

Monolayer Oxide Films



Shuqiu Wang
Mansfield College
University of Oxford

A thesis submitted for the degree of
Doctor of Philosophy
Trinity Term 2019

Preface

The work reported in this thesis is original work that was carried out by the author from October 2015 to August 2019. Some of the work contained in this thesis has been published in peer-reviewed scientific publications and presented at scientific conferences. These include:

Publications:

1. 'Influence of the support on stabilizing local defects in strained monolayer oxide films'
S. Wang, X. Hu, J. Goniakowski, C. Noguera and M. R. Castell.
Nanoscale, 11, 2412 – 2422, 2019.
2. 'Atomic and electronic structure of an epitaxial Nb₂O₃ honeycomb monolayer on Au(111)'
S. Wang, J. Goniakowski, C. Noguera and M. R. Castell.
Physical Review B, 100, 125408, 2019.
3. 'Growth and Atomic Structure of NbO_x Nanostructures on Au(111) in the Submonolayer Regime'
S. Wang, and M. R. Castell.
Submitted to Journal of Physical Chemistry C, 2019.
4. 'Domain boundaries in a (2 × 2) honeycomb Ti₂O₃ monolayer on Au(111)'
S. Wang, X. Hu, J. Goniakowski, C. Noguera and M. R. Castell.
In preparation.
5. 'Maximising the resolving power of the scanning tunneling microscope'
L. Jones, **S. Wang**, X. Hu, S.U. Rahman and M.R. Castell.
Advanced Structural and Chemical Imaging, 4, 7, 2018.

Oral presentations:

1. 'Defects in Monolayer Films with the Honeycomb Structure: Ti₂O₃ and Nb₂O₃ on Au (111)'
S. Wang, X. Hu, J. Goniakowski, C. Noguera, M. R. Castell.
The 21st International Vacuum Conference (IVC-21), Malmö, Sweden, 2019
2. 'Defects in honeycomb Ti₂O₃ ultrathin films on Au(111)'
S. Wang, X. Hu, J. Goniakowski, C. Noguera and M. R. Castell.
The 34th European Conference on Surface Science, Aarhus, Denmark, 2018.
Nominated for the ECOSS prize for the best oral presentation.
3. 'Maximising the resolving power of the scanning tunneling microscope'
S. Wang, L. Jones, X. Hu, S.U. Rahman and M.R. Castell.
The 34th European Conference on Surface Science, Aarhus, Denmark, 2018.

Poster presentations:

1. 'Influence of the support on stabilizing local defects in strained monolayer oxide films'
S. Wang, X. Hu, J. Goniakowski, C. Noguera, M. R. Castell.
The 21st International Vacuum Conference (IVC-21), Malmö, Sweden, 2019.
2. 'Maximising the resolving power of the scanning tunneling microscope'
S. Wang, L. Jones, X. Hu, S.U. Rahman and M.R. Castell.
The 21st International Vacuum Conference (IVC-21), Malmö, Sweden, 2019.
3. 'Nanostructures and ultrathin films of NbO_x grown on Au(111)'
S. Wang, X. Hu, M. R. Castell.
The 13th European Conference on Surface Crystallography and Dynamics, San Sebastian, Spain, 2017.
4. 'Nanostructures and ultrathin films of NbO_x grown on Au(111)'
S. Wang, X. Hu, M. R. Castell.
Solid Surface Group Symposium, Royal Society of Chemistry, London, UK, 2016.

Abstract

This thesis focuses on the monolayer films and nanostructures of Ti oxide and Nb oxide supported on the gold substrate. Particular emphasis have been placed on learning about the point and extended defects that occur in the films.

The thesis begins with a significant improvement in the resolving power of the STM that can be achieved through automated distortion correction and multi-frame averaging. The broad utility of this approach is demonstrated with three examples: the Si(111)-(7 × 7) reconstruction, the Ti₂O₃ (2 × 2) film on Au(111) and the (4 × 4) reconstructed SrTiO₃(111) surface.

Ti₂O₃ monolayer films with a honeycomb lattice often contain local defects in which the hexagonal elements are replaced by four, five, seven, and eight-membered rings. The structure and energetics of Stone-Wales and divacancy defects in the Ti₂O₃ monolayers are investigated using scanning tunneling microscopy (STM) and density functional theory (DFT). The substrate significantly influences the energetics, and hence favors vacancy-type defects, in compressively strained 2D materials. A variety of non-stoichiometric defects are observed and they can be generated by applying a voltage pulse using the STM tip.

An epitaxial (2 × 2) honeycomb Nb₂O₃ monolayer is grown on an Au(111) surface. The films form a well-ordered honeycomb lattice and adopt a (2 × 2) periodicity with respect to the Au(111) substrate. The Nb atoms are located in Au(111) three-fold hollow sites and the O atoms are located in on-top positions. The existence of a strong interfacial interaction is characterized by a large electron transfer to the Au substrate, an increase of the Nb oxidation state, and substantial film rumpling. High resolution STM images are able to discriminate between Nb atoms adsorbed in fcc or hcp hollow sites on the surface.

A variety of monolayer niobium oxide (NbO_x) nanostructures are grown on Au(111) surfaces. The NbO_x nanostructures can be classified as atomic clusters consisting of only a few atoms, or larger triangular islands of various sizes. The atomic clusters have rectangular, pentagonal and hexagonal shapes, and they can merge to form larger clusters. The atomic clusters have stoichiometries ranging from NbO to NbO_{1.5}. The triangular islands have a close-packed structure. Triangular islands of different sizes have similar atomic structures and stoichiometries close to NbO. The nanostructures can be converted into (2 × 2) Nb₂O₃ honeycomb monolayer films when annealed for prolonged periods in 10⁻⁶ Pa of oxygen.

The structures and properties of defects in monolayer films of Ti₂O₃ and Nb₂O₃ on Au (111) are compared. For both systems, a rich variety of defects including island edges and domain boundaries are observed. Characteristic domain boundaries consist of 4, 5, 7 and 8-membered rings. For the Nb₂O₃ monolayer films, a larger variety of structures within domain boundaries have been observed. Furthermore, the edge structures for both systems have been studied. While the Ti₂O₃ forms disordered edges containing nonhexagonal rings, the Nb₂O₃ forms armchair and zigzag edges containing only hexagonal rings. It is surprising that although both Ti₂O₃ and Nb₂O₃ form the same structure, the defects in these systems are distinctly different.

Acknowledgements

Without the support of many people in many places, this thesis could not have been written. First of all I would like to thank my supervisor Prof Martin R. Castell. He often explains a complicated concept in a simple way and guides me to think deeply and critically. We had many frank exchange of opinions and ideas, and the results were mostly positive. His guidance in science and career has helped me overcome my weakness and nurture my interest in fundamental physics. I am very fortunate to be in his group.

Thanks to my surrogate advisors. To Dr Jacek Goniakowski and Dr Claudine Noguera who performed density functional theory calculations for this thesis. They gave inspirations and theoretical insights behind the interesting discoveries I played a role in my PhD. Their enthusiasm for beautiful explanations was contagious. Jacek's curiosity in solving difficult problems was wonderful. It is truly inspiring and encouraging for me to see Claudine as a female global leader of solid state physics. To Prof Jan Seidel who taught me the value of teamwork in science and introduced me to the field of magnetic domain walls. To Prof Lewys Jones who transferred his knowledge of multiple frame averaging to me. He is not only an excellent scientist, mathematician but also a genius artist. To Prof J.C. Seamus Davis, who I was extremely fortunate to meet at the end of my PhD, has taught me how to be clear about my goals so as to proceed efficiently.

Thanks to my groupmates who are both friends and teachers. To Xiao who taught me STM imaging and the UHV system, and did a lot of hard work which has been the critical foundation for this thesis. To Yakun who gave a lot of happiness and energy to our STM subgroup. I am thankful to Peiyu as we supported each other through our PhDs and shared our ups and downs. To Fubiao and Yuhan for laughter, support and shared memories. Wish them all the best for their PhDs. To Krish who often popped his head into my office to ask 'how are things'. To Merel, Ben and Atif who have been a pleasure to work with. Tabby and Aditiya have been lovely people to share an office with. I'd like to thank Chris Spencer for maintaining the UHV equipment and replying rapidly when the instrument has problems. I'd like thank Peter Flaxman who spent so much time making delicate components for the microscope.

I'd like to thank my friends. To Jiawei who helped me laugh through all the obstacles which appeared in my path towards PhD. To Anela for being sharp and thorough, and she has given me great support and smart tactics in my searching for a postdoc position. I'd like to thank Ghazi for sharing our progress and dreams over coffee breaks in the park. To friends in our corridor as we have worked hard and supported each other in the late nights. I want to thank my housemates. To Luigi for sharing a bottle of wine, watching movies, and laughing. To Ruth for being sweet, cute and supportive. I will miss our family breakfast and hotpot with Ruth and Alex. To Albert for barbecue on 4th July, turkey on Thanksgiving Day and Irish coffee on Saturdays. I'd also like to thank my college advisor Prof Jason Smith, for encouraging me to pursue the most exciting and important scientific problems during my postdoc search. I'd like to thank my OxFEST mentor Dr Alison Crossley for encouraging me to meet interesting people and exchange ideas.

Finally, this thesis would not have been possible without the love and support from my parents. They have given me a lot of freedom, and have encouraged me through the four years that is challenging, thrilling and surreal.

Contents

Chapter 1. Introduction	1
1.1 Background	1
1.2 Plan of thesis	3
Chapter 2. Experimental Methods.....	6
2.1 Ultrahigh Vacuum (UHV) System	6
2.2 Sample preparation	8
2.3 Scanning Tunneling Microscopy (STM).....	10
2.4 Low Energy Electron Diffraction (LEED).....	13
2.5 Image Processing — Multiple Frame Averaging.....	16
2.6 Conclusions.....	17
Chapter 3. Literature Review	19
3.1 Surface relaxation and reconstruction.....	19
3.2 Oxide monolayers	21
3.2.1 Structures determined by stoichiometry.....	23
3.2.2 Structures determined by charge transfer	25
3.3 Monolayer films with honeycomb structure.....	27
3.3.1 Van der Waals and covalent honeycomb monolayers	27
3.3.2 Oxide honeycomb monolayers.....	29
3.4 Defects in the honeycomb structure.....	33
3.4.1 Extended linear defects.....	34
3.4.2 Local defects.....	39
3.4.3 Edge terminations.....	42
3.5 Monolayer oxide nanostructures	46
3.5.1 Atomic clusters	46
3.5.2 Larger nanostructures.....	48
3.6 Perspective.....	51
Chapter 4. Maximising the signal-to-noise ratio of the scanning tunneling microscope	52
4.1 Introduction.....	52
4.2 Methods	53
4.3 Results.....	54
4.4 Discussion	63
4.5 Conclusions.....	65
Chapter 5. Local defects in the Ti₂O₃ honeycomb monolayer.....	67
5.1 Introduction.....	67

5.2 Experimental methods	67
5.3 Results and discussion	68
5.4 Conclusions	82
Chapter 6. Nb₂O₃ honeycomb monolayer	84
6.1 Introduction	84
6.2 Experimental methods	84
6.3 Experimental results and discussion	85
6.4 Theoretical results and discussion	91
6.5 Point defects in (2 × 2) Nb ₂ O ₃ monolayer on Au(111)	95
6.6 Conclusions	96
Chapter 7. NbO_x nanostructures on Au(111) in the submonolayer regime	98
7.1 Introduction	98
7.2 Experimental methods	98
7.3 Results and discussion	99
7.4. Conclusions	113
Chapter 8. Domain boundaries in the Ti₂O₃ and Nb₂O₃ honeycomb monolayers	115
8.1 Introduction	115
8.2 Domain boundaries in Ti ₂ O ₃ (2 × 2) honeycomb structure	116
8.3 Domain boundaries in Nb ₂ O ₃ (2 × 2) honeycomb structure	126
8.4 Conclusions	134
Chapter 9. Island edges of the Ti₂O₃ and Nb₂O₃ honeycomb monolayers	136
9.1 Introduction	136
9.2 Results and discussion	137
9.3 Conclusions	153
Chapter 10. Conclusions	155
10.1 Overview	155
10.2 Ti ₂ O ₃ and Nb ₂ O ₃ monolayers with a (2 × 2) honeycomb structure	156
10.3 Defects in Ti ₂ O ₃ and Nb ₂ O ₃ honeycomb structures	156
10.4 NbO _x atomic clusters and nanostructures	158
10.5 Future work	158
Appendix A Supporting Information of Chapter 5	161
Appendix B Supporting Information of Chapter 6	165
Appendix C Supporting Information of Chapter 7	168
Appendix D Supporting Information of Chapter 8	171
References	173

Chapter 1. Introduction

1.1 Background

Monolayer oxide films consist of a single layer of atoms or polyhedron units. They are important materials in heterogeneous catalysis both as inhibitor and catalyst. Noble metal nanoparticles can be encapsulated by ultrathin oxide films at elevated temperature and the metal catalysts may thereby become deactivated.¹ Oxide ultrathin films themselves may also be novel catalysts for a variety of reactions such as water splitting² and the water gas shift reaction.³ In fundamental research, oxide monolayers are interesting systems that can exhibit unconventional structures, such as quasicrystalline⁴ and labyrinth-like structures.⁵ These systems are interesting because they are not only a surface but also an interface. The surface structures are modified with respect to the bulk structures because the surface atoms experience inter-atomic forces from the bulk and no force from the vacuum whereas the bulk atoms experience forces from surrounding atoms within the bulk. The interface structures are modified with respect to that in the bulk phase because the interfacial structures are influenced by the substrate. Being both a surface and an interface significantly modifies the film structures with respect to the bulk structures.

The surface structures of titanium oxides are particularly interesting because of their photocatalytic properties. They are also of fundamental interest because Ti oxide is a transition metal oxide with more complex surface structures than a simple oxide such as MgO. The surface structure of Mg oxide is a slice of their bulk termination whereas the surface of Ti oxide exhibits a variety of structures completely different from their bulk counterpart. A metal supported TiO_x monolayer contains one atomic layer, and can be characterized using techniques that require conductance. The growth of monolayer TiO_x films has been reported on a Pt(111) substrate.⁶⁻⁸ Several surface structures of a TiO_x monolayer are grown by varying the growth conditions of the oxide. The TiO_x has stoichiometry ranging from TiO to TiO_2 with the Ti atoms being 2+, 3+ or 4+. The fact that Ti atoms can bond to three or four O atoms result in a variety of TiO_x surface structures. Previously monolayer TiO_x films have been successfully grown on an Au(111) substrate in our group.^{5,9} It is therefore with new motivation that in this thesis, the surface chemistry of TiO_x monolayers, defect structures in the films and the physical origin of these structures have been studied in the pursuit of a deeper understanding of these TiO_x monolayers.

Similar interest has been raised for niobium oxide monolayers. NbO_x is an important material for supporting Pt nanoparticles in methanol oxidation¹⁰ and a dielectric material for capacitors.¹¹ Nb has oxidation states ranging from 2+ to 5+. There are only a few reports that address to NbO_x monolayer films. NbO_x monolayers have been grown on Pt(111)¹² and $\text{Cu}_3\text{Au}(100)$.¹³ NbO_x/Pt has a (2×2) structure with poor crystallinity but the quality of the low energy electron diffraction pattern was not sufficient to derive the atomic structure of the corresponding film. $\text{NbO}_x/\text{Cu}_3\text{Au}$ exhibits a mixing of the oxide and the reactive substrate and thus is not an ideal system for studying the oxide-metal

interface. A calculated freestanding Nb_2O_3 film has a honeycomb structure and exhibits interesting topological states.¹⁴ A Nb_2O_3 film supported on a MoS_2 substrate has also been calculated. The topological states are retained under the van der Waals interfacial interactions between Nb_2O_3 and MoS_2 . This thesis reports a systematic investigation on the growth and atomic structures of NbO_x monolayers supported on $\text{Au}(111)$.

1.2 Plan of thesis

This thesis covers the growth of Ti and Nb oxide monolayer oxide films, characterization of the film structures at atomic resolution and investigation of the atomic structure and stabilizing mechanism of the films and defects.

Metallic Ti is deposited on a bare $\text{Au}(111)$ surface and annealed in an oxidizing atmosphere. The metallic Ti is oxidized into TiO_x . The surface energy of Ti oxide is significantly lower than the surface energy of a bare Au surface. Covering an Au surface with a monolayer of TiO_x has lower system energy than growing TiO_x islands on the Au surface and exposing the bare Au surface to vacuum. Therefore Ti oxide forms a monolayer film that wets the surface. The Nb oxide monolayer has been grown in a similar manner. Ti and Nb oxide films have an epitaxial M_2O_3 (2×2) honeycomb structure that can act as a suitable template for metal atom adsorption.⁵ A rich variety of defects including local defects, domain boundaries and island edges are observed in both systems. Their structures are characterized using a combination of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED), and modeled using density functional theory (DFT).

Chapter 2 is a general introduction to the experimental system and surface characterization techniques. Emphasis is put on STM and image processing methods. The signal to noise ratio of the STM images is improved after image processing.

Chapter 3 introduces a honeycomb structure and the structures of oxide monolayers. Monolayer films with a honeycomb lattice, such as graphene and hexagonal boron nitride, have been extensively investigated. The investigations on defects in graphene provide insights into the stabilizing mechanisms for defect structures. Five-membered rings induce tension in a hexagonal lattice of graphene whereas seven-membered rings induce expansion. The coupling of five and seven-membered rings lowers the strain energy induced by defects. The honeycomb structure has been observed in a Ti_2O_3 monolayer which interacts with $\text{Pt}(111)$ and $\text{Au}(111)$ substrates via strong ionic and metallic bonding. Other metal supported oxide systems with a honeycomb structure include $\text{V}_2\text{O}_3/\text{Pd}(111)$ and $\text{FeWO}_3/\text{Pt}(111)$. A variety of defects including linear defects, local defects and island edges occur in the honeycomb structure. Oxides can also form nanostructures, such as atomic clusters and nanoislands, in the submonolayer regime.

From Chapter 4 onwards, original work is presented. Chapter 4 shows a method to denoise STM images by means of averaging of a large number of images. This is an imaging implementation that involves averaging over multiple frames, image registration and plane subtraction.

Chapter 5 shows that growing a Ti_2O_3 monolayer film on an $\text{Au}(111)$ substrate generates a variety of defects. The divacancy defects in an Au-supported Ti_2O_3 film have lower energies than the corresponding structure in a freestanding film. The interaction between the oxide and the Au substrate results in compressive strain in the oxide film. Formation of divacancy defects relieves the compressive strain and thus it is favored.

Chapter 6 reports the experimental discovery and theoretical analysis of an epitaxial (2×2) honeycomb Nb_2O_3 monolayer on $\text{Au}(111)$. The oxide monolayer is grown by Nb deposition and subsequent annealing in oxidizing atmosphere. STM images show that the

films form a well-ordered honeycomb lattice, and LEED patterns confirm that the films adopt a (2×2) periodicity with respect to the Au(111) substrate. The Nb₂O₃ film is stabilized by a strong interfacial interaction with the Au substrate.

Chapter 7 describes the growth of Nb oxide nanostructures on Au(111). The Nb oxide can form nanostructures of atomic clusters and triangular islands. The nanostructures can be converted into Nb₂O₃ (2×2) structure via a thermally activated process in an oxidative atmosphere.

Chapter 8 focuses on the domain boundaries in (2×2) structures of Ti₂O₃ and Nb₂O₃. The Ti₂O₃ film shows characteristic domain boundaries consist of 4, 5, 7 and 8-membered rings. Whereas the Nb₂O₃ monolayer film shows a larger variety of structures within domain boundaries, and their structures are harder to define than those in Ti₂O₃.

Chapter 9 presents the island edges in (2×2) structures of Ti₂O₃ and Nb₂O₃. The Ti₂O₃ island edge mainly reconstructs into nonhexagonal rings. The island edges of Nb₂O₃ often forms regular armchair and zigzag edges consisting of hexagonal rings. The Nb₂O₃ island edges can reconstruct into pentagonal rings depending on growth conditions.

Chapter 10 concludes this thesis. This thesis focuses on the growth and atomic structures of Ti₂O₃ and Nb₂O₃ (2×2) structures, with emphasis on defects that occur in the films. Although the Ti₂O₃ and Nb₂O₃ has the same structure, the defects behavior in these systems are distinctly different. Future proposed development include interactions of metal atom (Fe, Cu) with the honeycomb monolayers, ternary oxide monolayers of Ti-V, V-Nb and oxidation-reduction behavior of the oxide films.

Chapter 2. Experimental Methods

In this chapter, the experimental procedures and techniques for preparation and characterization of oxide nanostructures on metal substrates are summarized. Most of the experiments are conducted in an ultrahigh vacuum (UHV) system and various equipment are attached to it that are used to grow monolayer oxide films and nanostructures. The preparation of oxide monolayers using metal deposition and oxidation are discussed. The oxide monolayers are characterized using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). The scanning tunneling microscope images are processed using a multiple frame averaging method to enhance the signal-to-noise ratio of the image.

2.1 Ultrahigh Vacuum (UHV) System

The UHV system is important for providing cleanliness and preventing contamination in surface science experiments. The UHV system allows the vacuum conditions for metal deposition and gas dosing that are required for the growth of oxide films and nanostructures. The UHV system is also necessary for STM because the UHV system decreases surface adsorption and helps maintain a clean surface so that the surface can be characterized at atomic resolution.

One JEOL JSTM 4500XT instrument has been used. The JEOL system consists of two main chambers as shown in Fig. 2.1. The Treatment Chamber (the left chamber in Fig. 2.1) is maintained at a base pressure of $10^{-7} \sim 10^{-8}$ Pa and it is used for sputtering, annealing and LEED. The Imaging Chamber (on the right-hand side in Fig. 2.1) is maintained at low 10^{-8} Pa and it is used for epitaxial structure growth and STM imaging. A typical high-resolution STM image that shows fine surface features is often taken at $\sim 1 \times 10^{-8}$ Pa. The pressure in both chambers is maintained by pumping out gases using one ion pump per chamber (2 in Fig. 2.1). Samples are transferred from air to UHV through the loadlock that is pumped down to 10^{-6} Pa by a turbomolecular pump (TMP, 1 in Fig. 2.1), backed by a rotary pump.

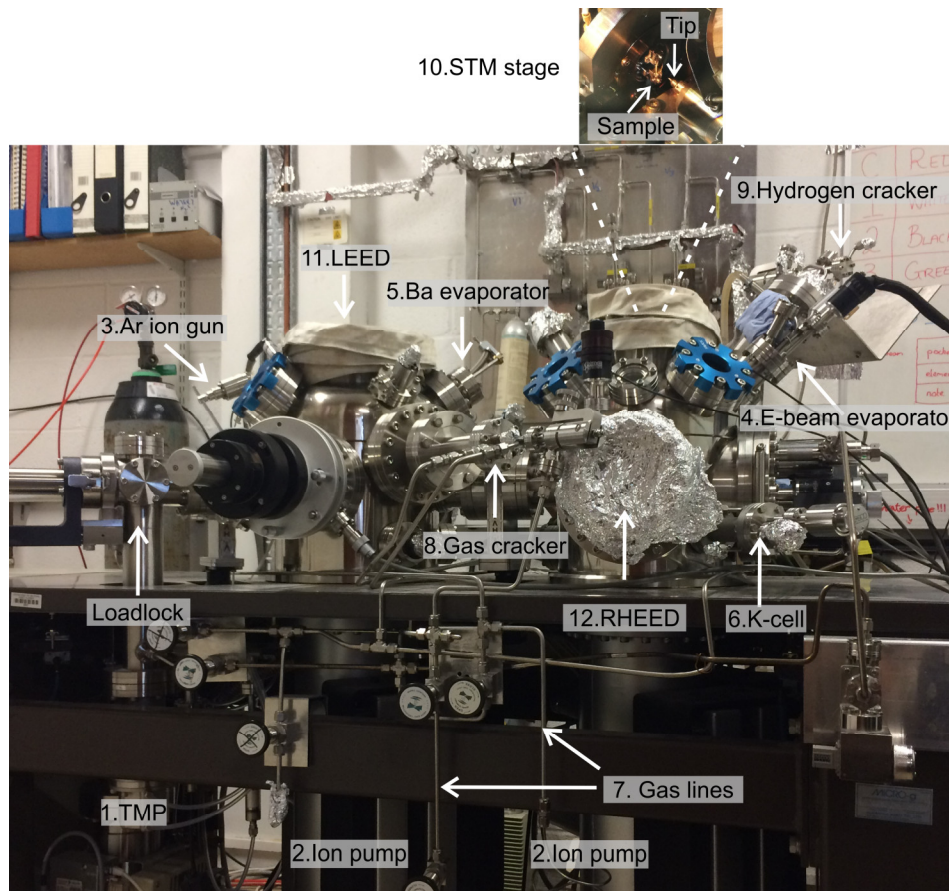


Fig 2.1. The JEOL-4500XT UHV system. The left chamber is the Treatment Chamber and the right chamber is the Imaging Chamber. Various parts are labeled.

The UHV chambers are equipped with various tools for sample preparation and characterization. Surface preparation equipment includes two direct current resistive annealing power supplies, an argon ion sputtering gun (3), an electron beam (E-beam) evaporator (4), a barium evaporator (5), one Knudsen cell (K-cell) evaporator (6), various gas line inlets (7), a thermal gas cracker (8), and a hydrogen cracker (9). Surface characterization techniques include an STM (10), a LEED optical system (11), and a reflection high-energy electron diffraction (RHEED) system (12).

UHV is also used for large-scale systems such as gravitational wave detectors LIGO and synchrotron radiation. UHV is critical for eliminating temperature fluctuations and sound waves that may cover the signal of gravitational waves in LIGO. UHV is used in synchrotron to decrease beam-gas interaction such as scattering.

2.2 Sample preparation

2.2.1 Preparation of the Au substrate

The nanostructures presented in this thesis were grown on Au(111) thin films supported on mica, and Au(111) single crystals. The Au thin films on mica are supplied by Agilent Technologies UK. The size of the samples is $2 \times 7 \text{ mm}^2$. To control the temperature of the Au/mica substrate, these crystals are heated indirectly by mounting them on a strontium titanate backplate. The strontium titanate is heated by resistive heating. Since the Au thin film is a good heat conductor, a low current through the sample can lead to high temperature. One end of the gold is scratched to avoid the current running through the gold. The temperature is calculated from an empirical power (P) - temperature (T) curve $T = 2.30893 - 38.793P^2 + 323.34P + 21.976$.¹⁵ Furthermore, a polished Au single crystal (SurfaceNet GmbH, Germany) cut to reveal the (111) termination was cleaned by repeated sputtering and annealing cycles. The size of the sample is $4 \times 7 \text{ mm}^2$. The Au single crystal

in heated using an indirect heater which has a heating plate below the sample. A current is passed through the metal wires behind the heating plate and the plate is heated up.

The gold crystal is heated up to 600°C to eliminate water, hydrocarbons and other contaminants from the surface. This process is known as degassing. The crystal is subsequently sputtered by 0.75~1 keV Ar⁺ ions for 15 to 25 minutes with a sputtering current of 7.5 μA. The sputtering is performed with an argon ion sputtering gun (PSP Vacuum Technology Ion Source ISIS3000). After sputtering, the surface is annealed in UHV at 600°C for 1.5 hours. The procedure leads to atomically flat and clean Au(111) herringbone reconstructions as observed by the STM.

2.2.2 Preparation of the Au substrate

Oxide films and nanostructures are grown on Au(111) by metal evaporation and subsequent oxidation. Metallic Ti and Nb are evaporated onto Au(111) surfaces using an electron beam evaporator (Oxford Applied Research EGN4). Ti and Nb metal rods are supplied by Johnson Matthey plc, U. K. and have a purity of 99.99%. The substrates are kept at a temperature in the range of 25-600°C. After evaporation, oxygen is introduced and the substrate is heated to 500-600°C for 15-60 minutes to oxidize the metal and form oxide nanostructures. The samples are then cooled down in an oxygen atmosphere, preventing reduction of the oxides during annealing. The substrate temperature, oxygen partial pressure and annealing time are critical parameters that control oxide structures. These parameters will be discussed with the results in the following chapters.

2.2.3 Electron beam (e-beam) evaporator

The e-beam evaporator is used to evaporate Ti and Nb metal and deposit the metal onto the Au(111) substrate. It is attached to the imaging chamber of the UHV system (4 in Fig. 2.1). A current is first induced through a tungsten wire. The charge tungsten wire gives

off an electron beam that bombards the end of a metal rod. The metal rod is heated up and is melted, which generates the vapor of metal atoms. These ions collide with an ion collector, which induces a flux current. The amount of metal deposits is proportional to the product of the flux current and the deposit time. These evaporated atoms then precipitate onto the substrate.

2.3 Scanning Tunneling Microscopy (STM)

STM is one of the most detailed and precise techniques for surface characterization. STM provides three-dimensional real-time topography and electronic structure of surfaces with atomic resolution. STM characterizes surfaces locally, including both periodic and non-periodic structures such as nanoparticles and defects. This is an essential distinction compared with spectroscopy and electron diffraction which both long-range ordered structures.

The STM operates via a quantum tunneling effect. When two conductors are close enough to each other and a voltage is applied, electrons can tunnel through the vacuum barrier. In STM, a sharp metal tip approaches a conductive surface to within 1 nm. By applying a voltage between the tip and the conductor, a tunneling current is induced. The tunneling current (I) is exponentially dependent on the tip-sample distance (d), which is written as $I \propto e^{-2\kappa d}$. κ is a constant related to the decay length for the wave function in the vacuum. Thus a change in tip-sample distance is reflected in a dramatic change in the tunneling current. This gives STM high surface sensitivity in the z -direction with a resolution down to 0.1 Å. STM probes information from the topmost atomic layer of a surface.

2.3.1 Interpretation of STM images

An STM image is a compound of both topography and local density of states from a surface. Fig. 2.2 shows energy level diagrams for the STM tip and the sample, where E_{vac}

is the vacuum level, E_f is the Fermi level (Fermi energy), ϕ_T is the work function of the tip and ϕ_S is the work function of the sample. The tip and the sample are separated by a macroscopic distance in Fig. 2.2a and there is no interaction between the tip and the sample. As the tip-sample distance decreases, the tip and the sample reach thermodynamic equilibrium and their Fermi energies are equal (Fig. 2.2b). Their vacuum levels are not equal due to the presence of the electric fields in vacuum. Thus there is a trapezoid potential barrier between the tip and the sample. Applying a positive bias to the sample results in electrons to tunnel from the tip into the empty states of the sample (Fig. 2.2c). Applying a negative bias to the sample causes a tunneling current from the filled states of the sample towards the tip (Fig. 2.2d).

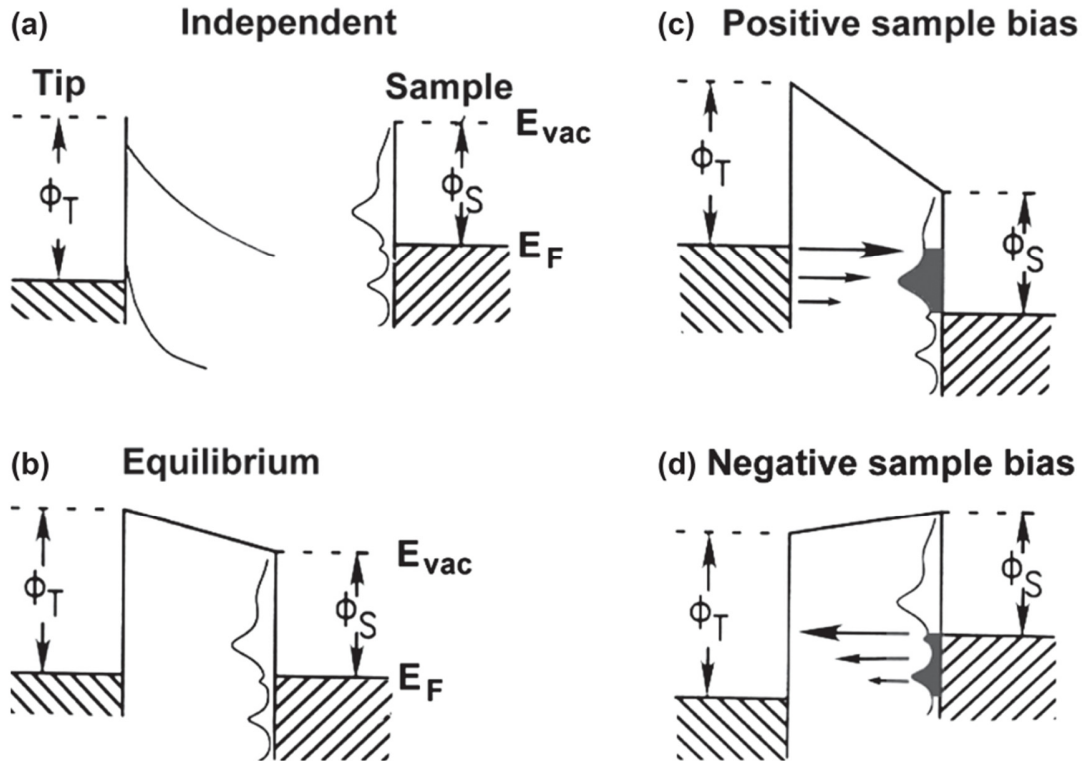


Fig 2.2. Energy level diagrams for the STM tip and sample. (a) The tip and the sample are independent. (b) The tip and the sample are interacting. They are in thermodynamic equilibrium and their fermi energies are equal. (c) Applying a positive sample bias results in electrons to tunnel from the tip to the empty states of the sample. (d) Applying a negative bias causes electrons to tunnel from the filled states of the sample to the tip.¹⁶

For example, on a $\text{TiO}_2(110)$ surface with the (1×1) reconstruction, the O atoms (red balls in Fig. 2.3a) stick out and are closer to the STM tip than the Ti atoms (grey balls).¹⁷ However, the Ti atoms are imaged as the bright rows and the O atoms are imaged as the dark rows in an empty state STM image (Fig. 2.3b). The Ti atoms have stronger STM signal because the conduction band of TiO_2 is dominated by the Ti states.

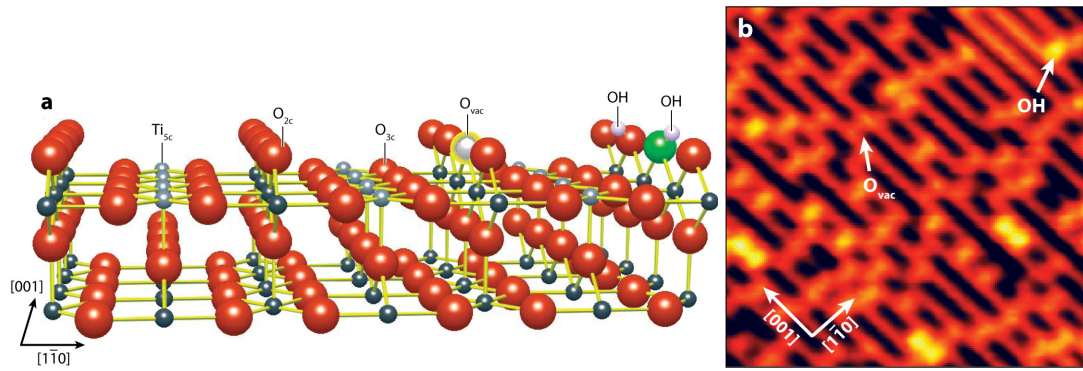


Fig 2.3. $\text{TiO}_2(110)$ surface with the (1×1) reconstruction. (a) An atomic model showing the Ti atoms in grey and O atoms in red. (b) An empty state STM image of the $\text{TiO}_2(110)$ surface. Image width 10 nm, $V_s = 1.48$ V, $I_t = 0.08$ nA.¹⁷

2.3.2 Scanning tunneling spectroscopy (STS)

Scanning tunneling spectroscopy (STS) is used to probe the local electronic structures. STS is implemented by maintaining the tip at a constant height above an atom. The tunneling current is measured as a function of electron energy by varying the sample bias, giving rise to an I-V curve. Taking the slope of the I-V curve yields a differential dI/dV spectrum that tells the local density of states in the sample and the tip. Measuring a dI/dV spectrum at each atom on a surface allows to visualize the spatial arrangement of the local density of states at given energies.

Fig. 2.4 shows an example of using STS to investigate Zn impurities in a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSSCO) superconductor.¹⁸ Fig. 2.4a is a topographic STM image showing the BiO termination of the BSSCO crystal. Fig. 2.4b shows a dI/dV map taken simultaneously with

Fig 2.4a. A Zn dopant is located in the center of the image and shows a cross-shaped four-fold symmetric structure. One dI/dV spectrum taken at a usual Cu site (black line in Fig. 2.4c) shows two superconducting coherence peaks. One dI/dV spectrum taken at the Zn atom shows one intragap conductance peak whereas the superconducting coherence peaks are suppressed.

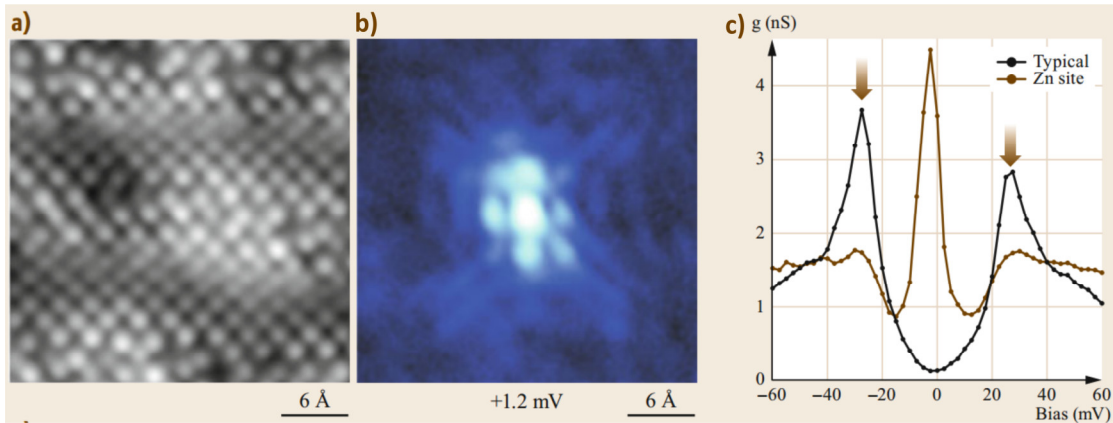


Fig. 2.4. The topograph (a) and the LDOS map (b) of a BiO termination layer of a Zn-doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ crystal. (a) and (b) are acquired simultaneously. (c) Differential tunneling conductance spectra taken at a typical Cu site and a Zn atom on the Zn-BSCCO crystal.¹⁸

2.4 Low Energy Electron Diffraction (LEED)

In contrast to the long-time imaging in STM, LEED enables faster monitoring of surface order and periodicity. Fig. 2.5 shows a schematic of a LEED system. Electrons are emitted from a charged tungsten filament. They are given a kinetic energy of 20-200 eV and focused into an electron beam by passing through the Wehnelt cylinder (indicated as ‘W’ in Fig. 2.5). The electron beam bombards the surface, penetrate a few atomic layers and are thus highly sensitive to surfaces. The electrons are scattered by surface atoms. Elastically scattered electrons are accelerated towards the fluorescent screen and form the diffraction pattern which reveals the crystallography of the topmost layers. Inelastically scattered electrons mainly lose energy via plasmon- and phonon- excitation and electron-

electron interactions. The inelastically scattered electrons are shielded by the second grid at a suppressor voltage. Hence, they will not reach the fluorescent screen which prevents blurring the diffraction pattern.

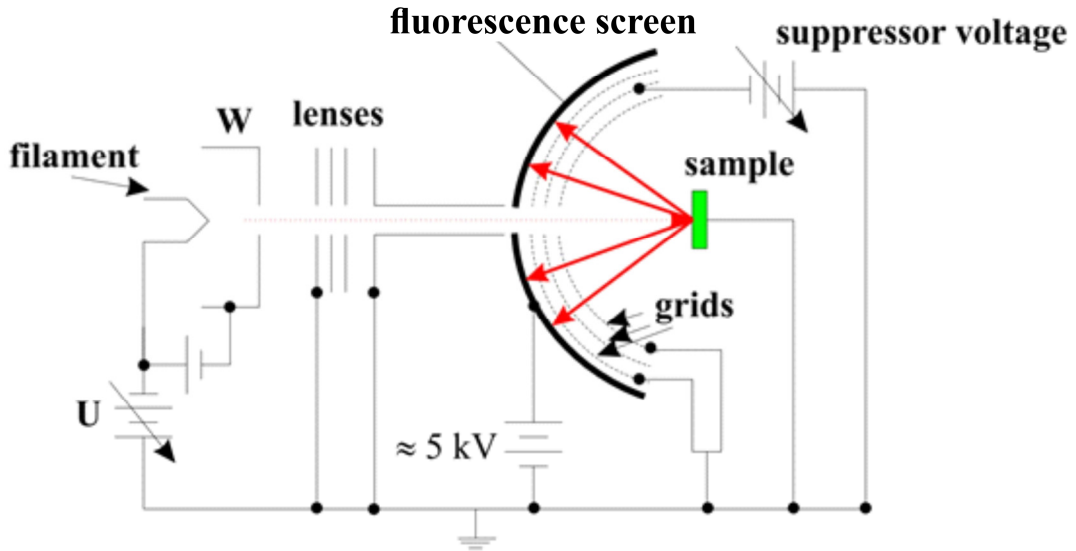


Fig. 2.4. The schematic of a LEED system, showing how electrons are generated, focused and scattered to visualize the diffraction pattern.

A basic LEED pattern is the Bravais array, i.e., the spots consisting of a single reciprocal unit cell which corresponds to a surface with single ordered domains. $\vec{a}$, $\vec{b}$ are the basis vectors of the substrate lattice and $\vec{a}_s$, $\vec{b}_s$ of the superstructure on the substrate. The superstructure vectors are related to the substrate vectors by a matrix m_{ij}

$$\begin{bmatrix} \vec{a}_s \\ \vec{b}_s \end{bmatrix} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \begin{bmatrix} \vec{a} \\ \vec{b} \end{bmatrix}$$

In the reciprocal space, $\vec{a}^*, \vec{b}^*$ are reciprocals to $\vec{a}, \vec{b}$, and $\vec{a}_s^*, \vec{b}_s^*$ are reciprocals to $\vec{a}_s, \vec{b}_s$.

The substrate reciprocal lattice is related to the reciprocal superlattice vectors by a matrix m_{ij}^*

$$\begin{bmatrix} \vec{a}^* \\ \vec{b}^* \end{bmatrix} = \begin{bmatrix} m_{11}^* & m_{12}^* \\ m_{21}^* & m_{22}^* \end{bmatrix} \begin{bmatrix} \vec{a}_s^* \\ \vec{b}_s^* \end{bmatrix}$$

Since $(m_{ij}^*)^{-1} = m_{ij}^T$, the vectors of the superstructure on the substrate are expressed as

$$\begin{bmatrix} \vec{a}_s \\ \vec{b}_s \end{bmatrix} = \begin{bmatrix} m_{11}^* & m_{21}^* \\ m_{12}^* & m_{22}^* \end{bmatrix} \begin{bmatrix} \vec{a} \\ \vec{b} \end{bmatrix}$$

Fig. 2.5 is an example of a $c(2 \times 2)$ superlattice on a fcc(100) surface. The left-handed panel shows the schematic of a $c(2 \times 2)$ reconstruction and the right panel shows a simulated LEED diffraction pattern.

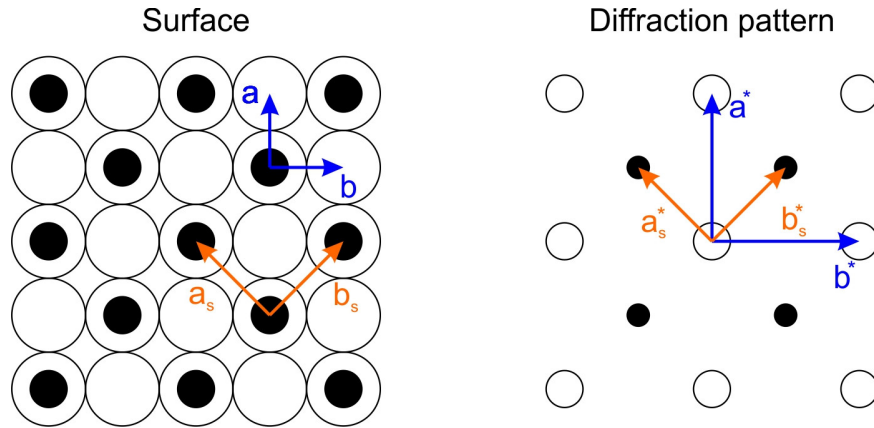


Fig. 2.5. Surface atom arrangement and LEED diffraction pattern with a Bravais array. Substrate atoms are white and superstructure atoms are black.

In reciprocal space, the reciprocal vectors of the substrates are

$$\begin{bmatrix} \vec{a}^* \\ \vec{b}^* \end{bmatrix} = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \vec{a}_s^* \\ \vec{b}_s^* \end{bmatrix}$$

Hence, the superstructure in the real space is

$$\begin{bmatrix} \vec{a}_s \\ \vec{b}_s \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} \vec{a} \\ \vec{b} \end{bmatrix}$$

2.5 Image Processing — Multiple Frame Averaging

STM images can be corrupted by scanning distortions and noise. A software package named Smart Align, developed by Jones et al.,¹⁹ was used to correct image distortions and achieve data with a higher signal-to-noise ratio. SmartAlign is programmed by Dr Lewys Jones and I apply the software package to align multiple STM images to a common field-of-view (rigid registration) and average them into one frame (non-rigid registration). The procedures are described in more details below.

2.5.1 Rigid Registration

A series of STM images are taken at the same field-of-view (FOV) and imaging conditions, including the tunneling current, sample bias, scanning speed and orientation. The FOVs of the multiple frames are not exactly the same due to sample drifts. Rigid alignment is based on cross-correlation and it is used to correct these drifts and crop a common area among all the images. The common area is subsequently used in the image averaging described in Section 2.5.2. The images are aligned by using correlation functions which are generalized into a parameter α . High α values of 0.6~1.0 are chosen for ‘plain’ structures, such as surface reconstructions; while low α values of 0.1~0.4 are chosen for

outstanding features, such as nanoparticles. Moreover, there are two registration modes for high- and low-SNR images. The high-SNR mode evaluates the offset up to all the nearest neighbors of each image to register. This is suitable for most of the datasets. The low-SNR mode defaults a linear displacement between every two images. This mode helps align very noisy images. Rigid registration creates an image stack of the same FOV. It not only aligns the images for non-rigid registration in Section 2.5.2, but also helps in the study of surface dynamics described in Chapter 7.

2.5.2 Non-rigid Registration

Distortion and scanning noise in STM images are corrected using non-rigid registration. Non-rigid registration averages the rigid-aligned image stack into a reference image. By comparing each raw frame with the reference, the noise and distortion of the raw images are corrected. This is considered as one cycle. Applying 3-6 registration cycles to one image series provides an averaged image of high SNR. Non-rigid registration includes affine-only cycles and non-rigid cycles. The affine-only cycle preserves straight lines and corrects linear distortions such as shear and small-angle rotations. This applies to most datasets. The non-rigid cycle transforms straight lines into non-linear features and corrects non-linear distortions. This cycle is more intensive and may damage the raw images of high noise levels or images rotated using symmetry. It is applicable to images of high SNR and with the same scanning orientation. Detailed examples that demonstrate how multiple frame averaging enhances STM images are provided in Chapter 4.

2.6 Conclusions

The results in this thesis are produced via the following process. Ti and Nb oxide nanostructures and films are grown on a reconstructed Au(111) single crystal substrate in a UHV system. The surface structures are characterized using STM and LEED. The STM

images are processed using multiple frame averaging and occasionally processed using a median filter to denoise the STM images. The processed STM images are then compared with DFT simulations carried out by collaborators to validate the atomic models.

Chapter 3. Literature Review

This chapter provides a background on monolayer oxide films, defects that occur in the films and monolayer nanostructures. Different film structures are discussed. Particularly oxide monolayers with a honeycomb lattice are discussed and compared to honeycomb monolayers that interact with the substrate via van der Waals bonding. Local defects, extended linear defects and edge terminations that occur in the honeycomb monolayers are discussed. Moreover, the structures of atomic clusters and nanostructures of monolayer thickness are reviewed. The focus of this chapter is to provide a broad and representative, but not exhaustive review, of experimental and theoretical studies of the atomic structures and stability of oxide monolayers, defects in the films and nanostructures, and the underlying physical mechanisms involved in stabilizing the structures.

3.1 Surface relaxation and reconstruction

Surface relaxation and reconstruction occurs when a bulk crystal is terminated along a given plane. The atoms at the surface experience no force from vacuum on one side whereas experience forces exerted from surrounding atoms in the bulk crystal on the other side. The altered chemical and electronic environment of surface atoms with respect to

atoms in the bulk results in rearrangement of atoms. Surface relaxation describes a process where the surface layer(s) of a bulk crystal is (are) shifted with respect to the bulk unit cells by a translational lattice offset. The surface atoms change their locations whereas the pristine bulk unit cell is maintained. Surface reconstruction refers to the rearrangement of surface atoms into unit cells and periodicities different from those of an unreconstructed bulk surface. This process leads to novel two-dimensional structures at the surface layer of a bulk crystal. For example, oxide surfaces, when going through surface reconstruction, often form layers with atomic structures, stoichiometry and coordination different from those in the bulk. The structures of oxide surfaces are stabilized by the interplay of a series of mechanisms including polarity compensation, strain release, charge transfer and finite size effect.^{20,21}

A surface reconstruction is often described by a matrix notation and Wood's notation.²² In the matrix notation, the basic translational vectors a_s and b_s of a reconstructed surface layer are related to the basic translational vectors a and b of one unreconstructed atomic layer within the bulk.

$$a_s = G_{11}a + G_{12}b$$

$$b_s = G_{21}a + G_{22}b$$

Thus the crystallographic relation between the reconstructed layer and a pristine bulk layer is described by:

$$G = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$$

Wood's notation is $X(hkl) m \times n - R\Phi$, where X indicates the bulk crystal, (hkl) is the termination plane of the crystal. The unit cell of a reconstructed layer is defined by the multiples of a pristine bulk unit cell, with the basic translational vectors a multiplied by

m and b multiplied by n . The rotation angle of the unit cell of the reconstructed layer with respect to the pristine layer is defined by Φ .

The matrix notation can directly indicate changes in the layer symmetry, such as from rectangular to hexagonal, whereas Wood's notation cannot. However, Wood's notation is more widely used due to its simplicity. In this chapter, the surface structures are described using Wood's notation.

3.2 Oxide monolayers

Oxide monolayers consist of one layer of atoms or polyhedron units,²⁰ and are of technological interest in the fields of catalysis and corrosion.^{23,24} They are also effective model systems for encapsulation of metal nanoparticles in catalysis. When metal nanoparticles are supported on reducible oxide substrate, an oxide film from the substrate may migrate onto the metal particle at high temperature.²³ The encapsulation is due to strong metal-support interaction,²⁵ and can lead to deactivation of the catalytic reactivity of the metal particles, or novel film properties such as enhanced CO oxidation.²³ In fundamental research, oxide monolayers are attractive materials systems because they have properties that do not exist in bulk oxides such as modified crystallography and stoichiometry as well as unusual electronic and magnetic behavior.

The origin of monolayer wetting a substrate can be explained by the energetics of the surface and the film.²⁶ The layer-by-layer growth occurs for situations where the surface energy of the substrate (δ_s) is more than the sum of the surface energy of the film (δ_f) and the interface energy (δ_i), that is, $\delta_s > \delta_f + \delta_i$, as shown in Fig. 3.1. The adatoms of the deposits have stronger interaction with the substrate than with other adatoms, and thus the deposits wet the surface as a monolayer film. The film grows in a layer-by-layer mode.

The film growth may also be influenced by kinetic effect, which can lead to growth modes deviate from those in Fig. 3.1.

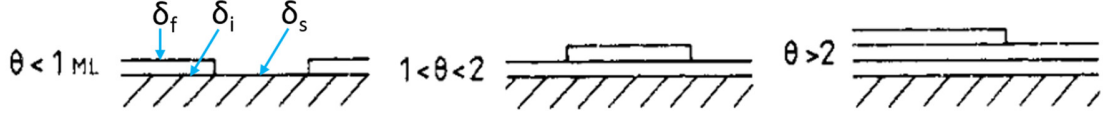


Fig. 3.1 Layer-by-layer film growth as a function of film coverage (θ).²⁶

Oxide monolayers may grow as a relaxed layer that forms a coincidence structure with the substrate and these films show a moiré pattern, such as FeO_x on $\text{Pt}(111)$ and $\text{Au}(111)$, and CoO_x on $\text{Au}(111)$.^{27–32} Fe and Co oxides have lower surface energy than a bare Au surface and thus they wet the surface as a monolayer. The structures of the films are barely affected by the structure of the substrate. Alternatively, monolayer films may be constrained to match the substrate lattice as experimentally observed in many oxide monolayers grown on metals, systems such as $\text{NiO}(100)-(1 \times 1)/\text{Ag}(100)$,³³ $\text{WO}_3-c(2 \times 2)/\text{Pd}(100)$,³⁴ $\text{CoO}(100)-c(4 \times 2)/\text{Pd}(100)$,³⁵ $\text{V}_2\text{O}_3 (2 \times 2)/\text{Pd}(111)$,³⁶ $\text{Ti}_2\text{O}_3 (2 \times 2)/\text{Au}(111)$ ^{5,9,37–39} and $\text{FeWO}_3 (2 \times 2)/\text{Pt}(111)$.⁴⁰ For example, the $\text{V}_2\text{O}_3 (2 \times 2)$ has lower surface energy than the $\text{Pd}(111)$ surface, and the film strongly interact with the substrate. Thus V_2O_3 wets the surface as a monolayer and its atomic structure is determined by the large interfacial interaction with Pd.

The oxide monolayers have shown various novel structures that are not observed in the bulk phase. The nanostructure of oxide monolayers are determined by various factors such as the stoichiometry of the oxide phase, lattice mismatch between film and substrate, interfacial charge transfer, adhesion energy of the film, polarity effect and the chemical

potential of the growth atmosphere. Some of these factors and their effect on the oxide structures will be discussed below using several examples.

3.2.1 Structures determined by stoichiometry

The cations in transition metal oxides can adopt a variety of oxidation states which can result in a variety of bulk crystal stoichiometries and structures (e.g., FeO, Fe₃O₄ and Fe₂O₃). Analogously, monolayer films of transition metal oxides can also form a myriad of complex surface structures. For example, in the system of TiO_x films supported on Pt(111), the oxidation states of the Ti ions range from +2 to +4, and a Ti atom can have a variety of coordination with O atoms. The reducibility of Ti atoms results in a variable stoichiometry and structural flexibility of the film. This capability allows the films to reach thermodynamically stable structure under various chemical potentials.

TiO_x/Pt(111) films show a variety of kagomé, zigzag, wagon-wheel, rectangular and hexagonal structures, and their stoichiometries range from TiO to TiO₂.^{6–8,41–44} A series of TiO_x zigzag and hexagonal structures show atomic structures determined by their stoichiometry. The TiO_x monolayer films contain small patches of TiO(111) islands separated by periodic linear defects, see the first column in Fig. 3.2. STM images show the Ti atom locations as bright spots, as confirmed by STM simulations (the second column in Fig. 3.2). The TiO(111) domains consist of three-fold coordinated Ti atoms and the linear defects contain four-fold coordinated Ti atoms. The four-fold coordinated Ti atoms appear brighter than three the 3-fold coordinated Ti atoms due to higher density of states. The schematics for these structures are shown in the third column of Fig. 3.2.

A zigzag (z-TiO_x) structure is grown by depositing 0.8 monolayer equivalent (MLE, 1 MLE = 1.5×10^{15} atoms/cm²) Ti on Pt(111) substrate and annealing in 10⁻⁵ Pa O₂ at 823 K.^{42,43} The structural model of the z-TiO_x structure is shown in Fig. 3.2c. The z-TiO_x is an

incommensurate layer with a rhombic unit cell of $6.8 \text{ \AA} \times 9.1 \text{ \AA}$ (highlighted in the first row in Fig. 3.2) with respect to the Pt(111) substrate. Each unit cell contains six Ti atoms and eight O atoms, giving rise to a $\text{TiO}_{1.33}$ stoichiometry and a Ti oxidation state of 2.7. Two of the Ti atoms are three-fold coordinated (Ti^{3+}) and four other Ti atoms are four-fold coordinated (Ti^{4+}). The $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio is 0.5.

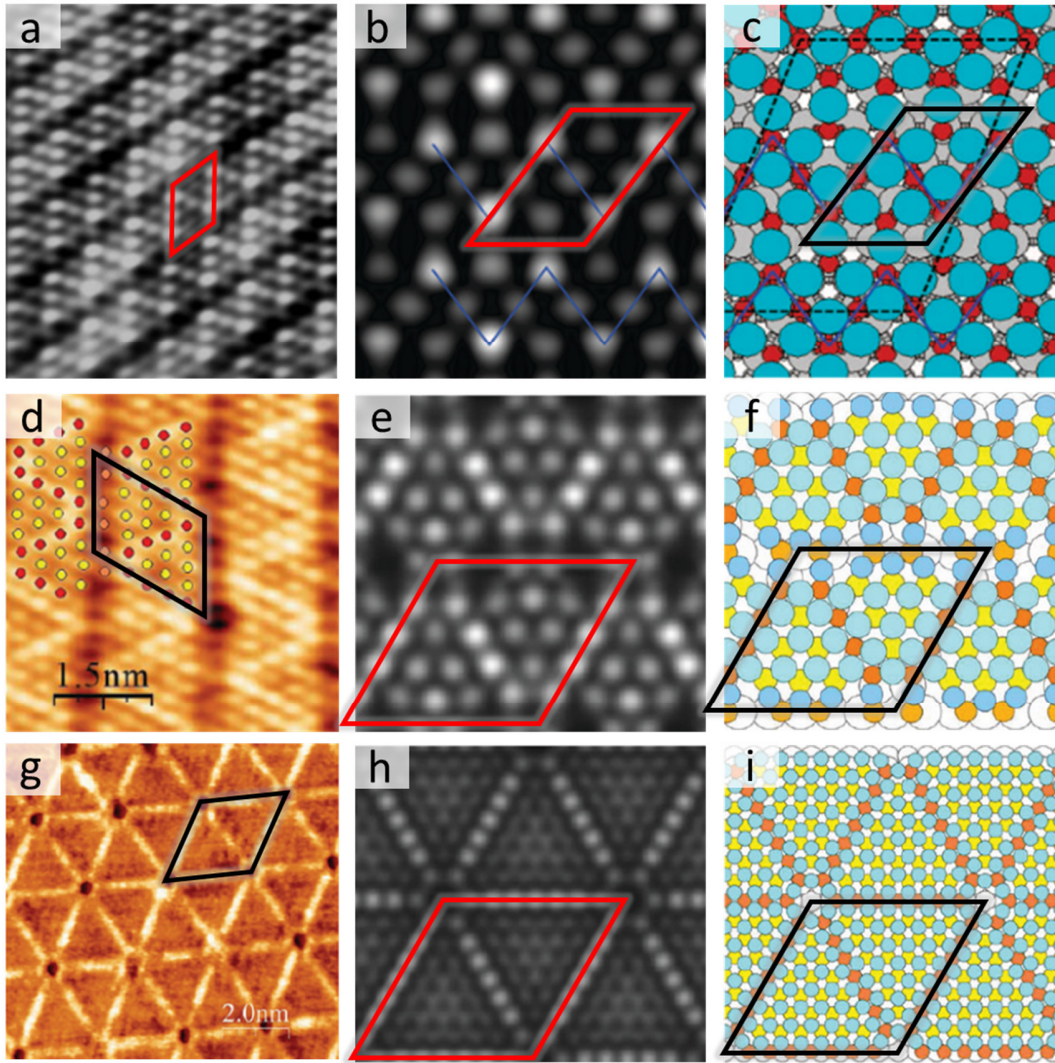


Fig. 3.2. Zigzag structures and hexagonal structures of a TiO_x monolayer film on Pt(111). (a) Experimental STM image ($V_s = 1 \text{ V}$, $I_t = 1.5 \text{ nA}$, image width 10.7 nm), (b) simulated STM image at $+1 \text{ V}$ and (c) atomic model of the TiO_x zigzag structure.^{6,42,43} (d) Experimental STM image ($V_s = 1.0 \text{ V}$, $I_t = 1.5 \text{ nA}$, image width 5.2 nm), (e) simulated STM image at $+1 \text{ V}$ and (f) atomic model of the TiO_x $\text{h}(6 \times 6)$ structure.^{6,41} (g) Experimental STM image ($V_s = 1 \text{ V}$, $I_t = 1.22 \text{ nA}$, image width 10 nm), (h) simulated STM image at $+1 \text{ V}$ and (i) atomic model of the TiO_x $\text{h}(9 \times 9)$ structure.⁴¹

Annealing the z-TiO_x structure in UHV at 673 K results structural transformation into a h(6 × 6), also known as a z'-TiO_x structure (middle row of Fig. 3.2).⁸ The h(6 × 6) structure is a commensurate layer with a periodicity of 16.6 Å, which corresponds to the 6 × 6 periodicity of Pt(111). The unit cell is highlighted in Fig. 3.2d-f. Each unit cell contains 24 Ti atoms and 30 O atoms, giving rise to a stoichiometry of TiO_{1.25} and a Ti oxidation state of 2.5 (Fig. 3.2f). The 24 Ti atoms are classified into 12 three-fold coordinated Ti atoms and 12 four-fold coordinated Ti atoms, yielding a Ti³⁺/Ti⁴⁺ ratio of 1.

Annealing the h(6 × 6) structure in UHV at 1000 K generates a h(9 × 9) structure, as shown in the bottom row in Fig. 3.2.⁴¹ The h(9 × 9) structure is a commensurate layer with a hexagonal structure. The unit cell has a periodicity of 24.9 Å, which corresponds to the 9 × 9 periodicity of the Pt(111) substrate. One unit cell contains 63 Ti atoms and 72 O atoms (see Fig. 3.2i). The h(9 × 9) structure has a TiO_{1.14} stoichiometry and the Ti oxidation state is 2.3. Each unit cell contains 42 Ti³⁺ atoms and 21 Ti⁴⁺ atoms, and thereby the Ti³⁺/Ti⁴⁺ ratio is 2.

The above examples show that the structure of the TiO_x monolayer is determined by its stoichiometry. From z-TiO_{1.33}, to h(6 × 6)-TiO_{1.25} and then to (9 × 9)-TiO_{1.14}, the oxidation state of Ti decreases from 2.7 to 2.3 and is characterized by an increase of Ti³⁺ atoms and a decrease of Ti⁴⁺ atoms. The (9 × 9)-TiO_{1.14} has the highest proportion of Ti³⁺ atoms and its close-packed structure is the densest.

3.2.2 Structures determined by charge transfer

Charge transfer between the oxide layer and the substrate can result in strong adhesion of the oxide film onto the metal substrate. The high adhesion energy stabilizes monolayer structures that cannot exist as a freestanding film. Freestanding CoO(111) monolayers,

i.e., a layer of Co atoms and a layer of O atoms, are unstable due to charge polarity. When supported on electronegative substrate such as Au and Pt, the CoO(111) monolayer films are stabilized by transferring electrons to the substrate. CoO(111) monolayers on Au and Pt have been investigated using a combination of STM and DFT.^{30,32,45} The Co oxide is synthesized by depositing Co onto Au and Pt substrates (held to 380 K) in 10^{-6} mbar oxygen, and post annealed at 523 K in 10^{-6} mbar oxygen. As shown in Fig. 3.3a CoO_x monolayer on Au(111) forms a hexagonal lattice with a periodicity of 3.3 Å, and a slightly rotated moiré pattern with a periodicity of 37 Å. The CoO_x/Au interface is Au-Co-O, see Fig. 3.3b. 0.19 electron is transferred from CoO_x to the Au substrate per Au (1 × 1) area. Similarly, CoO_x islands on Pt(111) display a hexagonal lattice with an interatomic spacing of 3.1 Å, present in Fig. 3.3c. The CoO_x islands are an incommensurate layer that forms a coincidence structure with the Pt substrate. The CoO_x structure has a moiré pattern with a larger periodicity of 27 Å which is rotated with respect to the atomic spacing in the oxide. The CoO_x/Pt interface is Pt-Co-O, shown in Fig. 3.3d. 0.24 electron is transferred from CoO_x to the Pt substrate per Pt (1 × 1) area. In contrast to the large charge transfer to Au and Pt substrates, DFT calculations predict that only 0.08 electron is transferred from CoO_x to the less electronegative Ag substrate per Ag (1 × 1) area, indicate that the CoO_x–Ag(111) interaction is weak. This is in agreement with experiment that the monolayer CoO_x structure is not observed on Ag(111).

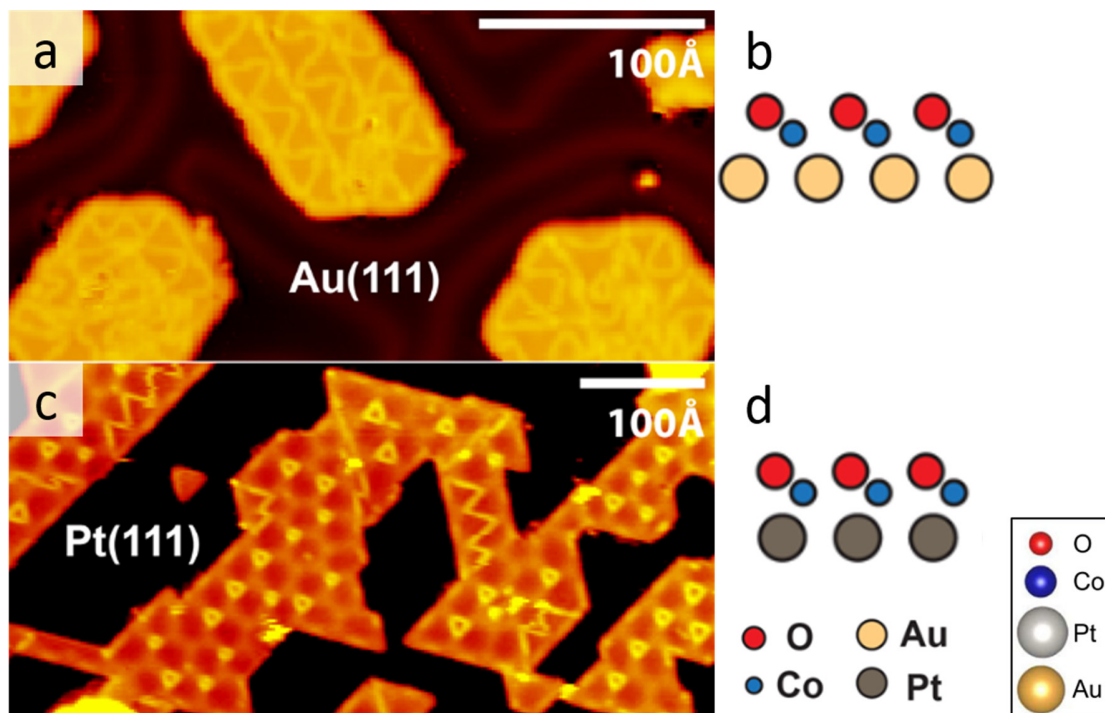


Fig. 3.3. CoO_x monolayer islands grown on Au(111) and Pt(111). Experimental STM image showing (a) CoO_x islands on Au(111) ($V_s = -1.1$ V, $I_t = 0.22$ nA, image width 31.5 nm). (c) CoO_x islands on Pt(111) ($V_s = -0.7$ V, $I_t = 0.28$ nA, image width 56 nm). Side views of (b) CoO_x/Au(111) and (d) CoO_x/Pt(111) interfaces.³²

3.3 Monolayer films with honeycomb structure

Two-dimensional materials of monolayer thickness often have a honeycomb lattice. These films consist of fully coordinated atoms. The honeycomb structure has been observed in various system such as monolayers of graphene,⁴⁶ silicene,⁴⁷ hexagonal boron nitride,⁴⁸ phosphorus,⁴⁹ stanene,⁵⁰ germanene⁵¹ as well as oxides.

3.3.1 Van der Waals and covalent honeycomb monolayers

Graphene and hexagonal boron nitride are honeycomb monolayers derived from van der Waals solids. The van der Waals solids consist of atomic layers where the intralayer atoms are fully coordinated via covalent bonds and the interlayer atoms are bonded via van der Waals forces. Because of the weak interlayer interactions, the monolayers are considered as freestanding films. Graphene consists of a flat layer of carbon atoms arranged in a

simple hexagonal lattice (Fig. 3.4a).⁴⁶ Hexagonal boron nitride has a flat layer of alternating boron and nitrogen atoms, and this heteroelemental nature adds chemical and polar complexity to the system (see Fig. 3.4b).⁵² Other honeycomb monolayers that interact with substrates via van der Waals interactions include stanene, germanene and phosphorene. They have buckled film structures constituted by Sn, Ge, and P atoms, respectively.^{49–51,53} A comprehensive review on elemental 2D materials has been given in Ref.[⁵⁴].

Silicene has a buckled honeycomb structure, where the atoms are subdivided into two planes of silicon atoms, as shown in Fig. 3.4c.⁴⁷ One hexagonal ring contains alternating upper buckled Si atoms (light brown) and lower buckled Si atoms (dark brown). Silicene has mainly been reported to be epitaxially grown on Ag(111) substrate using molecular beam epitaxy.⁴⁷ Silicene is bound to the silver substrate via covalent bond.^{47,50,51} Silicene is stabilized by its interfacial interaction with the Ag substrate thus it is a surface reconstruction structure rather than a two-dimensional material.

There is also a bilayer silica film with a honeycomb structure. Bilayer silica consists of two layers of tetrahedral structural units in which four oxygen atoms surround a silicon atom (Fig. 3.4d).⁵⁵ Bilayer silica has been grown on Ru(0001), Pt(111), graphene substrates and interact with the substrate via van der Waals interactions.

These monolayers have excellent properties such as high mechanical stiffness, high electrical, optical and thermal conductivity, tunable band gap, and novel optoelectronic properties. The properties can be tuned with high flexibility by generation of defects or assembly into heterostructures.⁵⁶ Apart from the above honeycomb structures, crystalline monolayers of water (ice) can form a H-bonded puckered honeycomb network.⁵⁷

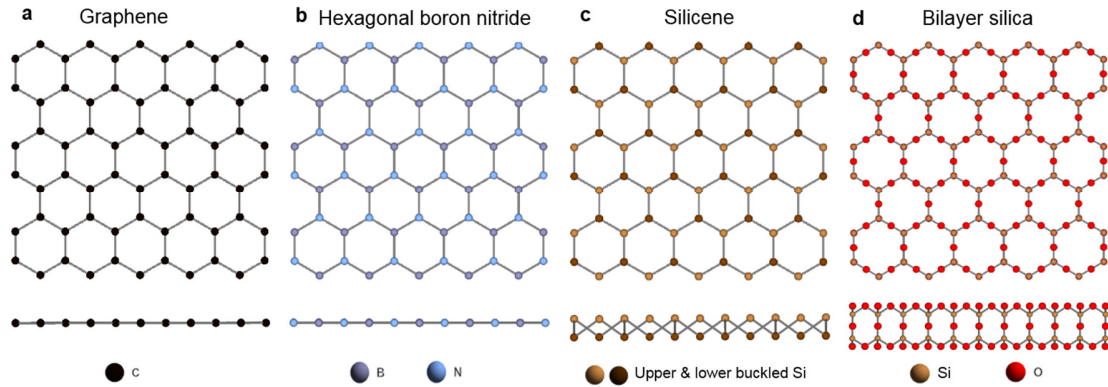


Fig. 3.4. Atomic structures of films with a honeycomb lattice including (a) graphene, (b) hexagonal boron nitride, (c) silicene and (d) bilayer silica.

3.3.2 Oxide honeycomb monolayers

Two types of oxide honeycomb monolayer have been experimentally and theoretically investigated, including M_2O_3 and M_3O_2 . In M_2O_3 the metal atoms form a honeycomb lattice by sharing one oxygen atom with three neighboring metal atoms. The M_2O_3 honeycomb structure has been extensively studied. It has been theoretically modelled as a freestanding film of V_2O_3 , Ti_2O_3 , Cr_2O_3 , Fe_2O_3 ,⁵⁸ and Nb_2O_3 .¹⁴ The latter oxide was suggested to display topologically protected edge states, which could survive upon deposition on a MoS_2 substrate. This would likely not happen for honeycomb M_2O_3 structures synthesized on metals due to stronger oxide/substrate interaction and charge transfer. Simulations of such systems include V_2O_3 on $Pd(111)$,^{36,59} Ti_2O_3 ⁴³ and $FeWO_3$ ⁴⁰ on $Pt(111)$ and M_2O_3 ($M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni$)^{37,60,61} on $Au(111)$. The schematic of a supported M_2O_3 structure is shown in Fig. 3.5a. The metal atoms (green) sit at three-fold hollow sites of the (111) plane of the substrate, and the oxygen atoms (red) sit at the top sites of the substrate surface (grey). A M_2O_3 unit cell is highlighted in Fig. 3.5a. The interfacial stacking is substrate-metal-oxygen (Fig. 3.5e).

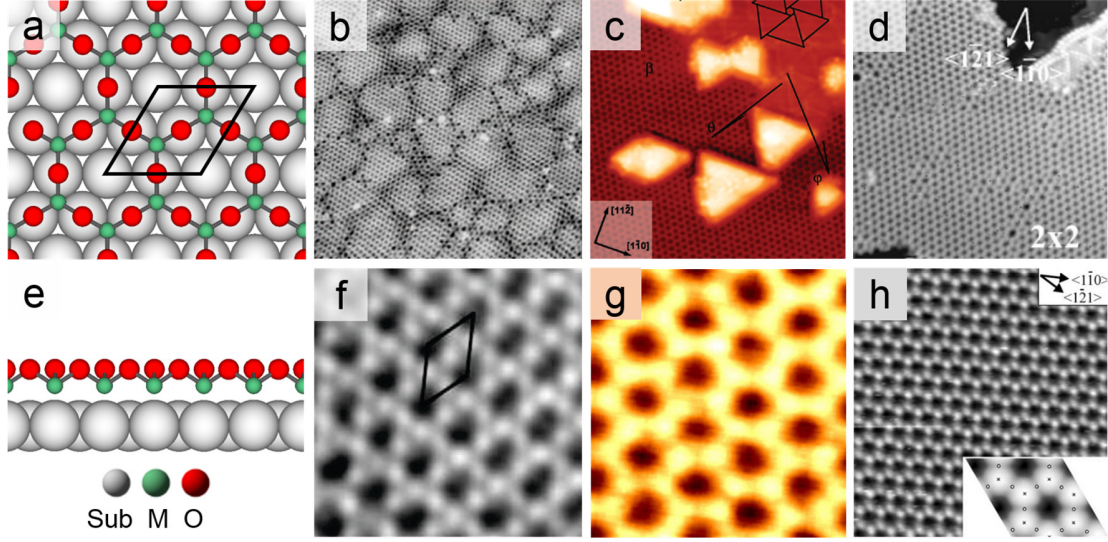


Fig. 3.5. The schematics of the honeycomb structure showing the (a) top view and (e) side view of the M_2O_3 honeycomb structure. STM images of (b) the (2.15×2.15) Ti_2O_3 on Pt(111),⁶ (c) the (2×2) Ti_2O_3 on Au(111),^{5,9} and (d) the (2×2) V_2O_3 on Pd(111).^{36,62} Atomically resolved structures of (f) Ti_2O_3 /Pt(111),⁶ (g) Ti_2O_3 /Au(111),^{5,9} and (h) V_2O_3 /Pd(111).^{36,62} The STM parameters are (b) $V_s = 1.0$ V, $I_t = 1.0$ nA, image width 30 nm, (c) $V_s = 1.0$ V, $I_t = 0.2$ nA, image width 24 nm, (d) $V_s = 0.1$ V, $I_t = 1.0$ nA, image width 14 nm, (f) $V_s = -0.4$ V, $I_t = 1.1$ nA, image width 3 nm, (g) $V_s = 1.0$ V, $I_t = 0.2$ nA, image width 3 nm,, (h) $V_s = 0.04$ V, $I_t = 1.0$ nA, image width 8 nm.

The supported M_2O_3 monolayers of V and Ti have been experimentally grown by depositing metal on (111) substrates followed by annealing in oxygen. Fig. 3.5b shows one STM image of the honeycomb structures of Ti_2O_3 on Pt(111).⁸ The Ti_2O_3 monolayer forms a hexagonal motif and exhibits a moiré-like modulation.⁶ The Ti_2O_3 film contains several periodic domains with size around 60 Å. Two domains are separated by domain boundaries and a cross-shaped local defects, known as DV(5555-6-7777).⁶³ Filled state STM images show bright protrusions arranged in a kagome lattice (Fig. 3.5f), which corresponds to the location of oxygen atoms in the honeycomb lattice. LEED pattern shows the honeycomb structure has a (2.15×2.15) periodicity. The (2.15×2.15) periodicity can be interpreted by that the Ti_2O_3 monolayer is coupled with the topmost layer of a Pt(111) surface. The coupled Ti_2O_3 -Pt bilayer has a lattice parameter between a

hypothetical freestanding Ti_2O_3 film and an unreconstructed $\text{Pt}(111)$ layer. Thus the bilayer forms a coincidence structure with the second layer of $\text{Pt}(111)$, which gives rise to a moiré-like modulation in the STM images in Fig. 3.5b.

Fig. 3.5c shows one STM image of a surface of a Ti_2O_3 monolayer on $\text{Au}(111)$.^{5,9} The $\text{Ti}_2\text{O}_3/\text{Au}$ monolayer has a hexagonal lattice in the STM images and it forms highly ordered and continuous honeycomb films. The honeycomb structure coexists with a TiO pinwheel monolayer structure and a TiO_2 triangular island multilayer structure.⁹ Typical empty state STM images show bright spots at the vertices of a honeycomb lattice, as shown in Fig. 3.5g.⁹ They represent the location of Ti atoms because DFT calculations show Ti atoms have higher density of states than the O atoms in empty states.⁵

Fig. 3.5d shows one STM image of a V_2O_3 monolayer grown on $\text{Pd}(111)$. The film exhibits a hexagonal lattice in the STM images, and it is well-ordered and continuous. There are several domain boundaries and local structural defects in the monolayer. Atomically resolved STM images show the location of V atoms as bright spots (Fig. 3.5h), which is confirmed by simulations (inset in Fig. 3.5h).

While unsupported Ti_2O_3 and V_2O_3 honeycomb structures are perfectly flat,⁵⁸ the supported films exhibit film rumpling. The supported films are stabilized by strong interactions with the substrate, mainly related to electrostatics.^{5,64} The adhesion energy for $\text{Ti}_2\text{O}_3/\text{Au}(111)$ is -3.8 eV per Ti_2O_3 unit and the adhesion energy for $\text{V}_2\text{O}_3/\text{Pd}(111)$ is -2.54 eV per V_2O_3 unit.

The honeycomb lattice has also been observed in a Cu_3O_2 monolayer supported on $\text{Au}(111)$.^{65,66} Here the O atoms form a honeycomb lattice by sharing one Cu atom with each neighbor. The Cu_3O_2 film shows a hexagonal pattern in the STM images, as shown in Fig. 3.6a-b. The film can be separated into stripy or triangular domains depending on

the annealing temperature. The film has a weak crystallographic relationship with the Au substrate, and this results in structures with a moiré pattern. The Cu_3O_2 hexagonal lattice has a periodicity of 5.8 Å. The film has a honeycomb lattice and each hexagonal ring contains six Cu atoms (white) and six O atoms (red and pink), as shown in Fig. 3.6c. Three O atoms (pink) are located below the Cu plane and three O atoms (red) are located above the Cu plane. The bright spots in the filled state STM images in Fig. 3.6b are arranged in a kagome lattice and thus they correspond to the location of Cu atoms. Two types of sites are observed within the three-fold hollow sites of the Cu atoms. The brighter sites represent the O atoms in the upper plane and the darker sites correspond to the O atoms in the lower plane. DFT calculations predict a charge transfer of 0.06 electron per Cu_3O_2 from Cu_3O_2 to Au(111). This results in a weak interfacial interaction between Cu_3O_2 and Au(111), which is consistent with the formation of a moiré-like structure.

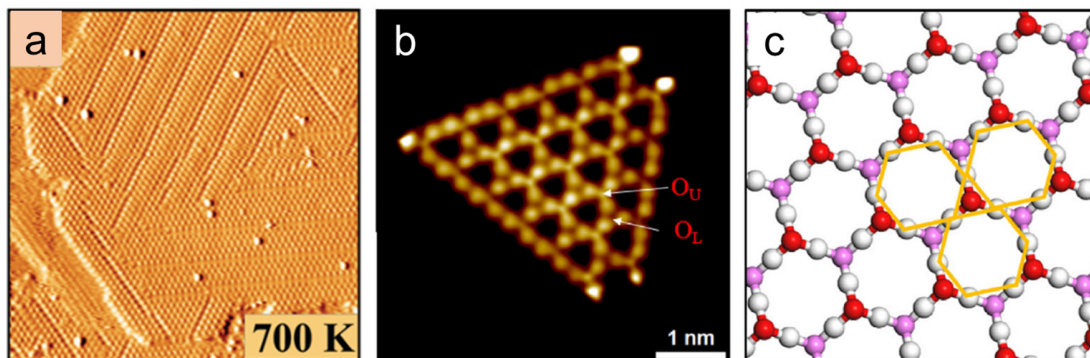


Fig. 3.6. STM images showing a Cu_3O_2 monolayer supported on Au(111). (a) The surface structure of $\text{Cu}_3\text{O}_2/\text{Au}(111)$ with a moiré-like modulation.⁶⁵ (b) A close-up of one Cu_3O_2 island showing the atomically resolved kagome lattice.⁶⁶ (c) A schematic of the Cu_3O_2 honeycomb lattice. The STM parameters are (a) $V_s = 0.5$ V, image width 40 nm, and (b) $V_s = -0.3$ V, $I_t = 3.5$ nA, image width 5 nm.

3.4 Defects in the honeycomb structure

The surface structures of various honeycomb monolayers were briefly introduced in Section 3.3. This section now focuses on how defects in honeycomb monolayers appear in the film. The most commonly attributed defect at the honeycomb films is a single vacancy. It is easy to introduce single vacancies into van der Waals monolayers by irradiation with electrons or ions, or during growth.⁶⁷ These defects have been intensively studied in the last decades. For example in graphene, a C atom vacancy has been investigated using transmission electron microscopy (TEM),^{68,69} STM,⁷⁰ scanning tunneling spectroscopy (STS)⁷⁰ and DFT.⁷¹ The removal of one C atom results in one reconstructed five-membered ring and one unsaturated bond at a C atom. The dangling bond results in the presence of a magnetic moment,⁷¹ which has been predicted using DFT.⁷¹ The single vacancy leads to a sharp resonance peak around the Fermi level and this had been measured using STS.⁷⁰ The C vacancy leads to a strong reduction of the carrier mobility and enhanced chemical reactivity.

The O atom vacancy has been extensively studied in various films such as CeO₂(111)/Cu(111) and FeO(111)/Pt(111).^{72–76} O vacancies can be systematically introduced into oxide thin films by vacuum annealing, electron bombardment, exposure to atomic hydrogen and during crystal growth. O vacancies are critical for catalytic reactions on oxide surfaces. For example, the hydroxyl groups in CeO₂/Cu and FeO/Pt react to form H₂ when many O vacancies are present at the surfaces whereas the hydroxyl groups react to produce H₂O when there are few O vacancies.^{73,76}

3.4.1 Extended linear defects

Extended linear defects in honeycomb monolayer films are of increasing interest as they have a significant impact on the properties of the films. For example in graphene, enhanced conductance at the defect site can lead to functionalization as a metallic wire,⁷⁷ and weakened mechanical strength.⁷⁸ These property modifications are determined by the atomic structures of the linear defects,^{79–82} which are characterized by the incorporation of non-hexagonal units.

A grain boundary is formed between two crystallites in a polycrystalline material. The crystal orientation changes abruptly across the grain boundary. Grain boundaries have been extensively studied in monolayer films of graphene and hexagonal boron nitride.^{78,81,83,84} These films interact with their substrate via van der Waals interactions and consequently, a number of different orientations of the grains could be realized. For example, a 57° grain boundary contains alternating pentagons and heptagons repeated linearly between two misoriented grains. The 57° boundary has been reported in graphene, hexagonal boron nitride and bilayer silica, as shown in Fig. 3.7. The degree of misorientation between the two grains determines the locations and arrangements of the polygons, which has been quantitatively analyzed using modeling in Ref.[^{52,80,85}].

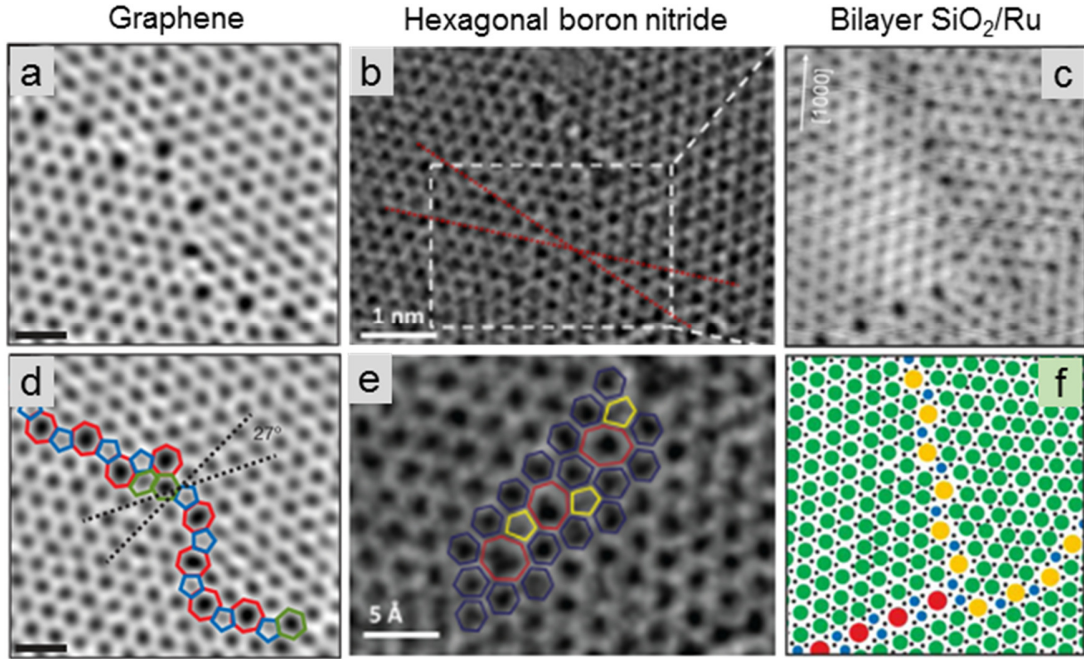


Fig. 3.7. Structures of 57° grain boundaries. (a) Scanning transmission electron microscope images of a 57° boundary between two graphene grains with a misorientation angle of 27°. (b) TEM images of a 57° boundary between two hexagonal boron nitride grains with a misorientation angle of 21°. (c) STM images of a 57° boundary between two bilayer silica grains with a misorientation angle of 30°. (d-f) The same images from (a-c) with the grain boundary structure highlighted by color-coded rings. Image parameters are (a) image width 3.2 nm, (b) image width 16.1 nm, (c) image width 7.4 nm, $V_s = 0.1$ V and $I_t = 0.1$ nA, (e) image width 8.1 nm.

A zero degree grain boundary is a domain boundary, which is formed between two crystallites that are related by a translational lattice offset. A domain boundary is a typical structure in monolayer films that grow epitaxially on a substrate, and thus the films have a single orientation with respect to the substrate. Domain boundaries have been reported in supported honeycomb monolayers of SiO_2 on $\text{Ru}(0001)$ and $\text{Mo}(112)$, germania (GeO_2) on $\text{Ru}(0001)$, Ti_2O_3 on $\text{Pt}(111)$, V_2O_3 on $\text{Pd}(111)$ and silicene on $\text{Ag}(111)$.^{6,36,86–90} Monolayer SiO_2 and GeO_2 consist of tetrahedral-shaped $[\text{SiO}_4]$ or $[\text{GeO}_4]$ structural units arranged in a planar honeycomb lattice. Ti_2O_3 and V_2O_3 monolayers are a hexagonal network in which each hexagonal ring contains six metal atoms and six oxygen atoms.

In SiO₂, GeO₂, Ti₂O₃, and V₂O₃ monolayers, a domain boundary often contains four, five, seven and eight-membered rings and can form a variety of boundary structures. A 48 boundary consists of alternating four and eight-membered rings and it is named after the ring sizes of the building blocks.^{86,88} The 48 boundary has been observed in monolayers of GeO₂ on Ru(0001) and SiO₂ on Mo(112), as shown in the first row in Fig. 3.8. A 5577 boundary contains alternating pairs of five and seven-membered rings and the two pentagons share an edge.^{89,90} The 5577 boundary has been observed in monolayer SiO₂ on Mo(112) and Ru(0001) (see the second row in Fig. 3.8).^{89,90} A 558 boundary contains periodically repeated units of a pair of pentagons and one octagon.^{6,36} The 558 boundary has been observed in graphene on Ni(111), Ti₂O₃ on Pt(111) and V₂O₃ on Pd(111) (the third row in Fig. 3.8).^{6,36,77} A 5775 boundary also contains a pair of pentagons and a pair of heptagons in one structural unit. However, in contrast to the 5577 boundary, the two pentagons in the 5775 structure are separated and have vertices bonded to each other.^{6,36} The 5775 defect has been reported in Ti₂O₃ on Pt(111) and V₂O₃ on Pd(111), as shown in Fig. 3.8h-i.^{6,36}

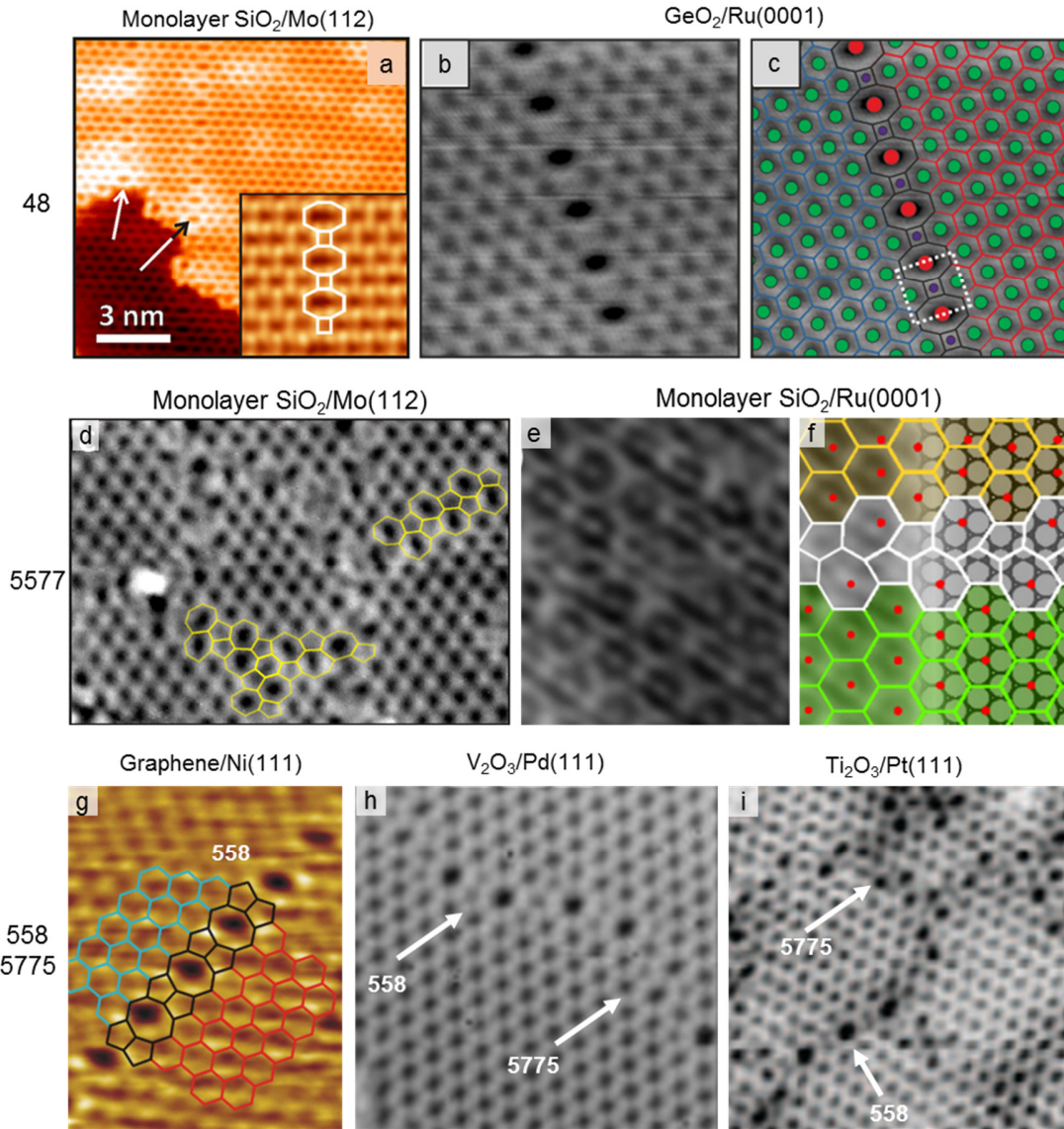


Fig. 3.8. Atomically resolved STM images of various domain boundaries in honeycomb monolayers. A 48 domain boundary observed in (a) SiO₂ on Mo(112) and (b-c) GeO₂ on Ru(0001).^{86,89} A 5577 boundary observed in (d) SiO₂ on Mo(112) and (e-f) SiO₂ on Ru(0001).^{89,90} A 558 boundary observed in (g) graphene/Ni(111), (h) Ti₂O₃ on Pt(111) and (i) V₂O₃ on Pd(111).^{6,36,77} A 5775 boundary observed in (h) Ti₂O₃ on Pt(111) and (i) V₂O₃ on Pd(111).^{6,36} The STM parameters are: (a) image width 13.8 nm, 2 V, 0.1 nA, (b-c) image width 5.5 nm, 2.4 V, 4.5 nA, (d) image width 8 nm, 1.2 V, $I_t = 0.15$ nA, (e-f) image width 3 nm, 2 V, $I_t = 0.9$ nA, (g) image width 2.5 nm, 0.1 V, (h) image width 6.3 nm, 0.1 V, $I_t = 1.0$ nA, (i) image width 9.9 nm, 1 V, 1.0 nA.

Silicene is a monolayer of Si atoms arranged in a buckled honeycomb lattice.⁴⁷ The domain boundaries in a silicene (4×4) structure are shown in Fig. 3.9a. The boundaries appear as bright spots in a linear or zigzag-like arrangement in STM images. Its domain boundary mainly consists of hexagonal rings (Fig. 3.9c). The strain due to the mismatch between two domains is relieved via vertically shifting the Si atoms. The Si atoms are subdivided into three planes in the domain boundaries whereas they are subdivided into two planes in the pristine (4×4) structure (the bottom panels in Fig. 3.9b-c).⁸⁷ The boundary structure has stronger bias-dependent behavior than the domain structure. The local density of states in both phases mainly originate from the Si $3p_z$ orbitals. The Si atoms in the domain boundary are observed to shift up and down, indicating that it is a metastable structure.

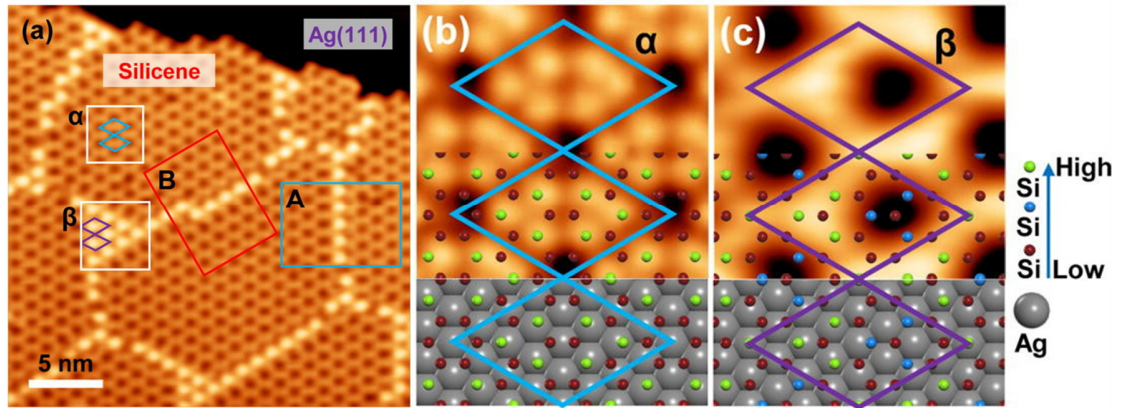


Fig. 3.9. STM images of domain boundary structures in silicene on Ag(111). (a) STM images showing a (4×4) structure of silicene on Ag(111). STM images showing (b) atomically resolved defect-free (4×4) structure, and (c) domain boundaries two laterally shifted domains. The schematic of pristine buckling structure is shown at the bottom panel of (b). The schematic of modified buckling structure at the boundaries is shown at the bottom of (c). The STM parameters are: (a) image width 27 nm, $V_s = 1.75$ V and $I_t = 1.0$ nA, (b) image width 2.7 nm, $V_s = 1$ V and $I_t = 0.5$ nA, (c) image width 2.7 nm, $V_s = -1$ V and $I_t = 1.0$ nA.

3.4.2 Local defects

A honeycomb structure often contains local structural defects where the hexagons are replaced by 4, 5, 7 and 8-membered rings. The non-hexagons can be generated through Stone-Wales (S-W) transformations. This mechanism was first predicted in graphene and involves rotating a C-C dimer by 90° to transform four hexagons into two pentagons and two heptagons.⁹¹ The resultant structure is known as an S-W defect, as shown in Fig. 3.10a. A further series of related defects incorporating divacancies (DV) results in larger structures of non-hexagonal elements. The simplest divacancy defect consists of one octagon and two pentagons and is called a DV(5-8-5) defect which is named after the ring sizes of the building blocks. The schematic for a DV(5-8-5) is shown in Fig. 3.10b. Other structures include the DV(555-777) defect, containing three pentagons and three heptagons, and the DV(5555-6-7777) defect, containing four pentagons and four heptagons surrounding a hexagon.⁹² Fig. 3.10c-d show the schematics for the two divacancy defects. These structures have been widely investigated in graphene,^{63,93} h-BN,⁹⁴ transition metal dichalcogenides,⁹⁵ bilayer silica⁹⁶ and ice monolayers.^{97,98} The TEM images of these defects in graphene are shown in the second row of Fig. 3.10.

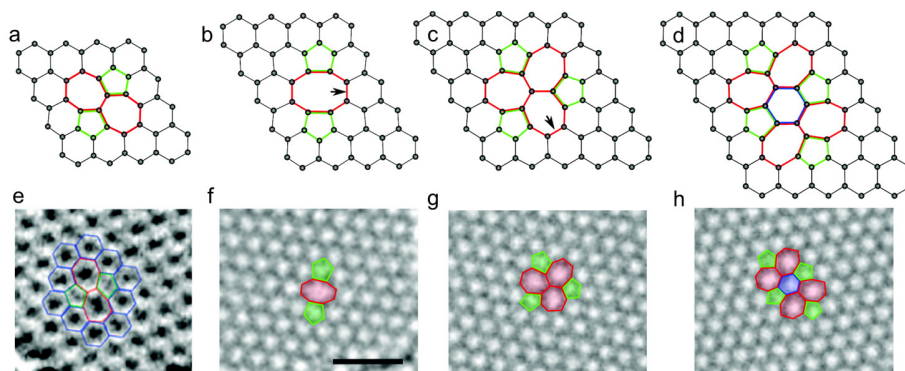


Fig. 3.10 Local structural defects in graphene. Atomic models of (a) a S-W defect, (b) a DV(5-8-5) defect, (c) a DV(555-777) defect and (d) a DV(5555-6-7777) defect.⁶⁷ Carbon atoms are in black. The second row shows TEM images of these defects.^{67,93} Scale bars are 1 nm. 5-membered rings are in green, 6-membered rings within the defect are colored in blue, and 7 and 8-membered rings are colored in red.

Generally, these defects have relatively high formation energies (e.g. 5-8 eV in graphene)⁶⁷ mainly due to the bond distortions in the non-hexagonal rings. Small 4 and 5-membered rings result in bond compression, whereas large 7 and 8-membered rings result in bond expansion. The strain resulting from 5 and 7-membered rings is lower than for 4 and 8-membered rings.⁹⁹ 5 and 7-membered rings often form defect pairs that have relatively low strain energy. In graphene, both DV(5-8-5) and DV(555-777) defects have two missing carbon atoms but the latter, although it is larger, has a lower formation energy due to smaller bond distortions.

Mechanically straining the graphene lattice results in a change in the formation energies of the S-W defect and the DV(5-8-5) defect.^{100,101} An alternative approach to investigate the influence of lattice strain on the defects is to grow the 2D material via epitaxial growth on lattice-mismatched or patterned substrates.^{77,102,103} This results in compression or tension of the supported film and has been reported in graphene supported on a Ni(111) substrate,⁷⁷ where the small lattice mismatch between graphene and Ni(111) allows the carbon hexagons to be in registry with the substrate. However, the Ni(111) substrate barely influences the behavior of the defects because the energy gain from the interfacial van der Waals interaction (0.7 eV per two carbon atoms)¹⁰⁴ is small compared with the high energy cost of distorting the C-C bonds (5-8 eV).⁶⁷

The generation of the S-W defects in graphene is linked to a C-C dimer to undergo a rotation. The energy barrier of S-W rotation has been calculated for an unsupported (Fig. 3.11a-c) and a Ni supported graphene monolayer (Fig. 3.11d-f).^{105,106} The intermediate atomic arrangement in the unsupported graphene shows that the C-C dimer in rotation is tilted out of the graphene plane. There are two under-coordinated carbon atoms in the neighboring graphene rings. This intermediate state has an energy of 9.28 eV with respect

to the pristine lattice shown in Fig. 3.11c. A similar atomic configuration has also been calculated for the transition state of S-W rotation in an unsupported h-BN monolayer.¹⁰⁷

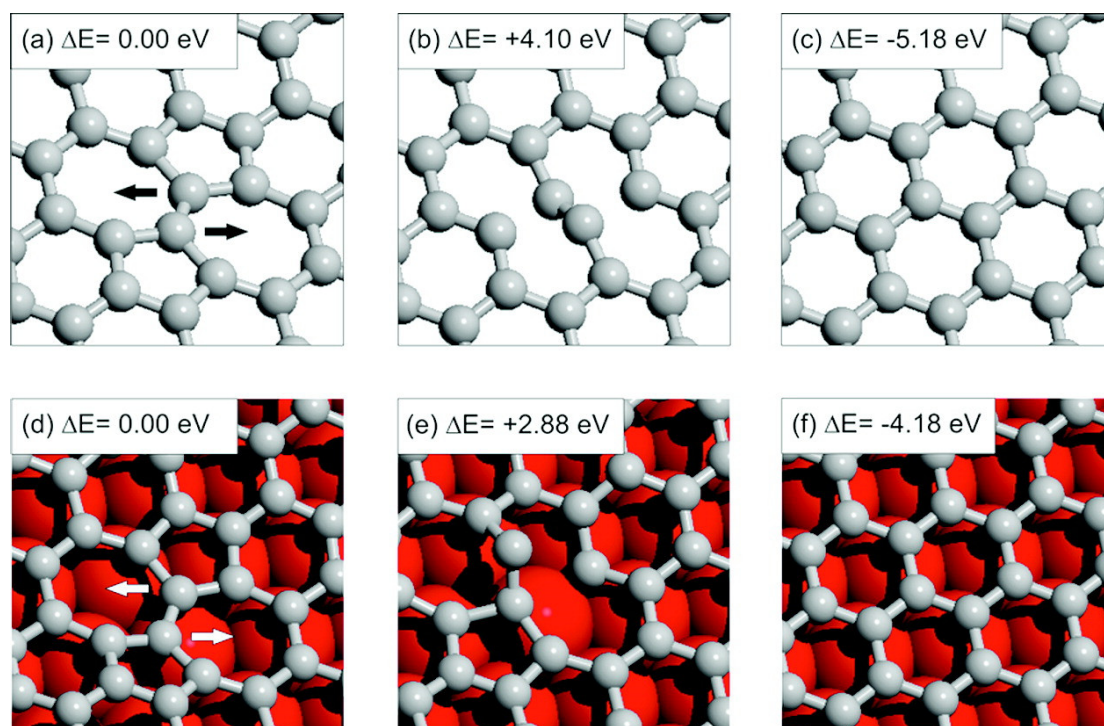


Fig. 3.11. Calculated reaction pathways for the creation of a S-W defect in (a-c) an unsupported and (d-f) a Ni(111) supported graphene film. The relaxed geometries for the intermediate states are in (b) unsupported graphene and (e) Ni-supported graphene. C atoms are grey and Ni atoms are red.

The atomic configuration of the intermediate state in graphene supported on Ni(111) is shown in Fig. 3.11e. The presence of the Ni(111) surface hinders the downward tilting of the C-C bond, resulting in asymmetric tilting which is in contrast to the symmetric tilting of the C-C bond in the freestanding layer. One under-coordinated C atom in the neighboring graphene lattice is coordinated to the Ni surface, leading to a stabilization of the reaction intermediate and a reduction of the reaction barrier to 7.06 eV. A similar atomic configuration of the transition state has been observed in unsupported silicene.¹⁰⁸

3.4.3 Edge terminations

The edge terminations of 2D materials lead to novel properties such as high catalytic activity,¹⁰⁹ enhanced photoluminescence,¹¹⁰ and novel energy states.^{111,112} A variety of edge structures within these honeycomb monolayers have been explored theoretically and experimentally.^{113–119} When a honeycomb lattice is cut along the zigzag direction, the edge is terminated by a zigzag structure containing hexagonal rings. The structure is called ZZ-66, named after the ring sizes of the building blocks.^{114,115,118–122} The atomic structure of the ZZ-66 edge in graphene is shown in Fig. 3.12a & c. When a honeycomb lattice is cut along the armchair direction, the edge is terminated by an armchair structure containing hexagonal rings, called AC-66.^{114,115,118,119,121,122} Fig. 3.12b & d show the structural model and a TEM image of the atomic structure of the AC-66 edge in graphene. The ZZ-66 and AC-66 edges have been experimentally and theoretically studied in graphene,^{113–115,122–124} and theoretically predicted in silicene,^{116,120} hexagonal boron nitride,^{117,125} and germanene.¹¹⁹

These terminations can reconstruct into four-, five-, and seven-membered rings, which may lead to novel properties not observed in regular edge structures. The zigzag edges in graphene can reconstruct to form structure unit cells such as alternating pentagon and heptagon (ZZ-57), as shown in Fig. 3.12e & h.^{111,115,121,122} The armchair edges in graphene can reconstruct to form structure unit cells such as alternating pentagon and hexagon (AC-56, present in Fig. 3.12f & i),¹²³ and one hexagon and two heptagons (AC-677, see Fig. 3.12g & j).¹¹⁵

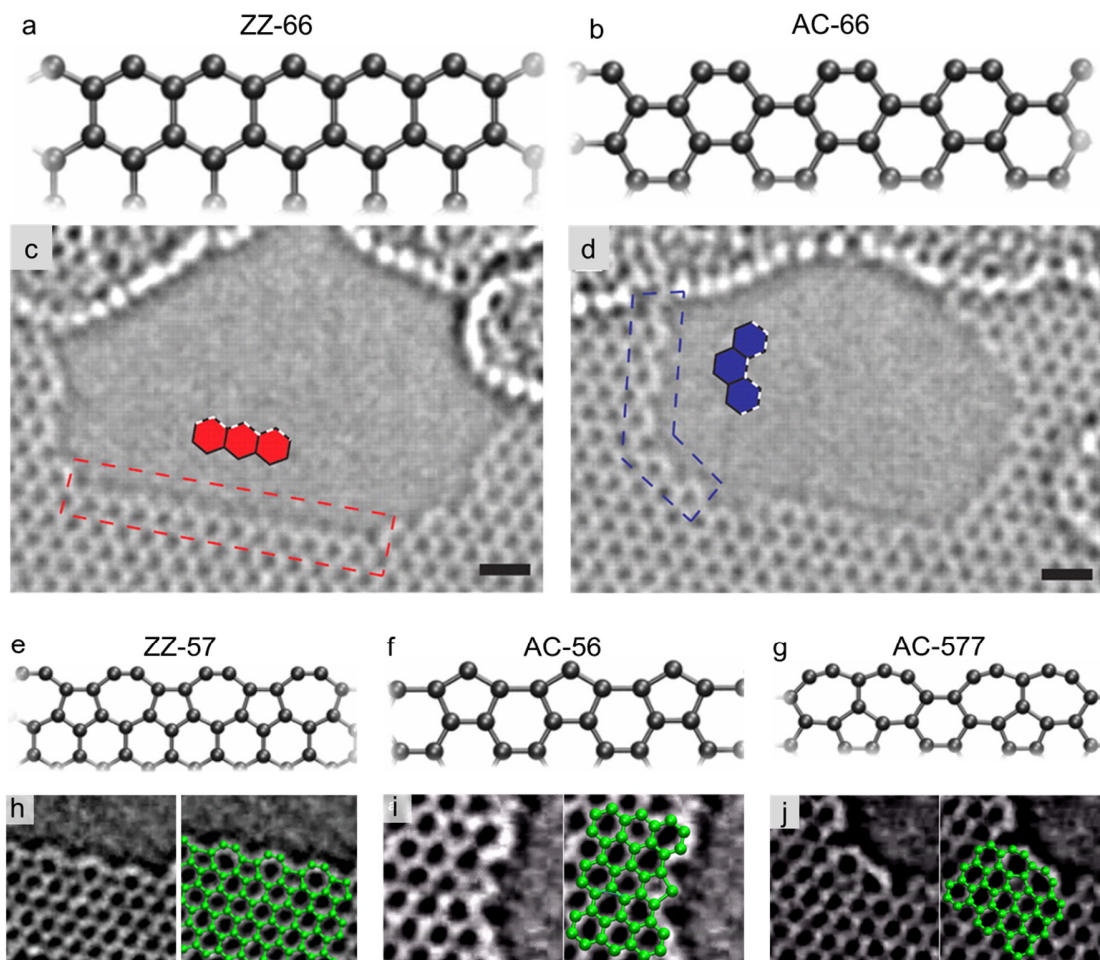


Fig. 3.12. Schematics and atomic structures of regular ZZ-66, AC-66 edges and reconstructed ZZ-57, AC-56 and AC-577 edges in graphene. The atomic models are shown in (a-b) and (e-g). (c-d) & (h-j) are TEM images showing the edge structures. In (c-d), the inset diagrams exemplify an armchair (blue) and zigzag (red) arrangement. Images in (h-j) show TEM images on the left panel, and a highlighted structure assignment on the right. The image widths are (c) 5 nm, (d) 5 nm, (h) 1.4 nm, (i) 1.2 nm and (j) 1.4 nm.

In parallel to the development of edge terminations in van der Waals monolayer, previous work has revealed the presence of island edges in M_2O_3 honeycomb monolayer films. Regular zigzag and armchair edge units have been observed in $V_2O_3/Pd(111)$,³⁶ as shown in Fig. 3.13a. The V_2O_3 island edge starts from an armchair edge, roughly 15 hexagons long, on the left of the image and makes a 60° turn at the corner. The armchair edge then turns 30° and transforms into a zigzag edge of three hexagons long. After a 90° turn, the edge switches into a 6-hexagon long armchair edge, a 3-hexagon long zigzag edge and finally a 3-hexagon long armchair edge. The armchair and zigzag edges in V_2O_3 mainly contain hexagonal rings. The regular zigzag edges have also been observed in $FeWO_3/Pt(111)$, as shown in Fig. 3.13b.⁴⁰

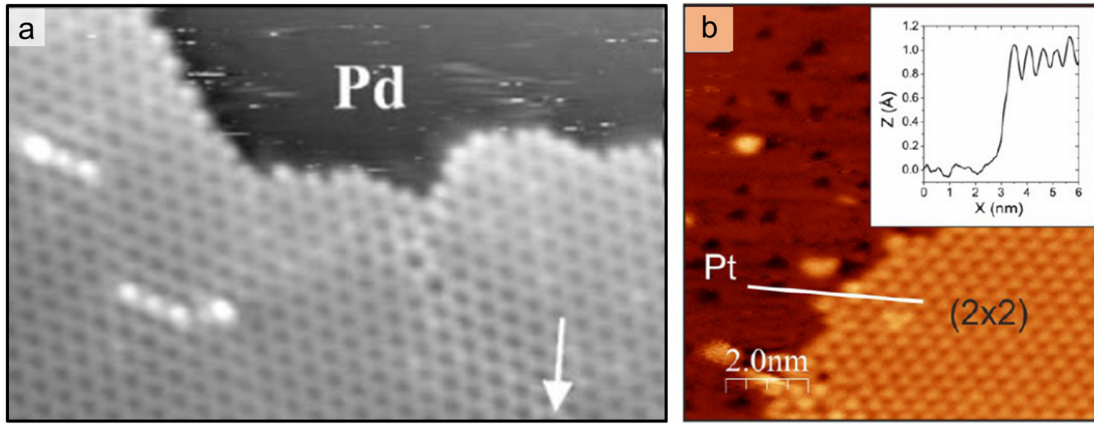


Fig. 3.13. STM images showing the edge structures in M_2O_3 (2×2) honeycomb monolayers. (a) A V_2O_3 film contains AC-66 and ZZ-66 edges in the top of the image.⁶² (b) A $FeWO_3$ film contains ZZ-66 edges.⁴⁰ STM parameters are (a) image width 12.6 nm, $V_s = 1.0$ V and $I_t = 1.0$ nA, (b) image width 10 nm, $V_s = 1$ V and $I_t = 0.15$ nA.

The ZZ-66 and reconstructed AC-56 edges have also been observed in the $Cu_3O_2/Au(111)$ monolayer (see Fig. 3.14a-b).⁶⁶ Both edges are terminated with O atoms and the O atoms are coordinated to two Cu atoms, as shown in Fig. 3.14d-e. There are two types of ZZ-66 edges, including one terminated by upper O atoms and the other terminated by lower O

atoms. The most present edge structure in $\text{Cu}_3\text{O}_2/\text{Au}(111)$ is the regular zigzag edge with lower O atom terminations (Fig. 3.14d). Annealing Cu_3O_2 nanostructures at 600 K results in islands with predominantly zigzag edges. These islands have triangular, truncated triangular and truncated hexagonal shapes. Two examples of these islands are shown in the third column of Fig. 3.14.

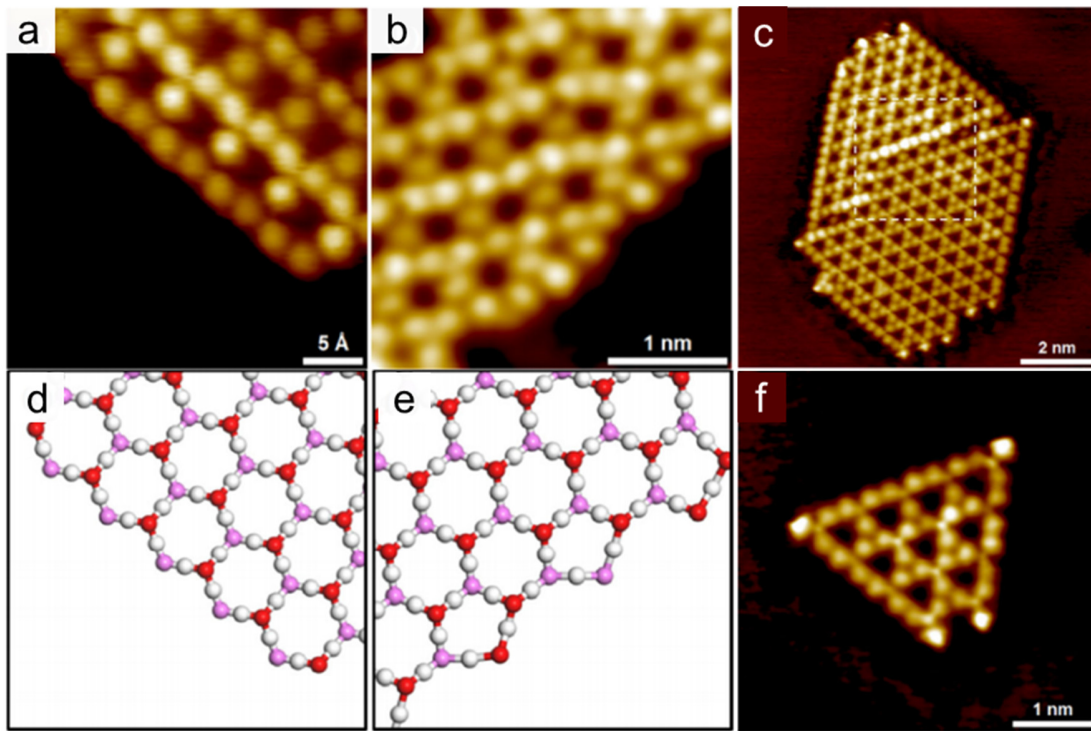


Fig. 3.14. Edge structures in Cu_3O_2 honeycomb monolayers.⁶⁶ STM images showing (a) ZZ-66 edges and (b) AC-56 edges in Cu_3O_2 , and structural models for both structures shown in (d) and (e). (c & f) STM images showing two structures terminated with the ZZ-66 structures. STM parameters are (a) image width 3 nm, $V_s = -0.9$ V and $I_t = 0.2$ nA, (b) image width 10 nm, $V_s = -0.8$ V and $I_t = 1.0$ nA. (c) image width 10 nm, $V_s = -0.3$ V and $I_t = 2.9$ nA, (f) image width 5 nm, $V_s = -0.3$ V and $I_t = 2.4$ nA.

3.5 Monolayer oxide nanostructures

Monolayer oxide nanostructures are attractive systems for the investigation of catalytic mechanisms in chemical reactions.¹²⁶ Oxide nanostructures are also effective model systems for developing an understanding of the nature of cluster size effects and cluster-substrate interactions. Monolayer oxide nanostructures on metal supports have been successfully grown either with the aim of the formation of size-selected clusters for catalysis or as inverse catalyst systems.^{127–133}

3.5.1 Atomic clusters

When an oxide nanostructure is of the order of a few nanometers in size, it may have a novel crystal structure, stoichiometry and properties that are not observed in the bulk analogue. This has been observed for the example for the oxides of V, Fe, Co and Ni.^{134–}

¹³⁷ The metal supports also have a significant influence on oxide nanostructures. For atomic clusters, strong cluster-substrate interactions can change the inherent structure of the atomic clusters compared with their freestanding counterparts. Many atomic clusters of transition metal oxides such as V_6O_{12} or Nb_3O_7 are predicted to form a cage structure in the gas phase whereas they form a planar structure on metal supports in experiments.^{138–}

¹⁴⁴ Fig. 3.15a shows the lowest energy structure for an unsupported V_6O_{12} cluster calculated using DFT.¹⁴¹ One V_3O_3 six-membered ring is connected to one V_3O_6 six-membered ring through three bridging oxygen bonds forming a triangular prism. The lower V_3O_6 ring contains three dangling O atoms bond to each V atom. The cage-like V_6O_{12} cluster consists of V^{5+} and V^{3+} cations. Fig. 3.15b shows the atomic structure of a V_6O_{12} cluster supported on Rh(111) substrate.¹⁴⁰ DFT calculations demonstrate that the structure consists of six V atoms located in Rh(111) three-fold hollow sites, six O atoms located in Rh on-top positions, and six dangling O atoms bonded to each V atom.^{134,140}

The planar V_6O_{12} cluster features V^{4+} cations. Fig. 3.15c shows an experimental STM image of the planar V_6O_{12} cluster. There is strong hybridization between V states and O states in the STM images. DFT modeling also shows a hypothetical unsupported planar V_6O_{12} cluster is less stable than the cage structure.¹⁴¹ The unsupported planar V_6O_{12} cluster is stabilized by 15.7 eV when supported on Rh(111) due to the strong bonding interaction with Rh.¹⁴⁰

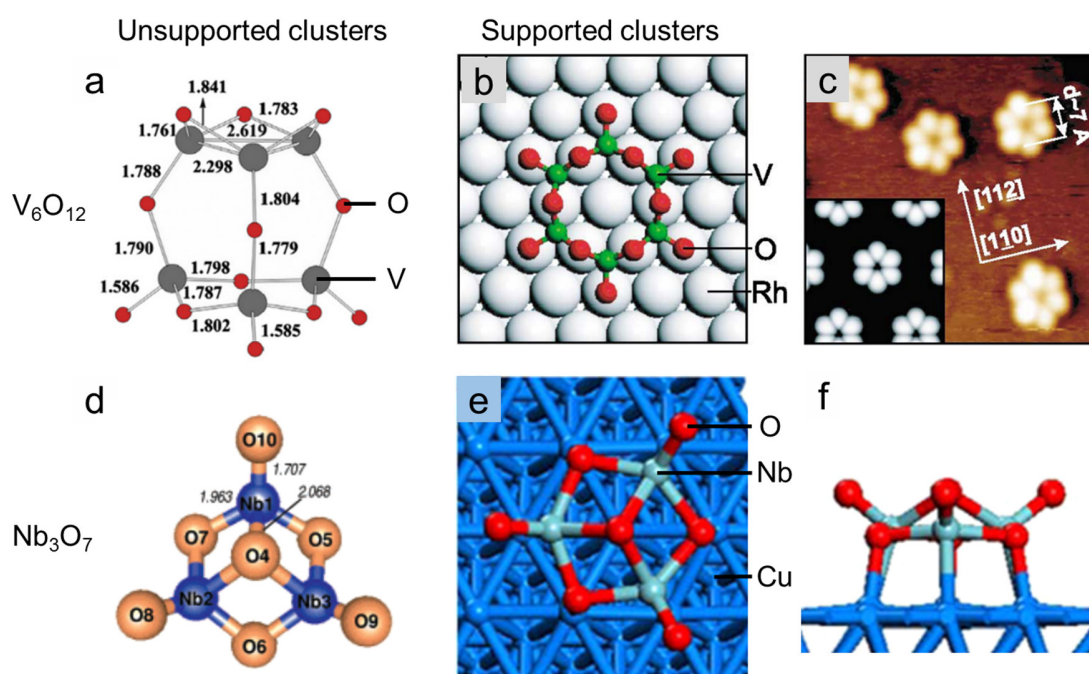


Fig. 3.15. Atomic structure of V_6O_{12} and Nb_3O_7 cluster. (a) Calculated unsupported V_6O_{12} cluster with a cage structure.¹⁴¹ The bond lengths are in Å.¹³⁸ (b) Calculated Rh(111)-supported V_6O_{12} cluster with a planar hexagonal structure.¹⁴⁰ (c) STM images and simulations (inset) of Rh-supported V_6O_{12} cluster (image width 6.3 nm, $V_s = 0.5$ V and $I_t = 0.1$ nA). (d) Calculated unsupported Nb_3O_7 cluster with a cage structure.¹⁴² A calculated Cu(111)-supported Nb_3O_7 cluster with a planar triangular structure shown in (e) top view and (f) side view.

Fig. 3.15d shows an unsupported Nb_3O_7 cluster with a cage structure calculated using DFT.¹⁴² There is a 6-membered ring consisting of three Nb atoms and three O atoms. A 3-fold coordinated O atom is in the center of the cluster and three terminal O atoms are

attached to each Nb atom. Nb₃O₇ clusters supported on Cu(111) have a planar structure modeled using DFT, as shown in Fig. 3.15 e-f. The Nb atoms are located close to Cu(111) bridge sites, four O atoms are located in Cu on-top positions and three dangling O atoms are bonded to each Nb atom.¹³⁸ The planar Nb₃O₇ cluster structure has strong interaction with the Cu substrate and there is charge redistribution at the Nb₃O₇-Cu interface.¹³⁸

A similar influence of the support on modifying cluster structures was also observed in other Nb, Mo, Ti, W oxide clusters on Cu(111) and Cu₂O/Cu(111),^{138,139,145,146} Ni oxide clusters on MgO/Ag(100),¹³⁷ and W₃O₉ on Cu(110)-O(2 × 1).¹⁴⁷ The strong cluster-substrate interactions in these systems are characterized by electron transfer to or from the substrate, modification of the cation oxidation states, structural distortions of the cluster and support, and the modification of the electronic structure of the cluster.

3.5.2 Larger nanostructures

There is also growing interest in the formation of larger monolayer oxide nanostructures that contain tens to hundreds of atoms. These oxide islands are confined on the metal supports.¹²⁸ These structures have been investigated for the systems of FeO_x/Pt(111),^{126,135,148–150} CoO_x/Au(111),^{32,45,136} and MgO_x/Au(111).^{131,151,152} These oxide nanostructures contain metal and oxygen-terminated edges, and their island shapes are determined by the relative stability of the edges.^{32,152} The edges exhibit properties that are different from those of the island center, such as enhanced chemical reactivity,¹⁵⁰ increased work function,¹⁵¹ and higher conductance.^{135,151}

One notable example is the study of Fe oxide nanostructures grown on Pt(111) substrates.^{126,128,129,135,150} Fe oxide is catalytically active at small length scales and has proven useful as a catalyst for the water-gas-shift reaction¹⁵³ and preferential oxidation of CO.^{126,128,154} FeO_x nanostructures are grown by depositing Fe in an oxygen atmosphere

and flash-annealed to form FeO_x nanostructures. The Fe oxide nanostructures are one monolayer thick, an example of which is shown in Fig. 3.16a.¹³⁵ The FeO_x nanostructures have triangular, truncated triangular shapes, or coalesce of both. An atomically resolved STM image of the FeO_x nanostructures shows a triangular island with a moiré pattern (Fig. 3.16b).

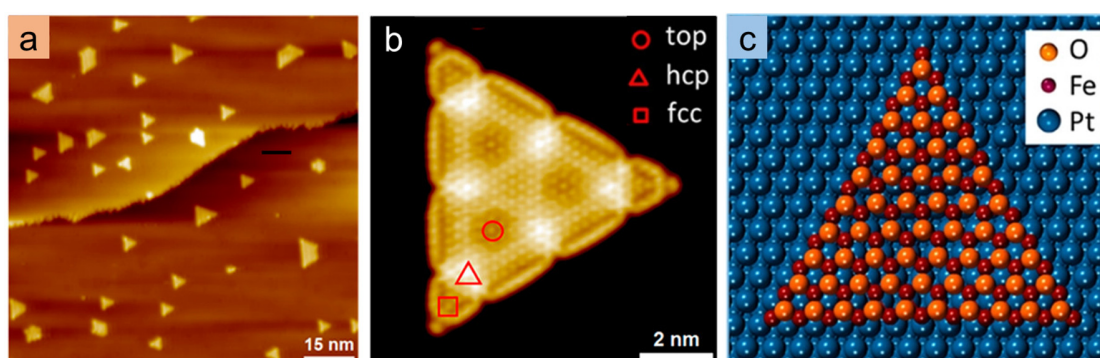


Fig. 3.16. FeO_x nanostructures supported on a Pt(111) surface. Panel (a) shows the distribution of islands (image width 40 nm), and panel (b) is a close-up of one Fe₃₇₈O₃₅₁ island showing atomic resolution with moiré domains (image width 10 nm, $V_s = 0.01$ V and $I_t = 4.4$ nA). The hcp, top, and fcc domains are highlighted by a triangle, circle, and square, respectively. Panel (c) is a DFT-calculated structural model of Fe₆₆O₅₅ on Pt(111).¹³⁵

The physical origin of the moiré-like structure is that Fe atoms occupy successively top, hcp and fcc sites of Pt(111) surface, and resulting in the formation of top, hcp and fcc domains within an oxide island. The schematic of one FeO_x island is shown in Fig. 3.16c. The three domains are characterized by their apparent heights in STM images (Fig. 3.16b) and can thereby be identified as top (circle), hcp (triangle) and fcc (square) domains.²⁷ FeO_x nanostructures mainly have a triangular shape and they show the preference of Fe terminated edge structures over O terminated edges (Fig. 3.16b-c). The Fe atoms in the edges are two-fold coordinated to O atoms and are known as coordinatively unsaturated

Fe (CUF) sites.¹³⁵ The Fe edges appear curvy in STM images due to the modulation of the adsorption sites of Fe atoms on Pt. The indentation corresponds to Fe atoms located at top sites of Pt(111). The FeO_x top domain shows lower density of states than that of the hcp and fcc domains when the energy is close to Fermi level.¹³⁵

The size of the FeO_x nanostructures affects the stability, with three differently sized islands shown in Fig. 3.17. The triangles have similar moiré-like surface structures and curvy edge structures, and the same atomic periodicity. Using a combination of STM and DFT to probe the size of the FeO_x nanostructures reveals that the most favored nanostructures tend to locate the vertex Fe atoms at fcc adsorption sites. This is because the Fe atoms at fcc sites tend to have stronger electronic interactions with the Pt surface than the Fe atoms located at top or hcp sites.

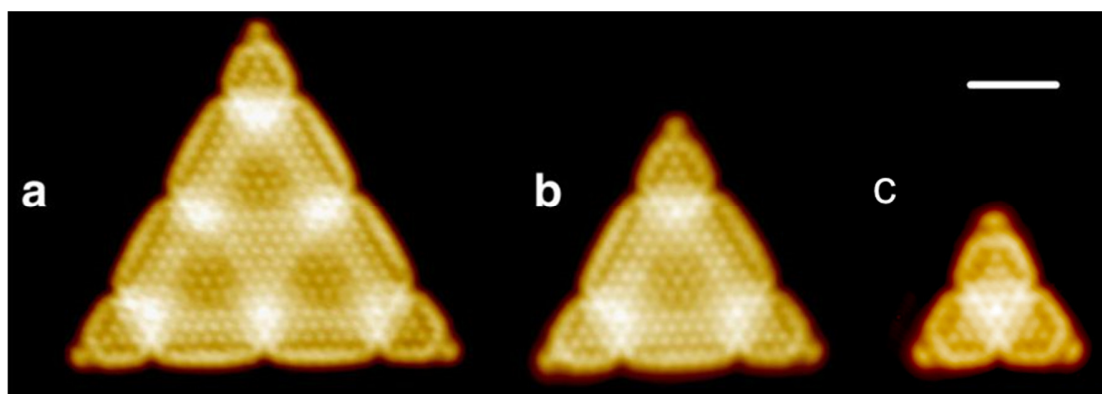


Fig. 3.17. Three frequently observed Fe oxide nanostructures (Fe₃₇₈O₃₅₁, Fe₁₉₀O₁₇₁, Fe₆₆O₅₅).^{129,135} The edges have 27, 19 and 11 Fe atoms, respectively. The atomic structure is visible in these images, as well as the moiré domains. The STM parameters are (a) $V_s = 0.006$ V and $I_t = 5.5$ nA, (b) $V_s = 0.007$ V and $I_t = 5.9$ nA, (c) $V_s = 0.01$ V and $I_t = 3.8$ nA. The scale bar is 2 nm.

The FeO_x nanostructures also display an interesting dynamic size effect that leads to enhanced oxidation resistance.¹²⁹ The FeO_x nanostructures with a width above 3.2 nm are more likely to be oxidized into a bilayer FeO₂ structure than the FeO_x nanostructures with

a width below 3.2 nm. This is counterintuitive because one may expect oxide nanostructures with a smaller size would be oxidized more easily due to the presence of a larger amount of unsaturated atoms. STM results show that the small nanostructures reconstruct via a collective in-plane shift of all O atoms. DFT modeling reveals that in small islands, the energy gain from oxygen adsorption is larger than the energy cost due to island reconstruction, and thereby the smaller islands prefer to reconstruct in an oxygen rich environment. For large islands, island reconstruction costs more energy than oxygen adsorption, and thereby they incorporate excess oxygen by transformation into bilayer FeO_2 .^{148,149}

3.6 Perspective

This chapter has covered a number of studies on the atomic structures of monolayer oxide films and nanostructures. There are further topics, not covered here, such as ternary oxide monolayer. Ternary oxide films consist of two types of metal atoms, such as FeWO_3 , FeTiO_3 and BaTiO_3 .^{5,40,155} These films exhibit unconventional structures such as labyrinth phases and quasicrystalline structure.^{4,5} Ternary oxide monolayers also have more degrees of freedom for modifying the oxide structural, electronic, and reactivity characteristics than binary oxide.⁵⁸ Another related important investigation of a monolayer oxide film is to study its catalytic reactivity to small gas molecules and metal atoms.^{28,39,129} The metal supported oxide monolayers can serve as an “inverse catalyst model” at two-dimension, so as to reveal the promotional effects of the metal-oxide interfaces, well-defined oxide morphology and uniform low-coordinated metal sites in a catalytic reaction.

Chapter 4. Maximising the signal-to-noise ratio of the scanning tunneling microscope

4.1 Introduction

From this chapter onwards, original work is presented. In this chapter, an image processing method has been demonstrated to significantly improve the resolving power of the scanning tunneling microscope (STM). The resolution of STM has barely improved since its inception.¹⁵⁶ Only small advances have been achieved through low noise electronics, enhanced vibration damping, and low temperature operation. These incremental gains stand in stark contrast to the advances made with the atomic force microscope (AFM). Where AFM was initially derived from the atomic resolution STM, it is now possible to take non-contact AFM (nc-AFM) images with intramolecular resolution.¹⁵⁷ The advantage however, that the STM still has over nc-AFM is that the scan speed is typically around two orders of magnitude faster. In effect this means that for the time taken to acquire one nc-AFM image it is possible to acquire around a hundred STM images. To date this has not been viewed as a particularly significant advantage because operator practice is such that only the best one of these hundred images will be used and

the others discarded. However, if all the hundred images are averaged then we would expect a ten-fold improvement in the signal-to-noise ratio (SNR) as the random noise diminishes with the square root of the number of averaged images.¹⁵⁸ This improved SNR leads to a commensurate increase in the resolving power of the STM. The reason that this kind of multi-frame averaging (MFA) has so far not been performed routinely is that unique and locally varying distortions in each of the images prevent them from being aligned in perfect registry with each other.

4.2 Methods

UHV-STM images were taken using two JEOL instruments, a JSTM4500s and a JSTM4500xt, both operating at a base pressure of 10^{-8} Pa. Constant current STM images were taken at room temperature using etched tungsten tips. The B-doped Si(111) samples were prepared by flashing at 1200 °C for 15 seconds to desorb the native oxide and cooled to room temperature to allow the 7×7 reconstruction to form. The 2×2 Ti_2O_3 honeycomb ultrathin films on Au(111) substrates were grown according to the description detailed in Chapter 5, 8, 9 and ref.[⁹]. The $\text{SrTiO}_3(111)-(4\times 4)$ reconstructions were generated on 0.5 wt% Nb-doped samples according to the recipe described in ref.[¹⁵⁹].

To estimate the reduction in image noise power (and resulting improvement in image signal-noise ratio), images were 3×3 pixel median-filtered and subtracted from the originals to leave an estimate of the noise only. From these noise-estimates, the standard deviation was plotted as a metric of the noise-power. This process was repeated for increasing numbers of averaged images leading to the inverse square-root trend behavior. For very large numbers of frames being averaged, the SNR becomes so high that the median-filtering approach to estimation of noise power no longer holds and the improvement becomes harder to track. For the template-matching step, repeat-tile

searching was performed using a thresholded cross-correlation approach. Local maxima in this cross-correlation indicate the positions of the repeats of the given motif which are then cropped out.

4.3 Results

4.3.1 The Si(111)-(7 × 7) reconstruction

Si(111) samples were flashed in UHV to generate the familiar (7 × 7) reconstruction.¹⁶⁰ The surface was imaged in empty states in the STM and sequential images were recorded with 33 nm image widths. One of these single images is shown in Fig. 4.1a, and represents a typical surface with a variety of atomic defects. The image in Fig. 4.1b is one where 41 scans of the same area have been averaged. To take full advantage of the MFA process it is helpful to perform data up-sampling (interpolating over a finer image mesh) before MFA is carried out. The original STM images of 512×512 pixels were interpolated to 2048×2048 pixels. The improvement in the image noise can be more easily seen in the magnified frames (the bordered region in Figs. 4.1a,b) shown in Figs. 4.1c,d. It is obvious that the MFA image of Fig. 4.1d is less noisy than that of the raw image in Fig. 4.1c. We have quantified this reduction in noise by plotting the noise power against the number of averaged frames, as shown in Fig. 4.1e. The noise power was calculated by median filtering the images using a 3×3 kernel and subtracting these median filtered images from the originals. This process results in images containing only noise, and the standard deviation of the noise in these images is related to the noise power. As expected for a system that is mainly governed by shot noise, the reduction in the noise power can be approximated by an inverse-square law. The red line in Fig. 4.1e is the least squares fit to our data with an exponent of -0.448, which can be compared to an exponent of -0.5 if our data were to perfectly follow Poisson statistics. The exponent measured in the experiment

deviates from the standard Gaussian distribution exponent of -0.5. Because the noise is measured with respect to the median filtered image, rather than the standard value. The latter is difficult to measure in STM experiments.

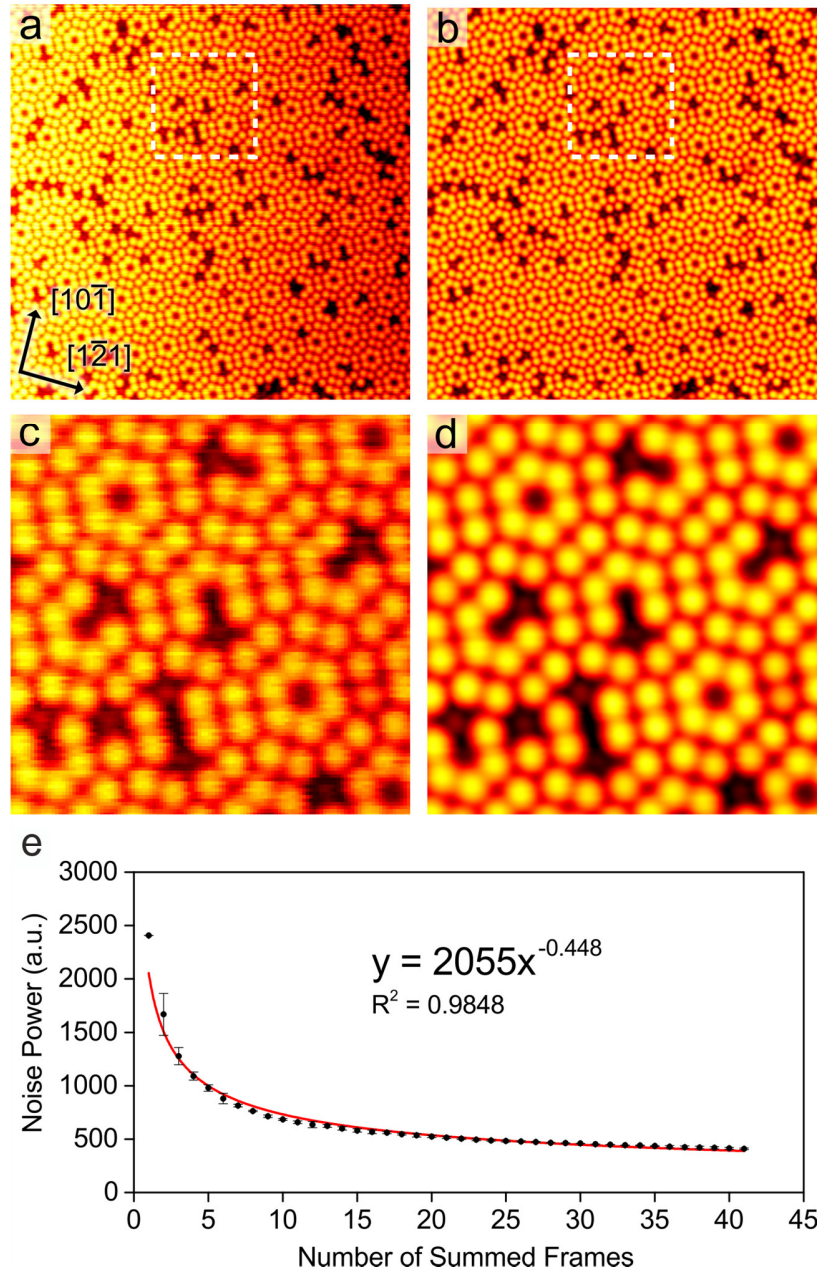


Fig. 4.1 STM data from the Si(111)-(7 × 7) reconstruction. (a) Raw single frame (image width 33.2 nm, $V_s = 1.3$ V, $I_t = 0.17$ nA). (b) Image after ramp-subtraction, alignment, scan-correction and averaging of 41 sequential frames. (c) Magnified region from (a) (image width 8.3 nm). (d) Magnified region from (b). (e) Fitting plot of noise power versus the number of summed frames. The plot shows the reduction in noise-power with increasing number of averaged images.

A relatively common feature in STM software packages is a process called *unit cell averaging*. The user creates the surface unit cell grid in the STM image, and the software averages all of the cells to create an image with an enhanced SNR. This process has variable results, and tends to only work well on images where the image is already of high quality and has few distortions. We performed unit cell averaging over defect free unit cells of the Si(111)-(7 × 7) reconstruction. This was achieved by selecting 3 separate crystallographically similar regions from a single STM image. Using the known 3-fold symmetry of the reconstruction,¹⁶⁰ we rotated all the images twice by 120° and thereby tripled the number of tiles to average to nine. The result of MFA is shown in the empty-states image in Fig. 4.2a. We performed a similar procedure on filled-states images, but this time we selected three tiles each from three separate images and additionally rotated them all twice by 120°, thereby generating 27 tiles to average. The filled-states MFA result is shown in Fig. 4.2b. The images in Fig. 4.2 contain ~100 adatoms each and are comfortably superior to the traditionally unit cell averaged results where alignment is not as accurate.

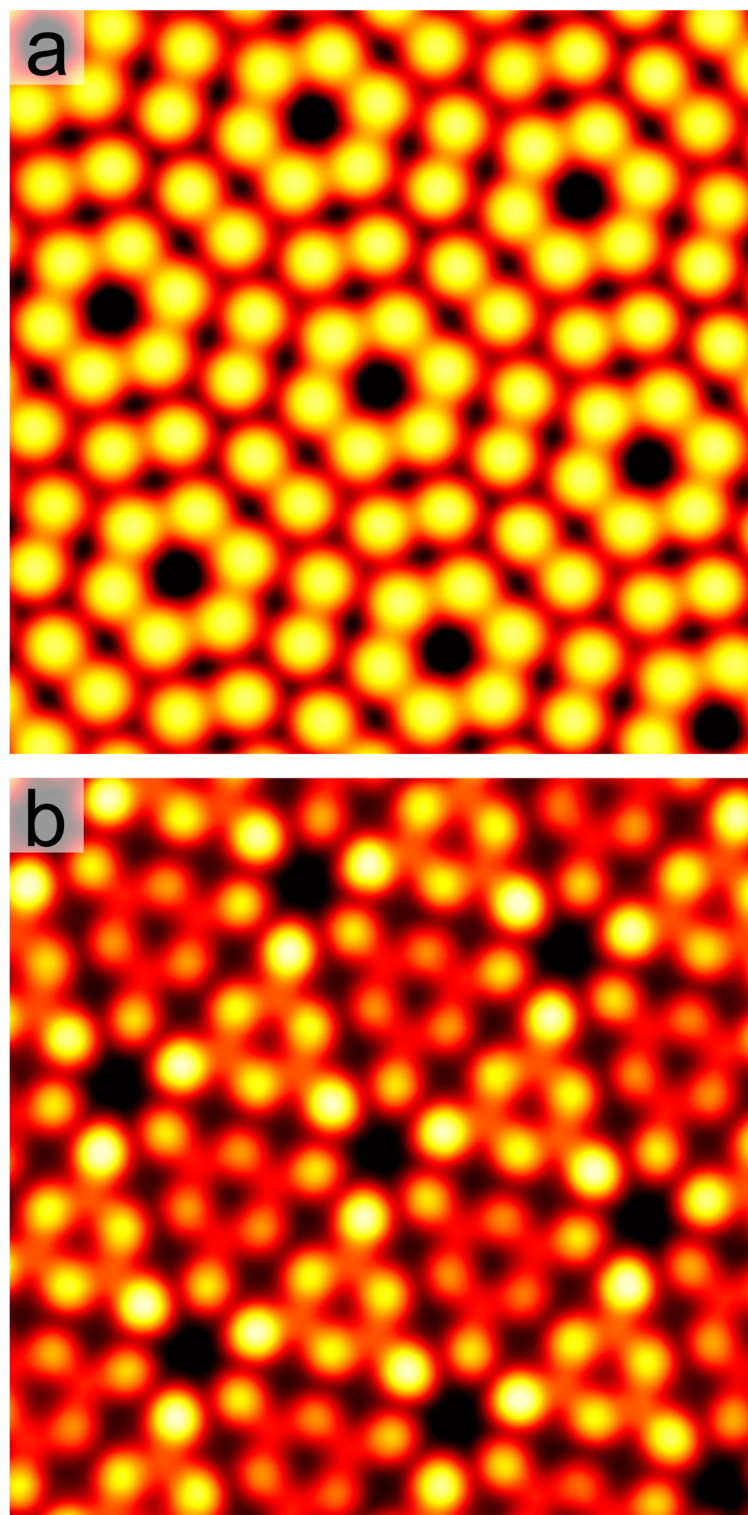


Fig. 4.2 MFA images of defect-free regions of ~ 100 adatoms of the Si(111)-(7×7) reconstruction. (a) Empty states image created from 9 averaged tiles (image width 7.2 nm, $V_s = 2.0$ V, $I_t = 0.7$ nA). (b) Filled states image from 27 averaged tiles (image width 7.2 nm, $V_s = -3.0$ V, $I_t = 1.0$ nA).

Additional resolution enhancement of Si(111) images can also be achieved with particularly favorable tips.¹⁶¹ Further SNR improvement is possible by exploiting known crystallographic relationships.¹⁶² For the Si(111) surface we could have additionally used the mirror symmetry of the (7×7) unit cell to further double the number of tiles that we averaged. For the high-quality images we used for Fig. 4.2 this mirror symmetry enhancement would have resulted in little additional benefit. However, in situations where the number of tiles is limited and the raw data is noisy, then full use of the crystallographic surface symmetry relationships should be made.¹⁶³

4.3.2 Ti₂O₃ ultrathin films

To demonstrate the sensitivity that can be achieved with MFA, STM images of honeycomb Ti₂O₃ ultrathin films grown epitaxially on Au(111) substrates were averaged.⁹ Panels (a-c) of Fig. 4.3 show high magnification empty states STM images of the honeycomb Ti₂O₃ (2×2) overlayer. To generate the MFA images 176 tiles of 4.2×4.2 nm² defect-free areas were cropped from 88 raw frames of a continuous honeycomb overlayer. The 88 frames were recorded sequentially from the same area with no change in tip configuration and only minor changes in the STM imaging parameters. Fig. 4.3a shows a typical raw image of one of the 176 tiles where the hexagonal rings can be identified, but where the image noise forms a significant barrier to seeing the fine atomic scale structure. The result of processing the 176 tiles, which were tripled to 528 tiles using the known 3-fold surface symmetry of this structure^{5,9} is shown in Fig. 4.3b. In this image the bright spots, corresponding to the Ti atoms,⁵ can now be clearly distinguished.

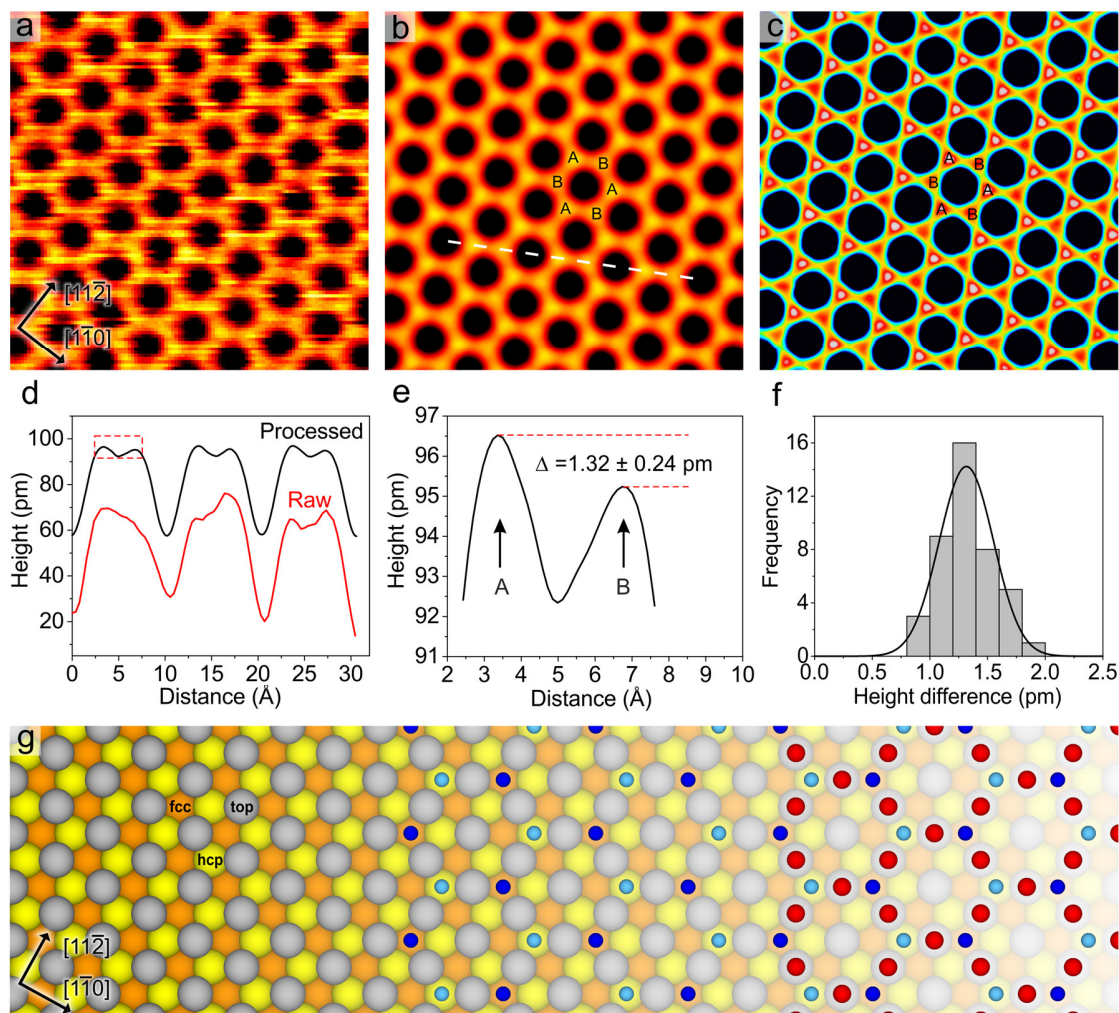


Fig. 4.3 STM images and detailed analysis of the (2×2) honeycomb Ti_2O_3 ultrathin film on Au(111). (a) Raw STM image of the honeycomb structure (image width 4.2 nm, $V_s = 1.0$ V, $I_t = 0.22$). (b) Average of 528 tiles (image widths 4.2 nm, $V_s = 1.0$ V, $I_t = 0.22$ -0.25 nA). The SNR is significantly improved and scan-distortions are corrected. Individual Ti atoms can be distinguished and are marked as A and B. (c) The same data as in (b) but with an exaggerated colour-scale to highlight the small differences in peak height between A and B sites. (d) Line-profile from the raw and processed images from the dashed white line shown in (b). The profiles are offset by 40 pm from each other for clarity. (e) Enlargement from (d) showing the 1.32 pm difference in height of the A and B sites. (f) Histogram of the height difference measured from 42 A-B pairs. (g) Model for the bare Au(111) surface (left part of figure) with hcp (yellow), fcc (orange), and top (grey) sites indicated. Ti atoms located on the fcc and hcp sites are in dark and light blue, respectively (centre of figure). O atoms are shown in red (right part of figure).

In Fig. 4.3c the same data is shown as in Fig. 4.3b, but with an exaggerated colour scale. In this image it can be seen that half of the Ti sites, marked as ‘A’ sites, are marginally brighter than the other half, marked as ‘B’ sites. This height difference can also be seen in the linescan indicated as a dashed white line in Fig. 4.3b and shown in Fig. 4.3d. The MFA processed image linescan (black) consistently shows a small difference in the height of the A sites and the B sites, whereas this difference is not apparent in the raw data (red) from a single tile. The height difference from the MFA processed data, highlighted in the dashed red box in Fig. 4.3d, is shown in Fig. 4.3e. Measurements of 42 A-B site pairs were taken (Fig. 4.3f) resulting in an average height difference of 1.32 ± 0.24 pm.

The origin of the asymmetry of the height of the A sites and B sites in the MFA images of Fig. 4.3b,c can be explained through an analysis of the structure of the Ti_2O_3 overlayer. Fig. 4.3g is a diagram of the structure showing the bare $\text{Au}(111)(1 \times 1)$ surface on the left, only the location of the Ti atoms shown in the centre, and the full Ti_2O_3 overlayer shown on the right. The Ti atoms (blue balls) are located in three-fold hollow sites on the $\text{Au}(111)$ surface, and the O atoms (red balls) are located in the outermost layer, on the ‘top’ sites. There are two types of three-fold hollow sites, namely hcp sites (yellow) and fcc sites (orange), as indicated in Fig. 4.3g. The structure of the overlayer results in half of the Ti atoms sitting in hcp sites, and the other half in fcc sites. Density functional theory calculations show that the Ti atoms located on the hcp sites are marginally higher by less than a picometre than the ones on the fcc sites. It is according to this calculation that we assign the A and B sites to the fcc and hcp locations, respectively. These measurements show that through MFA we can perform atomic height determination to sensitivities comfortably better than a picometre.

4.3.3 Chiral unit identification on SrTiO₃(111)

STM is an invaluable tool for visualising chiral crystal terminations^{159,164} and molecular arrangements on surfaces.¹⁶⁵ Individual chiral units can sometimes be very challenging to identify accurately in raw STM data. Here we demonstrate the utility of performing MFA in order to enhance the image SNR and thereby to be able to reliably automate the identification of chiral units. The STM images shown in Fig. 4.4 are of the SrTiO₃(111)-(4 × 4) reconstruction. This is an unusual crystal termination in that the surface unit cells have chirality associated with them. The surface exhibits domains of each of the two types of unit cell that are non-superimposable mirror images of one another,^{159,164} as shown in Figs. 4.4a,b. We assign left-handed chirality with a blue label to the units shown in Fig. 4.4a, and right-handed chirality with a green label to the units shown in Fig. 4.4b. Unintentionally, we were able to generate more high-resolution images that contained a majority of left-handed units, which is why the left-handed image (Fig. 4.4a) is constructed from 297 averaged defect-free tiles and has a better SNR than the right-handed image (Fig. 4.4b) that is constructed from only 15 tiles.

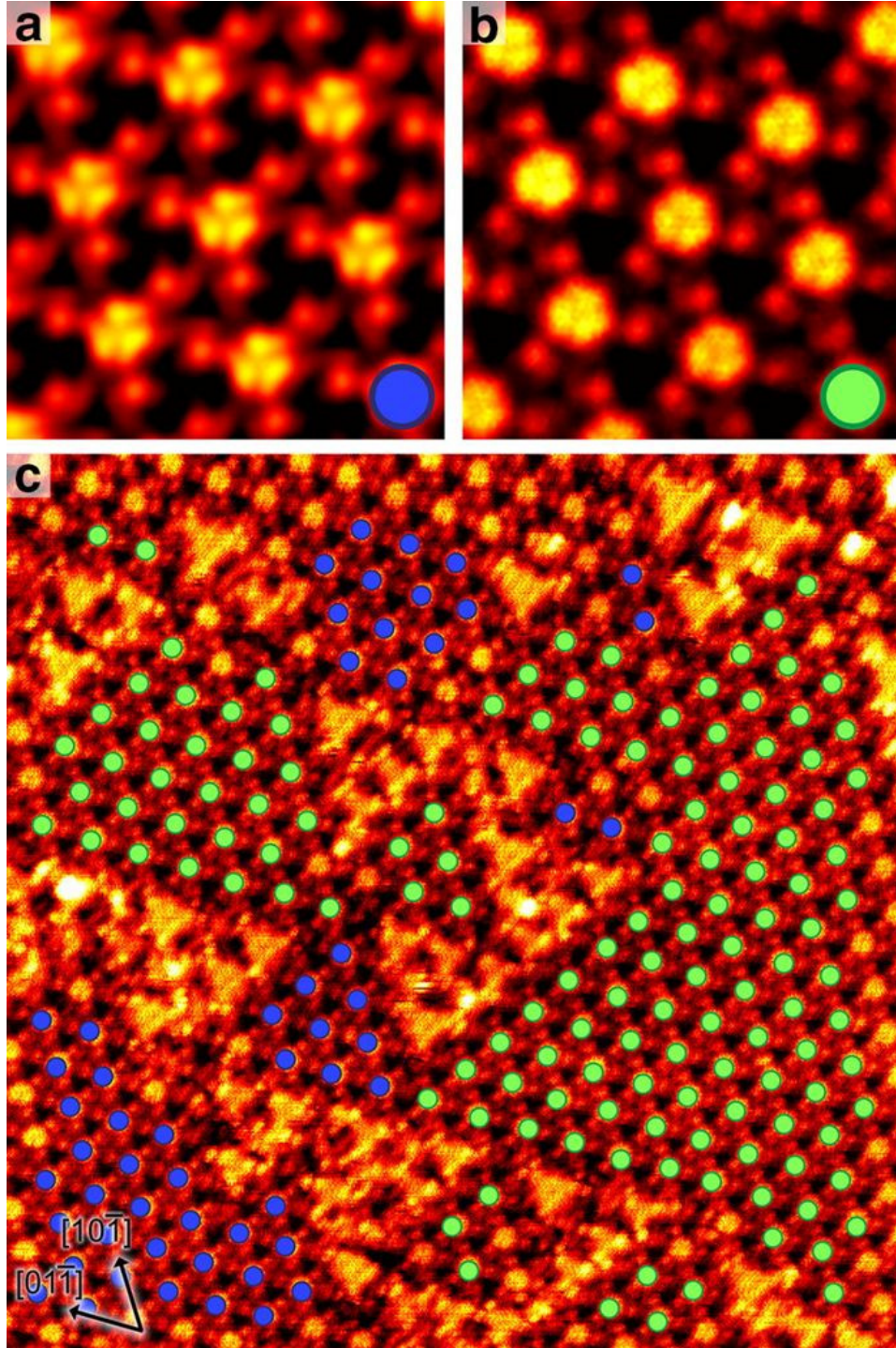


Fig. 4.4 STM images of the $\text{SrTiO}_3(111)-(4 \times 4)$ reconstruction. (a) Left-handed chiral units image constructed by averaging 297 defect-free tiles (image width 4.2 nm, $V_s = 2.0$ V, $I_t = 0.5$ nA). (b) Right-handed chiral units image constructed by averaging 15 defect-free tiles (image width 4.2 nm, $V_s = 2.0$ -2.5 V, $I_t = 0.5$ -0.65 nA). (c) Large area image where the reconstructed units associated with the left (blue) and right (green) chiralities have been automatically identified and labelled (image width 42 nm, $V_s = 2.0$ V, $I_t = 0.5$ nA).

Owing to the similarity of the two types of unit cell, it can be challenging to distinguish chirality in raw noisy images. We select a defect-free unit cell from the raw image and use cross-correlation function to correlate it with other motifs – this process is known as a template matching tool. After applying the template-matching tool on an image that contained both chiralities, it was possible to automatically identify the left and right-handed units, as shown in Fig. 4.4c. It is immediately apparent that unit cells of the same chirality prefer to be located next to each other, which results in extended chiral domains, separated by disordered regions. It can also be seen in Fig. 4.4c that a few (4×4) unit cells have not been identified with either chirality. This occurs where there are local defects, or where the unit cell is near the image boundary and the template is too large to be entirely overlaid on the image.

The example of chiral recognition presented here uses a single crystal termination, but of course the same approach could readily be used for STM and AFM images of adsorbed chiral molecules. In our example this automated procedure of the identification of repeating motif units is only possible on images that contain fine structural detail. This emphasizes the necessity for correcting for scanning artefacts and using subsequent image averaging to enhance the SNR. Other methods for automated feature extraction, such as those based on Fourier transforms,¹⁶⁶ may also be used for chiral unit recognition.

4.4 Discussion

Artefacts present in individual STM images can include affine-distortion (shear/stretch), non-linear scanning distortion, and abrupt image contrast changes resulting from structural tip changes. These artefacts arise due to thermal drift between the sample and the tip, piezo-scanner hysteresis, or from the laboratory environment, and are generally exacerbated as field-of-view or scanning time increase. Thus the resolution of a single

STM image is determined by the combination of imaging / instrumental artefacts and the intrinsic limit to resolution due to quantum mechanical interactions. In reality it is the artefacts that limit the resolving power of most STMs. Imaging artefacts are often hidden by using filters such as median (real-space), Wiener and low-pass (Fourier-space) filters.¹⁶⁷ In Fourier-space, signals are transformed into frequencies so that we can focus on the signal with the highest frequencies. Nevertheless, median filters can distort the lattice or blur structural features. Wiener filters and low-pass filters involving Fourier transforms can introduce artificial periodicities or modify existing periodic features. A further point is that filters contain subjective elements where the researcher selects a specific filter to give the impression of resolution enhancement. However, we have shown in this chapter that the MFA approach does not require any filtering steps. The scan-corrected images are reliable and highly reproducible due to the simple averaging process. Previous studies from electron microscopy have shown that both the precision of image features (image intensity/feature-height),¹⁹ and the lateral spatial precision of features,¹⁶⁸ improves proportionally to the square-root of the number of frames averaged. Here we evaluate the signal-noise ratio (SNR) of aligned images for an increasing number of frames with similar findings. In the extreme case where many hundreds of frames are averaged, the median-filter and subtraction method becomes less sensitive to image noise and becomes limited by the finite sampling of the image data. This does not indicate that the precision is no longer improving, but merely that the resolvability of features or noise has become limited by pixel-size instead of SNR. In practice, the data in Fig. 4.1e shows that MFA of 30 images is sufficient for most applications because the rate of improvement diminishes significantly beyond this number.

The use of MFA techniques applied to STM images relies on obtaining images from the same area and under the same imaging conditions. Keeping sample bias and tunneling setpoint conditions the same is trivial, however the microscopist does not have control over the condition of the apical atom of the tip. Tip changes at the atomic level can result in significant changes in image contrast (e.g. Fig. 6 in ref.[¹⁶⁹]) and will often be the limiting factor that determines the number of sequential images that can be obtained. However, even as few as ten images will deliver a significantly improved SNR and it is common in STM to have this number of scans without a tip change.

We anticipate that MFA will find further application in STM images that suffer from serious distortions and thermal drift, such as those obtained during high-temperature imaging, and facilitate studies of surface diffusion.¹⁹ Accurate alignment of images allows movies to be created that directly reveal dynamic behaviour without the distractions inherent in unprocessed sequences.¹⁷⁰ It is also possible to use automation to extract rare kinetic events that would be very time consuming to identify manually. The sensitivity of MFA may also provide new insights into the investigation of metal surfaces with corrugations less than 0.1 Å.¹⁶⁷

4.5 Conclusions

With the three examples presented here, we have demonstrated the *fidelity*, *sensitivity*, and *selectivity* that can be achieved for STM data when using a multi-frame averaging (MFA) approach. This approach is made possible by the robust and automated non-rigid registration afforded by the SmartAlign software package. We demonstrate the approximately square-root relationship improvement in SNR upon image averaging, a sub-picometre precision height measurement, and the automated identification of chiral unit cells on a surface. These automated tools, which do not require prior knowledge of

the surface structure, promise to facilitate more rapid and higher-precision studies of surfaces, making full use of the experimentalists recorded data sets. This advance allows a new study of surface pico-science to be developed where subtle variations in surface structure can now be seen, that hitherto were not detected because they were buried in noise. In future developments, it would be interesting to combine MFA with automated probe microscopy,¹⁷¹ to remove the substantial operator time commitment in obtaining hundreds of STM images of the same area.

Chapter 5. Local defects in the Ti_2O_3 honeycomb monolayer

5.1 Introduction

This chapter explores the structural and electronic properties of local defects in Ti_2O_3 monolayers supported on Au(111). Previous work in the literature has revealed the presence of defects consisting of four, five, seven and eight-fold rings in monolayer films of Ti_2O_3 on Pt(111), V_2O_3 on Pd(111)^{6,36} and Cu_3O_2 on Cu(111).¹⁷² In this chapter, a series of defects with different arrangements of polygons are reported in the Ti_2O_3 honeycomb structure. The role of epitaxial strain in determining the structures and energies of stoichiometric defects of a Ti_2O_3 vacancy is investigated using STM and DFT. The DFT calculations are performed by Dr Jacek Goniakowski and Dr Claudine Noguera (CNRS, FR). Non-stoichiometric defects that do not have the Ti_2O_3 stoichiometry are also investigated.

5.2 Experimental methods

The experiments were performed in an ultrahigh vacuum (UHV) system at a base pressure of 10^{-8} Pa. STM measurements were carried out in a JEOL instrument (JSTM 4500XT) at room temperature using etched tungsten tips in constant current mode. The Ti_2O_3

honeycomb ultrathin films on Au(111) substrates were grown according to the description detailed in Ref.[⁹]. Mica-supported Au(111) single crystals (Agilent Technologies, U.K.) were used as substrates. Au(111) substrates were sputtered by Ar⁺ ions and UHV annealed to 600 °C for 1.5 h resulting in the herringbone reconstruction. Ti vapor is deposited using an e-beam evaporator (Oxford Applied Research EGN4) from a 99.99% pure Ti rod supplied by Goodfellow, U.K. The surfaces are then annealed in 10⁻⁶ Pa O₂ for 0.5 h to create the (2 × 2) Ti₂O₃ honeycomb ultrathin films. Most STM images presented in this chapter are the results of multiple frame averaging (MFA) using a software package called Smart Align with the general method described in Ref.[¹⁹] and the specific application to STM described in Chapter 4. The STM images were smoothed using ImageJ packages.

5.3 Results and discussion

5.3.1 The pristine Ti₂O₃ (2 × 2) honeycomb structure.

The structural model of the titanium oxide monolayer epitaxial film on Au(111) is shown in Fig. 5.1a. The film has Ti₂O₃ stoichiometry and a honeycomb structure. The film adopts the 2 × 2 periodicity of the Au(111) substrate with the Ti atoms located in Au(111) three-fold hollow sites and the O atoms located in on-top positions.^{5,9} A Ti₂O₃ (2 × 2) unit cell is highlighted in Fig. 5.1a. DFT calculations show that the films incorporate substantial rumpling with the O atoms shifted away from the substrate with respect to the Ti atoms by 0.7 Å, as shown in Fig. 5.1b(i). Despite the O atoms being closest to the STM tip during scanning, typical empty states STM images show the Ti locations as bright spots in the images (Fig. 5.1c). A calculated STM image in the bottom right corner of Fig. 5.1c demonstrates good correspondence between theory and experiment for this system.

DFT calculations for the Ti₂O₃ monolayer were also carried out on a hypothetical freestanding film. These simulations result in a flat film with a lattice parameter of 6.35

Å, as shown in Fig. 5.1b(ii). The rumpling of the supported film is due to the effect of electron transfer from the film to the electronegative Au substrate. This causes Coulomb interactions to push the O anions away from the substrate, and attract the Ti cations towards the substrate.^{173,174} The resulting equilibrium in-plane lattice parameter of the Au-supported honeycomb film can be estimated to be about 5.9 Å. This value is much smaller than that of the unsupported film, but somewhat larger than the (2×2) -Au(111) periodicity of 5.77 Å. This indicates that the pseudomorphic Ti_2O_3 film is in a state of in-plane elastic compression.

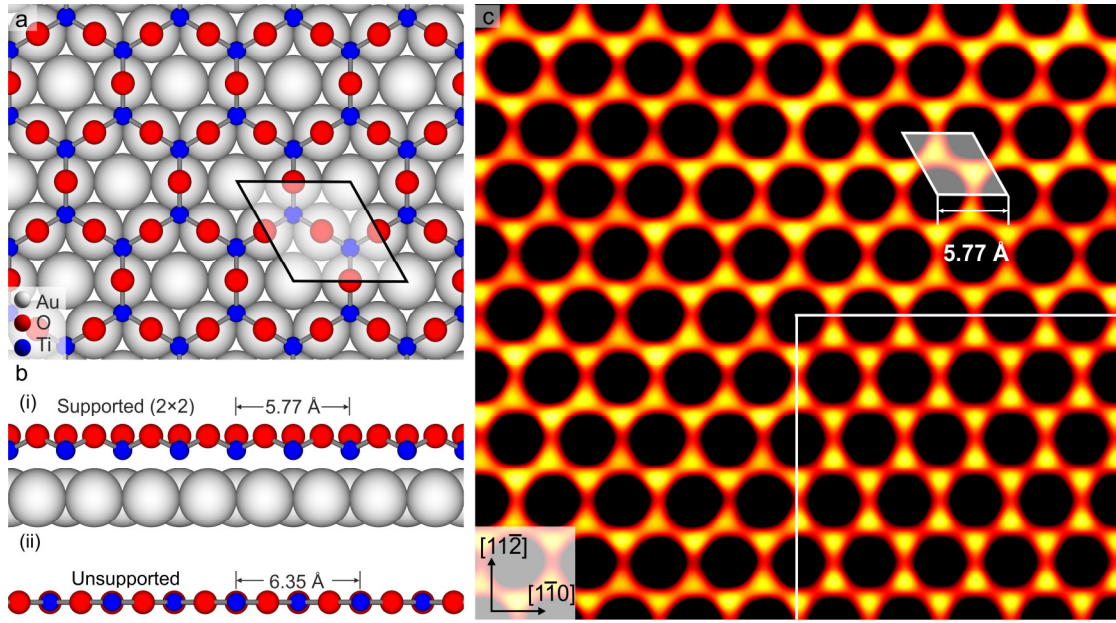


Fig. 5.1 Pristine Ti_2O_3 (2×2) honeycomb structure. (a) A schematic of the Ti_2O_3 monolayer with a honeycomb lattice on Au(111). Ti atoms (blue) are located in Au(111) (grey) three-fold hollow sites, and O atoms (red) are located in on-top positions. A Ti_2O_3 2×2 unit cell is highlighted. Side views of the calculated structures of supported (i) and freestanding (ii) Ti_2O_3 films. (c) Experimental STM image of the pristine film with a 2×2 Ti_2O_3 unit cell highlighted. The atomically resolved (2×2) honeycomb lattice with a periodicity of 5.77 Å serves as a calibration lattice for the experimental STM images. The STM image is averaged from 88 raw frames to enhance the signal-to-noise ratio (image width 5.2 nm, $V_s = 0.9$ -1.0 V and $I_t = 0.22$ -0.24 nA). The inset shows a DFT simulation of the STM image ($E - E_F = +2$ V, distance from the center of the first Au substrate plane is 5.2 Å).

5.3.2 Visualization of defects.

The relationship between the Stone-Wales (S-W), DV(5-8-5), DV(555-777) and DV(5555-6-7777) defects can be represented through the S-W transformation in combination with a divacancy (DV) formation, as illustrated in Fig. 5.2. The first row in Fig. 5.2 shows the initial structure in each case. The atoms in motion are highlighted throughout the process to help visualize the bond rotation. The middle row qualitatively shows the movement in each case. The final optimized structures are shown in the bottom row where 5, 6, 7 and 8-membered rings are clustered in various arrangements.

The first column in Fig. 5.2 shows the formation of a S-W defect. A Ti_2O unit (Fig. 5.2a) can be thought to undergo a bond rotation of 90° to form a S-W defect where four hexagons are replaced by two pentagons and two heptagons (Fig. 5.2i). The second column in Fig. 5.2 shows the formation of a DV(5-8-5) defect. The Ti_2O_3 cluster highlighted in Fig. 5.2b is removed. The resultant four dangling bonds (Fig. 5.2f) recombine to form two pentagons and one octagon. The coordination of the Ti and O atoms is maintained for this, and indeed for all the defects, as is the Ti_2O_3 stoichiometry. The Ti_2O_3 vacancy here is called a “divacancy” because it incorporates two missing Ti atoms, and from a structural point of view this is analogous to two missing carbon atoms in graphene. The DV(5-8-5) defect can transform into a DV(555-777) defect via a S-W transformation, as shown in the third column in Fig. 5.2. A Ti_2O unit shared amongst an octagon and three hexagons (Fig. 5.2c) undergoes a 90° rotation to form a DV(555-777) defect (Fig. 5.2k). The DV(555-777) defect contains three pairs of alternating 5 and 7-membered rings. Following the same mechanism, the DV(555-777) defect undergoes a S-

W rotation and results in a loop of four pentagon-heptagon pairs surrounding a hexagon, as shown in the right-hand column of Fig. 5.2. This structure is called the DV(5555-6-7777) defect.

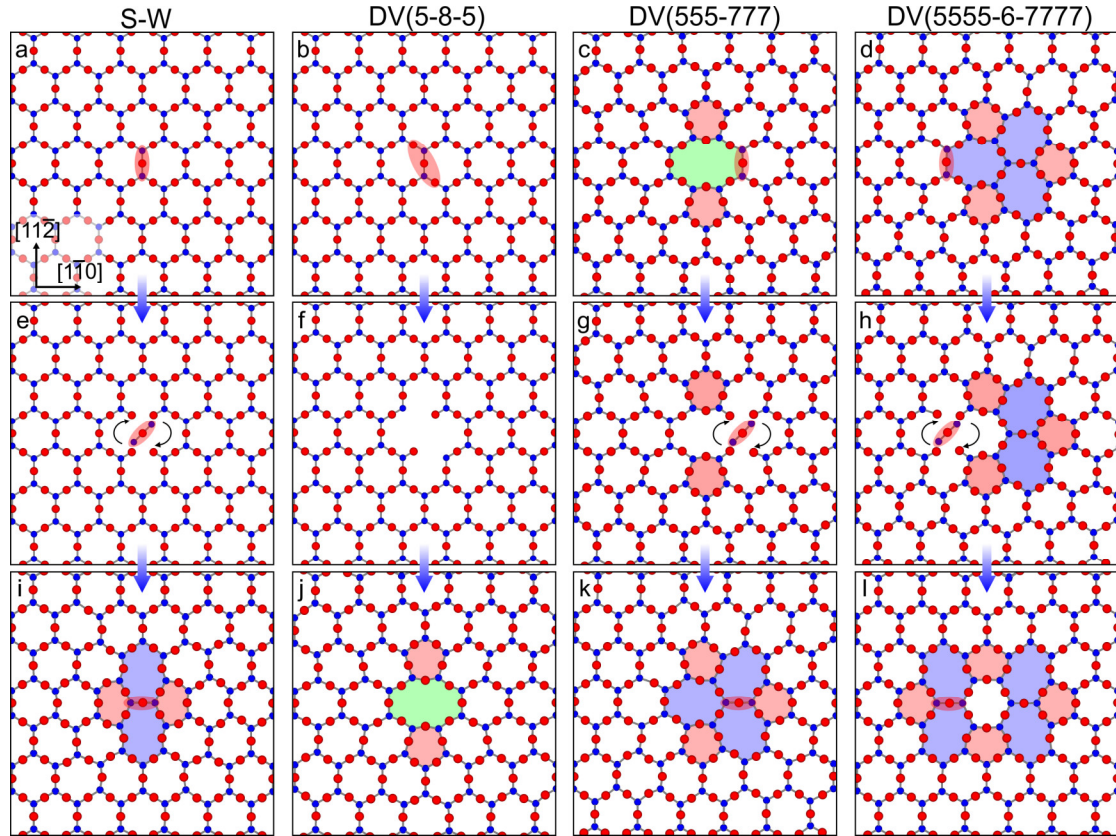


Fig. 5.2 Schematic representation of the relationship of the Stone-Wales (S-W), DV(5-8-5), DV(555-777) and DV(5555-6-7777) defects. The initial structures are shown in (a-d), in which the atoms that move are indicated by an oval. The movements in each case are qualitatively shown in (e-h), where the rotation is indicated by black arrows. The final optimized structures are shown in (i-l). The pentagons, heptagons and octagons are highlighted in pink, blue and green. Ti and O atoms are blue and red balls, respectively. The Au substrate atoms are not shown.

In the experiments there are three mechanisms that give rise to S-W and DV defects in the Ti_2O_3 honeycomb films. The first mechanism is incorporation of defects during crystal growth or when two separately nucleated domains meet. The second is coalescence of atomic vacancies, where in our case, a cluster of two Ti and three O vacancies agglomerate

to form a DV defect. The third mechanism relates to the use of STM. We have observed on a small number of occasions that during scanning tip-surface interactions can give rise to DV defects and S-W rotations. Presumably this occurs when the tip makes contact with the honeycomb film and some of the monolayer atoms are transferred onto the STM tip.

5.3.3 Defect structures in the Ti_2O_3 honeycomb monolayer.

Experimental STM observations of the defect structures are presented in the top row of Fig. 5.3. The main feature in the images is the clustering of polygons embedded in the honeycomb lattice. The geometry of the clusters is the same as in the models in the bottom row of Fig. 5.2, hence the structures are referred to as S-W, DV(5-8-5), DV(555-777) and DV(5555-6-7777) defects. Atomic models, including the Au substrate atoms, are shown in the third row of Fig. 5.3. Image simulations (the second row of Fig. 5.3) calculated from these atomic models are in good agreement with the experimental STM images. The only visible difference is the bright region to the left of the DV(5-8-5) defect in the experimental image (Fig. 5.3b), probably due to contamination.

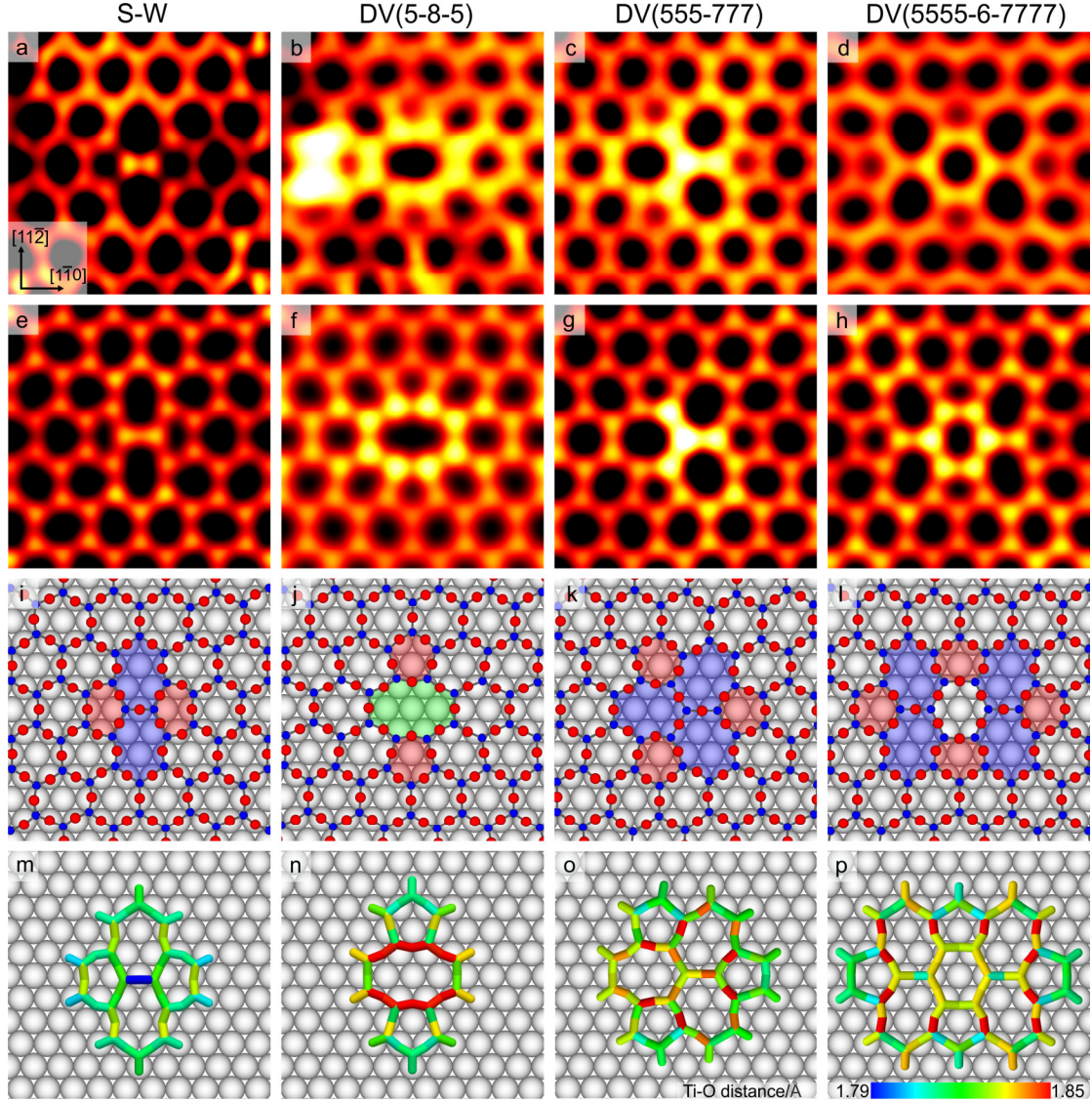


Fig. 5.3 Defect structures in Ti_2O_3 honeycomb. Experimental STM data (a-d), and corresponding DFT simulations (e-h) of S-W, DV(5-8-5), DV(555-777) and DV(5555-6-7777) defects. The atomic models including the Au(111) substrate atoms are shown in (i-l) with Ti atoms in blue, O atoms in red and Au atoms in grey. The STM images from (a), (c) & (d) are generated from 4, 138 and 4 frames using multiple frame averaging (MFA). The experimental STM parameters of (a-d) are $V_s = 0.95$ V and $I_t = 0.22$ nA; $V_s = 0.9$ V and $I_t = 0.22$ nA; $V_s = 1.0$ V and $I_t = 0.2$ nA; $V_s = 0.9$ V and $I_t = 0.22$ nA, respectively, with image widths of 2.9-3.0 nm for all cases. Panels (m-p) show variations of bond lengths for the defects. The bonds are colored according to an increase (red and yellow) or decrease (blue) of the bond length.

The bottom row of Fig. 5.3 shows the calculated variations of the Ti-O bond lengths which illustrate the strain within the structures. The bonds are colored according to an increase (red and yellow), decrease (blue), or negligible variation (green) in the bond length with respect to 1.82 Å, the value found in the pristine supported layer. In the S-W defect, the bond expansion is relatively weak and only the central Ti-O bonds are slightly compressed (Fig. 5.3m). Conversely in the divacancy defects, the Ti-O bonds are considerably expanded because the surrounding film is stretched to fill in some of the area due to the missing Ti₂O₃ unit. The DV(5-8-5) defect has twelve of the most elongated Ti-O bonds (1.85 Å, colored in red in Fig. 5.3n), indicating that bond expansion is localized in the octagon. The DV(555-777) defect has six significantly expanded bonds (1.85 Å, colored in red) and several moderately expanded bonds (1.82-1.84 Å, in yellow and orange). When compared with the DV(5-8-5) defect, the DV(555-777) defect is larger, but its lattice distortions are smaller and not concentrated in the central ring. The structural characteristics of the DV(555-777) and DV(5555-6-7777) defects are similar, except that the latter involves more distorted bonds.

Analogous defect structures to the ones shown in Fig. 5.3 were also calculated for hypothetical freestanding Ti₂O₃ films. The bond distortions in the freestanding films are much larger than in the supported films. The presence of a solid substrate diminishes the degree of distortion suffered by the defective layers because the in-plane Ti-O bond stretching can be accommodated by a reduction of film rumpling.

The calculated defect formation energies in the supported Ti₂O₃ film are reported in Table 1 and range between 0.3 eV and 1.4 eV. The energies are calculated by subtracting a pristine Ti₂O₃ film from a Ti₂O₃ film containing the defect. Interestingly, these energies are significantly lower than those of similar defects in other honeycomb monolayers, e.g.,

graphene (5-7.6 eV),⁶⁷ h-BN (8.7-19.7 eV),⁹⁴ or bilayer silica (2.8-9 eV).¹⁷⁵ Moreover, their relative stability is different. Remarkably, the formation energy of the Ti₂O₃ DV(555-777) defect is considerably lower than that of the S-W defect, whereas the DV(5555-6-7777) and S-W defects are essentially isoenergetic. This finding stands in stark contrast to the usual hierarchy in other monolayers with a honeycomb structure, where S-W defects are by far systematically favored over the various divacancy defects.

Table 1. Calculated formation energies (in eV) for local structural defects in supported and freestanding Ti₂O₃ films, compared with literature values for freestanding layers of graphene, silicene, h-BN and bilayer SiO₂.

Defect	Supported Ti ₂ O ₃	Freestanding Ti ₂ O ₃	Graphene ⁶⁷	Silicene ¹⁰⁸	h-BN ⁹⁴	Bilayer SiO ₂ ¹⁷⁵
S-W	1.1	1.1	5.0	2.1	8.7	2.8
DV(5-8-5)	1.4	5.9	7.6	3.7	19.7	9.0
DV(555-777)	0.3	4.4	6.7	2.8	-	5.7
DV(5555-6-7777)	1.0	5.2	7.2	-	-	4.8

In the following discussion, we thoroughly investigate the origin of this unusual behavior and specifically analyze the role of the Au substrate. To clarify the support effect, we start by considering defects in a calculated hypothetical freestanding honeycomb Ti₂O₃ film. A perfectly flat structure is favored in an unconstrained film shown in Fig. 5.1b(ii), with an in-plane lattice parameter of 6.35 Å, which is much larger than that of the (2 × 2)-Au(111) substrate (5.77 Å). The calculated energies of the defects in the freestanding film are reported in Table 1. The hierarchy of the formation energies is analogous to those in graphene and in most other 2D materials. Because in calculations of defect energies the

overall number of Ti-O bonds is preserved, the defect energetics are therefore mainly driven by the degree of bond distortion. In the S-W defect in the freestanding monolayer, the Ti-O bonds are slightly contracted with an elastic energy cost of 0.2 eV. However in the divacancy defects, the Ti-O bonds are considerably elongated with energy costs of +3.5, +4.0, and +4.5 eV for DV(555-777), DV(5555-6-7777), and DV(5-8-5) defects, respectively. These elastic contributions account for the main part of the defect formation energies (second column in Table 1) and provide a good estimate of the relative stability of divacancy defects in the freestanding film: S-W $\ll$ DV(555-777) < DV(5555-6-7777) < DV(5-8-5). More generally, this conclusion also applies to defect formation in other freestanding films.

As discussed previously, to achieve a 2×2 pseudomorphic structure with the Au(111) surface, the Ti_2O_3 monolayer is in a state of in-plane compressive strain of the order of 2%. It is this substrate-induced strain that is responsible for the drastically different divacancy defect energies compared with the freestanding case. The removal of a Ti_2O_3 unit in the divacancy defects results in a large tensile strain in the freestanding film, while, in the supported film, it results in a release of the compressive strain. Consequently, the elastic contribution to the defect energy changes from large and positive (of the order of +4.0 eV) in the freestanding film, to small and negative (of the order of -0.5 eV) in the supported film. This qualitatively different elastic response of supported and freestanding films to the defect creation is the main reason for the substantially different defect energies. In particular, it explains that the energies of the S-W defects in supported and unsupported Ti_2O_3 films are similar because S-W defects only induce a small film distortion and are barely influenced by the external strain. However, the divacancy defects have lower energies in supported films because they introduce a large amount of lattice

distortions and release the compressive strain. Interestingly, in the latter, the optimal arrangement of adjacent 5 and 7 member rings in the DV(555-777) defect produces the smallest strain in the freestanding films and the most efficient compressive strain release in the supported case, leading to the lowest defect energy. More generally, film structures that are buckled due to their interaction with a substrate may more readily accommodate elastic distortions produced upon defect formation, which in turn may lead to relatively low defect energies. This is clearly the case in our Au-supported honeycomb-Ti₂O₃ films but is likely also to be the case in silicene.

STM experiments provide additional information that cannot readily be modeled using *ab initio* methods due to the large number of atoms involved. After image processing using multiple frame averaging (MFA), the STM image (Fig. 5.4a), averaged over 138 frames, reveals an anisotropic strain field surrounding the DV(555-777) defect, a feature which is not visible in single images. The three rows of hexagons adjacent to each heptagon are marginally brighter than the other lattice atoms. The elevation of the Ti atoms extends several unit cells beyond the divacancy defect. The brightness of the Ti atoms decreases with the increase of their distance from the defect core. In particular, measurements between the first and second pairs of Ti atoms adjacent to the heptagon show an average height difference of 0.83 ± 0.19 pm (Fig. 5.4b). It demonstrates the power of MFA in that it allows STM to resolve surface features into the sub-picometer regime.

The origin of the anisotropic strain field in Fig. 5.4a can be explained in terms of atomic displacements. The Ti atoms in the defect cores move away from their three-fold hollow adsorption sites in order to optimize the bonding. These displacements increase their elevation and their associated local density of states (LDOS) resulting in brighter spots in the STM images. These bright spots are mainly located along the heptagon directions,

implying that there are greater lattice distortions adjacent to the heptagons. Similar anisotropic strain fields of a DV(555-777) defect have been theoretically predicted in 2D silica and graphene.^{175,176}

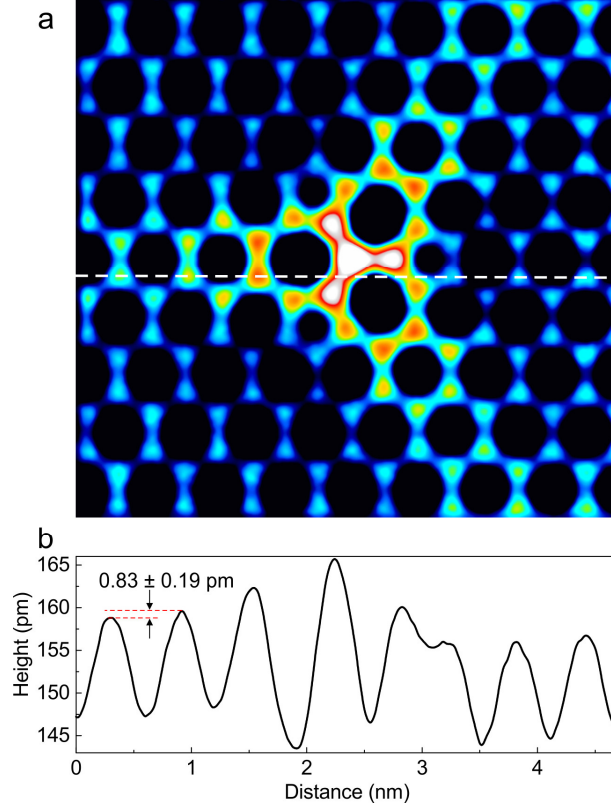


Fig. 5.4 Atomic structure of the strain field around a DV(555-777) defect. (a) STM image using a look-up table that has been chosen for maximum contrast. The STM image is averaged from 138 frames (image width 4.7 nm, $V_s = 1.0$ V and $I_t = 0.2$ nA). (b) Height profile along the dashed white line shown in (a) showing the 0.83 pm height difference between the first and second pairs of Ti atoms adjacent to the heptagon. The height difference is measured from six pairs of Ti atoms.

We have also observed a defect loop of six alternating pentagons and heptagons (Fig. 5.5a), previously called a ‘flower’ defect in graphene and 2D silica.^{96,177} The defect core is a crystalline domain of seven hexagons rotated by 30° with respect to the pristine honeycomb lattice. A model atomic structure is shown in Fig. 5.5b. The defect conserves the number of Ti and O atoms relative to the pristine lattice and maintains Ti₂O₃

stoichiometry. The Ti atoms in the rotated central domain are moved to the top sites and the O atoms are moved to bridge sites. Elevation of these Ti atoms leads to increased brightness in the defect core atoms in the STM image (Fig. 5.5a).

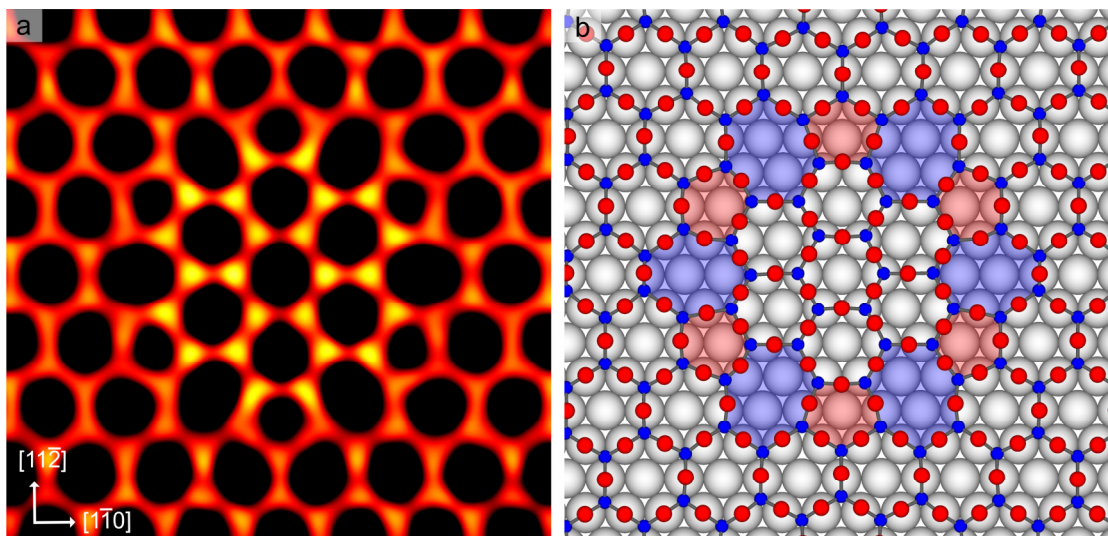


Fig. 5.5 ‘Flower’ defect consisting of six pentagon-heptagon pairs. (a) STM image averaged from 12 frames (image width 4.0 nm, $V_s = 0.9$ V, $I_t = 0.22$ nA) and (b) an atomic model schematic of the ‘flower’ defect.

5.3.5 Non-stoichiometric defects in Ti_2O_3 (2×2) honeycomb structure.

A vacancy located at the Ti site has been systematically observed in a Ti_2O_3 (2×2) honeycomb structure (Fig. 5.6). The vacancy is likely to be a Ti atom vacancy and leave three dangling O atoms (the right inset) because the Ti_2O_3 film is grown in an oxidative atmosphere. The Ti vacancy is either formed during crystal growth or generated by applying a voltage pulse of 3 ~ 5 V.

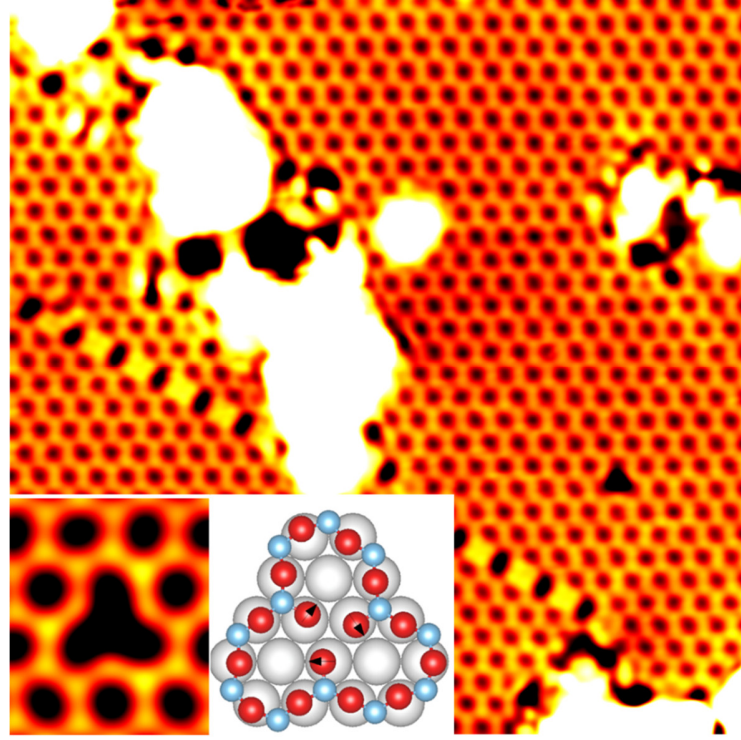


Fig. 5.6 STM images showing a vacancy at the Ti site in the honeycomb lattice. (Image width 13.5 nm, $V_s = 0.95$ V, $I_t = 0.22$ nA). The left inset shows a close-up image of the vacancy (averaged from three raw images, image width 1.7 nm, $V_s = 0.95$ V, $I_t = 0.22$ nA) and the right inset shows a schematic.

A variety of non-stoichiometric defects have been summarized in Fig. 5.7. Experimental STM observations of the defect structures are presented in the top row of Fig. 5.7. Fig. 5.7a shows a vacancy at a Ti site with a triangular shape in the honeycomb lattice. Fig. 5.7b shows a 5-membered ring and a vacancy at Ti site. Fig. 5.7c shows a vacancy where one Ti atom is missing and three bright spots surround the Ti vacancy. Fig. 5.7d shows a heart-shape defect where three Ti atoms are missing. Atomic models are shown in the third row of Fig. 5.7. Image simulations (the second row of Fig. 5.7) calculated from these atomic models are in good agreement with the experimental STM images. Hence the structures are referred to as Ti, TiO, TiO₃ and Ti₃O₅ vacancy defects.

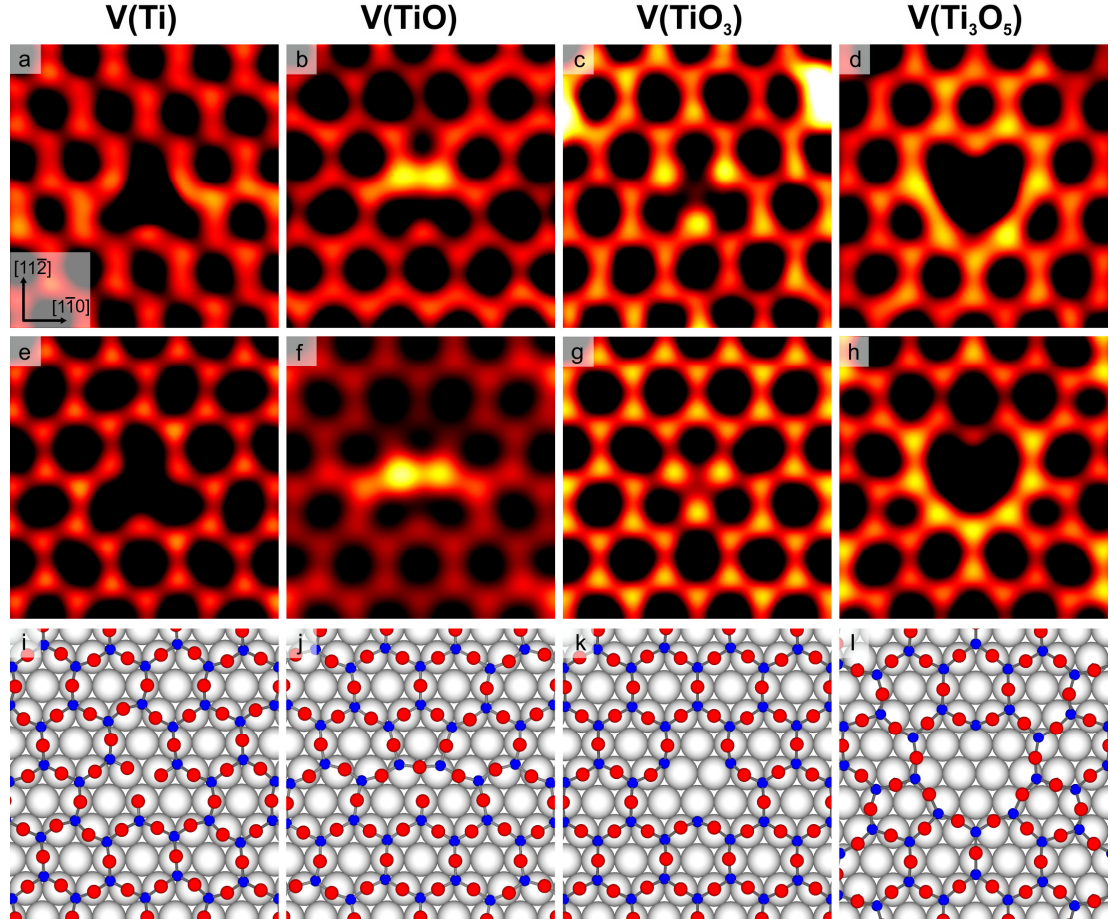


Fig. 5.7. Non-stoichiometric defects in the Ti_2O_3 films on Au(111). Experimental STM data (a-d), and corresponding DFT simulations (e-h) of Ti, TiO, TiO_3 and Ti_3O_5 vacancies. The atomic models are shown in (i-l) with Ti atoms in blue, O atoms in red and Au atoms in grey. The STM images from (c-d) are generated from 42 and 10 frames using MFA. The experimental STM parameters of (a-d) are $V_s = 0.8$ V and $I_t = 0.18$ nA, $V_s = 0.9$ V and $I_t = 0.22$ nA, $V_s = 0.51$ V and $I_t = 0.22$ nA and $V_s = 0.95$ V and $I_t = 0.22$ nA respectively, with image widths of 2.3 nm for all cases. STM simulations are taken at $E - E_F = +2$ V and the distance from the center of the first Au substrate plane is 5.2 Å.

A Ti atom and a TiO cluster are Ti-rich with respect to Ti_2O_3 ($\text{TiO}_{1.5}$). The removal of a Ti atom or a TiO cluster results in a Ti-poor and O-rich film of $\text{Ti}_{1-x}\text{O}_{1.5}$. This film can be grown by oxidizing a $\text{TiO}_{1.5}$ film. A TiO_3 cluster and a Ti_3O_5 cluster are O-rich with respect to $\text{TiO}_{1.5}$. The removal of a TiO_3 cluster and a Ti_3O_5 cluster results in a Ti-rich and O-poor film of $\text{TiO}_{1.5-x}$. This film is grown by reducing a $\text{TiO}_{1.5}$ film.

The most frequently observed defect in STM experiments is the Ti vacancy defect. A Ti atom is removed from the honeycomb lattice and the removal leaves three dangling O atoms at the defect site (Fig. 5.7i). The honeycomb film with the presence of vTi has stoichiometry of $\text{Ti}_{1-x}\text{O}_{1.5}$. The Ti_2O_3 film is grown in an atmosphere with the presence of oxygen which favors a slightly oxygen-rich film structure. Preliminary DFT calculation predicts that vTi defects have lower energies than other non-stoichiometric defects at an oxygen chemical potential of $-1 \sim -2$ eV. The prediction is in agreement with the experimental observation that a vTi defect has relatively high occurrences in a sample grown by annealing in 10^{-6} Pa O_2 at 600°C .

5.4 Conclusions

We have used STM to observe a series of local structural defects in the Ti_2O_3 honeycomb layer on Au(111). DFT simulations have further determined in detail the atomic and electronic structures of the S-W and divacancy defects as well as their formation energetics. Whilst these defects are topologically similar to their counterparts in graphene and other 2D honeycomb materials, the relatively strong interaction of the oxide monolayer with the Au substrate significantly affects the defect energies and hierarchy. Moreover, we show that the elastically compressed monolayer film favors the formation of divacancy-type defects because they facilitate the release of the compressive strain. These results broaden the perspective under which such defects may be considered in other 2D materials, such as graphene or h-BN films, and open the door to new ideas in relation to the design of defect structures through a judicious combination of monolayer film and substrate. It is further probable that in monolayer films in a state of elastic tension, it will be difficult to form vacancy-type defects whereas other defects of the interstitial-type may be favored to release the tensile strain. Our study provides a solid atomic and

electronic structure-based understanding of the peculiarities of local structural defects in supported ultrathin oxide films and is the starting point for further investigations into more complex defects in 2D oxide nanostructures. The defect cores with increased Ti brightness in the STM images are correlated with a downshifted Ti d-Au hybridization band that will influence their chemical reactivity, for example by decreasing the CO binding energy.¹⁷⁸ The occurrences of non-stoichiometric defects is related to the chemical conditions that used to grow the Ti_2O_3 film. Furthermore, enhancement of the signal-to-noise ratio of STM images using MFA provides a better comparison between experiments and simulations and reveals fine surface features that hitherto were buried in noise.

Chapter 6. Nb₂O₃ honeycomb monolayer

6.1 Introduction

This chapter focuses on the experimental discovery of a well-ordered (2×2) Nb₂O₃ honeycomb monolayer on the Au(111) surface. Its large scale crystal structure is characterized with STM and LEED, its fine atomic structure is analyzed via high-resolution STM images, and its electronic properties are determined using DFT. The DFT calculations in this chapter are performed by Dr Jacek Goniakowski and Dr Claudine Noguera (CNRS, FR). Nb atom vacancies have been observed, with their atomic structure characterized using STM.

6.2 Experimental methods

The experiments were performed in a UHV system at a base pressure of 10^{-8} Pa. Measurements were carried out in a JEOL JSTM 4500XT instrument which includes STM and LEED analysis facilities. Polished Au single crystals (SurfaceNet GmbH, Germany) cut to reveal the (111) termination were cleaned by repeated sputtering and annealing cycles. Mica-supported Au(111) single crystals (Agilent Technologies, U.K.) were also used as substrates. Both types of Au(111) substrates were sputtered by Ar⁺ ions (0.75-1 keV) and UHV annealed to 600 °C for 1.5 h resulting in the herringbone reconstruction.

Nb vapor was deposited using an e-beam evaporator (Oxford Applied Research EGN4) from a 99.99% pure Nb rod supplied by Goodfellow, U.K. The samples were then annealed in 10^{-6} Pa O₂ at 600 °C for 1 h to create the (2 × 2) niobium oxide ultrathin films. Constant current STM images were produced at room temperature using etched tungsten tips. Most STM images presented in this chapter are the results of MFA using a software package called Smart Align with the general method described in¹⁹ and the specific application to STM described in Chapter 4.

6.3 Experimental results and discussion

6.3.1 Crystal structure of niobium oxide monolayers

Fig. 6.1 shows STM images of the evolution of the surface structures upon increasing the coverage from 0.16 monolayer (ML, where 1 ML coverage corresponds to an Au surface fully covered by one layer of niobium oxide) to 1.83 ML. Fig. 6.1a shows an Au(111) surface following the deposition of 0.16 ML of Nb and subsequent oxidation. Niobium oxide on Au(111) forms a film structure with a honeycomb lattice as well as an island structure with a triangular shape. Bare patches of the Au(111) substrate (dark areas) coexist with the oxide islands. The herringbone reconstruction is lifted underneath the oxide film and distorted in the bare regions. As the coverage is increased from 0.16 ML to 0.85 ML, several separately nucleated honeycomb domains meet and transform into continuous domains [Fig. 6.1(a-d)]. The stripy pattern in the center of Fig. 6.1d is surrounded by the honeycomb structure. It is possibly a Cu(2 × 1) structure on Au(111) and the Cu atoms come from the Cu gaskets used for UHV sealing. The surface structures are dominated by honeycomb units and triangular islands. Some defects are seen in the honeycomb lattice, such as atomic vacancies [bottom right in Fig. 6.1c] and domain boundaries [top left in Fig. 6.1c]. Domain boundaries are formed to accommodate the

epitaxial offset between two domains. Depositing more Nb on a NbO_x surface of 0.85 ML coverage and annealing the surface in oxygen increases the oxide coverage to 1.83 MLs (Fig. 6.1e). Disordered structures grow on top of the honeycomb structures and triangular islands. Depositing more Nb onto the NbO_x surface of 1.83 MLs and annealing the surface in oxygen increases the oxide coverage to 2.2 MLs. The honeycomb structure is no longer observed and the surface is covered by disordered structures.

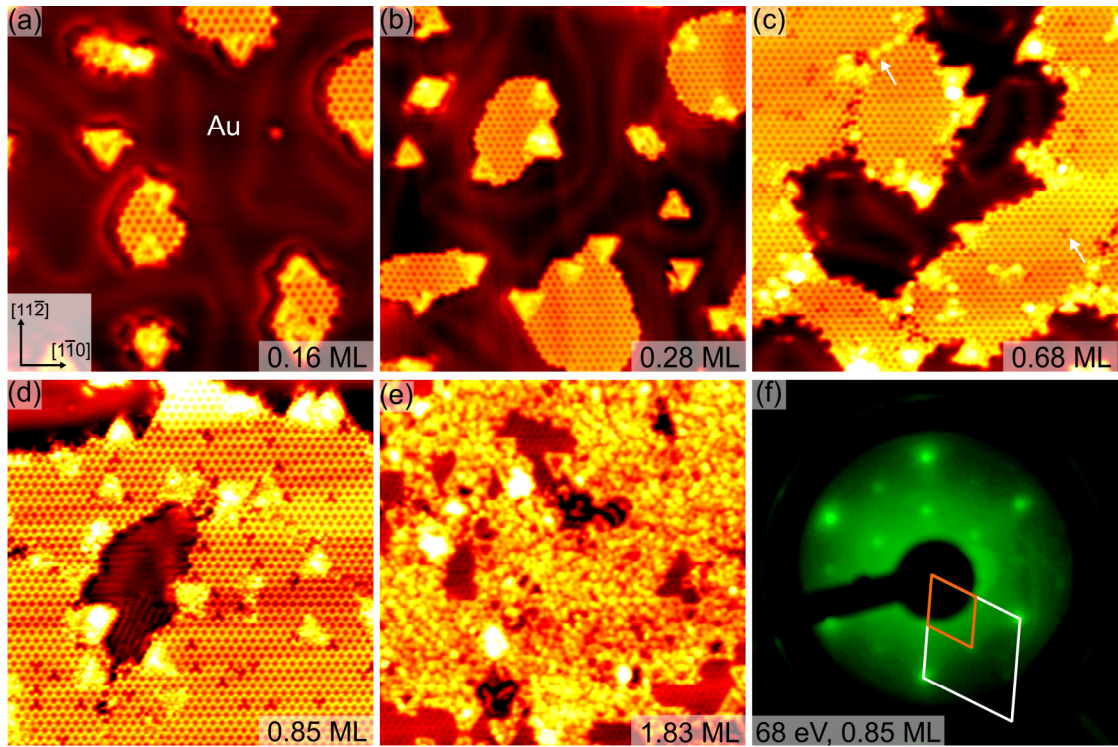


Fig. 6.1. Overview of niobium oxide grown on Au(111) at increasing coverage. STM images of niobium oxides at (a) 0.16 ML, (b) 0.28 ML, (c) 0.68 ML, (d) 0.85 ML, and (e) 1.83 ML. Atomic vacancies and domain boundaries are indicated by arrows in (c). (f) LEED pattern (taken at 68 eV) showing a (2×2) superstructure (orange rhombus) on an Au(111) surface (white rhombus) covered by 0.85 ML of oxide. The STM images from (a-d) are generated from 19, 71, 14, 8 frames using multiple frame averaging (MFA) to enhance the signal-to-noise ratio, as described in the Appendix B. The experimental STM parameters are (a) image width 21.0 nm, $V_s = 0.45$ V and $I_t = 0.26$ nA; (b) image width 27.0 nm, $V_s = 0.4$ -1 V and $I_t = 0.26$ nA; (c) image width 24.7 nm, $V_s = 1$ V and $I_t = 0.16$ nA; (d) image width 24.0 nm, $V_s = 1$ V and $I_t = 0.18$ nA; (e) image width 30.0 nm, $V_s = 1$ V and $I_t = 0.25$ nA.

The LEED pattern taken at 0.85 ML coverage (Fig. 6.1f) indicates a commensurate (2×2) superstructure (indicated by an orange rhombus) with respect to the Au(111) substrate (white rhombus), which corresponds to an overlayer lattice constant of 5.77 Å. The unit cell of the oxide film is aligned along the $[1\bar{1}0]$ directions of the Au(111) substrate.

Annealing the niobium oxide surface covered by 0.9 ML honeycomb at 800 °C in UHV and 10^{-6} Pa O₂ barely affects the coverage or the crystal structure of the honeycomb monolayer. Annealing the honeycomb surface at 400 °C in 10^{-4} Pa O₂ also has little effect. This stability is in contrast to that of the honeycomb monolayers of V₂O₃ and Ti₂O₃ which transform into more oxidized phases under elevated temperatures and higher oxygen pressures.^{6,9,36}

6.3.2 Atomic structure of niobium oxide honeycomb films

Fig. 6.2 shows the atomic structure of the (2×2) oxide phase. Experimental STM images with two different tip terminations show bright protrusions at the vertices (Fig. 6.2a) or the bridge sites (Fig. 6.2c) of the honeycomb network, respectively. The hexagonal network has an average periodicity of 5.8 ± 0.1 Å which corresponds to the (2×2) periodicity of Au(111) surface, in agreement with the LEED pattern (Fig. 6.1f).

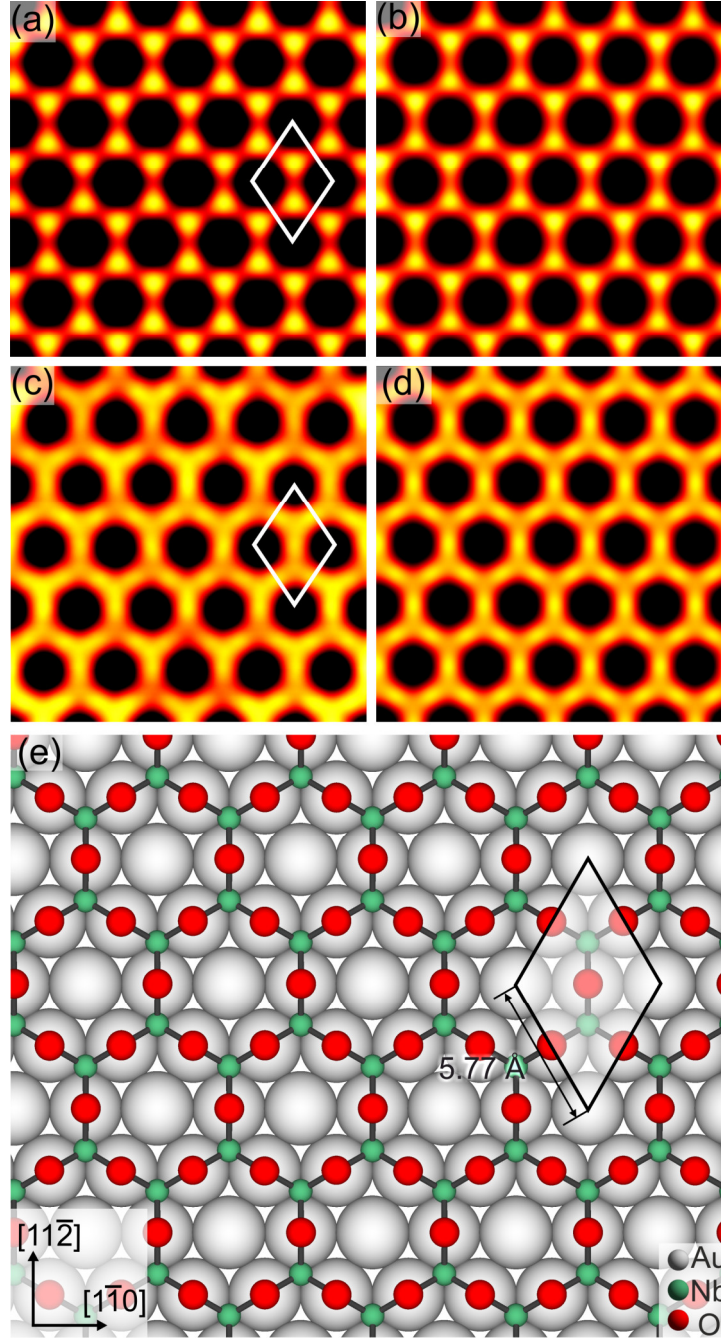


Fig. 6.2. Pristine Nb_2O_3 (2×2) honeycomb structure. (a) Experimental empty states STM image (averaged from 290 frames, image width 2.9 nm, $V_s = 0.8$ V and $I_t = 0.16$ nA). (b) DFT simulation of the empty states STM image ($E - E_F = +1$ V, distance from the center of the first Au substrate plane is 6.0 Å). (c) Experimental filled states STM image (averaged from 46 raw frames, image width 2.9 nm, $V_s = -0.5$ V and $I_t = 0.18$ nA). (d) DFT simulation of the filled states STM image ($E - E_F = -0.5$ V, distance from the center of the first Au substrate plane is 6.0 Å). (e) A schematic of the Nb_2O_3 monolayer with a honeycomb lattice on Au(111). Nb atoms (green) are three-fold coordinated with O atoms (red). Au atoms are in grey. A (2×2) Nb_2O_3 unit cell is highlighted in (a), (c) & (e).

The atomic structure and crystallographic orientation with respect to the Au(111) surface of the niobium oxide honeycomb phase are similar to those observed for the epitaxial honeycomb (2×2) $\text{Ti}_2\text{O}_3/\text{Au}(111)$ system with the Ti atoms located in Au(111) three-fold hollow sites and the O atoms located in on-top positions.⁵ We adopt the previous interpretation for the Ti_2O_3 monolayer directly and assign the Nb atoms to bright protrusions imaged in Fig. 6.2a, and that O atoms are imaged in Fig. 6.2c. The structural model of the niobium oxide honeycomb monolayer is shown in Fig. 6.2e. Each unit cell [highlighted in Fig. 6.2(a, c & e)] contains two Nb atoms and three O atoms. Each Nb atom is coordinated with three O atoms and each O atom is coordinated with two Nb atoms. The stoichiometry of the honeycomb phase is Nb_2O_3 . Image simulations [Fig. 6.2(b & d)] are in good agreement with the experimental STM images. The theoretical calculations are discussed in detail in section 6.4.

6.3.3 Observation of Nb atoms in hcp and fcc adsorption sites

After image processing using MFA, STM images show fine surface features that cannot be observed in single frames. The STM image [left of Fig. 6.3a], averaged over 176 frames without other image filtering, shows that half of the Nb sites, marked as ‘A’ sites are marginally brighter than the other half, marked as ‘B’ sites. The difference between ‘A’ and ‘B’ sites are visualized in the right panel of Fig. 6.3a using another look-up table that has been chosen for maximum contrast. The height difference can also be seen in the profile taken along the highlighted A-B pair in Fig. 6.3a and shown in Fig. 6.3b. Measurements of 66 A-B site pairs were taken from this image resulting in an average height difference (Δh) of 1.83 ± 0.20 pm.

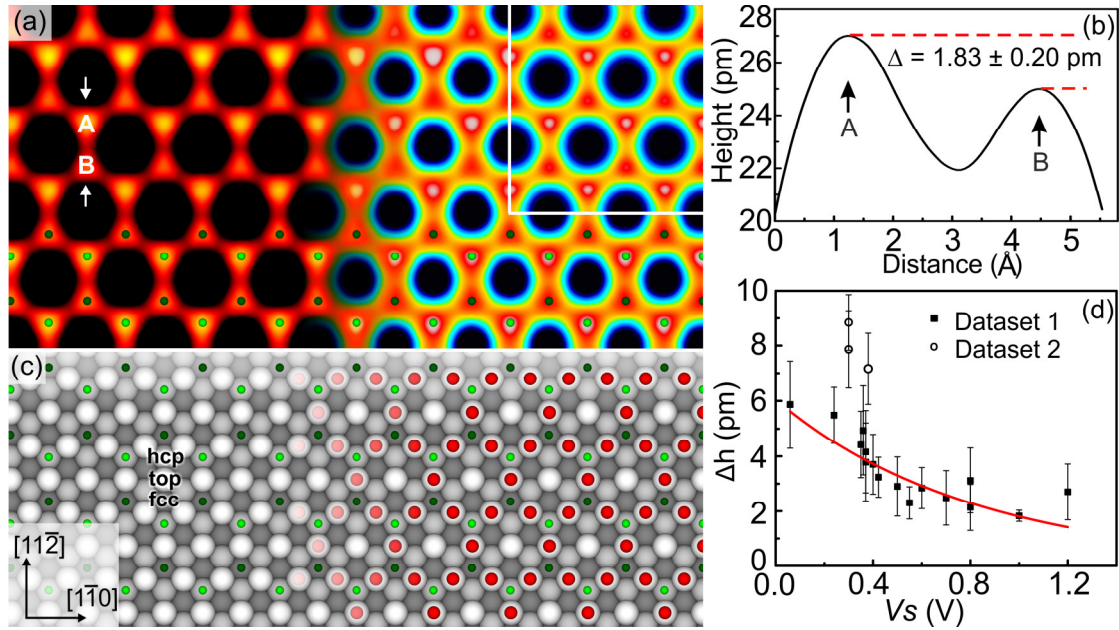


Fig. 6.3. STM image and detailed analysis of the (2×2) honeycomb Nb_2O_3 monolayer structure on $\text{Au}(111)$. (a) (Left) experimental empty states STM image (averaged from 176 raw frames, image width 5.2 nm, $V_s = 1.0$ V and $I_t = 0.18$ nA). (Right) the same data as in the left part but with a different look-up table that has been chosen for maximum contrast. The top right inset shows a calculated STM image showing that the hcp sites appear brighter than fcc sites ($E - E_F = +2$ V, distance from the center of the first Au substrate plane is 6.0 Å). (b) Line profile from the highlighted A-B pair in (a) showing the 1.83 pm difference in height of the A and B sites. (c) Epitaxial model of the (2×2) honeycomb Nb_2O_3 monolayer on $\text{Au}(111)$ with top (white), hcp (light grey) and fcc (dark grey) sites indicated. Nb atoms located on the hcp and fcc sites are in light and dark green, respectively. O atoms are shown in red. (d) Plot of A-B pair height difference (Δh) vs the sample bias (V_s) illustrating that Δh decreases with increasing V_s . Each data point is extracted from one single STM image so that the Δh of various A-B pairs is measured under the same tip condition and imaging parameters.

The measurements of Δh have only small variations within each image, but show more significant average differences depending on tip termination and imaging parameters.

Measurements of multiple A-B site pairs were taken from single STM images resulting in a variety of values for Δh . Eighteen Δh averages were plotted against the sample bias, as shown in Fig. 6.3(d). The data sets are separated into two regions of lower (filled squares, classified as Dataset 1) and higher (open circles, classified as Dataset 2) values of Δh . This suggests that in our experiments there are two generally stable types of tips. The majority

of the data sets fall in the lower region, which ranges from 1.83 to 5.87 pm with a preponderance of values around 3 pm. The decrease of Δh can be approximated by an inverse exponential fit with the sample bias. An increase in sample bias will generally result in an increase in the tip-sample separation and have a reduction of atomic corrugation height in the images. The three data points above 6 pm are not included in the red line fit and are probably due to a different apical tip termination.¹⁷⁹

The origin of the difference of the height of the A sites and B sites in Fig. 6.3a can be explained by analyzing the structure of the Nb₂O₃ overlayer. Fig. 6.3c is a schematic showing an Au(111) surface where the top three atomic Au layers can be seen with the location of the Nb atoms on the left and the full Nb₂O₃ overlayer on the right. The Nb atoms (green balls) are located in threefold hollow sites on the Au(111) surface, and the O atoms (red balls) are located on the ‘top’ sites (white). There are two types of threefold hollow sites, namely hcp sites (light grey) and fcc sites (dark grey), as indicated in Fig. 6.3c. The structure of the overlayer results in half of the Nb atoms sitting in the hcp sites, and the other half in fcc sites. A calculated STM image (in the top right corner of Fig. 6.3a) is in good agreement with the experimental STM image. In simulations, the Nb atoms located on the hcp site are marginally brighter than the ones on the fcc sites. It is according to this simulation that we assign the A and B sites to the hcp and fcc locations, respectively.

6.4 Theoretical results and discussion

(This section is carried out by Dr. Jacek Goniakowski and Dr. Claudine Noguera.)

6.4.1 Atomic structure of Nb₂O₃ (2 × 2) honeycomb monolayers on Au(111)

Atomistic simulations confirm that Nb atoms preferentially occupy the hollow (fcc and hcp) surface sites, whereas oxygen atoms, which bridge two neighboring cations are

located in on-top surface Au sites (Fig. 6.3c). There is a slightly different local environment of the fcc and hcp Au hollow adsorption sites and this results in the Nb cations in the hcp sites being located 1 pm further away from the surface than those in the fcc sites. Compared to the hypothetical calculated freestanding honeycomb monolayer which is perfectly flat (Fig. 6.4b), the Au-supported Nb₂O₃ film has significant structural polarization (rumpling) $\delta_{\text{ZNb-O}} = 0.93 \text{ \AA}$, the anions relaxing outwards and the cations approaching the Au(111) surface (Fig. 6.4a). Such film rumpling helps accommodate the lattice mismatch between the gold substrate and the freestanding honeycomb monolayer [$a_{\text{Nb}_2\text{O}_3} \sim 6.67 \text{ \AA}$, $a_{\text{Au}}(2 \times 2) = 5.77 \text{ \AA}$] while allowing a quasi-negligible contraction of the cation-anion distance ($d_{\text{Nb-O}} = 1.91 \text{ \AA}$) with respect to the freestanding reference ($d_{\text{Nb-O}} = 1.93 \text{ \AA}$).

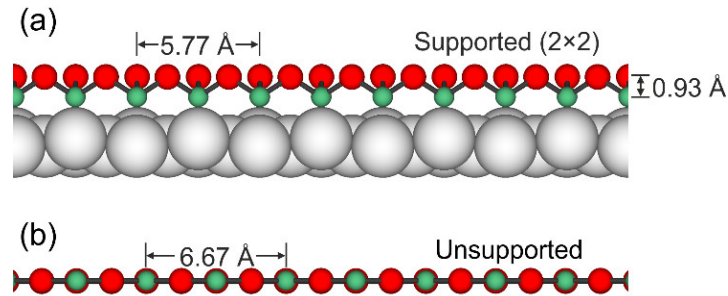


Fig. 6.4. Side views of the calculated structures of (a) Au(111)-supported and (b) freestanding Nb₂O₃ films. Nb atoms are shown in green, O atoms are shown in red and Au atoms are shown in grey.

6.4.2 Adhesion energy

The oxide-metal interaction strength can be estimated by the adhesion energy $E_{\text{adh}} = -[E(\text{Nb}_2\text{O}_3/\text{Au}) - E(\text{Nb}_2\text{O}_3) - E(\text{Au})]$, where $E(\text{Nb}_2\text{O}_3/\text{Au})$, $E(\text{Nb}_2\text{O}_3)$, and $E(\text{Au})$ are the total energies of the oxide-covered slab, a freestanding fully relaxed oxide layer, and the bare gold slab, respectively. The calculated adhesion energy is 2.34 J/m^2 (4.2 eV per Nb₂O₃ formula unit or 14.6 eV/nm^2), typical of strongly interacting metal/oxide interfaces

or other honeycomb transition metal oxides on Au(111).^{60,180} The calculated adhesion energy is 4.2 eV per Nb₂O₃ formula unit. This number can be decomposed into two contributions, namely the elastic energy necessary to constrain the lattice parameter of the freestanding honeycomb monolayer to that of the gold substrate (-1.8 eV) and the oxide-metal interaction energy gained when bringing the oxide film into contact with the Au(111) surface (6.0 eV). Despite the large lattice mismatch between the freestanding oxide monolayer and the substrate lattices (16%), the efficient release of strain due to film rumpling enables the elastic term (unfavorable for adhesion) to remain roughly a third of the strength of the oxide-metal interaction term.

6.4.3 Electronic structure

The substrate-induced changes of the electronic structure can be best assessed via modifications of the cation magnetic moments μ_{Nb} , charges Q_{Nb} , and the LDOS with respect to the freestanding reference monolayer.

The freestanding flat Nb₂O₃ honeycomb monolayer is a Mott-Hubbard semiconductor with purely cationic states at the top of the valence band and at the bottom of the conduction band, Fig. 6.5a. The Fermi level is located in the half-filled majority band of $d_{xz}+d_{yz}$ character, in agreement with reference [14]. The filled majority d_{z^2} state, which contains the second valence electron of the Nb⁺³ cation, is located about 1 eV below the Fermi level. While the Bader charge $Q_{\text{Nb}} = 1.61$ e does not straightforwardly represent the Nb⁺³ formal charge, the cation magnetic moment $\mu_{\text{Nb}} = 1.89 \mu_{\text{B}}$ is very close to the expected formal +2 value.

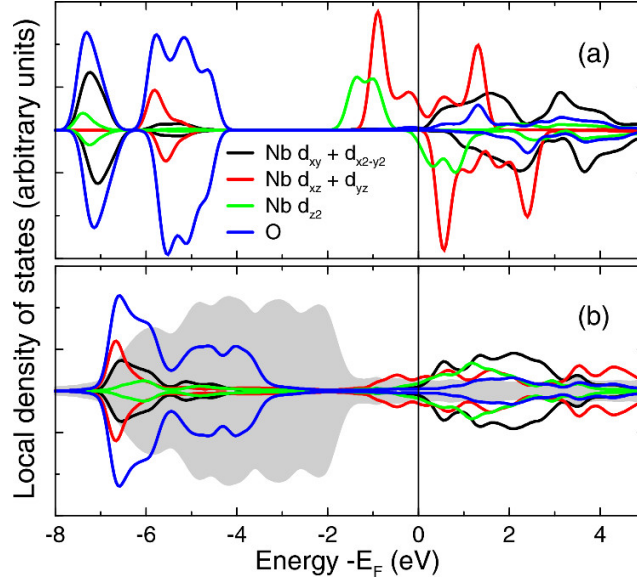


Fig. 6.5. Atom- and orbital- projected densities of states of (a) a freestanding and (b) an Au-supported Nb_2O_3 honeycomb monolayer. A broadening of 0.2 eV has been systematically applied. The energy scales of the two systems are aligned by their Fermi levels.

All these electronic characteristics are substantially different in the Au-supported Nb_2O_3 monolayer. There is a well pronounced depletion of the purely Nb d states at the top of the valence band, consistent with the reduced cation contrast in the filled state STM images (Fig. 6.2c). As shown in Fig. 6.5b, due to the rumpled geometry of the supported film, the d_{z^2} component loses its atomic-like character and hybridizes with the rest of the Nb d band. A similar difference can also be seen in the $d_{xz}+d_{yz}$ band, which is significantly larger. Both d_{z^2} and $d_{xz}+d_{yz}$ states lose their spin polarized character and are visibly depleted. The cation magnetic moment μ_{Nb} is entirely quenched ($\mu_{\text{Nb}} = 0 \mu_{\text{B}}$) and the cation charge is increased by 0.55 e ($Q_{\text{Nb}} = 2.16 \text{ e}$). These changes are associated with a particularly large electron transfer from the film towards the Au substrate, $Q_{\text{Au}} = -1.28 \text{ e}$ per Nb_2O_3 unit. Although Bader charges and magnetic moments do not straightforwardly account for the formal oxidation states, the calculated changes are consistent with an increase of the Nb oxidation state from 3+ in the freestanding film to 4+/5+ in the supported one, with some uncertainty in their assignment due to the metallic character of

the system. Similar changes in cation oxidation states have previously been reported in Ti_2O_3 and V_2O_3 honeycomb monolayers on $\text{Au}(111)$ substrates.⁶⁰

The origin of such a large electron transfer can be traced back to the important offset between the Fermi levels of the separated systems: the freestanding film and the bare gold surface, whose calculated work functions are equal to 3.5 eV and 5.4 eV, respectively, within the present computational set-up. Due to the relatively small electronegativity of niobium, the valence band maximum in the freestanding honeycomb monolayer is located nearly 2 eV above the Fermi level of the gold substrate. Such a band misalignment is consistent with a depletion of the majority Nb d_{z^2} and $d_{xz}+d_{yz}$ orbitals and an electron transfer towards the Au surface once the two systems are in contact, and was also invoked in other $\text{M}_2\text{O}_3/\text{Au}$ systems.⁶⁰

As a consequence of this electron transfer, the gold surface becomes negatively charged and electrostatically repels (attracts) anions (cations), thus inducing positive film rumpling.^{173,174} This electronic polarization allows a contraction of the Nb_2O_3 layer and effectively reduces the lattice mismatch with the gold substrate.

6.5 Point defects in (2×2) Nb_2O_3 monolayer on $\text{Au}(111)$

Fig. 6.6 shows STM images of a common triangular vacancy defect in the (2×2) Nb_2O_3 monolayer on $\text{Au}(111)$. Fig. 6.6 shows the vacancy located at the Nb site in the honeycomb lattice. Experimental STM images with two different tip terminations show the vacancy via Nb state (Fig. 6.6a) and O state (Fig. 6.6b). This defect is a Nb atom vacancy. Because the Nb_2O_3 monolayer is grown in an oxidative atmosphere, the presence of oxygen favors the Nb_2O_3 film to be slightly oxygen-rich. A Nb atom is removed from a Nb_2O_3 film which leaves a single Nb vacancy in the honeycomb lattice and three dangling O atoms surrounding the Nb site (Fig. 6.6c). The stoichiometry of the

honeycomb film then becomes $\text{Nb}_{2-x}\text{O}_3$. These defects are present after annealing a $\text{Nb}_2\text{O}_3/\text{Au}(111)$ surface in 10^{-4} Pa O_2 at 400°C , which further supports the interpretation of the triangular defect as a Nb atom vacancy.

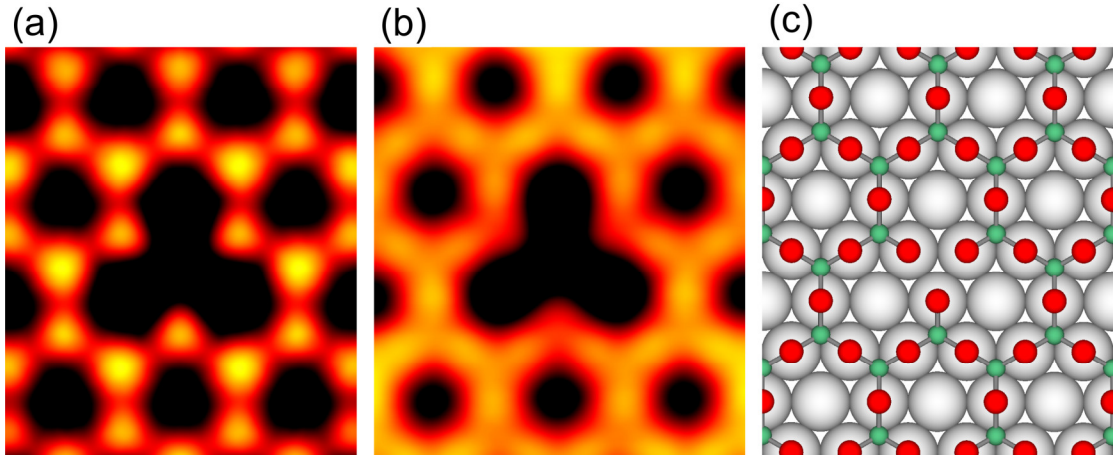


Fig. 6.6. (a) Experimental empty states STM image (averaged from 150 raw frames, image width 1.7 nm, $V_s = 1$ V and $I_t = 0.18$ nA) and (b) filled states STM image of the Nb vacancy defect (averaged from 60 raw frames, image width 1.7 nm, $V_s = -0.5$ V and $I_t = 0.18$ nA). (c) A schematic of the Nb vacancy defect.

6.6 Conclusions

A honeycomb (2×2) Nb_2O_3 monolayer was successfully grown on an $\text{Au}(111)$ substrate by Nb deposition and oxidation, and studied using STM, LEED and DFT simulations. The results of our investigations show that the structure is consistent with a particularly strong interaction between the Nb_2O_3 film and the $\text{Au}(111)$ substrate. It is accompanied by large interfacial electron transfer, a change of Nb oxidation state and substantial film rumpling. The rumpling reduces the in-plane lattice parameter of the oxide monolayer compared with a freestanding film and thereby improves the lattice matching with the $\text{Au}(111)$ substrate. Careful STM image processing using multiple frame averaging was able to discriminate between Nb fcc and hcp adsorption sites in qualitative agreement with the simulations. A triangular vacancy located at Nb site has been observed and interpreted as

a Nb atom vacancy. This new two-dimensional oxide enriches the family of oxide monolayers of M_2O_3 stoichiometry on metal substrates and raises the enticing prospect of the creation of mixed cation $A_xB_{2-x}O_3$ ($0 \leq x \leq 2$) honeycomb structures.

Chapter 7. NbO_x nanostructures on Au(111) in the submonolayer regime

7.1 Introduction

Here we report on an investigation of the growth of Nb oxide nanostructures on Au(111). Because Nb has oxidation states ranging from 2+ to 5+, this gives rise to various Nb-O coordination motifs, which can in turn result in the formation of a variety of oxide nanostructures. Previous computational results show that Cu(111) and Cu₂O/Cu(111) supported Nb oxide trimer clusters (Nb₃O₅ and Nb₃O₇) have planar structures, and Nb oxide tetramer clusters (Nb₄O₇ and Nb₄O₁₀) have cage structures.¹³⁸ In this chapter we show that planar Nb oxide atomic clusters can be grown on an Au(111) surface. Furthermore, larger Nb oxide nanostructures with triangular shapes and of various sizes are observed on Au(111). The structure of these nanostructures is characterized using STM and atomic models are proposed. The stability of the nanostructures is studied using in-situ STM imaging at elevated temperatures.

7.2 Experimental methods

The experiments were performed in a UHV system at a base pressure of 10⁻⁸ Pa. Measurements were carried out in a JEOL JSTM 4500XT instrument which includes STM

analysis facilities. Polished Au single crystals (SurfaceNet GmbH, Germany) cut in the (111) termination were cleaned by repeated sputtering and annealing cycles. Mica-supported Au(111) single crystals (Agilent Technologies, U.K.) were also used as substrates. Both types of Au(111) substrates were sputtered by Ar^+ ions (0.75-1 kV) and UHV annealed to 600 °C for 1.5 h resulting in the herringbone reconstruction. Nb vapor was deposited using an e-beam evaporator (Oxford Applied Research EGN4) from a 99.99% pure Nb rod supplied by Goodfellow, U.K. The surfaces were then annealed in 10^{-6} Pa O_2 at 500-600 °C for 15-60 mins to create the niobium oxide nanostructures. Constant current STM images, using etched tungsten tips, were taken at room temperature and elevated temperatures. Constant current STM images in Fig. 7.7 were taken at elevated temperatures in the range 100-600 °C. Most of the STM images presented in this chapter are the result of MFA using a software package called Smart Align with the general method described in Ref.[¹⁹] and the specific application to STM described in Chapter 4.

7.3 Results and discussion

7.3.1 Morphology of niobium oxide films

Fig. 7.1a-b shows the Au(111) surfaces following Nb deposition at room temperature and annealing in 10^{-6} Pa O_2 at 500 °C for 15 minutes. Fig. 7.1a shows an Au(111) surface covered by 0.07 monolayer (ML, where 1 ML coverage corresponds to an Au surface fully covered by one layer of Nb oxide). Nb oxide (NbO_x) forms three main types of nanostructures namely atomic clusters, islands with a close-packed structure, and monolayer epitaxial films with a honeycomb (2×2) structure. The (2×2) honeycomb structure is well-ordered and unrotated with respect to the Au(111) substrate and serves as an excellent reference to determine the exact periodicity and orientation of the other

structures. Atomic clusters consist of several bright protrusions with widths ranging from 0.8 to 2 nm in the STM images. The close-packed islands have widths ranging from 2 to 4 nm. More than 90% of the observed close-packed islands have a triangular shape. The remaining fraction being related structures such as hexagons, truncated triangles and structures merged from these. We therefore interpret the triangular island in Fig. 7.1a as the favored structure of close-packed islands under the conditions of our experiments. Fig. 7.1b shows a NbO_x/Au(111) surface prepared under the same experimental conditions as in Fig. 7.1a but at a higher Nb oxide coverage of 0.25 ML. The merging of several nanostructures results in the formation of larger islands. These merged structures act as the precursor of the (2 × 2) oxide monolayer films.

Fig. 7.1c shows the morphology of the Au(111) surface following Nb deposition at room temperature and annealing in 10⁻⁶ Pa O₂ at 600 °C for 30 minutes. Nb oxide forms triangular islands and the (2 × 2) honeycomb structure. When the oxide coverage is increased to 0.31 ML (Fig. 7.1d), the honeycomb monolayer films grow larger while the triangular islands have similar widths to the islands observed at lower coverages. The herringbone reconstruction is lifted underneath the oxide nanostructures and distorted in the bare regions (Fig. 7.1a-d).

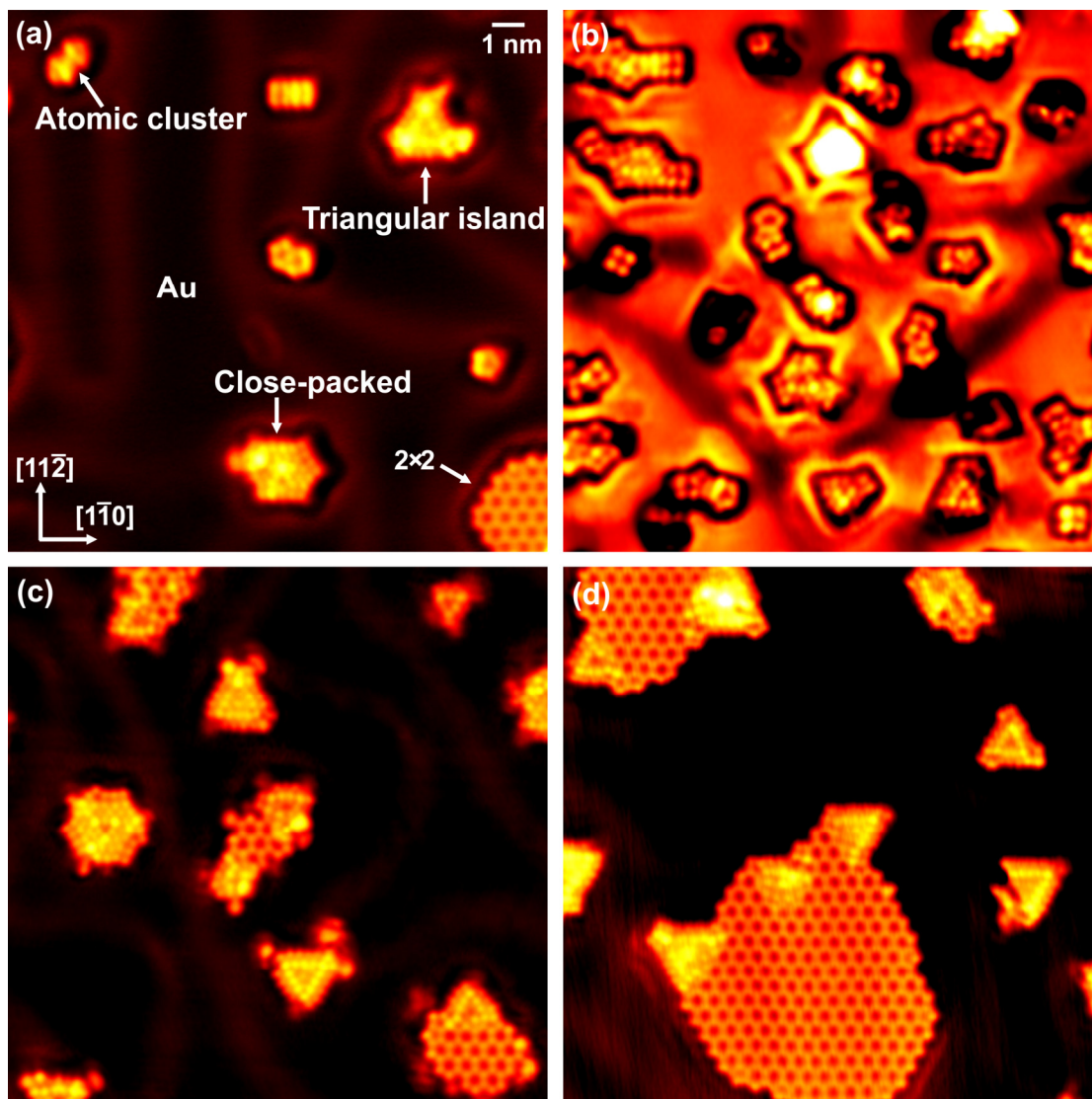


Fig. 7.1. STM images of niobium oxide nanostructures grown on Au(111). Nanostructures at the coverages of (a) 0.07 ML and (b) 0.25 ML following Nb deposition at room temperature and annealing in 10^{-6} Pa O_2 at 500 °C for 15 minutes. Nanostructures at the coverages of (c) 0.14 ML and (d) 0.31 ML following Nb deposition at room temperature and annealing in 10^{-6} Pa O_2 at 600 °C for 30 minutes. The STM images from (a-d) are generated from 119, 86, 13, 71 frames using MFA to enhance the signal-to-noise ratio, details described in the Appendix C. The image widths for all panels are 18.0 nm. The experimental STM parameters are (a) $V_s = 0.4$ -1 V and $I_t = 0.28$ nA, (b) $V_s = 0.25$ -0.6 V and $I_t = 0.24$ nA, (c) $V_s = 1$ V and $I_t = 0.24$ nA and (d) $V_s = 0.4$ -1 V and $I_t = 0.26$ nA.

7.3.2 Structure of NbO_x atomic clusters

Fig. 7.2 shows NbO_x atomic clusters with rectangular shapes of different sizes. The first row in Fig. 7.2 shows the STM images of each cluster. The STM images (in Fig. 7.2 top row) show atomic clusters consisting of four, six, eight and ten bright protrusions. All rectangular clusters are found in three rotational orientations, corresponding to the three-fold symmetry of the Au(111) substrate and thereby demonstrate an epitaxial relationship with Au(111). The clusters consist of a single layer of Nb and O atoms. The maxima in the clusters are systematically higher than the Nb atoms in the Nb₂O₃ (2 × 2) structure by 0.2 ± 0.1 Å, indicating that the clusters are monolayer thin. This height difference is independent of the applied sample bias.

All the clusters consist of a square unit cell of four bright spots. The clusters in Fig. 7.2b-c also include a rectangular unit cell of four bright spots. Line scans taken along the $[1\bar{1}0]$ direction for the four structures reveal a distance of 4.0 ± 0.3 Å between the two maxima in a square and a distance of 3.0 ± 0.3 Å between the maxima in the width of rectangle. Maxima distances for individual clusters are shown in the first panel of Fig. 7.2 and each distance is averaged from 20-60 bond measurements.

The simulated STM image of a Nb₄O₈ cluster in Fig. 7.2e reproduces the experimental image of the tetramer cluster in Fig. 7.2a. The cluster is an eight-membered ring consisting of four Nb atoms sitting close to the Au-hollow sites and four O atoms close to the Au-top site (Fig. 7.2f). Four peripheral O atoms are attached to the Nb atoms and they slightly stick out from the 2D plane (Fig. 7.2g). The bright spots in the simulated STM image originates the hybridization between a Nb atom and a dangling O atom.

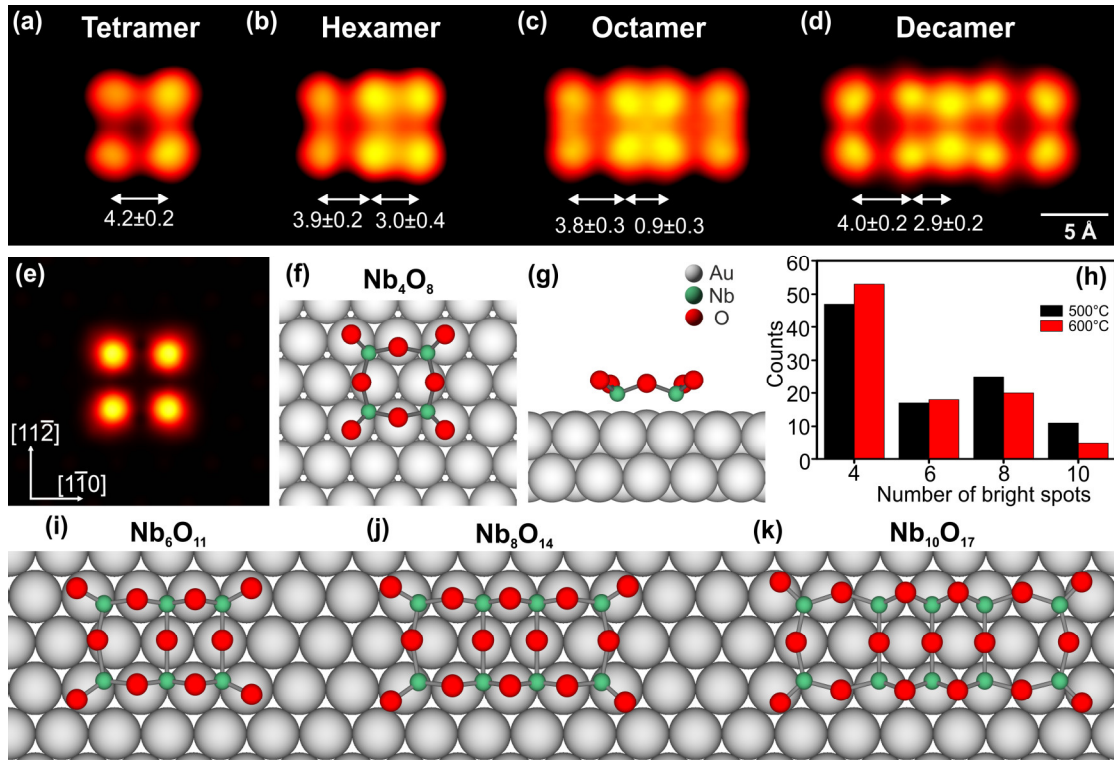


Fig. 7.2. Structures of rectangular atomic clusters. (a-d) Experimental STM data of tetramer, hexamer, octamer and decamer clusters. The bond lengths are in Å. (e) A simulated STM image of the tetramer cluster. (f) Top view and (g) side view of the atomic models for the tetramer clusters, with Nb atoms in green, O atoms in red and Au atoms in grey. (h) Occurrence histogram for rectangular Nb oxide clusters of different sizes. (i-k) Schematics for the hexamer, octamer and decamer clusters. The STM images from (a-d) are generated from 56, 112, 240 and 36 frames using MFA. Image parameters are (a) $V_s = 1.0$ V, $I_t = 0.22$ nA, (b) $V_s = 1.0$ V, $I_t = 0.22$ nA, (c) $V_s = 1.0$ V, $I_t = 0.18$ nA, and (d) $V_s = 0.4$ V, $I_t = 0.22$ nA. The STM simulations parameters are $E - E_F = +1$ V, distance from the center of the first Au substrate plane is 6 Å.

The atomic structures of the rectangular clusters in Fig. 7.2b-d can be derived by scaling up the model of a Nb₄O₈ cluster, because they all have the well-defined square elements. As shown in Fig. 7.2i-k, the stoichiometries for the hexamer, the octamer and the decamer are Nb₆O₁₁, Nb₈O₁₄ and Nb₁₀O₁₇, respectively. The Nb₄O₈ cluster is the most oxygen-rich and the oxygen stoichiometry decreases as the cluster grows larger.

The tetramer is the most frequently observed structure among the rectangular clusters, followed by the octamer, hexamer and decamer clusters, as shown in Fig. 7.2h. Growth of

rectangular clusters at different annealing temperature has little effect on their statistics (Fig. 7.2h). The tetramer cluster is the most favored cluster structure because it is the most oxidized structure. This allows the Nb atoms to have higher oxidation states which may be closer to the common oxidation state for a Nb atom is 5+. This is consistent with DFT simulations that Nb atoms supported on an Au surface tend to stick to as many O atoms as possible.

Freestanding Nb oxide atomic clusters have been modeled using density functional theory.¹⁸¹ The freestanding four-fold Nb oxide cluster is Nb₄O₁₀, which reduces to NbO_{2.5} whereas the Au supported tetramer cluster has stoichiometry of Nb₄O₈, which breaks down to NbO₂. Thus the electronegative Au substrate receives electrons from Nb and stabilizes the sub-oxygen stoichiometric Nb oxide clusters. The freestanding Nb₄O₁₀, Nb₆O₁₅, Nb₈O₂₀ and Nb₁₀O₂₅ clusters systematically show a square Nb₄O₈ unit cell. The unit contains four Nb atoms, four bridging O atoms and four terminal O atoms and it is similar to the schematic shown in Fig. 7.2f. Thus the Au substrate acts as a support but it does not change the inherent square structure of the Nb oxide clusters compared their freestanding counterpart. This is in contrast to the V₆O₁₂ cluster on Rh(111) that the strong V₆O₁₂-Rh interaction leads to a planar structure that does not exist in the gas phase.

Experimental STM observations of polygonal and merged clusters are presented in the top row of Fig. 7.3. The main feature in the images is the clustering of (a) five, (b) six, (c) seven, (d) eight and (e) sixteen bright spots. The maxima in the clusters are higher than the Nb atoms in the Nb₂O₃ (2 × 2) structure by 0.2 ± 0.1 Å and this height difference is independent of the applied sample bias. The bright maxima are interpreted as the location of Nb atoms and the schematics are shown in the bottom panel of Fig. 7.3. The Nb atoms

in the clusters are bond to a terminal O atom because the oxide structures are grown in an oxidative atmosphere.

Fig. 7.3(a) shows a pentamer structure. The bottom-left interior angle of the pentamer cluster is close to 120° which is the angle between the $[1\bar{1}0]$ and $[\bar{1}10]$ directions of Au(111), and it deviates from the interior angle of a regular pentamer of 108° . The difference indicates that the pentamer cluster is distorted when supported on Au(111), which suggests a strong NbO_x-Au interaction. The maxima distance in the pentamer is 4.0 ± 0.5 Å which corresponds to two connected Nb-O bonds. An atomic model of a pentamer cluster is shown in Fig. 7.3f. The cluster is a 10-membered ring containing five Nb atoms, five bridging O atoms and five peripheral O atoms, and its stoichiometry is Nb₅O₁₀.

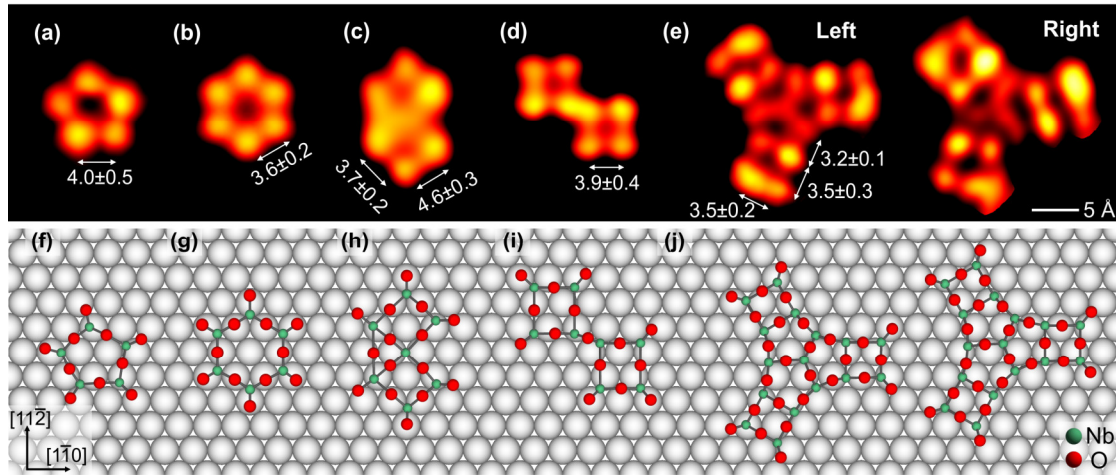


Fig. 7.3. Structure of NbO_x atomic clusters. Experimental STM data and proposed atomic models of (a & f) pentamer, (b & g) hexagonal hexamer and merged clusters containing (c & h) seven, (d & i) eight and (e & j) sixteen maxima. The maxima distance is in Å. Nb and O atoms are green and red balls, respectively. The Au substrate atoms are not shown. The STM images in (a-e) are generated from 60, 75, 56, 56, 26 (left) and 12 (right) frames using MFA. Image parameters are (a) $V_s = 1.0$ V, $I_t = 0.18$ nA, (b) $V_s = 0.8$ V, $I_t = 0.21$ nA, (c) $V_s = 1.0$ V, $I_t = 0.22$ nA, (d) $V_s = 1.0$ V, $I_t = 0.22$ nA, (e) left: $V_s = 0.4$ V, $I_t = 0.24$ nA, right: $V_s = 0.2$ V, $I_t = 0.25$ nA.

Fig. 7.3b & g show the structure of a hexagonal hexamer cluster. The hexamer has a preferred orientation with the $[11\bar{2}]$ direction of the Au(111) substrate. The maxima

distance is 3.6 ± 0.2 Å. A tentative atomic model of a Nb₆O₁₂ structure is shown in Fig. 7.3g. Six Nb atoms are located close to Au-hollow sites, six bridging O atoms are located close to Au-top sites and six dangling O atoms are attached to the Nb atoms. A similar hexamer cluster has been observed in the V₆O₁₂ cluster grown on Rh(111).¹⁴⁰ DFT calculations indicate that the V₆O₁₂ cluster is a 12-membered ring containing six V atoms and six O atoms, with six peripheral O atoms attached to the V atoms.

Fig. 7.3c shows a cluster of seven maxima. The central axis of the cluster goes along the $[11\bar{2}]$ direction of the Au(111) substrate. The maxima distances are classified into 3.7 ± 0.2 Å and 4.6 ± 0.3 Å. Fig. 7.3h shows an atomic model of this structure. It is formed by attaching two tetramer clusters to one common corner in which one Nb atom is shared by the two adjoining squares. One Nb atoms next to the common corner is further connected to its counterpart in the other square by an O atom. The cluster has Nb₇O₁₅ stoichiometry. Fig. 7.3d shows a cluster of eight maxima. The cluster has a preferred orientation with respect to the $[11\bar{2}]$ direction of the Au(111) substrate. The cluster consists of two square unit cells with an average maxima distances of 3.9 ± 0.4 Å. The atomic model is shown in Fig. 7.3i. Two tetramer clusters are bridged by a Nb-O-Nb bond at one corner. The cluster has Nb₈O₁₅ stoichiometry.

Fig. 7.3e shows two Nb₁₆O₂₇ clusters that have chirality associated with them. The cluster exhibits two types of structures that are non-superimposable mirror images of one another. The maxima distances in the cluster range from 3.2 Å to 3.5 Å. The Nb₁₆O₂₇ cluster consists of three Nb₄O₈ tetramers that are connected by a central Nb₄O₃ cluster Fig. 7.3j. The cluster has two adsorption configuration on Au(111), one with the central Nb atom in the Au-hcp site and the other with the central Nb atom in the Au-fcc site, resulting in two types of chiral structures.

7.3.3 Structure of NbO_x triangular islands

Fig. 7.4 shows STM images of the NbO_x nanostructures with a close-packed structure and a triangular shape. The edges consist of bright atomic features in the STM images. The bright spots exhibit a hexagonal surface structure with an atomic periodicity of 3.17 ± 0.23 Å. The lattice mismatch between the NbO_x nanostructure and the (1×1) unit cell of Au substrate (2.89 Å) gives rise to an incommensurate structure and thus the triangular islands display a moiré-like modulation in the STM images (Fig. 7.5d). The outermost atomic row at the edge has apparent height similar to the heights of Nb sites in the (2×2) honeycomb structure. The second atomic row is higher than the Nb sites in the (2×2) honeycomb structure by 0.3 Å. The apparent heights of the edges are independent of the applied sample bias in the STM images. Fig. 7.4b shows a triangular island merged with the (2×2) honeycomb structure. The straight boundary between two structures implies that there is no rotation between the triangle and the honeycomb structure.

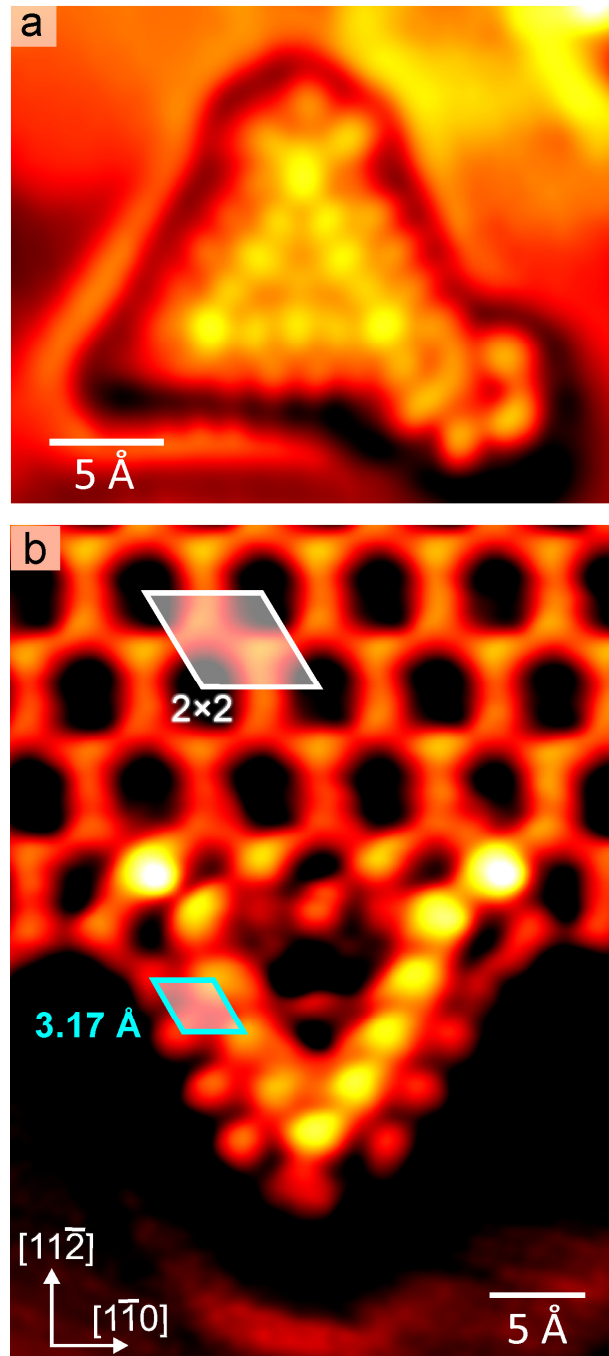


Fig. 7.4. Structure of NbO_x triangular islands. (a) STM image of an isolated triangular island. (b) STM image of a triangular island merged with the honeycomb structure, with unit cells indicated. The STM images are generated from (a) 86 and (b) 64 frames using MFA. Image parameters are (a) image width 4.5 nm, $V_s = 0.2\sim 0.3$ V, $I_t = 0.24$ nA, and (b) image width 3.2 nm, $V_s = 0.059$ V, $I_t = 0.24$ nA.

We imaged numerous samples containing NbO_x triangles with STM and show their size distribution in Fig. 7.5. Their sizes are categorized by the number of Nb atoms (N) along the bright atomic line of the triangle. The bright atomic lines are generally defect-free, whereas the outermost edge lines often contain defects such as vacancies or adatoms and the number of Nb atoms is sometimes unclear. Fig. 7.5a-g shows a series of NbO triangles with their sizes ranging from $N = 3$ to $N = 9$. The NbO_x triangles of various sizes have the same characteristic bright atomic lines and the 3.17 Å periodicity at the edges.

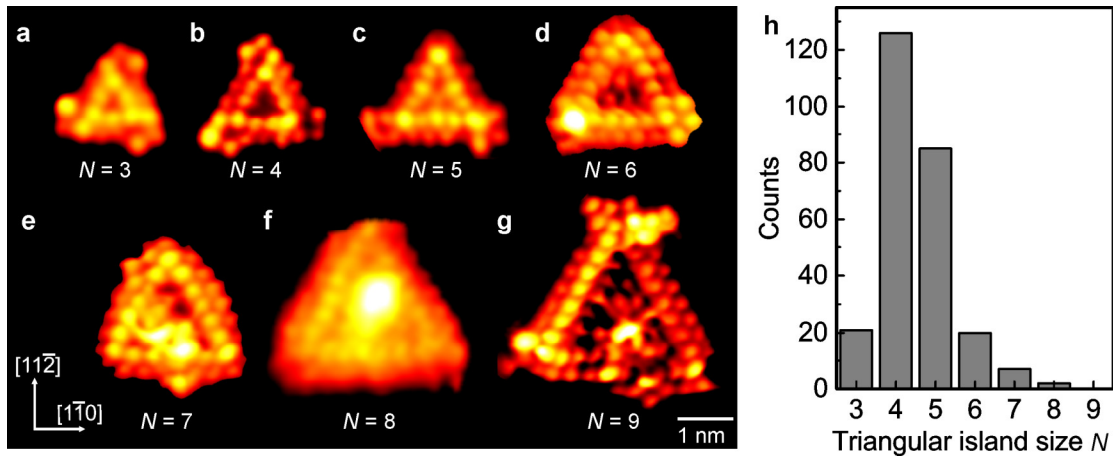


Fig. 7.5. Structures of rectangular triangular NbO_x islands. (a-g) Experimental STM data of triangular islands ranging from $N = 3$ to $N = 9$. (h) Size-distribution histogram of the triangular NbO_x islands grown by annealing Nb in 10^{-6} Pa O₂ at 600 °C for 30 minutes. The STM images from (a-e) & (g) are generated from 56, 71, 86, 64, 64 and 64 frames using MFA. Image parameters are (a) $V_s = 1.0$ V, $I_t = 0.22$ nA, (b) $V_s = 0.4$ -1.0 V, $I_t = 0.26$ nA, (c) $V_s = 0.2$ -0.3 V, $I_t = 0.24$ nA, (d) $V_s = 0.059$ V, $I_t = 0.24$ nA, (e) $V_s = 0.059$ V, $I_t = 0.24$ nA, (f) $V_s = 0.9$ V, $I_t = 0.19$ nA and (g) $V_s = 0.059$ V, $I_t = 0.24$ nA.

The frequency of each triangle structure as a function of its size (N) is plotted in the histogram shown in Fig. 7.5h. The triangle structures are grown by annealing Nb in 10^{-6} Pa O₂ at 600 °C for 30 minutes. The triangles with a side length of $N = 4$ are most frequently observed (48 % of 262 triangles analyzed), followed by triangles with $N = 5$ (32 %). The small triangles ($N = 3$ -6) often contain defects such as adatoms or vacancies at their corners. The large triangles ($N = 7$ -8) contain defects in the center, on the edges

and corners. The largest structure ($N = 9$) contains many defects across the island. Triangles with sizes above $N = 9$ were not observed. Most of the triangular islands have the same edge structures with a $3.17 \text{ \AA}$ periodicity. The triangular islands contain a variety of structural centers. The centers of the small triangles ($N = 3, 4$) appear as black holes in the STM images. The medium triangles ($N = 5$) contains one faint atomic feature in the structural center and the medium triangles ($N = 6$) has three faint spots. The large triangles ($N = 7-9$) contain defects in their structural centers and the defects appear higher than the edges in STM images.

We propose the models for the NbO_x close-packed island with four Nb atoms on the edge, as shown in Fig. 7.6. The close-packed island is a laterally expanded $\text{NbO}(111)$ where the Nb atoms are separated by $3.17 \text{ \AA}$. The 10% lattice mismatch between the NbO layer and the (1×1) unit cell of $\text{Au}(111)$ lead to a coincidence structure. The Nb atoms shift gradually from Au-hollow sites to Au-bridge sites (Fig. 7.6c). The step edges are aligned along the $[1\bar{1}0]$ direction of $\text{Au}(111)$. The edges are decorated with dangling O atoms because the structures are grown in an oxidative atmosphere.

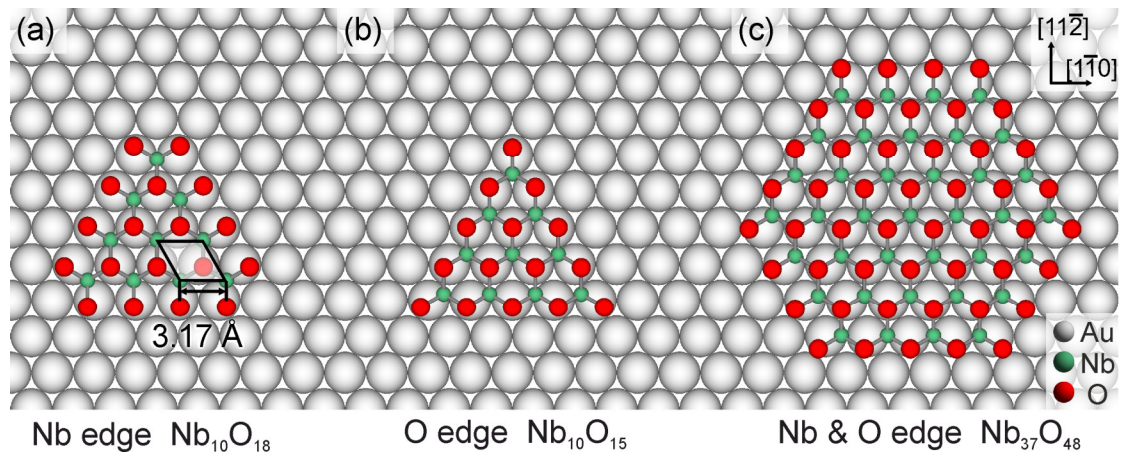


Fig. 7.6. Structural models of the triangular island with four Nb atoms on the edge. The overlayer has a lattice constant of $3.17 \text{ \AA}$ and is aligned with the $[1\bar{1}0]$ direction of $\text{Au}(111)$. (a) Nb terminated islands. (b) O terminated islands. (c) An island containing Nb and O edges.

STM results reveal that the monolayer close-packed NbO_x structure adopts a triangular shape under the oxidative conditions of synthesis, indicating that one type of edge is preferred over the other. Fig. 7.6a shows a model of a triangular islands with Nb-terminated edges and Fig. 7.5b shows an island model with O-terminated edges. Atomic models for the other sizes of triangular structures have a scaling relationship with the triangle model in Fig. 7.6a-b and thus are not shown here.

Additionally, STM results show hexagonal NbO_x close-packed islands with atomic spacing of 3.17 ± 0.40 Å and widths ranging from 2 to 4 nm (Fig. 7.1a & c). The hexagonal-shaped structures contain both Nb and O-terminated edges (Fig. 7.6c).

7.3.4 Thermal stability of NbO_x nanostructures on Au(111)

Fig. 7.7 shows the results of elevated temperature imaging experiments of NbO_x/Au(111) surfaces exposed to 10^{-6} Pa O₂. The STM image of Fig. 7.7(a) shows a NbO_x/Au(111) surface at room temperature. The surface contains dispersed atomic clusters, triangular islands and the honeycomb structure. The NbO_x/Au(111) surface was then heated to 300 °C and kept at this temperature for 1 h to minimize thermal drift. An STM image taken at 300 °C [Fig. 7.7(b)] shows that several clusters and nanocrystals have merged and larger islands have formed. The NbO_x/Au(111) surface was then heated to 360 °C and kept at this temperature for 1 h. An STM image taken at this temperature [Fig. 7.7(c)] shows mainly large islands merged from atomic clusters, triangular islands and the honeycomb structure, while isolated atomic clusters are now only rarely seen. After the NbO_x/Au(111) surface was heated to and kept at 400 °C for 1 h, the STM image taken at this temperature [Fig. 7.7(d)] shows further ripening of nanoislands and increased formation of the honeycomb structure. After the sample was heated to and kept at 500 °C for 1 h, in-situ STM imaging [Fig. 7.7(e)] of the NbO_x/Au(111) surface shows extensive

formation of the honeycomb structure and triangular islands, while atomic clusters are no longer observed. The sample was then heated to and kept at 600 °C for 1 h, where in-situ STM imaging shows that the morphology at 600 °C is similar to the surface heated to 500 °C.

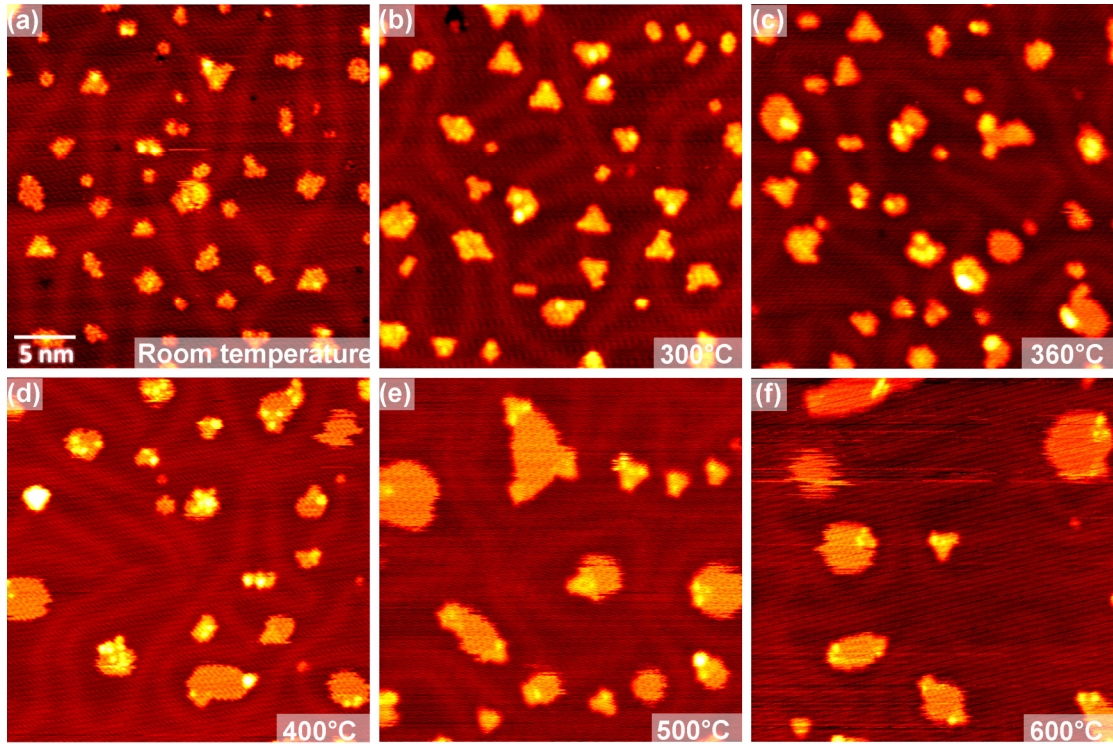


Fig. 7.7. Sequence of STM images of a niobium oxide decorated Au(111) surface exposed to 10^{-6} Pa O_2 at elevated temperature. (a) The $NbO_x/Au(111)$ at room temperature, covered with the honeycomb structure, triangular islands and atomic clusters. (b) After 1 h exposure to O_2 at 300 °C, ripening of atomic clusters is observed. (c) After 1 h exposure to O_2 at 360 °C, atomic clusters, triangular islands and honeycomb merge, and larger islands are formed. (d) After 1 h exposure to O_2 at 400 °C, the formation of the honeycomb structure increases. (e) After 1 h exposure to O_2 at 500 °C, the surface is mainly dominated by the honeycomb structure and triangular islands. (f) After 1 h exposure to O_2 at 600 °C, the experimental conditions have little further effect on the surface morphology. Image width for all the panels is 30 nm. The imaging conditions are (a) $V_s = 1.0$ V, $I_t = 0.16$ nA, (b) $V_s = 1.0$ V, $I_t = 0.17$ nA, (c) $V_s = 1.0$ V, $I_t = 0.18$ nA, (d) $V_s = 1.0$ V, $I_t = 0.16$ nA, (e) $V_s = 1.2$ V, $I_t = 0.16$ nA, and (f) $V_s = 1.2$ V, $I_t = 0.16$ nA.

In the experiments atomic clusters are converted into the (2×2) honeycomb structure. Some of the triangular islands can transform into the (2×2) structure. The triangles also act as pin-point defects that anchor the (2×2) structure undergoing diffusion. The (2×2) island to the left of the movie is merged with a triangle and its edges diffuse around the triangular island. Whereas the (2×2) island in the top-right corner of the movie is isolated, and its edges diffuse more rapidly than the (2×2) island pinned by a triangle. The triangles are present on the surface after annealing in oxygen for 6h at 600°C. They do not fully convert into the (2×2) structure with time.

7.4. Conclusions

The growth of a variety of niobium oxide clusters and nanostructures has been reported, to occur on an Au(111) surface as the result of the oxidation of metallic Nb. The structure and the stoichiometry have been elucidated by high resolution STM images. The planar Nb oxide clusters do not exist as stable entities in the gas phase but form spontaneously at the Au(111) surface. The oxygen-rich clusters are favored than other structures because Nb tends to be oxidized when supported on an Au(111) surface. The NbO_x triangular islands locally exhibit a hexagonal structure at the edges with an atomic periodicity of 3.17 Å. Despite a 10% lattice mismatch to the substrate, an epitaxial growth of the nanostructures is observed. The diffusion of the Nb-oxide nanostructures has been followed in elevated-temperature STM experiments and they coalesce into the (2×2) honeycomb structure.

The control over the synthesis of size-selected triangular islands is yet to be explored in this system and will be the subject of future investigations with possible interest for catalytic applications. It would also be informative to study the electronic properties of the characteristic bright lines in the triangular islands. Further theoretical modeling of the

atomic clusters and triangular islands is required to provide a thorough understanding of the properties and structures of the NbO_x/Au(111) system.

Chapter 8. Domain boundaries in the Ti_2O_3 and Nb_2O_3 honeycomb monolayers

8.1 Introduction

Here we investigate the domain boundary structures in epitaxial (2×2) honeycomb monolayer films of Ti_2O_3 and Nb_2O_3 supported on Au(111). A domain boundary is formed between two misaligned honeycomb domains. The lattice shift gives rise to a boundary gap consisting of four crystallographies. Four types of domain boundary structures are observed in the $\text{Ti}_2\text{O}_3/\text{Au}(111)$ honeycomb, with their atomic structures characterized using STM and modeled using DFT. The calculation of formation energies of the structural units gives a fundamental understanding of the stabilization mechanism of the domain boundaries in the $\text{Ti}_2\text{O}_3/\text{Au}(111)$ honeycomb. A larger variety of domain boundaries were observed in the $\text{Nb}_2\text{O}_3/\text{Au}(111)$ honeycomb film. The Nb_2O_3 boundaries are visualized using STM but their atomic structures are harder to define. The Ti_2O_3 and Nb_2O_3 films are grown using methods described in Chapter 5 and 6, respectively. The DFT calculations are performed by Dr Jacek Goniakowski and Dr Claudine Noguera (CNRS, FR).

8.2 Domain boundaries in Ti_2O_3 (2×2) honeycomb structure

8.2.1 Domain boundary crystallography in (2×2) Ti_2O_3 on Au(111)

Fig. 8.1 shows a domain boundary gap that occurs when one Ti_2O_3 domain is shifted with respect to another Ti_2O_3 domain by one Au periodicity (**a**). The shift is indicated by a black arrow in Fig. 8.1. The edges of Ti_2O_3 domains have terminations along the armchair (A) or the zigzag (Z) orientation. The two domains can align with the axis normal to the termination. The alignment is indicated using '1' and the related crystallographies are A1 for an armchair-terminated boundary and Z1 for a zigzag-terminated boundary. One domain can be laterally shifted with respect to the other domain by one Au periodicity. The lateral shift is represented by '2' and the related crystallographies are A2 for an armchair-terminated boundary and Z2 for a zigzag-terminated boundary. Thereby a domain boundary can have four types of crystallographies.

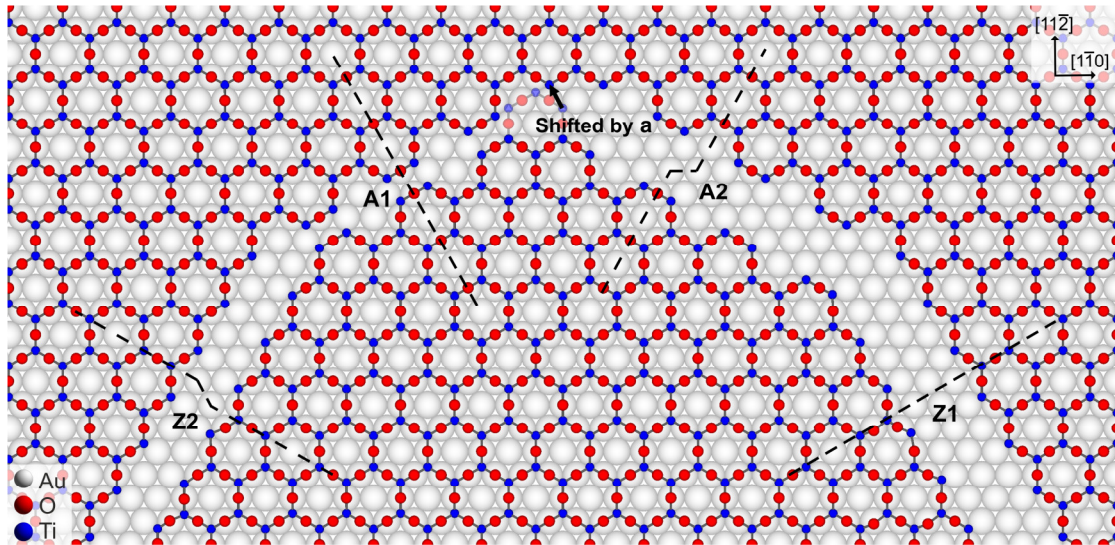


Fig. 8.1. Four crystallographies of one domain boundary in Ti_2O_3 . The boundary gap is generated by shifting one Ti_2O_3 domain with respect to the other by one Au periodicity (highlighted by a black arrow). The boundary gaps are labeled as A1, A2, Z1 and Z2. The alignments and the shifts between the two domains are visualized using dashed lines.

8.2.3 Structures of domain boundaries in (2×2) -Ti₂O₃/Au(111) film

Fig. 8.2 shows six representative STM images of domain boundary structures in the Ti₂O₃ honeycomb film. The panels below each STM images show the schematics where differently colored polygons represent the sizes of the rings including squares (orange), pentagons (red), hexagons (white), heptagons (blue) and octagons (green).

In Fig. 8.2a, two Ti₂O₃ domains form a boundary gap with the A1 crystallography. The gap is filled with alternating four and eight-membered rings and the boundary structure is called an A1-48 boundary. The boundary is frequently observed, as shown in Fig. 8.2(a, c, e, f). Fig. 8.2b shows two Ti₂O₃ domains that meet at a boundary with the Z1 crystallography. The boundary consists of several 5775 units and a lateral offset in the middle of the boundary. The offset is bridged by a pair of five-membered rings. Two domains in Fig. 8.2c form a boundary gap containing two segments with the A1 crystallography and two segments with the Z2 crystallography. The A1 segments are filled with four 48 units and the Z2 segments are filled with four shifted 558 units. In Fig. 8.2d, two Ti₂O₃ domains meet along their zigzag orientation and result in one Z1 segment and two Z2 segments. The Z1 segment contains two 5775 structures. The Z2 segments consist of two shifted 558 structures. In Fig. 8.2e, two domains form a long boundary consisting of four types of crystallographies. From the top of the image, the boundary starts with an A1 boundary containing 48 units, turns by 90° into a Z1-5775 boundary, transforms into two alternating Z2-558 and A2-5577 segments with a 60° turn, and makes another 60° turn into the A1 crystallography filled with the 5775 units. The STM image in Fig. 8.2f shows a Ti₂O₃ film merged from three domains. In the upper part of the images, three domains are separated by two A1-48 domain boundaries. In the lower part of the images, one complex boundary consists of A2-5577, Z2-558, Z1-5775 and A1-48 structural units.

Fig. 8.2 points to the limited domain boundary structures present in the Ti_2O_3 (2×2) honeycomb film.

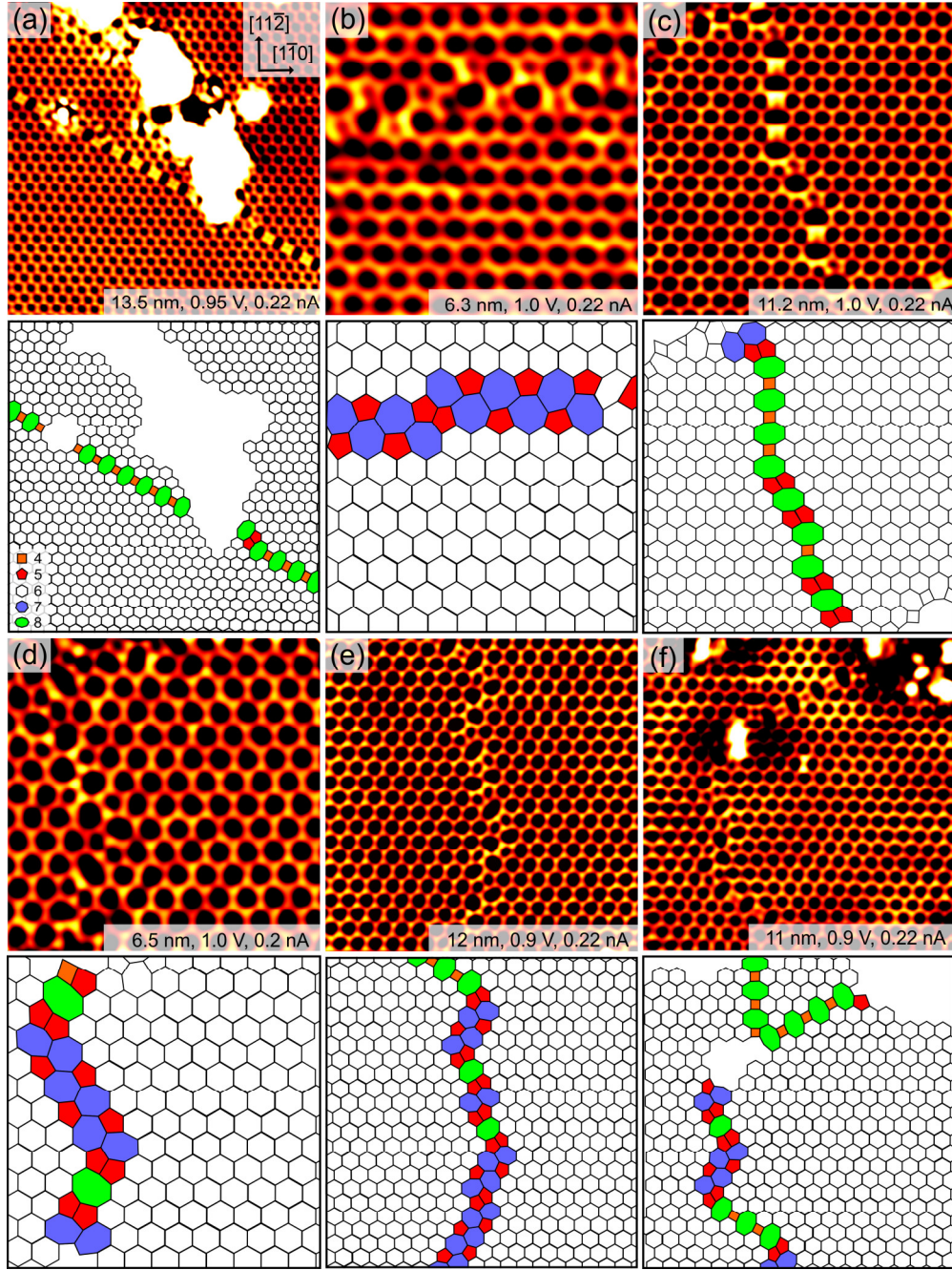


Fig. 8.2. Domain boundaries in Ti_2O_3 . STM images showing (a) an A1-48 boundary, (b) a Z1-5775 boundary, (c) a boundary of A1-48 and Z2-558 units, (d) a boundary of Z1-5775 and Z2-558 units. (e-f) complex boundaries consisting of A1-48, A2-5577, Z1-5775 and Z2-558 segments. For each image, schematics are shown below which display polygonal rings color-coded according to their sizes. The STM images from (a-c, e-f) are generated from 15, 11, 88 7, and 8 frames using MFA.

8.2.4 Atomic structures of domain boundaries

Fig. 8.3 shows the atomic structure of A1-48, A2-5577, Z1-5775 and Z2-558 boundaries in the Ti_2O_3 (2×2) monolayer. Four, five, seven and eight-membered rings combine to form periodic cells in the domain boundaries. Atomic models are shown in the third row of Fig. 8.3 and their periodic cells along the boundary are indicated by a black rectangle. Two Ti_2O_3 domains are laterally aligned in the A1 and Z1 boundaries and the symmetric axis is indicated in cyan in the first and third columns of Fig. 8.3. Two Ti_2O_3 domains are laterally shifted by one Au periodicity along the $[1\bar{1}0]$ orientation and the shift is highlighted in the second and fourth columns of Fig. 8.3. Image simulations (the second row of Fig. 8.3) calculated from these atomic models are in good agreement with the experimental STM images. One visible difference is that there is only one 5577 segment observed in the experimental image in Fig. 8.3b.

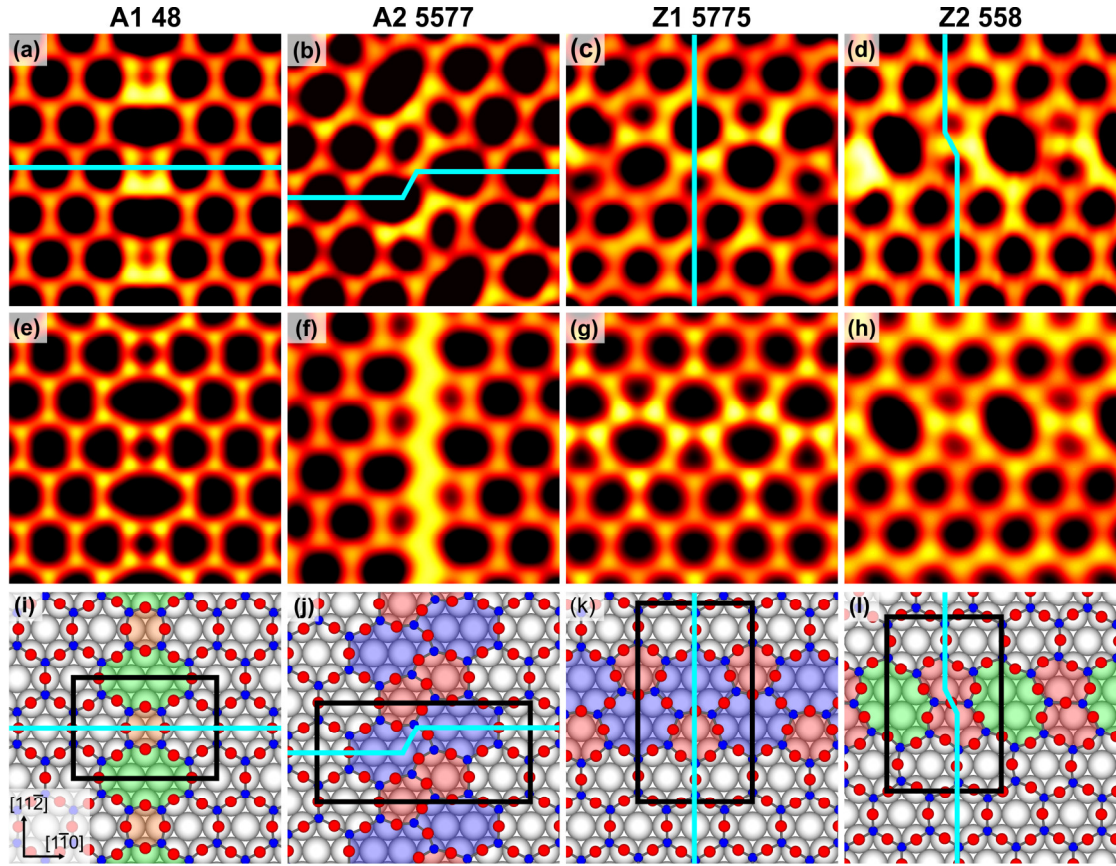


Fig. 8.3 Domain boundary structures in Ti_2O_3 honeycomb. (a-d) Experimental STM data, and (e-h) corresponding DFT simulations of A1-48, A2-5577, Z1-5775 and Z2-558 structures. (i-l) The atomic models including the Au(111) substrate atoms with Ti atoms in blue, O atoms in red and Au atoms in grey. The STM images from (a, b, d) are generated from 88, 7, and 88 frames using MFA. The experimental STM parameters of (a-d) are $V_s = 1.0$ V and $I_t = 0.22$ nA; $V_s = 0.9$ V and $I_t = 0.22$ nA; $V_s = 1.0$ V and $I_t = 0.20$ nA; $V_s = 1.0$ and $I_t = 0.22$ nA, respectively, with image widths of 2.7-2.8 nm for all cases. The periodic cells of the boundary structure are indicated. The alignment and the lateral shift between the two domains is highlighted in cyan. The simulation parameters $E - E_F = +2$ V, and distance from the center of the first Au substrate plane of 5.2 Å.

The solutions for the four domain boundary structures in $\text{Ti}_2\text{O}_3/\text{Au}(111)$ are summarized in Fig. 8.4. Each crystallography presents one domain boundary structure. From the left of the schematic, the boundary gap begins with a Z2 crystallography filled with the shifted 558 unit, makes a 30° turn into the A1 crystallography filled with the 48 unit, transforms into the A2 crystallography filled with the shifted 5577 unit by a 60° turn and transforms into the Z1 crystallography filled with the 5775 unit by a 30° turn.

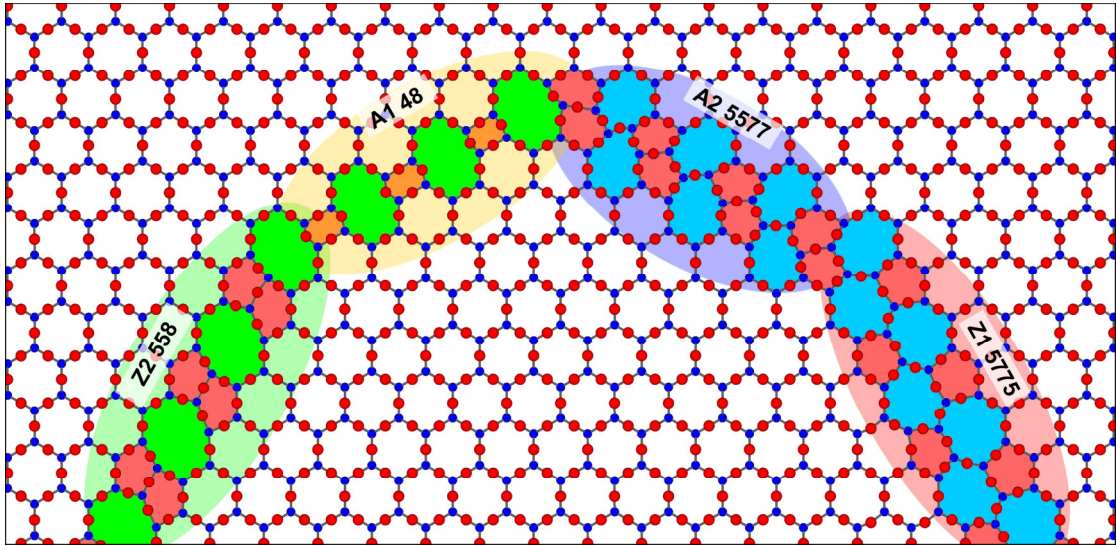


Fig. 8.4. Structural solutions of four types of Ti_2O_3 domain boundaries: A1-48 (yellow), A2-shifted 5577 (blue), Z1-5775 (red) and Z2-shifted 558 (green).

Stress induced by the interaction between the domains and these boundary cores is released by two main structural effects. On the one hand, compressive or tensile stresses are released by a contraction or an expansion of the Ti-Ti distances (the first row in Fig. 8.5), respectively, involving principally the distances between domain edges and boundary cores and the distances between edge and sub-edge atomic rows, in the direction perpendicular to the boundary. Compared to the pristine monolayer, we find a particularly strong $d_{\text{Ti-Ti}}$ expansion at the A2-5577 boundary, a moderate contraction at the A1-48

boundary, and a comparable in strength, but less homogeneous distortion at the Z1-5775 and Z2-585 ones. These distortions attenuate progressively within the domains. Inside the boundary cores, the Ti-Ti distances are also modified, but more weakly than those described above. Associated to these distortions are in-plane displacements of the cations (anions) off their preferential hollow (top) sites at the Au(111) surface, which gives rise to contractions (expansions) of the Ti-Au (O-Au) distances, as shown in the bottom row of Fig. 8.5.

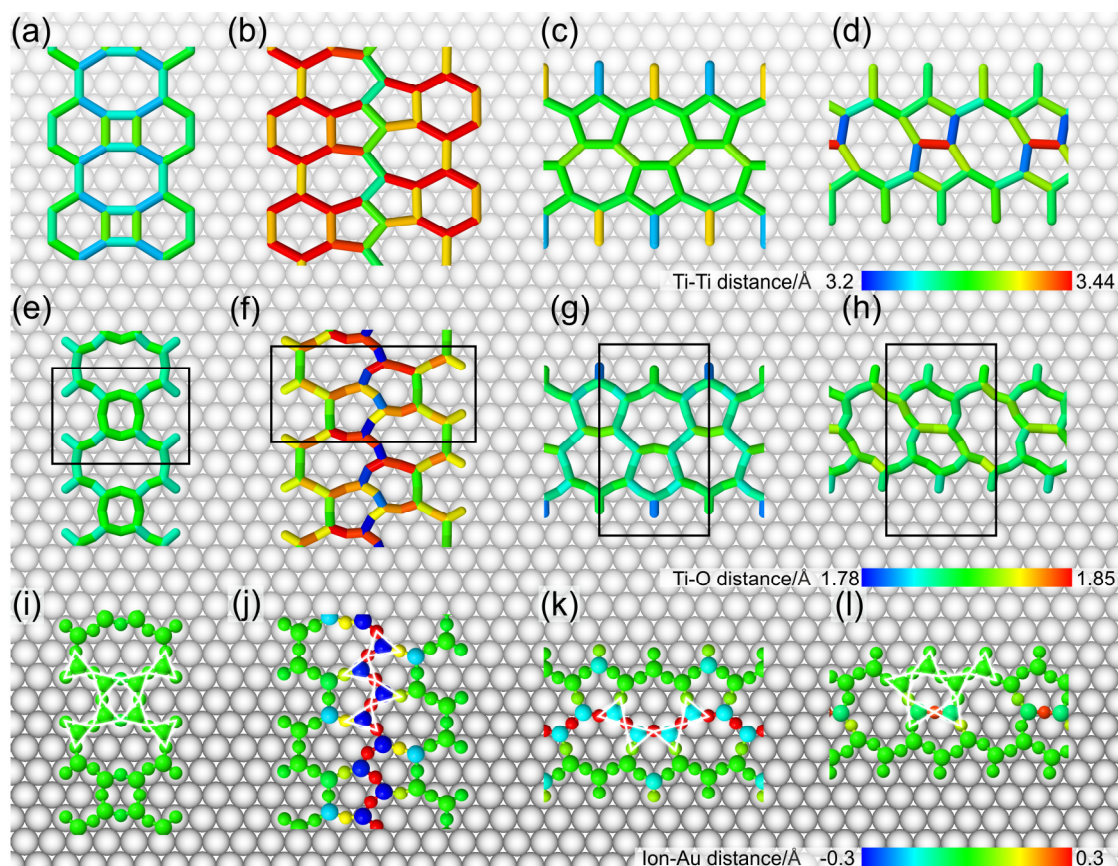


Fig. 8.5. DFT calculations showing variations of bond lengths and displacements of ions for the domain boundaries of A1-48, A2-5577, Z1-5775 and Z2-558. The bonds are colored according to an increase (red and yellow) or decrease (blue) of the bond length. The Ti-Ti bond lengths are shown in the first row, the Ti-O bond lengths are shown in the second row and the Ti-Au and O-Au distances are shown in the bottom row. TiO₃ entities undergoing rotations are indicated with triangles in the bottom row.

On the other hand, the core-domain interactions induce in-plane rotations of the TiO_3 entities (highlighted with triangles in Fig. 8.5i-l) which enable an efficient accommodation of both the stress and the structural mismatch while preserving the angles between the three Ti-O bonds around each cation. Thanks to such rotations, the Ti-O bond lengths at the (compressed) A1-48 boundary are only slightly modified despite a substantial contraction of the Ti-Ti distances and a reduced film rumpling (see Fig. 8.5e). Conversely, the symmetry-driven absence of such rotations in the vicinity of Z1-5775 boundary results in a visible contraction of the Ti-O distances at the summits of the 5-membered rings, Fig. 8.5g. Finally, at the Z2-585 boundary, (opposite) sequences of rotations at opposite edges of the two shifted domains release the strain while preserving the structure of the TiO_3 entities, Fig. 8.5l, and help accommodate the structural mismatch. Unsurprisingly, disorientations between TiO_3 entities are systematically the largest in the boundary cores, where the O-O-O angles may differ by as much as 30° from those in the pristine honeycomb monolayer, as in the case of the A2-5775 domain boundary (DB).

With this perspective, the much larger modifications of the Ti-Ti and Ti-O bond lengths and ion positions with respect to the Au substrate found at the A2-5775 boundary, Fig. 8.5, can be principally assigned to the presence of a substantial tensile strain necessary to bridge the large distance between the two domains. Indeed, despite important outward relaxations of the two domain edges, the Ti-Ti distances between the domains and the boundary core remain large. This induces expansions of the corresponding Ti-O distances since, contrary to boundaries under a compressive strain, they cannot be preserved by rotations of TiO_3 entities. As a consequence, the boundary core is particularly strongly

constrained. Not only are its cations placed in the least favored Au-top sites, but also the TiO_3 entities along the core chain are significantly distorted and disoriented.

To summarize, despite substantial structural rearrangements at the boundaries, the anion-cations distances and the preferential ion positions on the Au surface are only weakly impacted, except for the case of the A2-5577 boundary.

8.2.5. Formation energies of domain boundaries

Table 8.1 summarizes the calculated DB formation energies. Consistent with the amplitude of structural effects described above, we find that they are systematically small ($E_{\text{form}} \sim 0.7$ eV/unit), except in the case of the A2-5577 boundary ($E_{\text{form}} \sim 1.9$ eV/unit). In particular, these values are much smaller than the energy cost of under coordinated ions at a domain edge (of the order of 2.0-2.5 eV per a two-fold coordinated Ti and a dangling O atom), showing that the main driving force for boundary formation between domains is the recovery of full coordination of edge ions. Moreover, the particularly small formation energies of the A1-48, Z1-5775, and Z2-558 DBs show that, provided that the Ti-O bond lengths are approximately preserved (the elastic contribution due to changes of Ti-O bond lengths does not exceed 0.1 eV/unit for the considered DBs), the precise network connectivity and the moderate ion displacements with respect to the Au substrate have only a small energetic impact.

Termination	Armchair		Zigzag	
Domain boundary	A1-48	A2-Shifted 5577	Z1-5775	Z2-Shifted 558
Formation energy (eV/Å)	0.05	0.19	0.07	0.06
Formation energy (eV/unit)	0.54	1.91	0.78	0.64
Unit counts	308	16	72	61

Table 8.1. Calculated formation energies of the four domain boundaries with respect to the perfect Au-supported Ti_2O_3 monolayer and occurrences of the domain boundaries.

The considerably larger value of E_{form} at the A2-5577 boundary may in part be assigned to the change of cations position with respect to the Au substrate and the in-plane rotation of TiO_3 entities. We have estimated these two contributions with the dedicated model calculations mentioned above. We found that the energy cost of a lateral shift of the perfect monolayer with respect to the substrate, such that 50% of its cations occupy the Au-top positions and 50% remain in their favored hollow sites, is of nearly 0.15 eV per the Au-top cation. At the A2-5577 boundary four Au-top cations (per 5577 unit) are involved, which accounts for about 0.6 eV/unit of E_{form} . Regarding rotations of TiO_3 entities, we find that small ones ($\Delta\phi < 25^\circ$) have a negligible energy cost (about 0.03 eV/Ti), but the latter increases to about 0.10 eV/Ti for rotations with $\Delta\phi \sim 35^\circ$, such as found along the core chain at the A2-5577 boundary. Thus they account for nearly 0.4 eV/unit of E_{form} .

8.2.6. Discussion on Ti_2O_3 domain boundaries

The statistical analysis of the experimentally observed four domain boundaries is summarized and compared to the calculated formation energies in Table 8.1. We find that 71% (324 out of 457) of the domain boundaries have armchair-like orientations whereas 29% (133 out of 457) of the domain boundaries have zigzag-like orientations. Within the armchair domain boundaries, 95% of the structural units are aligned boundaries with the A1-48 structure and 5% are shifted boundaries with the A2-5577 structure. Thus aligned A1-48 boundaries dominate the armchair domain boundary structures. Within the zigzag domain boundaries, nearly equal proportion of Z1 and Z2 DBs are found (54% and 46%, respectively).

Interestingly, a clear correlation can be found between measured frequencies of occurrence of the different types of DBs and the calculated DB formation energies. Indeed, the significant difference in occurrence of the A1 and A2 DBs can be directly linked to

the large difference of formation energy of these two DBs. Similarly, roughly equal occurrences of Z1 and Z2 DBs correlate well with essentially the same formation energies of these two boundaries. However, this correlation does not hold when comparing the armchair- and zigzag-oriented DBs, since the latter have formation energies comparable to the A1 DB while being observed much less frequently.

This result suggests that the experimental system has not reached its thermodynamic equilibrium, and that the observed DB configurations are to some extent influenced by their kinetics of formation. Anyway, a kinetic bias is likely present since, at the actual (low temperature) thermodynamic equilibrium, the system should expose a single domain with no boundaries. Several, qualitatively different kinetic effects can be evoked. On the one hand, diffusion of ions and formation of rings at AC and ZZ boundaries may be subject to different energy barriers, leading to different occurrence frequencies. On the other hand, since DBs form upon coalescence of islands, the observed DB orientations may be biased by the initial orientations of island edges.

8.3 Domain boundaries in Nb₂O₃ (2 × 2) honeycomb structure

8.3.1 Structures of domain boundaries in (2 × 2)-Nb₂O₃/Au(111) film

Fig. 8.6 shows STM images of a monolayer Nb oxides on an Au(111) substrate. Nb oxide forms a (2 × 2) honeycomb structure and a triangular island structure. Several domain boundaries (indicated by an arrow in the upper part of Fig. 8.6a) and non-stoichiometric defects (see the arrow in the bottom of Fig. 8.6a) occur in the honeycomb film. The Nb₂O₃ (2 × 2) structure is similar to the Ti₂O₃ (2 × 2) structure and its domain boundary has the same crystallography as that for Ti₂O₃ (shown in Fig. 8.1).

The first row of Fig. 8.6 shows several boundary gaps with the A1 crystallography. Fig. 8.6a presents a large Nb₂O₃ island merged from four Nb₂O₃ domains. In the upper part of

the image, two domains meet at an A1 gap filled with a 48 structure. The A1-48 boundary is interrupted by a non-stoichiometric defect. In the bottom left corner, two domains run into a boundary of several segments. The boundary starts with a Z2 gap, transforms into another Z2 gap by a 120° turn after interrupted by a non-stoichiometric defect, and transforms into an A1 gap by a 30° turn. The A1 gap consists of a 48 structure on the top and two harder-to-define cells on the bottom. In the bottom right corner, two domains meet at an A1 gap with harder-to-define units. Fig. 8.6b shows a Nb₂O₃ island merged from four domains. The four domains meet at four gaps with the A1 crystallography. The A1 gap is filled with several segments that appear brighter than Nb atoms in a pristine honeycomb film and two segments that appear slightly darker. The two types of segments are different structures and they will be discussed in section 8.3.2. In Fig. 8.6c, two Nb₂O₃ islands meet at an A1 gap with bright units. The fine structure in the A1 gap is unclear even though the Nb atoms in the Nb₂O₃ honeycomb are resolved under the same tip condition, pointing to the difficulty to image this domain boundary structure.

In the second row of Fig. 8.6, two Nb₂O₃ islands with a lateral offset along the armchair orientation of the honeycomb lattice run into an A2 boundary. The A2 boundary can be filled with disordered structures that consist of polygons of four, five, six and seven-membered rings [Fig. 8.6(d-e)]. Alternatively, several Nb oxide vacancies are located at the domain boundaries, which leaves trenches in the lattice (Fig. 8.6f). The fact that experiments show only disordered A2 boundaries does not mean that A2 boundary does not form an ordered structure. An ordered A2 boundary structure may have a high formation energy due to the presence of a large amount of Nb-O bond distortion and the shift of Nb atoms out of their preferential hollow sites. Their formation may be hindered

in the present experimental conditions and they may be formed by increasing the annealing temperature during oxide growth.

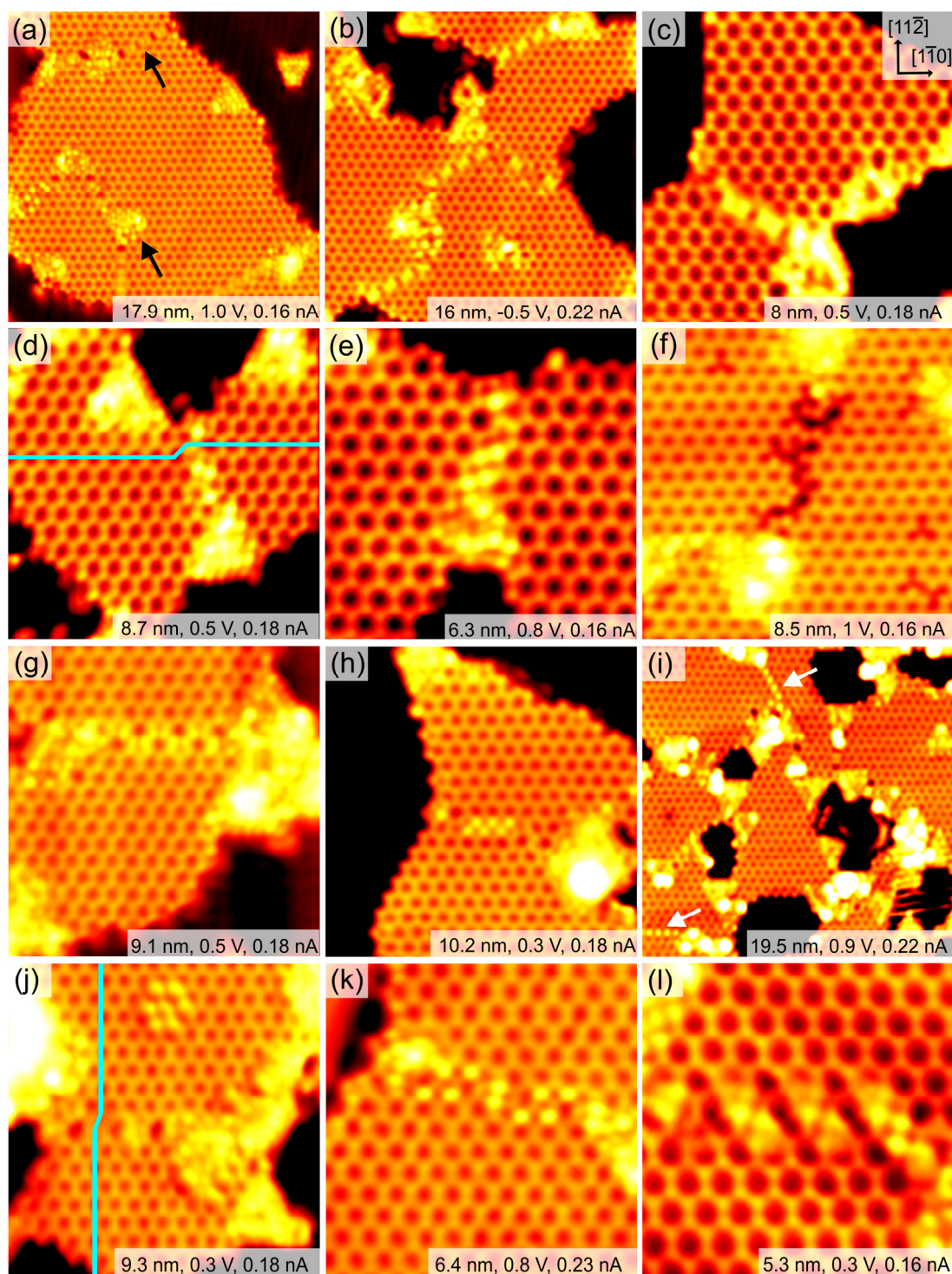


Fig. 8.6 shows STM images of a Nb₂O₃ film supported on an Au(111) substrate. (a-c) mainly show the A1 boundary gap. (d-f) show the A2 boundary gap. (g-i) show the Z1 boundary gap. (j-l) show the Z2 boundary gap. The lateral misalignment in A2 and Z2 gaps is indicated by a cyan line. STM images in (a-h) are averaged from 26, 16, 8, 17, 12, 16, 23, 26, 1, 17, 16 and 27 images.

The third row in Fig. 8.6 shows that two Nb₂O₃ domains that are aligned along their armchair orientation meet at the zigzag orientation and give rise to the boundary gap with the Z1 crystallography. The Z1 gap can be filled with a 5775 unit cell (see Fig. 8.6g), similar to the 5775 structure observed in Ti₂O₃ (discussed in section 8.2.4). The gap can also be filled with several bright spots arranged in a zigzag pattern (Fig. 8.6h) or a straight line (indicated by a white arrow in Fig. 8.6i). The latter two structures have narrow gaps, indicating that two Nb₂O₃ domains prefer to approach each other as much as possible.

The bottom row in Fig. 8.6 shows the domain boundary structures for the Z2 crystallography. A shifted 558 structure has been observed (Fig. 8.6j) and it resembles the 558 boundary found in Ti₂O₃ (see section 8.2.4). The Z2 gap can also be filled with a periodic cell of four bright spots and two distorted hexagonal rings (Fig. 8.6k). One complex boundary structure has also been observed in Fig. 8.6l and its atomic structure is difficult to define.

In general, two types of nanostructures and a variety of defects are observed on the surfaces of Nb oxide supported on Au(111) shown in Fig. 8.6. Most domain boundaries only have a short section of three to four unit cells and are often interrupted by non-stoichiometric defects. These systems are away from the thermodynamic equilibrium for the honeycomb monolayer film.

8.3.2 Atomic structures of domain boundaries

Experimental STM observations of three domain boundary structures with the A1 crystallography are presented in the top row of Fig. 8.7. The proposed models are shown below the STM images. The first column presents the atomic structure of an A1-48 domain boundary. The top two Nb atoms in the square ring appear brighter than the bottom two Nb atoms in Fig. 8.7a. This asymmetry is possibly due to two of the Nb atoms located

on the hcp sites of Au(111) and two other Nb atoms sitting on the fcc sites of Au(111). The periodic cell has $\text{Nb}_{10}\text{O}_{15}$ stoichiometry and it is stoichiometric with respect to the Nb_2O_3 honeycomb. The second column shows the atomic structure of an A1-6-66 domain boundary. We assign the bright spots in the STM image as the location of a Nb atom because a typical empty state STM image of Nb_2O_3 is dominated by the Nb state (Chapter 6). One row of atoms are removed from the A1 gap and the vacant is filled by the expansion of Nb-Nb distances in the honeycomb lattice. The gap consists of two distorted hexagonal rings in the upper part of the highlighted unit cell and one distorted hexagon in the center of the cell. Thus it is called an A1-6-66 domain boundary. The periodic cell has Nb_8O_{12} stoichiometry which is consistent with the Nb_2O_3 stoichiometry of (2×2) honeycomb. The third row shows a complex boundary structure imaged via Nb state (upper panel in Fig. 8.7c) and O state (lower panel in Fig. 8.7c). We assign the bright spots in the upper panel to the location of Nb atoms and the bright spots in the lower panel to the location of O atoms, and obtain an atomic structure shown in Fig. 8.7f. A Nb_2O cluster sits in the center of an octagonal ring in an A1-48 structure and the octagon is divided into two six-membered rings. This DB structure is called an A1-4-66 structure. Its stoichiometry is $\text{Nb}_{12}\text{O}_{16}$ ($\text{NbO}_{1.33}$) which is sub-stoichiometric compared to Nb_2O_3 .

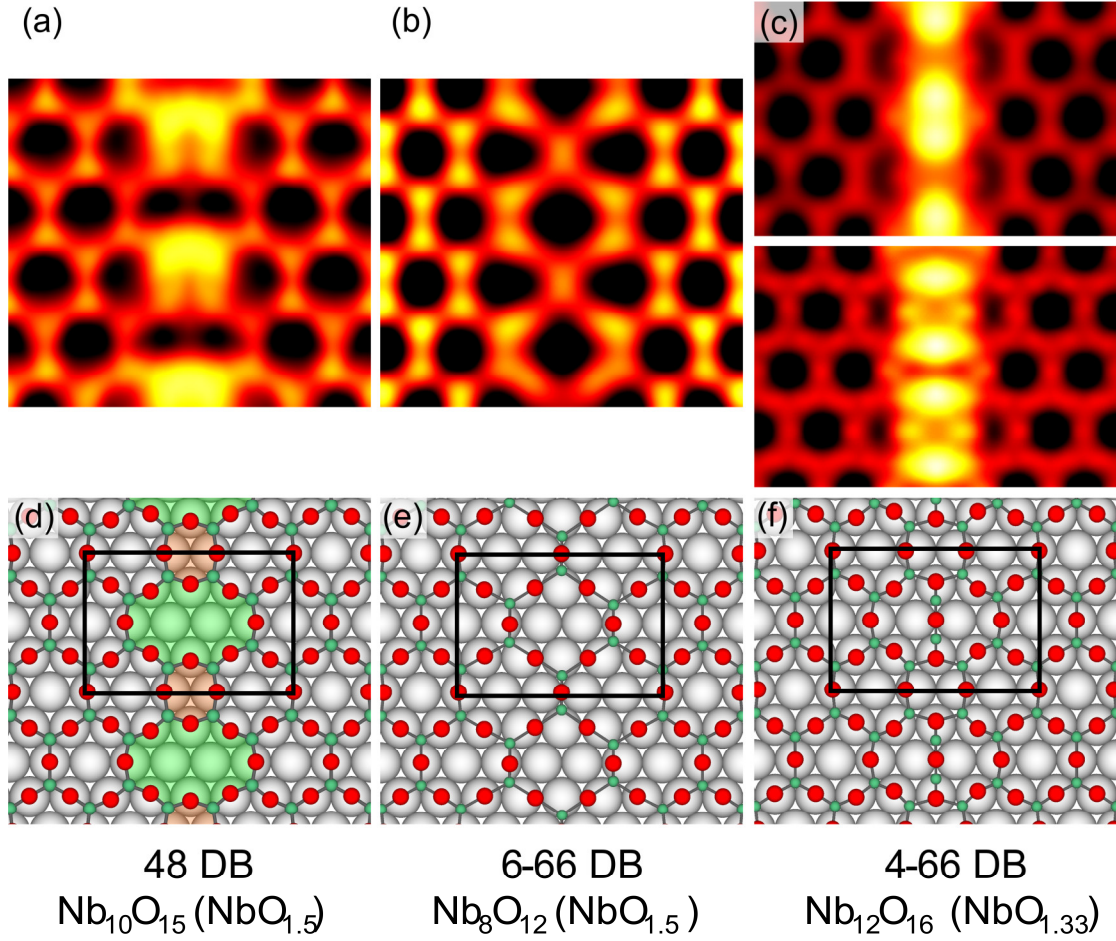


Fig. 8.7. Domain boundary structures in Nb_2O_3 with the A1 crystallography. (a-c) Experimental STM data of 48, 6-66 and 4-66 structures. The upper panel in (c) shows the 4-66 structure via Nb state and the lower panel shows the structure via O state. The atomic models are shown in (d-f) with Nb atoms in green, O atoms in red and Au atoms in grey. The STM images from (a-c) are generated from 18, 54, 6 and 7 frames. The experimental STM parameters of (a-c) are $V_s = 0.2$ V, $I_t = 0.16$ nA; $V_s = 0.3$ V, $I_t = 0.16$ nA; $V_s = 0.2$ V, $I_t = 0.16$ nA; $V_s = 0.1-0.3$ V, $I_t = 0.16$ nA.

Fig. 8.8 shows the atomic structures of the Z1 domain boundary and their schematics are shown below the STM images. The first column presents a Z1-5775 boundary with $\text{Nb}_{12}\text{O}_{18}$ (Nb_2O_3) stoichiometry (Fig. 8.8d). Z1 boundary can also be decorated with bright spots arranged in a straight line (Fig. 8.8b) or a zigzag line (Fig. 8.8c). The bright spots are $0.25 \sim 0.35$ Å higher than the Nb atoms in the pristine honeycomb and the relative height is independent of the applied bias. They are possibly a Nb^{4+} atom which may have

higher density of states than a Nb^{3+} atom. They may also be small molecules, such as a H atom, a hydroxyl group or an O atom, adsorbed at the domain boundary. Fig. 8.8e-f show two proposed models in which the bright spots are interpreted as Nb^{4+} atoms. The linear Z1-44 boundary consists of compressed four-membered rings and these rings are connected by a Nb atom at the corners. The zigzag-like Z1-44 boundary contains elongated four-membered rings that are connected to each other by sharing a Nb-O-Nb edge. The linear Z1-44 boundary has $\text{Nb}_{14}\text{O}_{22}$ ($\text{NbO}_{1.57}$) stoichiometry and the zigzag Z1-44 boundary has $\text{Nb}_{12}\text{O}_{22}$ ($\text{NbO}_{1.67}$) stoichiometry, which are oxygen-rich with respect to the Nb_2O_3 honeycomb.

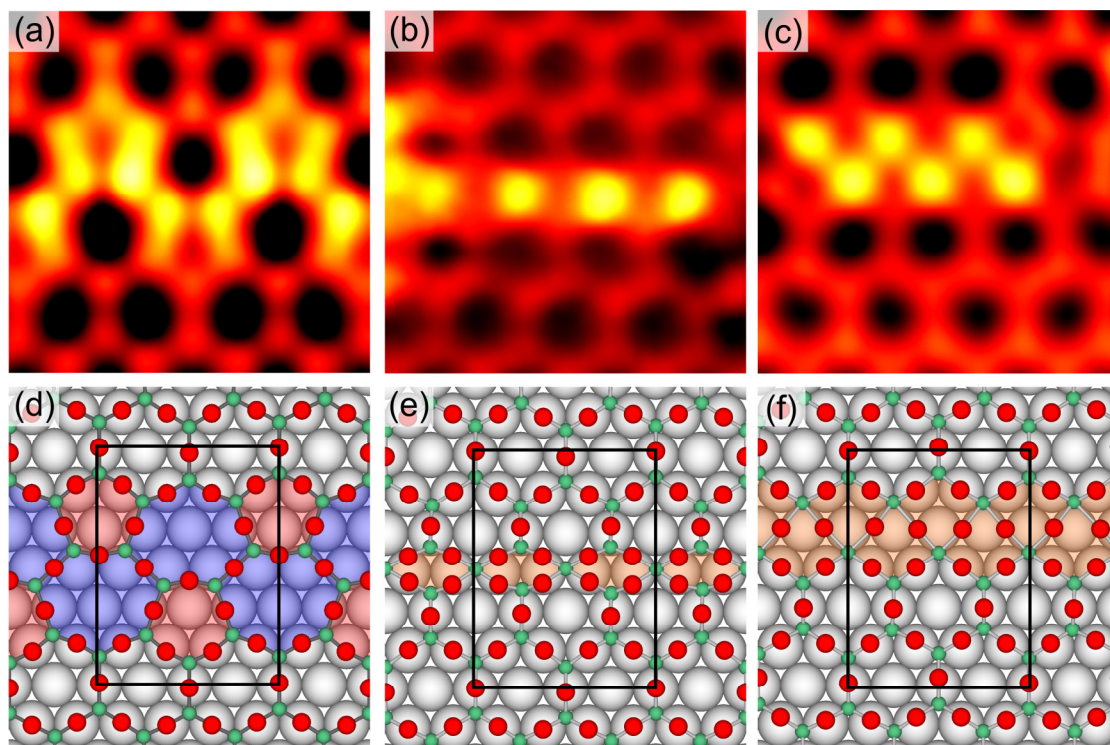


Fig. 8.8. Domain boundary structures in Nb_2O_3 with the Z1 crystallography. (a-c) Experimental STM data of 57, linear-44 and zigzag-44 structures. The atomic models are shown in (d-f) with Nb atoms in green, O atoms in red and Au atoms in grey. The four, five and seven-membered rings are colored in orange, red and purple. The STM images (a) and (c) are generated from averaging 48 and 26 frames. The experimental STM parameters of (a-c) are $V_s = 0.5$ V, $I_t = 0.18$ nA; $V_s = 0.3$ V, $I_t = 0.18$ nA; $V_s = 0.9$ V, $I_t = 0.22$ nA.

Fig. 8.9 shows the atomic structure of a shifted Z2-558 boundary in Nb_2O_3 and its structural model is shown in Fig. 8.9b. The stoichiometry of the boundary is Nb_2O_3 .

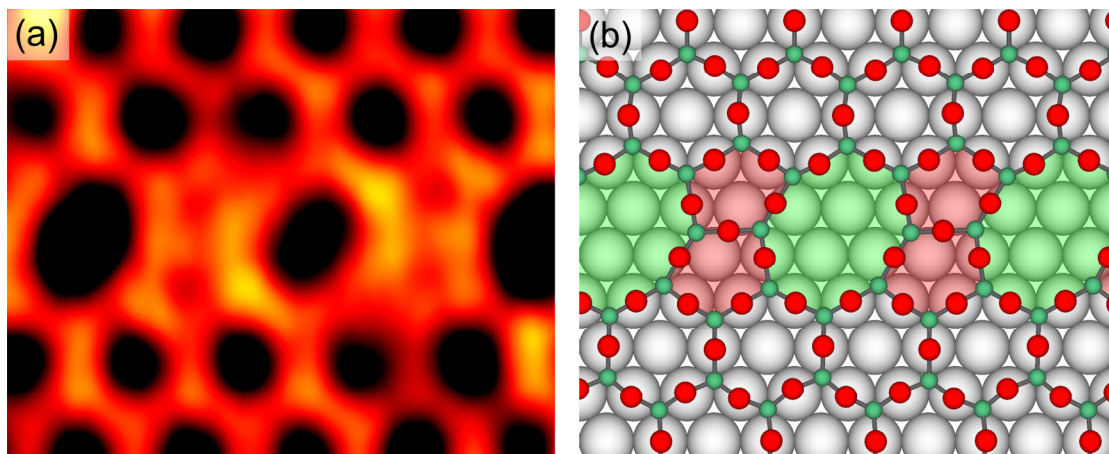


Fig. 8.9. Domain boundary structures in Nb_2O_3 with the Z1 crystallography and a shifted 558 structure. (a) STM observation and (b) a proposed model. The STM image is averaged from 17 frames. The experimental STM parameters are $V_s = 0.3$ V, $I_t = 0.18$ nA.

Comparison between the domain boundaries in Nb_2O_3 and Ti_2O_3 shows that there is a larger variety of boundary structures in Nb_2O_3 than in Ti_2O_3 . The differences in the domain boundary structures of Nb_2O_3 and Ti_2O_3 possibly originate from the electronic configuration of the metal atoms. A Nb atom has five electrons in the outermost orbitals. It can bond to three or four O atoms and transfer the remaining charge to the Au substrate. Thus a boundary of the Nb_2O_3 film can have a variety of stoichiometries and thereby several boundary structures. A Ti atom has four electrons in the outermost orbitals. It mainly bond to three O atoms and transfer the remaining charge to the Au substrate. A boundary of the Ti_2O_3 film is constrained to the Ti_2O_3 stoichiometry thus it forms a limited number of edge structures.

8.4 Conclusions

This chapter reports the structures of domain boundaries in two (2×2) honeycomb monolayers of Ti_2O_3 and Nb_2O_3 supported on an Au(111) substrate. There are four types

of crystallographies in a (2×2) honeycomb monolayer domain boundaries. Our combined STM and theory study reveals that each crystallography in Ti_2O_3 is filled with a specific type of boundary structure. Their stabilization mechanisms are related to the efficiency of strain relief within the domain boundary structure. Most domain boundaries observed in Ti_2O_3 have been found in Nb_2O_3 . A larger variety of boundaries such as complex structural units, non-stoichiometric units, disordered boundaries and trenches are present in Nb_2O_3 . In order to understand the physical origin of the structural differences in the domain boundaries of Ti_2O_3 and Nb_2O_3 , complete atomic models of Nb_2O_3 boundaries would be needed. This is difficult to establish directly by STM images due to the complex signal in the STM image concerning the relative contrast of Nb and O as a result of the interplay of geometric and electronic effects. Therefore, further DFT modeling aims to test a selection of boundary structures, to understand the STM signal and to search for the low energy configurations. The coexistence of the NbO_x ($1 < x < 1.5$) triangular islands and non-stoichiometric defects with the Nb_2O_3 results in difficulty to define the stoichiometry of the Nb oxide surface. Further experiments will provide a Nb_2O_3 film with easier to define stoichiometry by diminishing the triangular islands and non-stoichiometric defects by e.g., annealing at higher temperature for prolonged periods.

Chapter 9. Island edges of the Ti_2O_3 and Nb_2O_3 honeycomb monolayers

9.1 Introduction

Monolayer oxides may be novel catalysts in chemical reactions such as water splitting² and CO oxidation.¹⁵⁰ Chemical reactions often take place at catalytically active centers that incorporate under-coordinated atoms,¹⁴⁹ inhomogeneous surface potential¹⁸² or dangling O atoms.²³ These active centers have been observed to be located at the edges of oxide nanoislands supported on metal substrates such as $\text{FeO}_x/\text{Pt}(111)$,¹²⁶ $\text{MgO}/\text{Ag}(001)$,¹⁸³ $\text{CoO}_x/\text{Au}(111)$ ⁴⁵ and $\text{CoO}_x/\text{Pt}(111)$.⁴⁵ Particularly one report has directly visualized that CO oxidation takes place at the unsaturated Fe sites at the island edges of FeO_x on $\text{Pt}(111)$.¹⁵⁰ However, little information is available on the edge structures of M_2O_3 honeycomb structure and their structural transition when exposed to reactive gases. In this chapter the edge structures of Ti_2O_3 and Nb_2O_3 monolayers on $\text{Au}(111)$ are investigated. The DFT calculations are performed by Dr Jacek Goniakowski and Dr Claudine Noguera (CNRS, FR).

9.2 Results and discussion

9.2.1 Island edges of the Nb₂O₃ (2 × 2) honeycomb structure

Fig 9.1 shows a series of STM images recorded from numerous samples prepared by Nb deposition at room temperature and annealing in 10⁻⁶ Pa O₂ at 600 °C for 1 h (Fig. 9.1a-b) and 6 h (Fig. 9.1c-d). The details of sample preparation are described in Chapter 6. Several Nb oxide nanostructures are formed including Nb₂O₃ honeycomb structure, atomic clusters and NbO_x (1 < x < 1.5) triangular islands (Chapter 7). Bare Au(111) surface is present with the oxide structures and exhibits a distorted herringbone structure. The Au(111) regions covered by oxides do not show any herringbone structure indicating that the herringbone reconstruction is lifted. This observation is in contrast to that of the Cu₃O₂ honeycomb structure supported on Au(111). The herringbone structure of Au(111) is maintained. Cu₃O₂ forms elongated islands with their edges aligned with the [11 $\bar{2}$] orientation of Au(111) and their structures constrained in the fcc regions of Au(111).⁶⁶ This difference points to the weak interfacial interaction between Cu₃O₂ and Au(111) versus the strong interaction between Nb₂O₃ and Au(111).

STM images show that Nb₂O₃ forms several islands with widths of 15 ~ 25 nm on the Au(111) surface. A small island in the center of Fig. 9.1a has a hexagonal shape indicating that it is close to thermodynamic equilibrium. Its edges mainly have a ZZ-66 structure. A large island at the top of Fig. 9.1a has a less regular shape. The large island has not reached thermodynamic equilibrium in one hour because more mass transport is required for the larger islands. The island edge consists of short sections of ZZ-66, AC-66, AC-56 structures and defects imaged as bright spots in the STM images. Two more examples of large Nb₂O₃ islands are shown in Fig. 9.1b.

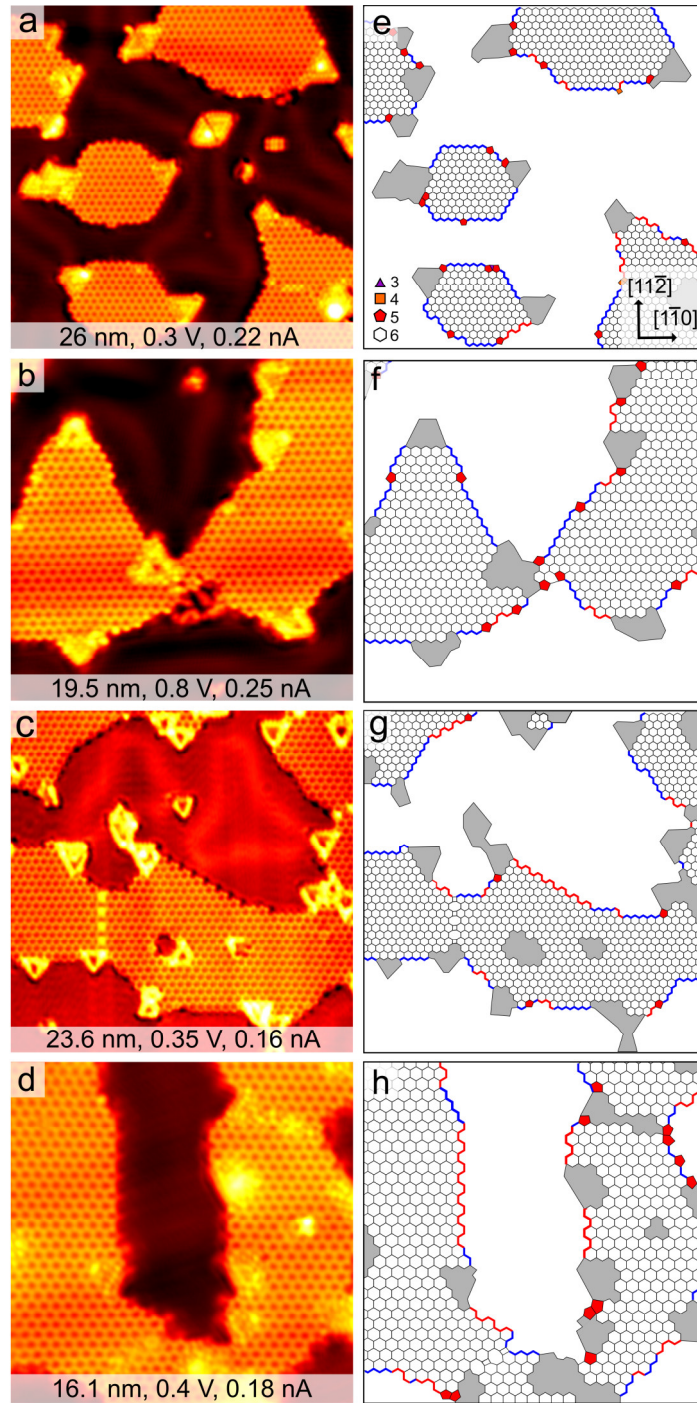


Fig. 9.1. STM images of island edges in Nb_2O_3 honeycomb monolayers grown by annealing Nb in 10^{-6} Pa O_2 at 600 °C for (a-b) 1h and (c-d) 6h. Nb_2O_3 honeycomb contains mainly hexagonal rings within the islands edges. The dominant edge structures are AC-66 and ZZ-66. For each STM image, schematics are shown in the right panel (e-h) where the AC-66 edges are highlighted in red, ZZ-66 edges are highlighted in blue, and the hexagonal network of the monolayers is marked with black outlines. Other oxide nanostructures and defects are in grey. The STM images from (a-d) are generated from 26, 21, 27 and 20 frames using multiple frame averaging (Chapter 4).

The above samples were then annealed to 600°C in O₂ for 5 h, giving rise to a total annealing period of 6 h (Fig. 9.1c-d). The Nb₂O₃ islands observed after annealing of 6 h are larger than the Nb₂O₃ islands annealed for 1 h, as a result of island ripening. The Nb₂O₃ islands form long and straight edges that have a zigzag-like structure along the $[1\bar{1}0]$ direction and armchair-like structure along the $[11\bar{2}]$ direction. The Nb₂O₃ islands annealed for 6 h have more straight edges than the Nb₂O₃ islands annealed for 1 h. A prolonged annealing period promotes the mass transport process for the Nb₂O₃ islands and allows the atoms to diffuse into low energy adsorption sites.

The second column of Fig. 9.1 shows four schematics that duplicate the critical information from the above STM images. The hexagonal honeycomb lattice is in black outlines, edge structures are in red or blue, and local defects or triangular islands are in grey. The Nb₂O₃ island edges mainly consist of hexagonal rings, and are categorized into ZZ-66 (blue) and AC-66 (red) structures. 45.8% of the polygons at the island edges are arranged into a ZZ-66 structure and 47.8% of the polygons are arranged into an AC-66 structure. Therefore ZZ-66 and AC-66 are low energy structures in the thermodynamic conditions of 600°C and 10⁻⁶ Pa O₂. The edges sometimes contain pentagonal rings incorporated in or attached to a Nb₂O₃ island edge (3.5% of the overall polygons). The pentagonal rings appear at the island corners or intersection between Nb₂O₃ honeycomb and NbO_x nanostructures. The Nb₂O₃ islands occasionally form an alternating pentagon and hexagon structure (discussed below), resembling the AC-56 edge in graphene.¹¹⁵ The remaining 2.9% of the polygons are square, heptagonal rings or bright spots. These irregularities may originate from a Nb atom sitting at the elbow of a ZZ-66 structure, incorporation of Au atoms into the island edge or surface adsorption of atoms and small molecules from the UHV chamber such as C and H₂O onto the edge sites.

For comparison, Cu_3O_2 islands can form AC-66 and ZZ-66 edges structures.⁶⁶ Cu_3O_2 islands mainly form an AC-66 structure which is driven by a kinetic effect. The AC-66 edge of Cu_3O_2 runs parallel to the herringbone lines of Au(111) and a ZZ-66 edge runs perpendicular to the herringbone lines. A Cu_3O_2 island grows faster along the zigzag direction than along the armchair direction, resulting in the dominance of armchair edges in a Cu_3O_2 island. The Au substrate can determine the edge type of a Cu_3O_2 island. On the contrary, AC-66 and ZZ-66 edges in a Nb_2O_3 island are not influenced by the herringbone of Au(111) because the interaction between Nb_2O_3 and Au(111) lifts the Au reconstruction. Comparing the two Au-supported oxide system shows that the interaction between Cu_3O_2 -Au is weaker than the interaction between Nb_2O_3 -Au. Furthermore, the armchair edge of Cu_3O_2 is metastable structures and it can be converted into a zigzag edge that has lower formation energy. The oxide-Au interaction does not sufficiently stabilize the armchair edges of Cu oxide. Whereas the armchair edges in Nb_2O_3 are resistant to UHV annealing at 600°C for 10 h and annealing in 10^{-4} Pa oxygen at 300°C, indicating that the armchair edges are stable, possible due to the electrostatic interaction with Au.

9.2.2 Atomic structures of island edges in Nb_2O_3 monolayers

Experimental STM images of the atomic structures of the Nb_2O_3 island edges are shown in the top row of Fig. 9.2. The main feature in the images is the ordered arrangement of polygons in the termination of a honeycomb lattice. The structures are referred to as ZZ-66, AC-66 and AC-56 edges. Atomic models are shown in the third row of Fig. 9.2. Image simulations (the second row of Fig. 9.2) calculated from these atomic models are in good agreement with the experimental STM images.

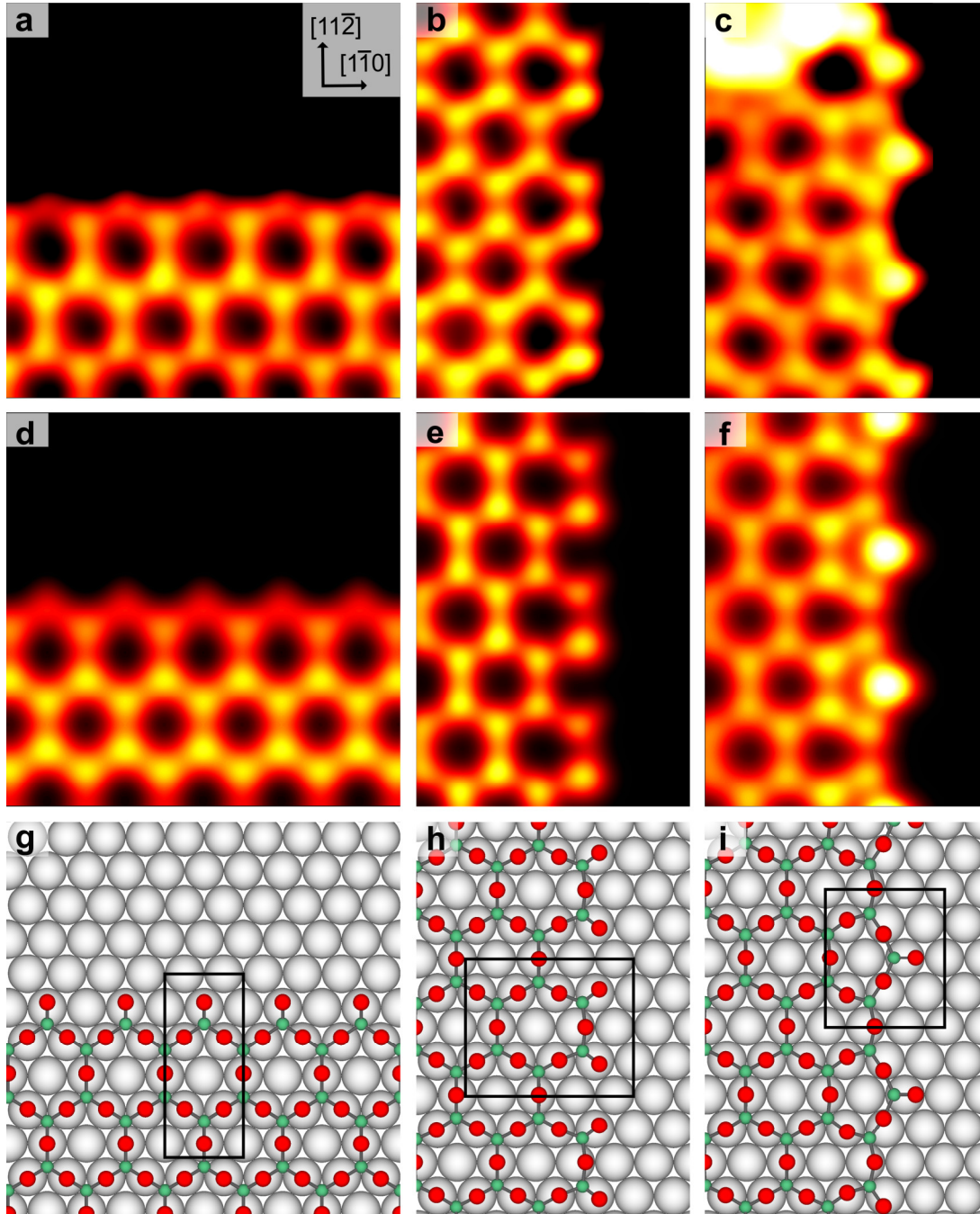


Fig. 9.2. Atomic structures of the island edges in a Nb_2O_3 monolayer supported on $\text{Au}(111)$. Experimental STM data (a-c), and corresponding DFT simulations (d-f) of ZZ-66, AC-66 and AC-56 edge structures. The atomic models are shown in the bottom row (g-i). Periodic cells are indicated by a black rectangle. Au, Nb and O atoms are shown in grey, green and red, respectively. The STM images from (a-c) are averaged from 36, 8 and 17 frames. The experimental STM parameters of are (a) $V_s = 0.5$ V and $I_t = 0.16$ nA; (b) $V_s = 1.0$ V and $I_t = 0.18$ nA; (c) $V_s = 0.6$ V and $I_t = 0.23$ nA, respectively, with image widths of (a) 2.9 nm and (b-c) 2.0 nm. The STM simulations parameters are $E - E_F = +1$ V, distance from the center of the first Au substrate plane is 5.2 Å).

Preliminary DFT calculations show that an edge structure containing Nb atoms bond to a dangling O atom have lower energies than a bare edge structure terminated by Nb atoms at an oxygen chemical potential of -2 eV. Each Nb atom in the outermost atomic row in the Nb₂O₃ edges is bonded to an additional O atom, as shown in the bottom row of Fig. 9.2.

The periodic cell of the ZZ-66 edge includes 3 three-fold coordinated Nb atoms and one Nb-O terminal bond (Fig. 9.2g). The unit cell stoichiometry is Nb₄O₇, which reduces to NbO_{1.75}. Fig. 9.2h shows that the unit cell of an AC-66 edge consists of four three-fold coordinated Nb atoms and two Nb-O bonds. The periodic cell of the AC-66 edge has stoichiometry of Nb₆O₁₁, which breaks down to NbO_{1.83}. The unit cell of an AC-56 structure consists of a pentagonal rings. There are 3 three-fold coordinated Nb atoms and one Nb-O bond. The stoichiometry of the unit cell indicated in Fig. 9.2i is Nb₄O_{6.5}, which reduces to NbO_{1.63}. Thus the AC-66 structure is the most oxidized and the AC-56 structure is the most reduced edge among the three edge structures. The three edge structures are more oxidized than the Nb₂O₃ film due to the presence of the Nb-O terminal bonding at the edge.

Further STM experiments also show that the AC-66 structure (Fig. 9.2h) is transformed into the AC-56 structure (Fig. 9.2i) after annealing in UHV at 800°C for 1 h. This is plausible because the AC-66 structure has higher oxygen stoichiometry than the AC-56 structure. The AC-66 structure is reduced into the AC-56 structure, consistent with the experimental condition of UHV annealing. An AC-56 unit can also be considered as a NbO cluster added to the armchair bowl of an AC-66 unit. A NbO cluster is oxygen-poor with respect to the Nb₂O₃ stoichiometry of the honeycomb phase and an AC-66 structure is reduced by the addition of a NbO cluster.

9.2.3 Chemical reactivity of Nb₂O₃ island edges.

STM images in Fig. 9.3(a, b) presents the Nb oxide surface structures on Au(111) after exposure to 10^{-6} Pa O₂ at 600°C. Nb₂O₃ forms large and continuous films. 45.8% of the hexagonal rings at the edge terminations are organized into a ZZ-66 structure and 47.8% of the hexagons are arranged into an AC-66 structure, giving rise to an AC/ZZ ratio of 1.04. The sample was then exposed to 10^{-6} Pa CO and heated to 600°C for 2.5 h. STM images recorded from this surface [Fig. 9.3(c, d)] show an increase of the occurrences of the AC-66 edges to 64% and a decrease of the occurrences of the ZZ-66 edges to 35%, giving rise to an AC/ZZ ratio of 1.83. Thus the ZZ-66 edge structure is converted into the AC-66 edge structure. Many of the Nb oxide islands exhibit long and straight edges composed of AC-66 units.

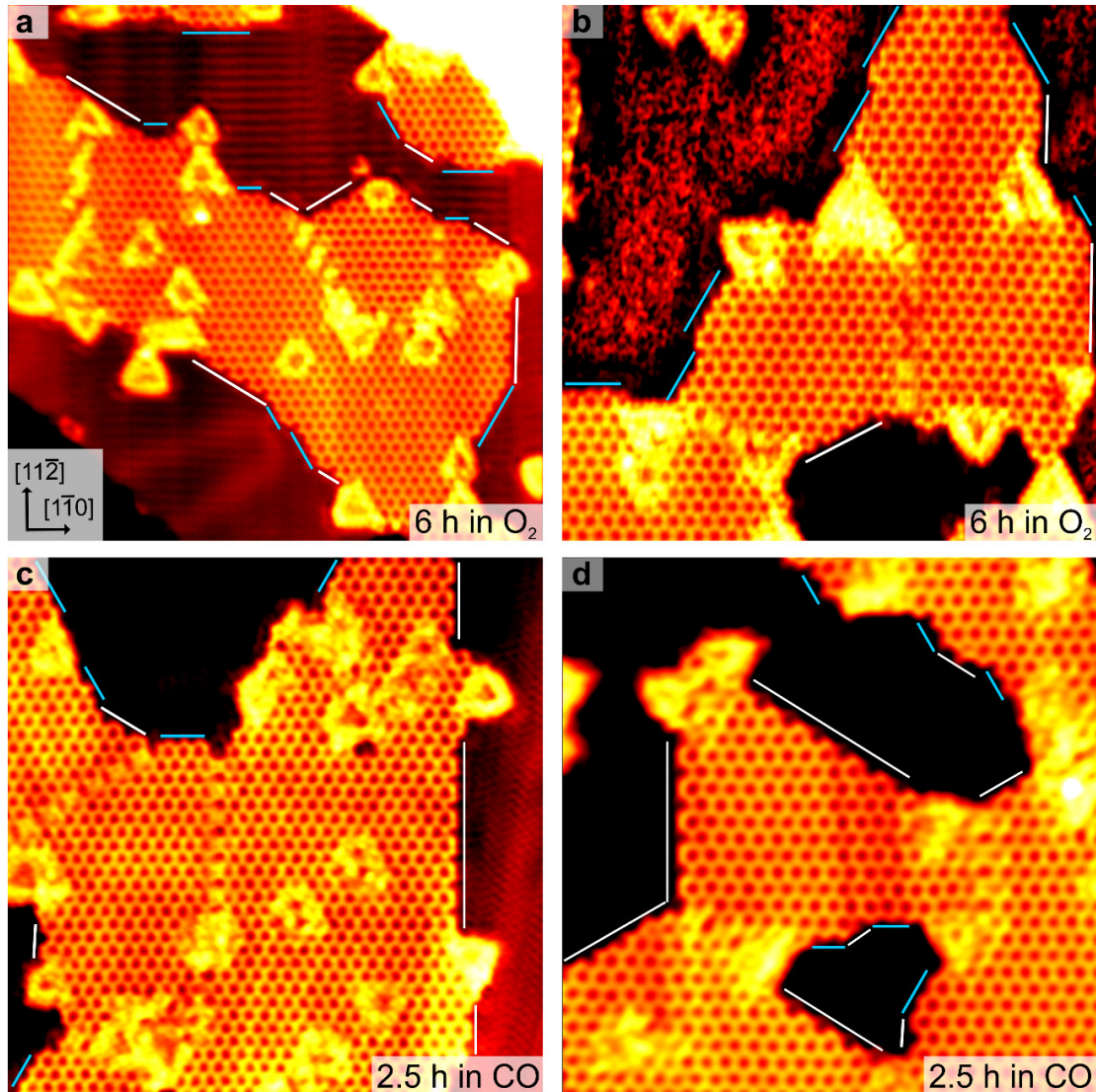


Fig. 9.3. STM images showing a Nb oxide surface on Au(111) annealed in O₂ for 6 h and then annealed in CO for 2.5 h at 600°C. (a-b) The Nb₂O₃ islands grown by annealing in 10⁻⁶ Pa O₂ for 6 h shows an AC-66/ZZ-66 ratio of ~1. (c-d) After 2.5 h exposure to 10⁻⁶ Pa CO, the AC-66/ZZ-66 ratio is increased to 1.83. The STM images from (a, c, d) are averaged from 35, 4 and 7 frames. The experimental STM parameters of are (a) 0.7 V, 0.16 nA, image width of 24.9 nm; (b) 0.8 V, 0.16 nA, 18.4 nm; (c) 0.5 V, 0.22 nA, 20 nm; (d) 1 V, 0.18 nA, 16.8 nm, respectively.

9.2.4 Island edges in Ti₂O₃ (2 × 2) honeycomb structure

The Ti₂O₃ honeycomb film is grown following the procedures described in Chapter 5. Fig.

9.4 shows six representative STM images of island edges in the Ti₂O₃ honeycomb film.

The island edges can be straight, concave or convex. The panels below each STM images

show the schematics where differently colored polygons represent the sizes of the rings ranging from three to eight-membered rings. The edges consist of 3, 4, 5, 6 and 7-membered rings. They often assemble into structural units of regular 66 edges, 46, 56, 474, 47374 and 47474 units.

Fig. 9.4(a & d) show a convex edge and the edge is aligned with the $[1\bar{1}0]$ direction. From left to right, the island edge consists of a 474 unit, a 56 unit, a second 474 unit, a 47374 unit, a defect of 3, 4, 5 and 7-membered rings, another 474 unit, another 47374 unit, and ends with a 56 unit. Fig. 9.4(b & e) show two island edges. On the left hand side, an island edge starts with a 56 unit, a 474 unit and several defects of polygonal rings. The edge then makes a 30° turn and become aligned with the $[11\bar{2}]$ direction. It consists of three sections of alternating 56 units and 47474 units. On the right hand side, an island edge consists of a 4-membered ring, a 474 unit, two 56 units, a 47474 units and a 474 units. After being interrupted by several defects of 3, 4 and 8-membered rings and a bright island, the edge transforms into a zigzag edge decorated with a 4-membered ring, a 7-membered ring and a 47 unit. In Fig. 9.4(c & f), there are two island edges showing the common units observed above and a short regular 66 edge in the bottom right corner of the image. Fig. 9.4(d & j) shows a concave edge containing the 4, 5, 6 and 7-membered rings. Fig. 9.4(e & k) show a hole in the Ti_2O_3 honeycomb monolayer. The hole is mainly surrounded by 4 and 7-membered rings. Fig. 9.4(f & l) show a high resolution image of two Ti_2O_3 island edges. The Ti atoms at the edge appear brighter than the Ti atoms in the honeycomb domains.

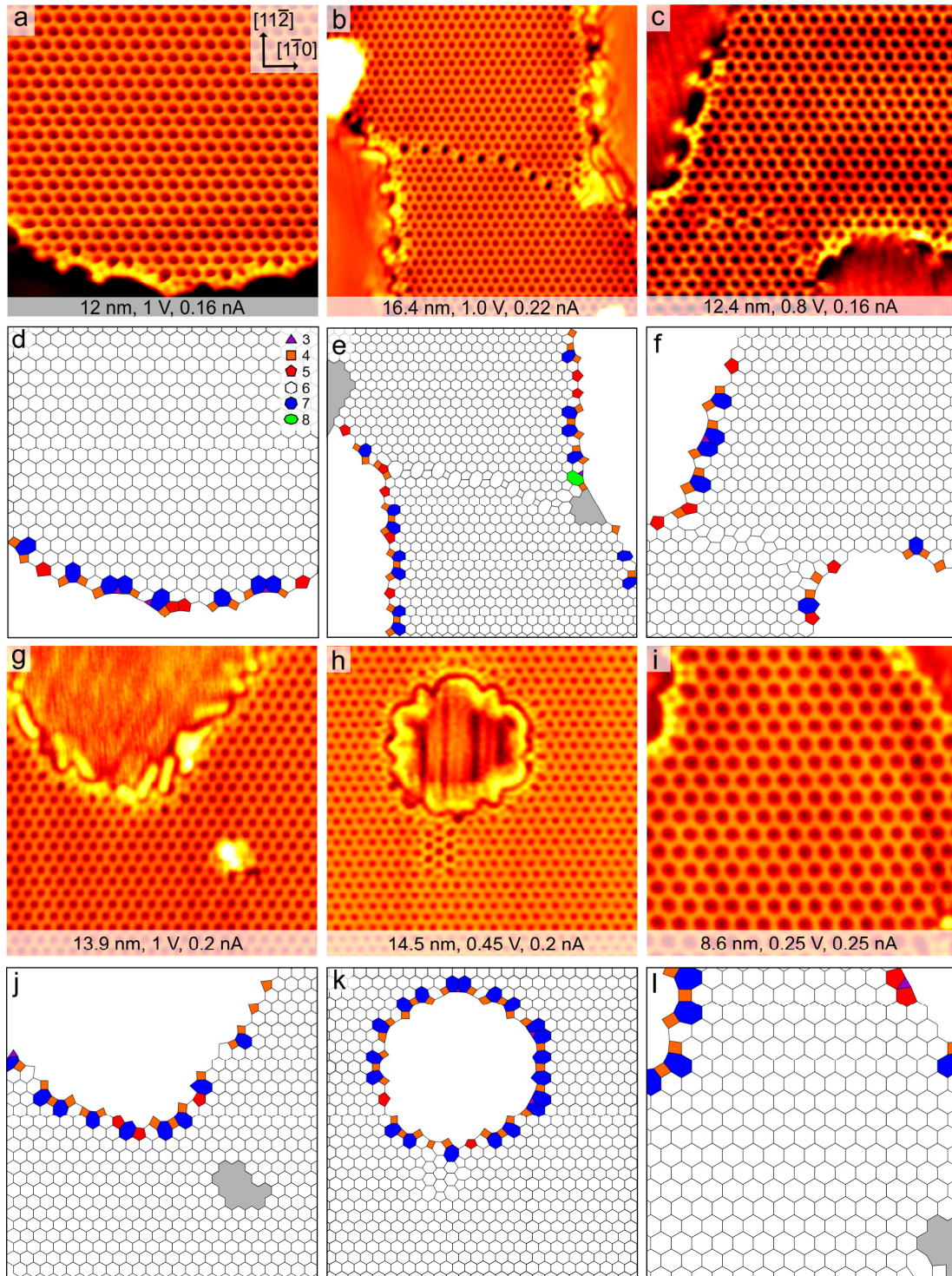


Fig. 9.4. STM images of island edges in Ti_2O_3 honeycomb monolayers grown by annealing Ti in 10^{-6} Pa O_2 at 600 °C for 1h. (a-c) & (g-i) STM images show that Ti_2O_3 honeycomb contains a variety of polygonal rings within the islands edges. (d-f) & (j-l) Schematics below the STM images show Ti_2O_3 honeycomb monolayers with the edge structures highlighted. The polygonal rings are color-coded. Defects are colored in grey. The STM images in (a, b, g) are averaged from 16, 88 and 22 frames.

9.2.5 Atomic structures of island edges in Ti_2O_3 monolayers

The first row in Fig. 9.5 shows the atomic structure of the structural unit cells in Ti_2O_3 island edges. The terminations of the honeycomb lattice consists of three to seven-membered rings. Atomic models are shown below the STM images. The bright spots in the STM images are associated with the location of Ti atoms. Ti atoms located at the outermost atomic row appear brighter than Ti atoms in the pristine honeycomb lattice. Because Ti atoms in the edges shift out of the three-fold hollow sites of Au, they are geometrically elevated with respect to Ti atoms in the hollow sites in the pristine lattice (Fig. 9.5g-l). Shifting Ti out of hollow sites also increases the density of states of Ti atoms between 0 ~ 1.5V, indicating that Ti atoms at the island edges exhibit electronic behavior different from Ti atoms in the pristine honeycomb film. Some of the Ti atoms in the outermost atomic row of a Ti_2O_3 edge are terminated with O atoms, giving rise to a Ti-O cluster. Because one Ti atom has four electrons in its 4s and 3d orbitals and its common oxidation state is 4+. The Ti atom in the Ti_2O_3 film has an oxidation state in the range of 3+ to 4+. Thus Ti atoms in the Ti_2O_3 film are possibly bonded to more than three O atoms so that they will be closer to the ideal 4+. The remaining Ti atoms are three-fold coordinated with O atoms.

One armchair edge is terminated with an AC-56 (Fig. 9.5a) or an AC-47474 structure (Fig. 9.5b). An AC-56 unit cell includes a pentagonal ring with four three-fold coordinated Ti atoms and one Ti-O cluster. The unit cell stoichiometry of the AC-56 structure according to Fig. 9.5a is $\text{Ti}_4\text{O}_{6.5}$, which reduces to $\text{TiO}_{1.63}$. An AC-47474 unit cell is composed of three square rings and two heptagonal rings. There are 14 three-fold coordinated Ti atoms and two Ti-O clusters in one unit cell. The stoichiometry of the AC-47474 structure is

$\text{Ti}_{16}\text{O}_{25}$, which breaks down to $\text{TiO}_{1.56}$. The AC-47474 edge is more reduced than the AC-56 edge and its stoichiometry is closer to the Ti_2O_3 film.

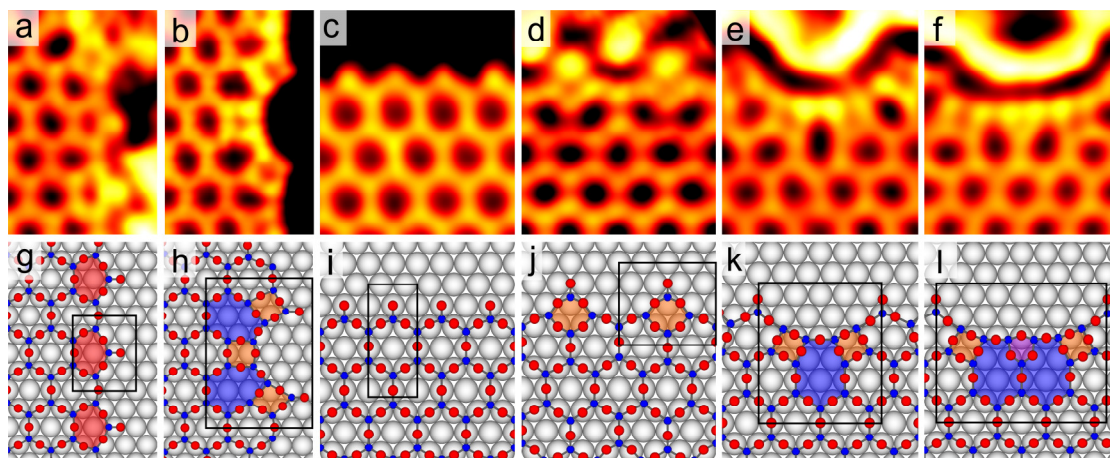


Fig. 9.5. Atomic structures of the island edges within a Ti_2O_3 monolayer. (a-f) Experimental STM data and (g-l) schematics of AC-56, AC-47474, ZZ-66, ZZ-46, ZZ-474 and ZZ-47374 structures. The periodic cell of each structure is indicated. The STM images from (a, d, e, f) are generated from 3, 22, 3 and 3 frames using MFA. The experimental STM parameters of (a-f) are 1 V, 0.22 nA; 0.45V, 0.2 nA; 0.25 V, 0.25 nA; 1 V, 0.2 nA; 0.45 V, 0.2 nA; 0.45 V, 0.2 nA.

One zigzag edge can be terminated with a ZZ-66, a ZZ-46, a ZZ-474 or a ZZ-47374 structure (Fig. 9.5c-f). The ZZ-66 structure is a line of hexagonal rings (Fig. 9.5c) and each unit cell consists of 3 three-fold coordinated Ti atoms and one Ti-O cluster (Fig. 9.5i). The stoichiometry in a ZZ-66 unit cell is Ti_4O_7 , which reduces to $\text{TiO}_{1.75}$. Fig. 9.5d shows a ZZ-46 structure where one Ti-O cluster is attached to the elbow of two hexagonal rings. One ZZ-46 unit cell has a square ring with 4 three-fold coordinated Ti atoms and one Ti-O cluster. The unit cell stoichiometry according to Fig. 9.5j is Ti_5O_8 that breaks down to $\text{TiO}_{1.6}$. In Fig. 9.5e one -474 structure is incorporated into the edge of the Ti_2O_3 film and is surrounded by hexagonal rings. One unit cell of ZZ-474 consists of 13 three-fold coordinated Ti atoms and one Ti-O cluster in a hexagonal ring. The stoichiometry is $\text{Ti}_{14}\text{O}_{22}$ that breaks down to $\text{TiO}_{1.57}$. Fig. 9.5f shows a ZZ-47374 structure that includes a

triangular ring sandwiched by two heptagonal rings and then connected to two square rings on both sides. There are 18 three-fold coordinated Ti atoms in one unit cell and one Ti-O cluster. The unit cell stoichiometry is $\text{Ti}_{29}\text{O}_{29}$ which reduces to $\text{TiO}_{1.53}$. The four edge structures along the zigzag orientation of the honeycomb lattice are more oxidized than the Ti_2O_3 film due to the presence of the Ti-O cluster. The ZZ-47374 structure is the most reduced zigzag edge and its stoichiometry is closest to the pristine Ti_2O_3 film.

In Fig. 9.6 several schematics show a honeycomb lattice terminated with the structural units observed in Ti_2O_3 (Fig. 9.5). The first row in Fig. 9.6 presents four edges aligned with the armchair direction of the honeycomb lattice. Each edge is 12-hexagon long and consists specific structural units. Fig. 9.6a shows a hypothetical regular AC-66 edge. There are six hexagons in the outermost column and each hexagon consists of two Ti-O clusters, yielding 12 Ti-O clusters in total. Fig. 9.6b presents an AC-56 edge. There is one Ti-O cluster in each pentagonal ring and the edge in Fig. 9.6b includes six Ti-O clusters. The edge in Fig. 9.6c has three unit cells of AC-47474 and each unit cell consists of two Ti-O clusters, resulting in six Ti-O clusters in total. Fig. 9.6d shows an edge of alternating AC-56 and AC-47474 structures. The number of Ti-O cluster is 6. Comparison among the four panels shows that reconstructed armchair edges have a smaller number of Ti-O clusters than the regular armchair edges.

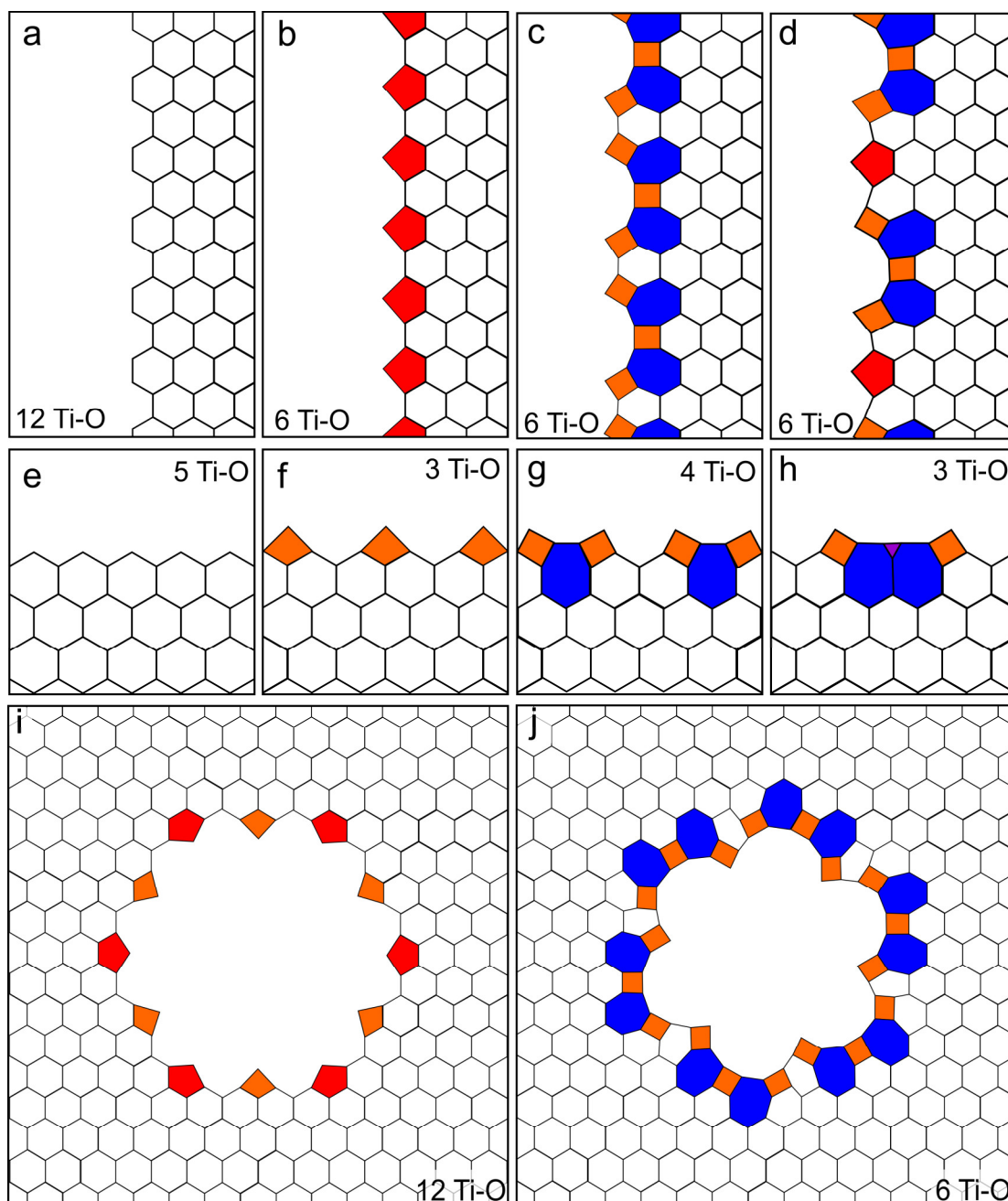


Fig. 9.6. A summary of structures of armchair edges, zigzag edges and holes in a honeycomb lattice. For a straight edge, reconstructed edges have fewer Ti-O terminal bonds than regular edges. For a hole in the lattice, 47 structures have fewer Ti-O terminal bonds than 46 and 56 structures.

The second row of Fig. 9.6 shows four zigzag edge structures with a length of five hexagons. Fig. 9.6e shows a ZZ-66 edge of five hexagonal rings. The outermost atomic

row is composed of five Ti-O clusters according the schematic shown in Fig. 9.5i. Fig. 9.6f shows a ZZ-66 structure and there are three Ti-O clusters in the three square rings. A ZZ-474 edge has two periodic cells and four Ti-O clusters located in the square rings (Fig. 9.6g). A ZZ-47374 edge has one periodic cell that includes two Ti-O unit in the square rings and one Ti-O unit in the hexagonal ring. The reconstructed zigzag edges have a smaller number of Ti-O units than the regular ZZ-66 edge.

The third row in Fig. 9.6 shows two schematics for a hole in the honeycomb lattice. The edge in Fig. 9.6i reconstructs into 4 and 5-membered rings. There are six squares and six pentagons. Each nonhexagonal ring is attached to a Ti-O cluster and there are 12 Ti-O clusters in Fig. 9.6i. Fig. 9.6j shows a hole with its edges reconstructed into 4 and 7-membered rings. Six square rings stick out of the edges and each square consists of one Ti-O terminal bond, leading to 6 Ti-O clusters. This configuration decreases the number of Ti-O clusters in a hole configuration.

In a highly curved edge, the AC-47474, ZZ-474 and ZZ-47374 edges have fewer Ti-O bonds than the AC-56 and ZZ-46 edges, and thus the former have stoichiometries closer to the Ti_2O_3 stoichiometry. Whereas in a straight edge, the AC-47474, ZZ-474 and ZZ-47374 edges have similar amounts of Ti-O bonds to the AC-56 and ZZ-46 edges. Therefore the curvature of the edges influences the number of Ti-O terminal bonds and thereby influences the edge stoichiometry and their atomic structures.

9.2.6 Comparison between edges in honeycomb monolayers of oxides and graphene

Interestingly, the edge structures of Ti_2O_3 and Nb_2O_3 (2×2) honeycomb structure are distinctly different from the edge structures in graphene. The edge structures in graphene form regular armchair and zigzag edges composed of hexagonal rings.¹²² The edges of graphene are stabilized by saturating the intralayer C-C bond at the edges and their

formation energy is barely influence by the interlayer van der Waals bonding with the substrate. Whereas reconstructed edges often have lower stability than regular edges in graphene because they have more unsaturated C atoms than the latter.¹¹⁴ The stability of reconstructed edge in graphene can be enhanced via adsorption of hydrogen atoms from a molecular atmosphere or nickel atoms from the substrate.^{114,184} On the contrary, the honeycomb monolayers of Ti_2O_3 and Nb_2O_3 can often form a variety of reconstructed edges with different nonhexagonal rings. The stoichiometry is related to the number of M-O terminal bonding at the edges.

The edge structures of a M_2O_3 honeycomb monolayer are influenced by three main factors including the optimization of the M_2O_3 stoichiometry, the presence of M-O bonding and the non-ideal location of the metal atoms relative to the Au(111) substrate.

In the Ti_2O_3 film, the film optimizes its stoichiometry to Ti_2O_3 at the edges and forms reconstructed edge structures with few Ti-O terminal bonding rather than regular edges with more Ti-O bonds (Fig. 9.5). Because one Ti atom has four electrons in its outermost orbitals. A Ti atom in the honeycomb lattice transfers three electrons to three O atoms and the remaining charge the Au substrate. Thus a Ti atom at the edge does not have extra charge to bond with a dangling O atom and it prefers to maintain three-fold coordination. Whereas the edge structures in the Nb_2O_3 films mainly form regular edges with the presence of Nb-O terminal bonding. The stoichiometry at the Nb oxide edges prefers to be more oxygen rich (Fig. 9.2). Because a Nb atom has five electrons in its outermost orbitals. A three-fold coordinated Nb atom in a pristine lattice transfers three electrons to the surrounding O atoms and the remaining charge to the Au substrate. A Nb atom at the edge can further transfer charge to the dangling O atom. The Nb atom at the edge is thus closer to the common Nb^{5+} than the Nb atoms in the honeycomb lattice.

On the other hand, in the reconstructed edges of the Ti_2O_3 film, the Ti atoms shift out of its preferential Au-hollow adsorption sites, which can cost up to 0.15 eV per Ti atom when the Ti is moved to the Au-top site (Chapter 8). The energy cost is compensated by maintaining the network connectivity of one Ti atom coordinated with three O atoms. The Nb atoms at the Nb_2O_3 edges are located in the preferential hollow sites which maximizes their charge transfer to the Au substrate. This is again consistent with the fact that a Nb atom tends to approach the Nb^{5+} oxidation state.

9.3 Conclusions

We present STM and DFT results for the Nb_2O_3 honeycomb nanoislands and STM observation for the Ti_2O_3 honeycomb that reveal a variety of edge structures. Nb_2O_3 honeycomb mainly forms regular AC-66 and ZZ-66 edges. Ti_2O_3 honeycomb always forms reconstructed edges of three to seven-membered rings. The oxidized edges are favored in Nb_2O_3 while the edges with stoichiometry close to Ti_2O_3 are favored in Ti_2O_3 . Because a Nb has one additional electron in the outermost orbitals than a Ti atom, the Nb atoms at the Nb_2O_3 film edge prefer to attach to additional O atoms and Nb_2O_3 forms more oxidized edges.

The oxide honeycomb monolayers exhibit a variety of edge structures that are either regular or reconstructed. Whereas the graphene edges have limited edge structures of regular edges. The structural difference between oxide honeycomb films and graphene possibly originate from their interaction with the substrate and their capability to vary the stoichiometry. The Ti and Nb oxide monolayers are supported the Au substrate with high adhesion energies (3.8 eV per Ti_2O_3 and 4.2 eV per Nb_2O_3) so that the structures and defects of the films are influenced by Au. Whereas graphene has van der Waals bonding

with the substrate that has little impact on the film structures and barely stabilizes unsaturated C atoms. Furthermore, oxide monolayer films are a binary material that can vary its stoichiometry and form several reconstructed structures. However, graphene is a monolayer of carbon atoms and it cannot vary its stoichiometry.

The edge structures of the Nb_2O_3 honeycomb monolayer depend on the chemical conditions at the edge. Precise control of the Nb_2O_3 island edges via tuning the oxygen chemical potential, exposure to reactive gases and annealing temperature is yet to be explored. It would be interesting to visualize the oscillation between the occurrences of zigzag and armchair edges upon oxidation-reduction cycles (see research proposal in Fig. 9.7). This will lead to the understanding of reaction gases that influence the growth of the Nb_2O_3 islands and their shape evolution. A similar study has been reported for the growth of MoS_2 nanocrystals.¹⁸⁵

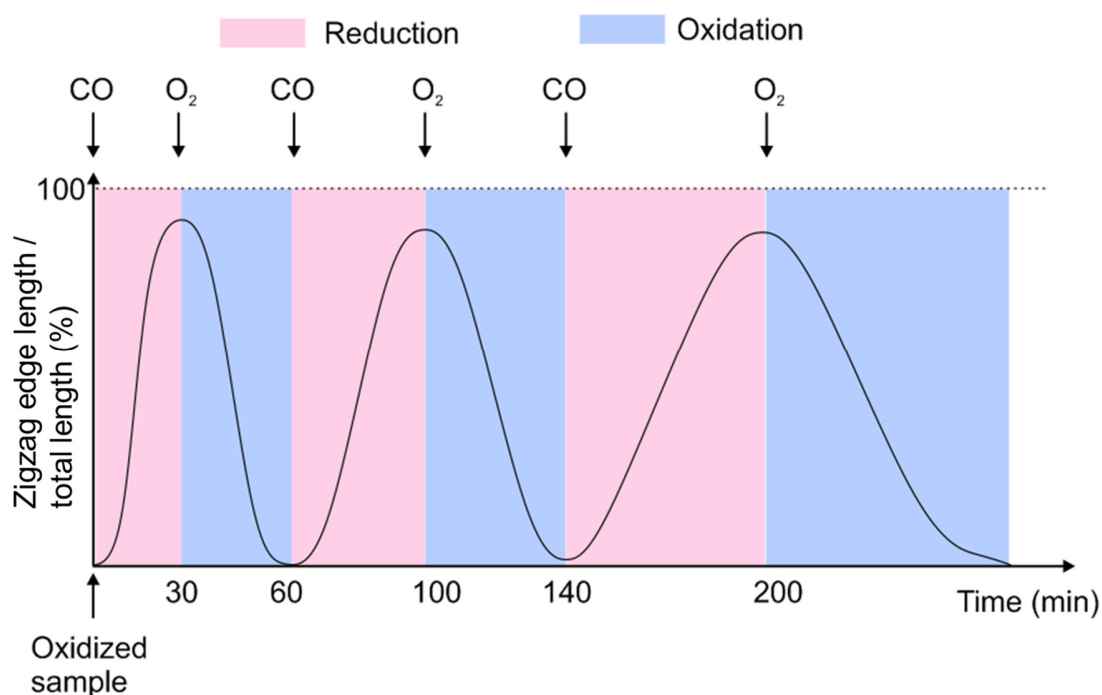


Fig. 9.7. A proposed experiment to measure the ratio of ZZ-66 edges to AC-66 edges of the Nb_2O_3 islands versus the time during three reduction-oxidation cycle.

Chapter 10. Conclusions

10.1 Overview

This thesis first reports work on an image averaging method that improves the signal-to-noise ratio of STM images in Chapter 4. Most of the STM images in this thesis are processed using this method. The results in Chapter 5-9 focus on the surface structures of monolayer oxide films of Ti_2O_3 and Nb_2O_3 , and NbO_x nanostructures. The five chapters provide fundamental understanding of transition metal oxide surfaces and oxide-metal interfaces. The work has encompassed several oxide materials including ultrathin films, nanostructures and atomic clusters. Oxide monolayers with a honeycomb structure contain a variety of defects, including single vacancies, local structural defects, domain boundaries and island edges. These defect structures are investigated from several perspectives including atomic structures, statistics, electronic structures, formation energies and stabilization mechanisms. The unifying thread through the five chapters on oxide surfaces is the interaction between the oxide and the Au(111) substrate.

10.2 Ti₂O₃ and Nb₂O₃ monolayers with a (2 × 2) honeycomb structure

The Ti₂O₃ and Nb₂O₃ monolayers supported on Au(111) have a (2 × 2) honeycomb structure, as determined by STM images. LEED patterns for Nb₂O₃ also confirms the (2 × 2) structure. DFT modeling shows that the metal atoms are located on the three-fold hollow sites of Au(111) and the O atoms are located on the top sites. Their atomic structures are significantly influenced by the crystallography of the top layer of Au(111). The honeycomb structures grow on Au(111) via pseudomorphism. The Ti₂O₃ film is in 2.2% elastic compression and the Nb₂O₃ monolayer is in 5.7% elastic compression. High resolution STM images, supported by simulations, are able to discriminate between metal atoms adsorbed in fcc or hcp hollow sites on the surface.

10.3 Defects in Ti₂O₃ and Nb₂O₃ honeycomb structures

A single vacancy on the metal atom site has been observed in Ti₂O₃ and Nb₂O₃. Because both films are grown in an oxidative environment, the three metal atoms adjacent to the vacancy site are more likely to be terminated with a dangling O atom than being a bare metal termination. Thus the vacancy defect is a Ti vacancy for Ti₂O₃ and a Nb vacancy for Nb₂O₃. The density of Ti vacancy defects is much lower than the density of Nb vacancy defects. Because the Ti vacancy defects are mobile in the honeycomb lattice, they tend to diffuse to the island edges. Whereas the Nb vacancy defects are immobile, they tend to stay in the honeycomb lattice. The different diffusion behavior between Ti and Nb vacancies is because the Ti atoms have lower adsorption energy (3.8 eV per Ti₂O₃ unit) than the Nb atoms (4.2 eV per Nb₂O₃ unit) in the honeycomb lattice. The Ti atoms are less constrained at the Au-hollow sites and diffuse more rapidly than the Nb atoms.

Local structural defects including S-W defects and vacancies of a Ti_2O_3 cluster, namely divacancy defects, have been solely observed in Ti_2O_3 . Local structure defects are clusters of polygonal rings consisting of five, six, seven and eight Ti atoms. The formation of a S-W defect has little effect on the Ti-O bond lengths. Whereas the formation of divacancy defects of 585, 555-777 and 5555-6-7777 result in Ti-O bond expansion. The formation of vacancy-type defects cause tension in a freestanding Ti_2O_3 film. Conversely, the formation of vacancy defects facilitate the relief of compressive strain in a Au-supported Ti_2O_3 film. Therefore the substrate influences defect energies, and hence favors vacancy-type defects in compressively strain monolayer films.

Since the (2×2) honeycomb structure is in registry with the Au(111), one honeycomb domain can be shifted with respect to another honeycomb domain by one Au periodicity. The shift gives rise to a boundary gap composed of four distinct crystallographies including one armchair boundary, one shifted armchair boundary, one zigzag boundary and one shifted zigzag boundary. For a Ti_2O_3 film, the four types of crystallography are filled with alternating 48, 5577, 5775 and 558 unit cells, respectively. Thus the domain boundaries in a Ti_2O_3 film exhibit a limited number of structures. One may naively think, because Ti_2O_3 and Nb_2O_3 have a similar (2×2) honeycomb structure, they would exhibit similar domain boundary structures. However this is not the case. A Nb_2O_3 film consists of a larger variety of domain boundary structures. Some of the domain boundaries in Nb_2O_3 are similar to those in Ti_2O_3 and they show 48, 5775 and 558 structures. More generally, the domain boundary structures are less defined and it is difficult to atomically resolve the atoms within the boundary. Some of the Nb_2O_3 boundaries are imaged as bright spots in STM images and their physical origin can possibly be surface adsorption, incorporation of Au atoms or highly coordinated Nb atoms.

The island edges in a Ti_2O_3 film consist of four, five and seven-membered rings indicating that the island edges prefer to reconstruct into nonhexagonal rings. However, a Nb_2O_3 film forms regular armchair and zigzag edges containing only hexagonal rings. The Nb_2O_3 film does not favor edge reconstruction. It is again surprising that although Ti_2O_3 and Nb_2O_3 have a similar crystal structure, their edges are distinctly different. The physical origin of the different edges structure in Ti and Nb oxide systems is possibly due to different polarity compensation mechanisms. This is being calculated using DFT at present.

10.4 NbO_x atomic clusters and nanostructures

Niobium oxide grows as a variety of atomic clusters and nanostructures on $\text{Au}(111)$. The sub-stoichiometric clusters are stabilized through their interaction with the electronegative Au. Consequently the supported clusters and nanostructures will have a different equilibrium structure and stoichiometry compared with clusters generated in the gas phase. The clusters and nanostructures can be converted into the (2×2) honeycomb structure through a thermally activated coalescence process in an oxidative environment.

10.5 Future work

The first future study is the interpretation of a defect containing paired bright dots located at two neighboring metal sites. The defect has been systematically observed in Ti_2O_3 and Nb_2O_3 (Fig. 10.1). However, its physical origin still remains unsolved. There are three possibilities for this defect. The first one is an O atom vacancy defect. The removal of an O atom leaves two under-coordinated Nb atoms. The electron density localized at the Nb sites is increased and thus the two Nb atoms appear brighter in the STM image. This hypothesis will be tested via water adsorption experiment that the O atom from a water molecule may fill in the O atom vacancy. Another possibility is that an O atom in the

honeycomb lattice is replaced by a C atom. This idea can be tested by dosing a small amount of ethane to introduce C atoms into the oxide film. The defect may also be a Cu atom (from the copper gaskets in the UHV chamber) replacing the Au atom below the O atom in the honeycomb lattice, which can be validated by depositing Cu atoms onto the Nb₂O₃ honeycomb.

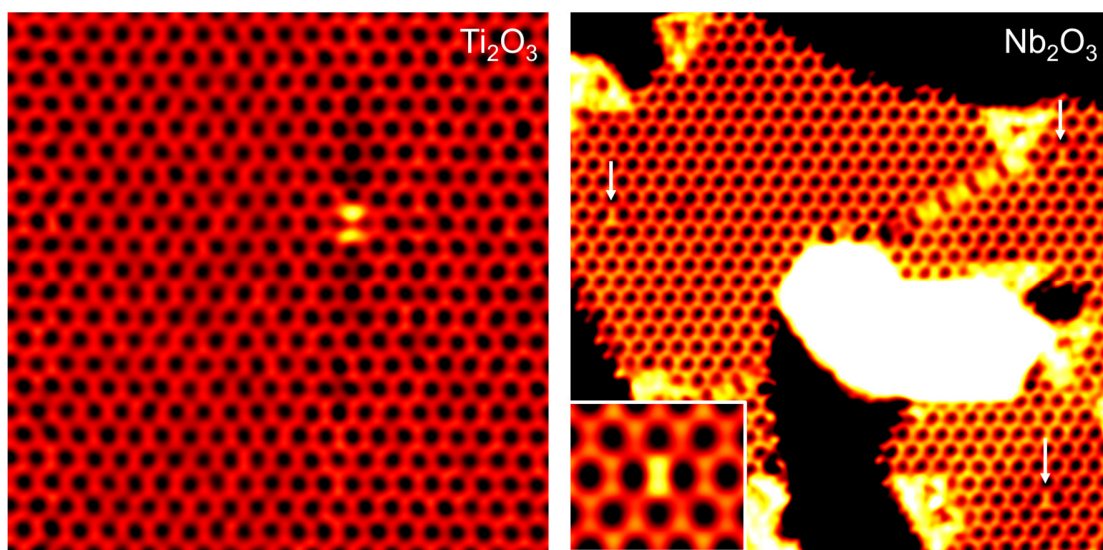


Fig. 10.1 STM images of defects consisting of paired bright spots at metal sites in a honeycomb lattice. Left: a defect in a Ti₂O₃ film (image width 11.3 nm, $V_s = 1$ V and $I_t = 0.2$ nA). Right: three defects in a Nb₂O₃ film (averaged from 21 raw frames, image width 16.5 nm, $V_s = 0.5$ V and $I_t = 0.18$ nA). The inset shows a high resolution images of the paired bright spots (averaged from 63 raw frames, image width 1.7 nm, $V_s = 0.5$ V and $I_t = 0.18$ nA).

The second future study is the interaction of Fe atoms with the Ti₂O₃ film. Following the deposition of metallic Fe atoms on to the Ti₂O₃ film at room temperature, several bright spots have been observed in the O atom sites (Fig. 10.2 a-c). The STM signal for the bright spots depend on the imaging bias. This bright spot is possibly due to the replacement of an Au atom with a Fe atom under an O atom in the honeycomb lattice (highlighted in yellow in Fig. 10.2d). The Au atoms “kicked out” by the Fe atoms coalesce into islands

forming a raft-like structure (yellow islands in Fig. 10.2a). In order to obtain a deeper understanding of the intercalation of Fe atoms in the $\text{Ti}_2\text{O}_3/\text{Au}$ interface, further theoretical insights in this system are required.

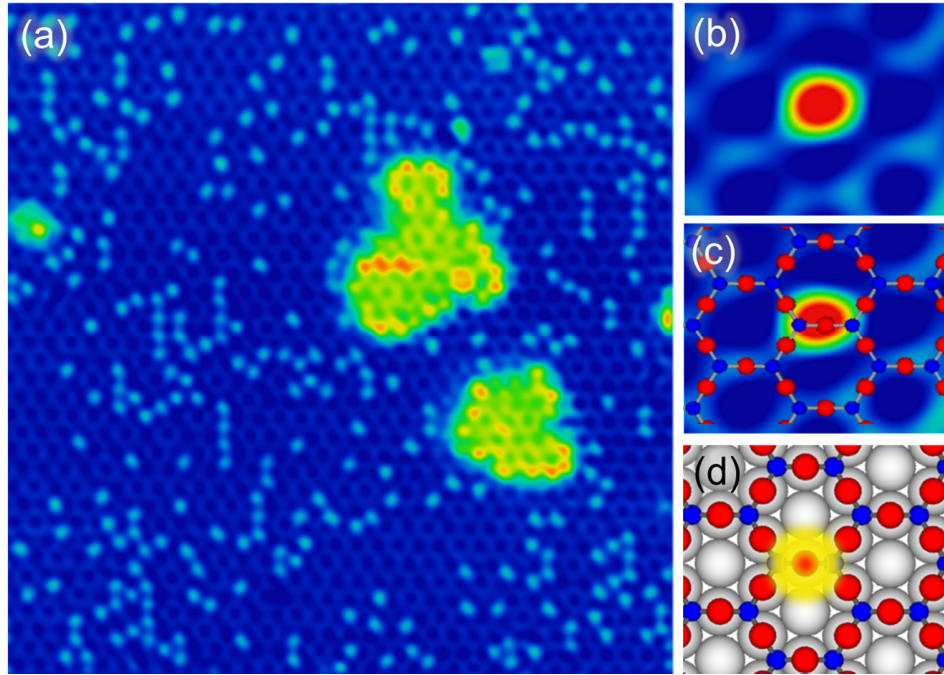


Fig. 10. STM images showing the intercalation of Fe atom within the $\text{Ti}_2\text{O}_3/\text{Au}$ interface. (a) Large scale STM image (averaged from 9 frames, image width 19.1 nm, $V_s = 0.9$ V and $I_t = 0.16$ nA). (b) High magnification STM image of a Fe atom spot (averaged from 9 frames, image width 1.5 nm, $V_s = 0.9$ V and $I_t = 0.16$ nA). (c) Applying a honeycomb grid onto the STM image in (b) shows that the bright spot is located at O site. (d) Schematic showing the Fe atom underneath the O atom.

Further studies on ternary oxide of Ti-V and Nb-V are also interesting. Combining two types of cations with different size and reducibility increases the degrees of freedom for modifying the structures, electronic and chemical properties of the oxide. Therefore a ternary oxide may exhibit novel structures and properties not observed in a binary oxide, such as mixing-induced change of cation oxidation states.⁵⁸ Ordered 2D ternary oxides can be grown by depositing the appropriate elements and choosing their growth conditions.^{5,40,186}

Appendix A Supporting Information of Chapter 5

A.1 Image processing procedures of multiple frame averaging.

Experimental STM images were processed using multiple frame averaging (MFA) to enhance the signal-to-noise ratio (see reference [19] and Chapter 4). followed by smoothing using ImageJ.

The STM image in Fig. 5.1c was generated from 88 STM images. 88 raw images were taken from the same area, of the same image size, with no change in tip configuration and only minor changes in the STM image parameters. The 88 images were aligned to generate a stack of images sharing a common field of view. The process is called rigid alignment.¹⁹ The resultant image stack was calculated into one averaged image which is called a reference image. Each raw image was compared to the reference image so that drift, noise and distortions of the raw images could be corrected. This process is called non-rigid alignment.¹⁹ 5 iterations of non-rigid alignment were performed to improve the signal-to-noise ratio, which finally produced an averaged image shown in Fig. 5.1c.

Fig. 5.3a was generated after averaging 4 frames. One raw STM image of the Stone-Wales (S-W) defect was taken. We used the known 2-fold symmetry of the S-W defect to rotate the image once by 180° and thereby doubled the number of the raw image to average. We

also used the known mirror symmetry of the S-W defect to flip the 2 images and thereby doubled the number of raw images to average. This process produced 4 raw frames. The 4 frames were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. Finally, the averaged image was smoothed using ImageJ and shown in Fig. 5.3a.

Fig. 5.3b was generated after smoothing one raw STM image using ImageJ. The STM image cannot be manipulated using symmetry because there is a bright region to the left of the DV(5-8-5) structure and this region breaks the symmetry of the image.

Fig. 5.3c was generated after averaging 138 frames. 23 raw STM images of the DV(555-777) were taken from the same area, of the same image size, with no change in tip configuration or in the STM image parameters. We used the known 3-fold symmetry of the DV(555-777) defect to rotate the image twice by 120° and thereby tripled the number of raw images to average to 69 frames. We also used the known mirror symmetry of the DV(555-777) defect to flip the 69 images and thereby doubled the number of raw images to average. This process produced 138 raw frames. The 138 frames were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. Finally, the averaged image was smoothed using ImageJ and shown in Fig. 5.3c.

Fig. 5.3d was generated after averaging 4 frames. One raw STM image of the DV(5555-6-7777) defect was taken. We used the known 2-fold symmetry of the DV(5555-6-7777) defect to rotate the image once by 180° and thereby doubled the number of the raw image to average. We also used the known mirror symmetry of the DV(5555-6-7777) defect to flip the 2 images and thereby doubled the number of raw images to average. This process produced 4 raw frames. The 4 frames were processed through 5 iterations of rigid

alignment and 5 iterations of non-rigid alignment, which generated an averaged image.

Finally, the averaged image was smoothed using ImageJ and shown in Fig. 5.3d.

Fig. 5.4 was generated from the same raw data and the same process as that for Fig. 5.3c, except that Fig. 5.4 was cropped from a larger field of view to show the strain field in the surrounding unit cells.

Fig. 5.5a was generated after averaging 12 frames. One raw STM image of the ‘flower’ defect was taken. We used the known 6-fold symmetry of the ‘flower’ defect to rotate the image once by 60° and thereby multiplied the number of the raw image to average by six. We also used the known mirror symmetry of the ‘flower’ defect to flip the 6 images and thereby doubled the number of raw images to average. This process produced 12 raw frames. The 12 frames were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. Finally, the averaged image was smoothed using ImageJ and shown in Fig. 5.5a.

The inset in Fig. 5.6 was generated after averaging 3 frames. One raw STM image of the vTi defect was taken. We used the known 3-fold symmetry of the vTi defect to rotate the image twice by 120° and thereby multiplied the number of the raw image to average by three. The three images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image.

Fig. 5.7c was generated after averaging 42 frames. 14 raw STM images of the defect were taken. They were rotated twice by 120° and thereby multiplied the number of the raw image to average by three. The three images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image.

Fig. 5.7d was generated after averaging 10 frames. Five raw STM images were taken. The five images were mirrored which doubled the number of raw images. The resultant 10

images were then processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment.

A.2 Generation of a Ti_2O_3 divacancy defect during STM imaging.

The formation of Ti_2O_3 divacancy defects via tip-surface interactions were sometimes observed during STM imaging. Fig. A1a shows a STM image of the pristine honeycomb surface. In the subsequent scan (Fig. A1b), a DV(5555-6-7777) defect and a S-W defect appear on the left part of the image. A Ti_2O_3 cluster is removed by the STM tip followed by rearrangement of the honeycomb lattice into pentagons and heptagons.

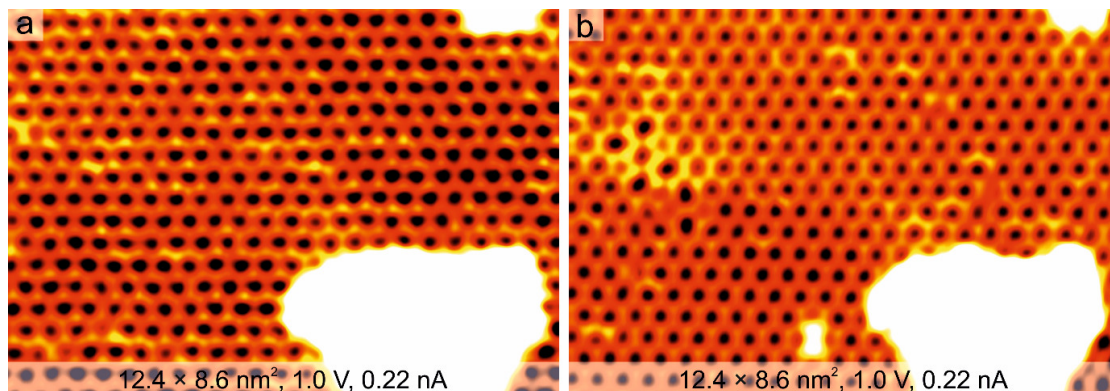


Fig. A1. The formation of divacancy defects in Ti_2O_3 -Au(111). Consecutive STM images showing (a) the pristine honeycomb film, and (b) the appearance of a DV(5555-6-7777) defect and a S-W defect.

Appendix B Supporting Information of Chapter 6

Image processing procedures of multiple frame averaging.

Experimental STM images were processed using multiple frame averaging (MFA) to enhance the signal-to-noise ratio (see reference [19] and Chapter 4).

The STM image in Fig. 6.1a was generated from 19 raw STM images. 19 images were taken from the same area, of the same image size, with no change in tip configuration and only minor changes in the STM image parameters. The 19 images were aligned to generate a stack of images sharing a common field of view. The process is called rigid alignment¹⁹. The resultant image stack was calculated into one averaged image which is called a reference image. Each raw image was compared to the reference image so that drift, noise and distortions of the raw images could be corrected. This process is called non-rigid alignment¹⁹. 5 iterations of non-rigid alignment were performed to improve the signal-to-noise ratio, which finally produced an averaged image shown in Fig. 6.1a.

The STM image in Fig. 6.1b was averaged from 71 raw STM images. The 71 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 6.1b.

The STM image in Fig. 6.1c was averaged from 14 raw STM images. The 14 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 6.1c.

The STM image in Fig. 6.1d was averaged from 8 raw STM images. The 8 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 6.1d.

Fig. 6.2a was generated from 20 raw STM images. The 20 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. We used the known 3-fold symmetry of the honeycomb structure to rotate the averaged image twice by 120° and thereby tripled the number of the image. We also used the known mirror symmetry of the honeycomb structure to flip the 3 images and thereby doubled the number of images. These processes produced 6 frames. We used the template matching tool to automatically identify defect free (5×5) unit from the 6 frames, yielding 290 tiles. The 290 tiles were processed through 5 iterations of non-rigid alignment, which generated an averaged image of a (5×5) unit cell shown in Fig. 6.2a.

Fig. 6.2c was generated from 6 raw STM images. The 6 raw images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. We used the known 3-fold symmetry of the honeycomb structure to rotate the averaged image twice by 120° and thereby tripled the number of the image. We also used the known mirror symmetry of the honeycomb structure to flip the 3 images and thereby doubled the number of images. These processes produced 6 frames. We used the template matching tool to automatically identify defect free (5×5) unit cells from the 6 frames, yielding 46 tiles. The 46 tiles were processed through 5 iterations of

non-rigid alignment, which generated an averaged image of a (5×5) unit cell shown in Fig. 6.2c.

Fig. 6.3a was generated from 20 raw STM images. The 20 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. We used the known 3-fold symmetry of the honeycomb structure to rotate the image twice by 120° and thereby tripled the number of the images. We also used the known mirror symmetry of the honeycomb structure to flip the 3 images and thereby doubled the number of images to average. These processes produced 6 frames. We used the template matching tool to automatically identify defect free (6×4) unit cells from the 6 frames, yielding 176 tiles. The 176 tiles were processed through 5 iterations of non-rigid alignment, which generated an averaged image of a (6×4) unit cell. This image of a (6×4) unit cell is colored using two look-up tables to generate two images of different contrast. The two images are joined together into one figure shown in Fig. 6.3a.

Fig. 6.6a was generated after averaging 150 frames. 25 raw STM images of the defect were taken. They were rotated twice by 120° and thereby multiplied the number of the raw image to average by three. We also used the known mirror symmetry of the honeycomb structure to flip the 75 images and thereby doubled the number of images. These processes produced 150 frames. The 150 frames were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image. Fig. 6.6b was generated from 60 images. 10 raw images were rotated twice by 120° and then mirrored, producing 60 frames. The averaged result of 60 frames is shown in Fig. 6.6c.

Appendix C Supporting Information of Chapter 7

Image processing procedures of multiple frame averaging.

Experimental STM images were processed using multiple frame averaging (MFA) to enhance the signal-to-noise ratio (see reference [19] and Chapter 4).

The STM image in Fig. 7.1a was generated from 119 raw STM images. 119 images were taken from the same area, of the same image size, with no change in tip configuration and only minor changes in the STM image parameters. The 119 images were aligned to generate a stack of images sharing a common field of view. The process is called rigid alignment.¹⁹ The resultant image stack was calculated into one averaged image which is called a reference image. Each raw image was compared to the reference image so that drift, noise and distortions of the raw images could be corrected. This process is called non-rigid alignment.¹⁹ 5 iterations of non-rigid alignment were performed to improve the signal-to-noise ratio, which finally produced an averaged image shown in Fig. 7.1a.

The STM image in Fig. 7.1b was averaged from 86 raw STM images. The 86 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 7.1b.

The STM image in Fig. 7.1c was averaged from 13 raw STM images. The 13 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 7.1c.

The STM image in Fig. 7.1d was averaged from 71 raw STM images. The 71 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 7.1d.

The STM image in Fig. 7.2a was averaged from 56 raw STM images. The 56 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 7.2a.

Fig. 7.2b was generated from 56 raw STM images. We used the known 2-fold mirror symmetry of the rectangular hexamer structure to flip the images and thereby doubled the number of the image to average. These processes produced 112 frames. The 112 tiles were processed through 5 iterations of non-rigid alignment, which generated an averaged image of a rectangular hexamer structure shown in Fig. 7.2b.

Fig. 7.2c was generated from 60 raw STM images. We used the known 2-fold symmetry of the rectangular octamer structure to rotate the 60 images by 180 degrees and thereby doubled the number of the images. We also used the mirror symmetry of the structure to flip the images and thereby doubled the number of the image to average. These processes produced 240 frames. The 240 tiles were processed through 5 iterations of non-rigid alignment, which generated an averaged image of a rectangular octamer structure shown in Fig. 7.2c.

Fig. 7.2d was generated from 9 raw STM images. We used the known 2-fold symmetry of the rectangular decamer structure to rotate the 9 images by 180 degrees and thereby doubled the number of the images. We also used the mirror symmetry of the structure to

flip the images and thereby doubled the number of the image to average. These processes produced 36 frames. The 36 tiles were processed through 5 iterations of non-rigid alignment, which generated an averaged image of a rectangular decamer structure shown in Fig. 7.2d.

The STM image in Fig. 7.3a was averaged from 60 raw STM images. The 60 images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated an averaged image shown in Fig. 7.3a.

Fig. 7.3b was generated from 25 raw STM images. We used the known 3-fold symmetry of the rectangular decamer structure to rotate the 25 images by 120 degrees and thereby tripled the number of the images to 75. The 75 tiles were processed through 5 iterations of non-rigid alignment, which generated an averaged image of a rectangular decamer structure shown in Fig. 7.3b.

The remaining STM images in this chapter were averaged from multiple STM images without any symmetry manipulation. The images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment.

Appendix D Supporting Information of Chapter 8

Image processing procedures of multiple frame averaging.

Experimental STM images were processed using multiple frame averaging (MFA) to enhance the signal-to-noise ratio (see reference [19] and Chapter 4).

The STM images from Fig. 8.2(a-c, e-f) are generated from 15, 11, 88 7, and 8 frames using MFA. The STM images were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment, which generated five averaged image shown in Fig. 8.2.

Fig. 8.3(a & d) were generated from the same raw data and the same process as that for Fig. 8.2d, except that Fig. 8.3(a & d) were cropped from a smaller field of view to show two unit cells for the 48 boundary and 558 boundary, respectively.

Fig. 8.3b was generated from the same raw data and the same process as that for Fig. 8.2e, except that Fig. 8.3b were cropped from a smaller field of view to show one unit cell for the 5577 boundary.

Fig. 8.3c is a single image processed using median filter.

The STM images in Fig. 8.6 were processed through 5 iterations of rigid alignment and 5 iterations of non-rigid alignment.

All the STM images in Fig. 8.7 are processed via mirror manipulation (the detailed procedure is similar to that described in Appendix A) and then averaged. Fig. 8.8a is processed using mirror symmetry and then averaged. Fig. 8.8b-c and Fig. 8.9a are averaged without symmetry manipulation.

References

- (1) Fu, Q.; Wagner, T. Interaction of Nanostructured Metal Overlayers with Oxide Surfaces. *Surf. Sci. Rep.* **2007**, *62*, 431–498.
- (2) Fester, J.; Makoveev, A.; Grumelli, D.; Gutzler, R.; Sun, Z.; Rodríguez-Fernández, J.; Kern, K.; Lauritsen, J. V. The Structure of the Cobalt Oxide/Au Catalyst Interface in Electrochemical Water Splitting. *Angew. Chem., Int. Ed.* **2018**, *57*, 11893–11897.
- (3) Rodriguez, J.; Ma, S.; Liu, P.; Hrbek, J.; Evans, J.; Pérez, M. Activity of CeO_x and TiO_x Nanoparticles Grown on Au(111) in the Water-Gas Shift Reaction. *Science* **2007**, *318*, 1757.
- (4) Förster, S.; Meinel, K.; Hammer, R.; Trautmann, M.; Widdra, W. Quasicrystalline Structure Formation in a Classical Crystalline Thin-Film System. *Nature* **2013**, *502*, 215–218.
- (5) Wu, C.; Castell, M. R.; Goniakowski, J.; Noguera, C. Stoichiometry Engineering of Ternary Oxide Ultrathin Films: Ba_xTi₂O₃ on Au(111). *Phys. Rev. B* **2015**, *91*, 155424.
- (6) Sedona, F.; Rizzi, G. A.; Agnoli, S.; Llabres i Xamena, F. X.; Papageorgiou, A.; Ostermann, D.; Sambi, M.; Finetti, P.; Schierbaum, K.; Granozzi, G. Ultrathin TiO_x Films on Pt(111): A LEED, XPS, and STM Investigation. *J. Phys. Chem. B* **2005**, *109*, 24411–24426.
- (7) Sedona, F.; Agnoli, S.; Granozzi, G. Ultrathin Wagon-Wheel-like TiO_x Phases on Pt (111): A Combined Low-Energy Electron Diffraction and Scanning Tunneling Microscopy Investigation. *J. Phys. Chem. B* **2006**, 15359–15367.
- (8) Sedona, F.; Granozzi, G.; Barcaro, G.; Fortunelli, A. Defect Evolution in Oxide Nanophases: The Case of a Zigzag-like TiO_x Phase on Pt(111). *Phys. Rev. B* **2008**, *77*, 115417.
- (9) Wu, C.; Marshall, M. S. J.; Castell, M. R. Surface Structures of Ultrathin TiO_x Films on Au(111). *J. Phys. Chem. C* **2011**, *115*, 8643–8652.
- (10) Wachs, I. E.; Chen, Y.; Jehng, J. M.; Briand, L. E.; Tanaka, T. Molecular Structure and Reactivity of the Group V Metal Oxides. *Catal. Today* **2003**, *78*, 13–24.
- (11) Zhao, Y.; Zhang, Z.; Lin, Y. Optical and Dielectric Properties of a Nanostructured NbO₂ Thin Film Prepared by Thermal Oxidation. *J. Phys. D* **2004**, *37*, 3392–3395.
- (12) Xie, L.; Wang, D.; Zhong, C.; Guo, X.; Ushikubo, T.; Wada, K. The Preparation of and Water Adsorption on Thin Films of Niobium Oxide on Pt(111). *Surf. Sci.* **1994**, *320*, 62–76.
- (13) Starr, D. E.; Mendes, F. M.; Middeke, J.; Blum, R. P.; Niehus, H.; Lahav, D.; Guimond, S.; Uhl, A.; Kluener, T.; Schmal, M.; *et al.* Preparation and Characterization of Well-Ordered, Thin Niobia Films on a Metal Substrate. *Surf.*

- Sci.* **2005**, *599*, 14–26.
- (14) Zhang, S. J.; Zhang, C. W.; Zhang, S. F.; Ji, W. X.; Li, P.; Wang, P. J.; Li, S. S.; Yan, S. S. Intrinsic Dirac Half-Metal and Quantum Anomalous Hall Phase in a Hexagonal Metal-Oxide Lattice. *Phys. Rev. B* **2017**, *96*, 205433.
 - (15) Marshall, M. S. J. Nanostructured Strontium Titanate Surfaces, University of Oxford, 2009.
 - (16) Hamers, R. Atomic-Resolution Surface Spectroscopy With The Scanning Tunneling Microscope. *Annu. Rev. Phys. Chem.* **1989**, *40*, 531–559.
 - (17) Diebold, U. Oxide Surfaces: Surface Science Goes Inorganic. *Nat. Mater.* **2010**, *9*, 185–187.
 - (18) Hamidian, M. H.; Sprau, P. O.; Edkins, S. D.; Davis, J. C. S.; Kazuhiro, F. Visualizing Electronic Quantum Matter. In *Springer Handbook of Microscopy*; 2019; pp. 1389–1411.
 - (19) Jones, L.; Yang, H.; Pennycook, T. J.; Marshall, M. S. J.; Van Aert, S.; Browning, N. D.; Castell, M. R.; Nellist, P. D. Smart Align—a New Tool for Robust Non-Rigid Registration of Scanning Microscope Data. *Adv. Struct. Chem. Imaging* **2015**, *1*, 8.
 - (20) Netzer, F. P. *Oxide Materials at the Two-Dimensional Limit*; Springer: Switzerland, 2016.
 - (21) Goniakowski, J.; Noguera, C. Insulating Oxide Surfaces and Nanostructures. *Comptes Rendus Phys.* **2016**, *17*, 471–480.
 - (22) Attard, G.; Barnes, C. *Surfaces*; Oxford Chemistry Primers, 1988.
 - (23) Shaikhutdinov, S.; Freund, H.-J. Ultrathin Oxide Films on Metal Supports: Structure-Reactivity Relations. *Annu. Rev. Phys. Chem.* **2012**, *63*, 619–633.
 - (24) Chen, H.; Bettayeb, M.; Maurice, V.; Klein, L. H.; Lapeire, L.; Verbeken, K.; Terryn, H.; Marcus, P. Local Passivation of Metals at Grain Boundaries : In Situ Scanning Tunneling Microscopy Study on Copper. *Corros. Sci.* **2016**, *111*, 659–666.
 - (25) Tauster, S. J.; Fung, S. C.; Baker, R. T.; Horsley, J. A. Strong Interactions in Supported-Metal Catalysts. *Science* **1981**, *211*, 1121–1125.
 - (26) Venables, J. A.; Spiller, G. D. T.; Hanbucken, M. Nucleation and Growth of Thin Films. *Reports Prog. Phys.* **1984**, *47*, 399–459.
 - (27) Merte, L. R.; Grabow, L. C.; Peng, G.; Knudsen, J.; Zeuthen, H.; Kudernatsch, W.; Porsgaard, S.; Laegsgaard, E.; Mavrikakis, M.; Besenbacher, F. Tip-Dependent Scanning Tunneling Microscopy Imaging of Ultrathin FeO Films on Pt(111). *J. Phys. Chem. C* **2011**, *115*, 2089–2099.
 - (28) Merte, L. R.; Bechstein, R.; Peng, G.; Rieboldt, F.; Farberow, C. A.; Zeuthen, H.; Knudsen, J.; Lægsgaard, E.; Wendt, S.; Mavrikakis, M.; *et al.* Water Clustering on Nanostructured Iron Oxide Films. *Nat. Commun.* **2014**, *5*, 4193.
 - (29) Ritter, M.; Ranke, W.; Weiss, W. Growth and Structure of Ultrathin FeO Films on Pt(111) Studied by STM and LEED. *Phys. Rev. B* **1998**, *57*, 7240–7251.

- (30) De Santis, M.; Buchsbaum, A.; Varga, P.; Schmid, M. Growth of Ultrathin Cobalt Oxide Films on Pt(111). *Phys. Rev. B* **2011**, *84*, 125430.
- (31) Deng, X.; Matranga, C. Selective Growth of Fe₂O₃ Nanoparticles and Islands on Au(111). *J. Phys. Chem. C* **2009**, *113*, 11104–11109.
- (32) Fester, J.; Bajdich, M.; Walton, A. S.; Sun, Z.; Plessow, P. N.; Vojvodic, A.; Lauritsen, J. V. Comparative Analysis of Cobalt Oxide Nanoisland Stability and Edge Structures on Three Related Noble Metal Surfaces: Au(111), Pt(111) and Ag(111). *Top. Catal.* **2017**, *60*, 503–512.
- (33) Steurer, W.; Surnev, S.; Fortunelli, A.; Netzer, F. P. Scanning Tunneling Microscopy Imaging of NiO(100)(1 × 1) Islands Embedded in Ag(100). *Surf. Sci.* **2012**, *606*, 803–807.
- (34) Doudin, N.; Kuhness, D.; Blatnik, M.; Barcaro, G.; Negreiros, F. R.; Sementa, L.; Fortunelli, A.; Surnev, S.; Netzer, F. P. Nanoscale Domain Structure and Defects in a 2-D WO₃ Layer on Pd(100). *J. Phys. Chem. C* **2016**, *120*, 28682–28693.
- (35) Allegretti, F.; Parteder, G.; Gragnaniello, L.; Surnev, S.; Netzer, F. P.; Barolo, A.; Agnoli, S.; Granozzi, G.; Franchini, C.; Podloucky, R. Strained c(4 × 2) CoO(100)-like Monolayer on Pd (100): Experiment and Theory. *Surf. Sci.* **2010**, *604*, 529–534.
- (36) Surnev, S.; Vitali, L.; Ramsey, M. G.; Netzer, F. P.; Kresse, G.; Hafner, J. Growth and Structure of Ultrathin Vanadium Oxide Layers on Pd(111). *Phys. Rev. B* **2000**, *61*, 13945.
- (37) Tumino, F.; Carrozzo, P.; Mascaretti, L.; Casari, C. S.; Passoni, M.; Tosoni, S.; Bottani, C. E. Two-Dimensional TiO_x Nanostructures on Au(111): A Scanning Tunneling Microscopy and Spectroscopy Investigation. *2D Mater.* **2015**, *2*, 045011.
- (38) Ragazzon, D.; Schaefer, A.; Farstad, M. H.; Walle, L. E.; Palmgren, P.; Borg, A.; Uvdal, P.; Sandell, A. Chemical Vapor Deposition of Ordered TiO_x Nanostructures on Au(111). *Surf. Sci.* **2013**, *617*, 211–217.
- (39) Farstad, M. H.; Ragazzon, D.; Walle, L. E.; Schaefer, A.; Sandell, A.; Borg, A. Water Adsorption on TiO_x Thin Films Grown on Au(111). *J. Phys. Chem. C* **2015**, *119*, 6660–6669.
- (40) Pomp, S.; Kuhness, D.; Barcaro, G.; Sementa, L.; Mankad, V.; Fortunelli, A.; Sterrer, M.; Netzer, F. P.; Surnev, S. Two-Dimensional Iron Tungstate: A Ternary Oxide Layer with Honeycomb Geometry. *J. Phys. Chem. C* **2016**, *120*, 7629–7638.
- (41) Barcaro, G.; Cavaliere, E.; Artiglia, L.; Sementa, L.; Gavioli, L.; Granozzi, G.; Fortunelli, A. Building Principles and Structural Motifs in TiO_x Ultrathin Films on a (111) Substrate. *J. Phys. Chem. C* **2012**, *116*, 13302–13306.
- (42) Barcaro, G.; Sedona, F.; Fortunelli, A.; Granozzi, G. Structure of a TiO_x Zigzag-like Monolayer on Pt(111). *J. Phys. Chem. C* **2007**, *111*, 6095–6102.
- (43) Barcaro, G.; Agnoli, S.; Sedona, F.; Rizzi, G. A.; Fortunelli, A.; Granozzi, G. Structure of Reduced Ultrathin TiO_x Polar Films on Pt(111). *J. Phys. Chem. C*

2009, *113*, 5721–5729.

- (44) Barcaro, G.; Fortunelli, A. Adsorption and Diffusion of Fe on a Titania Ultrathin Film. *J. Phys. Chem. A* **2009**, *113*, 14860–14866.
- (45) Fester, J.; Sun, Z.; Rodríguez-Fernández, J.; Walton, A.; Lauritsen, J. V. Phase Transitions of Cobalt Oxide Bilayers on Au(111) and Pt(111): The Role of Edge Sites and Substrate Interactions. *J. Phys. Chem. B* **2018**, *122*, 561–571.
- (46) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
- (47) Vogt, P.; De Padova, P.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asensio, M. C.; Resta, A.; Ealet, B.; Le Lay, G. Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon. *Phys. Rev. Lett.* **2012**, *108*, 155501.
- (48) Meyer, J. C.; Chuvilin, A.; Algara-siller, G.; Biskupek, J.; Kaiser, U. Selective Sputtering and Atomic Resolution Imaging of Atomically Thin Boron Nitride Membranes. *Nano Lett.* **2009**, *9*, 2683–2689.
- (49) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tománek, D.; Ye, P. D. Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility. *ACS Nano* **2014**, *8*, 4033–4041.
- (50) Zhu, F.-F.; Chen, W.-J.; Xu, Y.; Gao, C.-L.; Guan, D.-D.; Liu, C.-H.; Qian, D.; Zhang, S.-C.; Jia, J.-F. Epitaxial Growth of Two-Dimensional Stanene. *Nat. Mater.* **2015**, *14*, 1020–1025.
- (51) Dávila, M. E.; Xian, L.; Cahangirov, S.; Rubio, A.; Le Lay, G. Germanene: A Novel Two-Dimensional Germanium Allotrope Akin to Graphene and Silicene. *New J. Phys.* **2014**, *16*, 095002.
- (52) Liu, Y.; Zou, X.; Yakobson, B. I. Dislocations and Grain Boundaries in Two-Dimensional Boron Nitride. *ACS Nano* **2012**, *6*, 7053–7058.
- (53) Li, L.; Lu, S. Z.; Pan, J.; Qin, Z.; Wang, Y. Q.; Wang, Y.; Cao, G. Y.; Du, S.; Gao, H. J. Buckled Germanene Formation on Pt(111). *Adv. Mater.* **2014**, *26*, 4820–4824.
- (54) Mannix, A. J.; Kiraly, B.; Hersam, M. C.; Guisinger, N. P. Synthesis and Chemistry of Elemental 2D Materials. *Nat. Rev. Chem.* **2017**, *1*, 0014.
- (55) Löffler, D.; Uhlrich, J. J.; Baron, M.; Yang, B.; Yu, X.; Lichtenstein, L.; Heinke, L.; Büchner, C.; Heyde, M.; Shaikhutdinov, S.; *et al.* Growth and Structure of Crystalline Silica Sheet on Ru(0001). *Phys. Rev. Lett.* **2010**, *105*, 146104.
- (56) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. 2D Materials and van Der Waals Heterostructures. *Science* **2016**, *353*, 9439.
- (57) Carrasco, J.; Hodgson, A.; Michaelides, A. A Molecular Perspective of Water at Metal Interfaces. *Nat. Mater.* **2012**, *11*, 667–674.
- (58) Goniakowski, J.; Noguera, C. Intrinsic Properties of Pure and Mixed Monolayer Oxides in the Honeycomb Structure: M_2O_3 and $MM'O_3$ ($M, M' = Ti, V, Cr, Fe$). *J. Phys. Chem. C* **2019**, *123*, 7898–7910.

- (59) Kresse, G.; Surnev, S.; Schoiswohl, J.; Netzer, F. $V_2O_3(0001)$ Surface Terminations: A Density Functional Study. *Surf. Sci.* **2004**, 555, 118–134.
- (60) Goniakowski, J.; Noguera, C. Properties of $M_2O_3/Au(111)$ Honeycomb Monolayers ($M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni$). *J. Phys. Chem. C* **2019**, 123, 9272–9281.
- (61) Plessow, P. N.; Bajdich, M.; Greene, J.; Vojvodic, A.; Abild-Pedersen, F. Trends in the Thermodynamic Stability of Ultrathin Supported Oxide Films. *J. Phys. Chem. C* **2016**, 120, 10351–10360.
- (62) Surnev, S.; Kresse, G.; Sock, M.; Ramsey, M. G.; Netzer, F. P. Surface Structures of Ultrathin Vanadium Oxide Films on Pd(111). *Surf. Sci.* **2001**, 495, 91–106.
- (63) Chen, Q.; Robertson, A. W.; He, K.; Gong, C.; Yoon, E.; Lee, G. Do; Warner, J. H. Atomic Level Distributed Strain within Graphene Divacancies from Bond Rotations. *ACS Nano* **2015**, 9, 8599–8608.
- (64) Kresse, G.; Surnev, S.; Ramsey, M. G.; Netzer, F. P. First-Principles Calculations for V_xO_y Grown on Pd(111). *Surf. Sci.* **2001**, 492, 329–344.
- (65) Möller, C.; Fedderwitz, H.; Noguera, C.; Goniakowski, J.; Nilius, N. Temperature-Dependent Phase Evolution of Copper-Oxide Thin-Films on Au(111). *Phys. Chem. Chem. Phys.* **2018**, 20, 5636–5643.
- (66) Liu, Q.; Han, N.; Zhang, S.; Zhao, J.; Yang, F.; Bao, X. Tuning the Structures of Two-Dimensional Cuprous Oxide Confined on Au(111). *Nano Res.* **2018**, 11, 5957–5967.
- (67) Banhart, F.; Kotakoski, J.; Krashenninnikov, A. V. Structural Defects in Graphene. *ACS Nano* **2011**, 5, 26–41.
- (68) Meyer, J. C.; Kisielowski, C.; Erin, R.; Rossell, M. D.; Crommie, M. F. Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes. *Nano Lett.* **2008**, 8, 3582–3586.
- (69) Hashimoto, A.; Suenaga, K.; Gloter, A.; Urita, K.; Iijima, S. Direct Evidence for Atomic Defects in Graphene Layers. *Nature* **2004**, 430, 870–873.
- (70) Ugeda, M. M.; Brihuega, I.; Guinea, F.; Gómez-Rodríguez, J. M. Missing Atom as a Source of Carbon Magnetism. *Phys. Rev. Lett.* **2010**, 104, 096804.
- (71) Ma, Y.; Lehtinen, P. O.; Foster, A. S.; Nieminen, R. M. Magnetic Properties of Vacancies in Graphene and Single-Walled Carbon Nanotubes. *New J. Phys.* **2004**, 6, 1367–2630.
- (72) Jupille, J.; Thornton, G. *Defects at Oxide Surfaces*; Springer, 2015.
- (73) Chen, B.; Ma, Y.; Ding, L.; Xu, L.; Wu, Z.; Yuan, Q.; Huang, W. Reactivity of Hydroxyls and Water on a $CeO_2(111)$ Thin Film Surface: The Role of Oxygen Vacancy. *J. Phys. Chem. C* **2013**, 117, 5800–5810.
- (74) Xu, L.; Wu, Z.; Zhang, W.; Jin, Y.; Yuan, Q.; Ma, Y.; Huang, W. Oxygen Vacancy-Induced Novel Low-Temperature Water Splitting Reactions on $FeO(111)$ Monolayer-Thick Film. *J. Phys. Chem. C* **2012**, 116, 22921–22929.
- (75) Xu, L.; Wu, Z.; Zhang, Y.; Chen, B.; Jiang, Z.; Ma, Y.; Huang, W. Hydroxyls-

- Involved Interfacial Co Oxidation Catalyzed by FeO_x(111) Monolayer Islands Supported on Pt(111) and the Unique Role of Oxygen Vacancy. *J. Phys. Chem. C* **2011**, *115*, 14290–14299.
- (76) Xu, L.; Zhang, W.; Zhang, Y.; Wu, Z.; Chen, B.; Jiang, Z.; Ma, Y.; Yang, J.; Huang, W. Oxygen Vacancy-Controlled Reactivity of Hydroxyls on an FeO(111) Monolayer Film. *J. Phys. Chem. C* **2011**, *115*, 6815–6824.
 - (77) Lahiri, J.; Lin, Y.; Bozkurt, P.; Oleynik, I. I.; Batzill, M. An Extended Defect in Graphene as a Metallic Wire. *Nat. Nanotechnol.* **2010**, *5*, 326–329.
 - (78) Huang, P. Y.; Ruiz-Vargas, C. S.; Van Der Zande, A. M.; Whitney, W. S.; Levendorf, M. P.; Kevek, J. W.; Garg, S.; Alden, J. S.; Hustedt, C. J.; Zhu, Y.; *et al.* Grains and Grain Boundaries in Single-Layer Graphene Atomic Patchwork Quilts. *Nature* **2011**, *469*, 389–392.
 - (79) Ulrich, S.; Nilius, N.; Freund, H. J.; Martinez, U.; Giordano, L.; Pacchioni, G. Evidence for a Size-Selective Adsorption Mechanism on Oxide Surfaces: Pd and Au Atoms on SiO₂/Mo(112). *ChemPhysChem* **2008**, *9*, 1367–1370.
 - (80) Wei, Y.; Wu, J.; Yin, H.; Shi, X.; Yang, R.; Dresselhaus, M. The Nature of Strength Enhancement and Weakening by Pentagon–heptagon Defects in Graphene. *Nat. Mater.* **2012**, *11*, 759–763.
 - (81) Tison, Y.; Lagoute, J.; Repain, V.; Chacon, C.; Girard, Y.; Joucken, F.; Sporken, R.; Gargiulo, F.; Yazyev, O. V.; Rousset, S. Grain Boundaries in Graphene on SiC(0001) Substrate. *Nano Lett.* **2014**, *14*, 6382–6386.
 - (82) Botello-Méndez, A. R.; Declerck, X.; Terrones, M.; Terrones, H.; Charlier, J.-C. One-Dimensional Extended Lines of Divacancy Defects in Graphene. *Nanoscale* **2011**, *3*, 2868–2872.
 - (83) Li, Q.; Zou, X.; Liu, M.; Sun, J.; Gao, Y.; Qi, Y.; Zhou, X.; Yakobson, B. I.; Zhang, Y.; Liu, Z. Grain Boundary Structures and Electronic Properties of Hexagonal Boron Nitride on Cu(111). *Nano Lett.* **2015**, *15*, 5804–5810.
 - (84) Gibb, A. L.; Alem, N.; Chen, J. H.; Erickson, K. J.; Ciston, J.; Gautam, A.; Linck, M.; Zettl, A. Atomic Resolution Imaging of Grain Boundary Defects in Monolayer Chemical Vapor Deposition-Grown Hexagonal Boron Nitride. *J. Am. Chem. Soc.* **2013**, *135*, 6758.
 - (85) Liu, Y.; Yakobson, B. I. Cones, Pringles, and Grain Boundary Landscapes in Graphene Topology. *Nano Lett.* **2010**, *10*, 2178–2183.
 - (86) Lewandowski, A. L.; Schlexer, P.; Büchner, C.; Davis, E. M.; Burrall, H.; Burson, K. M.; Schneider, W.-D. D.; Heyde, M.; Pacchioni, G.; Freund, H.-J. J. Atomic Structure of a Metal-Supported Two-Dimensional Germania Film. *Phys. Rev. B* **2018**, *97*, 115406.
 - (87) Oh, Y.; Cho, Y.; Kwon, H.; Lee, J.; Jeon, I.; Ko, W.; Kim, H. W.; Ku, J.; Kim, G.; Suh, H.; *et al.* Electronic Structure and Switching Behavior of the Metastable Silicene Domain Boundary. *Appl. Phys. Lett.* **2017**, *110*, 263112.
 - (88) Weissenrieder, J.; Kaya, S.; Lu, J. L.; Gao, H. J.; Shaikhutdinov, S.; Freund, H. J.; Sierka, M.; Todorova, T. K.; Sauer, J. Atomic Structure of a Thin Silica Film on a

- Mo(112) Substrate: A Two-Dimensional Network of SiO₄ Tetrahedra. *Phys. Rev. Lett.* **2005**, *95*, 076103.
- (89) Yang, B.; Boscoboinik, J. A.; Yu, X.; Shaikhutdinov, S.; Freund, H. J. Patterned Defect Structures Predicted for Graphene Are Observed on Single-Layer Silica Films. *Nano Lett.* **2013**, *13*, 4422–4427.
 - (90) Mathur, S.; Vlaic, S.; Machado-Charry, E.; Vu, A. D.; Guisset, V.; David, P.; Hadji, E.; Pochet, P.; Coraux, J. Degenerate Epitaxy-Driven Defects in Monolayer Silicon Oxide on Ruthenium. *Phys. Rev. B* **2015**, *92*, 161410.
 - (91) Stone, A. J.; Wales, D. J. Theoretical Studies of Icosahedral C₆₀ and Some Related Species. *Chem. Phys. Lett.* **1986**, *128*, 501–503.
 - (92) Lee, G. Do; Wang, C. Z.; Yoon, E.; Hwang, N. M.; Kim, D. Y.; Ho, K. M. Diffusion, Coalescence, and Reconstruction of Vacancy Defects in Graphene Layers. *Phys. Rev. Lett.* **2005**, *95*, 205501.
 - (93) Kotakoski, J.; Krasheninnikov, A. V.; Kaiser, U.; Meyer, J. C. From Point Defects in Graphene to Two-Dimensional Amorphous Carbon. *Phys. Rev. Lett.* **2011**, *106*, 105505.
 - (94) Slotman, G. J.; Fasolino, A. Structure, Stability and Defects of Single Layer Hexagonal BN in Comparison to Graphene. *J. Phys.: Condens. Matter* **2013**, *25*, 045009.
 - (95) Lin, Y.-C.; Björkman, T.; Komsa, H.-P.; Teng, P.-Y.; Yeh, C.-H.; Huang, F.-S.; Lin, K.-H.; Jadcak, J.; Huang, Y.-S.; Chiu, P.-W.; *et al.* Three-Fold Rotational Defects in Two-Dimensional Transition Metal Dichalcogenides. *Nat. Commun.* **2015**, *6*, 6736.
 - (96) Burson, K. M.; Büchner, C.; Heyde, M.; Freund, H.-J. Assessing the Amorphousness and Periodicity of Common Domain Boundaries in Silica Bilayers on Ru(0001). *J. Phys.: Condens. Matter* **2017**, *29*, 035002.
 - (97) Nie, S.; Feibelman, P. J.; Bartelt, N. C.; Thürmer, K. Pentagons and Heptagons in the First Water Layer on Pt(111). *Phys. Rev. Lett.* **2010**, *105*, 026102.
 - (98) Maier, S.; Lechner, B. A. J.; Somorjai, G. A.; Salmeron, M. Growth and Structure of the First Layers of Ice on Ru(0001) and Pt(111). *J. Am. Chem. Soc.* **2016**, *138*, 3145–3151.
 - (99) Whitelam, S.; Tamblyn, I.; Haxton, T. K.; Wieland, M. B.; Champness, N. R.; Garrahan, J. P.; Beton, P. H. Common Physical Framework Explains Phase Behavior and Dynamics of Atomic, Molecular, and Polymeric Network Formers. *Phys. Rev. X* **2014**, *4*, 011044.
 - (100) Bissett, M. A.; Konabe, S.; Okada, S.; Tsuji, M.; Ago, H. Enhanced Chemical Reactivity of Graphene Induced by Mechanical Strain. *ACS Nano* **2013**, *7*, 10335–10343.
 - (101) Hao, F.; Chen, X. First-Principles Study of Lithium Adsorption and Diffusion on Graphene: The Effects of Strain. *Mater. Res. Express* **2015**, *2*, 105016.
 - (102) Li, H.; Tsai, C.; Koh, A. L.; Cai, L.; Contryman, A. W.; Fragapane, A. H.; Zhao, J.; Han, H. S.; Manoharan, H. C.; Abild-Pedersen, F.; *et al.* Activating and

- Optimizing MoS₂ Basal Planes for Hydrogen Evolution through the Formation of Strained Sulphur Vacancies. *Nat. Mater.* **2016**, *15*, 48–53.
- (103) Zhao, X.; Ding, Z.; Chen, J.; Dan, J.; Poh, S. M.; Fu, W.; Pennycook, S. J.; Zhou, W.; Loh, K. P. Strain Modulation by van Der Waals Coupling in Bilayer Transition Metal Dichalcogenide. *ACS Nano* **2018**, *12*, 1940–1948.
- (104) Ambrosetti, A.; Silvestrelli, P. L. Toward Tunable CO Adsorption on Defected Graphene: The Chemical Role of Ni(111) and Cu(111) Substrates. *J. Phys. Chem. C* **2017**, *121*, 19828–19835.
- (105) Jacobson, P.; Stöger, B.; Garhofer, A.; Parkinson, G. S.; Schmid, M.; Caudillo, R.; Mittendorfer, F.; Redinger, J.; Diebold, U. Disorder and Defect Healing in Graphene on Ni(111). *J. Phys. Chem. Lett.* **2012**, *3*, 136–139.
- (106) Ma, J.; Alfè, D.; Michaelides, A.; Wang, E. Stone-Wales Defects in Graphene and Other Planar Sp²-Bonded Materials. *Phys. Rev. B* **2009**, *80*, 033407.
- (107) Wang, R.; Yang, J.; Wu, X.; Wang, S. Local Charge States in Hexagonal Boron Nitride with Stone–Wales Defects. *Nanoscale* **2016**, *8*, 8210–8219.
- (108) Gao, J.; Zhang, J.; Liu, H.; Zhang, Q.; Zhao, J. Structures, Mobilities, Electronic and Magnetic Properties of Point Defects in Silicene. *Nanoscale* **2013**, *5*, 9785–9792.
- (109) Boukhvalov, D. W.; Katsnelson, M. I. Chemical Functionalization of Graphene with Defects. *Nano Lett.* **2008**, *8*, 4373–4379.
- (110) Barone, V.; Hod, O.; Scuseria, G. E. Electronic Structure and Stability of Semiconducting Graphene Nanoribbons. *Nano Lett.* **2006**, *6*, 2748–2754.
- (111) Warner, J. H.; Lin, Y.-C.; He, K.; Koshino, M.; Suenaga, K. Atomic Level Spatial Variations of Energy States along Graphene Edges. *Nano Lett.* **2014**, *14*, 6155–6159.
- (112) Son, Y. W.; Cohen, M. L.; Louie, S. G. Half-Metallic Graphene Nanoribbons. *Nature* **2006**, *444*, 347–349.
- (113) Acik, M.; Chabal, Y. J. Nature of Graphene Edges: A Review. *Japanese Journal of Applied Physics* **2011**, *50*, 070101.
- (114) Koskinen, P.; Malola, S.; Häkkinen, H. Self-Passivating Edge Reconstructions of Graphene. *Phys. Rev. Lett.* **2008**, *101*, 115502.
- (115) Koskinen, P.; Malola, S.; Häkkinen, H. Evidence for Graphene Edges beyond Zigzag and Armchair. *Phys. Rev. B* **2009**, *80*, 073401.
- (116) Ding, Y.; Wang, Y. Electronic Structures of Reconstructed Zigzag Silicene Nanoribbons. *Appl. Phys. Lett.* **2014**, *104*, 083111.
- (117) Huang, B.; Lee, H.; Gu, B.; Liu, F.; Duan, W. Edge Stability of Boron Nitride Nanoribbons and Its Application in Designing Hybrid BNC Structures. *Nano Res.* **2012**, *5*, 62–72.
- (118) Hu, T.; Han, Y.; Dong, J. Edge Reconstructions of Hexagonal Boron Nitride Nanoribbons : A First-Principles Study. *Physica E* **2013**, *54*, 191–196.

- (119) Pang, Q.; Zhang, Y.; Zhang, J. M.; Ji, V.; Xu, K. W. Electronic and Magnetic Properties of Pristine and Chemically Functionalized Germanene Nanoribbons. *Nanoscale* **2011**, *3*, 4330–4338.
- (120) Aghaei, S. M.; Monshi, M. M.; Torres, I.; Calizo, I. Edge Functionalization and Doping Effects on the Stability, Electronic and Magnetic Properties of Silicene Nanoribbons. *RSC Adv.* **2016**, *6*, 17046–17058.
- (121) Robertson, A. W.; Warner, J. H. Atomic Resolution Imaging of Graphene by Transmission Electron Microscopy. *Nanoscale* **2013**, *5*, 4079–4093.
- (122) Girit, C. O.; Meyer, J. C.; Erni, R.; Rossell, M. D.; Kisielowski, C.; Yang, L.; Park, C.-H.; Crommie, M. F.; Cohen, M. L.; Louie, S. G.; *et al.* Graphene at the Edge: Stability and Dynamics. *Science* **2009**, *323*, 1705–1708.
- (123) He, K.; Robertson, A. W.; Lee, S.; Yoon, E.; Lee, G.; Warner, J. H. Extended Klein Edges in Graphene. *ACS Nano* **2014**, 12272–12279.
- (124) He, K.; Lee, G.; Robertson, A. W.; Yoon, E.; Warner, J. H. Hydrogen-Free Graphene Edges. *Nat. Commun.* **2014**, *5*, 3040.
- (125) Zhao, R.; Li, F.; Liu, Z.; Liu, Z.; Ding, F. The Transition Metal Surface Passivated Edges of Hexagonal Boron Nitride (h-BN) and the Mechanism of h-BN's Chemical Vapor Deposition (CVD) Growth. *Phys. Chem. Chem. Phys.* **2015**, *17*, 29327–29334.
- (126) Fu, Q.; Li, W. X.; Yao, Y.; Liu, H.; Su, H. Y.; Ma, D.; Gu, X. K.; Chen, L.; Wang, Z.; Zhang, H.; *et al.* Interface-Confined Ferrous Centers for Catalytic Oxidation. *Science* **2010**, *328*, 1141–1144.
- (127) Marshall, M. S.; Castell, M. R. Scanning Tunnelling Microscopy of Epitaxial Nanostructures. *Chem. Soc. Rev.* **2014**, *43*, 2226–2239.
- (128) Fu, Q.; Yang, F.; Bao, X. Interface-Confined Oxide Nanostructures for Catalytic Oxidation Reactions. *Acc. Chem. Res.* **2013**, *46*, 1692–1701.
- (129) Liu, Y.; Yang, F.; Zhang, Y.; Xiao, J.; Yu, L.; Liu, Q.; Ning, Y.; Zhou, Z.; Chen, H.; Huang, W.; *et al.* Enhanced Oxidation Resistance of Active Nanostructures via Dynamic Size Effect. *Nat. Commun.* **2017**, *8*, 14459.
- (130) Surnev, S.; Fortunelli, A.; Netzer, F. P. Structure-Property Relationship and Chemical Aspects of Oxide-Metal Hybrid Nanostructures. *Chem. Rev.* **2013**, *113*, 4314–4372.
- (131) Pan, Y.; Benedetti, S.; Noguera, C.; Giordano, L.; Goniakowski, J.; Nilius, N. Compensating Edge Polarity: A Means to Alter the Growth Orientation of MgO Nanostructures on Au(111). *J. Phys. Chem. C* **2012**, *116*, 11126–11132.
- (132) Schoiswohl, J.; Sock, M.; Chen, Q.; Thornton, G.; Kresse, G.; Ramsey, M.; Surnev, S.; Netzer, F. Metal Supported Oxide Nanostructures: Model Systems for Advanced Catalysis. *Top. Catal.* **2007**, *46*, 137–149.
- (133) Schoiswohl, J.; Surnev, S.; Sock, M.; Eck, S.; Ramsey, M. G.; Netzer, F. P.; Kresse, G. Reduction of Vanadium-Oxide Monolayer Structures. *Phys. Rev. B* **2005**, *71*, 165437.

- (134) Schoiswohl, J.; Surnev, S.; Sock, M.; Ramsey, M. G.; Kresse, G.; Netzer, F. P. Thermodynamically Controlled Self-Assembly of Two-Dimensional Oxide Nanostructures. *Angew. Chem. Int. Ed.* **2004**, *43*, 5546–5549.
- (135) Liu, Y.; Ning, Y.; Yu, L.; Zhou, Z.; Liu, Q.; Zhang, Y.; Chen, H.; Xiao, J.; Liu, P.; Yang, F.; *et al.* The Structure and Electronic Properties of Interface-Confined Oxide Nanostructures. *ACS Nano* **2017**, *11*, 11449–11458.
- (136) Li, M.; Altman, E. I. Cluster-Size Dependent Phase Transition of Co Oxides on Au(111). *Surf. Sci.* **2014**, *619*, L6–L10.
- (137) Smerieri, M.; Pal, J.; Savio, L.; Vattuone, L.; Ferrando, R.; Tosoni, S.; Giordano, L.; Pacchioni, G.; Rocca, M. Spontaneous Oxidation of Ni Nanoclusters on MgO Monolayers Induced by Segregation of Interfacial Oxygen. *J. Phys. Chem. Lett.* **2015**, *6*, 3104–3109.
- (138) Nakayama, M.; Xue, M.; An, W.; Liu, P.; White, M. G. Influence of Cluster—support Interactions on Reactivity of Size-Selected Nb_xO_y Clusters. *J. Phys. Chem. C* **2015**, *119*, 14756–14768.
- (139) Yang, Y.; Zhou, J.; Nakayama, M.; Nie, L.; Liu, P.; White, M. G. Surface Dipoles and Electron Transfer at the Metal Oxide-Metal Interface: A 2PPE Study of Size-Selected Metal Oxide Clusters Supported on Cu(111). *J. Phys. Chem. C* **2014**, *118*, 13697–13706.
- (140) Schoiswohl, J.; Kresse, G.; Surnev, S.; Sock, M.; Ramsey, M. G.; Netzer, F. P. Planar Vanadium Oxide Clusters: Two-Dimensional Evaporation and Diffusion on Rh(111). *Phys. Rev. Lett.* **2004**, *92*, 206103.
- (141) Wang, L.-F.; Xie, L.; Fang, H.-L.; Li, Y.-F.; Zhang, X.-B.; Wang, B.; Zhang, Y.-F.; Huang, X. On the Structural and Electronic Properties of Hexanuclear Vanadium Oxide Clusters V₆O_n^{-/0} (n = 12–15): Is V₆O₁₂ Cluster Planar or Cage-Like? *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *131*, 446–454.
- (142) Fielicke, A.; Meijer, G.; Von Helden, G. Infrared Spectroscopy of Niobium Oxide Cluster Cations in a Molecular Beam: Identifying the Cluster Structures. *J. Am. Chem. Soc.* **2003**, *125*, 3659–3667.
- (143) Deng, H. T.; Kerns, K. P.; Castleman, A. W. Formation, Structures and Reactivities of Niobium Oxide Cluster Ions. *J. Chem. Phys.* **1996**, *100*, 13386–13392.
- (144) Zemski, K. A.; Justes, D. R.; Castleman, A. W. Reactions of Group V Transition Metal Oxide Cluster Ions with Ethane and Ethylene. *J. Phys. Chem. A* **2001**, *105*, 10237–10245.
- (145) Vajda, S.; White, M. G. Catalysis Applications of Size-Selected Cluster Deposition. *ACS Catal.* **2015**, *5*, 7152–7176.
- (146) Xue, M.; Nakayama, M.; Liu, P.; White, M. G. Electronic Interactions of Size-Selected Oxide Clusters on Metallic and Thin Film Oxide Supports. *J. Phys. Chem. C* **2017**, *121*, 22234–22247.
- (147) Wagner, M.; Surnev, S.; Ramsey, M. G.; Barcaro, G.; Sementa, L.; Negreiros, F. R.; Fortunelli, A.; Dohnalek, Z.; Netzer, F. P. Structure and Bonding of Tungsten

- Oxide Clusters on Nanostructured Cu-O Surfaces. *J. Phys. Chem. C* **2011**, *115*, 23480–23487.
- (148) Zeuthen, H.; Kudernatsch, W.; Peng, G.; Merte, L. R.; Ono, L. K.; Lammich, L.; Bai, Y.; Grabow, L. C.; Mavrikakis, M.; Wendt, S.; *et al.* Structure of Stoichiometric and Oxygen-Rich Ultrathin FeO(111) Films Grown on Pd(111). *J. Phys. Chem. C* **2013**, *117*, 15155–15163.
- (149) Zeuthen, H.; Kudernatsch, W.; Merte, L. R.; Ono, L. K.; Lammich, L.; Besenbacher, F.; Wendt, S. Unraveling the Edge Structures of Platinum(111)-Supported Ultrathin FeO Islands: The Influence of Oxidation State. *ACS Nano* **2015**, *9*, 573–583.
- (150) Kudernatsch, W.; Peng, G.; Zeuthen, H.; Bai, Y.; Merte, L. R.; Lammich, L.; Besenbacher, F.; Mavrikakis, M.; Wendt, S. Direct Visualization of Catalytically Active Sites at the FeO-Pt(111) Interface. *ACS Nano* **2015**, *9*, 7804–7814.
- (151) Nilius, N.; Benedetti, S.; Pan, Y.; Myrach, P.; Noguera, C.; Giordano, L.; Goniakowski, J. Electronic and Electrostatic Properties of Polar Oxide Nanostructures: MgO(111) Islands on Au(111). *Phys. Rev. B* **2012**, *86*, 205410.
- (152) Goniakowski, J.; Giordano, L.; Noguera, C. Polarity Compensation in Low-Dimensional Oxide Nanostructures: The Case of Metal-Supported MgO Nanoribbons. *Phys. Rev. B* **2013**, *87*, 035405.
- (153) Ratnasamy, C.; Wagner, J. P. Water Gas Shift Catalysis. *Catal. Rev.* **2009**, *51*, 325–440.
- (154) Park, E. D.; Lee, D.; Lee, H. C. Recent Progress in Selective CO Removal in a H₂-Rich Stream. *Catal. Today* **2009**, *139*, 280–290.
- (155) Halpegamage, S.; Ding, P.; Gong, X. Q.; Batzill, M. Ordered Fe(II)Ti(IV)O₃ Mixed Monolayer Oxide on Rutile TiO₂(011). *ACS Nano* **2015**, *9*, 8627–8636.
- (156) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. Surface Studies by Scanning Tunneling Microscopy. *Phys. Rev. Lett.* **1982**, *49*, 57–61.
- (157) Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G. The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy. *Science* **2009**, *325*, 1110–1114.
- (158) Zhou, W.; Oxley, M. P.; Lupini, A. R.; Krivanek, O. L.; Pennycook, S. J.; Idrobo, J.-C. Single Atom Microscopy. *Microsc. Microanal.* **2012**, *18*, 1342–1354.
- (159) Marks, L. D.; Chiaramonti, A. N.; Rahman, S. U.; Castell, M. R. Transition from Order to Configurational Disorder for Surface Reconstructions on SrTiO₃(111). *Phys. Rev. Lett.* **2015**, *114*, 226101.
- (160) Takayanagi, K.; Tanishiro, Y.; Takahashi, S.; Takahashi, M. Structure Analysis of Si(111)-7 × 7 Reconstructed Surface by Transmission Electron Diffraction. *Surf. Sci.* **1985**, *164*, 367–392.
- (161) Guo, H. M.; Wang, Y. L.; Du, S. X.; Gao, H. . High-Resolution Scanning Tunneling Microscopy Imaging of Si(111)-7 × 7 Structure and Intrinsic Molecular States. *J. Phys.: Condens. Matter* **2014**, *26*, 394001.

- (162) Straton, J. C.; Moon, B.; Bilyeu, T. T.; Moeck, P. Removal of Multiple-Tip Artifacts from Scanning Tunneling Microscope Images by Crystallographic Averaging. *Adv. Struct. Chem. Imaging* **2015**, *1*, 14.
- (163) Straton, J. C.; Bilyeu, T. T.; Moon, B.; Moeck, P. Double-Tip Effects on Scanning Tunneling Microscopy Imaging of 2D Periodic Objects: Unambiguous Detection and Limits of Their Removal by Crystallographic Averaging in the Spatial Frequency Domain. *Cryst. Res. Technol.* **2014**, *49*, 663–680.
- (164) Russell, B. C.; Castell, M. R. Surface of Sputtered and Annealed Polar SrTiO₃(111): TiO_x-Rich (n × n) Reconstructions. *J. Phys. Chem. C* **2008**, *112*, 6538–6545.
- (165) Fasel, R.; Parschau, M.; Ernst, K.-H. Amplification of Chirality in Two-Dimensional Enantiomorphous Lattices. *Nature* **2006**, *439*, 449–452.
- (166) Somnath, S.; Smith, C. R.; Kalinin, S. V.; Chi, M. F.; Borisevich, A.; Cross, N.; Duscher, G.; S., J. Feature Extraction via Similarity Search: Application to Atom Finding and Denoising in Electron and Scanning Probe Microscopy Imaging. *Adv. Struct. Chem. Imag.* **2018**, *4*, 3.
- (167) Wiesendanger, R.; Güntherodt, H.-J. *Scanning Tunneling Microscopy I*; Springer-Verlag Berlin Heidelberg, 1992.
- (168) Jones, L.; Wenner, S.; Nord, M.; Ninive, P. H.; Løvvik, O. M.; Holmestad, R.; Nellist, P. D. Optimising Multi-Frame ADF-STEM for High-Precision Atomic-Resolution Strain Mapping. *Ultramicroscopy* **2017**, *179*, 57–62.
- (169) Castell, M. R. Scanning Tunneling Microscopy of Reconstructions on the SrTiO₃(001) Surface. *Surf. Sci.* **2002**, *505*, 1–13.
- (170) Pennycook, T. J.; Jones, L.; Pettersson, H.; Coelho, J.; Canavan, M.; Mendoza-Sanchez, B.; Nicolosi, V.; Nellist, P. . Atomic Scale Dynamics of a Solid State Chemical Reaction Directly Determined by Annular Dark-Field Electron Microscopy. *Sci. Rep.* **2014**, *4*, 7555.
- (171) Woolley, R. A. J.; Stirling, J.; Radocea, A.; Krasnogor, N.; Moriarty, P. Automated Probe Microscopy via Evolutionary Optimization at the Atomic Scale. *Appl. Phys. Lett.* **2011**, *98*, 253104.
- (172) Yang, F.; Choi, Y.; Liu, P.; Stacchiola, D.; Hrbek, J.; Rodriguez, J. A. Identification of 5-7 Defects in a Copper Oxide Surface. *J. Am. Chem. Soc.* **2011**, *133*, 11474–11477.
- (173) Goniakowski, J.; Noguera, C. Polarization and Rumpling in Oxide Monolayers Deposited on Metallic Substrates. *Phys. Rev. B* **2009**, *79*, 155433.
- (174) Goniakowski, J.; Noguera, C.; Giordano, L.; Pacchioni, G. Adsorption of Metal Adatoms on FeO(111) and MgO(111) Monolayers: Effects of Charge State of Adsorbate on Rumpling of Supported Oxide Film. *Phys. Rev. B* **2009**, *80*, 125403.
- (175) Björkman, T.; Kurash, S.; Lehtinen, O.; Kotakoski, J.; Yazyev, O. V.; Srivastava, A.; Skakalova, V.; Smet, J. H.; Kaiser, U.; Krasheninnikov, A. V. Defects in Bilayer Silica and Graphene: Common Trends in Diverse Hexagonal Two-Dimensional Systems. *Sci. Rep.* **2013**, *3*, 3482.

- (176) Cretu, O.; Krashennnikov, A. V.; Rodríguez-Manzo, J. A.; Sun, L.; Nieminen, R. M.; Banhart, F. Migration and Localization of Metal Atoms on Strained Graphene. *Phys. Rev. Lett.* **2010**, *105*, 196102.
- (177) Cockayne, E.; Rutter, G. M.; Guisinger, N. P.; Crain, J. N.; First, P. N.; Stroscio, J. A. Grain Boundary Loops in Graphene. *Phys. Rev. B* **2011**, *83*, 195425.
- (178) Schlapka, A.; Lischka, M.; Groß, A.; Käsberger, U.; Jakob, P. Surface Strain versus Substrate Interaction in Heteroepitaxial Metal Layers: Pt on Ru(0001). *Phys. Rev. Lett.* **2003**, *91*, 016101.
- (179) Clarke, A. R. H.; Pethica, J. B.; Nieminen, J. A.; Besenbacher, F.; Lægsgaard, E.; Stensgaard, I. Quantitative Scanning Tunneling Microscopy at Atomic Resolution: Influence of Forces and Tip Configuration. *Phys. Rev. Lett.* **1996**, *76*, 1276–1279.
- (180) Le, H. L. T.; Goniakowski, J.; Noguera, C.; Koltsov, A.; Mataigne, J. M. Improving Adhesion at the Alumina/Zinc Interface by Stainless Steel Buffers. *J. Phys. Chem. C* **2017**, *121*, 25143–25151.
- (181) Wu, J. W. J.; Moriyama, R.; Nakano, M.; Ohshimo, K.; Misaizu, F. Compositions and Structures of Niobium Oxide Cluster Ions, $\text{Nb}_m\text{O}_n^{\pm}$, ($m = 2\text{--}12$), Revealed by Ion Mobility Mass Spectrometry. *Phys. Chem. Chem. Phys.* **2017**, *19*, 24903–24914.
- (182) Nilius, N.; Rienks, E. D. L.; Rust, H. P.; Freund, H. J. Self-Organization of Gold Atoms on a Polar FeO(111) Surface. *Phys. Rev. Lett.* **2005**, *95*, 066101.
- (183) Sterrer, M.; Risse, T.; Martinez Pozzoni, U.; Giordano, L.; Heyde, M.; Rust, H. P.; Pacchioni, G.; Freund, H. J. Control of the Charge State of Metal Atoms on Thin MgO Films. *Phys. Rev. Lett.* **2007**, *98*, 096107.
- (184) Liu, Y.; Dobrinsky, A.; Yakobson, B. I. Graphene Edge from Armchair to Zigzag: The Origins of Nanotube Chirality? *Phys. Rev. Lett.* **2010**, *105*, 235502.
- (185) Wang, S.; Rong, Y.; Fan, Y.; Pacios, M.; Bhaskaran, H.; He, K.; Warner, J. H. Shape Evolution of Monolayer MoS_2 Crystals Grown by Chemical Vapor Deposition. *Chem. Mater.* **2014**, *26*, 6371–6379.
- (186) Denk, M.; Kuhness, D.; Wagner, M.; Surnev, S.; Negreiros, F. R.; Sementa, L.; Barcaro, G.; Vobornik, I.; Fortunelli, A.; Netzer, F. P. Metal Tungstates at the Ultimate Two-Dimensional Limit: Fabrication of a CuWO_4 Nanophase. *ACS Nano* **2014**, *8*, 3947–3954.