Mechanical transfer of electrochemically grown molybdenum sulfide layers to silicon wafer

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Abstract

Large area MoS₂ ultra-thin film deposition is one of the big challenges in the recent years. Electrodeposition provides an opportunity to grow such ultra-thin films on large scale. However, the transfer of the electrochemically grown film is challenging. Standard transfer of those thin films is done by wet etching in which the underlying substrate is etched. In this work, the polymer coated electrodeposited MoS₂ films on Au are separated mechanically from the underlying substrate by using ultra-sonication. Collapse of micron-sized bubbles produced by ultra-sonication at the interface of Au and silicon substrate provides enough energy for separation due to their weak adhesion. The Au layer is then removed by standard Au-etchant (K/KI) and the polymer coated film is transferred to a desired substrate. Ammonium tetrathiomolybdate (ATTM) has been used as precursor material for the electrodeposition of the films. Initial electrochemically grown films consist of MoS₃ which is reduced to MoS₂ by a post-annealing step at 450–900 °C. Obtained films are investigated by AFM, Raman, UV–Vis and XPS. Crystal quality improves by increasing the post-annealing temperature. The thickness of the thinnest film was found to be equivalent to 2 monolayers of MoS₂, which is desirable for future electronics.

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Graphic abstract

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1 Introduction

After discovery of graphene as an atomically thin two-dimensional (2D) material [1], a complete new research area has been opened. Recently, 2D semi-conducting materials analogue to graphene, i.e. transition metal dichalcogenides (TMDCs), have attracted great attention due to their interesting optical and electronic properties and 2D nature. Among other 2D TMDCs, molybdenum disulfide (MoS₂) exhibits a non-zero band-gap, unlike conducting graphene, and it has interesting properties such as a tunable bandgap [2], optoelectronics [3], and spin–orbit coupling effects [4]. It can be used in switching devices such as a field effect transistor and in hydrogen evolution reaction because of its suitable band-structure [5, 6]. TMDCs thin films have been deposited by various deposition methods such as pulsed laser deposition [7], chemical vapor deposition (CVD) [8, 9], mechanical exfoliation [5], liquid-phase exfoliation [10], dip-coating [11, 12] and spin-coating [13]. Fabrication of

transistors is also reported by solution-based processes such as spin-coating and liquid-phase exfoliation [10, 14]. Each of these growth methods has advantages and disadvantages. Mechanical exfoliation method yields a good quality MoS₂ flakes but the lateral flake size and thickness of MoS₂ flake is not controllable with this method [5]. CVD also yields high quality MoS₂ flakes with large lateral size but it requires vacuum [9]. Similarly, ball milling can be used for large scale production of MoS₂ but it damages the crystal structure and causes a lot of defects [15]. MoS₂ and WS₂ monolayer flakes have been also obtained by dip-coating process but again thickness and lateral size is not controllable [11, 12]. However, a major challenge is to grow MoS₂ ultra-thin films on large scale and transferring those films to a desired substrate for different applications and characterization while preserving the quality of the films. In this work we present an alternative solution-based deposition methods which gives us an opportunity to control the thickness and lateral size of the grown layer. Ultra-thin films of MoS₂ have been

grown electrochemically on an Au substrate and transferred onto a silicon substrate by mechanical transfer method followed by gold etching. Such mechanical transfer method while the MoS_2 film is supported by a poly(methyl methacrylate) (PMMA) layer was recently reported [16], which is an alternative transfer method to chemical etching of the substrate. For chemical etching of the substrate, usually toxic etchants are used such as hydrofluoric acid (HF) for etching of SiO_2 [17]. In order to avoid toxic etchants for transfer, the environmental-friendly transfer method has been used in our approach. The MoS_2 films are mechanically separated by ultra-sonication from the silicon substrate along with Au layer because of its weak adhesion to the oxidized silicon surface. The Au layer is removed by a non-toxic gold-etchant such as potassium iodide. This mechanical transfer followed by gold etching doesn't harm the MoS_2 film and the underlying substrate can be reused. The obtained films have been characterized by various spectroscopic methods, i.e. Raman spectroscopy, UV–Vis and XPS before and after transfer.

2 Experiment

Ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, ATTM) was dissolved in di-ionized (DI) water in order to prepare 1 mM precursor solution for the electrodeposition. The aqueous solution of the precursor was ultra-sonicated for 20 min to get an uniform solution. Silicon wafers were cleaned with acetone and isopropanol and dried with nitrogen. Afterwards the wafers were treated with UV-ozone for 10 min to remove organic contaminations. A 50 nm gold layer was deposited on the silicon wafers by e-beam evaporation. However any standard deposited method can be used to deposit Au thin film such as physical vapor deposition or sputter coating. After preparing electrolyte and substrates for electrodeposition, the electrochemical setup was prepared. The Potentiostat consists of three electrodes: counter electrode (Pt), working electrode (Au deposited on a silicon wafer) and reference electrode (calomel electrode). The reduction potential of the calomel electrode is 0.27 V, which is referenced to standard hydrogen electrode at room temperature. The over-voltage was kept constant at 0.38 V and deposition time was varied in order to get films with different thicknesses. The growth substrate area was $1 \times 1 \text{ cm}^2$. The electrochemical setup is illustrated in Fig. 1. ATTM is a single source Mo-precursor with the molybdate ion surrounded by sulfur as main source of MoS_2 . After electrodeposition, the samples were pre-annealed at 120°C for 15 min to evaporate remaining solvent. Poly(methyl methacrylate) (PMMA) (4 wt%) material was dissolved in methyl ethyl ketone (MEK) solvent and stirred overnight. The PMMA solution was spin-coated on the electrochemically deposited MoS_x film at 1000 rpm for 60 s. It was

afterwards annealed at 150°C for 20 min. The polymer coated electrodeposited film on $\text{Au/SiO}_2/\text{Si}$ was then ultra-sonicated (Bandelen RK-100-H, 35 kHz) for 1 min. Ultra-sonication causes the $\text{PMMA/MoS}_x/\text{Au}$ stack to separate from the silicon wafer and to float on the surface of the DI-water. The floating $\text{PMMA/MoS}_x/\text{Au}$ layer stack was then transferred from DI-water to a gold etching solution (K/KI) in order to etch the Au layer. Undiluted standard gold etchant (651,818) was used and was bought from sigma-aldrich. After etching the gold, the PMMA/MoS_x layer stack was picked up with a cleaned silicon wafer with highly hydrophilic surface and annealed at 120°C for 30 min. Finally, the PMMA layer was removed with acetone. This way the MoS_x layer was successfully transferred of the conducting Au substrate to a silicon wafer. The transferred MoS_x sample was then annealed at target temperature (450, 500, 600, 700, 800, 900°C) with a heating rate of $20^\circ\text{C}/\text{min}$ and with an additional sulfur source in inert 95% Ar and 5% H_2 atmosphere. For this purpose, the sample was placed in the middle of a quartz tube and pure sulfur was placed in the upstream near the edge. The quartz tube was then placed in an oven. Initially the flow of Ar/H_2 was kept high to remove residual air. The target temperature was maintained for 120 min. The complete sequence of the experiment is illustrated in Fig. 1.

The electrodeposited films and the films after transfer were characterized with different spectroscopic techniques to study the surface morphology, composition of the film and crystal quality. Atomic force microscope (AFM) (Nanosurf) was used in tapping mode to analyze surface morphology and uniformity of the films. The thickness of the films is measured by a Dektak profilometer. UV–Vis spectroscopy (Cary 5000 UV–Vis–NIR Spectrometer) was done in a spectral range from 200 to 1100 nm in order to observe the excitonic finger print of MoS_2 . For UV–Vis measurements, an electrochemically deposited film was transferred to a quartz substrate before and after post-annealing. Raman measurements (Horiba Jobin–Yvon T64000) were carried out using 514.5 nm laser excitation source in order to identify the chemical structure based on unique molecular bond vibration and to analyze the crystallinity from the width of the peaks. The Raman signal was collected by a $\times 50$ objective and dispersed with 2400 lines/mm grating and detected by a CCD (charge coupled device) detector at -110°C (cooled by liquid nitrogen). In order to do x-ray photoelectron spectroscopy (XPS), the samples were introduced to the XPS vacuum vessel, which has a photoelectron spectrometer with a hemispherical analyzer (Specs Phoebos 100) and a Mg/Al X-ray gun (Specs XR-50). The analyzer was used in transmission mode with a pass energy of 50 eV and Mg K_α radiation ($E = 1253.6 \text{ eV}$) was used as source of excitation. The XPS data evaluation was done with the CASA XPS^{TM} software and Shirley method was used to subtract the

Fig. 1 **a** Electrochemical setup followed by post-annealing scheme **b** Scheme for the transfer of the electrodeposited film from Au covered growth substrate to a base silicon substrate and corresponding real image

background. The minor shift in the binding energy because of charging was corrected with respect to the C_{1s} peak.

3 Results and Discussion

Thermal decomposition of ATTM happens between 120 and 360 °C and converts to MoS₃. Above 800 °C in inert environment it turns into MoS₂ [18]. It has been reported that MoS₂ conversion temperature can be reduced from 800 to 450 °C using H₂ in an inert environment [18]. ATTM can be converted to MoS₃ at room temperature electrochemically according to Eq. 1 and 2. MoS₃ can be further reduced to MoS₂ by annealing above 450 °C in an inert environment. The thermolysis of electrochemically deposited MoS₃ takes place during post-annealing step and results in MoS₂ as one of the final reaction products. The chemical reactions that

occur during electrodeposition and post-annealing process are given below [19].

The color contrast of the optical microscope images shows that obtained films are uniform and cover large area (see Supplementary Data Fig. S1). Films with different thicknesses are obtained by varying the deposition time yielding a linear correlation (see Supplementary Data Fig. S2) which correlates with the difference in the color contrast of the optical microscope images (see Supplementary Data Fig. S1). ATTM solution with low concentration (1 mM) results in uniform and closed thin films. Ultra-thin films having thickness down to 1 nm have been successfully

obtained by electrodeposition, which is equivalent to thickness of a bi-layer of MoS_2 . Electrodeposition is one of the best ways to produce large area ultra-thin films of MoS_2 at room temperature and without using vacuum. The polymer coated electrodeposited film with Au layer is mechanically separated from silicon wafer by means of ultra-sonication as shown in Fig. 1b. Due to the operational principle of the ultra-sonication machine standing acoustical waves are produced. Millions of micron-sized bubbles are produced at the nodes of those standing waves. Initially, there is a negative pressure creating the bubbles. The size of these bubbles is getting bigger and bigger, until the pressure switches from negative to positive pressure. Due to this positive pressure bubbles are compressed and collapse. This implosion of bubble releases energy and transfer it to the environment. The imploding bubbles can provide enough energy to separate two layers [16]. As a result of ultra-sonication, the $\text{PMMA}/\text{MoS}_x/\text{Au}$ stack is separated from the silicon substrate because of low adhesion of Au to silicon. The PMMA layer protects the MoS_x layer during this procedure from breaking [16].

In Fig. 2 roughness of the electrodeposited film obtained from the AFM images before and after transfer is shown. The surface roughness of the 2.2 nm thick MoS_2 film is ~ 0.7 nm which indicates that the obtained films are uniform and closed. Furthermore, no big change in the roughness of the films with increasing thickness is observed due to the amorphous nature of the films. The obtained films are uniform and closed as can be seen from the small roughness values of the films in Fig. 2. The AFM images are given in Fig. S3.

The MoS_2 formation was investigated by non-destructive spectroscopic methods such as Raman, XPS and UV–Vis spectroscopy. In Fig. 3 the UV–Vis spectra of an

Fig. 2 Thickness vs roughness plot before and after transfer with inset of atomic force microscopy image electrodeposited layers

Fig. 3 UV–Vis of the 16 nm film before and after conversion to MoS_2 . Shown absorbance is calculated as one minus transmission

electrodeposited film before and after post-annealing are shown. In the spectrum of the film before post-annealing a gradual increase in the absorption is observed with decreasing wavelength. It doesn't exhibit any absorption peak which indicates the absence of MoS_2 content in the initial electrochemically deposited film. In contrast, the spectrum of the film after post-annealing exhibit clear characteristic peaks of MoS_2 at 612 nm and 674 nm, which indicates the conversion of electrochemically deposited film to MoS_2 . The peaks at 612 and 674 nm correspond to the A and B exciton of MoS_2 which are attributed to the direct transition at the K point of the Brillouin zone [20, 21]. In addition a broad peak is visible at around 400–450 nm which is attributed to contain two individual peaks i.e. the C and D excitons which are attributed to inter-band transitions [20].

In Fig. 4a Raman spectra of electrodeposited films post-annealed at different temperatures (450–900 °C) are shown. The Raman spectra of the annealed films exhibit two characteristic peaks at 382 cm^{-1} and 407 cm^{-1} , which correspond to the Raman active modes of MoS_2 , i.e. the E_{2g}^1 (in-plane vibrational mode) and A_{1g} (out of plane vibrational mode) [22]. According to group theory, there are four Raman active modes of MoS_2 [23] but only two of them are observed in the measured spectral range. The four Raman active mode of MoS_2 are A_{1g} (out-of-plane vibration (c-axis) of S atoms) at 407 cm^{-1} , E_{2g}^1 (in-plane vibration (basal plane) of Mo and S atoms) at 382 cm^{-1} , E_{1g} (in-plane vibration (basal plane) of S atoms) at 286 cm^{-1} , and E_{2g}^2 (in-plane vibration (basal plane) of Mo and S atoms) at 32 cm^{-1} . E_{1g} is invisible under back-scattering Raman geometry and for E_{2g}^2 the sensitivity factor is relatively small [24]. Among all Raman active modes of

Fig. 4 **a** Raman spectra of the MoS₂ films annealed at different temperature. **b** FWHM of E_{2g}^1 and A_{1g} peak vs post-annealing temperature

MoS₂, E_{2g}^1 and A_{1g} are widely studied and they also depend on the thickness of the MoS₂ films [22]. The Raman measurements allow to study the crystallinity of the MoS₂ films post-annealed at different temperatures. In Fig. 4b the full width at half maximum (FWHM) of both modes (E_{2g}^1 and A_{1g}) is plotted against the post-annealing temperature. The FWHM for both Raman active modes is large for low temperature and small for high temperature [25]. Decreasing FWHM with increasing temperature indicates that the crystalline quality of the MoS₂ improves for higher post-annealing temperatures. For comparison the Raman spectrum for geologically found bulk MoS₂ is also measured. It is found that the FWHM of the MoS₂ film annealed at 900 °C is essentially equal to the value of the reference MoS₂ crystal (FWHM _{A_{1g}} = 1.94 cm⁻¹ and FWHM _{E_{2g}^1} = 1.71 cm⁻¹). The minor difference in FWHM between electrochemically obtained MoS₂ and the geological MoS₂ crystal is attributed to the polycrystalline nature of the layers, which has more grain boundaries and related imperfections. A reported study shows that crystal grain size of MoS₂ increases with increasing post-annealing temperature [13]. Similarly, HR-TEM also shows high crystal quality for

samples annealed at 900 °C [13] which is consistent with our measured Raman results.

In Fig. 5 Raman spectra of MoS₂ films with different thicknesses (Bi-monolayer to bulk) are shown. A red-shift is observed for the peak position of the E_{2g}^1 mode and a blue-shift is observed for the peak position of the A_{1g} mode with increasing number of MoS₂ monolayers. Both peaks are moving away from each other with increasing number of MoS₂ monolayer. According to literature the difference between A_{1g} and E_{2g}^1 peak positions is 20 cm⁻¹ for MoS₂ monolayer and 27 cm⁻¹ for MoS₂ bulk [22, 26]. So in Fig. 5 the Raman spectrum with a difference of 22 cm⁻¹ between peak positions is attributed to MoS₂ bi-monolayer while the Raman spectrum with 27 cm⁻¹ difference between peak positions is attributed to bulk-like MoS₂, i.e. > 6ML. These results agree with the expected layer thickness from profilometer measurements. In Fig. 5, AFM image of transferred MoS₂ layer is shown. The thickness of the film is 1.9 nm which is equivalent to three monolayers of MoS₂ as thickness of the MoS₂ monolayer is 0.65 nm [27].

In Fig. 6 x-ray photoelectron spectra of the Mo_{3d} doublet and the S_{2s} singlet with corresponding peaks are shown. The spectrum in the upper panel is of a film after the

Fig. 5 Raman spectra of MoS₂ films with different thicknesses (left). Atomic force microscope image of a transferred MoS₂ film on silicon wafer (right)

Fig. 6 XPS spectrum: Mo_{3d} and S_{2s} peaks of the electrodeposited film before and after conversion to MoS₂

electrochemical deposition while the lower panel contains the spectrum of this film transferred to Si substrate and after annealing at 800 °C. The spectrum of the electrochemically deposited film exhibits a Mo_{3d} doublet with binding energy of 232.7 eV and 229.5 eV for the Mo3d_{3/2} and 3d_{5/2}, respectively, which is attributed to MoS₃ [28]. The atomic ratio between Mo_{3d} and S_{2s} peaks is found to be 1:2.85. It can also be deduced from the atomic ratio that the electrodeposited film contains MoS₃. In the lower panel, the spectrum of the transferred film annealed at 800 °C consists of a Mo_{3d} doublet with a binding energy of 232.2 eV and 229 eV for the Mo3d_{3/2} and 3d_{5/2}, respectively. The red-shift in the binding energy of the 3d state of Mo with respect to the MoS₃ counterpart is 0.5 eV, which is attributed to the formation of MoS₂ [29]. The peak intensity of the S_{2s} peak reduces when the film is annealed at 800 °C because the MoS₃ reduces to MoS₂. The Atomic ratio between Mo_{3d} and S_{2s} peaks is found to be 1:2.08, which is close to the ideal MoS₂ ratio. Hence the formation of MoS₂ is confirmed after annealing which is also verified by Raman and UV–Vis spectroscopy.

4 Conclusion

Ultra-thin films of MoS_x were successfully deposited by means of electrochemical deposition at room temperature. The film thickness was controlled by varying the electro-deposition time. A film thickness down to 1 nm was successfully achieved. For film thickness beyond a thickness of 10 nm the roughness stayed around 1 nm which is comparable to the thickness of monolayer of MoS₂. The roughness of the films was found to be essentially thickness independent as expected from smooth, uniform films covering the

surface completely. The electrochemically deposited films were successfully transferred from the initial Au substrate to a bare silicon substrate. The mechanical transfer method followed by environmental-friendly standard Au etching is a novel green method for thin film transfer without using toxic chemicals. It doesn't harm the MoS_x film during transfer process. Furthermore, the underlying growth substrate can be reused. The MoS_x films were successfully converted to MoS₂ by post-annealing with an additional sulfur source in Ar/H₂ environment. The reduction of the electrodeposited films to MoS₂ was confirmed by Raman, XPS, and UV–Vis spectroscopy. The crystallinity of the MoS₂ films was improved with higher post-annealing temperatures as confirmed by Raman measurements. The successful preparation and transfer of Bi-monolayer of MoS₂ was as well confirmed by Raman spectroscopy.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10800-021-01570-0>.

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