



# Tunable bandgap and spin-orbit coupling by composition control of $\text{MoS}_2$ and $\text{MoO}_x$ ( $x = 2$ and $3$ ) thin film compounds

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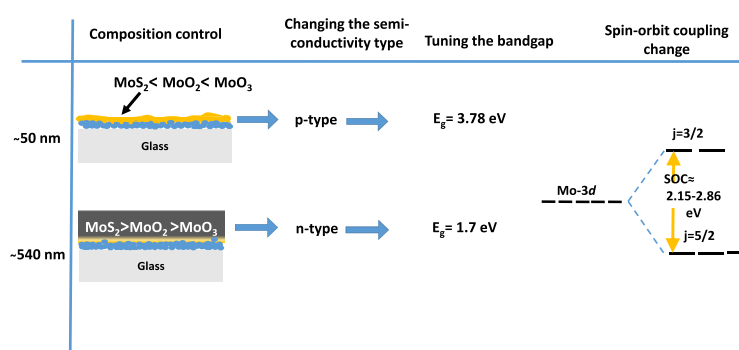
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## HIGHLIGHTS

- A composite form of  $\text{MoS}_2$ ,  $\text{MoO}_2$  and  $\text{MoO}_3$  thin film was electrodeposited.
- The relative content of these compounds was changed in different thickness of the layers.
- The bandgap and type of semiconductor were tuned by change on the composition.
- Spin-orbit coupling of Mo 3d doublet was enhanced by composition control.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We report on the  $\text{MoS}_2$  and  $\text{MoO}_x$  ( $x = 2$  and  $3$ ) composite thin layers, electrodeposited, onto a Fluorine doped Tin Oxide (FTO) substrate. Our results show a change in relative content of these compounds in different thicknesses ranging from ~20 to 540 nm. This change in the relative content at different thicknesses leads to a change in optical and electrical properties including bandgap and the type of semiconductor. A sharp transition from p to n-type of semiconductor is observed by scanning tunneling spectroscopy measurements. We find that the spin-orbit interaction of Mo 3d electrons in the  $\text{MoS}_2$  and  $\text{MoO}_3$  enhances by significant reduction of the  $\text{MoO}_3$  content in thicker layers.

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## 1. Introduction

In the past decade, low dimensional binary compounds with general formula  $\text{MX}_2$ , have attracted significant attention due to some

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unique properties of them [1–4]. In these compounds M is usually a transition metal and X is a chalcogenide. Among them probably Molybdenum disulfide ( $\text{MoS}_2$ ) is the most well-known material.  $\text{MX}_2$  compounds have potential applications in nanoelectronics, photoelectrochemistry, energy storage, etc. [5–12]. However, in a form of single  $\text{MX}_2$  compound, bandgap can be tuned by back-gate control or by impurity doping, but it technically requires some

additional preparation steps [13,14]. Hybrid configuration of the  $\text{MX}_2$  compounds can overcome this drawback. By appropriate combination of these binary compounds, different bandgaps can be obtained.

Various techniques such as chemical vapor deposition [15,17] or mechanical (liquid phase) exfoliation have been employed for fabrication of transition metal dichalcogenide compounds, but there are few attempts by electrodeposition [16,18–20]. This technique can provide low cost and high quality structures with controllable size made of various compounds. During the fabrication process of the  $\text{MoS}_2$  from Mo oxide compounds there are naturally  $\text{MoO}_x$  products; results in  $\text{MoS}_2$  and  $\text{MoO}_x$  composition.

In order to exploit electrical and optical properties of the  $\text{MoS}_2$  and  $\text{MoO}_x$  ( $x=2$  and  $3$ ) composition at first, some of their important properties should be referred, independently. In the monolayer  $\text{MoS}_2$ , the inversion symmetry is broken that results in a relatively (compared to the other transition metals) strong spin-orbit coupling in the Mo 3d electrons. This coupling leads to the valence band splitting which is abbreviated as SOS. The SOS in bilayer  $\text{MoS}_2$  mostly comes from inter-layer coupling. The strong SOS can lead to some important excitonic effects which are detectable using various techniques. The SOS value reported for this compound is around 150 meV.

$\text{MoO}_2$  is an unusual metal oxide which exhibits metal-like electrical conductivity (semimetal or a wide bandgap n-type semiconductor in bulk) [21,22]. During the last decade, optical and structural properties of this compound have been thoroughly investigated.  $\text{MoO}_2$  is a mixed ionic electronic conductor [23] and its electrical resistivity is very controversial. The SOS value of this material is less than that of  $\text{MoS}_2$  at which is around 130 meV.

Molybdenum trioxide ( $\text{MoO}_3$ ), with an orthorhombic symmetry is intrinsically n-type semiconductor with 3.2 eV bandgap. It has been widely investigated due to its high work function [24] and intercalation of  $\text{Li}^+$  and  $\text{H}^+$  ions [25]. These properties make it a promising candidate for photorechargeable and photoelectrochemical applications [26–28]. In contrast to the  $\text{MoS}_2$  and the  $\text{MoO}_2$ , this compound does not exhibit any symmetry-breaking valence band splitting.

The present paper explores the structural and optical properties of the electrodeposited  $\text{MoS}_2$ ,  $\text{MoO}_2$  and  $\text{MoO}_3$  compounds made on transparent FTO substrate. However, according to Ref. [16] a transition metal substrate is required to act as catalyst to have  $\text{MoS}_2$ , but this research proves that it is possible to have a composition of these compounds on a transparent substrate of the FTO. This paper provides a fabrication recipe to control each of these ( $\text{MoS}_2$ ,  $\text{MoO}_2$ ,  $\text{MoO}_3$ ) compounds and report on their interesting properties. In particular, this paper discusses on the optical (electrical) bandgap, spin-orbit coupling (SOC) and SOS of the Mo 3d electrons by change on the composition in different thickness of the layers.

## 2. Experiment

DC electrodeposition was carried out at room temperature to make thin layers from an electrolyte containing sodium molybdate ( $\text{Na}_2\text{Mo}_2\text{O}_4$ ) (0.5 M) with disodium sulfide ( $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ ) (30 g/l) similar to Ref. [16]. The pH value of the electrolyte was adjusted to 7 by adding dilute sulfuric acid. The products of chemical reactions in this solution depending on the electrodeposition conditions (substrate, temperature, pH and applied potential), can be  $\text{MoS}_2$  and  $\text{MoO}_x$  ( $x=2$  and  $3$ ).

A two electrode potentiostat having Pt as anode and FTO substrate as cathode was employed for the electrodeposition in this single-bath solution. Before electrodeposition, the FTO substrate was cleaned by ethanol and distilled water. Then the sample was located in a home-made chemical cell in front of a Pt counter electrode. A magnetic stirrer was used to mix the solution during deposition. In

a series of samples the electrodeposition was performed at different deposition times between 7 s and 10 min (7 s, 15 s, 30 s, 1 min, 2 min, 10 min) to achieve various thickness of the layers. Profilometry of the fabricated samples displayed the thickness from  $\sim 20$  to 540 nm ( $\pm 5$ nm). Applied DC potential was adjusted to 2.5 V (the minimum required potential for deposition from this electrolyte on the FTO) for all samples in which the current density during the deposition was kept at around 2  $\text{mA}/\text{cm}^2$ , well below 10  $\text{mA}/\text{cm}^2$  in accordance with previous reports to avoid reduction of  $\text{MoO}^{2+}$  ions as much as possible. The thick layers were black while thinner ones, below 1 min deposition time, were amber yellow and more transparent. The composition of the layers was expected to be affected by the interplay between  $\text{H}^+$  and Oxygen. This interplay in chemical reactions resulted in the change on final products and composition.

## 3. Results and discussion

### 3.1. Structural characteristics

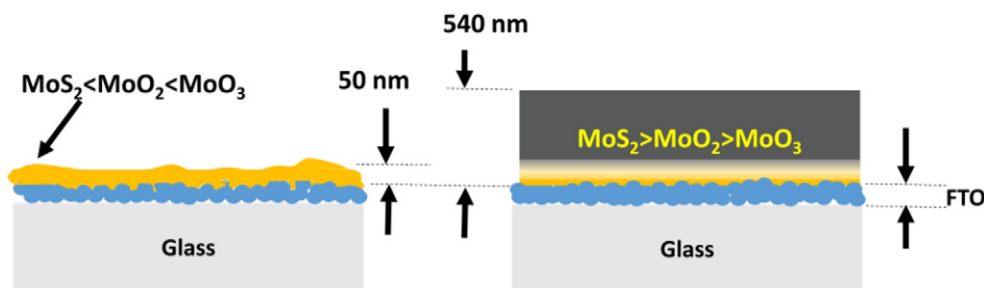
In this paper, mainly the results obtained from the thinnest and thickest layers are discussed which exhibit significant changes in optical and electrical properties. Fig. 1, illustrates the morphology and composition of the electrodeposited thin layers in two different thicknesses. Fig. 2a and b shows SEM micrograph of as-deposited samples with different deposition times of 30 s (with 100 nm thickness) and 10 min (with 540 nm thickness) respectively. It is clearly seen that at thinner one roughness of the substrate affects on the morphology of the layer, While thicker one shows large-scale flat islands. Fig. 2c and d exhibits TEM and selected area diffraction pattern (SAED) of the thicker composite layer. Interestingly, it is clearly seen that the structure of the fabricated composite is mostly polycrystalline. A rough orientation of the crystals, attributed to the  $\text{MoO}_2$  and  $\text{MoS}_2$  structures, is calculated from spot patterns.

In order to understand the chemical composition and for accurate analysis, XPS (X-ray photoelectron spectroscopy) spectra of the 30 s and 10 min as-deposited samples (shown in Fig. 3) were acquired. The obtained XPS data from 0 to 1200 eV is convoluted to analyze the XPS peaks. Best fitted Gaussian curves is used to determine the peak positions presented in Table 1. C 1 s calibration peak (284.8 eV) is employed to find the correct binding energy of all peaks.

According to Table 1, the relative content of the  $\text{MoS}_2$  has noticeable increase from 20 % to 43 %. This enhancement comes from less Oxygen evolution as well as less substrate effects on the thicker layer. However, chemical stability of  $\text{MoO}_3$  is the highest among these three compounds, the content of that decreases at higher deposition times and higher thicknesses.

The Molybdenum and Sulfur binding energies of each compound for two different thicknesses of the composite layer are shown in Table 2. Peak position of Oxygen is not shown due to the substrate effect and not possible accurate conclusion. In the XPS experiment, usually charge density around emitted-photoelectron has inverse relation with the binding energy, due to the repulsive Coulombic force of the electrons around a photoelectron. It is observed that, in the 100 nm sample, the peaks are shifted towards higher energies because of more formation of the  $\text{MoO}_2$  and the  $\text{MoO}_3$  compounds, indicating low density of the electrons. In contrast, energy downshift of the spectral peaks by increasing of the  $\text{MoS}_2$  content in 540 nm sample can indicate higher density of the electrons.

Fig. 4 shows the SOC of the Mo 3d electrons in the  $\text{MoS}_2$  at different thickness of the layer. The SOC, calculated from Mo  $3d_{3/2}$  and Mo  $3d_{5/2}$  peaks, increases from 2.15 to 2.86 eV at thicker layer. This effect is connected to the relative increasing of the  $\text{MoS}_2$  content. The observed SOC data are in agreement with reported results by several researches (as an example, see Senthilkumar et al. [29]). According to Table 2, the SOC of Mo 3d electrons in the  $\text{MoO}_3$  steps up from 3.28 to 3.74 eV. As it is expected the SOC in the  $\text{MoO}_3$  is higher than the



**Fig. 1.** Schematic representation of two distinct samples with 50 and 540 nm thickness. Morphology and relative content change are shown qualitatively by color gradient at thinner and thicker samples relatively.

MoO<sub>2</sub> because of direct relation between molecular mass and SOC. In addition, 2p peaks of the sulfur in the MoS<sub>2</sub> increases from 1.4 to 1.55 eV.

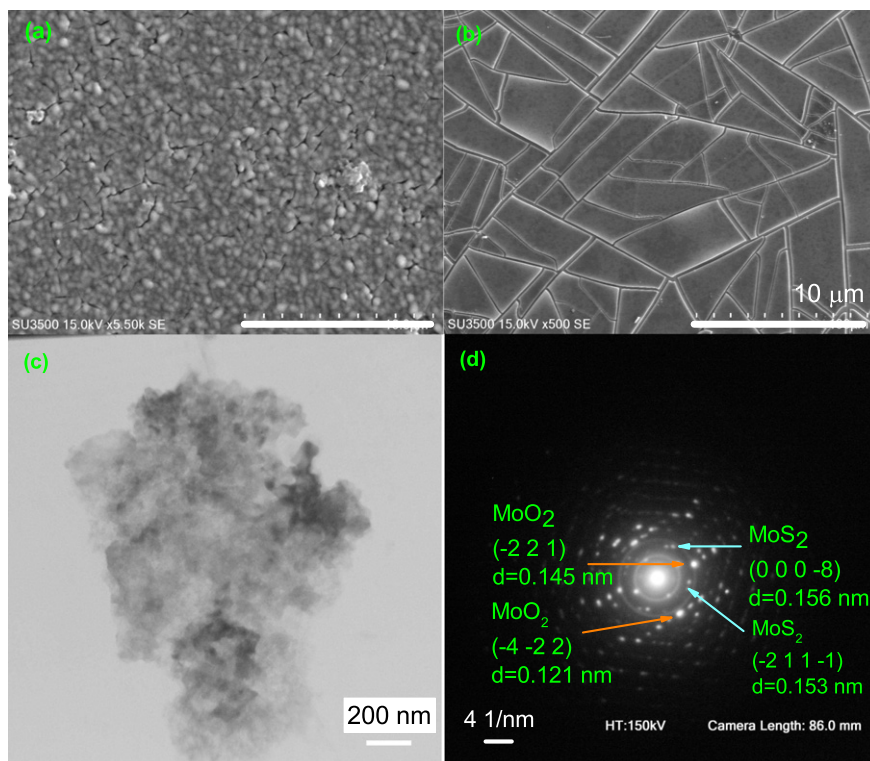
In the monolayer or bulk MoX<sub>2</sub> (x=O and S) compounds, inversion symmetry breaking or interlayer coupling, can lead to the valence and conduction band splittings in first Brillouin zone. The excitonic peaks that have arisen from this splitting are usually shown in the UV-Vis experiments. Apparently, in this composition, the valence band splitting is absent. With this, one can conclude that the presence of MoO<sub>2</sub> and MoO<sub>3</sub> suppress the valence band splitting. The Key point is that this splitting mostly depends on the SOS and crystal symmetries rather than SOC. The correlation between SOC and SOS for this composition is not very clear yet.

### 3.2. Optical and electrical properties

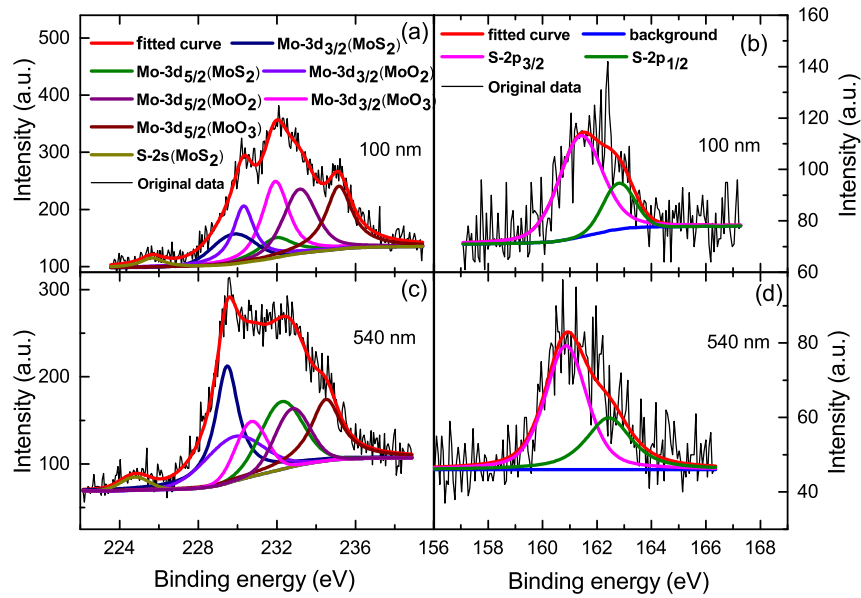
In the optoelectronics and material science, optical absorption measurements by UV-Vis spectroscopy is a powerful and common characterization technique. Fig. 5a shows the UV-Vis spectrum for different deposition times. Interestingly, by probing from 300 to

1100 nm various anomalies and peaks, attributed to the intraband and interband transitions, are observed by a redshift for thinner layers. The low energy peaks (where the excitonic peaks was expected to be observed), does not exactly coincide to the reported values of 623 and 683 nm for MoS<sub>2</sub> and neither very well separated from each other. However, high energy peaks related to interband transitions are in agreement with reported results.

Coexistence of the MoO<sub>2</sub> and the MoS<sub>2</sub> in this composition, can explain the absence of the excitonic peaks in UV-Vis spectrum at around 623 nm and 683 nm. It seems screening of the valence band splitting in the MoS<sub>2</sub> by the valence band splitting in the MoO<sub>2</sub> has significant effect on the possible suppression of the excitonic peaks in the UV-Vis spectrum. Illustration of this behavior is schematically presented in inset of the 5.a. This behavior causes energy separation of the Mo 3d degeneracy-lifted orbitals (due to the SOS coming from inversion symmetry breaking or inter-layer coupling) to be in both compounds beyond the resolution of the UV-Vis instrument. However, in this composition, the MoO<sub>3</sub> is also present, but no contribution due to excitonic effects is expected. Overall, these UV-Vis results had characteristics of the both MoS<sub>2</sub> and MoO<sub>x</sub> compounds



**Fig. 2.** SEM micrograph of the:(a) thin and;(b) thick layers exhibiting morphology and substrate effects;(c) TEM and;(d) SAED pattern of the thicker layer. From SAED pattern at least two series of points can be attributed to the MoS<sub>2</sub> and MoO<sub>2</sub> compounds.



**Fig. 3.** XPS spectra of the Mo 3d and S 2p electrons coincide to the binding energies of the Mo in the MoS<sub>2</sub>, MoO<sub>2</sub> and MoO<sub>3</sub> compounds at; (a, b) 100 nm and; (c, d) 540 nm layers.

**Table 1**

Relative content of compounds in as-deposited samples.

Compound	MoS <sub>2</sub>	MoO <sub>2</sub>	MoO <sub>3</sub>
Relative content (100 nm)	0.20	0.36	0.43
Relative content (540 nm)	0.43	0.29	0.28

Refs.[30,31]. It is worth to note that (by comparison of the insets in Figs. 5 and 4), the SOS and the SOC have two different origins. As it was discussed above, the first one is due to the inversion symmetry breaking or inter-layer coupling and the second one comes from the spin-orbit coupling of Mo 3d electrons ( $J = L \pm S$ ,  $L = 2$  and  $S = 1/2$ ).

Usually, the optical bandgap of the semiconductors can be calculated by plotting  $(\alpha h\nu)^2$  versus  $h\nu$  in UV-Vis spectrum where  $\alpha$  is absorption coefficient (Tauc plot). Fig. 5b shows the Tauc plot of indirect bandgap obtained from different thicknesses. The calculations indicate 3.78 eV energy gap for thinnest layer with 7 s deposition time, while the bandgap for 10 min deposited one is 1.77 eV. Complementary experiments for the deposition times, between these two values, exhibits a systematic and tunable bandgap. From this, it can be concluded that the bandgap is not strongly affected by dislocations or impurities.

Interestingly, an unusual step-like behavior below 15 s deposition time is observed. Such behavior can be attributed to the curved shape of layer which is formed on top of the rough FTO substrate. The FTO is made of the Fluorine doped Tin oxide nanoparticles (with approximately 200 nm particle diameter) deposited on a glass. This bending of the electrodeposited layer caused a lattice distortion and

affect the band structure. Our extended experiments at 5 V and 7.5 V (not shown here) showed no significant change on these features. The electrical bandgaps obtained from scanning tunneling spectroscopy measurements (NAMA-STM SS3) provided additional information about carrier correlations and charge densities. Fig. 6 exhibits the scanning tunneling spectroscopy of two samples with different thicknesses. Interestingly, it was observed that by increasing the thickness, bandgap decreases from 3.3 to 3 eV. According to these measurements the optical and electrical bandgaps are comparable. In addition, Fermi energy distance from conduction band decreases (from 2 to 1.2 eV), indicating a change from p-to n-type of the semiconductivity. At first approximation, the origin of this behavior can be ascribed to the composition change. A detailed explanation, based on the layer growth mechanism and the related parameters is offered as following. In the beginning of deposition, due to catalytic effect of the substrate, the protons penetrates and forms a bound state with Oxygen atoms to form water molecules that leaves Oxygen vacancies behind. This vacancies make the semiconductor p-type. After a while and separation of layer-growing points from FTO substrate, catalytic effect of the substrate is going to be smeared out. Accordingly, the Oxygen evolution decrease concomitant with the higher sulfur evolution leading to a higher electron charge density.

#### 4. Conclusions

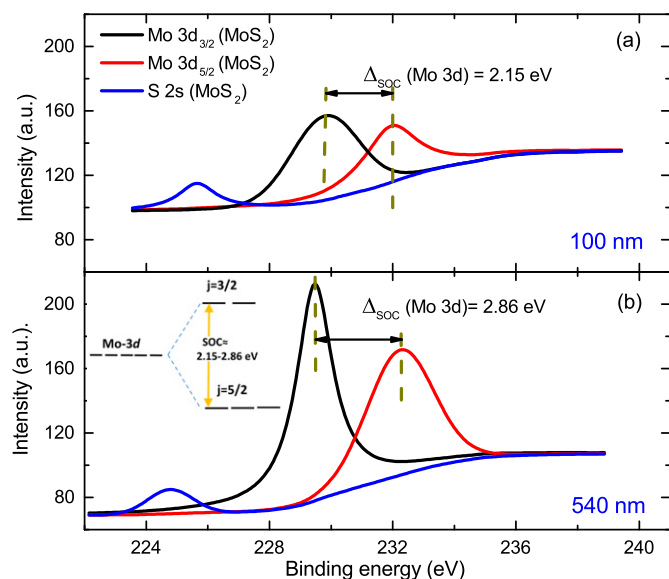
In conclusion, the MoS<sub>2</sub> and the MoO<sub>x</sub> ( $x = 2$  and 3) composites were electrodeposited on a transparent (FTO) substrate in the form of thin films with different thicknesses. The Optical and electrical

**Table 2**

Binding energy of Mo and S in as-deposited samples. Summary of the peak positions, spin-orbit coupling and related shifts in the Mo 3d and S 2p for 100nm and 540nm films.

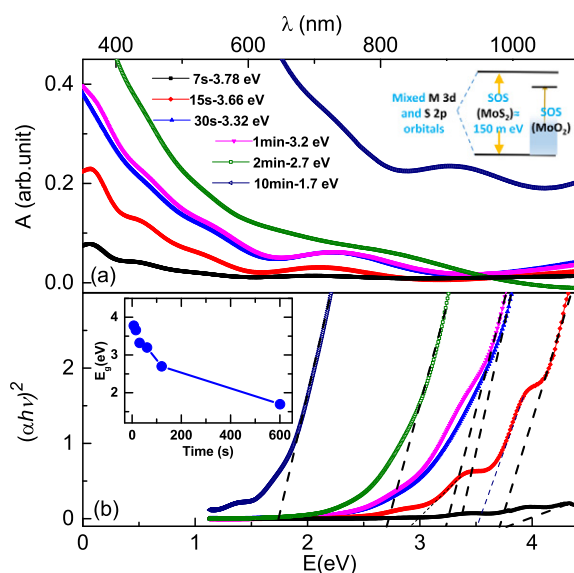
	Mo 3d <sub>3/2</sub>	Mo 3d <sub>5/2</sub>	$\Delta_{SOC}(\text{Mo } 3d)$	S-2p <sub>1/2</sub>	S-2p <sub>3/2</sub>	$\Delta_{SOC}(\text{S } 2p)$
<b>100 nm</b>						
MoS <sub>2</sub>	231.97	229.98	2.15	161.40	162.80	1.38
MoO <sub>2</sub>	233.18	230.30	2.85			
MoO <sub>3</sub>	235.15	231.96	3.28			
<b>540 nm</b>						
MoS <sub>2</sub>	232.24	229.47	2.87	160.86	162.43	1.53
MoO <sub>2</sub>	232.79	229.81	2.77			
MoO <sub>3</sub>	234.50	230.69	3.74			



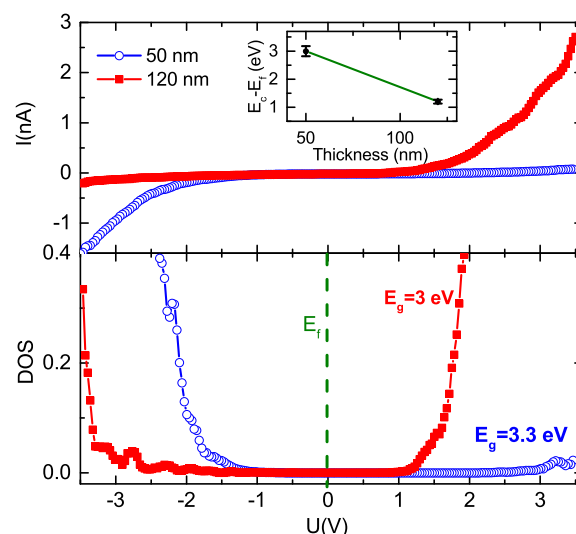


**Fig. 4.** Spin-orbit coupling of the Mo 3d electrons in MoS<sub>2</sub> for two different thickness. 2s peaks of the sulfur exhibit a significant downshift towards low binding energy. Inset in (b) shows schematic representation of the spin-orbit coupling of  $L = 2$  and  $S = 1/2$  in 3d orbitals.

characteristics were tuned by composition. This tunability enabled us to control the bandgap and the type of semiconductivity. The XPS and UV-Vis results demonstrated that the MoO<sub>2</sub> can suppress the SOS and valence band splitting of the MoS<sub>2</sub> compound. In addition, the SOC of the Mo 3d electrons were enhanced in the composites with higher MoS<sub>2</sub> content. This research suggests investigation of the electrodeposited hybrid chalcogenide compounds based on the composition control.



**Fig. 5.** (a) UV-Vis spectrum of the as-deposited thin films with different deposition times; (b) Tauc plot and bandgap (inset). The broad absorption band centered at 416 nm (2.98 eV) arising from the complicated interband transitions is also observed. However the excitonic peaks of spin orbit and interlayer couplings are not well resolved. The inset shows screening effect of MoO<sub>2</sub> valence band splitting on MoS<sub>2</sub> schematically.



**Fig. 6.** Scanning tunneling spectroscopy and DOS of the thick and thin films. Inset shows  $E_c - E_f$  change versus layer thickness.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.matdes.2017.02.085>.

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