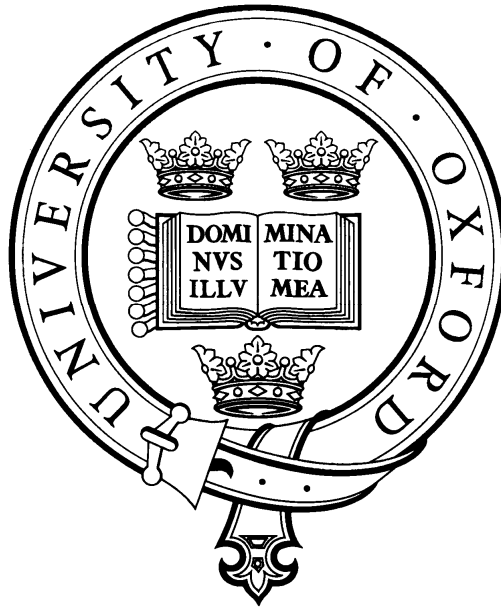


# Novel Functional Nano-Coatings on Glass by Spray Deposition



Weiliang Wang  
The Queen's College  
University of Oxford

A thesis submitted for the degree of  
*Doctor of Philosophy*  
Trinity 2010

# Novel Functional Nano-Coatings on Glass by Spray Deposition

Weiliang Wang, The Queen's College

Submitted for the degree of D.Phil., Trinity Term 2010

## ABSTRACT

Nanocomposite thin films with gold nanoparticles embedded in a host metal oxide prepared by spray pyrolysis deposition have been investigated. A single-step process has been developed using a one-pot solution containing precursors for both gold nanoparticles and host metal oxides. The films obtained display combined features of colouration, electrical conductivity and solar control. In this study two precursors for gold nanoparticles were used: preformed gold colloids and  $\text{HAuCl}_4$ . Three metal oxide host materials,  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$ , were investigated. These films were deposited at a substrate temperature of 200-600 °C. Powder X-ray diffraction analysis reveals the presence of metallic gold. SEM inspection typically showed particulate gold of 5-20 nm in diameter, distributed at the surface or within the host matrix. Optical spectroscopy showed an intense absorption in the visible region due to the characteristic surface plasmon resonance (SPR) effects of gold nanoparticles. The wavelength of the SPR peaks varies depending on the refractive index of surrounding host material which is significantly influenced by the substrate deposition temperature. On the other hand,  $\text{SnO}_2$  and  $\text{ZnO}$ , together with the introduction of dopants, were further investigated as suitable materials for transparent conducting oxides (TCO).  $\text{SnO}_2\text{:F}$  films were found to attain very low electrical resistivity, while  $\text{ZnO}$  films exhibit higher transparency in the visible. A double layered structure with a TCO layer of  $\text{SnO}_2\text{:F}$  on top of a layer embedded with gold nanoparticles has been employed to achieve the combined functionalities of conductivity and colouration. The electrical conductivity is significantly enhanced compared to a nanocomposite single layer film due to the introduction of the TCO top layer. In this thesis, spray pyrolysis deposition has demonstrated a simple and rapid approach to the production of a variety of thin films. It can be immediately integrated with current industrial coating equipment and scaled up for large-scale production process.

# ACKNOWLEDGEMENTS

First and foremost I would like to express my gratitude to my supervisors Prof. Peter Dobson and Dr. Steve Sheard for their continuing support, encouragement and advice throughout this project and the preparation of the thesis. Without their help and understanding this thesis would not be possible.

I also wish to thank all the other people that worked on the Nanocoat Project: Mr Simon Hurst, Drs Guillermo Benito, Troy Manning and Clare Hill from Pilkington European Technical Centre, Drs Peter Bishop, Virginie Buche, Kevin Cassar, Antonella di Trapani from Johnson Matthey Technology Centre, Prof. Ivan Parkin, Mr Paolo Melgari, Miss Gillian Walters from University College London. I am grateful for having spent such a productive time with these excellent people over the past four years whilst working on the project.

I would like to express my thanks to those who helped me along the road to completing this project; Prof. Patrick Grant, who kindly offered some of the equipment and allowed me to do the experiments in his lab, Drs Xin Zhao, Hongtao Zhang and Mr Richard Turner from Patrick's group for their help during this project; Drs Alison Crossley, Colin Johnston, Chris Salter, Gabriella Chapman from the Begbroke Science Park for help with characterisation and analysis; Mr Graham Hillsdon, Dr Peter Leigh of the Engineering department for their technical support; Xianfeng Chen, who firstly introduced me into the life of a researcher in Oxford; Huifeng Huang, Wang Xi, Lubin Zeng, Tong Hao, Jiwen Zhu and Christian Hofreiter for their precious friendship.

Finally I thank my parents who have supported me in every means and of course my wife, Jie, who has been with me all the time with patience.

# LIST OF PUBLICATIONS

## **Publications**

1. Wang, W.; Cassar, K.; Sheard, S.; Dobson, P.; Hurst, S.; Bishop, P.; Parkin, I., A Single-Step Route Towards Large-Scale Deposition of Nanocomposite Thin Films Using Preformed Gold Nanoparticles. Materials Research Society Proceedings, USA: **2009**.
2. Wang, W.; Cassar, K.; Sheard, S. J.; Dobson, P. J.; Bishop, P.; Parkin, I. P.; Hurst, S., Spray Deposition of Au/TiO<sub>2</sub> Composite Thin Films Using Preformed Nanoparticles. Nanotechnology in Construction 3, Proceedings. Springer-Verlag Berlin: Berlin, 2009; p 395-401.

## **Conferences attended**

1. The 3rd International Symposium on Nanotechnology in Construction (NICOM 3), Prague, Czech Republic. May **2009**. Oral presentation.
2. MRS Spring Meeting, San Francisco, USA. April **2009**. Poster presentation.

## **Patent**

1. Hurst, S.; et al. Coated substrate. WO/2010/106370, **2010**.

# TABLE OF CONTENTS

|                                                                           |      |
|---------------------------------------------------------------------------|------|
| ABSTRACT.....                                                             | i    |
| ACKNOWLEDGEMENTS .....                                                    | ii   |
| LIST OF PUBLICATIONS .....                                                | iii  |
| TABLE OF CONTENTS.....                                                    | iv   |
| LIST OF ABBREVIATIONS.....                                                | ix   |
| LIST OF FIGURES .....                                                     | xi   |
| LIST OF TABLES .....                                                      | xvii |
| CHAPTER 1 INTRODUCTION .....                                              | 1    |
| 1.1 Functional glass production.....                                      | 1    |
| 1.1.1 Body-tinted glass vs. coating-tinted glass .....                    | 2    |
| 1.1.2 Solar control coatings for energy-efficient windows .....           | 2    |
| 1.2 Challenge and limitations.....                                        | 4    |
| 1.3 How nanotechnology can help .....                                     | 5    |
| 1.3.1 Simulation of optical performance of nanocomposite thin films ..... | 8    |
| 1.4 Structure of thesis.....                                              | 10   |
| CHAPTER 2 LITERATURE REVIEW .....                                         | 11   |
| 2.1 Spray pyrolysis technique for thin film deposition .....              | 11   |
| 2.1.1 Introduction .....                                                  | 11   |
| 2.1.2 Spray pyrolysis system for thin film formation.....                 | 13   |
| 2.1.3 Processes during spray pyrolysis.....                               | 14   |
| 2.1.3.1 Atomisation of precursor solution.....                            | 15   |
| 2.1.3.2 Aerosol transport .....                                           | 15   |
| 2.1.3.3 Precursor decomposition .....                                     | 16   |
| 2.1.4 Influence of deposition parameters on thin film properties .....    | 18   |
| 2.1.4.1 Influence of substrate temperature .....                          | 18   |
| 2.1.4.2 Influence of precursor solution .....                             | 19   |
| 2.1.5 Preparation of thin films using spray pyrolysis.....                | 20   |
| 2.1.6 Conclusion.....                                                     | 21   |

|                                                             |                                                                                   |    |
|-------------------------------------------------------------|-----------------------------------------------------------------------------------|----|
| 2.2                                                         | Gold nanoparticles.....                                                           | 21 |
| 2.2.1                                                       | Introduction .....                                                                | 21 |
| 2.2.2                                                       | Quantum size effects and surface plasmons.....                                    | 22 |
| 2.2.3                                                       | Surface Plasmon Resonance.....                                                    | 22 |
| 2.2.4                                                       | Theoretical approach to SPR: the Mie Theory .....                                 | 25 |
| 2.2.5                                                       | Influence of the shape and structure of nanoparticles on optical properties ..... | 27 |
| 2.2.6                                                       | Synthesis of gold nanoparticles .....                                             | 30 |
| 2.2.7                                                       | Conclusion.....                                                                   | 31 |
| 2.3                                                         | Transparent conductive oxides.....                                                | 33 |
| 2.3.1                                                       | Introduction .....                                                                | 33 |
| 2.3.2                                                       | Deposition of TCO films.....                                                      | 35 |
| 2.3.3                                                       | Optical properties of TCO.....                                                    | 38 |
| 2.3.4                                                       | Electrical properties of TCO .....                                                | 41 |
| 2.3.5                                                       | Application of TCO.....                                                           | 43 |
| 2.3.6                                                       | Conclusion.....                                                                   | 45 |
| 2.4                                                         | Noble metal incorporated nanocomposite thin films .....                           | 45 |
| 2.4.1                                                       | Introduction .....                                                                | 45 |
| 2.4.2                                                       | Methods of nanocomposite film production .....                                    | 46 |
| 2.4.3                                                       | Properties and applications of noble metal incorporated nanocomposite films.....  | 51 |
| 2.4.3.1                                                     | Optical properties .....                                                          | 51 |
| 2.4.3.2                                                     | Catalytic properties .....                                                        | 52 |
| 2.4.3.3                                                     | Antibacterial property .....                                                      | 53 |
| 2.4.3.4                                                     | Other properties and applications.....                                            | 54 |
| 2.4.4                                                       | Conclusion.....                                                                   | 54 |
| CHAPTER 3 EXPERIMENTAL AND CHARACTERISATION TECHNIQUES..... |                                                                                   | 55 |
| 3.1                                                         | Introduction .....                                                                | 55 |
| 3.2                                                         | Apparatus set-up for spray deposition.....                                        | 55 |
| 3.3                                                         | Analytical techniques .....                                                       | 58 |

|                                                                                |                                                                    |     |
|--------------------------------------------------------------------------------|--------------------------------------------------------------------|-----|
| 3.3.1                                                                          | UV-visible-NIR spectroscopy .....                                  | 58  |
| 3.3.2                                                                          | X-Ray Diffraction (XRD) analysis.....                              | 60  |
| 3.3.3                                                                          | Scanning Electron Microscopy (SEM).....                            | 62  |
| 3.3.4                                                                          | Transmission Electron Microscopy (TEM).....                        | 67  |
| 3.3.5                                                                          | Four-point Probe Measurement.....                                  | 68  |
| 3.3.6                                                                          | Film thickness measurement using profiler.....                     | 69  |
| 3.4                                                                            | Conclusion.....                                                    | 70  |
| CHAPTER 4 SPRAY DEPOSITION OF TRANSPARENT CONDUCTIVE<br>OXIDE THIN FILMS ..... |                                                                    | 71  |
| 4.1                                                                            | Introduction .....                                                 | 71  |
| 4.2                                                                            | Spray deposition of SnO <sub>2</sub> and SnO <sub>2</sub> :F ..... | 72  |
| 4.2.1                                                                          | Precursor for SnO <sub>2</sub> .....                               | 72  |
| 4.2.2                                                                          | Spray deposition of SnO <sub>2</sub> .....                         | 72  |
| 4.2.3                                                                          | Spray deposition of SnO <sub>2</sub> :F .....                      | 75  |
| 4.2.4                                                                          | Discussion .....                                                   | 79  |
| 4.3                                                                            | Spray deposition of ZnO and doped ZnO thin films .....             | 81  |
| 4.3.1                                                                          | Spray deposition of ZnO thin film .....                            | 81  |
| 4.3.1.1                                                                        | Precursors for ZnO .....                                           | 81  |
| 4.3.1.2                                                                        | Spray deposition of ZnO films .....                                | 83  |
| 4.3.2                                                                          | Spray deposition of doped ZnO thin films .....                     | 88  |
| 4.3.2.1                                                                        | Al doped ZnO films.....                                            | 88  |
| 4.3.2.2                                                                        | B doped ZnO films.....                                             | 91  |
| 4.3.2.3                                                                        | In doped ZnO films .....                                           | 92  |
| 4.3.3                                                                          | Discussion on ZnO and doped ZnO .....                              | 93  |
| 4.3.3.1                                                                        | The effect of using different dopants .....                        | 93  |
| 4.3.3.2                                                                        | Influence of dopant concentration.....                             | 94  |
| 4.4                                                                            | Discussion on TCO .....                                            | 100 |
| 4.5                                                                            | Conclusion.....                                                    | 101 |
| CHAPTER 5 SPRAY DEPOSITION OF GOLD/METAL OXIDE<br>COMPOSITE THIN FILMS.....    |                                                                    | 102 |

|                                                                                                     |                                                                                                             |     |
|-----------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|-----|
| 5.1                                                                                                 | Introduction .....                                                                                          | 102 |
| 5.2                                                                                                 | Precursors .....                                                                                            | 103 |
| 5.2.1                                                                                               | HAuCl <sub>4</sub> & Au Nanoparticles.....                                                                  | 103 |
| 5.2.2                                                                                               | Precursors for TiO <sub>2</sub> , SnO <sub>2</sub> , ZnO .....                                              | 105 |
| 5.3                                                                                                 | Spray deposition of Au NPs thin films.....                                                                  | 105 |
| 5.4                                                                                                 | Spray deposition of Au/TiO <sub>2</sub> composite thin films .....                                          | 106 |
| 5.4.1                                                                                               | Au/TiO <sub>2</sub> thin films using preformed gold nanoparticles .....                                     | 106 |
| 5.4.2                                                                                               | Au/TiO <sub>2</sub> films using HAuCl <sub>4</sub> .....                                                    | 110 |
| 5.4.3                                                                                               | Summary .....                                                                                               | 114 |
| 5.5                                                                                                 | Spray deposition of Au/SnO <sub>2</sub> composite thin films .....                                          | 117 |
| 5.5.1                                                                                               | Au/SnO <sub>2</sub> films using preformed gold nanoparticles.....                                           | 117 |
| 5.5.2                                                                                               | Au/SnO <sub>2</sub> composite thin films using HAuCl <sub>4</sub> .....                                     | 122 |
| 5.5.3                                                                                               | Summary .....                                                                                               | 124 |
| 5.6                                                                                                 | Spray deposition of Au/ZnO composite thin films .....                                                       | 125 |
| 5.6.1                                                                                               | Au/ZnO films using preformed gold nanoparticles.....                                                        | 125 |
| 5.6.2                                                                                               | Au/ZnO composite films using HAuCl <sub>4</sub> .....                                                       | 130 |
| 5.6.3                                                                                               | Summary .....                                                                                               | 133 |
| 5.7                                                                                                 | Discussion .....                                                                                            | 136 |
| 5.7.1                                                                                               | Spray deposition mechanism.....                                                                             | 136 |
| 5.7.2                                                                                               | Optical properties and surface plasmon resonance effects.....                                               | 137 |
| 5.7.3                                                                                               | The incorporation of gold nanoparticles in host matrix .....                                                | 139 |
| 5.7.4                                                                                               | Comparison between using preformed Au NPs and HAuCl <sub>4</sub> ..                                         | 141 |
| 5.8                                                                                                 | Conclusion.....                                                                                             | 143 |
| CHAPTER 6 SPRAY DEPOSITION OF METAL OXIDE/GOLD-METAL<br>OXIDE COMPOSITE MULTILAYER THIN FILMS ..... |                                                                                                             | 144 |
| 6.1                                                                                                 | Introduction .....                                                                                          | 144 |
| 6.2                                                                                                 | Spray deposition of double-layered thin films of a SnO <sub>2</sub> + Au/SnO <sub>2</sub><br>composite..... | 145 |
| 6.2.1                                                                                               | Spray deposition experiment .....                                                                           | 145 |
| 6.2.2                                                                                               | Characterisations .....                                                                                     | 146 |

|                                            |     |
|--------------------------------------------|-----|
| 6.2.3 Discussion .....                     | 155 |
| 6.3 Conclusion.....                        | 156 |
| CHAPTER 7 CONCLUSIONS AND FUTURE WORK..... | 158 |
| 7.1 Summary of results.....                | 158 |
| 7.2 Future perspectives.....               | 161 |
| REFERENCES.....                            | 165 |

# LIST OF ABBREVIATIONS

|       |                                                            |
|-------|------------------------------------------------------------|
| a. u. | Arbitrary unit                                             |
| AACVD | Aerosol Assisted Chemical Vapour Deposition                |
| ALD   | Atomic Layer Deposition                                    |
| AZO   | Aluminium doped Zinc Oxide, ZnO:Al                         |
| BSE   | Backscattered Electron                                     |
| CVD   | Chemical Vapour Deposition                                 |
| EDX   | Energy-Dispersive X-ray spectroscopy                       |
| FIB   | Focused Ion Beam                                           |
| FPD   | Flat Panel Display                                         |
| GZO   | Gallium doped Zinc Oxide, ZnO:Ga                           |
| HDTV  | High Definition Television                                 |
| ICCD  | International Centre for Diffraction Data                  |
| IR    | Infra Red                                                  |
| ITO   | Tin doped Indium Oxide, In <sub>2</sub> O <sub>3</sub> :Sn |
| Low-E | Low-Emissivity                                             |
| MBTC  | Monobutyltin Trichloride                                   |
| NIR   | Near Infra Red                                             |
| NP    | Nanoparticle                                               |
| PET   | Polyethylene terephthalate                                 |
| PMMA  | Polymethyl methacrylate                                    |
| PV    | Photovoltaic                                               |
| SE    | Secondary Electron                                         |
| SERS  | Surface Enhanced Raman Scattering                          |

|       |                                      |
|-------|--------------------------------------|
| SPR   | Surface Plasmon Resonance            |
| TCO   | Transparent Conductive Oxide         |
| TGA   | Thermogravimetric Analysis           |
| TEM   | Transmission Electron Microscopy     |
| UV    | Ultraviolet                          |
| XANES | X-ray Absorption Near Edge Structure |
| XRD   | X-ray Diffraction                    |
| XPS   | X-ray Photoelectron Spectroscopy     |

# LIST OF FIGURES

## Chapter 1

Figure 1.1 Solar spectrum and desired transmission spectrum for solar control glass with high transmission in the visible range (350-750 nm) and low transmission in the infrared (750-2500 nm) [6]. .....4

Figure 1.2 Simulation of optical properties of gold embedded in  $\text{SnO}_2\text{:F}$  composite films on glass. The transmittance (T), reflectance (R) and absorptance (1-T-R) were calculated, in comparison with the transmittance of blank float glass provided by Pilkington Glass. The purple colour showed in the up-right corner is calculated as the transmitted colour the coating on glass.....9

## Chapter 2

Figure 2.1 Schematic diagram of chemical vapour deposition. The precursors are transformed from liquid phase (*l*) to gas phase (*g*) and experience reaction in the deposition chamber forming solids (*s*), either in a homogeneous reaction forming particles then diffuse to film growth, or in a heterogeneous reaction on the surface and form the film [29]..... 17

Figure 2.2 Schematic description of droplet transport before impacting onto substrate. The temperature of the substrate increases from A to D [39]. The droplets experience either wet spreading onto the substrate or evolution through precipitate, vapour to solid particles depending on the substrate temperature and finally deposition on the substrate. .... 17

Figure 2.3 Schematic presentation of the creation of a surface plasmon excited by the electromagnetic radiation (a) along the interface of a flat metal and dielectric and (b) corresponding to metal nanoparticles. A dipole is induced oscillating in phase with the electric field of the incoming light wave, where  $T$  = time period. Adapted from [54].....23

Figure 2.4 Size effects on the surface plasmon resonance of spherical gold nanoparticles. The results reproduced from the paper by Link and El-Sayed [62] show the UV-visible absorbance spectra of colloidal solutions of gold nanoparticles with diameters varying between 9 and 99 nm. ....26

Figure 2.5 Calculated absorption spectra of elongated ellipsoids with varying aspect ratios  $R$ . The dielectric constant of the host material is fixed at a value of 4. Reproduced from the paper by El-Sayed [66]. ....28

Figure 2.6 Calculated optical resonances of metal nanoshells (silica core, gold shell) over a range of core radius/shell thickness ratios. Reproduced from [69]. 29

Figure 2.7 Electromagnetic properties and fundamental physical processes and mechanisms over the wavelength for  $\text{In}_2\text{O}_3\text{:Sn}$  films.  $E_g$  is fundamental semiconductor band gap,  $\hbar\omega_p$  is plasma energy, and  $\hbar\omega_{PH}$  is phonon energy. Reproduced from [144] by Hamberg and Granqvist.. ....37

Figure 2.8 Photo showing Au nanoparticle doped coloured films on soda-lime-silica glass substrates heat treated at 500 °C. The position of Au SPR was tailored by changing the refractive index of the matrix. Adapted from [16] by Medda et al. and reproduced by permission of The Royal Society of Chemistry .....47

### Chapter 3

Figure 3.1 Schematic illustration of spray deposition system, comprising nozzle, syringe and X-Y table with hotplate. The substrate being coated is placed on the hotplate. Note the position of the nozzle and the needle tip. The nozzle and needle component is positioned 10 cm above the hotplate to attain fine and homogeneous droplets.....57

Figure 3.2 Raster scan pattern for coating glass substrate. The parameters are set as XLEN = 100 mm, YLEN = 100 mm, XPOS = 0, YPOS = 0, MARGIN = 10 mm, PITCH = 10 mm, COAT SPEED = 70 mm/s. Note the over-scan at the substrate edges and the relatively high coating speed to enhance uniformity. ....58

Figure 3.3 Schematic diagram of the double beam spectrometer. A typical double-beam spectrometer contains a diffraction grating, beam splitting system and a detector [241].....60

Figure 3.4 Diffraction of X-ray on the crystal lattice according to Bragg's law. ( $d$  is interplanar distance,  $\theta$  is Bragg's angle) .....61

Figure 3.5 Schematic configuration of XRD which consists of an X-ray source, a sample holder and a detector [243]. .....63

Figure 3.6 Illustrative diagram of electron beam interaction volume.....63

Figure 3.7 Variation of the backscatter coefficient as a function of atomic number ( $Z$ ). Backscatter coefficient is defined as the ratio of the number of backscattered electrons against incident electrons. Adapted from [245].....66

Figure 3.8 Schematic configuration of four point probe measurement. ....68

### Chapter 4

Figure 4.1 Typical XRD pattern of a  $\text{SnO}_2$  thin film deposited by spray pyrolysis using MBTC precursor at 500 °C. Note the presence of diffraction peaks for planes (110), (101), (200), (211) and (301). \* Note there is a peak that is difficult to identified but possibly attributed to  $\text{Sn}_2\text{O}_3$  (ICCD Reference Code 00-025-1259).. .....74

Figure 4.2 UV-visible-NIR transmittance spectra of blank float glass and spray deposited  $\text{SnO}_2$  thin film. Note the interference fringes and reduced IR transmission compared to the corresponding spectra for the blank float glass.....75

Figure 4.3 XRD pattern of a  $\text{SnO}_2\text{:F}$  thin film by spray deposition using MBTC and trifluoroacetic acid at 500 °C. Note the presence of diffraction peaks for

planes (110), (101), (211), (301), (321) and (312). \* Note the peaks that are difficult to identified but possibly attributed from  $\text{Sn}_2\text{O}_3$  (ICCD Reference Code 00-025-1259)..... 77

Figure 4.4 SEM image of spray deposited  $\text{SnO}_2$ . The scale bar is 1  $\mu\text{m}$ . The film consists of small crystallites with grain size of about 50 nm, along with larger grains of up to 500 nm. The contrast from the crystalline grains indicates a rough surface area.. ..... 79

Figure 4.5 Molecular structure of (a) Zinc acetate; and other zinc carboxylates developed by Johnson Matthey [246] (b) zinc 2-aminopyridine diacetate; (c) zinc 4-aminobutanoate; (d) zinc N,N-dimethylglycine. Note  $\text{Zn}^{2+}$  is coordinated by  $\text{O}^{2-}$  which is bonded to different ligands..... 82

Figure 4.6 XRD patterns of ZnO thin films deposited at different temperatures using zinc (2-aminopyridine) diacetate..... 85

Figure 4.7 XRD of ZnO thin films deposited using zinc aminobutyrate chloro.. 86

Figure 4.8 XRD of ZnO thin films deposited using N,N-dimethylglycin. Note that there is very little difference on the diffraction patterns from films deposited at different temperatures, indicating the films are poorly crystalline. .... 85

Figure 4.9 XRD pattern of ZnO:Al thin film by spray deposition at 425 °C. The film is polycrystalline of typical wurzite structure with (100), (002) and (101) planes. .... 87

Figure 4.10 UV-visible-NIR transmittance spectra of a ZnO:Al thin film as deposited and annealed in air or  $\text{H}_2$ . .... 90

Figure 4.11 XRD of ZnO:B thin film showing typical hexagonal ZnO pattern. .. 92

Figure 4.12 Influence of Al doping concentration on ZnO film resistance. Different doping levels from 5 at% to 0.5 at% and at different deposition temperatures were investigated. Note that 2 at% Al doped ZnO film shows lower resistance compared to other doping levels. .... 95

Figure 4.13 XRD patterns of Al doped ZnO films with varied doping levels from 0.5 at% to 5 at%. The intensity for (002) peak is reduced and the intensity for (101) peak is enhanced with increasing Al doping level. .... 96

Figure 4.14 SEM micrograph of ZnO:Al thin films with different Al doping concentrations of 5 at%, 2 at%, 1 at% and 0.5 at%. .... 99

## Chapter 5

Figure 5.1 (a) UV-visible spectrum of gold colloids in water stabilised by aminobenzoic acid. (b) TEM image of gold nanoparticle suspension in water on holey carbon film. The scale bar is 50 nm. .... 104

Figure 5.2 UV-visible spectrum of gold NP thin film. Note there is an SPR absorption band between 500 nm and 630 nm with a maximum at 558 nm..... 106

Figure 5.3 Visual images of appearance in transmission (top) and optical spectra (bottom) of Au/TiO<sub>2</sub> composite thin films on Pilkington float glass for a) as deposited at 200 °C; b) annealed at 400 °C and c) annealed at 600 °C. .... 108

Figure 5.4 Measured absorbance spectra of gold NP/TiO<sub>2</sub> thin films deposited with substrate temperatures from 200 °C to 550 °C. The intensity of SPR peaks is normalised for comparison. They also show a shift of the SPR peak w from 545 nm to 600 nm ith increasing substrate temperature (see inset). .... 109

Figure 5.5 Photo showing appearance of Au/TiO<sub>2</sub> composite thin films deposited on glass using HAuCl<sub>4</sub> at two substrate temperatures, 200°C (left) and 500 °C (right). .... 108

Figure 5.6 Transmittance spectra of Au/TiO<sub>2</sub> composite thin films deposited on glass at different substrate temperatures of 200-500 °C. The SPR peaks, which are positioned in the visible region from 545 nm up to 613 nm, red-shift with increasing deposition temperature. .... 112

Figure 5.7 XRD pattern obtained from a gold NP embedded titania film deposited on glass from HAuCl<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>Ti(C<sub>3</sub>H<sub>5</sub>O<sub>4</sub>). The peaks at 38.1°, 44.3° and 64.5° are assigned to the (111), (200) and (220) planes of cubic Au (ICCD reference code 01-089-3697). Peaks at 25.1° and 53.3° correspond to the (101) and (211) planes of anatase TiO<sub>2</sub> (ICCD reference code 01-071-1169). .... 113

Figure 5.8 SEM images of Au/TiO<sub>2</sub> films deposited at 250 °C using HAuCl<sub>4</sub> as the precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging where the bright spots are interpreted as gold NPs. The volume fraction of gold in TiO<sub>2</sub> is calculated as 1.5 vol%. .... 115

Figure 5.9 SEM images of Au/TiO<sub>2</sub> films deposited at 450 °C using HAuCl<sub>4</sub> as an alternative precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging where the bright spots are interpreted as gold NPs. The volume fraction of gold in TiO<sub>2</sub> is calculated as 1.5 vol%. .... 116

Figure 5.10 Transmittance spectra of Au/SnO<sub>2</sub> thin films spray deposited at different temperatures. SPR peaks are displayed for films deposited at 200 °C (553 nm) and 300 °C (575 nm) respectively, while the film deposited at 400 °C shows no SPR peak. .... 118

Figure 5.11 XRD patterns for Au/SnO<sub>2</sub> composite film using preformed gold NPs and for comparison a SnO<sub>2</sub> only film. .... 119

Figure 5.12 SEM images of Au/SnO<sub>2</sub> films deposited at 300 °C using a gold colloid as a source of gold NPs. Left: secondary electron mode image; right: backscattered electron mode image where the bright spots were interpreted as gold NPs. .... 120

Figure 5.13 EDX analysis of Au/SnO<sub>2</sub> films using preformed gold NPs. The spectra show different signal intensities for the elements detected. The bright spot area shows much higher Au signal intensity than Sn (upper graph) while the darker area shows increased Sn signal compared to Au (lower graph). .... 121

|                                                                                                                                                                                                                                                                                                                                                                    |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 5.14 Transmittance spectra of Au/SnO <sub>2</sub> thin films spray deposited at different temperatures using HAuCl <sub>4</sub> as a precursor. SPR peaks are observed for films deposited at 250 °C (553 nm) and 330 °C (588 nm) respectively, while the film deposited at 380 °C shows no SPR peak.....                                                   | 124 |
| Figure 5.15 Transmittance spectra of Au/ZnO thin films spray deposited at different temperatures using gold colloids as precursor. SPR peaks are displayed for films deposited at 250 °C (545 nm), 350 °C (568 nm) and 450 °C (575 nm) respectively, while the film deposited at 500 °C shows no SPR absorption. ....                                              | 126 |
| Figure 5.16 Transmittance spectra of Au/ZnO composite films which were as deposited at 350 °C and subsequently annealed at 600 °C. The SPR absorption was observed to red-shift after annealing. The band gap absorption edge is also seen as a step in the increasing transmittance due to a mixutre of amorphous crystalline material.....                       | 127 |
| Figure 5.17 XRD pattern for a typical Au/ZnO composite film using preformed gold NPs showing the presence of both Au and ZnO. ....                                                                                                                                                                                                                                 | 128 |
| Figure 5.18 SEM images of Au/SnO <sub>2</sub> films using gold colloids as a precursor which was deposited at 350 °C and then annealed at 600 °C. Left: secondary electron mode imaging; right: backscattered electron mode imaging, where the bright spots are interpreted as gold NPs.....                                                                       | 129 |
| Figure 5.19 Photo showing the appearance of Au/SnO <sub>2</sub> composite coating deposited on glass at 450 °C using HAuCl <sub>4</sub> .....                                                                                                                                                                                                                      | 127 |
| Figure 5.20 Transmittance spectra of Au/ZnO thin films spray deposited at different temperatures using HAuCl <sub>4</sub> as precursor. SPR peaks are displayed for films deposited at 250 °C (542 nm), 350 °C (559 nm), 450 °C (567 nm) and 500 °C (583 nm) respectively, while the film deposited at 550 °C shows no SPR absorption.....                         | 128 |
| Figure 5.21 XRD pattern for Au/ZnO composite film using preformed gold NPs showing the presence of Au and ZnO. ....                                                                                                                                                                                                                                                | 129 |
| Figure 5.22 SEM images of Au/ZnO films deposited at 450 °C using HAuCl <sub>4</sub> as a precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging, where the bright spots were interpreted as gold NPs. ....                                                                                                                   | 131 |
| Figure 5.23 SEM images of Au/ZnO films deposited at 450 °C using the HAuCl <sub>4</sub> precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging, where the bright spots were interpreted as gold NPs. At this higher magnification, the large ZnO particles are seen to be composed of smaller grains of 5-10 nm in size..... | 132 |
| Figure 5.24 Summary of SPR peak positions of Au/metal oxide composite films at different deposition temperatures. The gold NPs, either using preformed particles (solid symbol) or HAuCl <sub>4</sub> (hollow symbol) as precursors, were embedded into three different host materials: TiO <sub>2</sub> (black), SnO <sub>2</sub> (blue) and ZnO (red).....       | 135 |

Figure 5.25 Transmittance spectra corresponding to two methods of depositing Au/TiO<sub>2</sub> composite thin films at two different substrate temperatures using HAuCl<sub>4</sub> and preformed Au NPs.....139

## Chapter 6

Figure 6.1 Photo showing appearance of blank float glass (left), Au/SnO<sub>2</sub>:F composite coating on glass (middle) and composite coating with an additional SnO<sub>2</sub>:F layer on top (right).....143

Figure 6.2 Transmittance spectra of a single layer film of Au/SnO<sub>2</sub>:F composite (red trace) and double-layered film of Au/SnO<sub>2</sub>:F + SnO<sub>2</sub>:F, over the range from 250 nm to 3300 nm. The edges at 2800 nm for both films are attributed to the IR absorption by the float glass.....145

Figure 6.3 Reflectance spectra (in the range from 250 to 3300 nm) of a single-layered film of Au/SnO<sub>2</sub>:F composite (red trace), double-layered film of Au/SnO<sub>2</sub>:F + SnO<sub>2</sub>:F (blue), SnO<sub>2</sub>:F only film (dark yellow trace) and commercial Pilkington TEC 15 (nominally 15 Ω/□) and TEC 70 ((nominally 70 Ω/□)) glass (black traces). Note the reflectance of the double-layered film is between TEC 15 and TEC 70. ....149

Figure 6.4 (a) XRD patterns for a thin film of Au/SnO<sub>2</sub>:F composite (up) and a doubled-layered film of SnO<sub>2</sub>:F and Au/SnO<sub>2</sub>:F (bottom). (b) Re-scaled for comparison. Please note the broad peak between 20° to 40° (2θ) in the composite single layer which is probably due to the amorphous SnO<sub>2</sub> formed in the deposition.....151

Figure 6.5 SEM image of the top view of the double-layered thin film produced by spray deposition. The scale bar is 1 μm. Naturally only the top SnO<sub>2</sub>:F layer is visible. The impression of crystalline grains indicates a rough surface area. 152

Figure 6.6 Cross-sectional image of the double-layered film comprising a top layer of SnO<sub>2</sub>:F with thickness of about 1 μm and a bottom layer of Au/SnO<sub>2</sub>:F with thickness of 90 nm. The thickness of the SnO<sub>2</sub>:F only and Au/SnO<sub>2</sub>:F layers is obtained from the standard experimental conditions used in Chapter 4 and 5. ....153

Figure 6.7 Tilted cross-sectional image of the double-layered film of SnO<sub>2</sub>:F and Au/SnO<sub>2</sub>:F. An interfacial region between the layers (labelled as top of Au/SnO<sub>2</sub>:F layer) is enhanced due to the tilted imaging of the film. The scale bar is 1 μm. ....154

## LIST OF TABLES

Table 2.1 Summary of synthetic routes to gold nanoparticles. Typical methods were listed as below. The standard deviation indicates the monodispersity of the particles. The smaller it is, the more monodispersed the particles are.....32

Table 4.1 Sheet resistance of SnO<sub>2</sub>:F thin films deposited at different substrate temperature with different F doping concentration in the starting solution.....81

Table 6.1 Summary of electrical and optical properties of the double-layered composite film in comparison with the SnO<sub>2</sub>:F film and Au/SnO<sub>2</sub>:F composite film.....156

# CHAPTER 1

## INTRODUCTION

### 1.1 Functional glass production

There is growing demand for functional, value-added thin film coatings in the glass manufacturing industry. As stated in a report by Pilkington, a substantial glass manufacturer, the global market for flat glass in 2008 was about 53 million tonnes (6.6 billion m<sup>2</sup>), representing a value of around 22 billion Euros, out of which about 70% was consumed in building products and 10% for automotives, together with a growing production of specialty glass for solar applications, for example [1]. Europe has become the most mature market for value-added glass products. The values added to the commercial product include colouration, solar control and self-cleaning. The production of “specialised” glass has been viewed as a huge commercial business [2, 3]. Glass manufacturers aim to exploit the ability of producing multi-functional glass using new technologies associated with the well-established float line process - whereby molten glass is “floated” on top of a layer of molten tin. This method of manufacture was in fact developed commercially by the Pilkington brothers back in the 1950s [4].

More recently there has been intense development of the glass manufacturing industry in an attempt to reduce the inherent energy expenditure due to the emerging energy crisis and increasing demand for energy saving. This thesis addresses two aspects of energy cost relating to glass products: i) reducing the complexity of manufacturing coated glass and ii) designing a coating to give more effective energy control. These issues are discussed as follows.

#### **1.1.1 Body-tinted glass vs. coating-tinted glass**

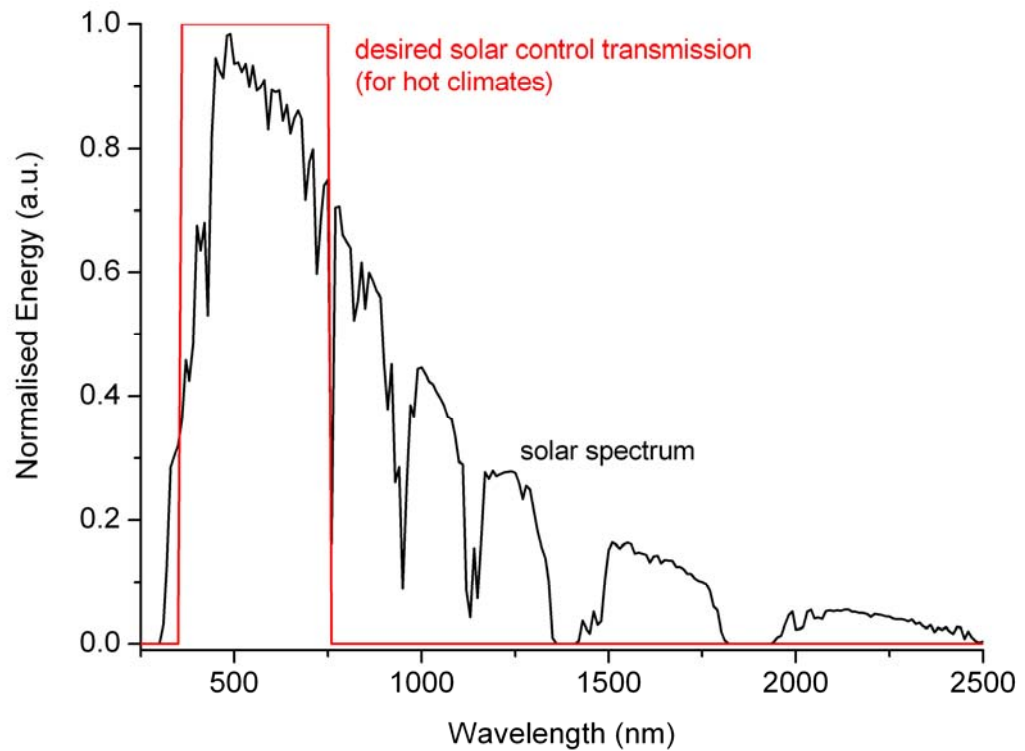
Tinted glass for applications in building facades is an important specialised glass product due to its aesthetic and functional value. The production of body-tinted glass (such as blue-coloured glass) is comparably expensive because of the lost income during the long time required to stabilise the modified (i.e. coloured) glass composition. Typically it takes 5 days for transition from clear to tint, 2 days between tints and 9 days from tint back to clear [5]. This causes a large waste of raw materials and energy consumption. An alternative approach is to apply a coloured thin film coating onto the glass at a later stage while maintaining constant glass composition. This “tinted glass by coating” approach applied to the product line could enable a manufacturing switch from base glass to coated glass with little or no lost production in between. Therefore an online coating technology is desirable for necessary development of such coating tinted glass.

#### **1.1.2 Solar control coatings for energy-efficient windows**

Solar control is a way of altering a glass window product’s infrared transmission to reduce the unwanted heating effect of sunlight which has been an area of intense research for some time [6]. In fact, windows are one of the great energy-wasters in buildings with an estimated average of about 25% of the total

building heat loss attributed to even the traditional double glazed sealed windows [6]. Also the heat gain that windows create during summer weather increase the running cost of an air conditioner. Solar control glass, which possesses modified reflectance and/or absorption characteristics over part of the sun's spectrum ( $0.75 - 3 \mu\text{m}$ ), can achieve a reduction in the total transmitted solar energy while retaining the visible transmittance.

In order to evaluate functional coatings for solar control glass it is necessary to further specify the desired properties of coatings by considering two different cases. In a cold climate, we wish to have a window which delivers as much heat energy (i.e. sunlight) into the building as possible. This implies that the window glass must be sufficiently transparent for solar radiation, benefiting from direct solar heating. In addition to considering the window glass transparency it is necessary to consider the internal heat loss due to thermal emission which should be decreased. Therefore, the near infrared (NIR) part of the sunlight ( $0.75 < \lambda < 3 \mu\text{m}$ ) should be transmitted for internal heating. In contrast, in a warm climate, the solar energy which enters through a window is a cause of heating which must be balanced by additional air conditioning. Thus one can save energy with a coating which is transparent for visible light at  $\lambda < 0.75 \mu\text{m}$  and reflects infrared light away from the building. A spectrally selective coating is therefore desired for energy efficiency. Therefore, such spectrally selective coatings are desirable in order for energy efficiency (see Figure 1.1 for warm climates). It is of great commercial interest for the glass industry to develop such a coating for window products with a deposition technology that is compatible with an industrial float line.



**Figure 1.1 Solar spectrum and desired transmission spectrum for solar control glass in hot climates with high transmission in the visible range (350-750 nm) and low transmission in the infrared (750-2500 nm) [6].**

## 1.2 Challenge and limitations

Therefore, to reduce the energy consumed during glass production and reduce the running costs for buildings and homes, production of multifunctional glass with the combined features of colouration and solar control is of significant commercial interest. However, to apply such coatings of suitable material on glass with compatible technology is still a challenge. First, there is a requirement to deposit a layer on a scale suitable for coating large areas, such as the full width of “float-line” glass i.e. 3 metres. What’s more, many processes involve the use of vacuum deposition which is expensive and not compatible with an on-line

coating process. Conventional deposition techniques such as chemical vapour deposition are restricted by the availability of suitable precursors. Exploration of compatible coating technologies developed to deposit thin film layers with controllable optical properties is therefore an essential objective.

### **1.3 How nanotechnology can help**

Nanotechnology, an area which exploits characteristics present at the nano- or submicron- scale, is driven by the desire to fabricate materials with novel and beneficial properties. The distinctly different optical properties of nanoparticles, as compared to their bulk counterparts, have stimulated considerable effort in a wide range of applications covering the industries of optics, microelectronics and biology [7]. Using nanoparticles offers a way of tailoring the optical properties of materials by forming composites of nanoparticles buried in a host material.

Nanocomposite materials based on noble nanoparticles embedded within a metal oxide host have been an intensive area of research due to their intriguing functional properties that can be modified by the nanoparticle size, shape and surrounding medium [8-10]. Noble metal nanoparticles, e.g. Au, Ag, Cu, generally exhibit a strong absorption peak in the visible range of the spectrum, due to the surface plasmon resonance (SPR) effect, which has led to applications in optical devices [11, 12]. The desired characteristics of the plasmon resonances can be achieved by careful design of the nanostructure, such as its size, shape and composition. Also dependent on the dielectric properties of the host matrix and the particles, the optical properties can be tailored to create intense absorption

bands at specific wavelengths. Dielectric materials, especially transition metal oxides, have been extensively investigated in their own right due to their functional properties, such as photocatalysis, electrochromism and solar control [13-16]. Among these metal oxides, transparent conductive oxides (TCOs) are a candidate for solar control because of their high transparency in the visible range and high electrical conductivity. This family of materials have been employed in a range of applications including larger flat-screen high-definition televisions (HDTV), low-emissivity (“low-e”) windows and thin film photovoltaics. The relatively high electrical conductance of TCOs also implies a reflectance band edge in the infrared due to free carrier plasma effects and the reflectance band edge can be shifted by tuning the free carrier concentration [6]. Therefore TCOs enable us to achieve some degree of solar control through high reflectance for the range  $\lambda > 0.7 \mu\text{m}$  of the solar spectrum (which carries about 50% of the solar energy) while retaining visible transparency.

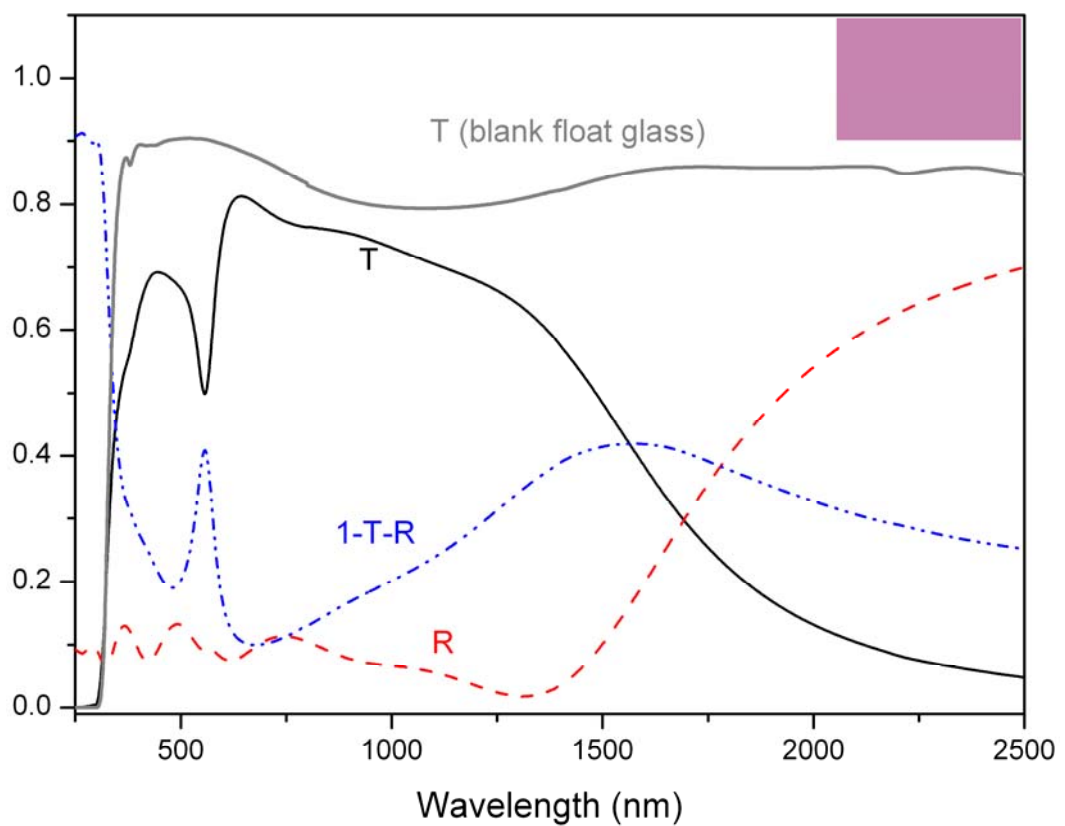
Nanocomposites, a class of materials comprising a host material and embedded metal particles, bear the combined functionalities of both phases and can be carefully selected to exploit the desired properties of either material. Such families of nanocomposites have shown potential applications in glass manufacturing, catalysis and the electronics industries [17]. The technology of incorporating metal nanoparticles within a TCO matrix enables a versatile approach to producing coloured coatings with a solar control property that have commercial viability. This requires an investigation into the background theory of nanoparticles and matrix material systems to allow the optical properties to be determined and to assist with any coating design work.

Also, there is a requirement to deposit layers onto glass on an industrial scale uniformly across the full width of a float glass production line (~ 3 metres) [5]. The main issue in such an application is that the process should be inexpensive and adaptable. Several approaches for the production of nanocomposite thin films incorporating metal nanoparticles into different metal oxide hosts have been developed. Among these methods, one scheme is to synthesise the host matrix with an addition of nanoparticles (or the metal ions as the precursor of nanoparticles) in a second step, or to some extent a layer-by-layer process in which the deposition of metal nanoparticles is followed by the deposition of host materials acting as the entrapping matrix [17]. Such a multi-step process would increase the complexity and cost, which is unattractive for industrial production. Another scheme is the deposition of composite thin films in a single step, where the precursors of noble metal nanoparticles and host matrix are premixed as a single source. The single-step route embraces the merits of simplicity and cost-effectiveness, which can also produce a more homogeneous composite film through control of the precursor properties, though the preparation of a stable one-pot solution is still challenging. Many deposition methods have been applied to produce composite thin films, such as magnetron sputtering, Chemical Vapour Deposition (CVD) and sol-gel processing. The conventional physical deposition methods are constrained by their operating environment (normally vacuum) and correspondingly their cost, while chemical processes (such as spray pyrolysis) are more flexible and scalable for large area applications.

### **1.3.1 Simulation of optical performance of nanocomposite thin films**

To verify the feasibility of using gold NPs/TCO nanocomposite coating for combined colouration and solar control, simulation of the optical properties of such films on glass has been conducted previously [18]. To simulate the optical properties of metal/dielectric composite thin films a software package, called CODE developed by W. Theiss [19] was used. The package provides a wide range of material properties in a database, calculates the reflectance and transmittance of the stack of material layers, simulates the visible appearance using colour coordinates (e.g. CIELAB [20]), and provides flexible fitting procedures to find out optimised parameters established in the models. The basic routine of simulation is firstly to set up the dielectric function models for gold nanoparticles and dielectric host matrix from the database of CODE (or models from the literature), then model the dielectric function of gold/host composites using an effective medium approximation [21] (such as the Maxwell-Garnett model [22, 23], the Bruggeman model [24]), and finally calculate the optical performance (reflectance, transmittance, absorbance, etc) of the stack of material layers comprising the composite thin film with the substrate. These operations have been fully implemented into the software. Using this software, the optical performance of nanocomposite thin films have been simulated, and a model system of gold NPs/TCO nanocomposite thin films has been identified for the coloured solar control products. A composite layer comprising gold incorporated in a host matrix of  $\text{SnO}_2\text{:F}$  was modelled using the Maxwell-Garnett approximation (0.5 vol% gold, composite layer thickness of 200 nm). The transmittance (T), reflectance (R) and absorptance (1-T-R) were calculated, in comparison with the transmittance of blank float glass provided by Pilkington

Glass. The transmittance starts to attenuate from 1300 nm which is associated with an increase of reflectance. An absorption peak at 578 nm was displayed due to the surface plasmon resonance of gold, which leads to a purple colour in transmission (Figure 1.2). The simulation has demonstrated the possibility of combining colouration and solar control by incorporating gold into TCO materials.



**Figure 1.2** Simulation of optical properties of gold embedded in SnO<sub>2</sub>:F composite films on glass. The transmittance (T), reflectance (R) and absorptance (1-T-R) were calculated, in comparison with the transmittance of blank float glass provided by Pilkington Glass. The purple colour showed in the up-right corner is calculated as the transmitted colour the coating on glass.

## 1.4 Structure of thesis

This thesis reports the investigation into spray deposition of gold/metal oxide composite thin films as well as transparent conductive oxides as the host materials for large area substrate applications. The chapters are organised as follows. In Chapter 2 the properties of the materials of interest, including gold nanoparticles, transparent conductive oxide and nanocomposite films are reviewed, along with a description of the spray deposition technique and its application for composite film deposition. In Chapter 3 the experimental set-up of spray deposition is described, and the various analytical techniques introduced and some physical background discussed. Chapter 4 presents the results of transparent conductive oxide thin films by spray deposition and two TCO materials,  $\text{SnO}_2$  and  $\text{ZnO}$  are investigated. Chapter 5 presents the results of spray deposition of gold/metal oxide thin films in a one-step process. In Chapter 6 an attempt towards coloured TCO composite films is reported by investigating the deposition of a double-layered structure. Finally Chapter 7 explores future work required to optimise the optical performance of thin film coatings on a large scale and development of the spray coating technology for higher quality of end products.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Spray pyrolysis technique for thin film deposition**

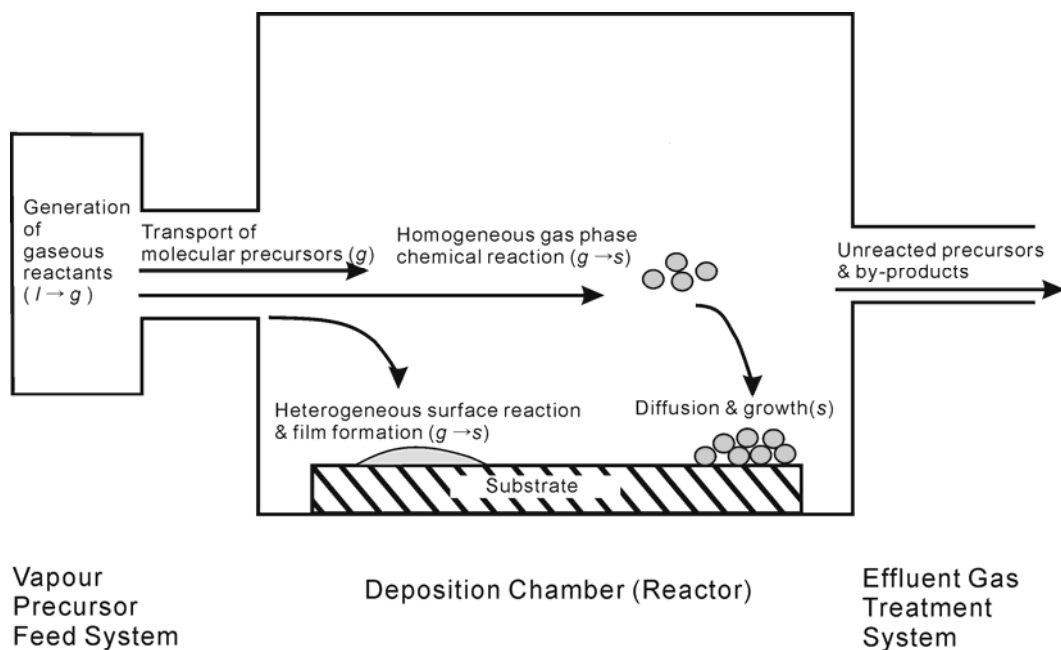
##### **2.1.1 Introduction**

Thin films of various materials have a wide range of applications from microelectronics to coatings of several square metres on window glass. A number of methods have been employed for thin film deposition which can be divided into two groups based on the nature of the process, i.e. physical or chemical. These have been described in standard text books and reviewed by many researchers from time to time [25-29]. A physical method describes a process of evaporation of a material and condensation of the vaporised form of the material onto a surface which usually involves the vacuum environment. The physical methods include evaporative deposition (in which the material to be deposited is heated to a high vapour pressure by electrically resistive heating in a low vacuum), laser ablation (in which a high power laser ablates the material from the target into a vapour) and sputtering (in which the material target is bombarded by a glowing plasma into a vapour form). However, these physical approaches involve sophisticated reactors and vacuum systems which increase the cost of production and has limitation on large-scale deposition process.

In contrast to the physical methods, the chemical approaches use chemical reactions in gas or liquid phase. Among these, chemical vapour deposition (CVD) is one of the gas-phase thin film technologies which relies on the reactive carrier gases to deliver precursors of desired materials to the substrate surfaces. The precursors either react or decompose at the surface to form thin films (see Figure 2.1 for schematic diagram of CVD reaction). This atomistic deposition method can provide highly pure materials with structural control at atomic or nanometre scale level [29]. Another gas-phase thin film deposition technique, atomic layer deposition (ALD), is a sequential chemical reaction process which keeps only one reactant in the chamber at a time. This provides an opportunity of precise control of very thin films at nano- or subnano- scale [30]. These gas-phase routes have restrictions in choice of the precursors which need to be volatile to form vapours during the reaction. Solution-based chemical deposition processes include spray pyrolysis, sol-gel, spin- and dip-coating which deliver liquid-phase precursor to the substrate surface where the reaction and film formation occur [31].

Among these, spray pyrolysis has been one of the major processing techniques to prepare thin and thick films, ceramic coatings and powders. It represents a very simple and relatively cost-effective processing method especially with regard to equipment costs. There are a number of advantages of this technique. First of all spray pyrolysis offers an extremely easy approach for preparing films of any composition by variation in the spray solution. It does not require high quality substrates or chemicals. Moreover, spray pyrolysis does not require a vacuum at any stage, which is a great advantage for a scaled-up industrial process. Compared to sol-gel methods which request repeatedly

coating layers to achieve desired thickness, the deposition rate can be easily controlled by changing the spray parameters and to achieve the desired film thickness. Even multilayered films can be easily prepared using this versatile technique. Therefore, spray pyrolysis deposition as a widely adopted technique has demonstrated its flexibility to be adapted into an industrial process.



**Figure 2.1 Schematic diagram of chemical vapour deposition. The precursors are transformed from liquid phase ( $l$ ) to gas phase ( $g$ ) and experience reaction in the deposition chamber forming solids ( $s$ ), either in a homogeneous reaction forming particles then diffuse to film growth, or in a heterogeneous reaction on the surface and form the film [29].**

### 2.1.2 Spray pyrolysis system for thin film formation

A typical spray system mainly consists of an atomiser (spray nozzle), precursor solution processor (or injector), substrate heater and temperature

controller. Different types of atomiser are often used in the spray pyrolysis process, including an air blast (in which the solution liquid is pulverized by gas such as compressed air or nitrogen), ultrasonic (in which ultrasonic frequencies are applied for fine aerosol generation) and electrostatic (in which the aerosol is produced and directed by a high electric field). Liquid and gas flow regulators are used to measure and control the feed rate of precursor solution and the flow of atomising gas. The spray nozzle can be moved vertically for adjusting spraying distance. In some cases the substrate heater is mounted on a moving table and is rastered across the spray nozzle using a stepping motor to achieve uniform deposition.

### **2.1.3 Processes during spray pyrolysis**

During the film formation by spray pyrolysis there are many processes occurring either sequentially or simultaneously. The formation of thin films by spray pyrolysis involves the atomization of a liquid solution containing precursors, droplet (aerosol) transportation towards a heated substrate, precursor decomposition and film formation on the substrate surface.

During aerosol generation and deposition a variety of fundamental physical and chemical phenomena are involved, for example, single particle physical processes such as nucleation, evaporation, condensation, solid-state diffusion and phase transformation; multi-particle physical processes such as collision, coalescence and agglomeration; transport and deposition of reactants and products of vapours and particles. The properties of films are influenced by the substrate temperature, properties of precursor solution, spray feed rate, carrier gas, droplet size and also the cooling rate after deposition. The deposition rate and

film thickness depend on the distance between the spray nozzle and substrate, substrate temperature, the concentration of precursor solution and the quantity of solution used. Successful film growth therefore requires understanding and tailoring of these characteristics as well as considering related factors. The following section will discuss the influence of the main spray pyrolysis parameters on the structure and properties of the films deposited.

#### **2.1.3.1 Atomisation of precursor solution**

Atomisation is a critical step in spray pyrolysis because it controls the droplet size distribution which finally determines film quality. There have been numerous reports in the past investigating the mechanism of liquid atomisation. Rizkalla and Lefebvre examined the influence of air and liquid properties on air blast atomisation [32] and Lampkin presented some applications of different spray nozzle set-ups [33]. Numerical calculation were reported to predict mean diameter, droplet size distribution and velocity [34, 35]. Other atomisation methods such as ultrasonic nebulisation [36] and electrostatic atomisation [37] were investigated and the generated droplet size distributions were compared with theoretical models.

#### **2.1.3.2 Aerosol transport**

During transportation, before impacting the substrates, the droplets experience several processes including: solvent evaporation, particle diffusion, precipitation and possible particle formation due to decomposition. External force fields (gravitational, electric, magnetic, or thermal) can influence droplet motion which determines both the trajectory of the droplets and evaporation. One of the forces due to temperature gradients is the thermophoretic force which

moves the droplets from high temperature regions to low temperature regions and therefore pushes the droplets away from the heated substrate.

The aerosol droplets also experience evaporation of the solvent during the transport to the substrate. This results in a reduction of droplet size and also a concentration gradient across the droplets. Therefore the precursor precipitates on the surface of the droplet which leads to possible formation of porous and hollow particles. This increases the film roughness which is not desired. Yu and Liao described the evaporating solution within a droplet during spray deposition by using a numerical model [38]. The effects of mass, momentum and heat transfer, as well as solute precipitation on solution evaporation, have been considered. Rapid increases in droplet temperature were observed at the beginning of solvent evaporation and at the moment of precursor precipitation on the droplet surface due to the heat resulting from precipitation. Therefore, as suggested, the concentration gradient across the aerosol droplet should be minimised to avoid the formation of hollow particles, which is an essential challenge.

It should be noted that it is desirable to have as many droplets as possible transported onto the substrate without forming powders. A film with high quality is formed when the droplets approach the substrate just as the solvent is completely removed.

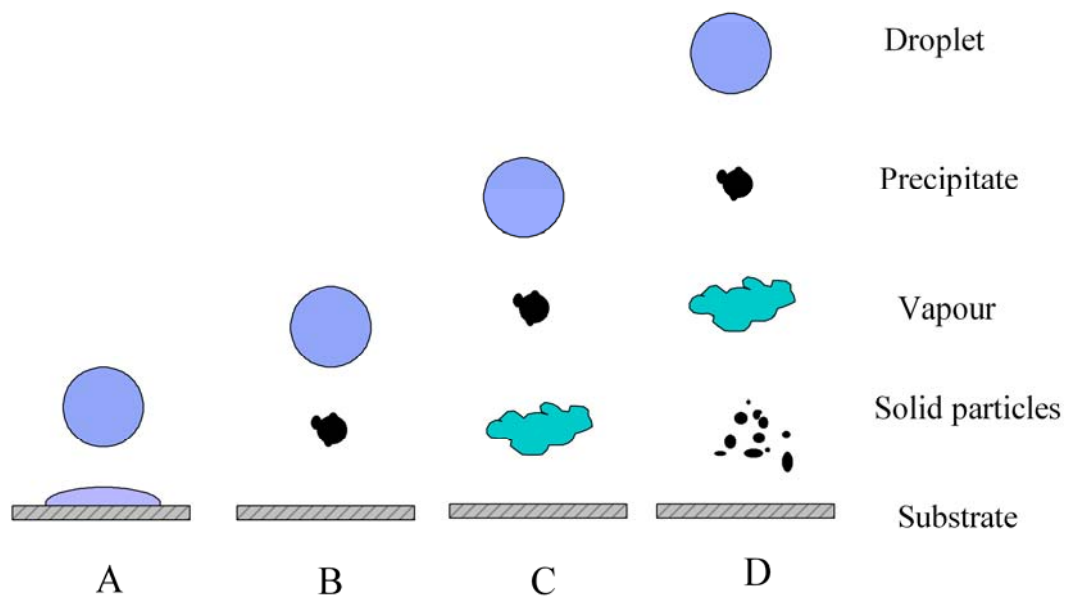
#### **2.1.3.3 Precursor decomposition**

After aerosol transport, many complex processes occur such as droplet impaction on the substrate surface and precursor decomposition. These processes

are significantly dependent on the deposition temperature and precursor properties.

Viguie and Spitz proposed different processes that occur with increased substrate temperature [39]. They described the evolution of droplets with increasing temperature through solvent evaporation and precursor decomposition before eventually impacting the target substrates, which is illustrated in Figure 2.2. As from process A to D, where the substrate temperature increases, the droplet experiences evolution to become a precipitate due to solvent evaporation (vapour loss due to precursor melting and evaporation) and finally becomes a solid particle by decomposition before reaching the substrate.

Therefore droplets with metal salts can either evaporate completely forming a film in a pseudo-CVD process or forming particles which are deposited on the substrate as solids [39, 40]. The droplets are deposited on the surface before complete evaporation or decomposition into solids only when the substrate temperature is lower than a critical point called Leidenfrost point [41, 42]. In this case, after the impaction onto the substrate, the droplets wet and spread over the substrate surface. During or after this process solvent still in the precursor starts to evaporate and the metal salts might precipitate from the droplet due to supersaturation and precursor decomposition occurs during this; forming solid deposits on the surface which gradually increase the coverage over the substrate with increasing deposition time and eventually a film is formed.



**Figure 2.2 Schematic description of droplet transport before impacting onto substrate. The temperature of the substrate increases from A to D [39]. The droplets experience either wet spreading onto the substrate or evolution through precipitate, vapour to solid particles depending on the substrate temperature and finally deposition on the substrate.**

## **2.1.4 Influence of deposition parameters on thin film properties**

### **2.1.4.1 Influence of substrate temperature**

Many processes involved in spray pyrolysis, such as aerosol transportation, solvent evaporation, droplet impact with spreading and precursor decomposition, are strongly temperature dependent. The substrate surface temperature therefore plays an important role in determining film morphology and properties.

Chen *et al* [43] presented four types of film morphologies depending on varied substrate temperature using electrostatic spray deposition: dense layer, dense layer with incorporated particles, porous top layer with dense bottom layer and fractal-like porous layer. The authors investigated different parameters and concluded that the substrate temperature is the main parameter determining the film morphology; higher deposition temperature leads to porous film formation. Stelzer *et al* [44] also investigated the morphology of terbium doped yttria thin films deposited using electrostatic spray deposition. By increasing the deposition temperature, the morphology of the films was shifted from a dense to a highly porous structure.

The influence of substrate temperature on the electrical and optical properties of zinc oxide films has been investigated [45]. It was found that films deposited at a relatively high temperature of 490 °C using an aqueous solution of zinc acetate resulted in the lowest electrical resistivity of down to 10  $\Omega\cdot\text{cm}$  with improved crystallinity. This was attributed to a decrease of film thickness and an increase in the structural homogeneity. Usually the films obtained at lower temperatures (300 °C for instance) are thicker and rougher than those obtained at high temperatures [46]. As the temperature increases, films become thinner and smoother.

#### **2.1.4.2 Influence of precursor solution**

The properties of the precursor solution are also important variables in the spray pyrolysis process. The nature of the solvent, type of salt, concentration of precursor and additives used, influence the physical and chemical properties of

the precursor solution which therefore change the structure and performance of the films deposited.

Chen's research revealed that the morphology of thin films can be changed by introducing additives to the precursor solutions [47]. The deposited  $\text{TiO}_2$  films changed from a cracked to a crack-free structure after the addition of acetic acid. The authors explained that the addition of acetic acid decreases the hydrolysability of the alkoxide precursor, titanium isopropoxide which improves the droplets drying process and forms a higher quality film. Pink *et al* reported the preparation of  $\text{SnO}_2$  films by spray pyrolysis using an inorganic and an organic precursor respectively [48]. Smooth but not uniform films were obtained using an inorganic precursor solution of  $(\text{NH}_4)_2\text{SnCl}_6$  in water, while very uniform but rough films were deposited using a solution of  $(\text{CH}_3\text{COO})_2\text{SnCl}_2$  in ethylacetate.

### **2.1.5 Preparation of thin films using spray pyrolysis**

Spray pyrolysis has been widely employed for deposition of different materials. These include a variety of metal oxides such as  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_3$ , metallic spinel type oxides such as  $\text{Co}_3\text{O}_4$ ,  $\text{LiCoO}_3$ , binary chalcogenides such as  $\text{CdSe}$ ,  $\text{CdTe}$ , and ternary chalcogenide such as  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$ . This has been extensively reviewed by Patil with references therein [49]. Also a spray deposition technique was used for thin film deposition with multiple components. Zhao *et al* produced different types of super-capacitors using spray pyrolysis, including polydiacrylate with  $\text{BaTiO}_3$ , fluoropolymer with carbon nanotubes and single wall carbon nanotubes [50-52]. The preparation of various films including TCO films and nanoparticles-incorporated composite

films will be further discussed in the following sections, together with comparison with other deposition techniques.

### **2.1.6 Conclusion**

In summary, spray pyrolysis is a versatile deposition technique to produce a variety of thin films. Compared to other deposition techniques e.g. sputtering in physical methods, CVD and sol-gel in chemical methods, the spray pyrolysis technique represents the advantages of simplicity, low cost and ability of scale-up under atmospheric conditions, which is well adapted to industrial production. The processes involved during spray deposition, including atomization of precursor solution, aerosol transportation and precursor decomposition, are influenced by the parameters including atomising air pressure, substrate temperature and precursor properties. Among these parameters, the substrate temperature is the most important factor which affects all the processes involved in spray pyrolysis and hence the end product properties of thin films. This will be carefully investigated in the experiments described later in the thesis.

## **2.2 Gold nanoparticles**

### **2.2.1 Introduction**

Gold is one of the Group 11 elements (Cu, Ag, Au) which have been of intense interest as a decorative material due to their intriguing functional properties such as extensive coloration and catalytic properties. The history of using noble metals dates back to 400-500 BC in Egypt and China and has been

used to provide coloured glass in medieval cathedral windows, vases, pottery and other ornaments [11].

### **2.2.2 Quantum size effects and surface plasmons**

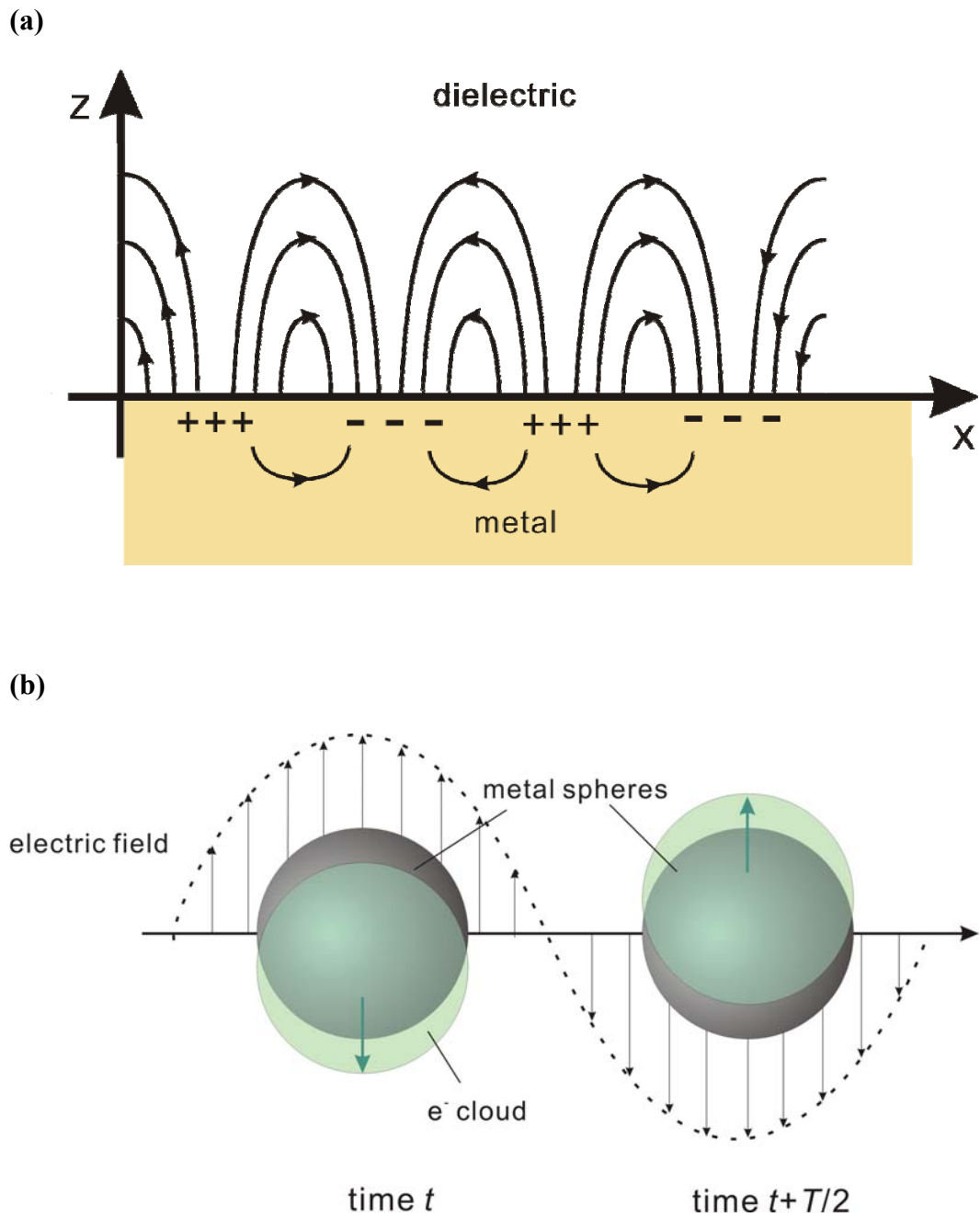
The properties of gold particles are dramatically influenced by their structure and size, from atomic to bulk [53]. Particles from the size of a single gold atom (about  $0.26 \times 10^{-9}$  m) up to around  $10^{-9}$  m show strong quantum confinement, i.e. the quantisation of electronic energy levels. Such particles can be regarded as clusters containing countable numbers of atoms in stable and preferred geometrical structure including hexagonal, cubic and icosahedral. Above about  $3 \times 10^{-9}$  m, the quantum confinement ceases and the electronic structure of the materials become much like the band structure of bulk solid. In the size range between  $3 \times 10^{-9}$  m and about  $5 \times 10^{-7}$  m, the optical properties of gold particles are dominated by surface plasmon resonance (SPR). For particle size above  $5 \times 10^{-7}$  m, the SPR absorption is no longer significant and the particles behave very much like bulk gold.

In this work, the gold particles investigated are in the range of 5-50 nm which are expected to have cubic crystal structure and show SPR effects rather than quantum confinement. The SPR effects will be discussed in detailed in the following subsection.

### **2.2.3 Surface Plasmon Resonance**

There are two modes of surface plasmons, the propagating plasmons and localised surface plasmons. Propagating plasmons are electromagnetic waves bounded by flat smooth metal-dielectric interfaces and arise from the oscillation

of conduction electrons in the metal. They propagate in the x- and y- directions along the interface and decay in the z- direction, as shown in Figure 2.3 (a). When the surface plasmons are confined to a small scale such as for nanoparticles, the localised optical modes are changed into localised surface plasmons. Figure 2.3 (b) shows the surface plasmons in a metal nanoparticle excited by electromagnetic radiation. The physical origin of the surface plasmon resonance effect is the coherent oscillation of the conduction band electrons induced by the interacting electromagnetic field. In a classical description, the electric field of an incoming light wave induces a polarization of the conduction electrons with respect to the much heavier ionic core of a nanoparticle. The net charge difference occurs at the surface of the nanoparticle, which in turn acts as a restoring force. As a consequence, a dipolar oscillation of the electrons with the same phase is created leading to an efficient energy exchange, and this is called surface plasmon resonance. When the frequency of the electromagnetic field becomes resonant with the coherent electron motion, a strong absorption in the visible region of the spectrum (for metal nanoparticles of gold, silver, and copper) is observed while maintaining mostly transparency. This is the origin of the colour seen in stained glass windows for example.



**Figure 2.3 Schematic presentation of the creation of a surface plasmon excited by electromagnetic radiation (a) along the interface of a flat metal and dielectric and (b) corresponding to metal nanoparticles. A dipole is induced oscillating in phase with the electric field of the incoming light wave, where  $T$  = time period. Adapted from [54].**

The frequency and the width of the surface plasmon absorption depend on the size and shape of the metal nanoparticle as well as the on the dielectric constant of the metal itself and the material surrounding it [55, 56].

#### 2.2.4 Theoretical approach to SPR: the Mie Theory

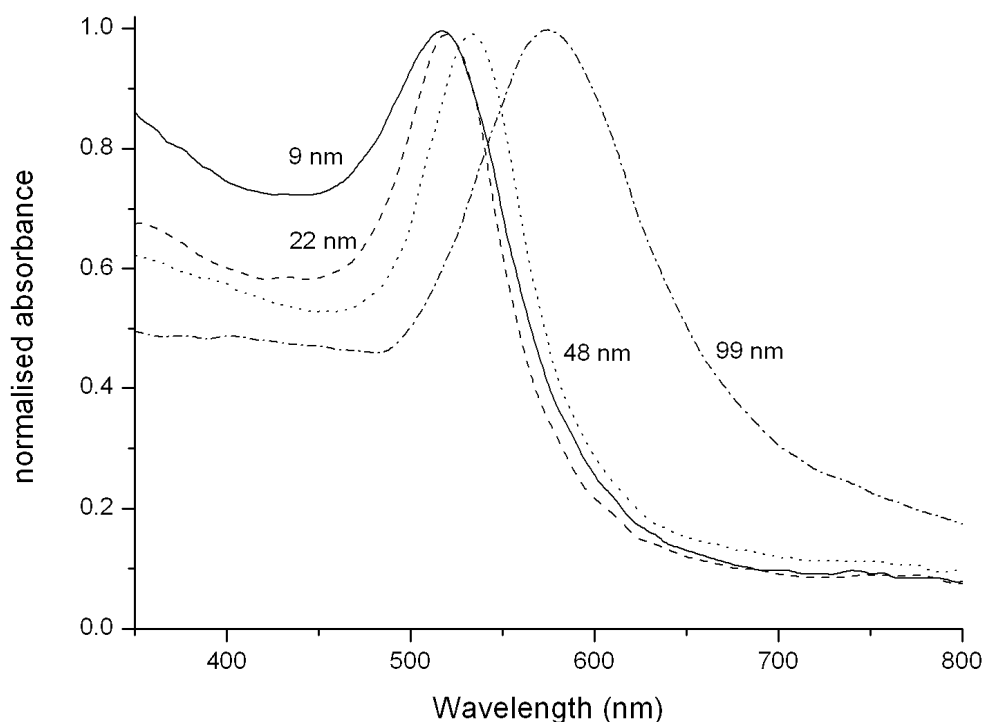
The linear optical properties such as scattering and extinction of small metal particles in relation to surface plasmon resonance were first explained theoretically by Mie in 1908 [57]. He solved Maxwell's equation and provided an electrodynamic calculation of the interaction of light with spherical metal nanoparticles. With the appropriate boundary conditions, his calculations give a series of multipole oscillations (dipole, quadrupole and higher modes.) for the scattering and extinction of electromagnetic radiation by spherical particles immersed in a continuous medium as a function of the particle radius [58, 59]. This chapter is primarily concerned with the role played by the size effect of the embedded nanoparticle and not specifically with the details of the analysis.

The effect of particle size on the peak resonant wavelength comes from two different mechanisms depending on the size range. For nanoparticles much smaller than the wavelength ( $2R \ll \lambda$ ), only the electric dipole term contributes significantly to the parameter described as the extinction cross section  $\sigma_{ext}$ , which is a measure of the fraction of light lost to scattering and absorption in a participating medium in unit area [60, 61]. Therefore the Mie theory reduces to the following relationship:

$$\sigma_{ext} = \frac{9\omega}{c} \varepsilon_m^{3/2} V_0 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2}$$

where  $V_0 = (4\pi/3) \cdot R^3$  is the volume of the spherical particle,  $\omega$  is the angular frequency of the exciting light,  $c$  is the velocity of light,  $\epsilon_m$  and  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$  are the dielectric functions of the surrounding medium and the metal, respectively. While  $\epsilon_m$  is assumed to be frequency independent,  $\epsilon(\omega)$  is complex and is a function of  $\omega$ . Note that a resonance condition is fulfilled when  $\epsilon_1(\omega) = -2\epsilon_m$  if  $\epsilon_2$  is small or weakly dependent on  $\omega$ . This is referred as the surface plasmon resonant condition.

The above equation has been extensively used to explain the absorption spectra of small nanoparticles. When the nanoparticles become larger, higher order modes become more important. This is because the light can no longer polarize the nanoparticles homogeneously and consequently the retardation effect of the electromagnetic field on the particle induces a shift and broadening of the surface plasmon resonance. These higher order modes have maxima at lower energies and therefore the plasmon band red-shifts with increasing particle size. Figure 2.4 shows the absorption spectra of different sized gold nanoparticles from the results reproduced from the paper by Link and El-Sayed [62]. The size effects contribute to the red-shift of the plasmon resonance peak position and the broadening of bandwidth with increasing particle size. Published data from several groups have confirmed that the SPR peak shifts from 520 nm up to 632 nm for gold nanoparticle size increasing from 9 nm to 140 nm, while the bandwidth  $\Delta\lambda$  increased from 80 nm to 160 nm [62-65].

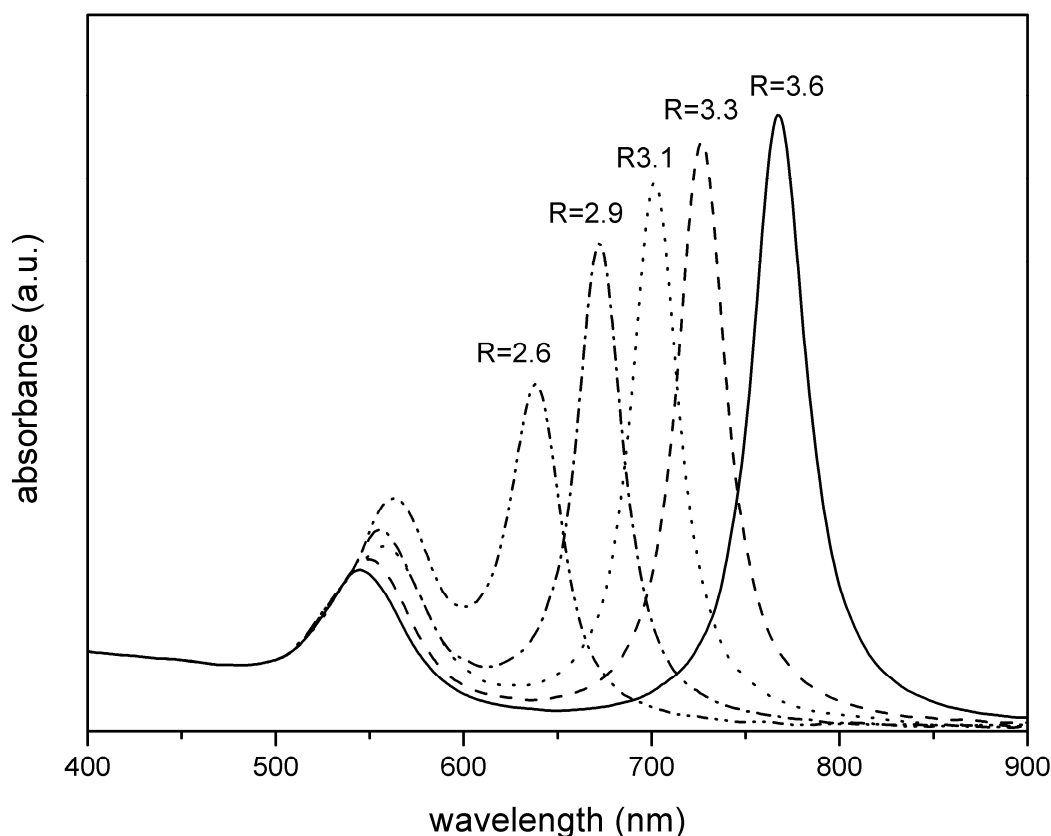


**Figure 2.4 Size effects on the surface plasmon resonance of spherical gold nanoparticles. The results reproduced from the paper by Link and El-Sayed [62] show the UV-visible absorbance spectra of colloidal solutions of gold nanoparticles with diameters varying between 9 and 99 nm.**

### **2.2.5 Influence of the shape and structure of nanoparticles on optical properties**

Although there is considerable interest in the size dependent effects, the optical properties are also influenced by other additional factors such as the shape and structure of the particles. A more drastic effect on the surface plasmon absorption is found if the shape of nanoparticles is changed to elongated rods. For gold nanorods, the plasmon absorption splits into two bands corresponding to the oscillation of the free electrons along and perpendicular to the long axis of the

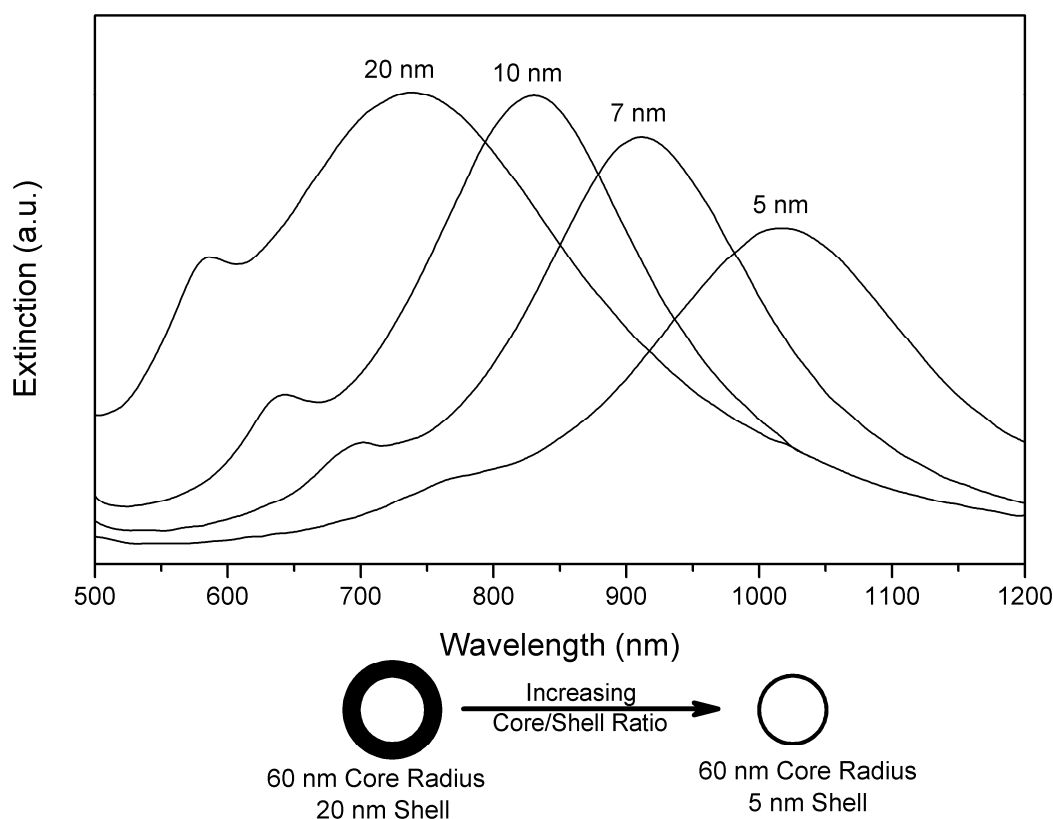
rods: the transverse mode and the longitudinal mode. The transverse mode shows resonance absorption at 520 nm, while the resonance of the longitudinal mode shifts to longer wavelength with increasing aspect ratio (the ratio of the length divided by the width of the rod). El-Sayed *et al* calculated the absorption spectra for the gold nanorods with different aspect ratios, as shown in Figure 2.5 which reproduces results from the paper [66]. From Figure 2.5 it can be seen that two plasmon peaks are present in the simulated absorption spectra corresponding to the transverse and longitudinal resonances. The longitudinal mode moves to longer wavelengths whereas the absorption peak of the transverse mode shifts slightly to shorter wavelength with increasing aspect ratio. The trend for the transverse mode of the surface plasmon oscillation of randomly orientated nanorods is in agreement with the results of experimental work by Martin and co-workers [67, 68], who also obtain a blue-shift of the plasmon peak using Maxwell-Garnett theory. Clearly, the effect on the longitudinal mode is much more significant showing a red-shift of over 100 nm. Furthermore, the relative absorbance intensity ratio of the longitudinal to the transverse mode increases with increasing aspect ratio.



**Figure 2.5** Calculated absorption spectra of elongated ellipsoids with varying aspect ratios  $R$ . The dielectric constant of the host material is fixed at a value of 4. Reproduced from the paper by El-Sayed [66].

In addition to changing nanoparticle size it is possible to create core-shell structures that exhibit interesting optical properties. Metal nanoshells, consisting of a dielectric core with a metallic shell of nanometre thickness, are a new class of composite nanoparticle whose optical resonance can be designed in a controlled manner. By varying the relative dimensions of the core and shell, the optical resonance of these nanoparticles can be varied over hundreds of nanometres in wavelength, across the visible and into the infrared region of the spectrum. An example of calculation results is shown in Figure 2.6 which is reproduced from the paper by Oldenburg *et al* [69]. A silica core with a size of

60 nm is covered by a shell layer of gold, the thickness of which is varied from 20 nm to 5 nm. The SPR peak is shifted to 1100 nm when the gold shell is only 5 nm thick (Figure 2.6).



**Figure 2.6** Calculated optical resonances of metal nanoshells (silica core, gold shell) over a range of core radius/shell thickness ratios. Reproduced from [69].

## 2.2.6 Synthesis of gold nanoparticles

Gold nanoparticles have been synthesised since ancient times for colouring materials and reported by Faraday for systematic investigation of the synthesis of gold colloids and their relation to colour [70]. Various methods have been developed aiming to grow gold nanoparticles with a desired size, monodispersion

and shape. The main routes include the citrate reduction method (first introduced by Turkevich [71] and later developed by Frens [72]) and the Brust-Schiffrin two-phase redox method [73]. Other methods include microwave, micelle, microbial, and sonolysis, which have been reviewed in [17]. These are summarised in Table 2.1.

### **2.2.7 Conclusion**

In this section gold nanoparticles have been reviewed which shows the intriguing optical properties of colouration owing to the surface plasmon resonance effects. The optical absorption property in the visible region is influenced by the particle size, shape and surrounding medium. Other properties (such as catalytic activity) and applications based on the properties of gold nanoparticles are discussed below in section 2.4, together with an introduction to nanocomposite films incorporated with gold nanoparticles.

**Table 2.1 Summary of synthetic routes to gold nanoparticles. Typical methods were listed as below. The standard deviation indicates the monodispersity of the particles. The smaller it is, the more monodispersed the particles are.**

| <b>Synthetic methods</b> | <b>Solvents</b>          | <b>Reducing/stabilising agents</b>                         | <b>Particle size (and standard deviation)</b>            | <b>Reference</b> |
|--------------------------|--------------------------|------------------------------------------------------------|----------------------------------------------------------|------------------|
| Citrate reduction        | water                    | trisodium citrate                                          | ca. 20 nm (12.5%)<br>16-147 nm                           | [71], [72]       |
| Brust-Schiffrin method   | toluene                  | sodium borohydride / dodecane thiol                        | 1.5 – 5.2 nm (26%)                                       | [73]             |
| Seeded growth            | water                    | ascorbic acid / cetyl trimethylammonium bromide (CTAB)     | 5-40 nm (40%)                                            | [74, 75]         |
| Microemulsion            | pentanol/ hexane/ water  | sodium hydroboride /cetyl trimethylammonium bromide (CTAB) | 7 nm (not reported)                                      | [76]             |
| Microwave                | water, methanol, ethanol | polyvinyl pyrrolidone (PVP)                                | 11 nm spherical,<br>30-50 nm polygonal<br>(not reported) | [77]             |
| Sonolysis                | water                    | sodium dodecylsulfate (SDS)                                | 10-20 nm (25%)                                           | [78]             |
| Solvothermal             | toluene                  | oleylamine                                                 | 2-3 nm (not reported)                                    | [79]             |

## 2.3 Transparent conductive oxides

### 2.3.1 Introduction

Transparent conductive oxides (TCOs) are a class of materials that display the remarkable combination of high electrical conductivity and optical transparency. This has formed the basis of many important technological applications, including flat panel displays, solar energy capture, energy efficient glass and other optoelectronic devices [6, 80].

The unique properties of high transparency and electrical conductivity are achieved by selecting a wide band gap oxide that has a high electron concentration by the introduction of native defects or substitutional dopants. Most of the useful oxide-based materials are *n*-type conductors that ideally have a wide band gap ( $>3\text{eV}$ ), the ability to be doped to degeneracy, and a conduction band shape that ensures the plasma absorption edge lies in the infrared range. Therefore the window of transparency in TCO materials (such as ITO,  $\text{SnO}_2\text{:F}$ ) extends from the band gap at the UV end to the plasma-absorption frequency at the IR end. The wavelength corresponding to the onset of infrared reflectance and the reflection intensity are dependent on the free carrier density and the effective mass of the carrier. There is also an additional effect with increasing carrier density leading to a widening of the TCO band gap attributed to the Burstein-Moss effect [81, 82].

Due to the increasing demand for high performance TCOs it is becoming more important to decrease the resistivity of TCO materials while maintaining their transparency. Comprehensive understanding of the fundamental inter-

relationships between conductivity and transparency is critical for further applications.

Gordon has reviewed the criteria for selection of TCOs and addressed the complex issues of balancing the material properties for particular applications [83]. Relevant criteria include optical and electrical performance, thermal stability and mechanical durability as well as compatible processing conditions (cost, deposition temperature, toxicity). In this review, he summarised that ZnO based TCOs (particularly ZnO:F) show the highest transparency ( $> 90\%$  of transmittance in the visible region) and are the easiest to etch, indicating their potential applications in photovoltaics. ITO still attains the highest conductivity (down to  $10^{-4} \Omega\cdot\text{cm}$ ), whereas SnO<sub>2</sub>:F suffers from a lower plasma frequency but has the benefit of lower production cost. It should be noted that due to the increasing demand for indium, films based around indium oxides are not considered as appropriate candidates for this work. However, in this thesis its use as a dopant (up to 5 at%) in ZnO as a bench mark material to be compared with other doped ZnO is considered. The most likely materials are fluorine doped tin oxide (SnO<sub>2</sub>:F) and aluminium doped zinc oxide (ZnO:Al) due to their overall cost-effectiveness. SnO<sub>2</sub> crystallises as a rutile structure, where the tin atoms are six coordinate and the oxygen atoms three coordinate, while ZnO crystallises mostly as a hexagonal wurzite structure. Through understanding the ability and constraints of the established materials we can choose suitable alternatives to meet specific application needs.

In the following sections, thin films of transparent conductive oxides will be reviewed in terms of their various deposition methods. Their fascinating optical

and electrical properties will be reported and the material properties that give rise to such behaviour will be investigated.

### **2.3.2 Deposition of TCO films**

The deposition technologies of TCO thin films have played an important role in the properties of the films; as the optical and electrical properties of the films strongly depend on their structure and morphology which is characteristically determined by the film deposition parameters. Various deposition technologies have been described in Section 2.1.1. Further details have been discussed in standard text books and reviewed by many researchers from time to time [25-29].

Spray pyrolysis is a relatively simple and cheap method which can be adopted for large-area substrate production at an industrial scale [84]. The sprayed droplet size and distribution, solution composition, gas and liquid flow rate, and substrate temperature, all determine the growth kinetics and hence the quality of the films. This technique has been reviewed previously in this chapter.  $\text{SnO}_2$  is one of the materials commonly prepared by spray pyrolysis and has been investigated by many workers [85, 86]. Different tin precursors are typically used including stannic chloride, tetrabutyl tin, diacetyl tin chloride. These are dissolved in the solvents such as ethanol, methanol and propanol due to their high volatility and low surface tension. Hydrochloride or acetic acid is added to produce crack-free films and improve the quality. Intentional doping with dopants of Sb [87-89], In [90] and F [91, 92] has been explored. It was reported that the addition of antimony in  $\text{SnO}_2$  films changes both the grain size and topography of the films [93]. Fluorine is an effective dopant due to its

comparable ionic radius with that of oxygen and therefore it substitutes the anionic site and acts as a donor. However, due to the volatility of fluorine, the F content is found to be much lower in as-deposited films compared to that in the starting solution.

Transparent conductive films of ZnO have also been successfully deposited by spray pyrolysis. Zinc acetate dissolved in a mixture of water and ethanol is often used as the spray solution, due to its high vapour pressure at a low temperature. A few drops of acetic acid are added to stabilise the solution against precipitation of zinc hydroxide. This helps produce optically transparent thin films of better quality. Romero *et al* compared the effects of zinc acetate and zinc chloride on the *c*-axis preferential orientation of ZnO [46]. Doping of ZnO films was also investigated not just because it improves the film electrical and optical properties, but also because it makes them highly stable. These dopants include Al [94, 95], Ga [96-98], F [99, 100], B[101, 102] and In [103-105]. Some researchers reported the effects of dopant concentration on the electrical properties. Lowest resistivity can be achieved when the doping ratio of [Al]/[Zn] is optimised. The optimised ratio, usually between 1 to 4 mol%, varies according to different reports in the literature. It can also be observed that, like undoped ZnO, the (002) plane is the most dominant growth plane, although the doping induces distortion in the lattice structure. Indium tin oxide prepared by a spray technique has also been investigated, exploring the structural properties as a function of thickness and substrate deposition temperature [106-108].

Chemical vapour deposition (CVD) is one of the most commonly used techniques in industry for thin film deposition which involves a reaction of gaseous species on a substrate. In this process, for example, vapour from a

volatile organometallic compound is transported to the substrate surface where it is decomposed through a heterogeneous reaction. This technique has been reviewed in detail by Choy (see [29] and the references therein). Ghoshtagore has studied the growth kinetics of SnO<sub>2</sub> films involving the reaction of SnCl<sub>4</sub> and (CH<sub>3</sub>)<sub>4</sub>Sn [109]. He also reported in his kinetic investigations that the deposition rate strongly depends on oxygen partial pressure, substrate temperature and stannic chloride partial pressure. Indium oxides doped by Sn or F have also been investigated using the CVD method [110-112]. Different precursors such as indium and tin acetylacetonates, indium 2-ethylhexanoate and tin chloride have been investigated and the effects of substrate temperatures (from 150-450 °C), atomic ratio of Sn:In and carrier gas flow rate on film properties have been explored. ZnO and doped ZnO films by CVD were also prepared [113-117]. Hu and Gordon have obtained aluminum doped zinc oxide films using diethylzinc, triethylaluminum and ethanol using atmospheric pressure CVD [117]. The films had resistivity as low as  $3.0 \times 10^{-4} \Omega\cdot\text{cm}$ , infrared reflectance close to 90% and visible transmission of 85%, which still attains the highest conductivity of ZnO:Al deposited by CVD ever reported.

Other chemical methods include sol-gel deposition [118-124], which involves immersion of a substrate in a chemical solution, withdrawal at a controlled rate and subsequent heat treatment. It should also be noted that thin film fabrication using nanoparticle deposition has been investigated. Recent studies [125-128] described specially prepared ITO films from a dispersion of ITO nanoparticles that were spin coated and subsequently annealed. The films obtained showed a resistivity comparable to that obtained by conventional

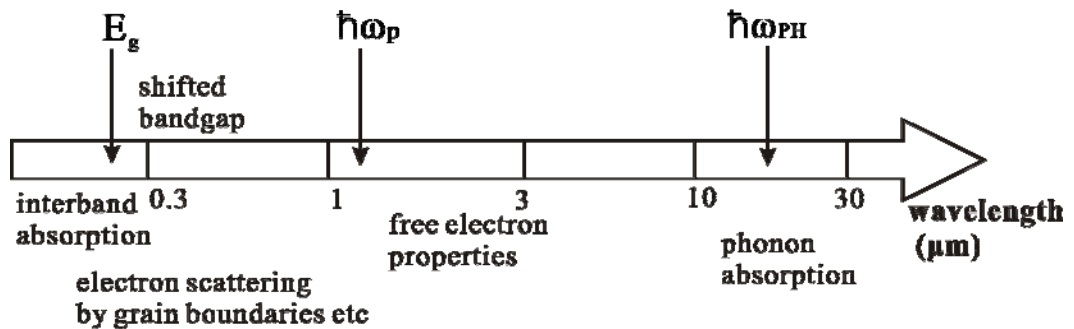
methods (about  $10^{-2} \Omega\cdot\text{cm}$ ) and encouraging IR reflectance has been demonstrated.

Physical methods, also called physical vapour deposition, include sputter deposition, pulse laser deposition and vacuum evaporation. These deposition techniques are widely used to make uniform thin film coatings on glass, polymers or metals. Vacuum or low pressure is usually required in the process. For example, in sputter deposition, a plasma is set up in a low pressure of inert or reactive gas, and energetic ions in the plasma bombard the target. The ions uniformly bombard the target and sputter atoms onto the substrate. In evaporation the raw material is heated in a vacuum so that a vapour from the material is transferred to the substrate at a sufficient rate. These methods have been adopted to deposit TCO films, e.g. ITO[129-132], ITO:ZnO[133, 134], ZnO:Ga[135-137], ZnO:Al[138-140], and ZnO:In[141]. Attempts have also been made to prepare ITO by radio frequency sputtering with the addition of trace Ag to increase conductivity [142, 143]. Such physical methods might give more uniform thin films, while it is not suitable for high-speed mass production.

### **2.3.3 Optical properties of TCO**

The electromagnetic properties of doped metal oxides have contributions from valence electrons, free electrons, and phonons. Their influence on the optical properties of the oxides plays a varying role over different wavelength regions. Hamberg and Granqvist reviewed and explained the optical properties at different wavelength regions taking ITO as an example [6, 144]. For ITO, the tin replaces some of the indium being quadra-valent which produces an excess of

conduction electrons leading to n-type conduction and formation of tin ions. Going from short to long wavelengths it is found that interband absorption is dominant at  $\lambda < 0.3 \mu\text{m}$  due to excitations across the fundamental band gap. The band gap is in fact shifted towards shorter wavelengths as a result of the free electrons entering states at the bottom of the conduction band of  $\text{In}_2\text{O}_3$ . The free electrons lead to the beginning of reflectance at a “plasma energy”, normally beyond  $1 \mu\text{m}$  in the near IR. The electrons are scattered by grain boundaries, impurities and lattice defects. Phonon effects come into play far into the thermal IR. For polycrystalline TCO films, the main scattering mechanisms for charge carriers are ionized impurity and neutral impurity scattering, thermal lattice vibration scattering and grain boundary scattering (see Figure 2.7).



**Figure 2.7 Electromagnetic properties and fundamental physical processes and mechanisms over the wavelength for  $\text{In}_2\text{O}_3\text{:Sn}$  films.  $E_g$  is fundamental semiconductor band gap,  $\hbar\omega_p$  is plasma energy, and  $\hbar\omega_{PH}$  is phonon energy. Reproduced from [144] by Hamberg and Granqvist.**

It is clear that the free electron is of great importance over a significant wavelength range. Within the free electron model, the optical properties of the TCO are described quite well by the simple Drude model but with a strongly

frequency-dependent electron scattering term for Fermi surface electrons [144]. To investigate the influence of free carrier concentration over the control of transmission and reflection in the infra-red, the following Drude model was set up as

$$\varepsilon = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\frac{1}{\tau_0})}$$

with  $\omega_p$ , the plasma frequency and  $\tau_0$ , the relaxation time, as

$$\omega_p = \frac{N_e e^2}{m_e \varepsilon_0}, \quad \tau_0 = \frac{m_e}{\rho_p N_e e^2}.$$

where  $N_e$  is the free carrier concentration,  $\rho_p$  the resistivity,  $m_e$  the effective mass. The carrier concentration not only determines the plasma wavelength in accordance with the equation above, but also governs the maximum achievable reflectivity in the infrared region. Therefore, increasing  $N_e$  will increase the plasma frequency and blue-shift the plasma reflectance edge.

Also, there are some other models to describe the electronic excitation, such as band gap transitions and interband transitions. For the band gap transitions, the OJL model by O'Leary, Johnson and Lim was proposed to describe the parabolic densities of states below and above the energy gap [145]. The interband transitions into the conduction band are represented by a simplified harmonic oscillator.

Hamberg and Granqvist calculated the optical properties of ITO deposited on a substrate with refractive index of 1.5 and investigated the influence of carrier concentration  $N_e$  and thickness [144]. They reported a band gap widening, onset of reflectance at a blue-shifted wavelength and a gradual disappearance of phonon induced structure due to the increase of  $N_e$ . In practice, the optical

properties of TCO thin films strongly depend on the deposition parameters, microstructure, level of doping and growth technique.

### 2.3.4 Electrical properties of TCO

Numerous investigations have been made on the electrical properties of TCO films to understand the conduction phenomenon involved [146-148]. Current understanding of conductivity in TCOs is based on a classical theory of charge transport in metals associated with the optical properties of the materials through the density of charge carrier and effective mass. In classical theory, free charge carriers can move under an applied field. The current generated is defined as

$$I_A = V/R_Q$$

where for a uniform electric field ( $E$ ) across  $L$ , gives

$$V = EL$$

the resistance  $R_Q$  is related to the length ( $L$ ), cross-sectional area ( $A$ ) and resistivity ( $\rho$ ) by

$$R_Q = \rho L/A$$

and the current is related to the number of electrons per unit volume ( $N_e$ ), the drift velocity ( $v_d$ ), the electron charge ( $e$ ), and the cross section area using

$$I_A = N_e e A v_d$$

In a crystalline lattice the electrons are not “free” and indeed are subjected to other forces which in fact alter their movement. For example, collision with lattice ions actually retards electron movement. The drift velocity is therefore related to the average time between collisions ( $\tau$ ) and defined as

$$v_d = (eE/m_e) \cdot \tau$$

and therefore,

$$\rho = m_e / (N_e e^2 \tau)$$

Two other terms are also derived from the above equations as

$$\sigma_e = 1/\rho = N_e e^2 \tau / m_e$$

$$\mu_e = e \tau / m_e$$

where  $\sigma_e$  is conductivity and  $\mu_e$  is carrier mobility. Therefore

$$\sigma_e = N_e e \mu_e$$

The above equations relate the conductivity to the number of charge carriers and their mobility. In the dielectric constant function expression (see Section 2.3.3), the plasma resonance frequency for free carrier conductors will increase with carrier density and decreasing free carrier mass; placing a limit on the optimum region of transparency associated with a particular conductivity.

The expression for the mobility of charge carriers depends on the relaxation time, which further depends on the drift velocity and the mean free path of the charge carriers. These parameters in turn depend on the mechanism by which the carriers are scattered by the lattice imperfections. Various electron scattering mechanisms are involved in TCOs, including lattice scattering, ionised impurity scattering, electron-electron scattering and grain boundary scattering. These have been described in the literature [149].

Optimised TCO thin films of  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO),  $\text{ZnO}:\text{Al}$  (AZO), and  $\text{ZnO}:\text{Ga}$  (GZO) usually present a resistivity of  $10^{-4} \Omega\cdot\text{cm}$ . Recent investigations of ITO films have demonstrated resistivity between  $7.2$  and  $8 \times 10^{-5} \Omega\cdot\text{cm}$  with free carrier concentration as high as  $2.5 \times 10^{21} \text{ cm}^{-3}$  [129, 150-154]. AZO films with  $\rho \approx 8.5 \times 10^{-5} \Omega\cdot\text{cm}$  [155] and GZO with  $\rho \approx 8.1 \times 10^{-5} \Omega\cdot\text{cm}$  [156] have also been reported. It should be noted that physical deposition methods, especially pulsed

laser deposition, are commonly employed to produce films with low resistivity. However an alternative method suitable for the larger area production of films on an industrial scale should be developed and the challenge is to produce TCO films with comparable electrical properties to those produced by smaller scale physical methods.

### **2.3.5 Application of TCO**

The unique combined electrical and optical properties of TCO films have seen many applications in the industries of optoelectronics, architecture and emerging renewable energy [83, 157, 158]. The dominant application for TCOs are flat panel displays (FPDs) as well as photovoltaics (PVs), followed by architectural building products.

**Low-emissivity windows in buildings.** One of the major applications of TCOs is in the spectrally selective products. Low-emissivity coating on window glass is used to improve energy efficiency because the free electrons reflect infrared radiation for wavelengths longer than the plasma wavelength. Fluorine-doped tin oxides have been widely produced in industry for low-E glass as it displays suitable infrared reflection with excellent durability and low cost. Double-glazed windows have been widely used for exceptionally good thermal insulation by sandwiching two low-E glass panes with a gap that is evacuated or filled with inert gas [159, 160].

**Thin film solar cells.** Solar cells are used to convert solar radiation to electricity. Recently TCO materials have received intense research attention in order to develop a suitable surface electrode for solar cell products [161, 162]. Such electrodes need a high optical transmittance for sufficient transport of light

into the active stack and a good electrical conductivity to attain a low transport loss of the generated electricity. For solar cells it is important to increase cell efficiency through optimisation of the light trapping effect to elongate the path length of the light through the active materials. This can be achieved by roughening the surface, for example using wet etching of sputter deposited ZnO:Al films [163, 164].

**Flat panel displays (FPDs).** FPDs are used in a wide variety of applications, from instrument panels for aircrafts and automobiles to consumer electronics. TCOs are employed in these devices as transparent conducting electrodes displaying each pixel (or larger zone) on the display screen. ITO (and potentially ZnO) is advantageous over other TCO materials, such as  $\text{SnO}_2$ , due to the fact that it can be easily patterned by etching and deposited at lower temperatures for thermally sensitive organic dyes and flexible substrate. It should be noted that various TCOs have been deposited on flexible substrates (such as polyethylene terephthalate, PET) by magnetron sputtering or pulsed laser deposition. This can be extended to broader applications such as flexible displays and other organic electronics [165-167].

Other applications include solar collectors which use photo-thermal conversion of solar energy to produce hot fluid or hot gas [168, 169], electromagnetic shielding, touch panel control, defrosting windows, oven windows [83], anodes for organic light emitting diodes [170, 171] to name a few diverse applications reported in the literature.

### **2.3.6 Conclusion**

Transparent conducting oxides have been reviewed through understanding the intrinsic dielectric properties and the corresponding optical and electrical properties. Their intriguing properties combining optical transparency, infrared reflectivity and electrical conductivity have lead to wide applications especially in the optoelectronics and energy related sectors. Such unique properties are strongly influenced by the free carrier concentration and carrier mobility. Careful selection of TCO materials according to the required characteristics such as optical transparency, electrical conductivity and cost should be considered. Among these materials, ZnO, SnO<sub>2</sub> and their doped oxides are of intense interest due to their much lower cost compared to In<sub>2</sub>O<sub>3</sub> based materials.

Various deposition techniques including chemical deposition and physical deposition methods have been reviewed and contrasted. Using chemical methods, especially the spray pyrolysis deposition technique, has the advantage of low cost for industrial production, although it is still challenging to achieve the optical and electrical properties that are comparable to that obtained by physical methods. It would be a compromise to produce TCO thin films with low cost by sacrificing part of the optical and electrical performance.

## **2.4 Noble metal incorporated nanocomposite thin films**

### **2.4.1 Introduction**

Nanocomposite materials based on noble metal nanoparticles (NPs, guest) within metal oxide matrices (host) have been an intense research area due to their

fascinating functional properties that can be tailored by the particle size, shape and surrounding materials. The choice of appropriate host metal oxide has received significant attention and initiates investigation into their merits such as optical transparency, insulating property, thermal stability and a weak interaction with the embedded nanoparticles [172-174]. Nanocomposites comprising host materials and embedded metal particles therefore present the combined functionalities of both phases and can be carefully selected to exploit the desired properties of either material. The review below will cover the preparation methods, properties and applications.

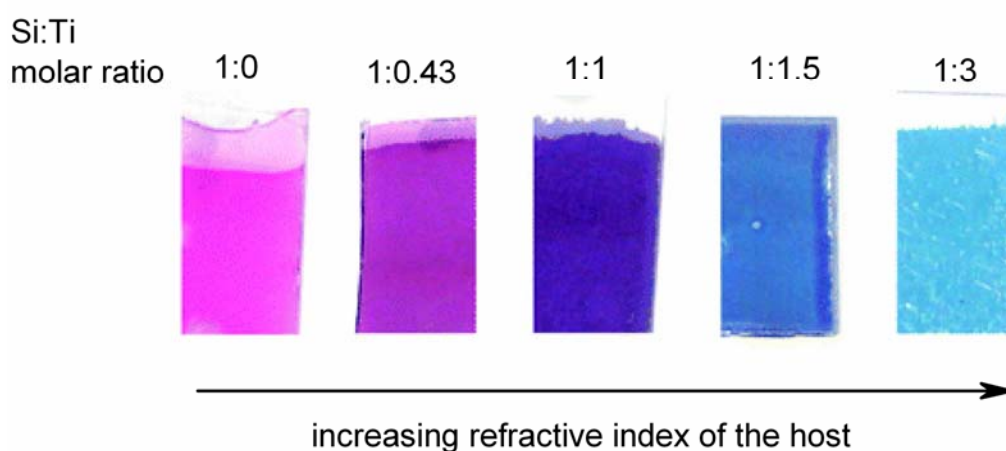
#### **2.4.2 Methods of nanocomposite film production**

Deposition of composite thin films is an essential issue for successful incorporation of the guest nanoparticles into the host, due to the nature of the two-component system. A homogeneous dispersion of nanoparticles entrapped by the host material is desired. Several strategies for the production of nanocomposite thin films incorporating metal nanoparticles into different metal oxide hosts have been developed. Among these methods, one scheme is to synthesise the host matrix with an addition of nanoparticles (or the metal ions as the precursor of nanoparticles) in a second step, or to some extent a layer-by-layer process in which the deposition of metal nanoparticles is followed by the deposition of host materials acting as the entrapping matrix [17]. Such a multi-step process does however increase the complexity and cost, which is unattractive for industrial production. Another scheme is the deposition of a composite thin film in a single step, where the precursors of noble metal nanoparticles and host matrix are premixed as a single source. The single-step route embraces the merits

of simplicity and cost-effectiveness, which can also produce a more homogeneous composite film through control of the precursor properties, though the preparation of a stable one-pot solution is still challenging. Many deposition methods have been applied to produce composite thin films, such as magnetron sputtering [175], Chemical Vapour Deposition (CVD) [176, 177] and sol-gel processing [178, 179]. The conventional physical deposition methods are constrained by their operating environment (normally vacuum) and correspondingly their cost; while chemical processes (such as spray pyrolysis) are more flexible and scalable for large area applications.

Sol-gel processing has been widely used in the preparation of composite films due to its versatility and simplicity. Spin coating and dip coating are common techniques and particularly used for metal particles embedded in the host materials. In this method, noble metal nanoparticles were either formed ex-situ and then embedded into the host materials or formed in-situ from metal ions followed by post-deposition heat treatment. Medda *et al* reported gold doped  $\text{SiO}_2/\text{TiO}_2$  films by dip coating [16]. They noted that the strong optical absorption peak due to the surface plasmon resonance can be shifted in position by controlling the refractive index of the host material by varying the  $\text{SiO}_2:\text{TiO}_2$  composition. This leads to different coloured coatings on glass substrates (see Figure 2.8). Work by Yang *et al* reported a spin coating process to fabricate  $\text{Au}/\text{SiO}_2$  using an aqueous precursor solution containing gold nanoparticles and tetraethyl orthosilicate with post-treatment annealing or UV irradiation [180]. Deposition of  $\text{Au}/\text{TiO}_2$  films by spin coating was also reported by Buso *et al* using surface functionalised gold nanoparticles compatible with titanium butoxide in ethanol. The optical properties were investigated for films with different gold

content and thermal treatment. It has been shown that in the process using preformed gold nanoparticles the functionalisation of gold nanoparticles is critical to help them be accommodated into the host material precursors, forming a stable solution and hence resulting in thin films with fine particle dispersion. Other sol-gel examples include Ag nanoparticles in Al doped ZnO [181], Ag/TiO<sub>2</sub> [182], Cu doped silica [183, 184] and Au/ZrO<sub>2</sub> [185]. It should be noted that the sol-gel process, due to the fact that it is a room temperature deposition method, usually requires multi-step treatment such as post-deposition annealing to remove excess solvents and organic ligands. In addition, repeated deposition cycles may be required to achieve the desired thickness. These steps are time-consuming and also increase the complexity. Cracks are commonly observed in such films.



**Figure 2.8 Photo showing Au nanoparticle doped coloured films on soda-lime-silica glass substrates heat treated at 500 °C. The position of Au SPR was tailored by changing the refractive index of the matrix. Adapted from [16] by Medda et al and reproduced by permission of The Royal Society of Chemistry.**

Magnetron sputtering, one of the major physical deposition methods has also been used to produce metal nanoparticle incorporated composite films. Many researchers have reported using this technique for deposition of (Ag, Au or Pt)/TiO<sub>2</sub> [186-188], (Ag, Au or Pt)/SiO<sub>2</sub> [189-191]. Such composite films usually have a multilayer structure. Recent work by Liao *et al* reported the deposition of gold in different oxides of ZnO, TiO<sub>2</sub> and SiO<sub>2</sub> using multi-target magnetron sputtering [192]. The multi-layered structures with gold layers are well separated by the metal oxide layers in the as-deposited films, but were destroyed after thermal treatment leaving large gold particles formed with a broad size distribution in the host. This is probably due to the migration of gold layers into the ZnO or TiO<sub>2</sub> layers.

Another physical method for layer-by-layer deposition is pulsed laser deposition. Recent work has involved incorporation of gold nanoparticles into SiO<sub>2</sub>/TiO<sub>2</sub> hosts [193, 194], silver and gold nanoparticles into amorphous ZrO<sub>2</sub> [195], and copper nanoparticles embedded into amorphous Al<sub>2</sub>O<sub>3</sub> [196]. It should be noted that these physical methods are usually carried out in a vacuum environment

A hybrid process combining radio-frequency sputtering and sol-gel approach was also reported by Armelao *et al* to prepare Au/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> films [11, 197, 198]. The size distribution of embedded particles can be well tailored. A novel structure of gold nanotubes was also formed using an anodised aluminium oxide template by sputtering.

Aerosol-assisted chemical vapour deposition (AACVD) is a novel technique for deposition of multicomponent films [28]. It is capable of depositing a uniform thin film with noble metal nanoparticles and non-volatile precursors in a

single step. Palgrave and Parkin reported their recent work on co-deposition of gold nanoparticles and semiconductor host materials ( $\text{WO}_3$ ,  $\text{TiO}_2$ ) in a single step by AACVD. Preformed gold nanoparticles [199] or  $\text{HAuCl}_4$  [200] as a gold precursor could be used and the films showed SPR red-shift and IR reflection upon annealing. Such a technique was extended by other work in their group using hybrid aerosol-assisted and atmospheric pressure CVD of gold doped vanadium oxide for thermochromic thin films leading to applications for energy efficiency [201-203].

Mulvaney *et al* reported the use of core-shell nanoparticles for construction of functional composite films [12, 204]. The films were deposited through self-assembly of silica coated gold nanoparticles on glass. The pre-coated shell layer serves to increase colloidal stability, aid dispersion in various media and alter the optical properties. The self-assembled core-shell films showed different colours through transmission from blue to purple to pink for silica layer thickness increasing from 1.5 nm to 17.5 nm. It was shown that a highly ordered structure can be achieved by careful control of the self-assembly deposition.

It should be noted that there are few reports on the gold NP embedded composite films prepared by spray pyrolysis. There are some restrictions imposed such as the preparation of a stable one-pot solution and possible thermophoretic problems. It would be challenging to produce the composite film by development of the spray pyrolysis technique.

### **2.4.3 Properties and applications of noble metal incorporated nanocomposite films**

The unique characteristics arising from the combination of incorporated noble metal nanoparticles and host materials, include the linear and non-linear optical properties, conductivity, catalytic activity, antibacterial properties and electrochromism. These properties are also dependent on the size and structure of the nanoparticles in addition to the intrinsic nature of the elements or compounds.

#### **2.4.3.1 Optical properties**

The most striking optical feature of noble metal doped composite films is the colour induced by the surface plasmon resonance (SPR) effect of noble metals whose size is reduced to the nano-scale. This has been discussed previously in Section 2.2. The resonant frequency and intensity of the SPR band for such nanocomposite films are dependent on the characteristics of the nanoparticles as well as the nature of the surrounding medium. Such properties have been used for the design and development of optical devices with controllable non-linear properties [205-210]. In the glass industry the production of protective and durable thin film coatings with noble metal nanoparticles has been developed for applications requiring coloured coatings and potentially for solar control [211]. Such tinted coatings can be used to replace body-tinted glass obtained by the conventional colouring technique which is commercially expensive and time consuming.

Another optical feature for noble metals is their photoluminescence property which was first reported by Mooradian in 1969 [212]. Enhancement of luminescence was observed for molecules absorbed on rough metal surface.

Nanoparticles of noble metal doped nanocomposites showing great enhancement of local field near the surface plasmon resonance peak would influence the fluorescence of the materials absorbed on or capped by the metal particles [213-215]. It was also found that two-phonon absorption in noble metals, which gives visible light emission, was associated with this enhancement [216]. The amplification is due to a resonant coupling with localised surface plasmons. Liao *et al* investigated the photoluminescence of gold: oxide composite multilayered films with gold sandwiched by oxide layers such as SiO<sub>2</sub>, ZnO or TiO<sub>2</sub> [192]. It was found that the SPR property of the composite films had a great influence on the photoluminescence position but little effect on the intensity. Basak *et al* found that thin films of poly(methyl methacrylate) (PMMA) incorporating silver nanoparticles showed a red-shift in the photoluminescence depending on the silver particle size [217]. Such optical properties of noble metals nanoparticles have led to applications for sensing and imaging techniques for diagnostics in the biotechnology industry. Specific examples relate to surface enhanced Raman scattering (SERS) in signal sensing [218-220]. Water soluble gold “nanodots” were also used for new biological labels due to their fluorescence in the spectrum from the visible to near infrared region [221].

#### **2.4.3.2 Catalytic properties**

Bulk gold is one of the least reactive metals, while nanoparticulate gold shows unique activity under mild conditions even at ambient temperature. When ultra-fine gold nanoparticles are deposited on metal oxides (which are regarded as supports), such as TiO<sub>2</sub>, CeO<sub>2</sub> and so on, their chemistry changes drastically and becomes significantly more active. The initial study by Haruta investigated the

adsorption properties and reactivity of gold in terms of their size dependency [222, 223]. It was found that the catalytic properties are significantly dependent on their supports and the dispersion of the particles as well. It is assumed that the gold-metal oxide perimeter interface acts as a site for activation of at least one of the reactants such as oxygen. Gold nanoparticles of a size less than 5 nm supported on base metal oxides or carbon are active catalysts showing high reactivity in CO oxidation, NO<sub>x</sub> reduction and water gas shift reaction [224-230]. Companies such as BASF, Johnson Matthey and 3M have interests in developing commercial applications for gold catalysts.

In addition, noble metal nanoparticles are used as catalytically active additives in semiconductor gas sensors as supported catalysts in order to increase both the selectivity and sensitivity of sensors [231, 232].

#### **2.4.3.3 Antibacterial property**

Silver in particular has shown interesting properties in antibacterial application such as wound dressing, ear piercing, plasters [233, 234]. Commercial antibacterial applications using silver ions (silver nitrates) rely on the diffusion of silver ions into solution which is not directly related to a photocatalytic mechanism. Page *et al* have shown that silver doped TiO<sub>2</sub> anatase films made by dip-coating demonstrated higher photocatalytic and antibacterial activity than parent titania hosts [182]. Such coatings have potential applications in a hospital environment. Zaporojtchenko *et al* developed a nanocomposite coating of silver and gold nanoparticle incorporated PTFE by co-sputtering, which showed enhanced antibacterial activity by addition of gold upon silver [235].

#### **2.4.3.4 Other properties and applications**

Noble metal nanoparticles have also been used in the semiconductor industry for reducing resistivity, providing freely connected conductive pathways by using embedded particles in thin films [236, 237].

Au/TiO<sub>2</sub> has been employed in photoelectrochemical solar cells due to the photocatalytic properties of TiO<sub>2</sub> that are further enhanced by gold dispersion, see for example dye sensitised nanocrystalline TiO<sub>2</sub> solar cells [238-240]. A three-fold enhancement in photocurrent generation has been achieved upon modification of TiO<sub>2</sub> films with Au nanoparticles. This improved photoelectrochemical performance is explained on the basis of improved interfacial charge-transfer kinetics of the TiO<sub>2</sub>/Au composite film.

#### **2.4.4 Conclusion**

Nanocomposite films incorporating noble metal nanoparticles into metal oxide host materials have been reviewed as a novel class of materials. The various preparation methods offer a versatile approach to such functional thin films, from those that are already commercially available, e.g. magnetron sputtering and conventional CVD to those newly developed e.g. AACVD, as well as hybrid methods. Such films present the combined and often enhanced properties of both guest particles and host materials, thus creating some intriguing features which lead to a number of products e.g. optical devices, coloured coatings, catalysts, antibacterial coatings, to name a few of the applications in the industries of electronics, glass manufacturing and biology. The properties of composite films can be tailored by careful control of particle size, shape and size distribution in addition to the intrinsic properties of the host metal oxide.

## **CHAPTER 3**

# **EXPERIMENTAL AND CHARACTERISATION TECHNIQUES**

### **3.1 Introduction**

This chapter describes the experimental methods for thin film deposition on a glass substrate using the spray pyrolysis technique, the apparatus set-up and operating parameters are explained. Analytical techniques employed in the characterisation of the films are also discussed in terms of their fundamental operating principles.

### **3.2 Apparatus set-up for spray deposition**

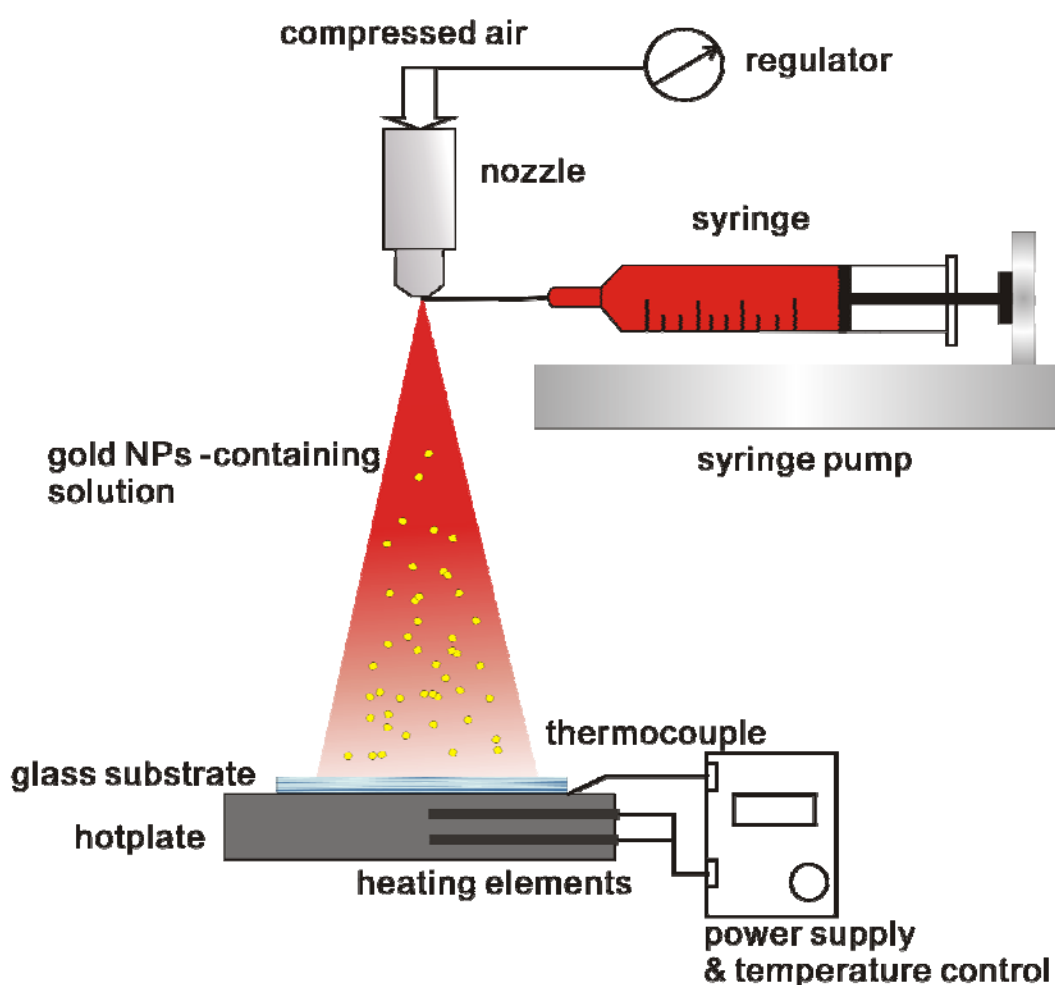
The laboratory-scale spray deposition system has been set up at the Begbroke Science Park, Oxford. It has been successfully used for depositing composite layers for dielectric devices [50, 52]. It comprises three major parts: the syringe pump as the injection system, the spraying nozzle with a needle delivery and the hotplate (Figure 3.1).

Basically, the precursor liquid contained in the syringe is first injected by the syringe pump (World Precision Instruments, Model Aladdin-1000 Programmable Syringe Pump) and after passing through the PVC tube is

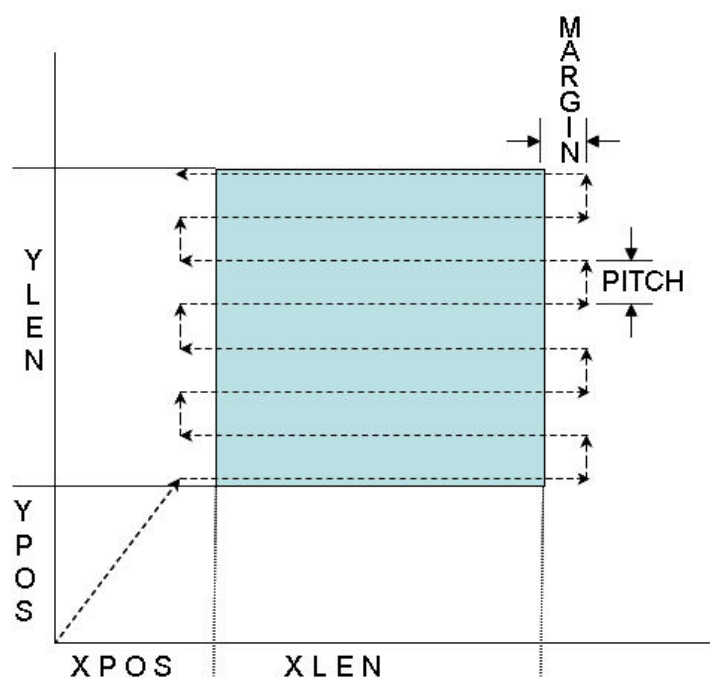
projected from the needle which is positioned underneath the nozzle driven by compressed air. The atomisation of the liquid droplets by the compressed air from the nozzle happens at the meeting point of the needle tip and the nozzle, which creates a sprayed aerosol that impacts onto the substrate heated by the hotplate. The hotplate is inserted with five cartridges of heating elements with a total maximum power of 2500 W supplied by Watlow Ltd. The hotplate is placed on an X-Y raster scanning system (Time and Precision Industries Ltd.). The scan pattern and parameters are controlled by a programmable controller (Compumotor RP240 controller) and summarised in the following diagram (Figure 3.2). The injected liquid flow rate (in the unit of ml min) is controlled by the syringe pump, the compressed air pressure (in the unit of psi) is controlled by a mass flow regulator and the table motion is controlled by the Compumotor RP240 controller. The hotplate temperature is controlled and monitored by a thermocouple and Eurotherm controlling unit. The sprayed droplet size and distribution can be controlled by variation of compressed air pressure and solution feed rate. The parameters for scan pattern as illustrated in Figure 3.2 were determined to allow a stable and uniform spray on the glass substrates.

In the following experiments, spray deposition was carried out under typical process conditions which were varied according to the specific properties of solutions in terms of evaporation rate and viscosity. In brief, the precursor solutions were injected by the syringe pump under a constant flow rate ( $1\text{--}2\text{ ml}\cdot\text{min}^{-1}$ ) and spread out by the compressed air at a pressure of 20-30 psi (138-206 kPa). The atomised droplets were sprayed onto Pilkington float glass substrates ( $50\text{ mm} \times 50\text{ mm} \times 4\text{ mm}$  or  $100\text{ mm} \times 100\text{ mm} \times 4\text{ mm}$  with a  $\text{SiO}_2$  barrier layer on top). Substrates were heated to the range of 150-600 °C. The

coated glass samples received further heat treatment (annealing) in some cases. They are placed in a furnace in air (or H<sub>2</sub> in Ar when specified) and heated up at a ramp rate of 5 °C/minute up to a temperature ranged 200-600 °C. The samples were then held for 30-60 minutes to remove any remaining organic ligands and further enhance the decomposition of the precursor.



**Figure 3.1** Schematic illustration of spray deposition system, comprising nozzle, syringe and X-Y table with hotplate. The substrate being coated is placed on the hotplate. Note the position of the nozzle and the needle tip. The nozzle and needle component is positioned 10 cm above the hotplate to attain fine and homogeneous droplets.



**Figure 3.2 Raster scan pattern for coating glass substrate. The parameters are set as XLEN = 100 mm, YLEN = 100 mm, XPOS = 0, YPOS = 0, MARGIN = 10 mm, PITCH = 10 mm, COAT SPEED = 70 mm/s. Note the over-scan at the substrate edges and the relatively high coating speed to enhance uniformity.**

### 3.3 Analytical techniques

#### 3.3.1 UV-visible-NIR spectroscopy

UV-visible-NIR spectroscopy was used to measure the intensity of the light passing through (e.g. colloidal solution) or reflected by the sample (e.g. thin films on glass). Depending on the light source which usually consists of more than one component a wide spectrum range from ultraviolet through visible to near infrared can be achieved. The spectra of transmittance (ratio of transmitted light

to incident light), reflectance (ratio of reflected light to incident light) and absorbance (negative logarithm of transmittance) indicated the optical properties of the particles in the solution or metal oxide host as well as the properties of TCO in the near infra red.

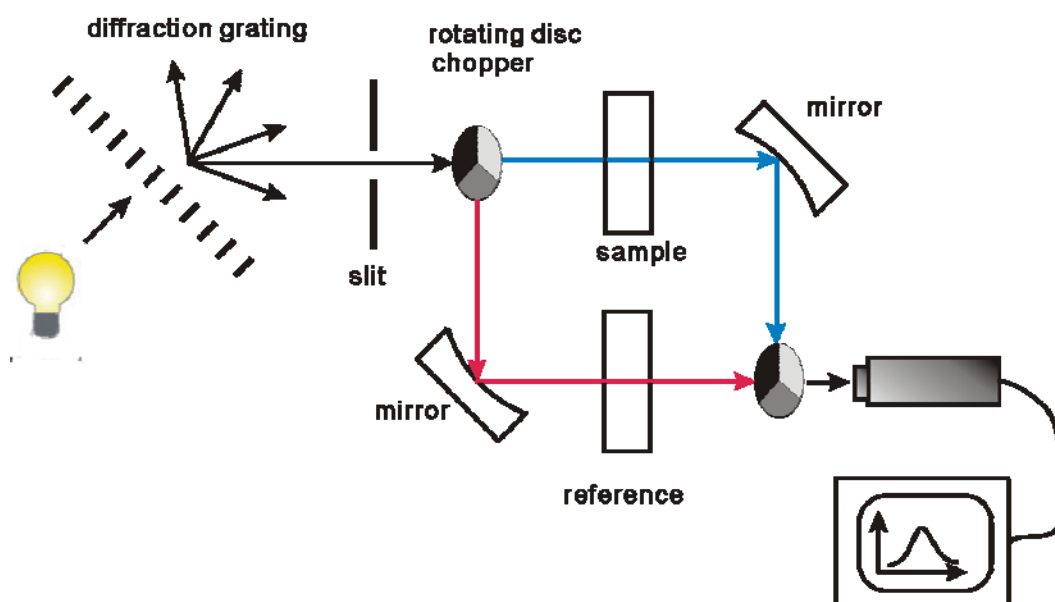
A UV-visible-NIR spectrometer usually consists of a combined light source, monochromator, light diffraction grating, beam splitting system, sample holders and detector. A diagram explaining the schematic configuration is shown in Figure 3.3. The light source of various wavelengths is diffracted by the grating monochromator and split into beams at a specific wavelength. The slit only allows light of a very narrow range of wavelengths into the rest of the spectrometer. The rotating disc is used as a chopper to transmit or reflect the monochromatic light of a specific wavelength into two beams. One of the beams passes through the sample (either a solution in a cuvette or a thin film coating on glass) and the other passes through a reference. The comparison between the intensity of the two beams can be defined as

$$A = -\log_{10} (I/I_0)$$

where  $A$  is absorbance,  $I_0$  is the intensity of incident light and  $I$  is of transmitted light.

In this work, a Varian Cary 5000 UV-visible-NIR dual-beam spectrometer was used to measure the transmittance and reflectance spectra of the thin films. This instrument has a wide scan range from 200 nm up to 3300 nm. The spectrometer was operated with a scanning speed of 10 nm/s and a resolution of 1 nm/step approximately over the full range. When measuring the absorbance of gold colloids the solution was contained in a plastic cuvette. When measuring the

transmittance and reflectance of the thin films the samples were placed in a clamped holder.



**Figure 3.3 Schematic diagram of the double beam spectrometer. A typical double-beam spectrometer contains a diffraction grating, beam splitting system and a detector [241].**

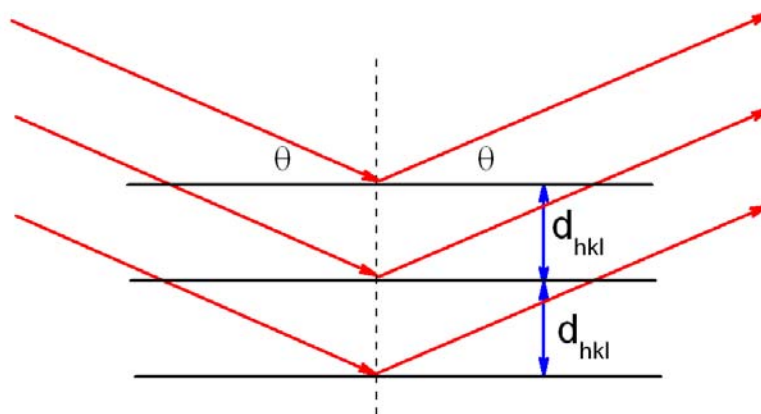
### 3.3.2 X-Ray Diffraction (XRD) analysis

XRD is a technique for examination of crystalline materials, typically powders and thin films. Compared to other techniques (such as EDX and TEM), XRD can be used to differentiate between phases having the same or very similar chemical composition but different crystal structure (cubic or tetragonal  $\text{BaTiO}_3$ , for example). XRD can also determine orientation for textured structure and analyse crystallite size and strains. It usually obtains an average value from a great number of individual grains rather than a particular local grain.

X-rays, generated due to the collision of electrons with a Cu target, interact and are scattered by the crystal lattice. The scattered X-ray radiation can be well detected only at given incident angles at which the reflected beams from the crystal planes are added by interference [242]. According to Bragg's law, the reflected beams give detectable maxima only when their differences in the distance travelled are equal to the integral multiple of wavelength ( $\lambda$ ). A radiation with wavelength  $\lambda$  is reflected from a set of planes with d-spacing only at conditions, when

$$n \lambda = 2 d_{hkl} \sin \theta$$

where  $n$  is an integer,  $hkl$  is the Miller index of the plane which defines the d-spacing. The intensities of the reflections are determined by the distribution of the electrons in the crystal lattice (which can also be referred as the unit cell). The intensity maximum at a particular angle is related to a particular plane spacing and therefore to the crystal structure of the thin film samples. XRD is therefore used to provide information on the crystalline phase presented, preferred crystal orientation and crystal size.

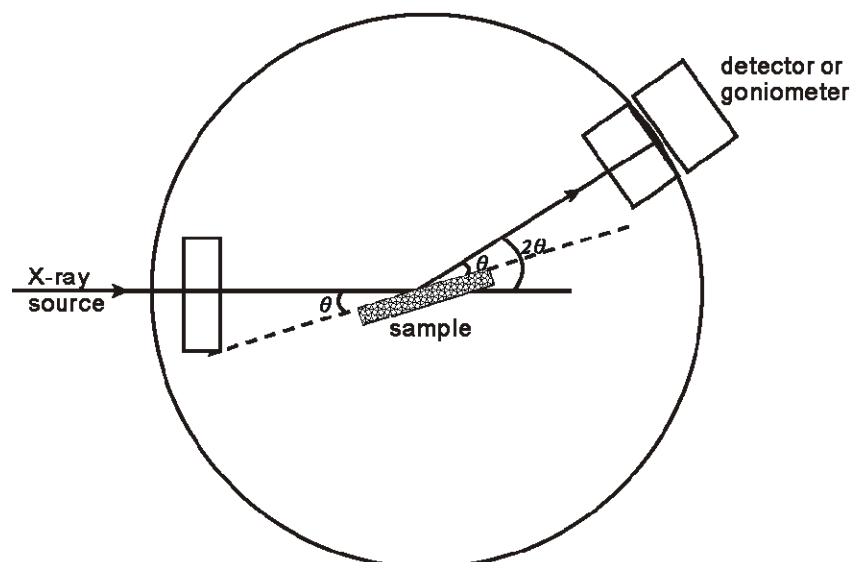


**Figure 3.4 Diffraction of X-ray on the crystal lattice according to Bragg's law. ( $d$  is interplanar distance,  $\theta$  is Bragg's angle).**

In this thesis XRD measurement was undertaken using a Philips PANalytical X-ray diffractometer (Model PW1820/00). The diffractometer comprises a  $\theta$ - $2\theta$  vertical goniometer where the X-ray tube is stationary, the sample moves by the angle  $\theta$  and the detector simultaneously moves by the angle  $2\theta$  (see Figure 3.5). The X-ray source is Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) with Ni foil to filter out other wavelengths of X-rays. The goniometer moves through  $20^\circ - 70^\circ$  ( $2\theta$ ) with respect to the X-ray source at a step size of  $0.5^\circ$  and scanning duration of 2-15 seconds per step depending on the properties of the sample. It should be noted that only crystallites with reflecting planes ( $h, k, l$ ) which are aligned parallel to the sample surface are detected in a  $\theta - 2\theta$  diffractometer and contribute to the reflected intensities. A broad peak in the background is usually indicative of non-crystalline materials (e.g. glass substrate). To identify the crystalline phases present in the sample, the peak positions in the XRD pattern are compared to the known compounds on the database of International Centre for Diffraction Data (ICCD). In this database the peaks at specific position of  $2\theta$  are labelled with ( $hkl$ ) values and correspond to a particular d-spacing, allowing identification of the various phases.

### **3.3.3 Scanning Electron Microscopy (SEM)**

SEM is an electron microscopy technique used to scan the sample surface with a high energy electron beam. These electrons interact with the atoms of the sample and produce signals detected by the machine to reveal the information about the sample's surface topography and composition.



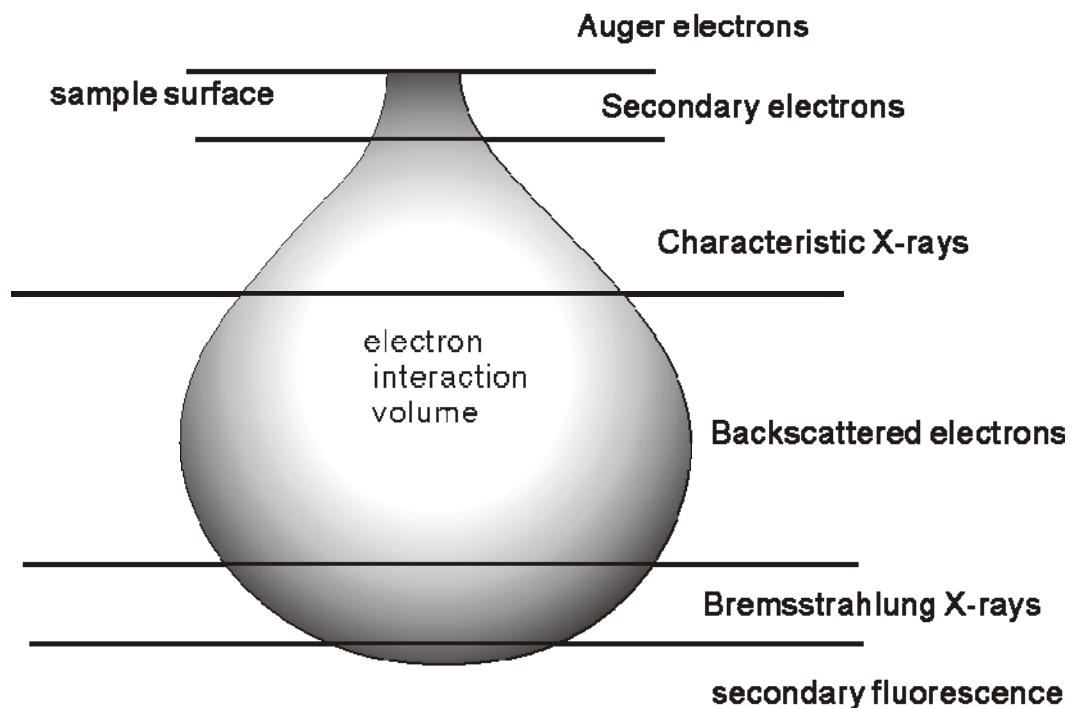
**Figure 3.5 Schematic configuration of XRD which consists of an X-ray source, a sample holder and a detector [243].**

Electrons, which can be generated by three types of electron guns (tungsten cathode,  $\text{LaB}_6$  cathode and field emission gun), interact with the specimen and result in different signals. Electron beam interactions with the specimen can be divided into two categories: elastic interactions and inelastic interactions. Elastic scattering occurs when the energy of the scattered electron is the same as the energy of the incident electron. There is no energy transferred from the beam into the specimen. Compared to elastic scattering that causes the beam to diffuse into the sample, inelastic scattering results when the incident electron loses energy in its interaction with the sample. Signals resulting from inelastic interactions include secondary electrons, characteristic X-rays, continuum X-rays, Auger electrons and cathodoluminescence radiation. Figure 3.6 shows the interaction volume produced by an electron beam focused into a sample. The shape of the interaction volume depends on the density of material, the beam energy and the tilt angle. The size of the interaction volume strongly depends on

the beam energy. The depth of electron penetration by the interaction volume is therefore a function of its angle of incidence, the magnitude of its current, the accelerating voltage and the average atomic number ( $Z$ ) of the sample. Of these, the accelerating voltage and the sample material density play the largest role in determining the depth of electron interaction. The penetration depth, which generally ranges around 1-5  $\mu\text{m}$ , can be calculated approximately using the following equation [244],

$$r(\mu\text{m}) = \frac{2.76 \times 10^{-2} \cdot A E_0^{1.67}}{\rho \cdot Z^{0.89}}$$

where  $\rho$  is the density of the material (in the unit of  $\text{g/cm}^3$ ),  $Z$  is the atomic number,  $A$  the atomic mass and  $E_0$  the accelerating voltage (kV).

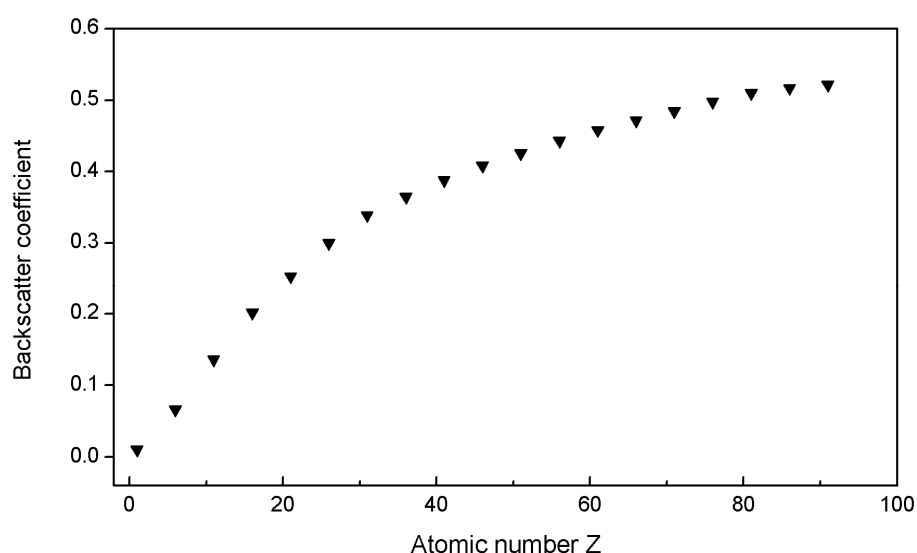


**Figure 3.6 Illustrative diagram of electron beam interaction volume.**

According to the types of signals produced by an SEM, there are two major modes of operation in this research: secondary electron mode and backscattered electron mode.

Secondary electrons are produced in the sample by direct excitation with the incident beam. The kinetic energy of the secondary electrons is usually low, and the electrons are easily captured by the ionised atoms in the specimen. The mean free path length of the secondary electrons in many materials is approximately 1 nm. Therefore, only those electrons originating from only a few nanometres of the specimen surface can escape to be detected as secondary electrons. This volume is very small compared to backscattered electrons and X-rays. Therefore secondary electrons are highly dependent on the morphology of the specimen surface; i.e. a highly curved surface reflects brighter in the secondary electron imaging mode.

Backscattered electrons are the high-energy electrons that are reflected or back-scattered out of the specimen by elastic scattering interaction with the specimen atoms. Approximately 30% of the incident electrons escape the sample by scattering. The intensity of the backscattered electrons strongly depends on the atomic number of the specimen; i.e. scattering is more likely to happen at regions exhibiting higher electron density. Regions with heavy elements backscatter more electrons than regions of light elements, and therefore these regions show up in the backscattered electron imaging mode. For this reason, the backscattered electron mode is used to distinguish different elements or phases in composite materials.



**Figure 3.7 Variation of the backscatter coefficient as a function of atomic number (Z). Backscatter coefficient is defined as the ratio of the number of backscattered electrons against incident electrons. Adapted from [245].**

Energy dispersive X-ray spectroscopy (EDX) is a technique for identifying the elemental composition of the specimen. In the EDX analysis, an elastic electron interaction occurs by exciting an electron in an inner shell and ejecting it from the shell forming an electron hole. The electron in the outer shell with higher energy may fill the hole and release the energy difference between the outer shell and inner shell in the form of X-rays. As the energy of the X-rays are characteristic of the difference in energy between the shells which relates to the atomic structure, an energy dispersive spectrum to measure the elemental composition of the specimen can be obtained by detecting the number and energy of the X-rays emitted from the specimen. It should be noted that many elements have overlapping peaks and therefore the analysis may not be effective. For inhomogeneous and rough samples the X-rays emitted do not completely escape

from the samples which reduces the accuracy of the analysis. EDX is usually used for qualitative analysis.

In this thesis SEM analysis was performed on a JEOL 6500F using voltages between 10 - 15 kV at a beam current of about 70  $\mu$ A. For those samples which are not conductive (i.e. Au/TiO<sub>2</sub>, Au/ZnO) a thin coating of platinum (1.5 nm) or carbon is typically applied before SEM analysis to enhance conductivity and reduce charging which causes image distortion.

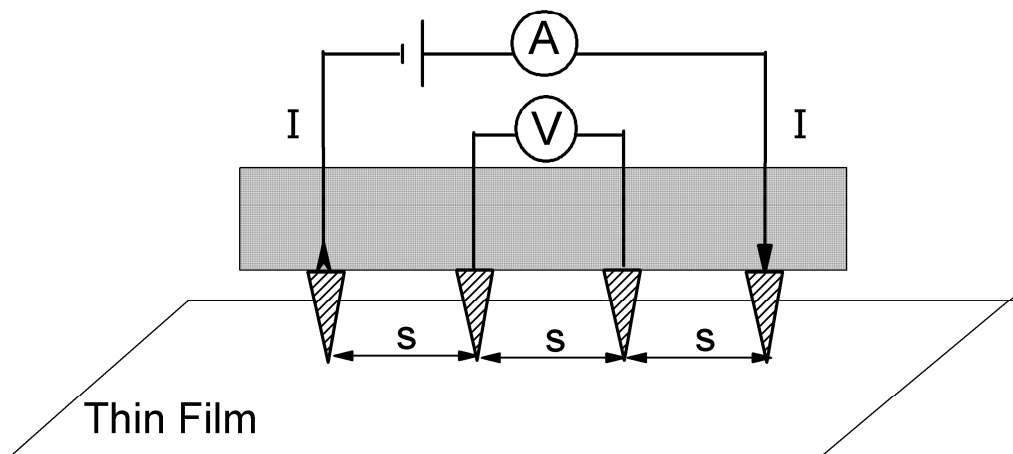
### **3.3.4 Transmission Electron Microscopy (TEM)**

TEM is an electron microscopy technique where a beam of electrons is transmitted through a thin specimen, interacting with the specimen when passing through. The electrons, produced from the source of a tungsten filament or field emission gun in a vacuum chamber, are accelerated and focused by a system of magnetic lenses. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light and X-rays: 200 kV electrons have a wavelength of 0.025 Angstrom. The electron beam then has sufficient energy to pass through the sample material. The specially prepared sample is a very thin (less than 100nm) slice of material. An objective lens provides the formation of either an image or diffraction pattern of the specimen. The electron intensity distribution behind the specimen is magnified with a three or four stage lens system and then focussed to a phosphor screen, CCD or film and an image is produced. Where the sample has less density, more electrons get through and the image is brighter. A darker image is produced in areas where the sample is denser and therefore fewer electrons pass through.

In this work TEM was used for the characterisation of gold NPs. The specimens were prepared by loading gold colloid droplets onto the copper grids coated with a holey carbon film (Agar Scientific) and subjected to imaging.

### 3.3.5 Four-point Probe Measurement

Four point probe based instruments use a long established technique to measure the resistivity of a thin film material. The four point probe set-up used here consists of four equally spaced tungsten metal tips with finite radius. Each tip is spring-loaded to ensure sufficient electrical contact and minimize sample damage during probing. The tip spacing,  $S$ , is about 1 mm. The average resistance of a thin layer is measured by passing a fixed valued of current through the outside two points of the probe and measuring the voltage across the inside two points (see schematic configuration in Figure 3.8).



**Figure 3.8 Schematic configuration of four point probe measurement.**

The electrical resistance,  $R$ , of a rectangular-shaped sample is given by [149]

$$R = \rho \cdot (l/wt)$$

where  $\rho$  is the resistivity and  $l$ ,  $w$ ,  $t$  are the length, width and thickness of the sample. When  $l = w$ , the equation becomes

$$R = \rho \cdot t = R_s$$

The sheet resistance,  $R_s$  is defined as the resistance of a square of the film area between opposite edges and is independent of the size of this square.

If the conducting film thickness is less than 40% of the spacing and the edges of the film are more than 4 times the spacing distance from the measurement point, then the average resistance of the film or the sheet resistance is given by [246]

$$R_s = (\pi/\ln 2) \cdot (V/I) = 4.53 \cdot (V/I)$$

Therefore one can calculate the resistivity if the thickness of a film is known, or one may obtain the thickness if the resistivity is known.

The accuracy of the sheet resistance measured by the four-point-probe technique is restricted by the surface contact between the tips and the film, the electrical connection and measuring resolution of the electronic equipment.

### **3.3.6 Film thickness measurement using profiler**

Veeco Dektak 6M Bench-Top Surface Profiler was used to measure the film thickness. A diamond tipped stylus is moved vertically in contact with a sample and then moved laterally across the sample for a specified distance. The size of the stylus is 12.5  $\mu\text{m}$  and the tracking force of the stylus is programmable down to 1 milligram. The vertical movement of the diamond stylus generates an

analogue signal which is converted into a digital signal and recorded simultaneously with the scanning. The signal variation reveals the topographical structure of the surface. This instrument can measure the film thicknesses from 5 nm up to 262  $\mu\text{m}$  with a thickness resolution down to 0.1 nm across the length of up to 15 cm. Usually a shorter length range (1-1.5 cm) is measured for accuracy.

### **3.4 Conclusion**

In this chapter the apparatus for spray pyrolysis deposition has been described which is simple and versatile. By optimising the compressed air pressure and solution feed rate and by programming the X-Y table motion, a uniform thin film can be produced.

To characterise the properties of the thin films obtained, various techniques are used. UV-visible-NIR spectroscopy is used to characterise the optical property in the range from 250 nm up to 3300 nm and four-point probe is used to characterise the electrical resistivity. XRD is used to identify the phases of materials in the films. Electron microscopy, especially SEM, is used to analyse the surface morphology as well as the composition and particle distribution in the host material.

## **CHAPTER 4**

# **SPRAY DEPOSITION OF TRANSPARENT CONDUCTIVE OXIDE THIN FILMS**

### **4.1 Introduction**

This chapter describes the deposition of Transparent Conductive Oxide (TCO) thin films by spray pyrolysis. Two widely studied TCO materials,  $\text{SnO}_2$  and  $\text{ZnO}$ , have been investigated by modifying experimental conditions with different precursors. Dopants were introduced to improve the conductivity and control the optical performance in the infrared. Fluorine was investigated as  $\text{SnO}_2$  dopant and three trivalent dopants for  $\text{ZnO}$ , B, Al and In, all of which are Group III elements, were investigated for comparison. It should be noted that In was investigated only as a benchmark dopant (up to 5 mol%) to be compared with Al. The electrical and optical properties as well as the microstructure have been characterised. The experimental conditions, including substrate temperature, dopant property and dopant concentration were altered and their influence on the thin film properties has been studied.

## **4.2 Spray deposition of SnO<sub>2</sub> and SnO<sub>2</sub>:F**

### **4.2.1 Precursor for SnO<sub>2</sub>**

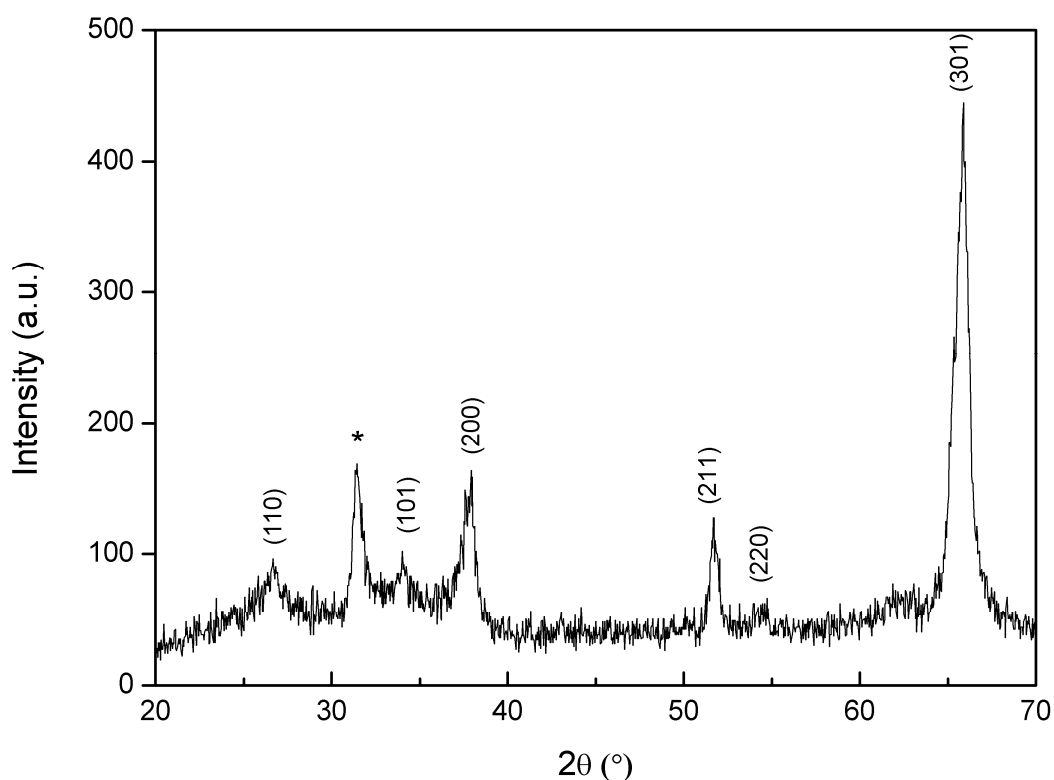
Deposition of SnO<sub>2</sub> thin films was carried out using monobutyltin trichloride (MBTC). MBTC has been used for producing tin oxide for infrared reflective glass coatings [247, 248]. Due to its organic (butyl) and inorganic (chloride) ligands MBTC is very soluble in a water-miscible solvent such as methanol or ethanol. This allows a wide range of Sn compound concentration in the solution as well as allowing mixing with other organic or inorganic dopant precursors such as trifluoroacetic acid (for F dopant) and auric acid (for gold nanoparticles). The high concentration of MBTC may allow rapid deposition of relatively thick films (150-1000 nm) at high volume glass throughput under certain conditions.

### **4.2.2 Spray deposition of SnO<sub>2</sub>**

The starting solution was prepared by dissolving 20 ml MBTC (0.12 mol) in 20 ml ethanol to obtain a solution of 3 mol·L<sup>-1</sup> concentration. The solution appeared pale yellow and clear without precipitation. Spray deposition was carried out at a constant solution feed rate of 1 ml·min<sup>-1</sup> and compressed air pressure of 25 psi (172.37 kPa). A range of different substrate temperatures between 200 and 500 °C were used. It was found that the electrical, optical and structural properties are dependent on the substrate temperature. At a substrate temperature below 300 °C, the deposited films displayed very high resistance (more than 2000 MΩ which is out of the range measured by the two-point-probe method), which is probably because the precursor was not fully decomposed and

oxidised, resulting in an amorphous film of SnO<sub>2</sub>. At temperatures above 300 °C the resistance of the as-deposited SnO<sub>2</sub> films decreased dramatically down to 1 kΩ/□ or less. Interference fringes were observed for the films deposited at above 350 °C, which is due to the varying film thickness. The thickness of the films deposited within a constant time period was found to increase with increasing substrate temperature, indicating a higher deposition rate at a higher substrate temperature. Using the MBTC precursor at this level of concentration a high deposition rate (200 nm/min) was achieved.

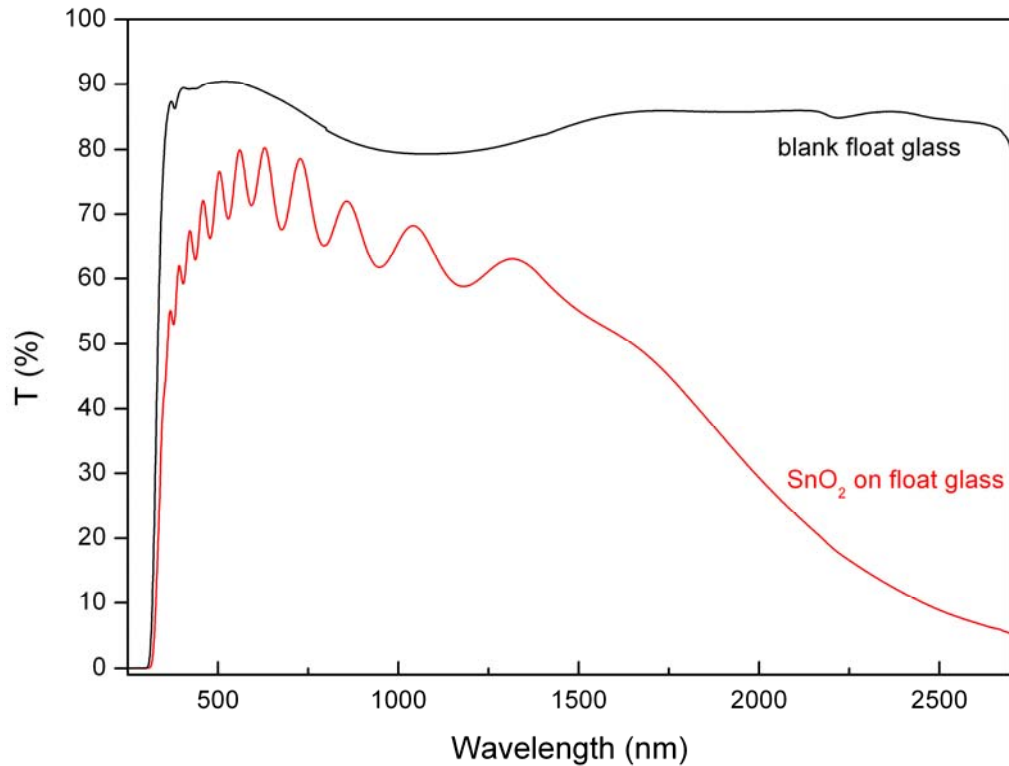
Figure 4.1 shows the X-ray diffraction pattern of a typical SnO<sub>2</sub> film deposited at 500 °C which has a sheet resistance of 50 Ω/□. The phases of cassiterite SnO<sub>2</sub> (110), (200) and (211) were identified (International Centre for Diffraction Data (ICCD) Reference Code 00-046-1088) [249]. The strongest diffraction peak is for the (301) plane rather than the (200) orientation. Similar examples in the literature have reported that the peak intensity of the (301) plane increased for increased film thickness [250]. There is a peak at 31.6° which is difficult to identify, but possibly attributed from Sn<sub>2</sub>O<sub>3</sub> (ICCD Reference Code 00-025-1259). It is indicative of the formation of oxygen-deficient SnO<sub>2</sub> which can also explain the reduced electrical resistivity of the film.



**Figure 4.1 Typical XRD pattern of a SnO<sub>2</sub> thin film deposited by spray pyrolysis using MBTC precursor at 500 °C. Note the presence of diffraction peaks for planes (110), (101), (200), (211), (220) and (301). \* Note there is a peak that is difficult to identified but possibly attributed to Sn<sub>2</sub>O<sub>3</sub> (ICCD Reference Code 00-025-1259).**

An optical transmission spectrum of the same film was measured and is presented in Figure 4.2 together with the corresponding spectrum for a blank float glass. An average transmittance of 78% in the visible region (350-700 nm) was obtained with the expected interference fringes. The bandgap, calculated from the absorption edge, is 3.81 eV. The transmittance in the infrared region is significantly attenuated from approximately 50% at 1500 nm to just 10% at 2500 nm. The reduction of transmission is probably due to the free carrier reflection of the infrared radiation due to oxygen vacancies formed in SnO<sub>2</sub> during the spray

deposition at a high substrate temperature (500 °C). It has also been reported that chlorine produces unintentional doping in SnO<sub>2</sub> films prepared from chlorine containing precursors such as SnCl<sub>4</sub>, C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub>. The chlorine content strongly decreases as the deposition temperature increases [251-253].



**Figure 4.2 UV-visible-NIR transmittance spectra of blank float glass and spray deposited SnO<sub>2</sub> thin film. Note the interference fringes and reduced IR transmission compared to the corresponding spectra for the blank float glass.**

#### **4.2.3 Spray deposition of SnO<sub>2</sub>:F**

Deposition of SnO<sub>2</sub>:F was carried out using MBTC as a precursor for tin oxide and trifluoroacetic acid as a precursor for the fluorine dopant. The starting solution was prepared with 10 ml MBTC (0.06 mol) and 0.083 ml trifluoroacetic

acid ( $13 \text{ mol}\cdot\text{L}^{-1}$ ) which were mixed and dissolved in 40 ml of ethanol to make a stock solution comprising  $1.5 \text{ mol}\cdot\text{L}^{-1}$  MBTC with atomic ratio of  $\text{F}:\text{Sn} = 0.05$ . The as-prepared solution was spray deposited onto float glass substrates using experimental conditions with a precursor feed rate of  $1 \text{ ml}\cdot\text{min}^{-1}$  and atomising air pressure of 25 psi (172 kPa). The substrate temperatures were varied from 350 to 550 °C.

Similar to the deposition of undoped  $\text{SnO}_2$  thin films, transparent and conductive thin films with interference fringes were obtained when deposited above 350 °C.

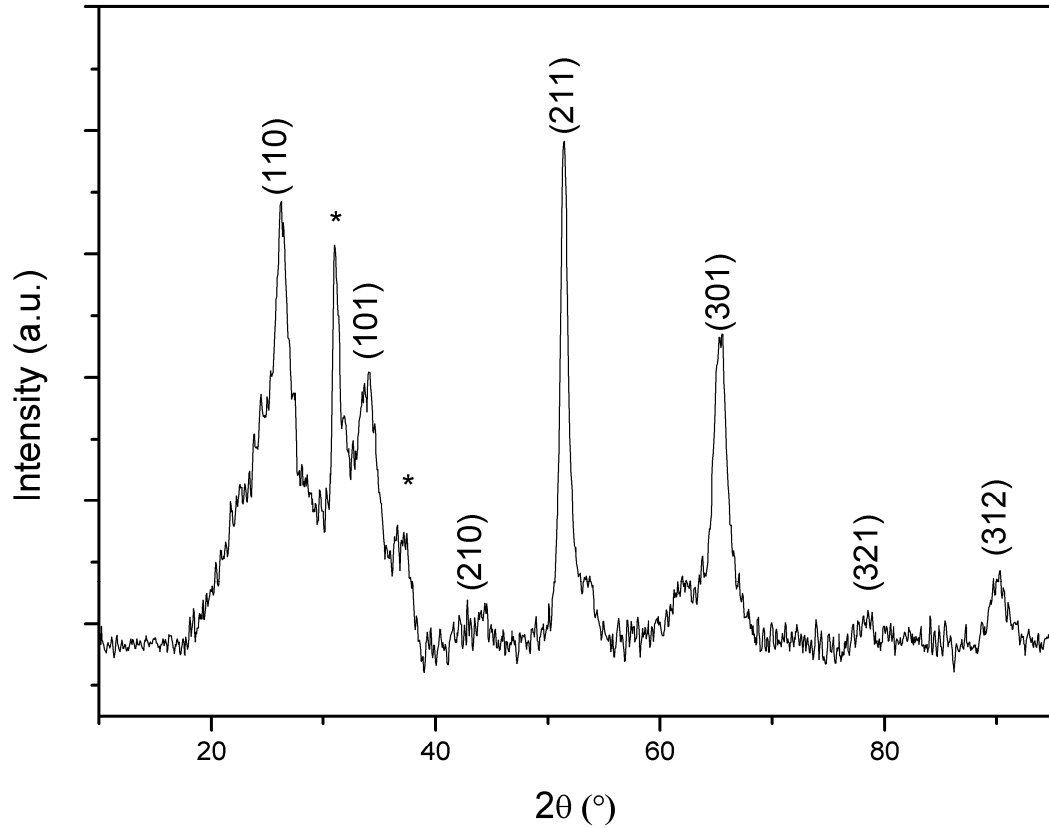
Powder X-ray diffraction indicates the presence of cassiterite  $\text{SnO}_2$  with phases (110), (101), (211) and (301) without additional peaks corresponding to fluorine (Figure 4.3). The crystallite size can be calculated according to Scherrer equation,

$$d = \frac{K\lambda}{B\cos\theta}$$

where  $K$  is the shape factor which is related to the particular instrument used and typically between 0.9 and 1,  $\lambda$  is the wavelength of incident X-ray,  $B$  is the full width at half maximum (FWHM) in radians and  $\theta$  is the Bragg angle. It should be noted that the equation is limited to nano-scale particles or films and  $B$  is influenced by not only crystallite size but also the lattice strain. Therefore, using the peak (211) in Figure 4.3 and  $K = 0.9$ ,  $\lambda = 0.154 \text{ nm}$ ,  $B = 0.82^\circ = 0.0143$ ,  $\theta = 25.73^\circ$ , the crystallite size is calculated as 10.77 nm. This is smaller than observed in the SEM images in Figure 4.4.

There are peaks at  $31^\circ$  and  $37^\circ$  which are difficult to identified but possibly attributed from  $\text{Sn}_2\text{O}_3$  (ICCD Reference Code 00-025-1259). It is again

indicative of the formation of oxygen-deficient  $\text{SnO}_2$  which can also explain the reduced electrical resistivity of the film.



**Figure 4.3 XRD pattern of a  $\text{SnO}_2\text{:F}$  thin film by spray deposition using MBTC and trifluoroacetic acid at 500 °C. Note the presence of diffraction peaks for planes (110), (101), (211), (301), (321) and (312). \* Note the peaks that are difficult to identified but possibly attributed from  $\text{Sn}_2\text{O}_3$  (ICCD Reference Code 00-025-1259).**

Four-point-probe measurement shows that the sheet resistance for  $\text{SnO}_2$  films varied with deposition temperature. It was observed that the films deposited at a temperature of 550 °C have the sheet resistance as low as  $25 \, \Omega/\square$ , while films deposited at 350 °C have a higher sheet resistance of up to  $3.5 \, \text{k}\Omega/\square$ .

The reduced sheet resistance with an increase in substrate temperature might be related to the crystal grains that grow to a larger size, causing a decrease in grain boundary scattering and hence improved electron mobility.

Figure 4.4 shows the scanning electron micrograph of SnO<sub>2</sub>:F thin films deposited at 450 °C. The surface of the film was imaged on an estimated scale of  $13 \times 10 \mu\text{m}^2$ . The high contrast of the crystal grains indicates a rough surface. The film consists of small crystallites with grain size of about 50 nm, along with larger grains of up to 500 nm, which are assumed to be over grown from the small grains. Cross-sectional SEM shows the thickness is about 700 nm. It has been reported that the thickness and grain size of the film are closely correlated [254, 255]. It is assumed that the larger grain size and correspondingly larger grain boundary contact surface would decrease the grain boundary potential leading to lower resistivity. Antonaia [254] also reported that the carrier mobility of the F doped SnO<sub>2</sub> film increased with grain size of the microcrystallite, which is another mechanism that might contribute to the decreased resistivity.

The resistivity of this film, according to the relationship between sheet resistance and thickness,  $\rho = R_s \cdot t$ , is therefore calculated as  $1.5 \times 10^{-3} \Omega\cdot\text{cm}$ , which is comparable to that of the films prepared by spray pyrolysis as  $1.03 \times 10^{-3} \Omega\cdot\text{cm}$  reported in [255] and  $6.4 \times 10^{-3} \Omega\cdot\text{cm}$  in [256]. It is also lower than that obtained by sol-gel method ( $\sim 24 \times 10^{-3} \Omega\cdot\text{cm}$ ) by Ray et al [257] and even comparable to that obtained by CVD ( $0.8\text{-}1.8 \times 10^{-3} \Omega\cdot\text{cm}$  [258]) and sputtering ( $1.63 \times 10^{-3} \Omega\cdot\text{cm}$  [259]).



**Figure 4.4 SEM image of spray deposited SnO<sub>2</sub>. The scale bar is 1 μm. The film consists of small crystallites with grain size of about 50 nm, along with larger grains of up to 500 nm. The contrast from the crystalline grains indicates a rough surface area.**

#### **4.2.4 Discussion**

**Growth mechanism.** Smears et al and Siefert et al have studied the growth mechanism of SnO<sub>2</sub> deposition by spray pyrolysis [260, 261]. They proposed a pseudo-CVD process that at an intermediate temperature (300-450 °C) the solvent evaporates before reaching the substrate. As a consequence the solid precipitate melts and evaporates without decomposition and diffuses to the substrate surface, leading to an adherent film. In this study the precursor for SnO<sub>2</sub>, butyltin trichloride, was used in the CVD process [248, 262]. Its relatively low boiling point (227 °C) compared to its decomposition temperature (300 °C)

and fast growth rate also suggest the process using butyltin trichloride is a good candidate precursor for the CVD process.

**Comparison between doped and non-doped SnO<sub>2</sub>.** Fluorine is a most effective dopant due to its comparable ionic radius with that of oxygen (F<sup>-</sup>: 1.33 Å, O<sup>2-</sup>: 1.40 Å), it therefore has a tendency to substitute the anionic sites and act as a donor. The F doping can be achieved by adding trifluoroacetic acid with various concentrations. It should be noted that the actual atomic ratio F:Sn present in the films is usually lower by a factor of 10 than that of the solution, as reported in the literature [263]. This is due to the volatile nature of fluorine compounds.

Non-doped (0 mol% F) and doped SnO<sub>2</sub> thin films (5 mol% F and 10 mol% F in the starting solution) were deposited at different temperatures and the sheet resistance measured. Results are shown in Table 4.. For non-doped SnO<sub>2</sub>, the sheet resistance decreased dramatically from over 600 kΩ/□ for substrates below 300 °C down to 20 kΩ/□ at 450 °C and 80 Ω/□ at 550 °C. A decrease in sheet resistance of doped SnO<sub>2</sub> with increased substrate temperature was also observed; from 1-3 k Ω/□ at 350 °C to 20 Ω/□ at 550 °C. The decreased sheet resistance is probably due to the enhanced crystallinity of SnO<sub>2</sub> films at an elevated substrate temperature. These observations also confirm that doping with fluorine further contributes to a decrease in sheet resistance which is due to O<sup>2-</sup> ion substitution with F<sup>-</sup>. The thickness of the 5 mol% F doped SnO<sub>2</sub> film deposited at 550 °C is measured as 900 nm, while the other SnO<sub>2</sub> films were deposited under similar conditions in terms of solution feed rate and atomising air pressure, indicating similar thickness.

**Table 4.1 Sheet resistance of SnO<sub>2</sub>:F thin films deposited at different substrate temperature with different F doping concentration in the starting solution.**

| SnO <sub>2</sub> : 0 mol% F |                          | SnO <sub>2</sub> : 5 mol% F |                          | SnO <sub>2</sub> : 10 mol% F |                          |
|-----------------------------|--------------------------|-----------------------------|--------------------------|------------------------------|--------------------------|
| T <sub>sub</sub> (°C)       | R <sub>sheet</sub> (Ω/□) | T <sub>sub</sub> (°C)       | R <sub>sheet</sub> (Ω/□) | T <sub>sub</sub> (°C)        | R <sub>sheet</sub> (Ω/□) |
| 350                         | 600 ×10 <sup>3</sup>     | 350                         | 3 ×10 <sup>3</sup>       | 350                          | 1.1 ×10 <sup>3</sup>     |
| 450                         | 20 ×10 <sup>3</sup>      | 450                         | 20                       | 450                          | 20                       |
| 550                         | 50                       | 550                         | 30                       | 550                          | 27                       |

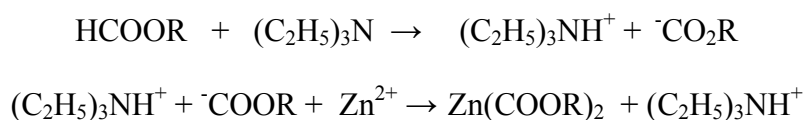
### 4.3 Spray deposition of ZnO and doped ZnO thin films

#### 4.3.1 Spray deposition of ZnO thin film

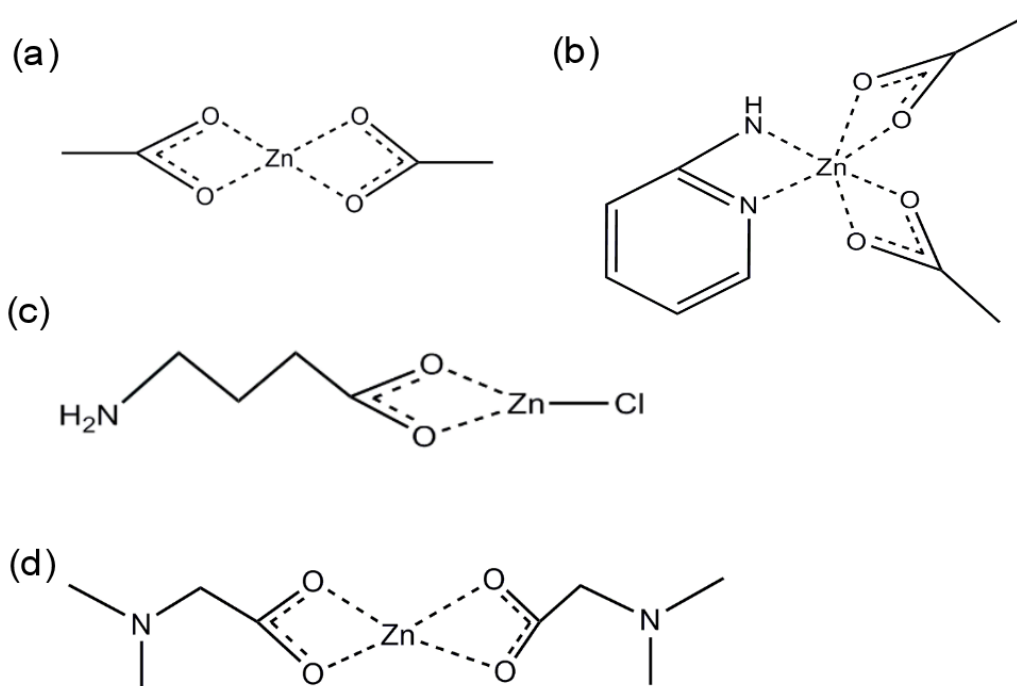
##### 4.3.1.1 Precursors for ZnO

Spray pyrolysis deposition of ZnO thin films were investigated using a series of zinc compounds with different ligands. These zinc compounds, mainly carboxylates, include conventional zinc acetate, zinc acetylacetonate, and those newly developed by Johnson Matthey (i.e. zinc bipyridine acetate, zinc aminobutyrate and zinc dimethylglycine, see Figure 4.5). The ligands have influence in the physical and chemical properties of the zinc compounds in terms of solubility in water and organic solvents, thermal decomposition temperature and reactivity. ZnO thin films deposited from these precursors are investigated by comparison of their crystallinity and optical properties.

The reaction scheme for the preparation of newly developed zinc carboxylates was reported by K. Cassar at Johnson Matthey [264]. Basically the synthetic route is to react  $\text{ZnCl}_2$  (or  $\text{Zn}(\text{NO}_3)_2$ ) with deprotonated carboxylic ligands to form zinc carboxylate precipitates in the solution.



The carboxylic acids used were dimethylglycine and 4-aminobutanoic acid. The precipitate solids were then filtered, washed and dried under low pressure at 40 °C. To prepare aqueous solutions of zinc carboxylate the compounds were dissolved in water with the addition of nitric acid to accelerate the dissolution.



**Figure 4.5** Molecular structure of (a) Zinc acetate; and other zinc carboxylates developed by Johnson Matthey [264] (b) zinc 2-aminopyridine diacetate; (c) zinc 4-aminobutanoate; (d) zinc N,N-dimethylglycine. Note  $\text{Zn}^{2+}$  is coordinated by  $\text{O}^{2-}$  which is bonded to different ligands.

By changing the ligands that coordinate with the zinc atom it is possible to change the properties of the zinc compound formed, such as its solubility in water and organic solvents as well as thermal decomposition temperature [264]. These precursors have in fact been developed so as to be dissolved in water and therefore to be compatible with further planned objectives that are part of the large industrial project; although organic solvents might also be an option in the future. Here these precursors were prepared in a water solution to make a  $0.1 \text{ mol}\cdot\text{L}^{-1}$  concentration and the film deposition experiments were conducted. A range of precursors have been evaluated aiming to find the best candidate for producing crystalline and transparent conductive ZnO suitable for control of its infrared properties.

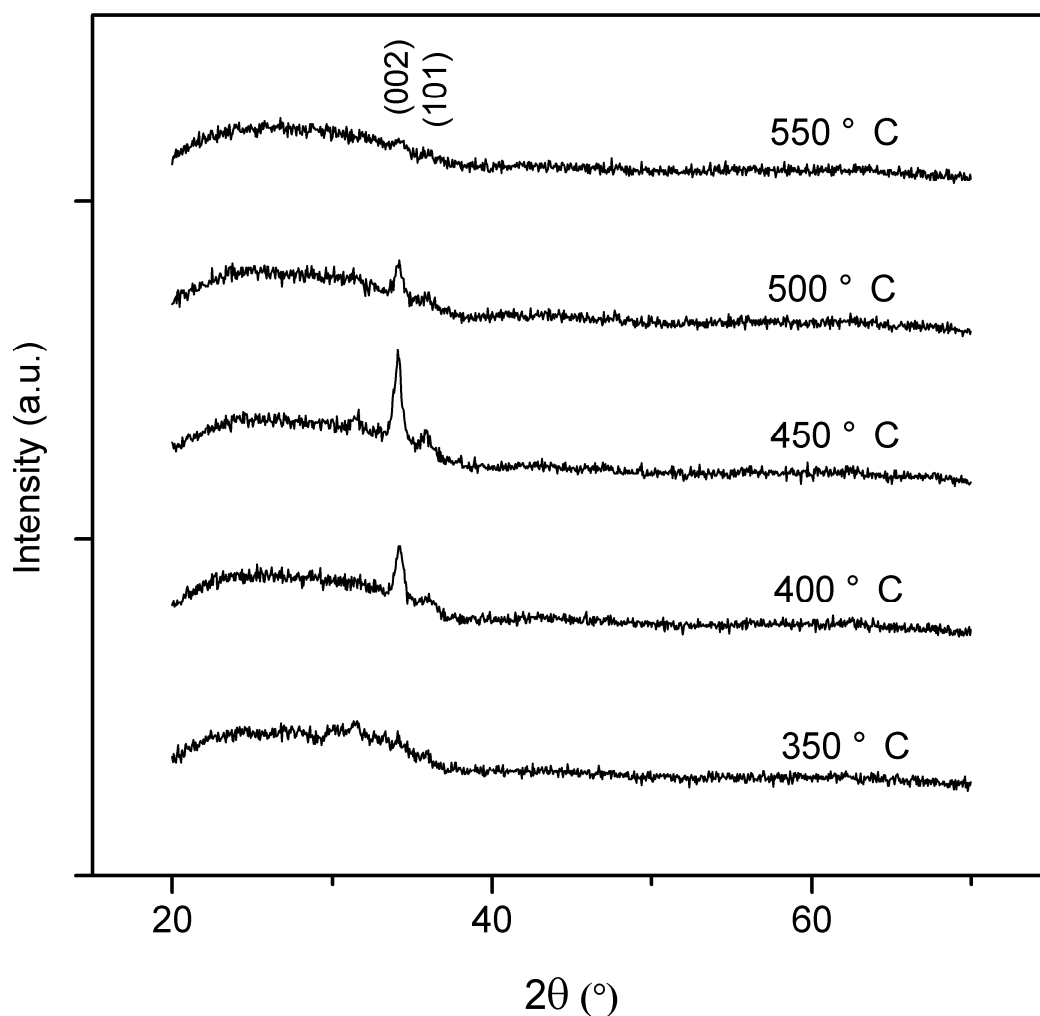
In this study, ethanol was also mixed with water for dissolving some of the zinc precursors (such as zinc acetate) not only because it has a high solubility of the metal carboxylates and suitable vapour pressure, but also because it functions as a favourable reducing agent during spray deposition. Using a mixed solvent of water and ethanol can improve the quality of deposited films.

#### **4.3.1.2 Spray deposition of ZnO films**

Zinc acetate was dissolved in water and ethanol at a ratio of 1:3 and was made to a  $0.1 \text{ mol}\cdot\text{L}^{-1}$  solution. Spray deposition was carried out at the processing conditions of  $1.5 \text{ ml}\cdot\text{min}^{-1}$  precursor feed rate and 25 psi atomising air pressure at substrate temperatures from 250 to 550 °C. Transparent thin films were obtained with optical spectra showing that all these films had high transmission in the visible region of spectra. XRD analysis shows that at temperatures above 400 °C, crystalline ZnO was formed in the film.

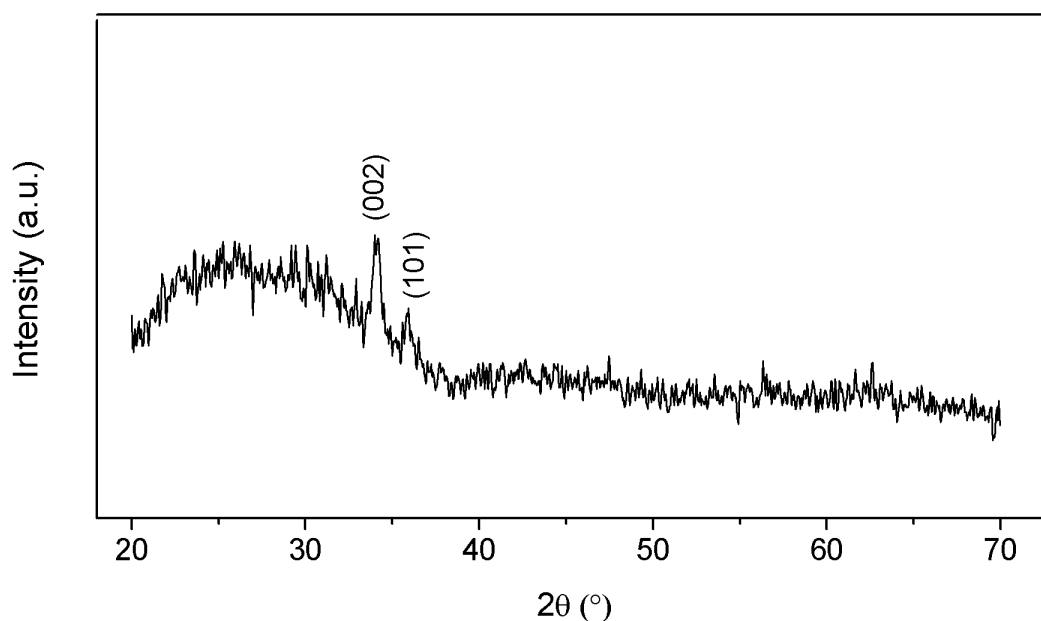
Zinc (bipyridine) diacetate, using a pyridine ligand, has some benefits such that the organometallic precursors decompose completely to give ZnO and the decomposition temperature is relatively low (down to 250 °C). The decomposition temperature can also be controlled (between 250-450 °C) by changing the functional groups on the pyridine ligand [264]. A solution was prepared with 0.1 mol·L<sup>-1</sup> zinc (2-aminopyridine) diacetate in H<sub>2</sub>O with a small amount of formic acid. The solution was spray deposited onto heated Pilkington float glass substrates with the processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure) at the temperatures between 350 °C and 550 °C. The films deposited were homogeneously transparent. XRD measurements were taken on each of the ZnO films which are shown in Figure 4.6.

At a substrate deposition temperature of 350 °C, no significant diffraction peaks for ZnO were observed, indicating that the ZnO formed in the film was still non-crystalline. For films deposited at and above 400 °C the diffraction pattern shows an intense peak at 34° (2θ), which is a characteristic of the ZnO (002) plane, and one at 37° (2θ) corresponding to the ZnO (101) plane. These peaks indicate the formation of some crystallinity in the films. The most intense peak was observed for the film deposited at 450 °C. Above this temperature the peak intensity was reduced. This is probably due to the higher substrate temperature which inhibits film deposition due to rapid evaporation of the precursor solution, resulting in a decrease in film thickness and X-ray diffraction intensity.



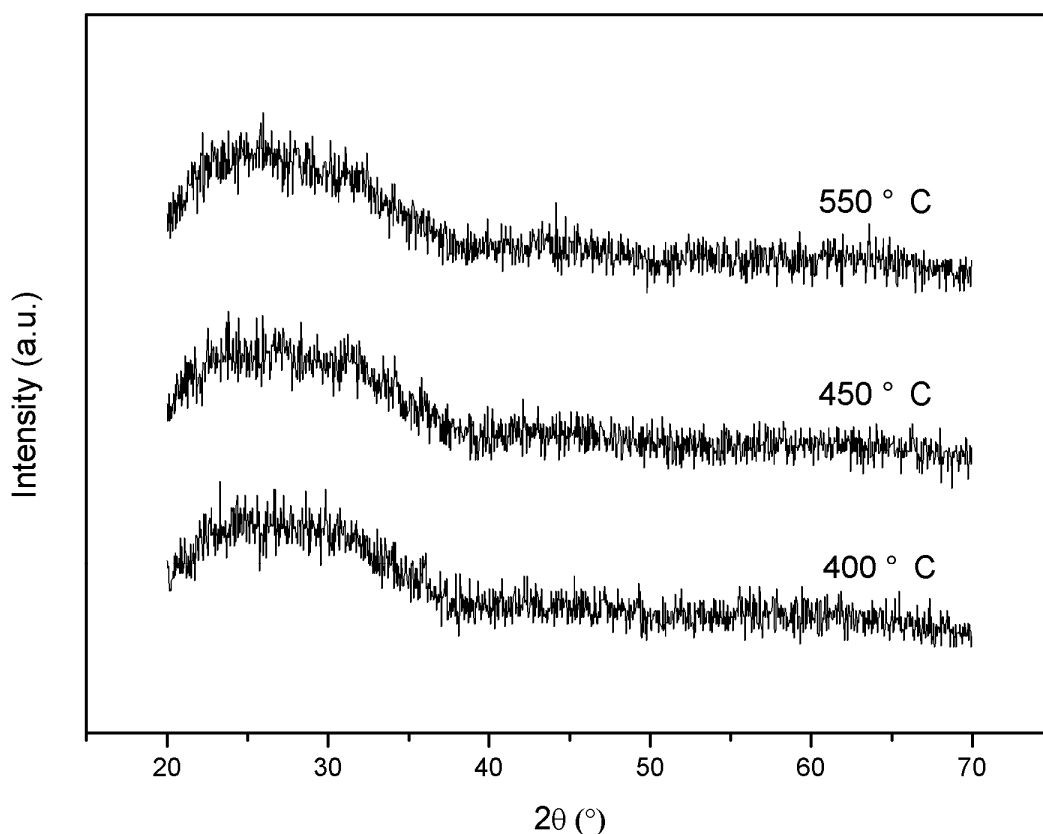
**Figure 4.6 XRD patterns of ZnO thin films deposited at different temperatures using zinc (2-aminopyridine) diacetate.**

Similarly, another zinc carboxylate precursor, zinc aminobutanoate chloro, was tested by spray deposition on float glass. Processing conditions ( $1.5 \text{ ml} \cdot \text{min}^{-1}$  precursor feed rate and 25 psi atomising air pressure) and different substrate temperatures from 300 to 550 °C were used for deposition. XRD results for the ZnO films deposited at 450 °C show peaks for the ZnO (002) and (101) planes, indicating a partially crystalline ZnO thin film was obtained using this precursor (Figure 4.7).



**Figure 4.7 XRD of ZnO thin films deposited using zinc aminobutyrate chloro.**

The films deposited from zinc N,N-dimethylglycine in H<sub>2</sub>O, however, did not show any significant peaks for crystalline ZnO when measured by XRD, indicating the crystallinity of ZnO deposited on the glass was poor (Figure 4.8). Deposition at even higher temperatures over 500 °C did not produce crystalline ZnO using this spray deposition system. Thermogravimetric analysis (TGA) suggests that because the decomposition temperature for zinc N,N-dimethylglycine is relatively high (above 400 °C) it might not decompose completely to allow the formation of crystalline thin films on the glass [264].



**Figure 4.8 XRD of ZnO thin films deposited using N,N-dimethylglycin. Note that there is very little difference on the diffraction patterns from films deposited at different temperatures, indicating the films are poorly crystalline.**

In summary, four different zinc precursor compounds, including conventional zinc acetate and newly developed zinc aminocarboxylates, have been studied for spray deposition to produce ZnO thin films on glass. The newly developed precursors of zinc (2-aminopyridine) diacetate and zinc aminobutyrate chloro have shown the potential to be suitable for crystalline ZnO deposition and used for further investigation of doped ZnO.

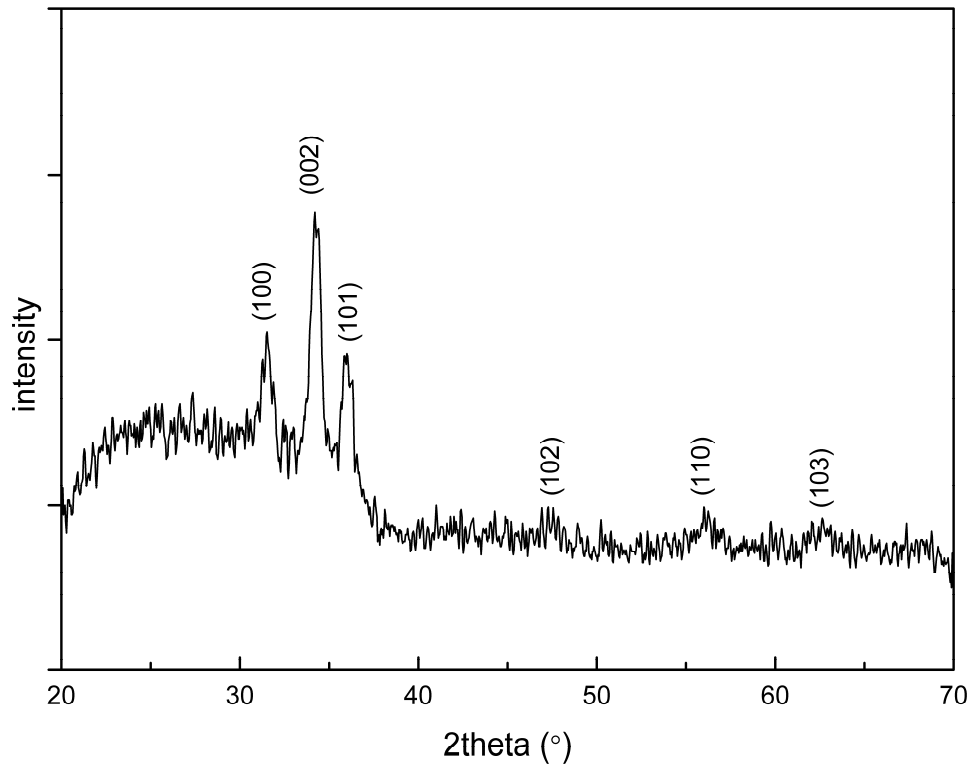
### **4.3.2 Spray deposition of doped ZnO thin films**

To reduce the electrical resistivity of ZnO films it is necessary to introduce cationic substitution with trivalent atoms. In this thesis, Al, B and In were used as dopants. The influence of different dopants and their concentration on the electrical and optical properties is investigated in the following sections.

#### **4.3.2.1 Al doped ZnO films**

Spray deposition of ZnO:Al thin films on Pilkington float glass was first investigated using  $0.1 \text{ mol}\cdot\text{L}^{-1}$  zinc aminopyridine diacetate and aluminium nitrate (with atomic ratio of Al to Zn being 4%) in  $\text{H}_2\text{O}$  with the addition of nitric acid for stabilisation of the solution. The experimental conditions used were  $1.5 \text{ ml}\cdot\text{min}^{-1}$  precursor feed rate at an atomising air pressure of 30 psi. The experiments were carried out with substrate temperatures between  $400^\circ\text{C}$  and  $550^\circ\text{C}$ . Transparent and conductive ZnO:Al films were obtained. Figure 4.9 shows the X-ray diffraction pattern of a typical ZnO:Al film deposited at  $450^\circ\text{C}$  indicating a polycrystalline thin film was formed of characteristic hexagonal wurzite structure with phases of (002), which is the preferred orientation for non-doped ZnO, together with the (100) and (101) phases (ICDD Reference Code 01-079-0208). It has been reported that doping changes the preferential growth of ZnO particles from (002) to (101) [265, 266]. The thickness of the film measured using a DekTak stylus profiler is approximately 300 nm. The lowest sheet resistance measured by the four-point-probe method is about  $0.98 \text{ M}\Omega/\square$  and therefore the resistivity is calculated as  $29.4 \Omega\cdot\text{cm}$ . Although this value is not favourably comparable with commercially available doped ZnO it is significantly

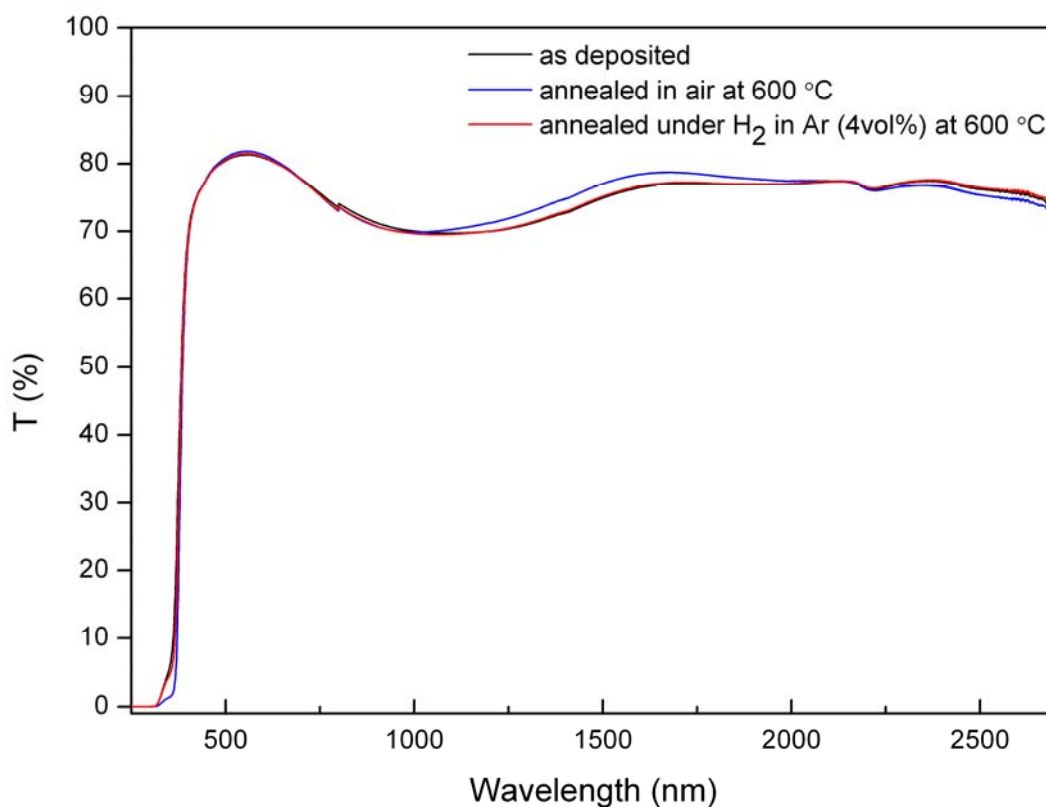
decreased from that expected for non-doped ZnO, indicating that some aluminium may have been successfully incorporated into the ZnO lattice.



**Figure 4.9 XRD pattern of ZnO:Al thin film by spray deposition at 425 °C. The film is polycrystalline of typical wurzite structure with (100), (002) and (101) planes.**

The optical transmission spectra show high transparency (over 80%) in the visible region. The bandgap, calculated from the absorption edge, is 3.35 eV. However, there is no reduced transmission in the infrared (Figure 4.10). This may be due to the phase separation of ZnO and Al<sub>2</sub>O<sub>3</sub> occurring during spray deposition, which results in the free carrier concentration from any aluminium doping not being high enough to give a plasma reflectance edge in the infrared. Annealing treatments were then carried out at different conditions, either 600 °C

in air for 2 hours or 600 °C in 4% H<sub>2</sub> in Ar for 2 hours. It was determined that annealing using these conditions did not decrease the resistivity and optical properties of the films (see Figure 4.10).

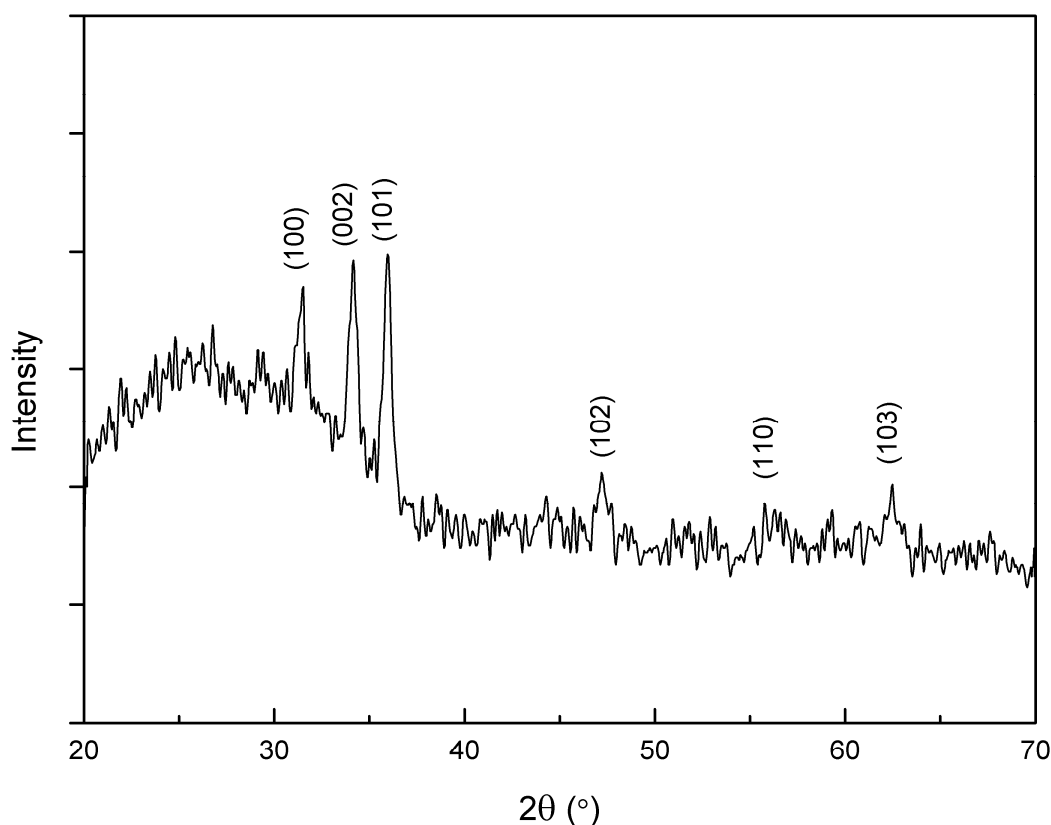


**Figure 4.10 UV-visible-NIR transmittance spectra of a ZnO:Al thin film as deposited and annealed in air or H<sub>2</sub>.**

Al doped ZnO films were also deposited from zinc acetate and aluminium nitrate in water and ethanol mixture. Similar results were obtained and the influence of Al doping level was also investigated. This is further discussed in section 4.3.3.2.

#### 4.3.2.2 B doped ZnO films

Spray deposition of ZnO:B thin films was also investigated using 0.1 M zinc aminodiacetate and boric acid (with atom ratio of B to Zn being 4 %) in H<sub>2</sub>O under typical experimental conditions. The ZnO:B thin film was deposited with processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure) and a substrate temperature at 450 °C. The film deposited was transparent with sheet resistance down to 78 MΩ/□ measured by the four-point-probe method. This is much higher than that of the ZnO:Al film (0.98 MΩ/□). XRD also showed a typical hexagonal wurzite structure for ZnO with planes of (100), (002), (101), (102), (110) and (103) (ICCD Reference Code 01-079-0208) (see Figure 4.11). It is also noted that the peak intensity for planes (100), (002) and (101) in B doped ZnO film is different from that obtained for Al doped ZnO, where the strongest peak in ZnO:B is at (101) while in ZnO:Al it is (002). It has been reported that the incorporation of dopant influences the crystallinity of ZnO films which might be due to the formation of stress caused by the ion size difference between Zn and dopants and the segregation of dopants at grain boundaries [122, 267]. The different nature of dopant in terms of ion size and electronegativity might induce the formation of preferred phases.



**Figure 4.11 XRD of ZnO:B thin film showing typical hexagonal ZnO pattern.**

#### **4.3.2.3 In doped ZnO films**

Spray deposition of ZnO:In thin films was also investigated using 0.1 mol·L<sup>-1</sup> zinc acetate and indium nitrate (with atomic ratio of In to Zn being 4 %) in H<sub>2</sub>O under typical experimental conditions. The ZnO:In thin film deposited at 450 °C with processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure) was transparent with sheet resistance down to 1.2 MΩ/□ measured by the four-point-probe method, indicating the doping effect of Indium. This is similar to that obtained for the ZnO:Al film (0.98 MΩ/□). The ZnO:In film was not further characterised because it is investigated as a benchmark to be compared with ZnO:Al regarding the electrical properties only. The characterisations of ZnO:In thin films by spray pyrolysis have been reported

in the literature [268, 269]. The XRD patterns, SEM images and optical spectra of the ZnO:In films are similar when compared to those of the ZnO:Al films investigated above.

Further details comparing the effects of different dopants and concentration on the electrical and optical properties of doped ZnO will be discussed in the next section.

### **4.3.3 Discussion on ZnO and doped ZnO**

#### **4.3.3.1 The effect of using different dopants**

In this study three different dopants, B, Al and In, have been used to investigate the influence on the electrical and optical properties of doped ZnO thin films. The role of the dopant is to establish electron donor centres in the host ZnO. Moreover, the donor centres must be spontaneously ionized in order to liberate highly mobile electrons in the conduction band of ZnO. It has been reported that doped ZnO films have high carrier concentration and low mobility in comparison with those of non-doped ZnO films. The increase of conductivity is due to the small amount of dopant providing a large number of free electrons in the films.

It is also observed that with the same dopant concentration of 5 at% of Zn, the sheet resistance of ZnO:Al and ZnO:In is much lower than that of ZnO:B. Portier et al introduced the concepts of electronegativity and chemical hardness to investigate the electrical properties of degenerate semiconductors [270]. They found that by comparison the computed electronic affinities of dopant oxides with those of various matrices are in agreement with experimental observations for ZnO, In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>.

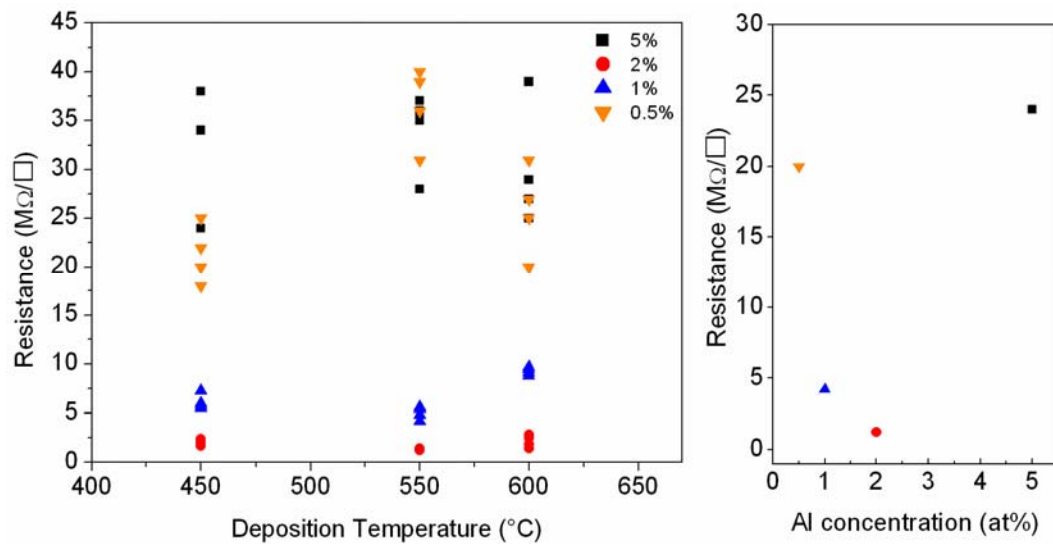
There are several factors that may affect the doping and corresponding electrical conductivity, including 1) the surface segregation of dopant (e.g. Al); 2) the phase separation of host (ZnO) and dopant (e.g.  $\text{Al}_2\text{O}_3$ ) along the lateral and vertical direction during the deposition process; 3) the different crystal structures between the host and dopant and 4) the different electronegativity and size which lead to different incorporation efficiency. Careful selection of suitable dopants based on comprehensive investigation is therefore essential in efficient doping and improving electrical and optical performance of TCOs.

#### **4.3.3.2 Influence of dopant concentration**

To investigate the influence of dopant concentration on the resistivity, a series of Al doped ZnO thin films with different Al concentration in the starting solution were deposited and characterised. The starting solution was prepared using zinc acetate and aluminium nitrate as precursors which were dissolved in an ethanol and water mixture (volume ratio being 3:1). Acetic acid was added for stabilisation. The concentration of zinc acetate was fixed at  $0.1 \text{ mol}\cdot\text{L}^{-1}$  and the Al concentration was varied as Al:Zn = (0.5, 1, 2, 5):100. The films were deposited with the processing conditions ( $1.5 \text{ ml}\cdot\text{min}^{-1}$  precursor feed rate and 25 psi atomising air pressure) and at  $450^\circ\text{C}$ ,  $550^\circ\text{C}$ , and  $600^\circ\text{C}$ , respectively.

Resistivity measurements using the four-point-probe method were taken on these films and shown in Figure 4.12. The resistance of the films is in the range between  $0.9 \text{ M}\Omega/\square$  and  $41 \text{ M}\Omega/\square$ , showing strong dependency on dopant concentration. The film with a minimum of resistance is that with 2% Al in the starting solution. It is assumed that for a lower dopant concentration (e.g. 0.5 at% Al), there is not enough Al to contribute free carriers in the films with sufficient

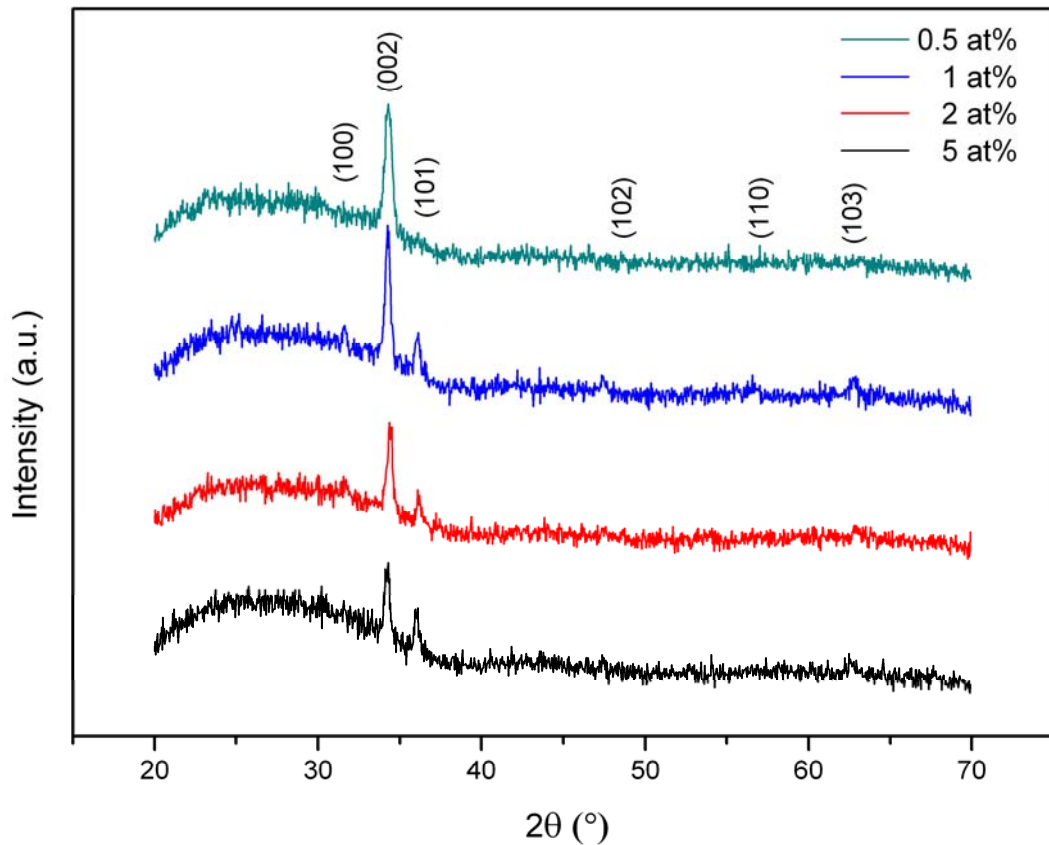
density. While at a higher Al content of 5 at%, a non-conducting  $\text{Al}_2\text{O}_3$  phase may be produced due to the extra availability of Al atoms. Optimisation between the Al atoms contributing conduction electrons and those producing  $\text{Al}_2\text{O}_3$  should be reached.



**Figure 4.12 Influence of Al doping concentration on ZnO film resistance. Different doping levels from 5 at% to 0.5 at% and at different deposition temperatures were investigated. Note that 2 at% Al doped ZnO film shows lower resistance compared to other doping levels.**

Figure 4.13 shows the X-ray diffraction patterns for the Al doped ZnO films deposited at 550 °C with different doping levels from 5 % to 0.5%. Typical (002) preferential orientation is observed for all these films, along with the (101) peak in some of the films, indicating the hexagonal structure. It should be noted that only for the 0.5 at% Al doped film the (101) peak was not detected. In contrast, there is no indication of the presence of  $\text{Al}_2\text{O}_3$  in the XRD pattern. There is also a tendency that with increasing Al doping level, the diffraction intensity for (002)

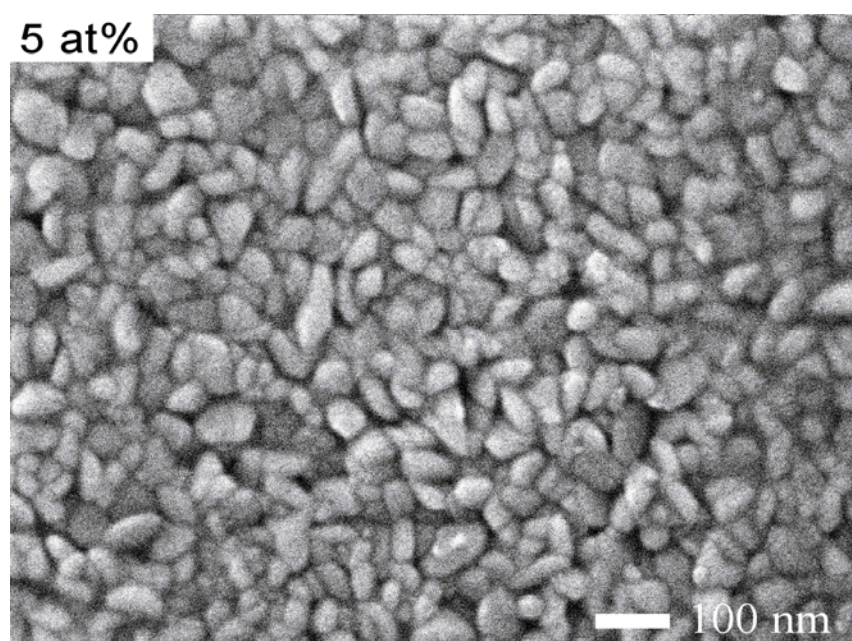
plane is reduced while for (101) plane it is enhanced. This is probably due to the introduction of Al which induces the lattice distortion and hence the formation of (101) plane.

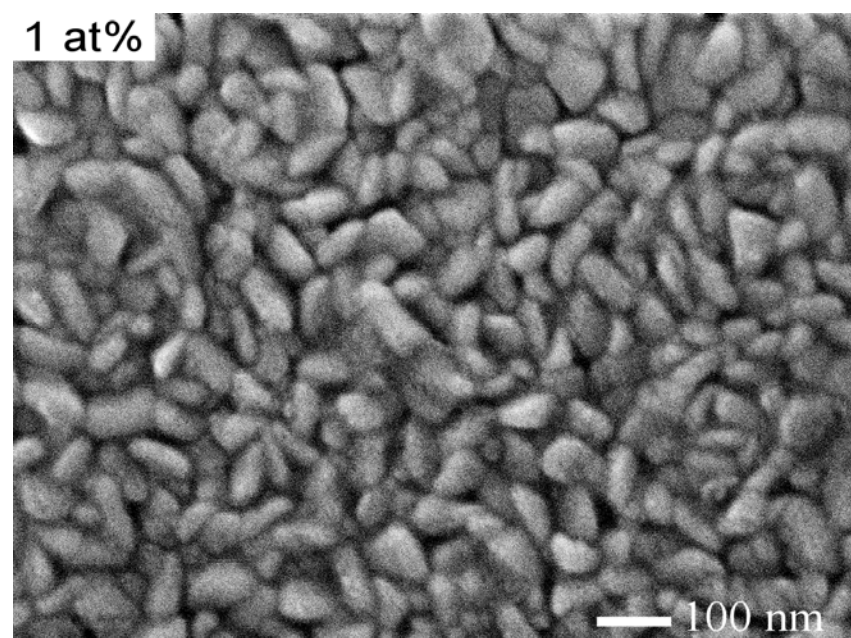
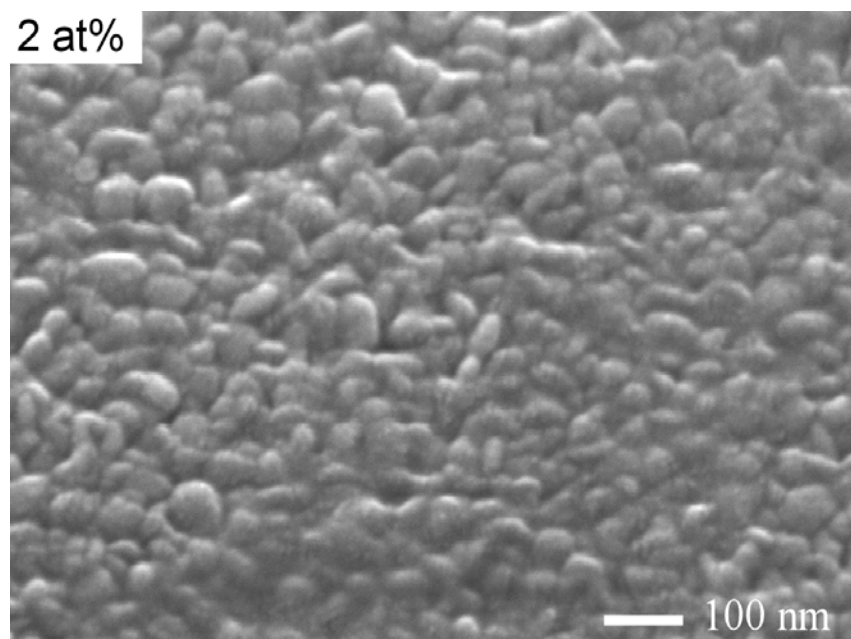


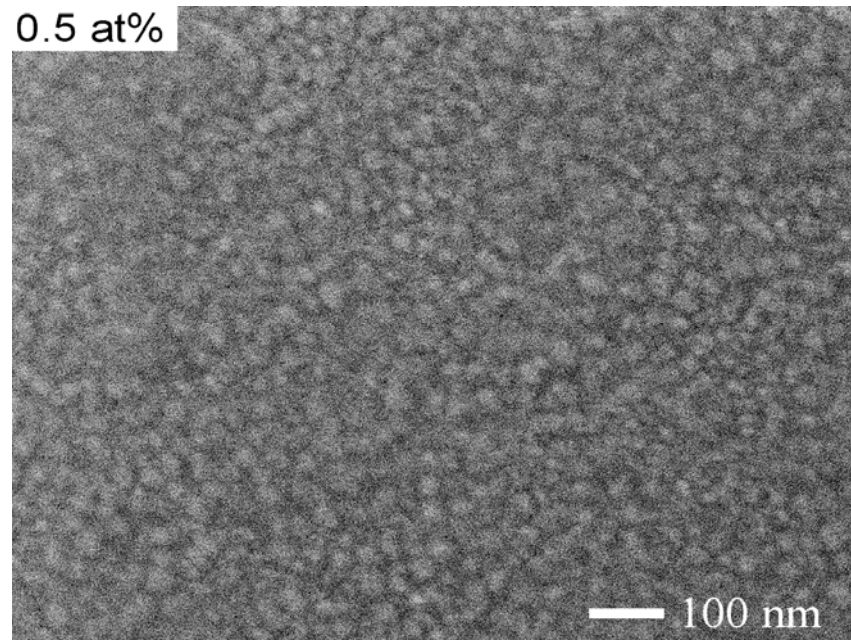
**Figure 4.13 XRD patterns of Al doped ZnO films with varied doping levels from 0.5 at% to 5 at%. The intensity for (002) peak is reduced and the intensity for (101) peak is enhanced with increasing Al doping level.**

The UV-visible-NIR spectra of these films were measured. However the transmittance showed irregular profile due to the sample and instrument problem. It is reported that increasing Al doping concentration results in blue shift of the UV absorption edge, indicating the broadening of the optical band gap [271]. This effect should be further investigated in the future.

Figure 4.14 shows the SEM images of the ZnO thin films potentially doped with 0.5, 1, 2 and 5 at% Al. Different morphologies are shown for the samples with different Al concentrations in the starting solution. The film deposited with 5 at%, 2 at% and 1 at% Al present grains of size around 50-100 nm. The film deposited with 0.5 at% Al has round shaped grains of size around 20-40 nm. It can also be observed that the 0.5 at% Al doped ZnO film shows less contrast due to the smaller grain size and thickness. The absence of the (101) peak in the XRD pattern also indicates a possible strong orientation perpendicular to the substrate surface. It therefore indicates that the addition of aluminium nitrate in the starting solution has an influence on the morphology of the film which correlates to the grain growth rate mechanism [46, 272]. Compared to the SnO<sub>2</sub> films (see Figure 4.4), the grain size of these ZnO films is much smaller than that of SnO<sub>2</sub>, which is probably due to the growth rate of films due to the different precursors used; higher growth rate results in larger grain size.







**Figure 4.14 SEM micrograph of ZnO:Al thin films with different Al doping concentrations of 5 at%, 2 at%, 1 at% and 0.5 at%.**

Thermodynamic analysis suggests that the segregation of aluminium from ZnO to form aluminium oxide during and after the deposition process is still an issue. As the doping of aluminium or gallium is related to physical chemistry thermodynamics, Ellingham diagrams (which provide information relating to the Gibbs free energy of metal oxides across a range of temperatures) should be used to explore the thermodynamic nature of the zinc oxide doped with aluminium and/or gallium [273]. Looking at the enthalpies of oxide formation, the enthalpy of the Zn-O is only -84 kcal/mol, which is low compared to possible dopants such as Al and Ga (whose enthalpies of formation are -404 kcal/mol and -256 kcal/mol, respectively). This indicates that the elements of Al and Ga are likely to form oxide inclusions in the material and not actually “dope” the ZnO.

## 4.4 Discussion on TCO

The optical properties of TCOs can be understood on the basis of Drude free electron theory. The interaction of an electromagnetic field with free carriers generated by the ionized impurity scattering results in polarisation of the field within a material and therefore induces a change in the relative dielectric constant. The plasma resonance frequency  $\omega_p$ , is determined by

$$\omega_p = (4\pi N e^2 / \epsilon_0 \epsilon_\infty m_e^*)^{1/2}$$

where  $m_e^*$  is the effective mass and  $N$  is the carrier concentration. The carrier concentration not only determines the plasma frequency but also the maximum achievable reflectivity in the infrared region. Large carrier concentration is desired for good conductivity and also reflection in the shorter infrared wavelength. However, it may also result in an increase in the optical absorption and decrease the overall transparency in the visible region [274]. It is a challenge to combine and balance the requirement of high conductivity with the simultaneous need of high transparency across the visible spectrum. Many researchers have investigated and proposed routes to achieving this [274]. One approach is to enhance conductivity via improved mobility of the carriers rather than increased concentration by introducing magnetic dopants. Another alternative is using multicomponent TCO films consisting of layered structure such as  $\text{InGaO}_3(\text{ZnO})_m$  [274]. These alternative methods not only allow the desired electrical transport and optical properties to be approached, but also broaden the range of materials with potential to act as novel functional transparent conductors.

## 4.5 Conclusion

Transparent and conductive oxide thin films of  $\text{SnO}_2$  and  $\text{ZnO}$  have been obtained by the spray pyrolysis deposition method. Butyltin trichloride and zinc carboxylates (zinc acetate, zinc aminopyridine diacetate) are found as suitable precursors to produce  $\text{SnO}_2$  and  $\text{ZnO}$ , respectively. Different dopants were introduced and the doping concentration was found to have influence on the electrical and microstructural properties of the films deposited. The electrical conductivity can be optimised by varying experimental conditions such as substrate temperature and dopant loading concentration. Optical reflection in the near infrared region was attained using F doped  $\text{SnO}_2$  which also displays high electrical conductivity, while the  $\text{ZnO}$  based films show high optical transparency in the visible region. This work has demonstrated that these two materials are good candidates for transparent conductors and can be used as host materials for additional functionalities.

## **CHAPTER 5**

# **SPRAY DEPOSITION OF GOLD/METAL OXIDE COMPOSITE THIN FILMS**

### **5.1 Introduction**

This chapter describes the spray deposition of nanocomposite thin films which comprise gold nanoparticles and metal oxides. The aim of this chapter is to produce coloured coatings on glass using such composite thin films. Two precursors for Au NPs were used: preformed gold colloids and  $\text{HAuCl}_4$ . Three metal oxides as host materials were investigated:  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$ .  $\text{TiO}_2$  was investigated due to its high refractive index which can produce intense colour when incorporated with gold NPs and therefore is studied as a prototype material.  $\text{SnO}_2$  and  $\text{ZnO}$  were studied due to their optical transparency and potentially solar control coatings when doped as discussed in Chapter 4. In this context a single-step process was performed using a one-pot solution containing precursors for both gold and metal oxide. The optical properties, thin film morphology and microstructure were investigated. The influence of the spray deposition conditions, especially substrate temperature, was also studied. The possibility of combining functionalities of colouration and conductivity by producing composite thin films is also discussed in this chapter. It should be noted that only

metal oxides incorporated with gold NPs are investigated in this chapter for colouration. Further development of combined functionalities using doped TCO will be reported in detail in Chapter 6.

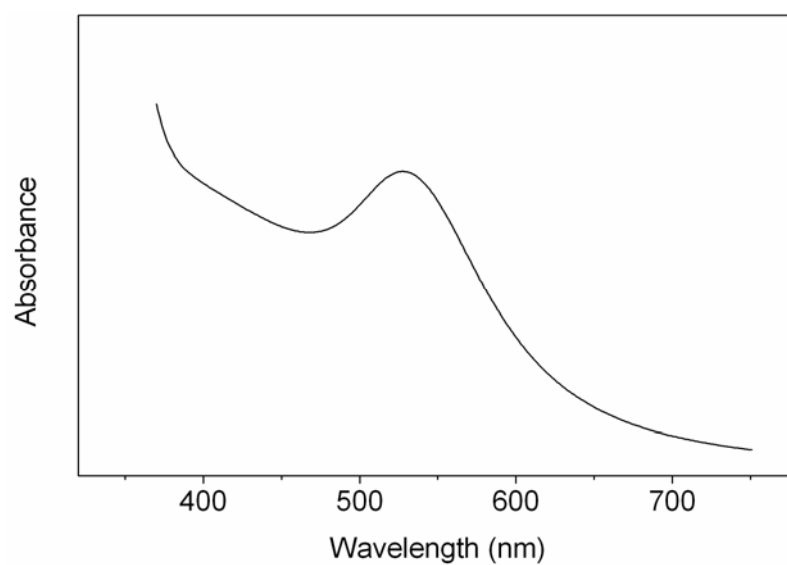
## **5.2 Precursors**

### **5.2.1 HAuCl<sub>4</sub> & Au Nanoparticles**

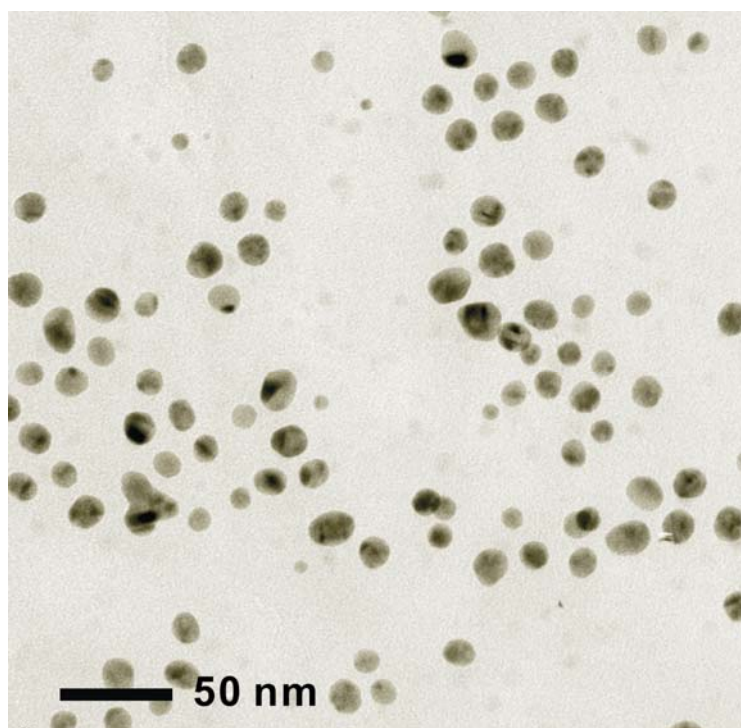
HAuCl<sub>4</sub> is a brown solid and its solution in water is light yellow. HAuCl<sub>4</sub> decomposes at around 150-200 °C and is easily reduced to stable gold nanoparticles in solution-phase synthesis, indicating it can be used as a precursor for Au NPs formation in composite films [200, 275].

Alternatively, gold nanoparticles were synthesised and supplied by Johnson Matthey. A typical synthetic method has been reported by K. Cassar [276]. Aminobenzoic acid was used as a capping agent and stabiliser which significantly enhances the solubility of gold NPs in water and alcohol allowing for a higher concentration up to 7.3 mmol·L<sup>-1</sup>. The gold NPs were dispersed in water or ethanol for compatibility with host precursors. The gold colloids in water solution are transparent and form a deep red colour. UV-visible spectrum measurement showed a SPR absorption maximum at 533 nm. TEM imaging of the colloid on a holey carbon film showed the gold nanoparticles to have a mean diameter of 5.9 nm with a narrow size distribution of ±1.3 nm calculated from 175 particles (Figure 5.1).

**(a)**



**(b)**



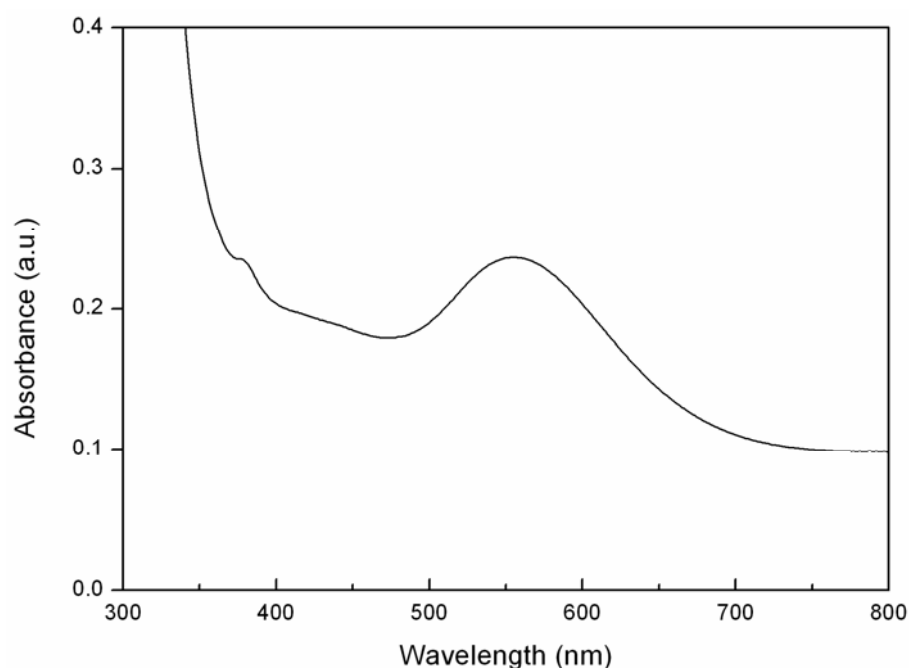
**Figure 5.1 (a) UV-visible spectrum of gold colloids in water stabilised by aminobenzoic acid. (b) TEM image of gold nanoparticle suspension in water on holey carbon film. The scale bar is 50 nm.**

### 5.2.2 Precursors for TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO

The precursors for the metal oxide hosts of TiO<sub>2</sub>, SnO<sub>2</sub> and ZnO, were selected for compatibility with gold colloids in terms of their solvent property and pH. Ammonium titanium lactate [(NH<sub>4</sub>)<sub>2</sub>Ti(C<sub>3</sub>H<sub>5</sub>O<sub>4</sub>), Johnson Matthey Catalysts VERTEC<sup>TM</sup> XL900] was used as the precursor for TiO<sub>2</sub> due to its compatibility with water and pH of about 9. The precursors used for SnO<sub>2</sub> and ZnO, i.e. monobutyltin trichloride and zinc aminobutanoate, are previously described in Chapter 4. Different solvents (water or ethanol) were selected in order to accommodate both precursors of gold and metal oxides.

### 5.3 Spray deposition of Au NPs thin films

Gold nanoparticle thin films were spray deposited onto Pilkington float glass at 180 °C under processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure) using gold colloids as introduced in section 5.2.1. The film was red in appearance when viewed in transmitted light as similarly observed with the gold colloidal solution. An intense absorption peak at 558 nm was displayed in the UV-visible spectrum which is due to the SPR effect of the gold NPs (Figure 5.2). The gold NPs are assumed to be capped by an aminobenzoate ligand and attached on the surface of the glass substrate. The absorption peak is moved to longer wavelengths compared to the value obtained for suspended gold NPs in water, i.e. 533 nm. This red-shift in the SPR is assumed to be from the effect of the glass substrate due to its higher refractive index than water..



**Figure 5.2 UV-visible spectrum of gold NP thin film. Note there is an SPR absorption band between 500 nm and 630 nm with a maximum at 558 nm.**

## **5.4 Spray deposition of Au/TiO<sub>2</sub> composite thin films**

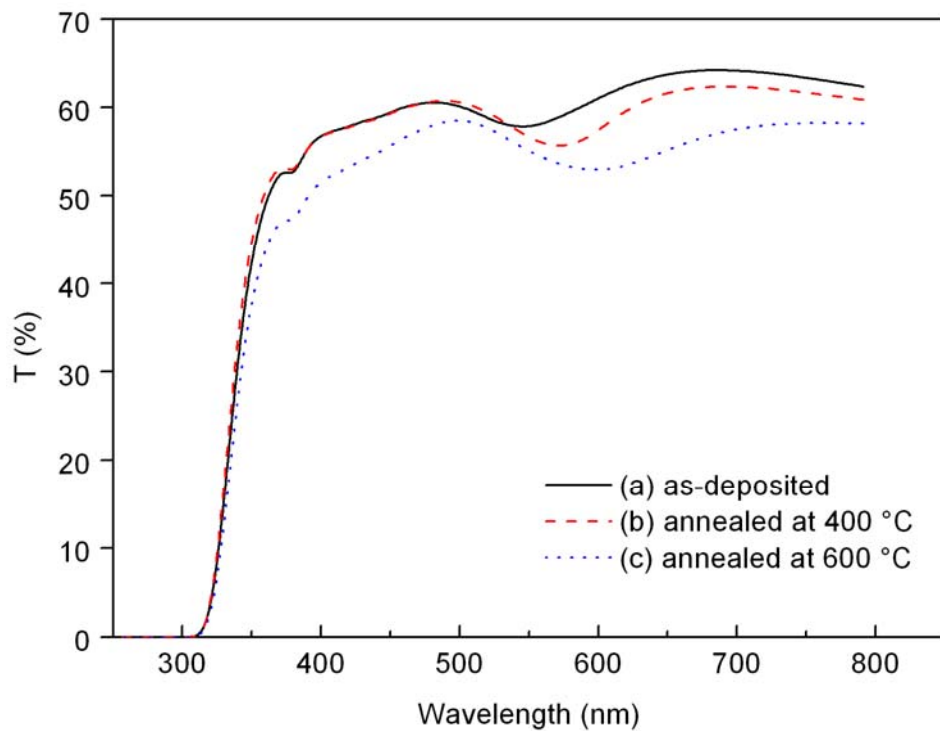
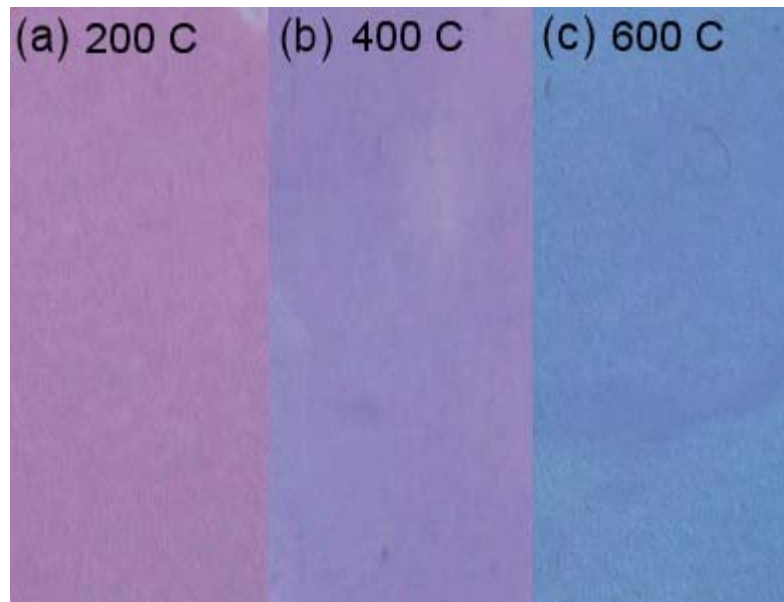
### **5.4.1 Au/TiO<sub>2</sub> thin films using preformed gold nanoparticles**

Au/TiO<sub>2</sub> nanocomposite thin films were firstly investigated using preformed gold NPs. A one-pot solution containing gold colloids and titanium precursor, ammonium titanium lactate, was prepared in water for spray deposition. The mixed solution shows a clear deep red colour which is from the SPR characteristics of gold NPs, and the prepared solution remained stable for over four weeks. The solution was atomised and sprayed on Pilkington float glass at 200 °C under processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure). The as-sprayed composite films appeared red in transmitted light. UV-visible spectroscopy of the film showed an absorption band

in the region of 543 nm indicating the deposition of gold nanoparticles in the film. An annealing treatment was applied at 400 °C or 600 °C for 30 minutes. With annealing the colour of the films either changed from red to purple (400 °C) or red to blue (600 °C).

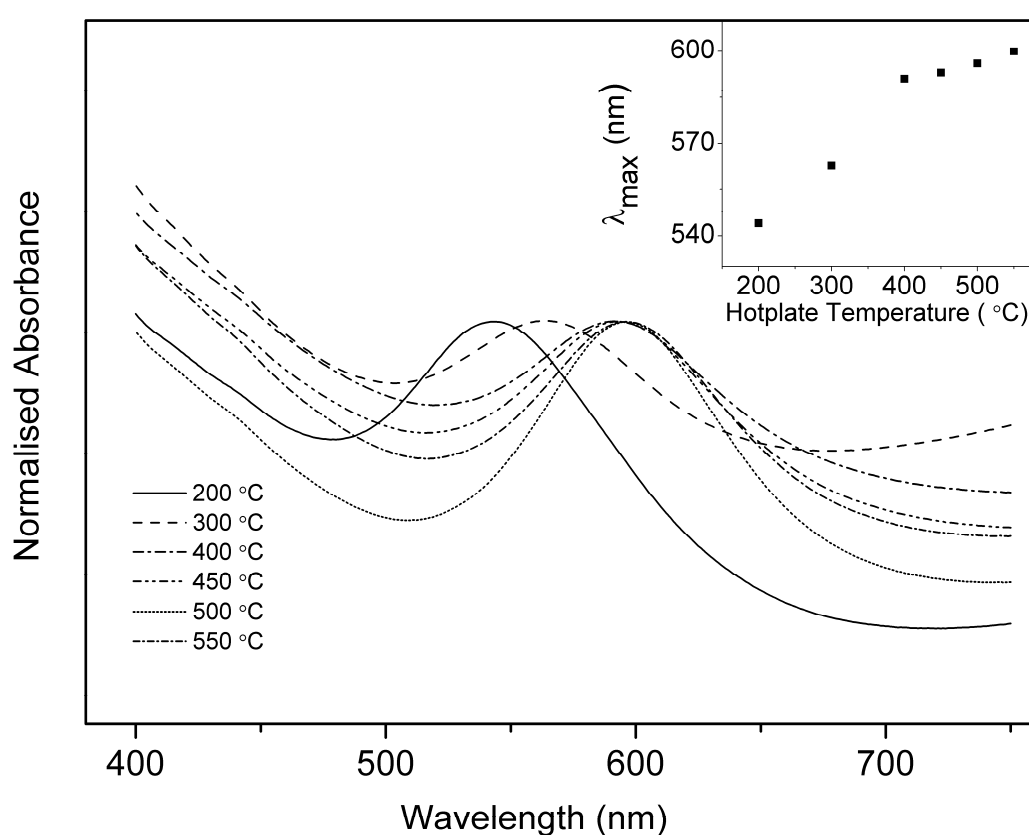
Optical spectroscopy showed an absorption peak shift from 543 nm (as deposited at 200 °C) to 572 nm (after 400 °C annealing) or to 599 nm (after 600 °C annealing) as illustrated in Figure 5.3. Film thickness, measured by profilometer, showed a corresponding decrease from 728 nm to 320 nm or 240 nm. The colour change can be explained by the effects of annealing removing organic ligands and causing densification of the TiO<sub>2</sub> host, which results in a higher refractive index of the host material [277, 278].

In order to compare the “spray followed by annealing” process, a direct spray deposition approach without annealing was investigated using the same solution and processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure) but at a range of different substrate temperatures from 200 °C to 550 °C. Transparent and coloured thin films were found to be successfully deposited at all these temperatures. These films were also robust under washing with good adherence to the glass substrate. The gold nanoparticles could not be removed from the TiO<sub>2</sub> host by repeated washing, indicating the gold nanoparticles were embedded in the film. The colour of the films deposited showed a transition from red to blue in transmitted light with increasing substrate temperature.



**Figure 5.3** Visual images of appearance in transmission (top) and optical spectra (bottom) of Au/TiO<sub>2</sub> composite thin films on Pilkington float glass for a) as deposited at 200 °C; b) annealed at 400 °C and c) annealed at 600 °C.

UV-visible spectroscopy showed that at relatively low substrate temperatures (200-400 °C), significant red-shift of the SPR peak was observed with increasing substrate temperature; the peaks occurred at 544, 562 and 585 nm corresponding to substrate temperatures of 200, 300 and 400 °C. It was observed that for temperatures above 400 °C, less red-shift occurred with a peak around 600 nm at 550 °C (Figure 5.4).

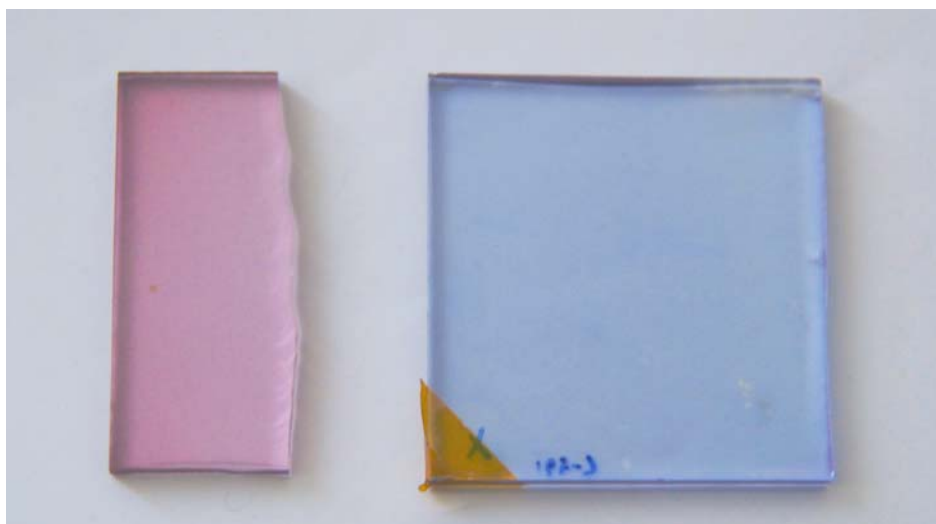


**Figure 5.4 Measured absorbance spectra of gold NP/TiO<sub>2</sub> thin films deposited with substrate temperatures from 200 °C to 550 °C. The intensity of SPR peaks is normalised for comparison. They also show a shift of the SPR peak w from 545 nm to 600 nm ith increasing substrate temperature (see inset).**

As we expect that the substrate temperature plays an important role in thin film formation during spray deposition, the SPR red-shift was attributed to the formation and densification of TiO<sub>2</sub> anatase with increasing substrate temperature, hence increasing the refractive index of TiO<sub>2</sub> as the host material [277, 278].

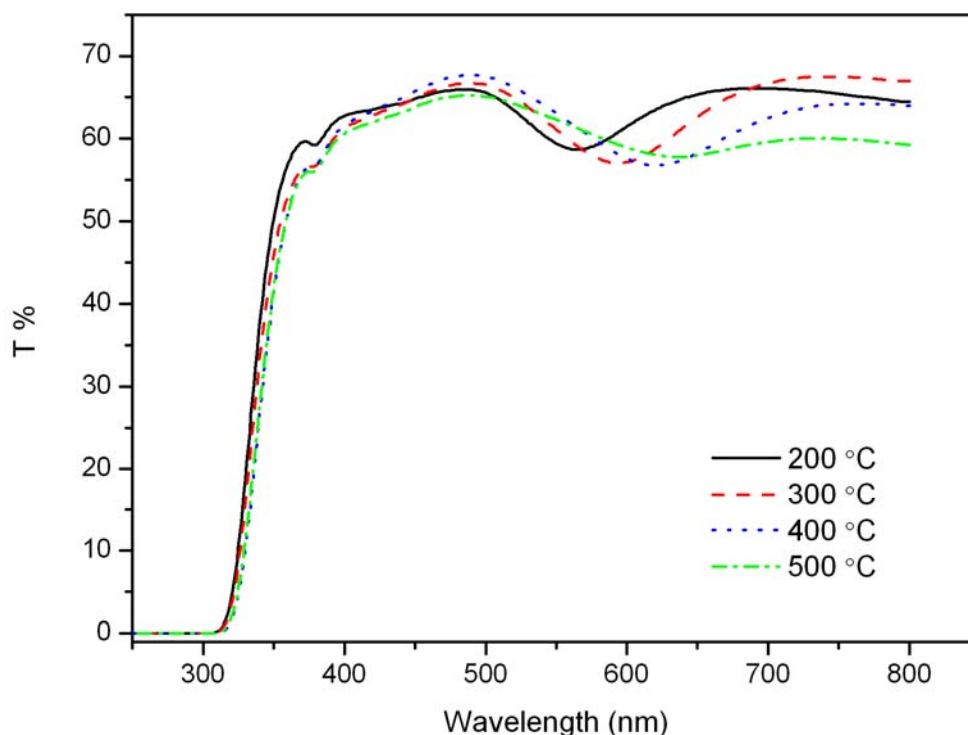
#### **5.4.2 Au/TiO<sub>2</sub> films using HAuCl<sub>4</sub>**

Spray deposition of Au/TiO<sub>2</sub> composite thin films was carried out using HAuCl<sub>4</sub> as an alternative precursor for metallic gold. The starting aqueous solution containing HAuCl<sub>4</sub> and titanium compound displayed a light yellow colour derived from the HAuCl<sub>4</sub>. The solution was sprayed onto Pilkington glass substrates under the processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure) at different temperatures from 200 °C to 500 °C. The films obtained were strongly coloured corresponding to an intense dip in the visible region of the transmittance spectra due to the SPR effects (see Figure 5.5). This has indicated that gold NPs were formed in-situ in the films during spray deposition.



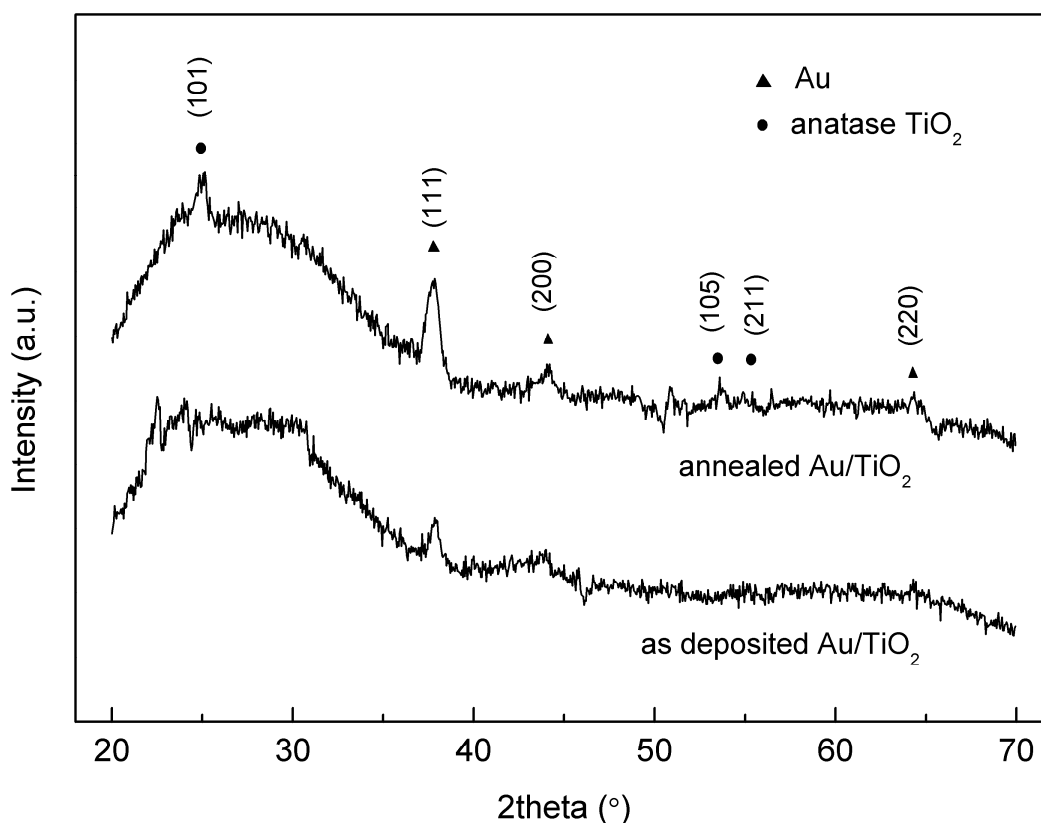
**Figure 5.5 Photo showing appearance of Au/TiO<sub>2</sub> composite thin films deposited on glass using HAuCl<sub>4</sub> at two substrate temperatures, 200°C (left) and 500 °C (right).**

It is again observed that the film colour is influenced by substrate temperature. At low temperatures (200-300 °C) the films deposited show a red appearance through transmitted light, corresponding to a narrow absorption band at the blue end of the light spectrum at around 545 nm. When deposited at higher temperatures (350-500 °C), the film appears blue in transmission, corresponding to the red-shift of the plasmon absorption peak up to 613 nm. This is similar to the observation when using preformed Au nanoparticles. It is assumed that the particulate Au NPs formed in-situ were embedded in a TiO<sub>2</sub> host material whose dielectric constant is increased when deposited at an increased substrate temperature. It's also noted that when the substrate temperature approaches 500 °C, a broader absorption peak was observed, probably because the deposition condition becomes more complex and the size distribution of the Au NPs formed in-situ is correspondingly more poly-dispersed (Figure 5.6).



**Figure 5.6 Transmittance spectra of Au/TiO<sub>2</sub> composite thin films deposited on glass at different substrate temperatures of 200-500 °C. The SPR peaks, which are positioned in the visible region from 545 nm up to 613 nm, red-shift with increasing deposition temperature.**

XRD patterns for the film deposited at 400 °C and the same film annealed at 600 °C for 2 hours indicated the presence of Au and TiO<sub>2</sub> anatase (Figure 5.7). It was found that the intensity of the peaks for gold and titania were enhanced after annealing, indicating a higher crystallinity achieved by thermal treatment. However, the intensity of the peaks for TiO<sub>2</sub> anatase was generally weak even after annealing. This has been observed in a similar experiment by Palgrave et al, which assumed that the inclusion of gold NPs (or HAuCl<sub>4</sub>) has an influence on the crystallisation of TiO<sub>2</sub> [9, 200].



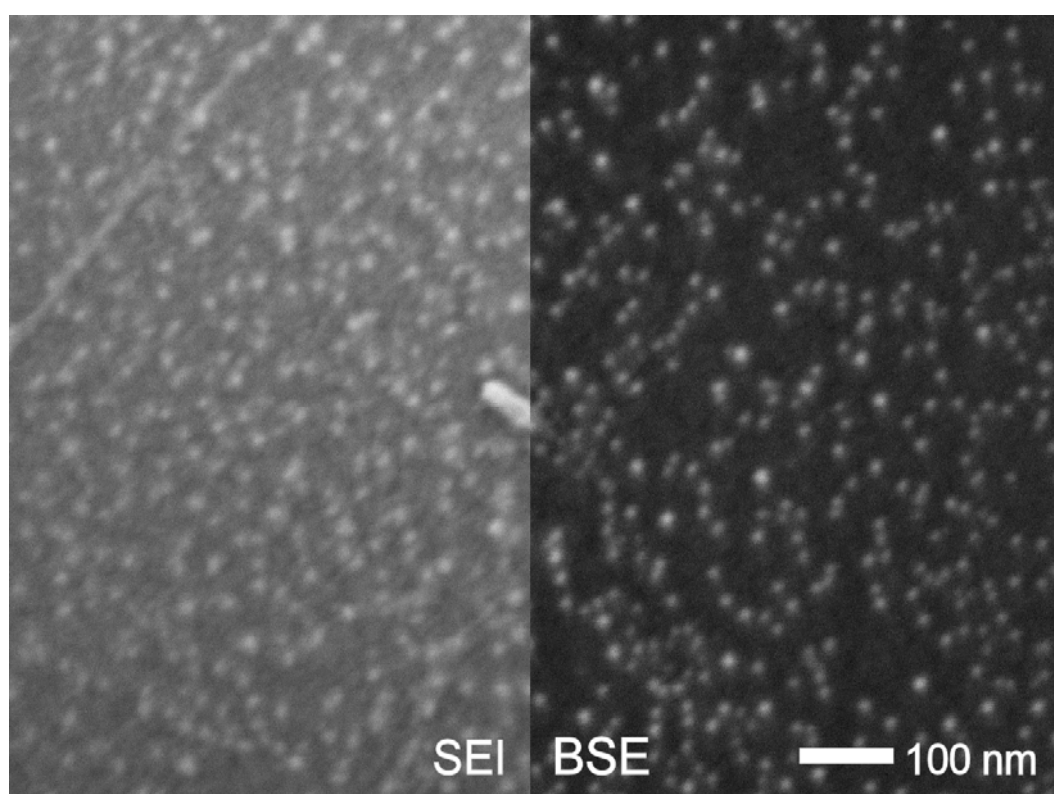
**Figure 5.7 XRD pattern obtained from a gold NP embedded titania film deposited on glass from  $\text{HAuCl}_4$  and  $(\text{NH}_4)_2\text{Ti}(\text{C}_3\text{H}_5\text{O}_4)$ . The peaks at  $38.1^\circ$ ,  $44.3^\circ$  and  $64.5^\circ$  are assigned to the (111), (200) and (220) planes of cubic Au (ICCD reference code 01-089-3697). Peaks at  $25.1^\circ$  and  $53.3^\circ$  correspond to the (101) and (211) planes of anatase  $\text{TiO}_2$  (ICCD reference code 01-071-1169).**

SEM imaging was carried out on the  $\text{Au/TiO}_2$  films deposited at  $250^\circ\text{C}$  and  $450^\circ\text{C}$ . For the film deposited at  $250^\circ\text{C}$ , secondary electron mode imaging (SEI) showed the presence of gold nanoparticles at or just below the surface of the film. The volume ratio of gold in  $\text{TiO}_2$  is calculated from the starting solution as 1.5 vol%. The particles appeared randomly distributed and around 10-15 nm in diameter. Backscattered electron mode imaging (BSE) showed bright particles

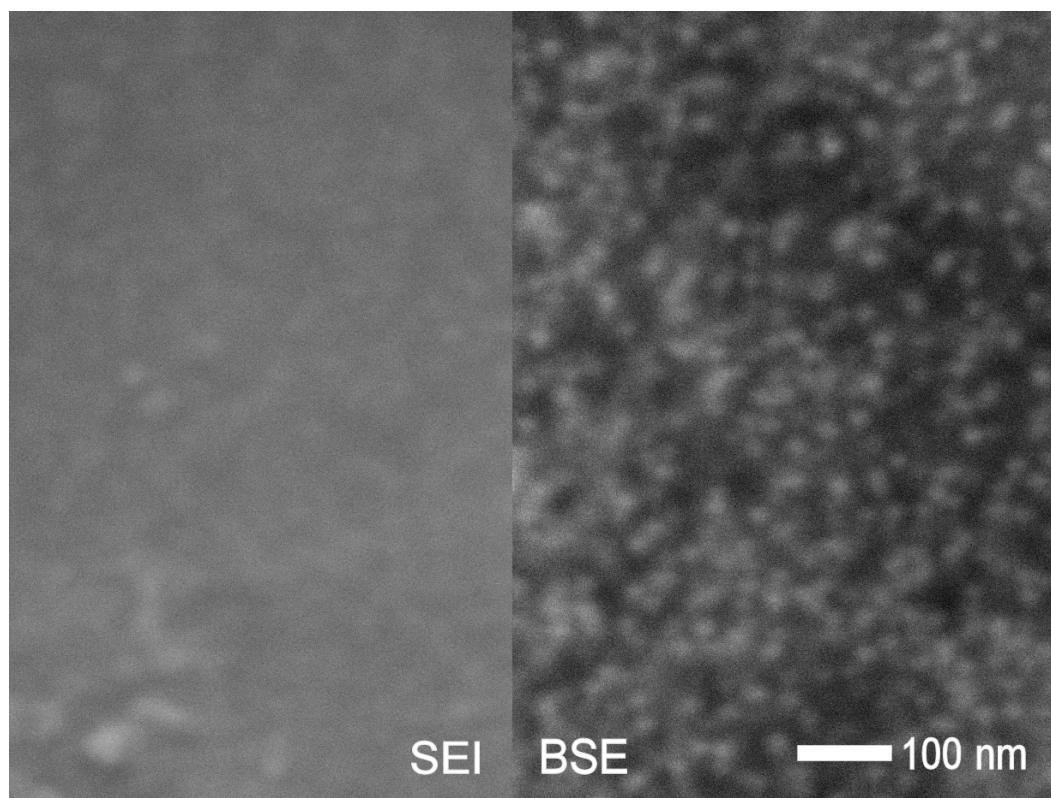
on a darker textured background, which is interpreted as gold nanoparticles embedded in a  $\text{TiO}_2$  host appearing bright due to their higher atomic weight (Figure 5.8). For the film deposited at 450 °C, SE imaging showed a very smooth surface of the film and no significant contrast was observed, whereas BSE imaging revealed a large number of bright particles present in the film; confirming that the gold NPs were mostly embedded into the  $\text{TiO}_2$  host (Figure 5.9). It was observed that the gold/ $\text{TiO}_2$  films deposited at 450 °C with an in-situ gold source contained more gold NPs with larger particle size (about 20-25 nm) and shorter particle-particle distance compared to films deposited at 250 °C. This indicates the growth of the gold NP size with increasing deposition temperature, which might explain why the SPR peaks are broader and the composite films appear correspondingly bluer.

### 5.4.3 Summary

In this section, Au/ $\text{TiO}_2$  composite films have been successfully deposited on float glass from a one-pot solution containing the precursors for gold NPs and  $\text{TiO}_2$ . Two types of gold precursors, preformed gold colloids and  $\text{HAuCl}_4$ , were used and a titanium precursor was chosen to accommodate the gold precursors. A spray pyrolysis deposition technique has been developed for a one-step process at a high deposition temperature. UV-visible transmittance spectra, XRD and SEM imaging have confirmed the incorporation of gold NPs in the  $\text{TiO}_2$  host. Compared to other chemical routes (e.g. sol-gel method), the spray pyrolysis deposition technique developed here is simple and fast which is conducted in a single step. This is regarded as a prototype for further investigation of other gold/metal oxide composite films by spray deposition.



**Figure 5.8 SEM images of Au/TiO<sub>2</sub> films deposited at 250 °C using HAuCl<sub>4</sub> as the precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging where the bright spots are interpreted as gold NPs. The volume fraction of gold in TiO<sub>2</sub> is calculated as 1.5 vol%.**



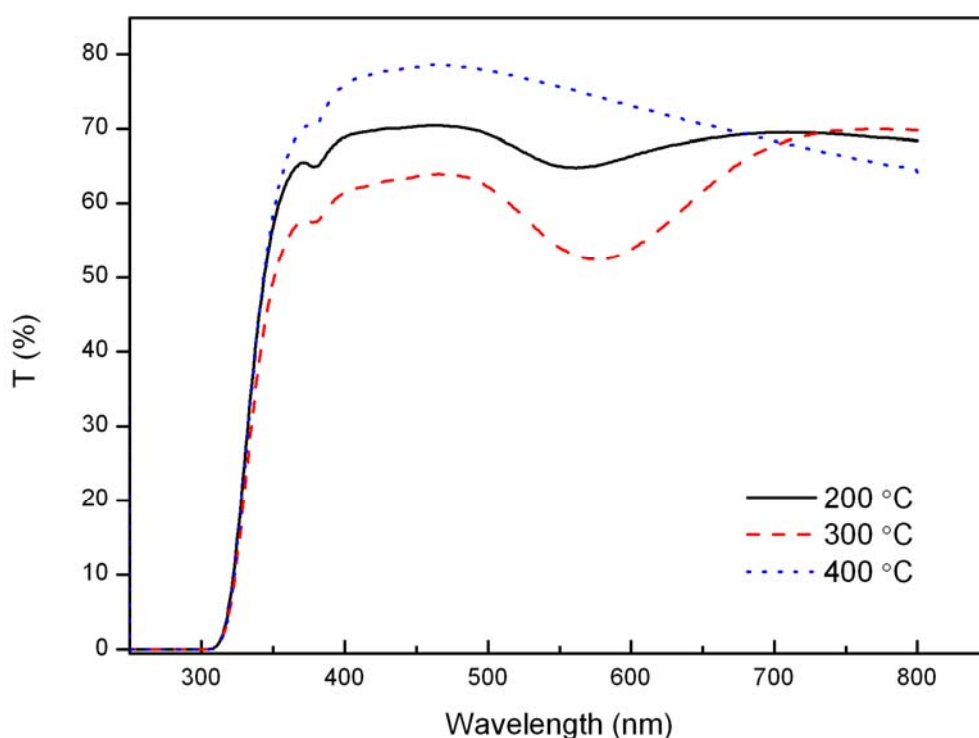
**Figure 5.9 SEM images of Au/TiO<sub>2</sub> films deposited at 450 °C using HAuCl<sub>4</sub> as an alternative precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging where the bright spots are interpreted as gold NPs. The volume fraction of gold in TiO<sub>2</sub> is calculated as 1.5 vol%.**

## 5.5 Spray deposition of Au/SnO<sub>2</sub> composite thin films

### 5.5.1 Au/SnO<sub>2</sub> films using preformed gold nanoparticles

Au/SnO<sub>2</sub> composite films were prepared by spray deposition using preformed Au NPs. A solution was prepared by mixing monobutyltin trichloride (MBTC) (14.7 g, 0.05 mol) and gold colloids (3.74 mmol·L<sup>-1</sup>, 0.086 mmol) in 50 ml ethanol to make a Au/Sn molar ratio of 0.17 mol%. The solution displayed a red appearance with high transparency, indicating a stable suspension without flocculation. It should be noted that aqueous gold colloids were not compatible with MBTC when dispersed in water, due to MBTC reacting with water forming HCl and hence changing the pH of the solution resulting in flocculation. The solution was used for spray deposition of Au/SnO<sub>2</sub> thin films onto float glass. A range of different temperatures from 200 °C to 400 °C were applied and the process parameters of 1.5 ml·min<sup>-1</sup> solution feed rate, 25 psi atomising pressure were used. The film deposited at a relatively low temperature of 200 °C showed a red colour in transmitted light, while the film deposited at 300 °C showed a purple colour, corresponding to an SPR absorption peak in the optical transmittance spectra at 558 nm or 578 nm respectively (Figure 5.10). Similar to the observations noted for Au/TiO<sub>2</sub> films, the red-shift in the SPR peak is due to the densification of the SnO<sub>2</sub> host material resulting in an increase of refractive index. However, spray deposition at an even higher temperature (over 350 °C) produced transparent films without any colouration, which was confirmed by transmission spectra showing no SPR peak (Figure 5.10). The film obtained is conductive, indicating a formation of SnO<sub>2</sub> only film. Although SnO<sub>2</sub> can be deposited on the glass substrate at a high temperature up to 500 °C through a fast

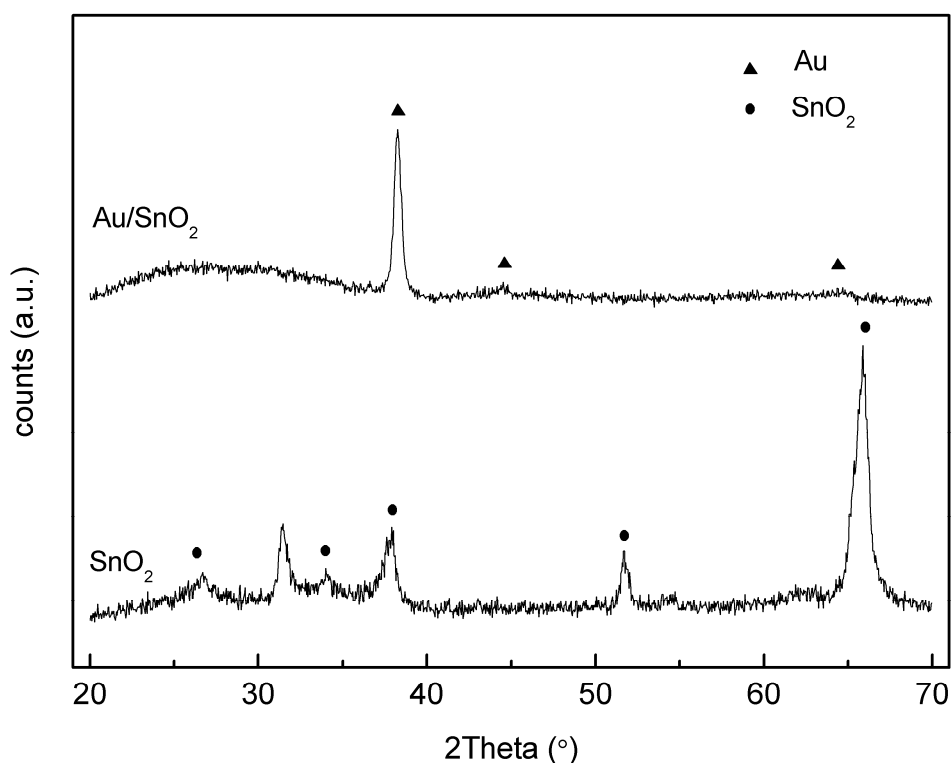
reaction process (as in section 4.3), the gold particles are not effectively embedded into the  $\text{SnO}_2$  host at a temperature just above  $350^\circ\text{C}$ . It's assumed that due to the high evaporation rate of ethanol and low decomposition temperature of MBTC, a phase segregation of the gold solids and monobutyltin trichloride solution occurs during deposition at a high substrate temperature, preventing the incorporation of gold NPs into the host.



**Figure 5.10 Transmittance spectra of Au/SnO<sub>2</sub> thin films spray deposited at different temperatures. SPR peaks are displayed for films deposited at 200 °C (553 nm) and 300 °C (575 nm) respectively, while the film deposited at 400 °C shows no SPR peak.**

An X-ray diffraction pattern for the Au NP/SnO<sub>2</sub> film deposited at 300 °C was recorded and is shown in Figure 5.11. Diffraction peaks for gold were clearly identified especially for the plane (111), while peaks for SnO<sub>2</sub> were

surprisingly not observed in the Au NPs/SnO<sub>2</sub> film. This is probably due to the addition of Au NPs that suppressed the crystallisation of SnO<sub>2</sub>, forming amorphous SnO<sub>2</sub> which cannot be detected by XRD.

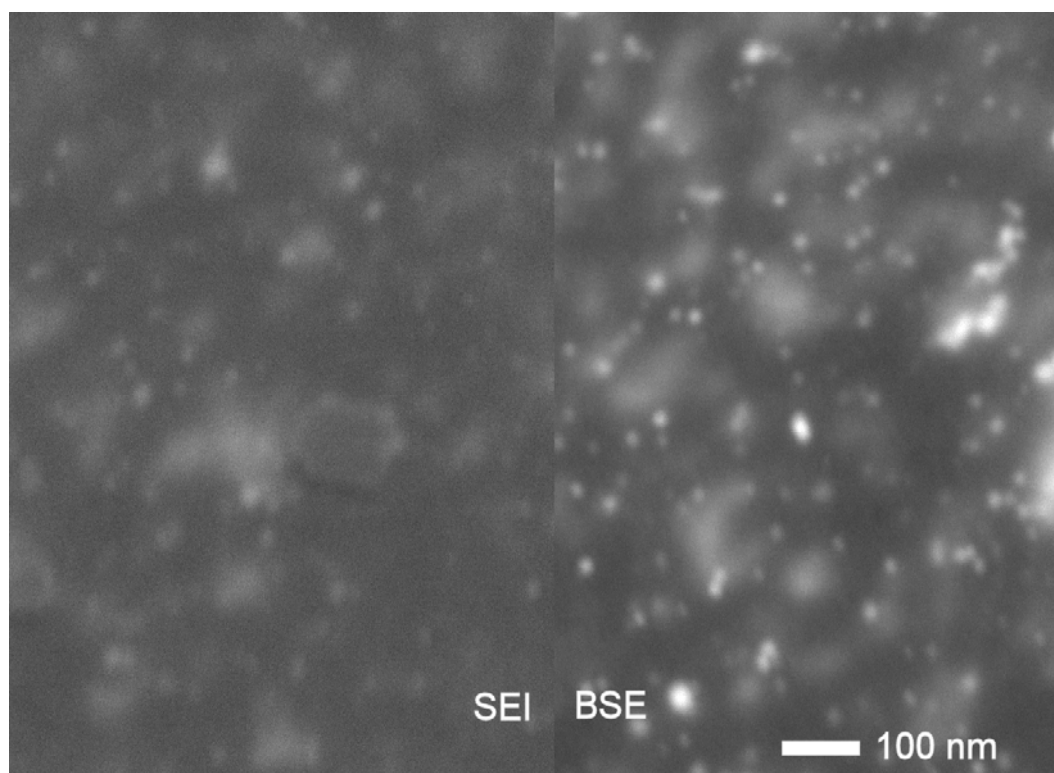


**Figure 5.11 XRD patterns for Au/SnO<sub>2</sub> composite film using preformed gold NPs and for comparison a SnO<sub>2</sub> only film.**

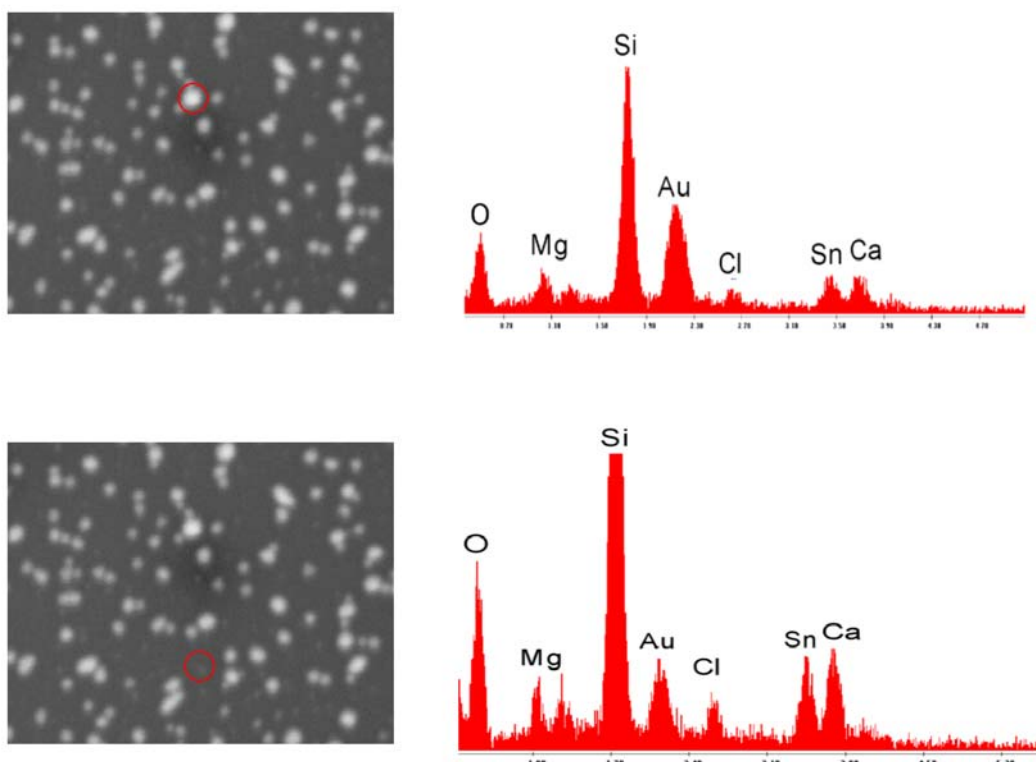
SEM imaging of the same film revealed the morphology of the film. SnO<sub>2</sub> in the film is generally amorphous, with a particulate structure distributed within the film which can be identified as gold nanoparticles when using the backscattered electron mode. The particle size is around 10 nm, which is consistent with the size of the preformed nanoparticles (Figure 5.12).

Energy dispersive X-ray spectroscopy (EDX) analysis investigated two areas in the film, the brighter area with spots and the darker area (see Figure 5.13). Both the two areas show the presence of Au and Sn. In the bright spot area, the

spectrum shows that the Au signal is higher than Sn, indicating a gold rich area consisting of single or aggregation of Au NPs. While in the darker area, the Sn signal is increased compared the Au signal, but the Au signal has not completely disappeared. The darker area can be interpreted as a composite area comprising both gold and SnO<sub>2</sub>, but with the gold NPs more deeply embedded in the SnO<sub>2</sub> host rather than located on the surface which is more difficult to image using the SEM secondary electron mode. EDX, however, with a deeper penetration depth due to higher electron beam energy, reveals the presence of gold even if incorporated within the SnO<sub>2</sub> host with some distance from the surface.



**Figure 5.12 SEM images of Au/SnO<sub>2</sub> films deposited at 300 °C using a gold colloid as a source of gold NPs. Left: secondary electron mode image; right: backscattered electron mode image where the bright spots were interpreted as gold NPs.**



**Figure 5.13 EDX analysis of Au/SnO<sub>2</sub> films using preformed gold NPs. The spectra show different signal intensities for the elements detected. The bright spot area shows much higher Au signal intensity than Sn (upper graph) while the darker area shows increased Sn signal compared to Au (lower graph).**

The Au/SnO<sub>2</sub> thin film deposited at 300 °C was annealed at 600 °C for 60 minutes. After annealing the film appeared to be red/pink with a powdery layer on top which could be easily wiped off. A colour change was observed from pink to blue after the powder was removed, which corresponded to a red-shift of the SPR peak. It is assumed that the as-sprayed film is a porous composite film comprising Au NP layer and Au/SnO<sub>2</sub> layer. After annealing the SnO<sub>2</sub> host is consolidated and becomes denser (hence resulting in a higher refractive index) so

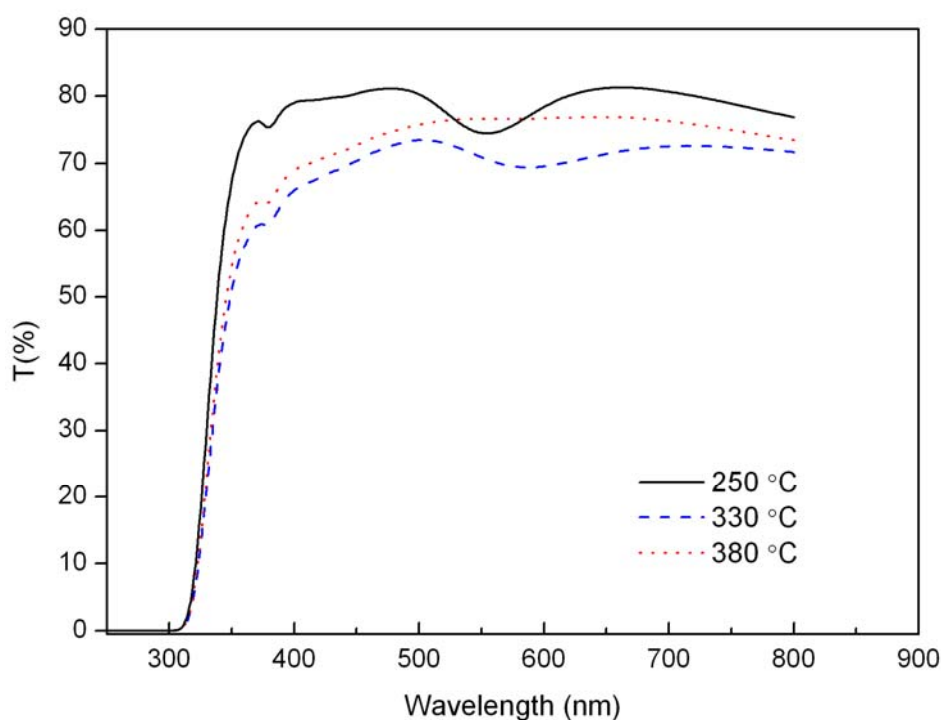
that the fraction of embedded Au NPs exhibit a red-shifted SPR peak. The excess Au NPs which are not effectively embedded into the SnO<sub>2</sub> host appear to migrate upwards and become loosely attached to the surface, where they can be wiped off. The Au NPs on the surface are surrounded by air and this results in SPR at a shorter wavelength creating a red appearance. The difference in film colour when cleaned of excess NPs is due to the difference in SPR peaks of the surface layer of NPs and those embedded in dense SnO<sub>2</sub> which give the blue layer.

It was also interesting to determine using the four-point-probe measurement that the film deposited at 200 °C had extremely high resistance of over 2000 MΩ/□, while the film deposited at 300 °C and 400 °C had resistance of 50 kΩ/□ 800 Ω/□ respectively. The drastic decrease in thin film resistance with increasing deposition temperature is probably attributed to the formation of oxygen vacancies in SnO<sub>2</sub>. Similar temperature dependency has been observed in the SnO<sub>2</sub> only films described in Section 4.2. The increased film density due to the consolidation of SnO<sub>2</sub> with increasing deposition temperature, is attributed to the red-shift in the SPR peak. It also indicates that it is possible to combine the functionalities of optical colouration and electrical conductivity using nanocomposites by incorporating gold NPs into a transparent conducting host by spray pyrolysis.

### **5.5.2 Au/SnO<sub>2</sub> composite thin films using HAuCl<sub>4</sub>**

Spray deposition of Au/SnO<sub>2</sub> composite thin films using HAuCl<sub>4</sub> as a precursor for Au NPs has also been investigated. The precursor solution was prepared by mixing monobutyltin trichloride (14.7 g, 0.05 mol) and HAuCl<sub>4</sub> (0.4 mg, 0.012 mmol) in 50 ml ethanol. The resultant solution was light yellow

and transparent. Spray deposition was carried out using this solution on float glass substrates under typical processing conditions ( $1.5 \text{ ml}\cdot\text{min}^{-1}$  precursor feed rate and 25 psi atomising air pressure) at different temperatures. The film deposited at  $250^\circ\text{C}$  showed a transparent red appearance in transmission, corresponding to an absorption band at 550 nm. This demonstrates the in-situ formation of Au NPs in  $\text{SnO}_2$  which results in SPR absorption. A higher temperature deposition at  $330^\circ\text{C}$  produced a film with blue colour, corresponding to a SPR peak at 588 nm. The red-shift is probably due to the further densification of  $\text{SnO}_2$  and corresponding higher refractive index. At a higher temperature of  $380^\circ\text{C}$ , however, the film deposited showed no colouration but some interference fringing was observed. A UV-visible transmittance spectrum showed no SPR band in the visible, indicating that no Au NPs were deposited and embedded in the  $\text{SnO}_2$  film (see Figure 5.14). Similar observations occurred for the films deposited at above  $380^\circ\text{C}$ . Four-point-probe measurements taken on these films showed that the sheet resistance decreased with increasing deposition temperature from  $200 \text{ k}\Omega/\square$  at  $330^\circ\text{C}$  to  $1 \text{ k}\Omega/\square$  at  $380^\circ\text{C}$ . This is consistent with the films deposited using preformed Au NPs described in the previous section.



**Figure 5.14 Transmittance spectra of Au/SnO<sub>2</sub> thin films spray deposited at different temperatures using HAuCl<sub>4</sub> as a precursor. SPR peaks are observed for films deposited at 250 °C (553 nm) and 330 °C (588 nm) respectively, while the film deposited at 380 °C shows no SPR peak.**

### 5.5.3 Summary

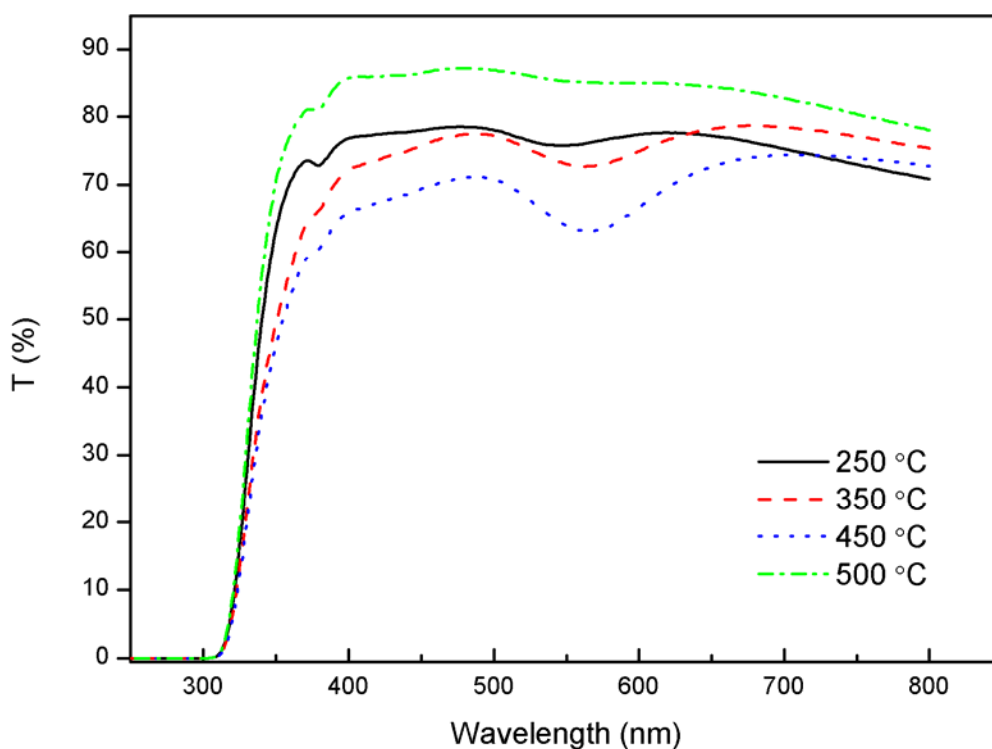
These experiments have demonstrated that Au/SnO<sub>2</sub> composite thin films can be deposited by the spray pyrolysis technique using two types of gold source; preformed gold NPs and HAuCl<sub>4</sub>. In contrast to the Au/TiO<sub>2</sub> films, successful incorporation of Au NPs into the films is more sensitive to the substrate temperature. No Au NPs were embedded in the SnO<sub>2</sub> host when the substrate temperature was too high. It is also remarkable to note that relatively conductive Au/SnO<sub>2</sub> composite films were obtained, indicating the possibility of producing both conducting and coloured thin films. It should be noted that in this section

only the deposition Au/SnO<sub>2</sub> films is reported. Au/SnO<sub>2</sub>:F films will be further discussed in the next chapter.

## **5.6 Spray deposition of Au/ZnO composite thin films**

### **5.6.1 Au/ZnO films using preformed gold nanoparticles**

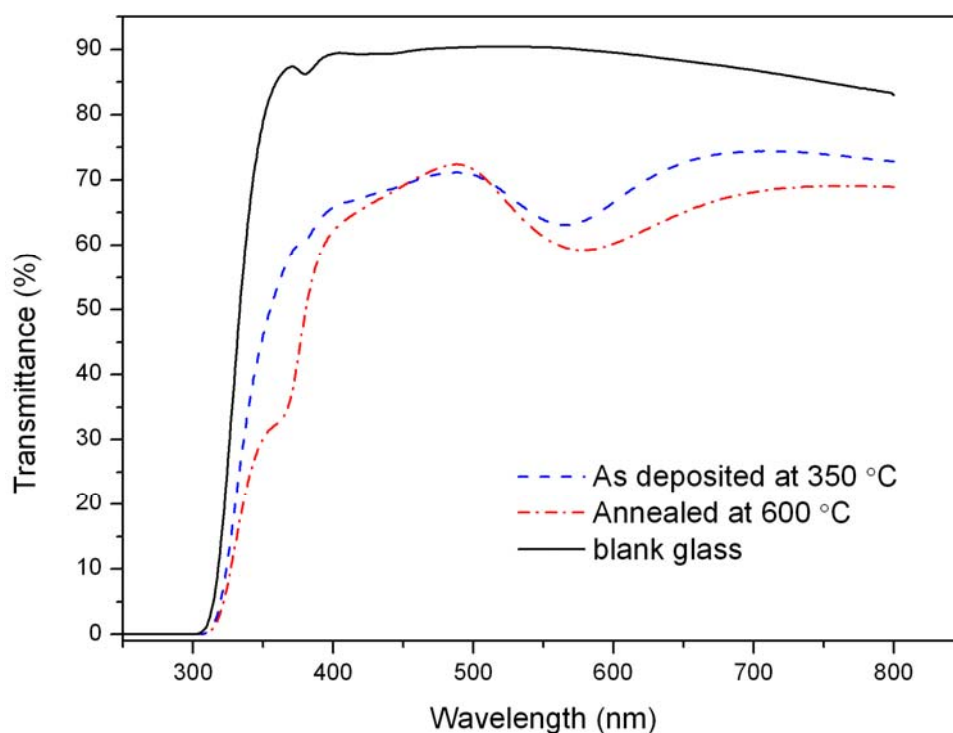
Au/ZnO composite thin films were investigated using gold colloids (3.74 mmol·L<sup>-1</sup>, 0.13 mmol) and zinc diaminobutanoate (0.1 mol·L<sup>-1</sup>, 2.5 mmol) in deionised H<sub>2</sub>O. Spray deposition was carried out on float glass at different temperatures from 250 °C to 550 °C with typical operating conditions (1.5 ml·min<sup>-1</sup> precursor feed rate, 25 bar atomised air pressure). It has been observed that thin films with a colouration feature were obtained when deposited over the temperature range of 250 to 450 °C, while at and above 500 °C only transparent films without colour were obtained. UV-visible transmittance spectra of these films were measured and shown in Figure 5.15. It is observed that for the films deposited at 250, 350 and 450 °C, the SPR absorption band position was at 545 nm, 568 nm and 575 nm respectively. This demonstrated the incorporation of gold NPs into the films and the corresponding SPR absorption. It is also noted that, similar to the previous observations with Au/TiO<sub>2</sub> and Au/SnO<sub>2</sub>, the SPR peak red-shifts with increasing substrate temperature. This is probably due to an increased refractive index of the host material.



**Figure 5.15 Transmittance spectra of Au/ZnO thin films spray deposited at different temperatures using gold colloids as precursor. SPR peaks are displayed for films deposited at 250 °C (545 nm), 350 °C (568 nm) and 450 °C (575 nm) respectively, while the film deposited at 500 °C shows no SPR absorption.**

The film deposited at 350 °C was further treated by annealing at 600 °C in air for 2 hours. A UV-visible spectrum shows that after heat treatment the SPR band red-shifts from 564 nm to 579 nm. The ZnO band gap absorption feature in the UV region was also observed, indicating band gap narrowing due to the densification and crystallisation of ZnO during annealing treatment (Figure 5.16). It is also noted that there is a step change of shape in the band gap absorption edge for the film annealed at 600 °C. Compared to the spectrum of blank float glass, the absorption edge of the as-deposited film is very close to that of the

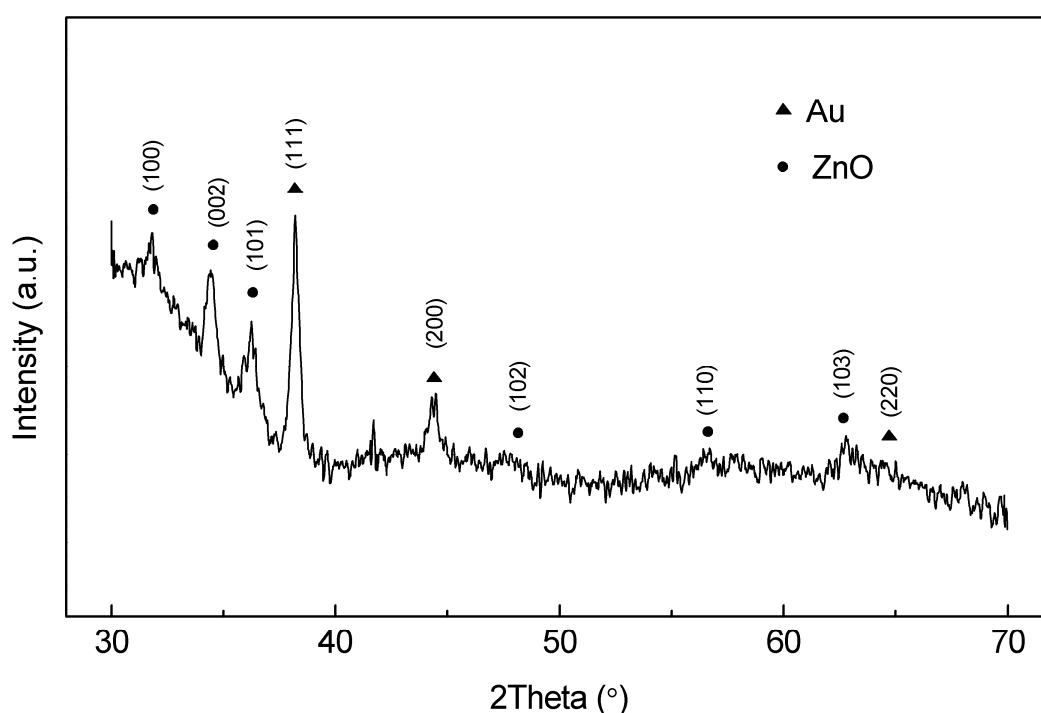
blank glass, while for the annealed film, a transition was observed from 310 nm to 350 nm, which is close to the band gap of ZnO (3.37 eV). This is possibly because of the incomplete oxidation of ZnO leading to mixtures of a less dense (non-crystalline) and crystalline film even after 2 hours of annealing. Similar observations have been reported by other researchers [279, 280].



**Figure 5.16 Transmittance spectra of Au/ZnO composite films which were as-deposited at 350 °C and subsequently annealed at 600 °C. The SPR absorption was observed to red-shift after annealing. The band gap absorption edge is also seen as a step in the increasing transmittance due to a mixture of amorphous and crystalline material.**

The XRD pattern for the annealed film in Figure 5.17 also indicates the presence of ZnO (ICCD reference code: 01-079-0206) and Au (ICCD Reference Code 01-089-3697). It should be noted that the peaks for gold in the diffraction

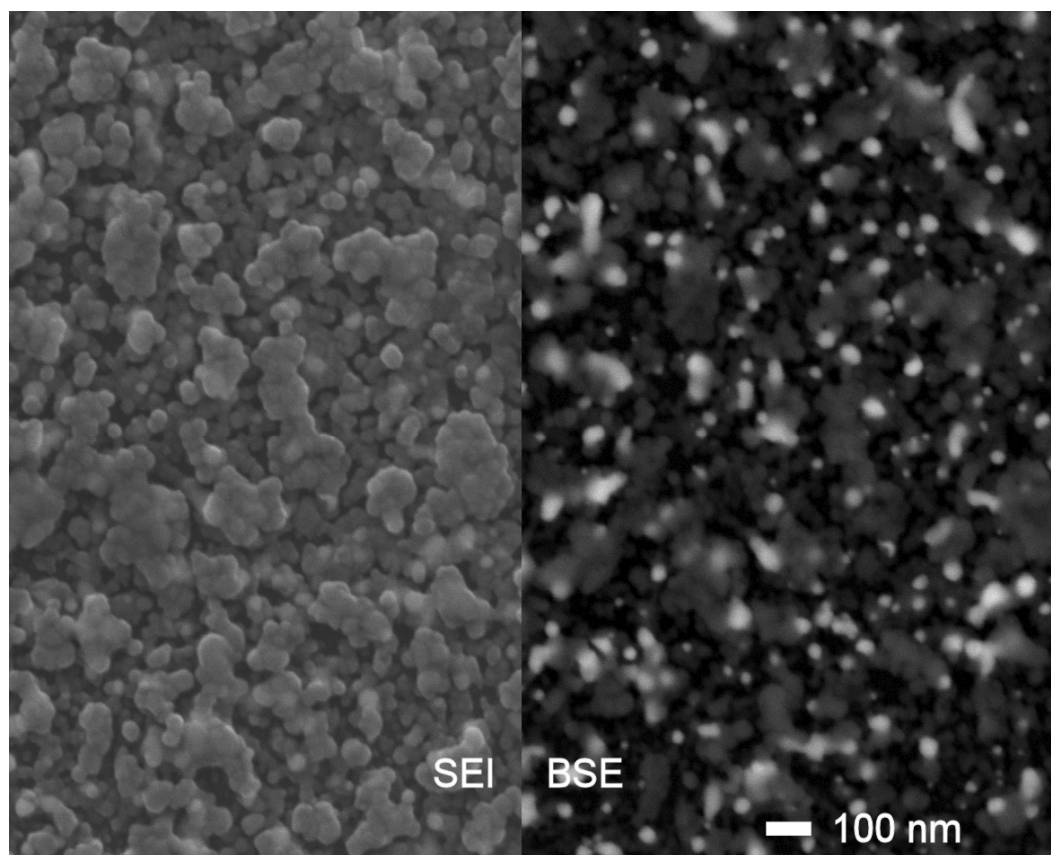
pattern are intense, probably because the gold particles were synthesised ex-situ under a controlled condition and displayed a sufficiently crystalline structure. In contrast, the peaks for ZnO are comparably weak, compared to that of the ZnO only films deposited at the same temperature as investigated in section 4.3.1. This is probably because of the incomplete oxidation resulting in poorly oxidised and crystalline structure despite the 2 hours of annealing. This is consistent with the observations from the optical spectra. It also suggests that the ZnO formation may be suppressed by the incorporation of gold NPs.



**Figure 5.17 XRD pattern for a typical Au/ZnO composite film using preformed gold NPs showing the presence of both Au and ZnO.**

SEM images for the annealed Au/ZnO film were taken and shown in Figure 5.18. It has been observed that the film consists of small round-shaped particles (with a size of 40-50 nm) along with irregular and large particles (with a size of

200-600 nm). These large particles seem to be composed of agglomerated and sintered small particles. Backscattered electron mode imaging indicates the presence of gold NPs (see brighter spots in Figure 5.18), which are either discretely distributed or agglomerated.



**Figure 5.18 SEM images of Au/SnO<sub>2</sub> film using gold colloids as a precursor which was deposited at 350 °C and then annealed at 600 °C. Left: secondary electron mode imaging; right: backscattered electron mode imaging, where the bright spots are interpreted as gold NPs.**

### 5.6.2 Au/ZnO composite films using $\text{HAuCl}_4$

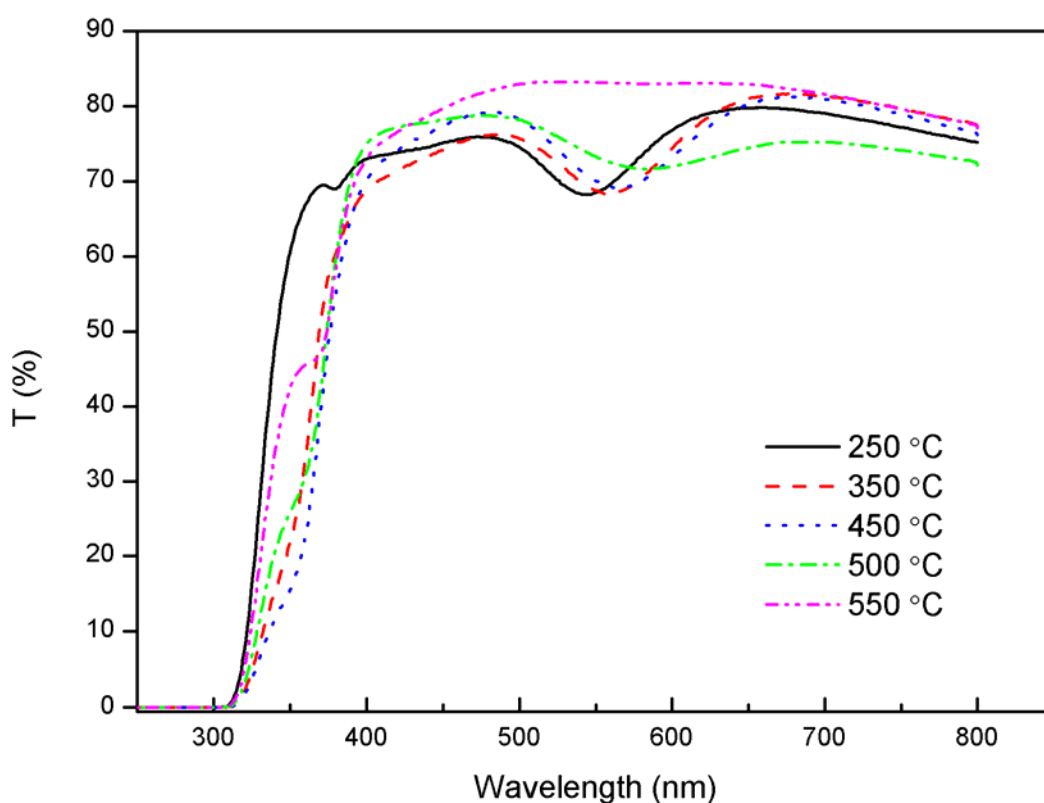
Au/ZnO films were also obtained by spray deposition using  $\text{HAuCl}_4$  (3 mg, 0.0088 mmol) and zinc aminobutanoate ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ , 5 mmol) in 50 ml  $\text{H}_2\text{O}$ . Typical processing conditions ( $1.5 \text{ ml}\cdot\text{min}^{-1}$  precursor feed rate and 25 psi atomising air pressure) and a range of different temperatures were applied. Transparent and coloured thin films were obtained for temperatures from  $200^\circ\text{C}$  to  $500^\circ\text{C}$ , while the films deposited at above  $500^\circ\text{C}$  show transparent layers without any colouration feature. The colour of the film is dependent on the deposition temperature; light red for films deposited at  $200\text{--}250^\circ\text{C}$  and purple/blue for films deposited at  $350\text{--}500^\circ\text{C}$  (see Figure 5.19).



**Figure 5.19** Photo showing the appearance of  $\text{Au/SnO}_2$  composite coating deposited on glass at  $450^\circ\text{C}$  using  $\text{HAuCl}_4$ .

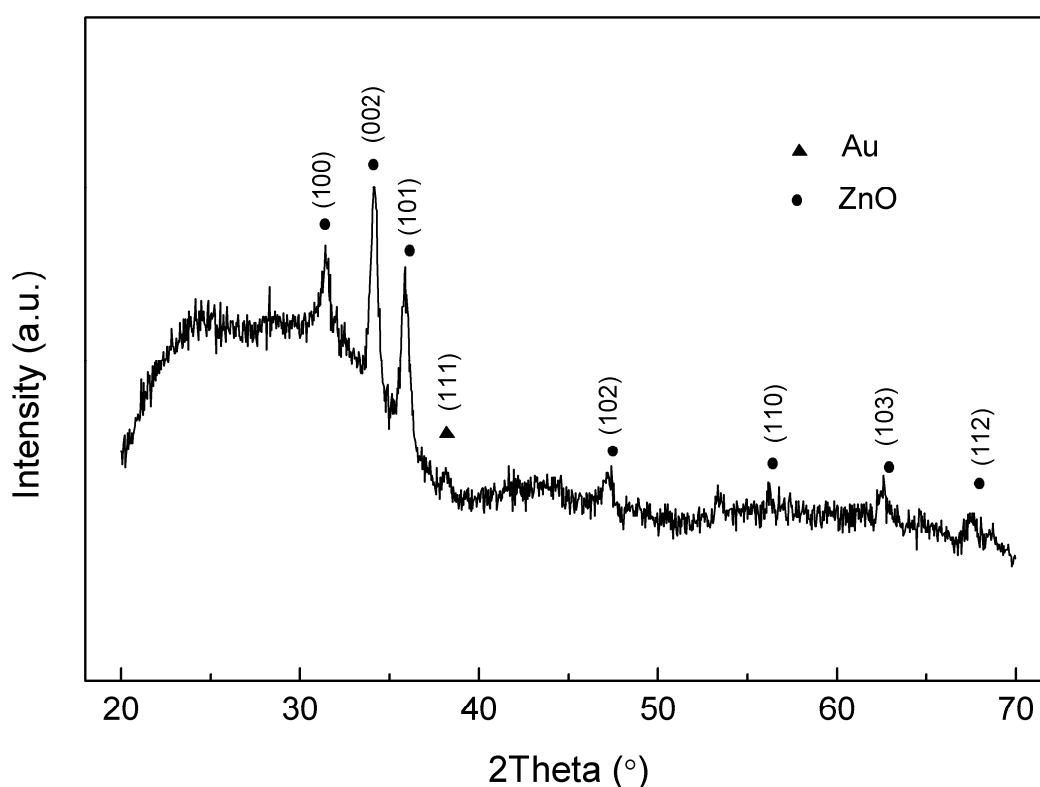
UV-visible transmittance spectra of the films showed SPR peaks displayed in the visible region and their positions red-shifted from 542 nm to 582 nm with increasing temperature from  $250$  to  $500^\circ\text{C}$  (see Figure 5.20). The spectrum for

the film deposited at 550 °C is almost “flat” in the visible region showing no SPR absorption. It has also revealed that the band gap absorption edge in the UV region shift from 330 nm to 360 nm (except the case at 250 °C). This is an indication of ZnO formation above 350 °C, which was also observed in the deposition of Au/ZnO using preformed gold NPs. This indicates that as the deposition temperature increases, the ZnO is oxidised and crystallised more completely.



**Figure 5.20 Transmittance spectra of Au/ZnO thin films spray deposited at different temperatures using HAuCl<sub>4</sub> as precursor. SPR peaks are displayed for films deposited at 250 °C (542 nm), 350 °C (559 nm), 450 °C (567 nm) and 500 °C (583 nm) respectively, while the film deposited at 550 °C shows no SPR absorption.**

The XRD pattern for the film deposited at 450 °C indicated the presence of ZnO with typical planes of (100), (002) and (101), as well as the presence of Au with a very weak peak displayed at 38° (2 $\theta$ ). The diffraction peak for Au is a lot weaker than that in the corresponding Au/ZnO film using preformed Au NPs (Figure 5.21). This is probably because the preformed Au NPs are larger and more crystalline, which can be concluded as the XRD pattern has higher intensity. It should also be noted that there is a broad peak between 25° and 35°. This is probably from not only the glass substrate but also the amorphous ZnO formed in the deposition which was mixed with the crystalline ZnO [281].

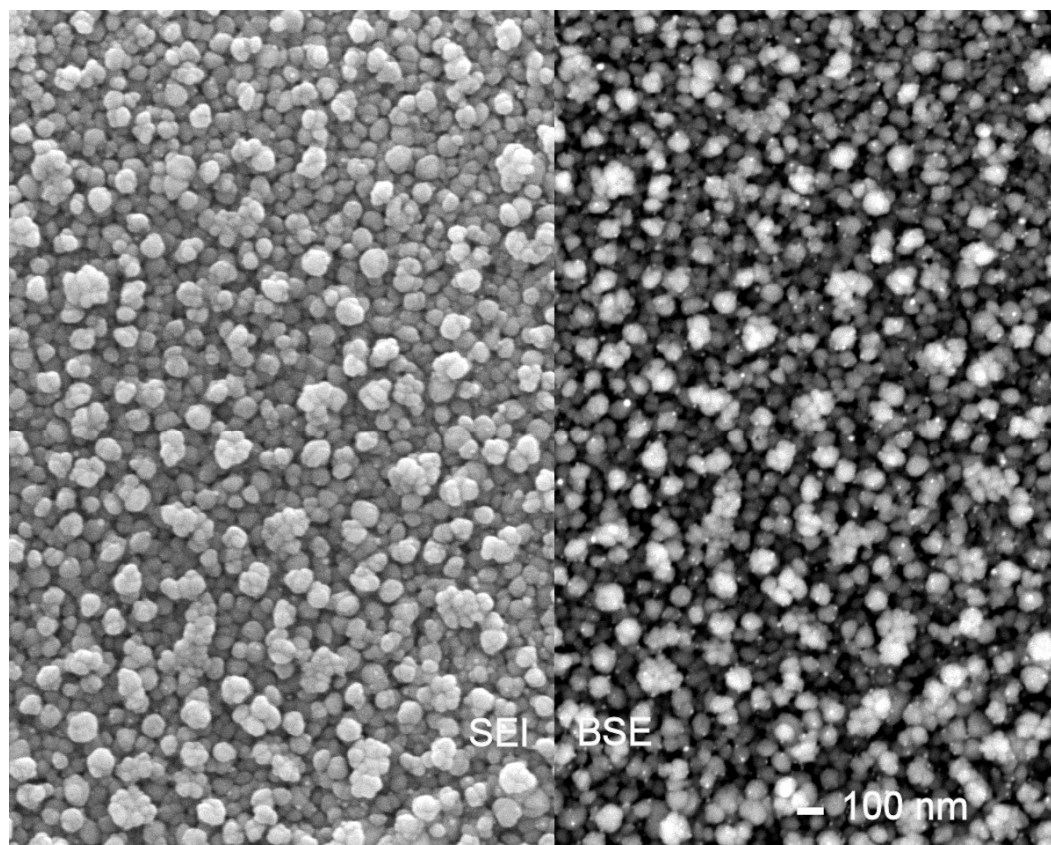


**Figure 5.21 XRD pattern for Au/ZnO composite film using HAuCl<sub>4</sub> as gold NP precursor showing the presence of Au and ZnO.**

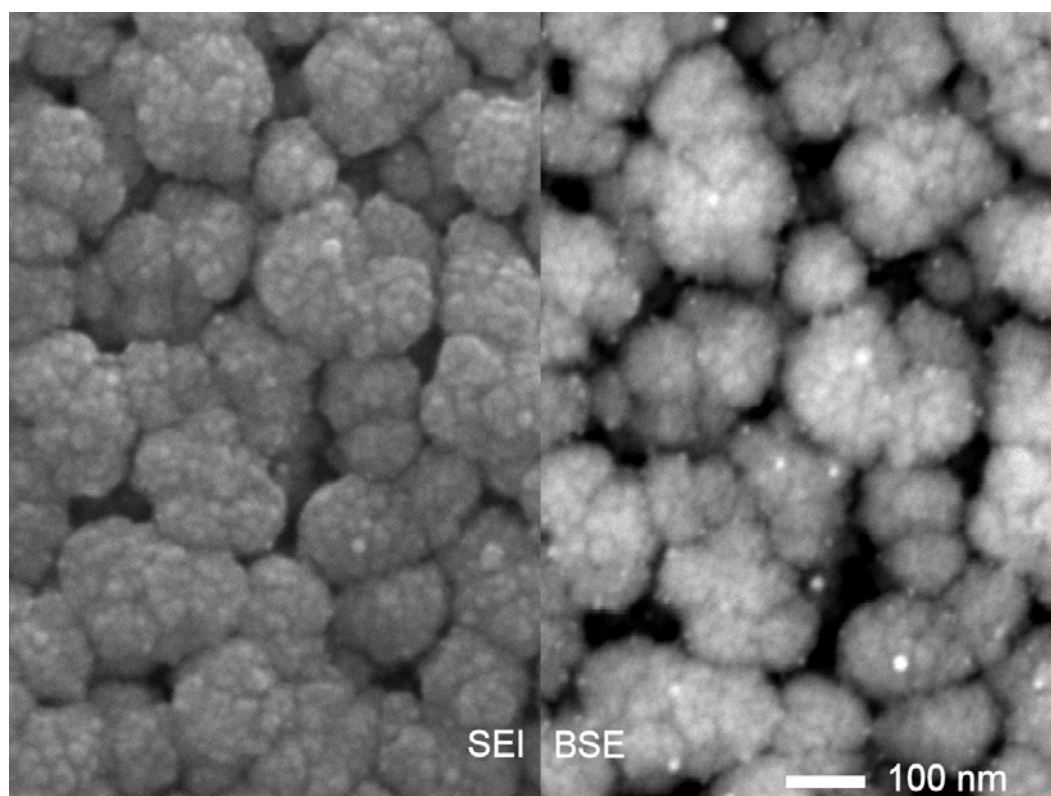
SEM images of the same film have been taken and presented in Figure 5.22. It is also noted that the morphology of the composite film is different from the ZnO only film due to the addition of HAuCl<sub>4</sub>. It is observed that the film is composed of round-shaped particles; the average size of which is 50 – 80 nm, while much smaller particles of about 5 nm are distributed on the surface of the large particles. Backscattered electron mode imaging indicates that the smaller particles are gold while the large particles are ZnO. At a higher magnification it is shown that the larger particles of ZnO are actually composed of smaller grains which are about 5–10 nm (Figure 5.23). This therefore indicates the composite films are deposited from smaller grains which grow and agglomerate into larger particles and finally form the thin film. SEM images of this film also confirmed the Au particles did indeed form in-situ during the deposition process. The average size is about 5 nm across, being smaller than the preformed Au NPs which are 15-20 nm.

### **5.6.3 Summary**

Au/ZnO nanocomposite films have been prepared by spray pyrolysis deposition using either gold colloids or HAuCl<sub>4</sub>. Gold NPs were successfully embedded in ZnO host except at a high substrate temperature. UV-visible transmittance spectra for these films showed the SPR absorption peak as well as the bandgap shift for ZnO. ZnO, together with SnO<sub>2</sub>, has demonstrated their capability to incorporate gold NPs which can lead to further applications such as in solar control.



**Figure 5.22 SEM images of Au/ZnO films deposited at 450 °C using  $\text{HAuCl}_4$  as a precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging, where the bright spots were interpreted as gold NPs.**



**Figure 5.23 SEM images of Au/ZnO films deposited at 450 °C using the H<sub>Au</sub>Cl<sub>4</sub> precursor. Left: secondary electron mode imaging; right: backscattered electron mode imaging, where the bright spots were interpreted as gold NPs. At this higher magnification, the large ZnO particles are seen to be composed of smaller grains of 5-10 nm in size.**

## 5.7 Discussion

### 5.7.1 Spray deposition mechanism

It has been demonstrated that gold/metal oxide composite thin films have been successfully deposited on glass by spray pyrolysis deposition. Three types of composite films, Au/TiO<sub>2</sub>, Au/SnO<sub>2</sub> and Au/ZnO, have been produced using compatible precursors for metal oxide and two gold precursors, gold colloids and HAuCl<sub>4</sub>. The spray deposition technique has been developed to meet the challenge of producing nanocomposite thin films at high deposition temperature in a single-step process. Spray pyrolysis deposition is a technique involving many processes, such as aerosol generation and transportation, solvent evaporation, droplet impact with substrate and precursor decomposition. It has been reported that the most important parameter in all these processes is the substrate temperature which has been reviewed in Chapter 2 and will be discussed in further detail in the following sub-sections. At low temperatures (normally below 200 °C), the droplets deposited are generally still rich in solvent. Therefore the droplets impact the surface of the substrate and form a thin and wet layer during deposition. The precursors for the host materials do not entirely decompose, resulting in non-dense and amorphous films with low refractive index. Only at higher temperatures do the solvents in the droplets evaporate during transportation. Subsequently the concentrated droplets impact on the substrate surface and start to decompose forming a dense thin film with a higher refractive index. While at higher temperatures (above 450 °C in our experiments, for example), the droplets are almost “dry” and the precursors in the droplets start to precipitate and decompose during transportation in the air flow. This situation

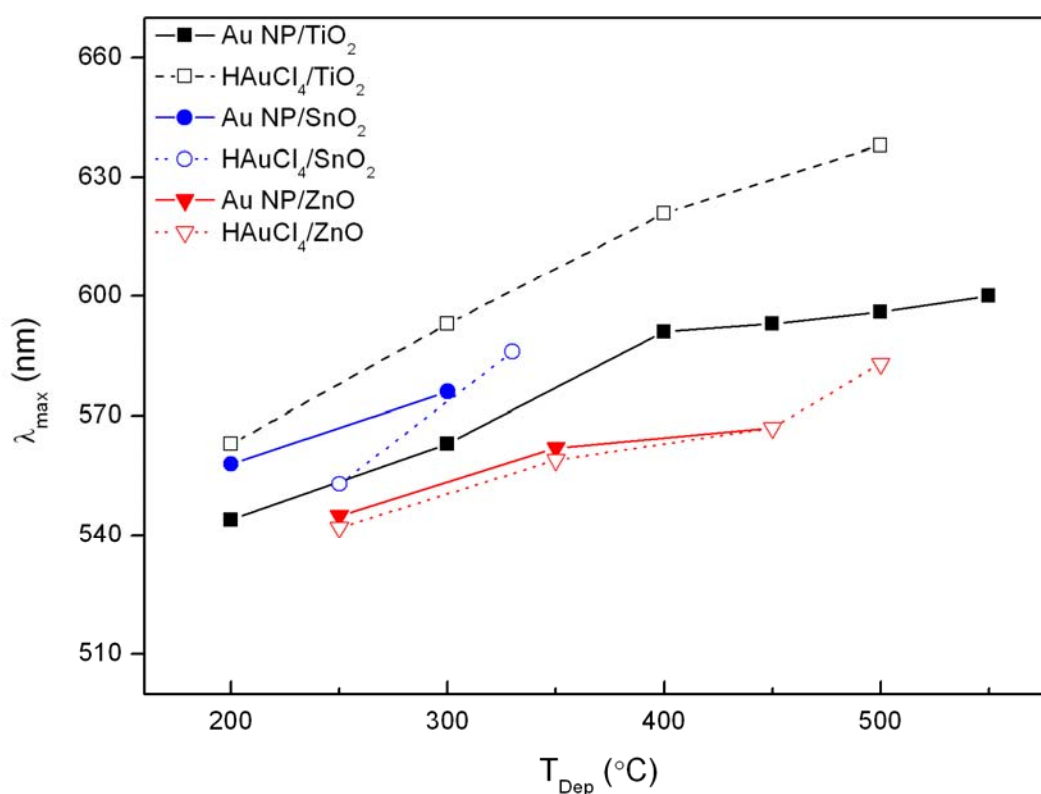
may form powders that cannot be adhered to the substrates. The deposition temperature therefore has a great influence not only on the morphology but also the crystallinity and density of the films, which determine the optical, electrical and catalytic properties [40]. For different precursor materials, the temperature window for successful deposition varies and needs to be investigated. Therefore the deposition temperature should be carefully controlled to establish the desired properties of the composite films.

### **5.7.2 Optical properties and surface plasmon resonance effects**

The most significant feature of these gold/metal oxide composite films (using preformed gold NPs or  $\text{HAuCl}_4$ ) is that they can all produce uniform and intense colour due to the surface plasmon resonance effects of the gold nanoparticles embedded within the films. As we know, SPR originates from the dipolar oscillation of the conduction band electrons of the noble metals which induces a dip in the intensity of the optical transmission in the visible spectrum. The intensity of the transmitted colour by the composite films is comparable to commercial body tinted glass, indicating the possibility of substituting the body-tinted glass process with a coating-tinted glass [9].

It has been observed that the optical properties of composite films are greatly influenced by the deposition temperature. In the experiments, colour change has been observed for composite films which were deposited at different substrate temperatures; consistently appearing red at a lower process temperature and blue at a higher temperature. This red-shift in the SPR absorption peak due to increased refractive index of surrounding materials by heat treatment has been reported previously in similar nanocomposites [8, 179, 277, 278].

Figure 5.24 summarises the wavelength of the SPR peak for gold NPs in different host materials at different deposition temperatures. It has been observed that the SPR peak position is greatly influenced by the refractive index of the host material, which is also temperature dependent. The Au/TiO<sub>2</sub> films generally display SPR peaks with longest wavelength, while the Au/ZnO films show the shortest. This is because the three host materials have different refractive indices; such that  $n(\text{ZnO}) < n(\text{SnO}_2) < n(\text{TiO}_2)$ , which results in a red-shift.



**Figure 5.24 Summary of SPR peak positions of Au/metal oxide composite films at different deposition temperatures. The gold NPs, either using preformed particles (solid symbol) or HAuCl<sub>4</sub> (hollow symbol) as precursors, were embedded into three different host materials: TiO<sub>2</sub> (black), SnO<sub>2</sub> (blue) and ZnO (red).**

One interesting exception is observed at a lower deposition temperature (200-300 °C) when the Au/SnO<sub>2</sub> films showed longer SPR wavelength than Au/TiO<sub>2</sub> films, indicating that the refractive index of SnO<sub>2</sub> is higher than TiO<sub>2</sub> when deposited at this temperature. This is probably because the precursor for SnO<sub>2</sub>, monobutyltin trichloride, decomposes and consolidates at a lower temperature (~300 °C) than the TiO<sub>2</sub> precursor (ammonium titanium lactate) (~400 °C). Therefore a dense SnO<sub>2</sub> host layer of a higher refractive index is likely to be formed even at such a lower temperature while TiO<sub>2</sub> is still incompletely oxidised and therefore of lower refractive index.

### **5.7.3 The incorporation of gold nanoparticles in host matrix**

In the composite thin film where the host material serves as a protecting and stabilising surrounding for the particles, the method employed to embed the particles in the host matrix is an important process to be considered. In the single-step deposition via a chemical route, successful deposition requires the preparation of a stable and homogeneous suspension containing the precursors of both particles and host material. There are constraints imposed on obtaining a stable single-source suspension due to issues relating to pH, choice of solvents and concentration which might result in immiscible solutions and subsequent flocculation. Therefore, careful investigation has been made in our experiments to determine compatible precursor components for preparation of a one-pot suspension for a single step deposition of coloured TCO.

In this work, two methods to obtain gold NPs have been employed. For the case of using preformed nanoparticles, the aqueous colloids are stabilised with aminobenzoate with a pH of 8.5. Ammonium titanium lactate is therefore chosen

as a precursor for titania to be compatible with aqueous gold colloids. However, using monobutyltin trichloride would react with water forming HCl which would change the pH of the gold colloid and result in flocculation. Therefore, gold NPs dispersed in ethanol were prepared and used so as to be compatible with the tin compound. In all the cases of in-situ formation of gold NPs in different hosts (i.e.  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$ ), it was found that  $\text{HAuCl}_4$  can be mixed with all the precursors with a variable ratio of concentration without flocculation.

Also the incorporation of gold nanoparticles into the host material during the deposition process is essential for successful deposition of a homogeneous composite thin film. In our spray deposition experiment, it has been discovered that gold NPs were not embedded into the host materials at a high substrate temperature, especially for the case of  $\text{Au/SnO}_2$  (over  $350\text{ }^\circ\text{C}$ ) and  $\text{Au/ZnO}$  (over  $450\text{ }^\circ\text{C}$ ). One of the probable reasons might be due to the low decomposition temperature of the tin (or zinc) compound and high evaporation rate of ethanol when compared to the titanium precursor. Droplets might therefore result in powder formation during aerosol transportation, which segregate from the gold particles in air. Moreover, high temperature not only increases droplet solvent evaporation rate and accelerates precursor decomposition, but also enhances thermophoretic forces which hinder the droplet's transportation. The thermophoretic force pushes the droplets away from a hot substrate, because the gas molecules from the hotter side of the droplet collide with higher kinetic energy than those from the cooler side [40]. The gold nanoparticles might therefore be prevented from embedding into the host material during the deposition process due to the action of thermophoresis. It is desired that most

droplets, together with gold NPs in them, strike and spread out over the substrate where decomposition and thin film formation occur.

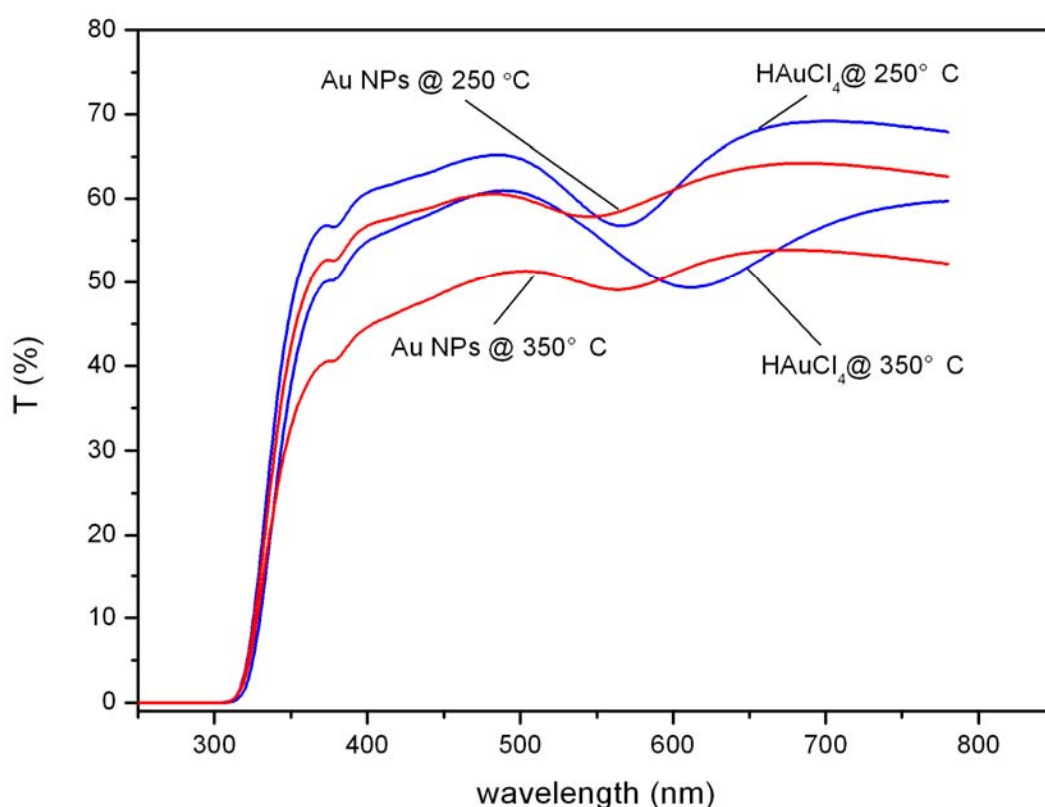
During the deposition process the host material not only serves as the entrapping agent but also the nucleation site and stabilisation matrix, which can assist with the embedding mechanism into the host matrix [200]. However, the addition of gold NPs can reduce the formation and crystallisation of the host material as observed in the XRD results that showed no significant diffraction peaks for  $\text{TiO}_2$  and  $\text{SnO}_2$  in the composite films.

#### **5.7.4 Comparison between using preformed Au NPs and $\text{HAuCl}_4$**

It has been demonstrated that gold/metal oxide composite thin films can be successfully deposited by a spray deposition technique in which the gold nanoparticles are formed either before the deposition or during the deposition. In both cases the films are robust with intense colour in which the position of the SPR peaks is dependent on the substrate temperature.

Figure 5.25 shows the optical spectra of typical  $\text{Au/TiO}_2$  films comparing both deposition methods. For the preformed nanoparticles, curves corresponding to two deposition temperatures at 250 °C and 350 °C demonstrate that the width of the SPR absorption is very similar. In contrast, the width of the SPR absorption for the in-situ growth deposition method shows significant broadening of the absorption feature at higher substrate temperature. This is interpreted as follows. The size of the preformed nanoparticles does not change during any of the thin film deposition processes, consistent with the unchanged shape of the absorption peaks. While for the particles formed in-situ, the size distribution is a function of the spray conditions and substrate temperature which impacts on the

nanoparticle growth process. Therefore a broader size distribution and hence absorption peak shape is observed when the particles are formed at a higher substrate temperature. It is also noticed that the intensity of the plasmon resonance peak of the gold nanoparticles formed in-situ using  $\text{HAuCl}_4$  is stronger and this is attributed to the higher concentration of  $\text{HAuCl}_4$ . In fact the concentration of  $\text{HAuCl}_4$  can be more conveniently varied over a wider range of precursor ratios resulting in more intense colouration and red-shift of the SPR peak [200]. The red-shift might be regarded as the contribution of larger gold nanoparticles and shorter inter-particle distance due to the higher gold concentration used.



**Figure 5.25** Transmittance spectra corresponding to two methods of depositing  $\text{Au/TiO}_2$  composite thin films at two different substrate temperatures using  $\text{HAuCl}_4$  and preformed Au NPs.

To summarise, using preformed gold NPs can provide well controlled particle size and monodispersity, albeit with restriction on the concentration and likely stability when mixed with precursors for the host material. In contrast using  $\text{HAuCl}_4$  as a convenient gold NP source provides wider flexibility in terms of concentration and compatibility with host precursors, but the experimental conditions need to be more carefully controlled to obtain a monodispersed particle size distribution.

## 5.8 Conclusion

A spray pyrolysis deposition technique has been developed to produce gold-incorporated nanocomposite thin films in a single-step process. Gold NPs, formed either ex-situ or in-situ, have been embedded into three different metal oxide hosts of  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$ . The films showed intense colouration due to the characteristic SPR absorption of gold NPs. XRD analysis indicated the presence of gold NPs in the films. It is found that substrate temperature plays an important role in the properties of the composite films in terms of microstructure and optical transmission. SPR peak position is dependent on the surrounding host medium which is influenced by the substrate temperature. It is noted that the gold/ $\text{SnO}_2$  composite films display colouration and reasonable conductivity, suggesting potential applications for coloured and transparent conductors. However, the films obtained with a single layer are not conducting enough to display a corresponding IR reflection due to the plasma edge effects associated with the available free carriers. A further investigation of Au NPs incorporated into doped TCO and their multi-layered films should be considered.

## **CHAPTER 6**

# **SPRAY DEPOSITION OF METAL OXIDE/GOLD-METAL OXIDE COMPOSITE MULTILAYER THIN FILMS**

### **6.1 Introduction**

This chapter investigates the deposition of double-layered thin films as a process step towards coloured TCO composite films. As is observed in Section 5.4, nanocomposite films of gold NPs incorporated into a  $\text{SnO}_2$  host not only display colour due to the SPR effect of the gold NPs but also allow conductivity from the  $\text{SnO}_2$ . This has indicated the possibility of producing a composite film by combining the functions of colouration, conductivity and even control of IR reflection. However, such kind of composite films typically possess a resistance in the order of  $\text{k}\Omega$ s, which is far too high to achieve the desired IR reflection for solar control via free carrier interactions. There are some restrictions on the production of a single-layered composite film when aiming for high conductivity. First, the incorporation of gold NPs deteriorates the crystalline structure of a TCO and may prevent it from achieving high conductivity. Second, there is the dilemma of trying to incorporate gold NPs whilst simultaneously producing a good quality film at a high temperature where the temperature gradient above the

heated substrate prevents incorporation of the NPs into the film due to a thermophoretic effect. Therefore it might be more advantageous to apply the NP and TCO layers in two stages; a TCO layer on top of a NP embedded composite layer which will act to protect the composite layer due to the mechanical properties of the TCO layer and attain a more robust film.

## **6.2 Spray deposition of double-layered thin films of a $\text{SnO}_2\text{:F}$ + Au/ $\text{SnO}_2\text{:F}$ composite**

### **6.2.1 Spray deposition experiment**

The float glass substrate was first deposited with a composite layer of Au/ $\text{SnO}_2\text{:F}$  according to the experimental conditions described in Section 5.5. Monobutyltin trichloride (14.7 g, 0.05 mol) and trifluoroacetic acid (1 ml, 0.013 mol) along with  $\text{HAuCl}_4$  (0.4 mg, 0.012 mmol) were dissolved in 50 ml of ethanol, resulting in a transparent and stable solution. Spray deposition using this solution was carried out on a float glass substrate at 340 °C and under typical processing conditions (1.5 ml·min<sup>-1</sup> precursor feed rate and 25 psi atomising air pressure). The as-deposited film displayed a transparent purple-blue appearance in transmission which is a consequence of the characteristic SPR effect from the gold NPs. A second layer of  $\text{SnO}_2\text{:F}$  was then deposited on top according to the experimental conditions described in Section 4.2. The solution containing monobutyltin trichloride (14.7 g, 0.05 mol) and trifluoroacetic acid (1 ml, 0.013 mol) was sprayed onto the as-prepared Au/ $\text{SnO}_2\text{:F}$  composite film at 450 °C. The resulting double-layered film displayed a deeper blue colour compared to the single layer film which is likely due to the additional layer of  $\text{SnO}_2\text{:F}$ . An

interference fringing appearance was also observed. Figure 6.1 shows the images of the two coatings on glass in comparison to the blank glass. These two films were analysed as deposited without further thermal treatment.



**Figure 6.1 Photo showing appearance of blank float glass (left), Au/SnO<sub>2</sub>:F composite coating on glass (middle) and composite coating with an additional SnO<sub>2</sub>:F layer on top (right).**

### 6.2.2 Characterisations

The two films, i.e. the initial Au NPs embedded composite thin film of Au/SnO<sub>2</sub>:F (referred to as the “composite single layer”) and the resulting combined double-layered film with a SnO<sub>2</sub>:F top layer (referred to as the “double layer”), were investigated by characterisation of their optical, electrical and microstructural properties for further comparison.

The sheet resistance of both films were measured based on the four-point probe technique. It was determined that the sheet resistance for the composite single layer was 30 k $\Omega/\square$ , while for the double-layered film it was drastically reduced to 50  $\Omega/\square$ . The thickness determined by SEM for both films are 92 nm and 1100 nm respectively, corresponding to a calculated resistivity as 0.28  $\Omega\cdot\text{cm}$  and  $5.5 \times 10^{-3} \Omega\cdot\text{cm}$ . The significantly decreased electrical conductivity for the

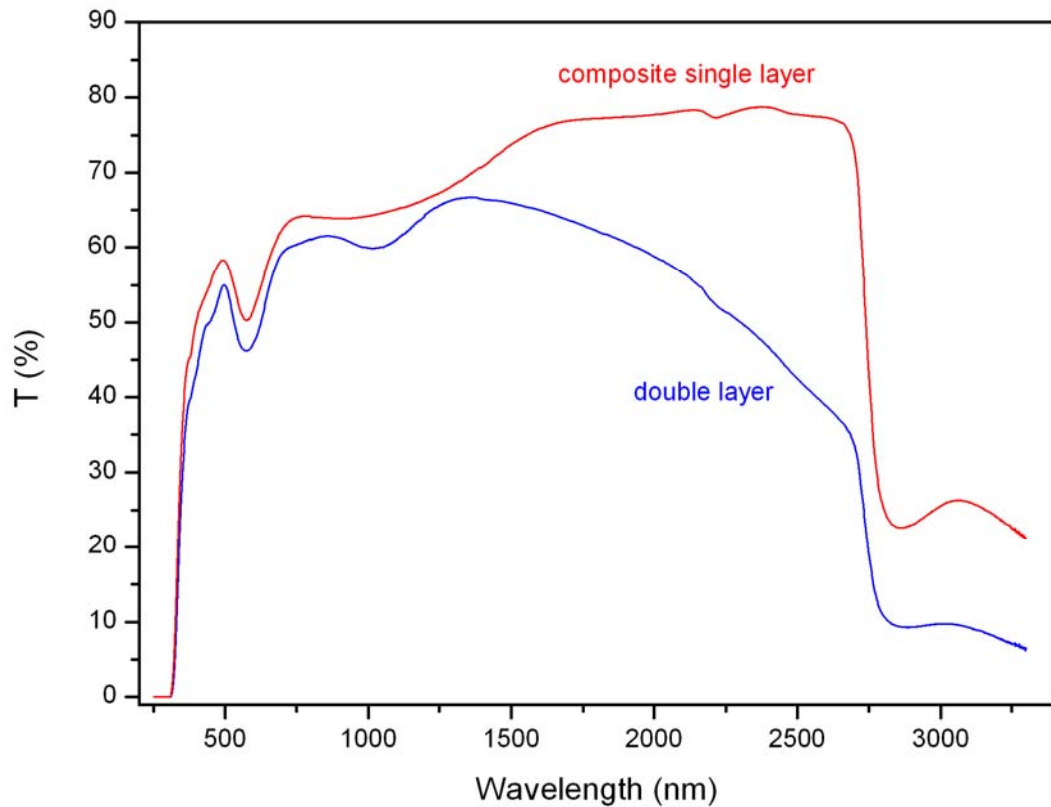
double-layered film can therefore be attributed to the additional conducting layer of SnO<sub>2</sub>:F on top.

The optical properties of both films were characterised by measurement over the range from visible to near infrared. Figure 6.2 and Figure 6.3 shows the transmittance and reflectance spectra for both films in the range from 250 nm to 3300 nm.

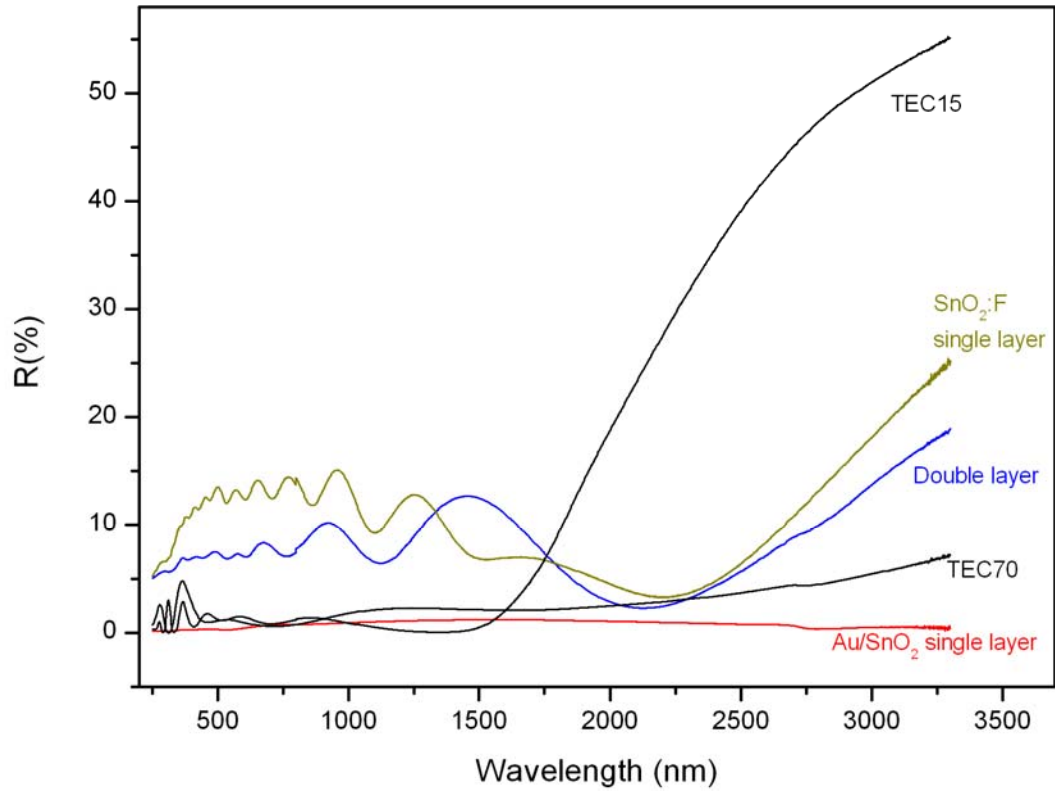
As seen in Figure 6.2, both the films show similar transmission properties in the visible region (300-750 nm), displaying an intense absorption peak at 580 nm. This is due to the characteristic SPR effect of gold NPs embedded in the SnO<sub>2</sub>:F host, which can be noted as the same observation discussed in Section 5.5. However, in the infrared region, the composite single-layered film shows high transparency to infrared radiation as observed before, while the double-layered film displays a significant attenuation in the infrared transmission from 64% at 1300 nm to 32% at 2700 nm. In addition, the interference effect observed with the double-layer film is not as intense as that observed in the SnO<sub>2</sub>:F only film, probably due to the insertion of the composite layer as an optical buffer layer. It should also be noted that there is a sharp edge at 2800 nm beyond which the transmission is dramatically reduced. This is because of the absorption from the float glass substrate. Nevertheless, this experiment has demonstrated the possibility of controlling the optical properties in both the visible and infrared regions by building up a double-layered film which combines the colouration feature derived from the Au NPs incorporated layer and the solar control from the TCO layer of SnO<sub>2</sub>:F.

The reflection spectra of the films with the double layer also show a higher reflectance in the infrared than that of the composite single layer (Figure 6.3).

Apparently the reflectance is still much lower than the commercially available SnO<sub>2</sub>:F coating (e.g. Pilkington TEC 15 glass which is nominally 15 Ω/□, see Figure 6.3 for comparison), but comparable to the SnO<sub>2</sub>:F single layer (dark yellow trace) investigated in Section 4.2, only slightly lower in the infrared. It should be noted that the reflectance of the double layer in the visible region is also lower than that of the SnO<sub>2</sub>:F only layer; probably due to the insertion of the composite layer which works as an optical buffer to reduce the reflection (see Figure 6.3).



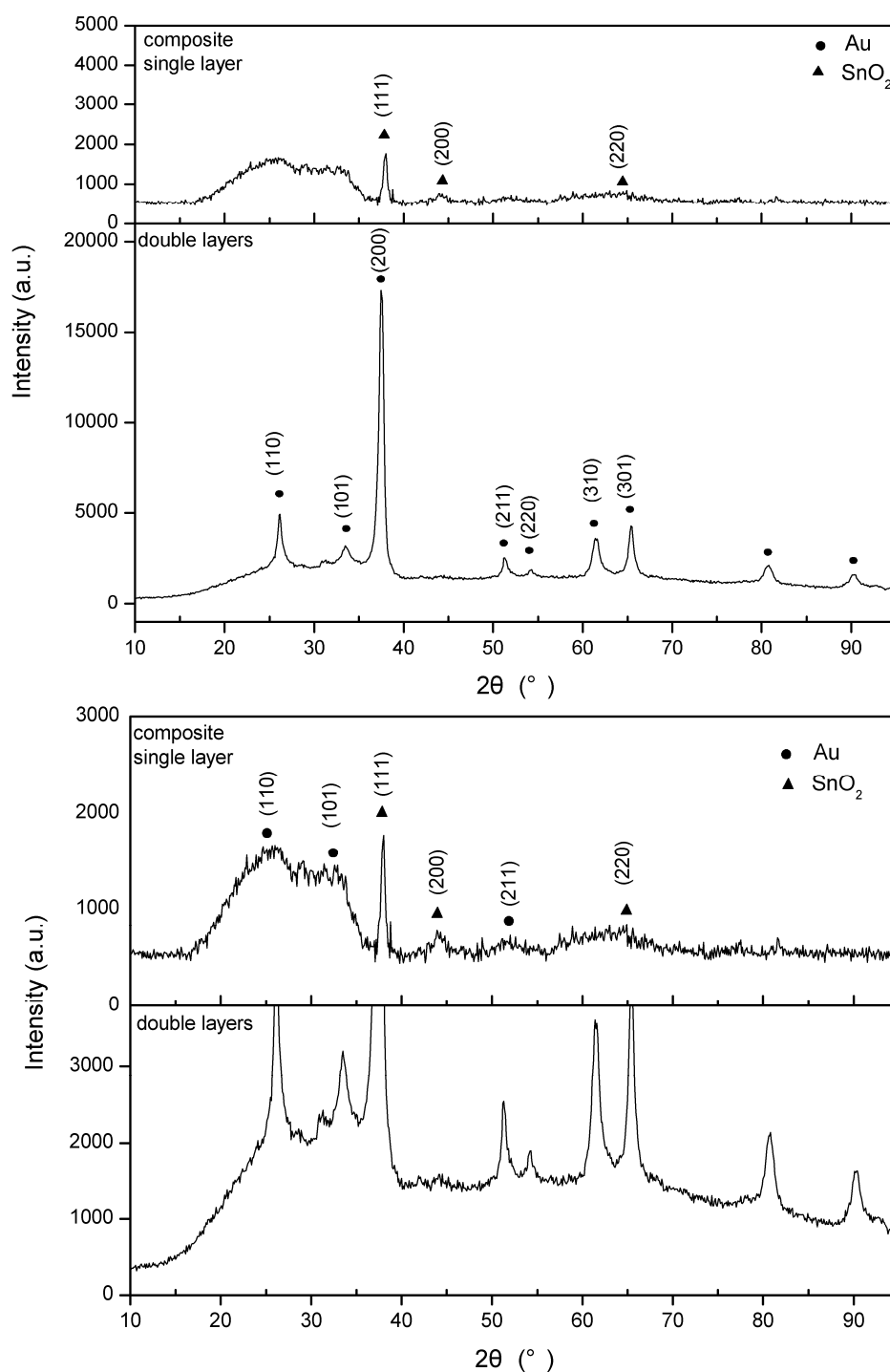
**Figure 6.2** Transmittance spectra of a single layer film of Au/SnO<sub>2</sub>:F composite (red trace) and double-layered film of Au/SnO<sub>2</sub>:F + SnO<sub>2</sub>:F, over the range from 250 nm to 3300 nm. The edges at 2800 nm for both films are attributed to the IR absorption by the float glass.



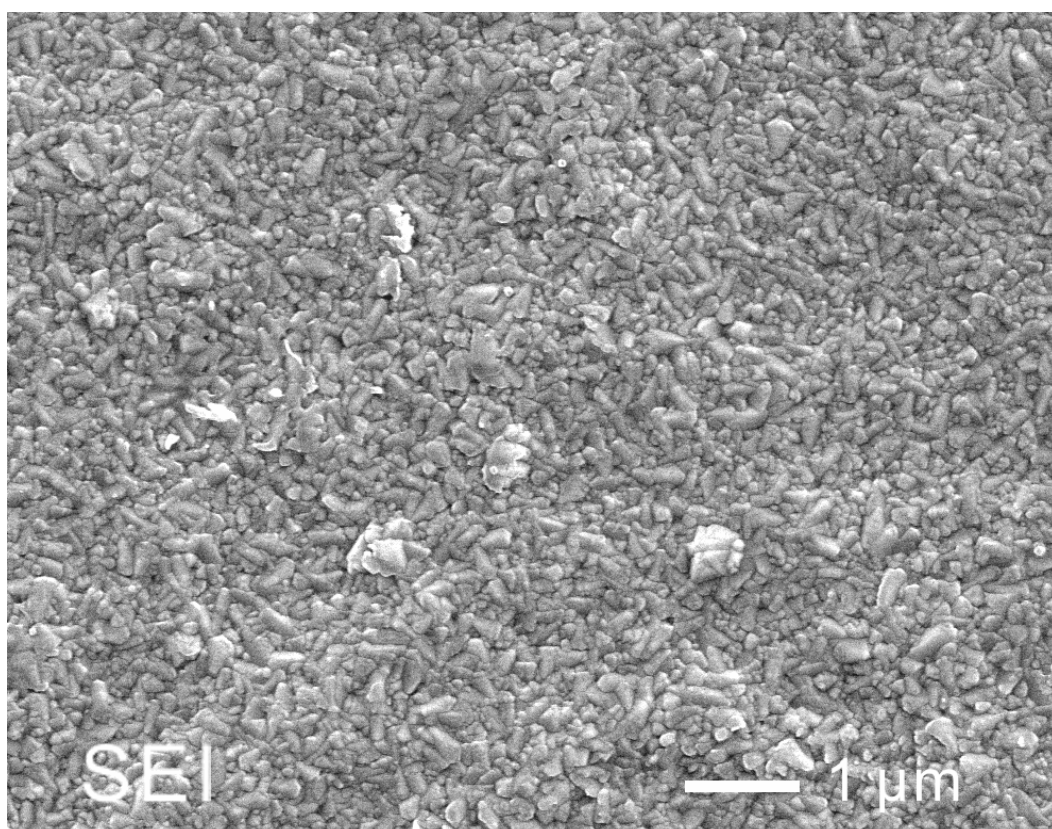
**Figure 6.3** Reflectance spectra (in the range from 250 to 3300 nm) of a single-layered film of Au/SnO<sub>2</sub>:F composite (red trace), double-layered film of Au/SnO<sub>2</sub>:F + SnO<sub>2</sub>:F (blue), SnO<sub>2</sub>:F only film (dark yellow trace) and commercial Pilkington TEC 15 (nominally 15  $\Omega/\square$ ) and TEC 70 ((nominally 70  $\Omega/\square$ )) glass (black traces). Note the reflectance of the double-layered film is between TEC 15 and TEC 70.

X-ray diffraction patterns for both films were recorded and shown in Figure 6.4. For the composite single layer, diffraction peaks for gold were clearly identified (ICCD Reference Code 03-065-2870), especially for plane (111), while peaks for SnO<sub>2</sub> were too weak to be observed in the Au/SnO<sub>2</sub> composite film (Figure 6.4a). Further analysis of this pattern carried out by scaling the signal intensity suggested that very weak diffraction peaks for SnO<sub>2</sub> (110) and (101) were present (Figure 6.4b). This is possibly due to the addition of Au NPs suppressing crystallisation of SnO<sub>2</sub> and forming amorphous SnO<sub>2</sub> which is difficult to detect by XRD. In contrast, the double layered film shows significant peaks for cassiterite SnO<sub>2</sub>, especially for planes (200), (110), (211), (310) and (301) (ICCD Reference Code 01-077-0447). However, the peak for gold (111) was not identified, possibly due to the close overlap with the peak for SnO<sub>2</sub> plane (002) at 37° (2θ) (see Figure 6.4b).

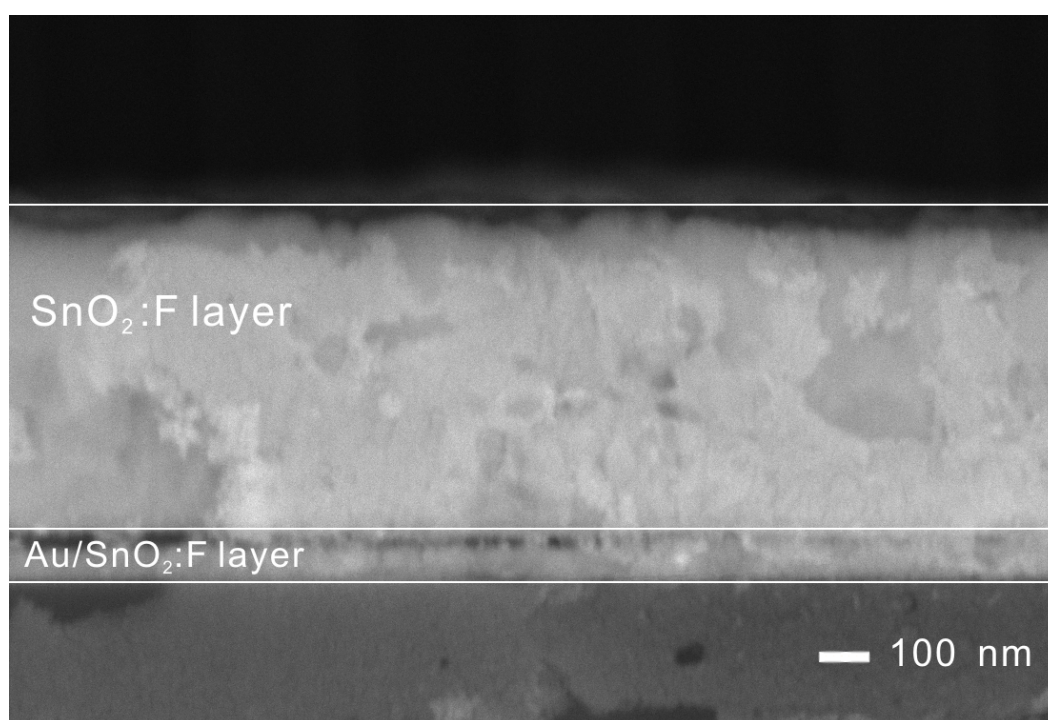
SEM imaging of the double-layered film was carried out for a top view and a cross-sectional image (Figure 6.5). The image viewed from the top showed a rough surface consisting of grains with size from approximately 50 nm to 200 nm, which has a similar morphology to that of the SnO<sub>2</sub>:F only films investigated in Section 4.2.3. A cross-sectional image of the double-layered film is shown in Figure 6.6. It is found that the film is clearly visible as two layers, the top layer of SnO<sub>2</sub>:F with a thickness of about 1 μm and the bottom layer of Au/SnO<sub>2</sub>:F with a thickness of 90 nm. A tilted cross-sectional view of the film is shown in Figure 6.7. Similarly, two layers were identified in the tilted view as SnO<sub>2</sub>:F and Au/SnO<sub>2</sub>:F composite layers. There is also an interfacial region between the layers enhanced due to the tilted imaging. It is also observed that there are brighter spots distributed in the composite layer interpreted as gold NPs.



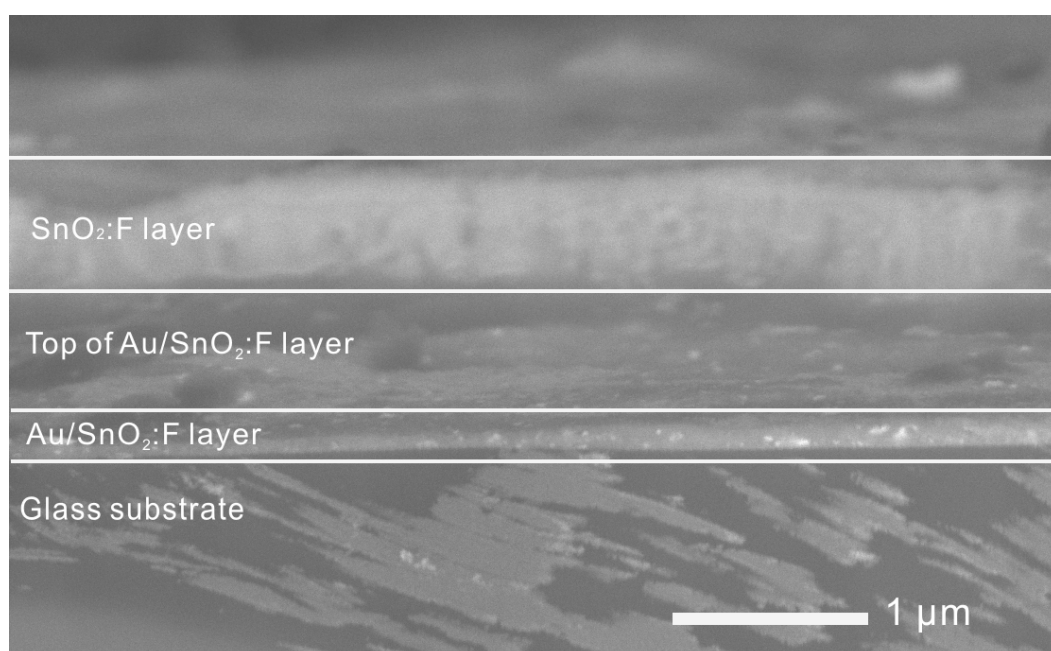
**Figure 6.4 (a) XRD patterns for a thin film of Au/SnO<sub>2</sub>:F composite (up) and a doubled-layered film of SnO<sub>2</sub>:F and Au/SnO<sub>2</sub>:F (bottom). (b) Re-scaled for comparison. Please note the broad peak between 20° to 40° (2θ) in the composite single layer which is probably due to the amorphous SnO<sub>2</sub> formed in the deposition.**



**Figure 6.5 SEM image of the top view of the double-layered thin film produced by spray deposition. The scale bar is 1  $\mu\text{m}$ . Naturally only the top  $\text{SnO}_2\text{:F}$  layer is visible. The impression of crystalline grains indicates a rough surface.**



**Figure 6.6** Cross-sectional image of the double-layered film comprising a top layer of SnO<sub>2</sub>:F with thickness of about 1  $\mu$ m and a bottom layer of Au/SnO<sub>2</sub>:F with thickness of 90 nm. The thickness of the SnO<sub>2</sub>:F only and Au/SnO<sub>2</sub>:F layers is obtained from the standard experimental conditions used in Chapter 4 and 5.



**Figure 6.7 Tilted cross-sectional image of the double-layered film of SnO<sub>2</sub>:F and Au/SnO<sub>2</sub>:F. An interfacial region between the layers (labelled as top of Au/SnO<sub>2</sub>:F layer) is enhanced due to the tilted imaging of the film. The scale bar is 1 μm.**

### 6.2.3 Discussion

In this chapter it has been demonstrated that a composite film with a double-layered structure was successfully deposited by spray pyrolysis. Such a film has the combined functionalities of colouration, electrical conductivity and control of the IR transmission and reflection.

Table 6.1 summarises the characteristics of this double-layered composite film which were compared with a single film of SnO<sub>2</sub>:F and Au/SnO<sub>2</sub>:F composite layer.

It was found that although the film of SnO<sub>2</sub>:F single layer demonstrates an excellent performance in terms of reducing the electrical resistivity (down to  $1.5 \times 10^{-3} \Omega\cdot\text{cm}$ ) and infrared transmission (as low as only 10% transmission), the film with the double-layered structure also shows comparable electrical properties (down to  $5.5 \times 10^{-3} \Omega\cdot\text{cm}$ ) and infrared control (as low as 37% transmission). Furthermore, due to the insertion of a composite layer with embedded gold NPs, the double-layered film also exhibits blue colouration resulted from the SPR absorption peak at 580 nm.

As discussed at the beginning of this chapter there are issues relating to successful incorporation of gold NPs into the host metal oxide when depositing at a high temperature. In this experiment the composite layer was deposited at only 340 °C whilst the second layer of SnO<sub>2</sub>:F was deposited at a much higher temperature of 450 °C. The temperature-affected properties of both layers can be controlled during spray deposition respectively. The gold NPs were found not to migrate to the second layer of SnO<sub>2</sub>:F (which has been observed elsewhere). The

top layer of SnO<sub>2</sub>:F not only serves to increase the electrical conductivity but also serves as a protective layer for achieving a more durable film.

**Table 6.1 Summary of electrical and optical properties of the double-layered composite film in comparison with a single-layered SnO<sub>2</sub>:F film and Au/SnO<sub>2</sub>:F composite film**

|                                               | Resistivity                                 | $\lambda_{\text{SPR}}$ | T% at 500 nm | T% at 2500 nm | Thickness  |
|-----------------------------------------------|---------------------------------------------|------------------------|--------------|---------------|------------|
| Double layer                                  | $5.5 \times 10^{-3} \Omega \cdot \text{cm}$ | 580 nm                 | 58%          | 37%           | 1000+90 nm |
| SnO <sub>2</sub> :F single layer              | $1.5 \times 10^{-3} \Omega \cdot \text{cm}$ | N/A                    | 70%          | 10%           | 800 nm     |
| Au/SnO <sub>2</sub> :F Composite single layer | 0.28 $\Omega \cdot \text{cm}$               | 579 nm                 | 55%          | 75%           | 100 nm     |

### 6.3 Conclusion

It has been demonstrated that a double-layered film can be deposited by spray pyrolysis in a two-step process to control the optical properties in both the visible and infrared regions by combining the colouration derived from an Au-NP incorporated composite layer and the infrared rejection from the TCO layer of SnO<sub>2</sub>:F. The optical and electrical properties of the NP embedded single layer and the double-layered film were characterised and compared. It has been shown that the double-layered film is not just a compromised option avoiding the restrictions observed when depositing a NP embedded single layer at a high temperature. It is also an effective approach to reducing the electrical resistivity

and attaining control on the infrared. It is also adaptable as a spray deposition method which can be appropriately scaled up in for an industry process.

## **CHAPTER 7**

### **CONCLUSIONS AND FUTURE WORK**

#### **7.1 Summary of results**

From the outset of this work the aim has been to produce a novel film possessing combined functionalities including colouration, electrical conductivity and solar control. Such kind of films should be able to be manufactured using an industrial production line. Spray pyrolysis deposition was investigated as a suitable candidate for production of various such films.

In this thesis it has been demonstrated that the spray pyrolysis technique is a versatile and effective approach for the deposition of a variety of thin films, including TCO films, composite films embedded with gold NPs and double-layered films combining a TCO layer and a NP embedded layer.

Spray deposition of gold NP embedded nanocomposite films is a major part of this work in which the incorporation of gold NPs is challenging. Such nanocomposite films have successfully been deposited with gold NPs embedded (either in-situ or ex-situ) in a single-step process. Two types of gold precursors, preformed gold colloids and  $\text{HAuCl}_4$ , have been investigated. In both cases a “one-pot” solution containing both the precursors for gold NPs and for metal

oxides ( $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ) was sprayed onto the glass substrates at a range of different temperatures. The microstructural and optical properties were characterised and analysed. The films showed intense colouration due to the characteristic SPR absorption of gold NPs. XRD analysis also indicated the presence of gold NPs in the films. Deposition using preformed nanoparticles maintains the size distribution of the NP and leads to more predictable colouration of the resulting films, while using  $\text{HAuCl}_4$  results in a more intense film colour due to the higher gold concentration achievable and also probably due to the broader particle distribution. It is found that the substrate temperature plays an important role in determining the properties of the composite films in terms of microstructure and optical performance. The SPR peak position and width are dependent on the particle size and distribution as well as the surrounding host medium, which are in fact influenced by the substrate temperature. It is also noted that the films comprising gold/ $\text{SnO}_2$  composite single layer display colouration and reasonable conductivity, indicating potential applications for coloured and transparent conductors.

The limitations associated with incorporating gold NPs into films during spray deposition at a high temperature have also been discussed. Due to the solvent properties (such as the evaporation rate) and the temperature gradient between the solvent and solid gold NPs, thermophoretic effects develop more significantly with increasing substrate temperature. Consequently it becomes more difficult to incorporate gold NPs into a metal oxide host to form a nanocomposite film when the temperature gradient exerts a sufficiently strong repelling upward thermophoretic force. A double-layered structure was therefore proposed and investigated aiming to enhance the incorporation of gold NPs.

Metal oxide host materials, especially TCO materials, have been investigated through spray pyrolysis deposition. Two types of TCO, namely ZnO and SnO<sub>2</sub>, together with the introduction of dopants, were spray deposited on glass substrates and their electrical and optical properties were studied. Again it was found that the structural properties and the correlated electrical properties of TCO films are strongly dependent on the substrate temperature, whilst the dopant concentration also plays a significant role. F doped SnO<sub>2</sub> films exhibit optical reflection in the near infrared region while ZnO based films display higher transparency. For ZnO thin film deposition, a series of zinc carboxylates as precursors including newly synthesised compounds have been screened for the most suitable candidates for further development.

Finally, a double layered structure combining a TCO layer of SnO<sub>2</sub>:F and a layer embedded with gold NPs has been employed to achieve the combined functionalities of conductivity and colouration. In such films the colouration is derived from the gold NP incorporated composite layer and the conductivity and infrared reflection from the TCO layer of SnO<sub>2</sub>:F. The electrical conductivity is significantly enhanced compared to a nanocomposite single layer film due to the introduction of the TCO top layer. Such structure is not just a compromised approach to resolving the problem of depositing a multifunctional single layer at a high temperature but it is also an effective approach for the successful deposition of films suitable for industrial scale up.

In summary, spray pyrolysis deposition offers a simple and rapid method for the production of a variety of thin films. It can be immediately integrated with current industrial coating equipment and scaled up for an industrial production process.

## **7.2 Future perspectives**

This thesis has demonstrated the versatility of the spray deposition technique and the successful deposition of gold NP/metal oxide composite films, yet further investigation and more comprehensive understanding of this process technique are needed. Besides many advantages offered, some problems need to be resolved to improve competitiveness against other techniques. Some suggestions for further work are given in the following areas.

### **7.2.1 Deposition of composite films and their properties**

Although the spray deposition technique has been well studied and implemented into many industrial production lines as a conventional process, there are still issues that may influence the properties of such films. One of the major problems is the low deposition rate which is mainly due to the thermophoretic effects. The problem of incorporating gold NPs into a host material arises from the repelling forces established by the thermal gradient. Some researchers have suggested using electrostatic spray deposition for higher deposition rates by comparison with air blast spray deposition [282]. Further investigation into improving the process rate is therefore needed.

It is also important to further improve the quality of the NP embedded composite films. It is desirable to incorporate the NPs into the host with a monodispersed particle distribution but this requires careful control of the precursors. For preformed gold NPs, the particle size and distribution, as well as the particle shape, can be finely controlled by tailoring the synthesis conditions. This will determine the final particle properties ex-situ and hence improve the properties of the as-prepared films. Therefore, the formulation of a stable “one-

pot” solution containing compatible gold NPs and host precursors would be essential to obtain high quality films. For in-situ formation of gold NPs using  $\text{HAuCl}_4$ , careful control of the conditions during the spray deposition process is required. The factors of concern include homogeneous temperature distribution of the substrate surface, moderate temperature to attain nano-scale particles and the surfactants that help control the particle nucleation and growth.

In addition, further analysis and assessment of the composite films are required. This is important in helping understand the formation and growth of NPs in the host material. Surface analysis techniques are needed to investigate the interaction between the particles and the host material, although using techniques such as X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Near Edge Structure (XANES) for example, remains a challenge due to their complexity. In addition cross-sectional SEM and Focus Ion Beam (FIB) analysis are necessary for film layer structure and gold particle distribution. Besides the materials analysis, further assessment of the films for practical suitability should be conducted. For example the thermal performance (such as solar heat gain coefficient) should be assessed in comparison with the commercially available solar control products, and the durability of the films against abrasion and strain needs to be characterised. Online measurement of the spray process, such as droplet size and distribution, temperature gradient, are important for further understanding of the process. Simulation of this process would be a beneficial addition as well.

### **7.2.2 Scale-up and integration into an industrial process**

In this thesis, it has been demonstrated that there is a possibility of transferring the results presented in this work to an industrial production process.

As explained before, there is a requirement to deposit layers onto glass on an industrial scale with uniformity across the full width of a float glass production line ( $\sim 3$  metres). It is expected that the technology of incorporating nanoparticles into a host material can be readily transferred to a typical industrial manufacturing line without the need for significant re-engineering. Industrial trials of spray pyrolysis using similar prototype composite films should be conducted on a scale up production line in order to solve the practical operation issues that will inevitably arise. For example, how can an array of spray nozzles be integrated across the line, or how to obtain efficient extraction of process waste. Indeed, the accurate control of film thickness and quality may need the introduction of new sensors and control systems to ensure that high quality continuous coating of films is achievable without interruption. Extension of this work along this direction requires a project team incorporating chemists, materials scientists and control engineers and this is the basis of a recently submitted new proposal.

### **7.2.3 Application of NPs embedded composite films**

It would also be interesting and useful to explore the applications of nanocomposite films in other areas such as catalytic and antibacterial applications. As reviewed in Chapter 2, there has been intense research in nanocomposite films due to their intriguing functionalities which are enhanced by the incorporation of noble metal nanoparticles. However, current production methods of films for these applications are still limited to sol-gel or physical deposition methods which can not be applied to a large-area online process. The spray deposition technique developed here will therefore offer an inexpensive and versatile approach using materials combining noble metal nanoparticles (gold, silver, copper) and

transition metal oxide (such as  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{WO}_3$ ). All these will rely on the development of new precursors and the formulation of the precursor solutions.

## REFERENCES

1. Pilkington and the Flat Glass Industry. Report. **2009**.
2. Allendorf, M. D., Research needs for coatings on glass. Summary of the US Department of Energy roadmapping workshop. *Thin Solid Films* **2001**, 392 (2), 155-163.
3. Muromachi, T.; Tsujino, T.; Kamitani, K.; Maeda, K., Application of functional coatings by sol-gel method. *J. Sol-Gel Sci. Technol.* **2006**, 40 (2), 267-272.
4. Pilkington, L. A. B. Manufacture of flat glass. U. S. Patent 2,911,759, **1959**.
5. NanoCoat project proposal. **2005**.
6. Granqvist, C. G., Transparent conductors as solar energy materials: A panoramic review. *Sol. Energy Mater. Sol. Cells* **2007**, 91 (17), 1529-1598.
7. Goddard, W. A., Handbook of nanoscience, engineering, and technology. CRC Press: Boca Raton, **2003**.
8. Buso, D.; Pacifico, J.; Martucci, A.; Mulvaney, P., Gold-Nanoparticle-Doped TiO<sub>2</sub> Semiconductor Thin Films: Optical Characterization. *Adv. Funct. Mater.* **2007**, 17 (3), 347-354.
9. Palgrave, R. G.; Parkin, I. P., Aerosol Assisted Chemical Vapor Deposition Using Nanoparticle Precursors: A Route to Nanocomposite Thin Films. *J. Am. Chem. Soc.* **2006**, 128 (5), 1587-1597.
10. Xu, X.; Stevens, M.; Cortie, M. B., In Situ Precipitation of Gold Nanoparticles onto Glass for Potential Architectural Applications. *Chem. Mater.* **2004**, 16 (11), 2259-2266.
11. Armelao, L.; Barreca, D.; Bottaro, G.; Gasparotto, A.; Gross, S.; Maragno, C.; Tondello, E., Recent trends on nanocomposites based on Cu, Ag and Au clusters: A closer look. *Coord. Chem. Rev.* **2006**, 250 (11-12), 1294-1314.
12. Ung, T.; Liz-Marzán, L. M.; Mulvaney, P., Gold nanoparticle thin films. *Colloids Surf. Physicochem. Eng. Aspects* **2002**, 202 (2-3), 119-126.
13. Ashraf, S.; Blackman, C.; Hyett, G.; Parkin, I., Aerosol assisted chemical vapour deposition of MoO<sub>3</sub> and MoO<sub>2</sub> thin films on glass from molybdenum polyoxometallate precursors; thermophoresis and gas phase nanoparticle formation. *J. Mater. Chem.* **2006**, 16 (35), 3575-3582.
14. He, T.; Ma, Y.; Cao, Y.; Jiang, P.; Zhang, X.; Yang, W.; Yao, J., Enhancement effect of gold nanoparticles on the UV-light photochromism of molybdenum trioxide thin films. *Langmuir* **2001**, 17 (26), 8024-8027.

15. Lahiri, D.; Subramanian, V.; Shibata, T.; Wolf, E. E.; Bunker, B. A.; Kamat, P. V., Photoinduced transformations at semiconductor/metal interfaces: X-ray absorption studies of titania/gold films. *J. Appl. Phys.* **2003**, *93* (5), 2575-2582.
16. Medda, S. K.; De, S.; De, G., Synthesis of Au nanoparticle doped SiO<sub>2</sub>-TiO<sub>2</sub> films: tuning of Au surface plasmon band position through controlling the refractive index. *J. Mater. Chem.* **2005**, *15* (32), 3278-3284.
17. Walters, G.; Parkin, I. P., The incorporation of noble metal nanoparticles into host matrix thin films: synthesis, characterisation and applications. *J. Mater. Chem.* **2009**, *19* (5), 574-590.
18. Wang, W., Nanocoat for large area energy efficient substrates (transfer report). **2007**.
19. W. Theiss Hard- and Software. <http://mtheiss.com/?Products:CODE>.
20. CIE 1976 colour space. For more details see F. W. Billmeyer, Principles of Color Technology (2nd edition), John Wiley (1981).
21. Aspnes, D. E., Optical properties of thin films. *Thin Solid Films* **1982**, *89* (3), 249-262.
22. Garnett, J. C. M., Colours in Metal Glasses and in Metallic Films. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* **1904**, *203* (359-371), 385-420.
23. Garnett, J. C. M., Colours in Metal Glasses, in Metallic Films and in Metallic Solutions.. II. *Proceedings of the Royal Society of London. Series A* **1905**, *76* (511), 370-373.
24. Bruggeman, D., The calculation of various physical constants of heterogeneous substances. I. The dielectric constants and conductivities of mixtures composed of isotropic substances. *Ann. Phys* **1935**, *24* (636), 132.
25. Maissel, L. I.; Glang, R., Handbook of thin film technology. MacGraw-Hill Book Company: New York [etc.], **1983**.
26. Smith, D. L., Thin-film deposition : principles and practice. McGraw-Hill: New York, **1995**.
27. Pulker, H. K., Coatings on glass. Elsevier: Amsterdam; New York, **1984**.
28. Hou, X.; Choy, K. L., Processing and Applications of Aerosol-Assisted Chemical Vapor Deposition. *Chem. Vap. Deposition* **2006**, *12* (10), 583-596.
29. Choy, K. L., Chemical vapour deposition of coatings. *Prog. Mater Sci.* **2003**, *48* (2), 57-170.

30. George, S. M., Atomic Layer Deposition: An Overview. *Chem. Rev.* **2009**, *110* (1), 111-131.
31. Sakka, S., Handbook of sol-gel science and technology : processing, characterization, and applications. Kluwer Academic Publishers: Boston, **2005**.
32. Rizkalla, A. A.; Lefebvre, A. H., Influence of liquid properties on airblast atomizer spray characteristics. *Journal of Engineering for Power-Transactions of the Asme* **1975**, *97* (2), 173-179.
33. Lampkin, C. M., Aerodynamics of nozzles used in spray pyrolysis. *Progress in crystal growth and characterization* **1979**, *1* (4), 405-416.
34. Ayres, D.; Caldas, M.; Semiao, V.; Carvalho, M. D., Prediction of the droplet size and velocity joint distribution for sprays. *Fuel* **2001**, *80* (3), 383-394.
35. Semiao, V.; Andrade, P.; Carvalho, M. D., Spray characterization: Numerical prediction of Sauter mean diameter and droplet size distribution. *Fuel* **1996**, *75* (15), 1707-1714.
36. Rajan, R.; Pandit, A. B., Correlations to predict droplet size in ultrasonic atomisation. *Ultrasonics* **2001**, *39* (4), 235-255.
37. Grace, J. M.; Marijnissen, J. C. M., A review of liquid atomization by electrical means. *J. Aerosol Sci* **1994**, *25* (6), 1005-1019.
38. Yu, H.-F.; Liao, W.-H., Evaporation of solution droplets in spray pyrolysis. *Int. J. Heat Mass Transfer* **1998**, *41* (8-9), 993-1001.
39. Viguie, J. C.; Spitz, J., Chemical Vapor Deposition at Low Temperatures. *J. Electrochem. Soc.* **1975**, *122* (4), 585-588.
40. Perednis, D.; Gauckler, L. J., Thin Film Deposition Using Spray Pyrolysis. *J. Electroceram.* **2005**, *14* (2), 103-111.
41. Muecke, U. P.; Messing, G. L.; Gauckler, L. J., The Leidenfrost effect during spray pyrolysis of nickel oxide-gadolinia doped ceria composite thin films. *Thin Solid Films* **2009**, *517* (5), 1515-1521.
42. Muecke, U. P.; Luechinger, N.; Schlagenhauf, L.; Gauckler, L. J., Initial stages of deposition and film formation during spray pyrolysis -- Nickel oxide, cerium gadolinium oxide and mixtures thereof. *Thin Solid Films* **2009**, *517* (5), 1522-1529.
43. Chen, C. H.; Kelder, E. M.; vanderPut, P.; Schoonman, J., Morphology control of thin LiCoO<sub>2</sub> films fabricated using the electrostatic spray deposition (ESD) technique. *J. Mater. Chem.* **1996**, *6* (5), 765-771.
44. Stelzer, N. H. J.; Goossens, A.; Schoonman, J., Synthesis of terbia doped yttria stabilized zirconia thin films by using the electrostatic spray

deposition (ESD) technique. *Solid-State Chemistry of Inorganic Materials* **1997**, 453, 543-548.

45. Afify, H. H.; Nasser, S. A.; Demian, S. E., Influence of substrate temperature on the structural, optical and electrical properties of ZnO thin films prepared by spray pyrolysis. *J. Mater. Sci.: Mater. Electron.* **1991**, 2 (3), 152-156.
46. Romero, R.; Leinen, D.; Dalchiele, E. A.; Ramos-Barrado, J. R.; Martín, F., The effects of zinc acetate and zinc chloride precursors on the preferred crystalline orientation of ZnO and Al-doped ZnO thin films obtained by spray pyrolysis. *Thin Solid Films* **2006**, 515 (4), 1942-1949.
47. Chen, C. H.; Kelder, E. M.; Schoonman, J., Effects of additives in electrospraying for materials preparation. *J. Eur. Ceram. Soc.* **1998**, 18 (10), 1439-1443.
48. Pink, H.; Treitinger, L.; Vite, L., Preparation of fast detecting SnO<sub>2</sub> gas sensors. *Japanese Journal of Applied Physics* **1980**, 19 (3), 513-517.
49. Patil, P. S., Versatility of chemical spray pyrolysis technique. *Mater. Chem. Phys.* **1999**, 59 (3), 185-198.
50. Zhao, X.; Hinchliffe, C.; Johnston, C.; Dobson, P. J.; Grant, P. S., Spray deposition of polymer nanocomposite films for dielectric applications. *Mater. Sci. Eng. B-Adv. Funct. Solid-State Mater.* **2008**, 151 (2), 140-145.
51. Zhao, X.; Koos, A. A.; Chu, B. T. T.; Johnston, C.; Grobert, N.; Grant, P. S., Spray deposited fluoropolymer/multi-walled carbon nanotube composite films with high dielectric permittivity at low percolation threshold. *Carbon* **2009**, 47 (3), 561-569.
52. Zhao, X.; Chu, B. T. T.; Ballesteros, B.; Wang, W.; Johnston, C.; Sykes, J. M.; Grant, P. S., Spray deposition of steam treated and functionalized single-walled and multi-walled carbon nanotube films for supercapacitors. *Nanotechnology* **2009**, 20 (6), 065605.
53. Daniel, M.-C.; Astruc, D., Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2003**, 104 (1), 293-346.
54. Willets, K. A.; Van Duyne, R. P., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, 58 (1), 267-297.
55. Link, S.; El-Sayed, M. A., Optical properties and ultrafast dynamics of metallic nanocrystals. *Annu. Rev. Phys. Chem.* **2003**, 54 (1), 331-366.
56. Ghosh, S. K.; Pal, T., Interparticle Coupling Effect on the Surface Plasmon Resonance of Gold Nanoparticles: From Theory to Applications. *Chem. Rev.* **2007**, 107 (11), 4797-4862.

57. Mie, G., Optical Properties of Colloidal Gold Solutions. *Ann. Phys* **1908**, *25*, 329.
58. Bohren, C. F.; Huffman, D. R., Absorption and scattering of light by small particles. Wiley: New York, **1983**.
59. Kreibig, U.; Vollmer, M., Optical properties of metal clusters. Springer: Berlin; New York, **1995**.
60. Mulvaney, P., Surface Plasmon Spectroscopy of Nanosized Metal Particles. *Langmuir* **1996**, *12* (3), 788-800.
61. Kreibig, U.; Genzel, L., Optical absorption of small metallic particles. *Surf. Sci.* **1985**, *156* (Part 2), 678-700.
62. Link, S.; El-Sayed, M. A., Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles. *The Journal of Physical Chemistry B* **1999**, *103* (21), 4212-4217.
63. Rodríguez-Fernández, J.; Pérez-Juste, J.; García de Abajo, F. J.; Liz-Marzán, L. M., Seeded growth of submicron Au colloids with quadrupole plasmon resonance modes. *Langmuir* **2006**, *22* (16), 7007-7010.
64. Brown, K. R.; Walter, D. G.; Natan, M. J., Seeding of colloidal Au nanoparticle solutions. 2. Improved control of particle size and shape. *Chem. Mater.* **1999**, *12* (2), 306-313.
65. Nakamura, K.; Kawabata, T.; Mori, Y., Size distribution analysis of colloidal gold by small angle X-ray scattering and light absorbance. *Powder Technol.* **2003**, *131* (2-3), 120-128.
66. Link, S.; Mohamed, M. B.; El-Sayed, M. A., Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant. *The Journal of Physical Chemistry B* **1999**, *103* (16), 3073-3077.
67. Foss, C. A.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R., Optical-properties of composite membranes containing arrays of nanoscopic gold cylinders. *J. Phys. Chem.* **1992**, *96* (19), 7497-7499.
68. Hornyak, G. L.; Martin, C. R., Optical properties of a family of Au-nanoparticle-containing alumina membranes in which the nanoparticle shape is varied from needle-like (prolate) to spheroid, to pancake-like (oblate). *Thin Solid Films* **1997**, *303* (1-2), 84-88.
69. Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L.; Halas, N. J., Nanoengineering of optical resonances. *Chem. Phys. Lett.* **1998**, *288* (2-4), 243-247.
70. Faraday, M., The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light. *Philosophical Transactions of the Royal Society of London* **1857**, *147*, 145-181.

71. Turkevich, J., A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discussions of the Faraday Society* **1951**, *11*, 55.
72. Frens, G., Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nature Phys. Sci* **1973**, *241* (105), 20–22.
73. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D.; Whyman, R., Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid–Liquid system. *J. Chem. Soc., Chem. Commun.* **1994**, *7*, 801-802.
74. Jana, N. R.; Gearheart, L.; Murphy, C. J., Evidence for Seed-Mediated Nucleation in the Chemical Reduction of Gold Salts to Gold Nanoparticles. *Chem. Mater.* **2001**, *13* (7), 2313-2322.
75. Sau, T. K.; Pal, A.; Jana, N. R.; Wang, Z. L.; Pal, T., Size Controlled Synthesis of Gold Nanoparticles using Photochemically Prepared Seed Particles. *J. Nanopart. Res.* **2001**, *3* (4), 257-261.
76. Chen, F.; Xu, G.-Q.; Hor, T. S. A., Preparation and assembly of colloidal gold nanoparticles in CTAB-stabilized reverse microemulsion. *Mater. Lett.* **2003**, *57* (21), 3282-3286.
77. Tsuji, M.; Hashimoto, M.; Nishizawa, Y.; Kubokawa, M.; Tsuji, T., Microwave-Assisted Synthesis of Metallic Nanostructures in Solution. *Chemistry - A European Journal* **2005**, *11* (2), 440-452.
78. Park, J.-E.; Atobe, M.; Fuchigami, T., Synthesis of multiple shapes of gold nanoparticles with controlled sizes in aqueous solution using ultrasound. *Ultrason. Sonochem.* **2006**, *13* (3), 237-241.
79. Mukherjee, B.; Ravishankar, N., A novel solvothermal method for nanoparticle thin films and coatings. *Nanotechnology* **2007**, *18* (2), 025603.
80. Ginley, D. S.; Bright, C., Transparent conducting oxides. *MRS Bull.* **2000**, *25* (8), 15-18.
81. Burstein, E., Anomalous Optical Absorption Limit in InSb. *Physical Review* **1954**, *93*, 632.
82. Moss, T. S., The Interpretation of the Properties of Indium Antimonide. *Proceedings of the Physical Society. Section B* **1954**, *67* (10), 775.
83. Gordon, R. G., Criteria for choosing transparent conductors. *MRS Bull.* **2000**, *25* (8), 52-57.
84. Mooney, J.; Radding, S., Spray pyrolysis processing. *Annu. Rev. Mater. Sci.* **1982**, *12* (1), 81-101.
85. Manificier, J. C., Thin metallic oxides as transparent conductors. *Thin Solid Films* **1982**, *90* (3), 297-308.

86. Gottlieb, B.; Koropecski, R.; Arce, R.; Crisalle, R.; Ferron, J., Characterization of fluorine-doped tin oxide produced by the pyrosol method. *Thin Solid Films* **1991**, *199* (1), 13-21.
87. Shanthi, E.; Dutta, V.; Banerjee, A.; Chopra, K. L., Electrical and optical properties of undoped and antimony-doped tin oxide films. *J. Appl. Phys.* **1980**, *51* (12), 6243-6251.
88. Kulaszewicz, S.; Lasocka, I.; Michalski, C., Properties of transparent conducting films of  $\text{SnO}_2\text{:Sb}$  and  $\text{In}_2\text{O}_3\text{:Sn}$  deposited by hydrolysis. *Thin Solid Films* **1978**, *55* (2), 283-288.
89. Shanthi, E.; Banerjee, A.; Chopra, K. L., Dopant effects in sprayed tin oxide films. *Thin Solid Films* **1982**, *88* (2), 93-100.
90. Vincent, C. A., Nature of semiconductivity in polycrystalline tin oxide. *J. Electrochem. Soc.* **1972**, *119* (4), 515-518.
91. Manificier, J. C.; Szepessy, L.; Bresse, J. F.; Perotin, M.; Stuck, R.,  $\text{In}_2\text{O}_3\text{:Sn}$  and  $\text{SnO}_2\text{:F}$  films - Application to solar energy conversion; part 1 - Preparation and characterization. *Mater. Res. Bull.* **1979**, *14* (1), 109-119.
92. Morris, G. C.; McElnea, A. E., Fluorine doped tin oxide films from spray pyrolysis of stannous fluoride solutions. *Appl. Surf. Sci.* **1996**, *92*, 167-170.
93. Shanti, E., V. Dutta, A. Banerjee, KL Chopra. *Journal of Applied Physics* **1980**, *51*, 6243.
94. Joseph, B.; Manoj, P. K.; Vaidyan, V. K., Studies on the structural, electrical and optical properties of Al-doped ZnO thin films prepared by chemical spray deposition. *Ceram. Int.* **2006**, *32* (5), 487-493.
95. Seeber, W. T.; Abou-Helal, M. O.; Barth, S.; Beil, D.; Höche, T.; Afify, H. H.; Demian, S. E., Transparent semiconducting ZnO:Al thin films prepared by spray pyrolysis. *Mater. Sci. Semicond. Process.* **1999**, *2* (1), 45-55.
96. Gomez, H.; Maldonado, A.; Olvera, M. d. l. L.; Acosta, D. R., Gallium-doped ZnO thin films deposited by chemical spray. *Sol. Energy Mater. Sol. Cells* **2005**, *87* (1-4), 107-116.
97. Babar, A. R.; et al., Gallium doping in transparent conductive ZnO thin films prepared by chemical spray pyrolysis. *J. Phys. D: Appl. Phys.* **2008**, *41* (13), 135404.
98. Tiburcio-Silver, A., Properties of gallium-doped ZnO deposited onto glass by spray pyrolysis. *Sol. Energy Mater. Sol. Cells* **1998**, *55* (1-2), 3.
99. Maldonado, A.; Tirado-Guerra, S.; Meléndez-Lira, M.; de la L. Olvera, M., Physical properties of ZnO:F obtained from a fresh and aged solution of zinc acetate and zinc acetylacetonate. *Sol. Energy Mater. Sol. Cells* **2006**, *90* (6), 742-752.

100. Rodríguez-Báez, J.; Maldonado, A.; Castañeda, L.; Delgado, G. T.; Castanedo-Pérez, R.; de la L. Olvera, M., On the effect of acetic acid on physical properties of chemically sprayed fluorine-doped ZnO thin films. *Thin Solid Films* **2007**, *515* (24), 8689-8694.
101. Pawar, B. N.; Jadkar, S. R.; Takwale, M. G., Deposition and characterization of transparent and conductive sprayed ZnO:B thin films. *J. Phys. Chem. Solids* **2005**, *66* (10), 1779-1782.
102. Lokhande, B. J.; Patil, P. S.; Uplane, M. D., Studies on structural, optical and electrical properties of boron doped zinc oxide films prepared by spray pyrolysis technique. *Physica B: Condensed Matter* **2001**, *302-303*, 59-63.
103. Kumar, P. M. R.; et al., On the properties of indium doped ZnO thin films. *Semicond. Sci. Technol.* **2005**, *20* (2), 120.
104. Tokumoto, M. S.; Smith, A.; Santilli, C. V.; Pulcinelli, S. H.; Craievich, A. F.; Elkaim, E.; Traverse, A.; Briois, V., Structural electrical and optical properties of undoped and indium doped ZnO thin films prepared by the pyrosol process at different temperatures. *Thin Solid Films* **2002**, *416* (1-2), 284-293.
105. Benouis, C. E.; Benhaliliba, M.; Sanchez Juarez, A.; Aida, M. S.; Chami, F.; Yakuphanoglu, F., The effect of indium doping on structural, electrical conductivity, photoconductivity and density of states properties of ZnO films. *J. Alloys Compd.* **2010**, *490* (1-2), 62-67.
106. Joseph Prince, J.; Ramamurthy, S.; Subramanian, B.; Sanjeeviraja, C.; Jayachandran, M., Spray pyrolysis growth and material properties of In<sub>2</sub>O<sub>3</sub> films. *J. Cryst. Growth* **2002**, *240* (1-2), 142-151.
107. Kodigala Subba, R.; et al., Optical, structural and electrical properties of tin doped indium oxide thin films prepared by spray-pyrolysis technique. *Semicond. Sci. Technol.* **2000**, *15* (7), 676.
108. Ramaiah, K.; Raja, V.; Bhatnagar, A.; Tomlinson, R.; Pilkington, R.; Hill, A., Optical, structural and electrical properties of tin doped indium oxide thin films prepared by spray-pyrolysis technique. *Semicond. Sci. Technol.* **2000**, *15* (7), 676-683.
109. Ghoshtagore, R. N., Mechanism of CVD thin film SnO<sub>2</sub> formation. *J. Electrochem. Soc.* **1978**, *125* (1), 110-117.
110. Maruyama, T.; Nakai, T., Fluorine-doped indium oxide thin films prepared by chemical vapor deposition. *J. Appl. Phys.* **1992**, *71* (6), 2915-2917.
111. Maruyama, T.; Fukui, K., Indium tin oxide thin films prepared by chemical vapour deposition. *Thin Solid Films* **1991**, *203* (2), 297-302.
112. Suzuki, A.; Maki, K., Transparent conductive thin films of Sn doped In<sub>2</sub>O<sub>3</sub> grown by aerosol-assisted CVD using In<sup>III</sup> acetylacetonate with 5 mol %

Sn<sup>IV</sup> bis-acetylacetonate dibromide dissolved in acetylacetone. *Chem. Vap. Deposition* **2006**, *12* (10), 608-613.

113. Sato, H.; Minami, T.; Miyata, T.; Takata, S.; Ishii, M., Transparent conducting ZnO thin films prepared on low temperature substrates by chemical vapour deposition using Zn(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>. *Thin Solid Films* **1994**, *246* (1-2), 65-70.
114. Kashiwaba, Y.; Sugawara, K.; Haga, K.; Watanabe, H.; Zhang, B. P.; Segawa, Y., Characteristics of c-axis oriented large grain ZnO films prepared by low-pressure MO-CVD method. *Thin Solid Films* **2002**, *411* (1), 87-90.
115. Haga, K.; Wijesena, P. S.; Watanabe, H., Group III impurity doped ZnO films prepared by atmospheric pressure chemical-vapor deposition using zinc acetylacetonate and oxygen. *Appl. Surf. Sci.* **2001**, *169-170*, 504-507.
116. Ataev, B. M.; Bagamadova, A. M.; Djabrailov, A. M.; Mamedov, V. V.; Rabadanov, R. A., Highly conductive and transparent Ga-doped epitaxial ZnO films on sapphire by CVD. *Thin Solid Films* **1995**, *260* (1), 19-20.
117. Hu, J.; Gordon, R. G., Textured aluminum-doped zinc oxide thin films from atmospheric pressure chemical-vapor deposition. *J. Appl. Phys.* **1992**, *71* (2), 880-890.
118. Frenzer, G.; Maier, W. F., Amorphous porous mixed oxides: Sol-gel ways to a highly versatile class of materials and catalysts. **2006**; Vol. 36, pp 281-331.
119. Ohyama, M.; Kouzuka, H.; Yoko, T., Sol-gel preparation of ZnO films with extremely preferred orientation along (002) plane from zinc acetate solution. *Thin Solid Films* **1997**, *306* (1), 78-85.
120. Natsume, Y.; Sakata, H., Zinc oxide films prepared by sol-gel spin-coating. *Thin Solid Films* **2000**, *372* (1-2), 30-36.
121. Lee, J. H.; Ko, K. H.; Park, B. O., Electrical and optical properties of ZnO transparent conducting films by the sol-gel method. *J. Cryst. Growth* **2003**, *247* (1-2), 119-125.
122. Lee, J. H.; Park, B. O., Transparent conducting ZnO : Al, In and Sn thin films deposited by the sol-gel method. *Thin Solid Films* **2003**, *426* (1-2), 94-99.
123. Alam, M. J.; Cameron, D. C., Optical and electrical properties of transparent conductive ITO thin films deposited by sol-gel process. *Thin Solid Films* **2000**, *377*, 455-459.
124. Gurlo, A.; Ivanovskaya, M.; Pfau, A.; Weimar, U.; Gopel, W., Sol-gel prepared In<sub>2</sub>O<sub>3</sub> thin films. *Thin Solid Films* **1997**, *307* (1-2), 288-293.

125. Ederth, J.; Heszler, P.; Hultåker, A.; Niklasson, G. A.; Granqvist, C. G., Indium tin oxide films made from nanoparticles: Models for the optical and electrical properties. *Thin Solid Films* **2003**, *445* (2), 199-206.
126. Ederth, J.; Johnsson, P.; Niklasson, G. A.; Hoel, A.; Hultåker, A.; Heszler, P.; Granqvist, C. G.; Van Doorn, A. R.; Jongerius, M. J.; Burgard, D., Electrical and optical properties of thin films consisting of tin-doped indium oxide nanoparticles. *Physical Review B - Condensed Matter and Materials Physics* **2003**, *68* (15), 1554101-15541010.
127. Ederth, J.; Hultåker, A.; Niklasson, G. A.; Heszler, P.; Van Doorn, A. R.; Jongerius, M. J.; Burgard, D.; Granqvist, C. G., Thin porous indium tin oxide nanoparticle films: Effects of annealing in vacuum and air. *Applied Physics A: Materials Science and Processing* **2005**, *81* (7), 1363-1368.
128. Ederth, J.; Hultåker, A.; Heszler, P.; Niklasson, G. A.; Granqvist, C. G.; Van Doorn, A.; Van Haag, C.; Jongerius, M. J.; Burgard, D., Electrical and optical properties of thin films prepared by spin coating a dispersion of nano-sized tin-doped indium oxide particles. *Smart Mater. Struct.* **2002**, *11* (5), 675-678.
129. Adurodija, F. O.; Izumi, H.; Ishihara, T.; Yoshioka, H.; Motoyama, M., Effect of Sn doping on the electronic transport mechanism of indium-tin-oxide films grown by pulsed laser deposition coupled with substrate irradiation. *J. Appl. Phys.* **2000**, *88* (7), 4175-4180.
130. Sato, Y.; Tokumaru, R.; Nishimura, E.; Song, P. K.; Shigesato, Y.; Utsumi, K.; Iigusa, H., Structural, electrical, and optical properties of transparent conductive  $\text{In}_2\text{O}_3$  -  $\text{SnO}_2$  films. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films* **2005**, *23* (4), 1167-1172.
131. Omoto, H.; Takamatsu, A.; Kobayashi, T., Effects of substrate temperature on tin-doped indium oxide films deposited by dc arc discharge ion plating. *Vacuum* **2006**, *80* (7 SPEC. ISS.), 783-787.
132. Rogozin, A.; Vinnichenko, M.; Shevchenko, N.; Kolitsch, A.; Möller, W., Plasma influence on the properties and structure of indium tin oxide films produced by reactive middle frequency pulsed magnetron sputtering. *Thin Solid Films* **2006**, *496* (2), 197-204.
133. Liu, D. S.; Wu, C. C.; Lee, C. T., A transparent and conductive film prepared by RF magnetron cosputtering system at room temperature. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* **2005**, *44* (7 A), 5119-5121.
134. Liu, D. S.; Lin, C. H.; Huang, B. W.; Wu, C. C., Electrical, optical and material properties of ZnO-doped indium-tin oxide films prepared using radio frequency magnetron cosputtering system at room temperature. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* **2006**, *45* (4 B), 3526-3530.

135. Hsu, L. S.; Yeh, C. S.; Kuo, C. C.; Huang, B. R.; Dhar, S., Optical and transport properties of undoped and Al-, Ga- And in-doped ZnO thin films. *Journal of Optoelectronics and Advanced Materials* **2005**, 7 (6), 3039-3046.
136. Bhosle, V.; Tiwari, A.; Narayan, J., Electrical properties of transparent and conducting Ga doped ZnO. *J. Appl. Phys.* **2006**, 100 (3).
137. Shirakata, S.; Sakemi, T.; Awai, K.; Yamamoto, T., Electrical and optical properties of large area Ga-doped ZnO thin films prepared by reactive plasma deposition. *Superlattices Microstruct.* **2006**, 39 (1-4), 218-228.
138. Park, S. M.; Ikegami, T.; Ebihara, K.; Shin, P. K., Structure and properties of transparent conductive doped ZnO films by pulsed laser deposition. *Appl. Surf. Sci.* **2006**, 253 (3), 1522-1527.
139. Kobayakawa, S.; Tanaka, Y.; Ide-Ektessabi, A., Characteristics of Al doped zinc oxide (ZAO) thin films deposited by RF magnetron sputtering. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* **2006**, 249 (1-2 SPEC. ISS.), 536-539.
140. Jeong, W. J.; Kim, S. K.; Park, G. C., Preparation and characteristic of ZnO thin film with high and low resistivity for an application of solar cell. *Thin Solid Films* **2006**, 506-507, 180-183.
141. Ramamoorthy, K.; Kumar, K.; Chandramohan, R.; Sankaranarayanan, K., Review on material properties of IZO thin films useful as *n*-TCOs in optoelectronic (SIS solar cells, polymeric LEDs) devices. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology* **2006**, 126 (1), 1-15.
142. Suzuki, M.; Maeda, Y.; Sawada, Y., Enhanced electrical conductivity of indium tin oxide films by Ag addition. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* **1998**, 37 (1), 34-38.
143. Hultåker, A.; Järrendahl, K.; Lu, J.; Granqvist, C. G.; Niklasson, G. A., Electrical and optical properties of sputter deposited tin doped indium oxide thin films with silver additive. *Thin Solid Films* **2001**, 392 (2), 305-310.
144. Hamberg, I.; Granqvist, C. G., Evaporated Sn-doped In<sub>2</sub>O<sub>3</sub> films: Basic optical properties and applications to energy-efficient windows. *Journal of Applied Physics* **1986**, 60 (11).
145. O'Leary, S. K.; Johnson, S. R.; Lim, P. K., The relationship between the distribution of electronic states and the optical absorption spectrum of an amorphous semiconductor: An empirical analysis. *J. Appl. Phys.* **1997**, 82 (7), 3334-3340.
146. Exarhos, G. J.; Zhou, X.-D., Discovery-based design of transparent conducting oxide films. *Thin Solid Films* **2007**, 515 (18), 7025-7052.

147. Ellmer, K.; Mientus, R., Carrier transport in polycrystalline transparent conductive oxides: A comparative study of zinc oxide and indium oxide. *Thin Solid Films* **2008**, *516* (14), 4620-4627.
148. Ellmer, K.; Mientus, R., Carrier transport in polycrystalline ITO and ZnO:Al II: The influence of grain barriers and boundaries. *Thin Solid Films* **2008**, *516* (17), 5829-5835.
149. Hartnagel, H., Semiconducting transparent thin films. Institute of Physics Pub.: Bristol [England]; Philadelphia, PA, **1995**.
150. Adurodija, F. O.; Izumi, H.; Ishihara, T.; Yoshioka, H.; Motoyama, M.; Murai, K., Pulsed laser deposition of crystalline indium tin oxide films at room temperature by substrate laser irradiation. *Jpn. J. Appl. Phys. Part 2 - Lett.* **2000**, *39* (4B), L377-L379.
151. Ohta, H.; Orita, M.; Hirano, M.; Tanji, H.; Kawazoe, H.; Hosono, H., Highly electrically conductive indium-tin-oxide thin films epitaxially grown on yttria-stabilized zirconia (100) by pulsed-laser deposition. *Appl. Phys. Lett.* **2000**, *76* (19), 2740-2742.
152. Ohta, H.; Orita, M.; Hirano, M.; Hosono, H., Surface morphology and crystal quality of low resistive indium tin oxide grown on yttria-stabilized zirconia. *J. Appl. Phys.* **2002**, *91* (6), 3547-3550.
153. Terzini, E.; Thilakan, P.; Minarini, C., Properties of ITO thin films deposited by RF magnetron sputtering at elevated substrate temperature. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology* **2000**, *77* (1), 110-114.
154. Suzuki, A.; Matsushita, T.; Aoki, T.; Yoneyama, Y.; Okuda, M., Pulsed laser deposition of transparent conducting indium tin oxide films in magnetic field perpendicular to plume. *Jpn. J. Appl. Phys., Part 2* **2001**, *40* (4 B).
155. Agura, H.; Suzuki, A.; Matsushita, T.; Aoki, T.; Okuda, M., Low resistivity transparent conducting Al-doped ZnO films prepared by pulsed laser deposition. *Thin Solid Films* **2003**, *445* (2), 263-267.
156. Park, S. M.; Ikegami, T.; Ebihara, K., Effects of substrate temperature on the properties of Ga-doped ZnO by pulsed laser deposition. *Thin Solid Films* **2006**, *513* (1-2), 90-94.
157. Lewis, B. G.; Paine, D. C., Applications and processing of transparent conducting oxides. *MRS Bull.* **2000**, *25* (8), 22-27.
158. Fortunato, E.; Ginley, D.; Hosono, H.; Paine, D. C., Transparent conducting oxides for photovoltaics. *MRS Bull.* **2007**, *32* (3), 242-247.
159. Garrison, J. D.; Collins, R. E., Manufacture and cost of vacuum glazing. *Solar Energy* **1995**, *55* (3), 151-161.

160. Collins, R. E.; Simko, T. M., Current status of the science and technology of vacuum glazing. *Solar Energy* **1998**, 62 (3), 189-213.
161. Goetzberger, A.; Luther, J.; Willeke, G., Solar cells: Past, present, future. *Sol. Energy Mater. Sol. Cells* **2002**, 74 (1-4), 1-11.
162. Miles, R. W., Photovoltaic solar cells: Choice of materials and production methods. *Vacuum* **2006**, 80 (10), 1090-1097.
163. Ruske, F.; Jacobs, C.; Sittinger, V.; Szyszka, B.; Werner, W., Large area ZnO:Al films with tailored light scattering properties for photovoltaic applications. *Thin Solid Films* **2007**, 515 (24), 8695-8698.
164. Hüpkes, J.; Rech, B.; Calnan, S.; Kluth, O.; Zastrow, U.; Siekmann, H.; Wuttig, M., Material study on reactively sputtered zinc oxide for thin film silicon solar cells. *Thin Solid Films* **2006**, 502 (1-2), 286-291.
165. Sugimoto, A.; Ochi, H.; Fujimura, S.; Yoshida, A.; Miyadera, T.; Tsuchida, M., Flexible OLED displays using plastic substrates. *Selected Topics in Quantum Electronics, IEEE Journal of* **2004**, 10 (1), 107-114.
166. Demiryont, H.; Shannon Iii, K. C. In *Innovative transparent electrode for flexible displays*, Orlando (Kissimmee), FL, USA, Byrd, J. C.; Desjardins, D. D.; Forsythe, E. W.; Girolamo, H. J., Eds. SPIE: Orlando (Kissimmee), FL, USA, 2006; pp 622519-622519.
167. Hsiao, S.; Tanaka, Y.; Ide-Ektessabi, A. In *Properties of Transparent Conductive Oxide Films on Flexible Substrates*, Warrendale, Pa.; Materials Research Society; 1999: 2007; p 210.
168. Tripanagnostopoulos, Y.; Souliotis, M.; Nousia, T., Solar collectors with colored absorbers. *Solar Energy* **2000**, 68 (4), 343-356.
169. Kalogirou, S.; Tripanagnostopoulos, Y.; Souliotis, M., Performance of solar systems employing collectors with colored absorber. *Energy and Buildings* **2005**, 37 (8), 824-835.
170. Ouerfelli, J.; Djobo, S. O.; Bernède, J. C.; Cattin, L.; Morsli, M.; Berredjem, Y., Organic light emitting diodes using fluorine doped tin oxide thin films, deposited by chemical spray pyrolysis, as anode. *Mater. Chem. Phys.* **2008**, 112 (1), 198-201.
171. Meyer, J.; Görrn, P.; Hamwi, S.; Johannes, H.; Riedl, T.; Kowalsky, W., Indium-free transparent organic light emitting diodes with Al doped ZnO electrodes grown by atomic layer and pulsed laser deposition. *Appl. Phys. Lett.* **2008**, 93, 073308.
172. Henrich, V. E.; Cox, P. A., The surface science of metal oxides. Cambridge University Press: Cambridge; New York, **1994**.

173. Vittadini, A.; Selloni, A., Small gold clusters on stoichiometric and defected TiO<sub>2</sub> anatase (101) and their interaction with CO: A density functional study. *J. Chem. Phys.* **2002**, *117* (1), 353-361.
174. De Marchi, G.; Mattei, G.; Mazzoldi, P.; Sada, C.; Miotello, A., Two stages in the kinetics of gold cluster growth in ion-implanted silica during isothermal annealing in oxidizing atmosphere. *J. Appl. Phys.* **2002**, *92* (8), 4249.
175. Qian, W.; Lin, L.; Deng, Y. J.; Xia, Z. J.; Zou, Y. H.; Wong, G. K. L., Femtosecond studies of coherent acoustic phonons in gold nanoparticles embedded in TiO<sub>2</sub> thin films. *J. Appl. Phys.* **2000**, *87* (1), 612-614.
176. Flahaut, E.; Agnoli, F.; Sloan, J.; O'Connor, C.; Green, M. L. H., CCVD Synthesis and Characterization of Cobalt-Encapsulated Nanoparticles. *Chem. Mater.* **2002**, *14* (6), 2553-2558.
177. Li, D.; Choi, C. J.; Kim, B. K.; Zhang, Z. D., Characterization of Fe/N nanoparticles synthesized by the chemical vapor condensation process. *J. Magn. Magn. Mater.* **2004**, *277* (1-2), 64-70.
178. Hida, Y.; Kozuka, H., Photoanodic properties of sol-gel-derived iron oxide thin films with embedded gold nanoparticles: effects of polyvinylpyrrolidone in coating solutions. *Thin Solid Films* **2005**, *476* (2), 264-271.
179. Yang, Y.; Shi, J.; Huang, W.; Dai, S.; Wang, L., Preparation and optical properties of gold nanoparticles embedded in barium titanate thin films. *J. Mater. Sci.* **2003**, *38* (6), 1243-1248.
180. Yang, K.; Fan, H.; Malloy, K. J.; Brinker, C. J.; Sigmon, T. W., Optical and electrical properties of self-assembled, ordered gold nanocrystal/silica thin films prepared by sol-gel processing. *Thin Solid Films* **2005**, *491* (1-2), 38-42.
181. Houn, B.; Huang, C.-J., Structure and properties of Ag embedded aluminum doped ZnO nanocomposite thin films prepared through a sol-gel process. *Surf. Coat. Technol.* **2006**, *201* (6), 3188-3192.
182. Page, K.; Palgrave, R. G.; Parkin, I. P.; Wilson, M.; Savin, S. L. P.; Chadwick, A. V., Titania and silver-titania composite films on glass-potent antimicrobial coatings. *J. Mater. Chem.* **2007**, *17* (1), 95-104.
183. Lutz, T.; Estournès, C.; Merle, J. C.; Guille, J. L., Optical properties of copper-doped silica gels. *J. Alloys Compd.* **1997**, *262-263*, 438-442.
184. Dutta, A.; Das, D.; Grilli, M. L.; Di Bartolomeo, E.; Traversa, E.; Chakravorty, D., Preparation of sol-gel nano-composites containing copper oxide and their gas sensing properties. *J. Sol-Gel Sci. Technol.* **2003**, *26* (1-3), 1085-1089.

185. Huang, W.; Shi, J., Synthesis and properties of ZrO<sub>2</sub> films dispersed with Au nanoparticles. *J. Sol-Gel Sci. Technol.* **2001**, *20* (2), 145-151.
186. Yoon, J. W.; Sasaki, T.; Koshizaki, N.; Traversa, E., Preparation and characterization of M/TiO<sub>2</sub> (M = Ag, Au, Pt) nanocomposite thin films. *Scripta Mater.* **2001**, *44* (8-9), 1865-1868.
187. Sasaki, T.; Koshizaki, N.; Koinuma, M.; Matsumoto, Y., Preparation of M/TiO<sub>2</sub> (M = Au, Pt) nanocomposite films using co-sputtering method. *Nanostruct. Mater.* **1999**, *12* (1), 511-514.
188. Maruyama, O.; Senda, Y.; Omi, S., Non-linear optical properties of titanium dioxide films containing dispersed gold particles. *J. Non-Cryst. Solids* **1999**, *259* (1-3), 100-106.
189. Mizsei, J.; Sipila, P.; Lantto, V., Structural studies of sputtered noble metal catalysts on oxide surfaces. *Sens. Actuators, B* **1998**, *B47* (1 -3 pt 3), 139-144.
190. Armelao, L.; Barreca, D.; Gasparotto, A.; Pierangelo, E.; Tondello, E.; Polizzi, S., Preparation of gold nanoparticles on silica substrate by radio frequency sputtering. *J. Nanosci. Nanotechnol.* **2005**, *5* (2), 259-265.
191. Tanahashi, I.; Yoshida, M.; Manabe, Y.; Tohda, T., Characterization and optical properties of Au/SiO<sub>2</sub> composite thin films. *Surf. Rev. Lett.* **1996**, *3* (1), 1071-1076.
192. Liao, H.; Wen, W.; Wong, G. K., Photoluminescence from Au nanoparticles embedded in Au:oxide composite films. *J. Opt. Soc. Am. B: Opt. Phys.* **2006**, *23* (12), 2518-2521.
193. Gyorgy, E.; Sauthier, G.; Figueras, A.; Giannoudakos, A.; Kompitsas, M.; Mihailescu, I. N., Growth of Au-TiO<sub>2</sub> nanocomposite thin films by a dual-laser, dual-target system. *J. Appl. Phys.* **2006**, *100* (11), 114302-114305.
194. Frey, K.; Beck, A.; Peto, G.; Molnár, G.; Geszti, O.; Gucci, L., Activity of TiO<sub>2</sub> overlayer deposited on Au/SiO<sub>2</sub>/Si(1 0 0) model system. *Catal. Commun.* **2006**, *7* (2), 64-67.
195. Zorica, K.; et al., Particle growth mechanisms in Ag-ZrO<sub>2</sub> and Au-ZrO<sub>2</sub> granular films obtained by pulsed laser deposition. *Nanotechnology* **2006**, *17* (16), 4106.
196. Serna, R.; et al., Optical evidence for reactive processes when embedding Cu nanoparticles in Al<sub>2</sub>O<sub>3</sub> by pulsed laser deposition. *Nanotechnology* **2006**, *17* (18), 4588.
197. Armelao, L.; Barreca, D.; Bottaro, G.; Gasparotto, A.; Maccato, C.; Tondello, E.; Lebedev, O. I.; Turner, S.; Tendeloo, G. V.; Sada, C.; Lavren, U.; ccaron; Scarontangar, Rational Design of Ag/TiO<sub>2</sub> Nanosystems by a Combined RF-Sputtering/Sol-Gel Approach. *ChemPhysChem* **2009**, *10* (18), 3249-3259.

198. Armelao, L.; Barreca, D.; Bottaro, G.; Gasparotto, A.; Maccato, C.; Maragno, C.; Tondello, E.; Štangar, U. L.; Bergant, M.; Mahne, D., Photocatalytic and antibacterial activity of TiO<sub>2</sub> and Au/TiO<sub>2</sub> nanosystems. *Nanotechnology* **2007**, *18* (37).
199. Palgrave, R. G.; Parkin, I. P., Aerosol Assisted Chemical Vapor Deposition Using Nanoparticle Precursors: A Route to Nanocomposite Thin Films. *J. Am. Chem. Soc.* **2006**, *128* (5), 1587-1597.
200. Palgrave, R. G.; Parkin, I. P., Aerosol Assisted Chemical Vapor Deposition of Gold and Nanocomposite Thin Films from Hydrogen Tetrachloroaurate(III). *Chem. Mater.* **2007**, *19* (19), 4639-4647.
201. Binions, R.; Piccirillo, C.; Palgrave, R. G.; Parkin, I. P., Hybrid Aerosol Assisted and Atmospheric Pressure CVD of Gold-Doped Vanadium Dioxide. *Chem. Vap. Deposition* **2008**, *14* (1-2), 33-39.
202. Saeli, M.; Binions, R.; Piccirillo, C.; Hyett, G.; Parkin, I. P., Templated growth of smart nanocomposite thin films: Hybrid aerosol assisted and atmospheric pressure chemical vapour deposition of vanadyl acetylacetonate, auric acid and tetraoctyl ammonium bromide. *Polyhedron* **2009**, *28* (11), 2233-2239.
203. Saeli, M.; Piccirillo, C.; Parkin, I. P.; Ridley, I.; Binions, R., Nano-composite thermochromic thin films and their application in energy-efficient glazing. *Sol. Energy Mater. Sol. Cells* **2010**, *94* (2), 141-151.
204. Liz-Marzan, L. M.; Mulvaney, P., The Assembly of Coated Nanocrystals. *The Journal of Physical Chemistry B* **2003**, *107* (30), 7312-7326.
205. Liao, H. B.; Xiao, R. F.; Fu, J. S.; Yu, P.; Wong, G. K. L.; Sheng, P., Large third-order optical nonlinearity in Au:SiO<sub>2</sub> composite films near the percolation threshold. *Appl. Phys. Lett.* **1997**, *70* (1), 1-3.
206. Tanahashi, I.; Yoshida, M.; Manabe, Y.; Tohda, T., Characterization and optical properties of Au/SiO<sub>2</sub> composite thin films. *Surf. Rev. Lett.* **1996**, *3* (1), 1071-1076.
207. Borsella, E.; Cattaruzza, E.; De Marchi, G.; Gonella, F.; Mattei, G.; Mazzoldi, P.; Quaranta, A.; Battaglin, G.; Polloni, R., Synthesis of silver clusters in silica-based glasses for optoelectronics applications. *J. Non-Cryst. Solids* **1999**, *245*, 122-128.
208. Uchida, K.; Kaneko, S.; Omi, S.; Hata, C.; Tanji, H.; Asahara, Y.; Ikushima, A. J.; Tokizaki, T.; Nakamura, A., Optical nonlinearities of a high concentration of small metal particles dispersed in glass: copper and silver particles. *J. Opt. Soc. Am. B: Opt. Phys.* **1994**, *11* (7), 1236-1243.
209. Cattaruzza, E.; Battaglin, G.; Calvelli, P.; Gonella, F.; Mattei, G.; Maurizio, C.; Mazzoldi, P.; Padovani, S.; Polloni, R.; Sada, C.; Scremin, B. F.;

- D'Acapito, F., Fast nonlinear refractive index of pure and alloy metallic nanoclusters in silica glass. *Compos. Sci. Technol.* **2003**, 63 (8), 1203-1208.
210. Ung, T.; Liz-Marzán, L. M.; Mulvaney, P., Optical properties of thin films of AuO/SiO<sub>2</sub> particles. *J. Phys. Chem. B* **2001**, 105 (17), 3441-3452.
  211. NanoCoat project proposal. **2006**.
  212. Mooradian, A., Photoluminescence of Metals. *Phys. Rev. Lett.* **1969**, 22 (Copyright (C) 2010 The American Physical Society), 185.
  213. Lai, C. W.; An, J.; Ong, H. C., Surface-plasmon-mediated emission from metal-capped ZnO thin films. *Appl. Phys. Lett.* **2005**, 86 (25), 251105-251103.
  214. Khurgin, J. B.; Sun, G., Enhancement of optical properties of nanoscaled objects by metal nanoparticles. *J. Opt. Soc. Am. B: Opt. Phys.* **2009**, 26 (12), B83-B95.
  215. Nakamura, T.; Hayashi, S., Enhancement of dye fluorescence by gold nanoparticles: Analysis of particle size dependence. *Jpn. J. Appl. Phys. Part 1 - Regul. Pap. Brief Commun. Rev. Pap.* **2005**, 44 (9A), 6833-6837.
  216. Beversluis, M. R.; Bouhelier, A.; Novotny, L., Continuum generation from single gold nanostructures through near-field mediated intraband transitions. *Physical Review B* **2003**, 68 (Copyright (C) 2010 The American Physical Society), 115433.
  217. Basak, D.; Karan, S.; Mallik, B., Size selective photoluminescence in poly(methyl methacrylate) thin solid films with dispersed silver nanoparticles synthesized by a novel method. *Chem. Phys. Lett.* **2006**, 420 (1-3), 115-119.
  218. Rivas, L.; Sanchez-Cortes, S.; García-Ramos, J. V.; Morcillo, G., Mixed silver/gold colloids: a study of their formation, morphology, and surface-enhanced Raman activity. *Langmuir* **2000**, 16 (25), 9722-9728.
  219. Kim, K.; Kim, K. L.; Lee, S. J., Surface enrichment of Ag atoms in Au/Ag alloy nanoparticles revealed by surface enhanced Raman scattering spectroscopy. *Chem. Phys. Lett.* **2005**, 403 (1-3), 77-82.
  220. Moskovits, M., Surface-enhanced Raman spectroscopy: a brief retrospective. *J. Raman Spectrosc.* **2005**, 36 (6-7), 485-496.
  221. Zheng, J.; Zhang, C.; Dickson, R. M., Highly Fluorescent, Water-Soluble, Size-Tunable Gold Quantum Dots. *Phys. Rev. Lett.* **2004**, 93, 077402.
  222. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N., Novel gold catalysts for the oxidation of carbon-monoxide at a temperature far below 0-degrees-C. *Chem. Lett.* **1987**, (2), 405-408.

223. Haruta, M., Size- and support-dependency in the catalysis of gold. *Catal. Today* **1997**, *36* (1), 153-166.
224. Bond, G. C.; Thompson, D. T., Catalysis by Gold. *Catalysis Reviews: Science and Engineering* **1999**, *41* (3), 319 - 388.
225. Hughes, M. D.; Xu, Y.-J.; Jenkins, P.; McMorn, P.; Landon, P.; Enache, D. I.; Carley, A. F.; Attard, G. A.; Hutchings, G. J.; King, F.; Stitt, E. H.; Johnston, P.; Griffin, K.; Kiely, C. J., Tunable gold catalysts for selective hydrocarbon oxidation under mild conditions. *Nature* **2005**, *437* (7062), 1132-1135.
226. Kim, W. B.; Rodriguez-Rivera, G. J.; Evans, S. T.; Voith, T.; Einspahr, J. J.; Voyles, P. M.; Dumesic, J. A., Catalytic oxidation of CO by aqueous polyoxometalates on carbon-supported gold nanoparticles. *J. Catal.* **2005**, *235* (2), 327-332.
227. Thompson, D. T., Using gold nanoparticles for catalysis. *Nano Today* **2007**, *2* (4), 40-43.
228. Sakurai, H.; Ueda, A.; Kobayashi, T.; Haruta, M., Low-temperature water-gas shift reaction over gold deposited on TiO<sub>2</sub>. *Chem. Commun.* **1997**, (3), 271-272.
229. Iizuka, Y.; Fujiki, H.; Yamauchi, N.; Chijiwa, T.; Arai, S.; Tsubota, S.; Haruta, M., Adsorption of CO on gold supported on TiO<sub>2</sub>. *Catal. Today* **1997**, *36* (1), 115-123.
230. Okumura, M.; Nakamura, S.; Tsubota, S.; Nakamura, T.; Azuma, M.; Haruta, M., Chemical vapor deposition of gold on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and TiO<sub>2</sub> for the oxidation of CO and of H<sub>2</sub>. *Catal. Lett.* **1998**, *51* (3-4), 53-58.
231. Mizsei, J.; Sipilä, P.; Lantto, V., Structural studies of sputtered noble metal catalysts on oxide surfaces. *Sensors Actuators B: Chem.* **1998**, *47* (1-3), 139-144.
232. Penza, M.; Martucci, C.; Cassano, G., NO<sub>x</sub> gas sensing characteristics of WO<sub>3</sub> thin films activated by noble metals (Pd, Pt, Au) layers. *Sensors Actuators B: Chem.* **1998**, *50* (1), 52-59.
233. Radheshkumar, C.; Münstedt, H., Antimicrobial polymers from polypropylene/silver composites--Ag<sup>+</sup> release measured by anode stripping voltammetry. *React. Funct. Polym.* **2006**, *66* (7), 780-788.
234. Panáček, A.; Kvítek, L.; Pucek, R.; Kolář, M.; Večerková, R.; Pizúrová, N.; Sharma, V. K.; Nevěčná, T. j.; Zbořil, R., Silver Colloid Nanoparticles: Synthesis, Characterization, and Their Antibacterial Activity. *The Journal of Physical Chemistry B* **2006**, *110* (33), 16248-16253.
235. Zaporozhchenko, V.; et al., Physico-chemical and antimicrobial properties of co-sputtered Ag-Au/PTFE nanocomposite coatings. *Nanotechnology* **2006**, *17* (19), 4904.

236. Mallick, K.; Witcomb, M. J.; Scurrall, M. S., Self-assembly of silver nanoparticles: Formation of a thin silver film in a polymer matrix. *Materials Science and Engineering: C* **2006**, 26 (1), 87-91.
237. Hong, C.-S.; Park, H.-H.; Moon, J.; Park, H.-H., Effect of metal (Al, Ga, and In)-dopants and/or Ag-nanoparticles on the optical and electrical properties of ZnO thin films. *Thin Solid Films* **2006**, 515 (3), 957-960.
238. Hagfeldt, A.; Grätzel, M., Molecular photovoltaics. *Acc. Chem. Res.* **2000**, 33 (5), 269-277.
239. Chandrasekharan, N.; Kamat, P. V., Improving the Photoelectrochemical Performance of Nanostructured TiO<sub>2</sub> Films by Adsorption of Gold Nanoparticles. *The Journal of Physical Chemistry B* **2000**, 104 (46), 10851-10857.
240. Cherepy, N. J.; Smestad, G. P.; Grätzel, M.; Zhang, J. Z., Ultrafast electron injection: Implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO<sub>2</sub> nanocrystalline electrode. *J. Phys. Chem. B* **1997**, 101 (45), 9342-9351.
241. Khandpur, R. S., Handbook of analytical instruments. McGraw-Hill: New York, **2007**.
242. Cullity, B. D., Elements of X-ray diffraction. Addison-Wesley Pub. Co.: Reading, Mass., **1956**.
243. Suryanarayana, C.; Norton, M. G., X-Ray diffraction : a practical approach. Plenum Press: New York, **1998**.
244. Kanaya, K.; Okayama, S., Penetration and energy-loss theory of electrons in solid targets. *J. Phys. D: Appl. Phys.* **1972**, 5 (1), 43.
245. Krinsley, D. H., Backscattered scanning electron microscopy and image analysis of sediments and sedimentary rocks. Cambridge University Press: Cambridge, U.K.; New York, **1998**.
246. Valdes, L. B., Resistivity measurements on germanium for transistors. *Proceedings of the IRE* **1954**, 42 (2), 420.
247. Lee, S. M.; Kim, D. L.; Youn, H. J.; Hong, K. S., Tin oxide films by chemical vapor deposition using a monobutyltin trichloride source: The effect of H<sub>2</sub>O on deposition behavior and electrical properties. *Jpn. J. Appl. Phys. Part 1 - Regul. Pap. Brief Commun. Rev. Pap.* **2000**, 39 (2A), 407-412.
248. Larkin, W. A. Process of applying tin oxide on glass using butyltin trichloride. US Patent 4130673, **1978**.
249. Laurent, J.-M.; Smith, A.; Smith, D. S.; Bonnet, J.-P.; Clemente, R. R., Morphology and physical properties of SnO<sub>2</sub>-based thin films deposited by

- the pyrosol process from dibutyltin diacetate. *Thin Solid Films* **1997**, 292 (1-2), 145-149.
250. Kim, K. H.; Chun, J. S., X-ray studies of SnO<sub>2</sub> prepared by chemical vapour deposition. *Thin Solid Films* **1986**, 141 (2), 287-295.
  251. Kane, J.; Schweizer, H. P.; Kern, W., Chemical vapor deposition of antimony-doped tin oxide films formed from dibutyl tin diacetate. *J. Electrochem. Soc.* **1976**, 123 (2), 270-277.
  252. Chambouleyron, I.; Constantino, C.; Fantini, M.; Farias, M., On the chlorine content in chemically sprayed tin oxide films: A quantitative analysis. *Solar Energy Materials* **9** (2), 127-138.
  253. Chen, Q.; Qian, Y.; Chen, Z.; Zhou, G.; Zhang, Y., Fabrication of ultrafine SnO<sub>2</sub> thin films by the hydrothermal method. *Thin Solid Films* **1995**, 264 (1), 25-27.
  254. Antonaia, A.; Menna, P.; Addonizio, M. L.; Crocchiolo, M., Transport properties of polycrystalline tin oxide films. *Sol. Energy Mater. Sol. Cells* **1992**, 28 (2), 167-173.
  255. Macedo, A. G.; Cava, C. E.; Canestraro, C. D.; Contini, L.; Roman, L. S., Morphology Dependence on Fluorine Doped Tin Oxide Film Thickness Studied with Atomic Force Microscopy. **2005**, 11 (SupplementS03), 118-121.
  256. Aukkaravittayapun, S.; Wongtida, N.; Kasecwatin, T.; Charojrochkul, S.; Unnanon, K.; Chindaudom, P., Large scale F-doped SnO<sub>2</sub> coating on glass by spray pyrolysis. *Thin Solid Films* **2006**, 496 (1), 117-120.
  257. Ray, S. C.; Karanjai, M. K.; DasGupta, D., Tin dioxide based transparent semiconducting films deposited by the dip-coating technique. *Surface and Coatings Technology* **1998**, 102 (1-2), 73-80.
  258. Remes, Z.; Vanecek, M.; Yates, H. M.; Evans, P.; Sheel, D. W., Optical properties of SnO<sub>2</sub>:F films deposited by atmospheric pressure CVD. *Thin Solid Films* **2009**, 517 (23), 6287-6289.
  259. Liao, B.-H.; Kuo, C.-C.; Chen, P.-J.; Lee, C.-C., Fluorine-doped tin oxide films grown by pulsed direct current magnetron sputtering with an Sn target. *Appl. Opt.* **2011**, 50 (9), C106-C110.
  260. Sears, W. M.; Gee, M. A., Mechanics of film formation during the spray pyrolysis of tin oxide. *Thin Solid Films* **1988**, 165 (1), 265-277.
  261. Siefert, W., Properties of thin In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> films prepared by corona spray pyrolysis, and a discussion of the spray pyrolysis process. *Thin Solid Films* **1984**, 120 (4), 275-282.
  262. Middleton, D. J., Grenier, Jodyne I., Method of making infrared reflective glass sheet. **1985**.

263. Manificier, J. C.; Szepessy, L.; Bresse, J. F.; Perotin, M.; Stuck, R.,  $\text{In}_2\text{O}_3$  : Sn and  $\text{SnO}_2$  : F films - application to solar energy conversion part II - Electrical and optical properties. *Mater. Res. Bull.* **1979**, 14 (2), 163-175.
264. Cassar, K., NanoCoat quarterly progress report. **2008**.
265. Lin, K.-m.; Tsai, P., Growth mechanism and characterization of ZnO: Al multi-layered thin films by sol-gel technique. *Thin Solid Films* **2007**, 515 (24), 8601-8604.
266. Nunes, P.; Malik, A.; Fernandes, B.; Fortunato, E.; Vilarinho, P.; Martins, R., Influence of the doping and annealing atmosphere on zinc oxide thin films deposited by spray pyrolysis. *Vacuum* **1999**, 52 (1-2), 45-49.
267. Srinivasan, G.; Rajendra Kumar, R. T.; Kumar, J., Influence of Al dopant on microstructure and optical properties of ZnO thin films prepared by sol-gel spin coating method. *Opt. Mater.* **2007**, 30 (2), 314-317.
268. Yoshino, K.; et al., Annealing effects of In-doped ZnO films grown by spray pyrolysis method. *Journal of Physics: Conference Series* **2008**, 100 (8), 082019.
269. Lucio-López, M. A.; Luna-Arias, M. A.; Maldonado, A.; de la L. Olvera, M.; Acosta, D. R., Preparation of conducting and transparent indium-doped ZnO thin films by chemical spray. *Solar Energy Materials and Solar Cells* **2006**, 90 (6), 733-741.
270. Portier, J.; Campet, G.; Poquet, A.; Marcel, C.; Subramanian, M. A., Degenerate semiconductors in the light of electronegativity and chemical hardness. *Int. J. Inorg. Mater.* **2001**, 3 (7), 1039-1043.
271. Wang, M.; Lee, K. E.; Hahn, S. H.; Kim, E. J.; Kim, S.; Chung, J. S.; Shin, E. W.; Park, C., Optical and photoluminescent properties of sol-gel Al-doped ZnO thin films. *Materials Letters* **2007**, 61 (4-5), 1118-1121.
272. Hong, R. J.; Helming, K.; Jiang, X.; Szyszka, B., Texture analysis of Al-doped ZnO thin films prepared by in-line reactive MF magnetron sputtering. *Appl. Surf. Sci.* **2004**, 226 (4), 378-386.
273. Gaskell, D. R., Introduction to the thermodynamics of materials. Taylor & Francis: Washington, D.C., **1995**.
274. Medvedeva, J. E., Unconventional approaches to combine optical transparency with electrical conductivity. *Appl. Phys. A: Mater. Sci. Process.* **2007**, 89 (1), 43-47.
275. Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J., Recent advances in the liquid-phase syntheses of inorganic nanoparticles. *Chem. Rev.* **2004**, 104 (9), 3893-3946.
276. Cassar, K.; Buche, V.; Bishop, P., NanoCoat Milestone 8 report. **2008**.

277. Deki, S.; Aoi, Y.; Yanagimoto, H.; Ishii, K.; Akamatsu, K.; Mizuhata, M.; Kajinami, A., Preparation and characterization of Au-dispersed TiO<sub>2</sub> thin films by a liquid-phase deposition method. *J. Mater. Chem.* **1996**, *6* (12), 1879-1882.
278. Lee, M.; Chae, L.; Lee, K. C., Microstructure and surface plasmon absorption of sol-gel-prepared Au nanoclusters in TiO<sub>2</sub> thin films. *Nanostruct. Mater.* **1999**, *11* (2), 195-201.
279. Silva, R. F.; Zaniquelli, M. E. D., Aluminium-doped zinc oxide films prepared by an inorganic sol-gel route. *Thin Solid Films* **2004**, *449* (1-2), 86-93.
280. Gao, X. D.; Li, X. M.; Yu, W. D., Structure and UV photoluminescence of nanocrystalline ZnO films prepared by thermal oxidation of ZnS films. *Mater. Sci. Eng., B* **2004**, *113* (3), 274-278.
281. Dejneka, A.; Aulika, I.; Makarova, M. V.; Hubicka, Z.; Churpita, A.; Chvostova, D.; Jastrabik, L.; Trepakov, V. A., Optical Spectra and Direct Optical Transitions in Amorphous and Crystalline ZnO Thin Films and Powders. *J. Electrochem. Soc.* **2010**, *157* (2), G67-G70.
282. Perednis, D. Thin film deposition by spray pyrolysis and the application in solid oxide fuel cells. PhD thesis, ETH, Zurich, Switzerland, 2003.