Magnetron sputtered MoS$_2$: optical and structural analysis

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Abstract. Transition Metal Dichalcogenide (TMDC) such as MoS$_2$ and WS$_2$, due to unique electronic and optical properties, have sizable band gap, allowing applications such as transistors, photo detectors and other electronic devices. So, fabrication and analysis of these films are important for new generation devices. The substrate temperature strongly effects on the sputtered MoS$_2$ films structure and were weakly influence on optical properties of MoS$_2$ films. The band gap ($E_g$) depends on thickness of the MoS$_2$ films.

1. Introduction
In recent years, various kinds of two-dimensional (2D) materials have received considerable attention as a promising material group for variety electronic applications. Among these materials, MoS$_2$ has attracted much attention, because of its remarkable physical properties and, a stable atomically thin structure has promoted novel applications [1]. MoS$_2$ is a member of the group transition metal dichalcogenides (TMDs) and crystallise with a layer-type structure which is connected in the intermolecular by Van-der-Waals forces. The crystal structure of MoS$_2$ is described as a stacking the sulphur and molybdenum atoms in layers are hexagonally packed with three layers of S-Mo-S. Within the layer each Mo atom are held together by strong covalent bond with six sulphur atoms, while between the layers the bonding is much weaker.

MoS$_2$ has an indirect band gap of 1.3eV, which increases as a function of decreasing film thickness. In monolayer MoS$_2$ (thickness≈0.65 nm), the band gap becomes direct with a width about 1.8eV [2]. MoS$_2$ has been extensively studied for their semiconducting properties as a channel material in conventional field-effect transistors, as well as phototransistors and other optoelectronic devices and has also shown promise in, sensors device for biomedicine. Group of Radisavljevic B et. al 2011 [3] obtained a significant improvement in the device performance with the use of a HfO$_2$ under gate dielectric and demonstrated a large mobility up to about 200 cm$^2$/Vs along with an on/off ratio of $10^6$. Qing Zhang et. al 2014 [4] shown molybdenum disulfide (MoS$_2$) is one of the most typical TMDCs and direct band gap of 1.8 eV in monolayer and layer dependence in band structure. This property of MoS$_2$ is inspiring, which will largely to compensate the weakness of gapless graphene, thus making it possible for MoS$_2$ material to be used in the next generation switching and optoelectronic devices. Therefore, recently many works have been studied to develop high-quality and large scale continuous MoS$_2$ thin films. The synthesis of MoS$_2$ thin films of better quality is highly required to increase the performance of the electronic devices. Different methods such as ALD, CVD and magnetron sputtering are usually adopted to deposit the MoS$_2$ layer on the silicon substrate. Among them, radio-frequency magnetron sputtering (RFMS) has several advantages such as low deposition temperature, ease to handle and the capability of depositing thin films of better quality [5].
have a strong influence on the structure and the properties of the deposited thin films. In traditional physics, it is known as the influence of substrate temperature on the structures and phases of films. As these results, the electrical, optical and electronic properties can change too.

There are different deposition techniques to prepare thin films in which the deposition temperature is one of the main parameters that should be controlled to get high quality films. In that article [6] analysed the effect of the substrate temperature on the structural, morphological, electrical and optical properties of thin films deposited by different techniques.

In this study, the effect of substrate temperature on the structural features that can be measured as a roughness and optical properties of the sputtered MoS$_2$ thin films has been studied.

2. Substrate Temperature Effect on Structural and Optical properties

The substrate temperature effect on the structural properties of the films including orientations of crystals growth and roughness surface, and the electrical properties including the density of charge carriers, and the optical properties including absorption coefficient, will change.

2.1. Structural properties

A large number of experimental results showed that the crystals growth orientations and preferential orientation of MoS$_2$ thin films are sensitive to the substrate temperature and found about the changes from amorphous to polycrystalline structure with substrate temperature increasing. Nozhnenkov M V [7] researched and found that MoS$_2$ films on the Al$_2$O$_3$ substrate prepared at substrate temperatures less than 110°C are quasi-amorphous and around 200°C are textured polycrystalline structures. Miika Mattinen et al. [8] demonstrated MoS$_2$ films are deposited on a variety of substrates, which reveal notable differences in growth rate, surface morphology, and crystallinity and also explored how the deposition temperature affects film crystallinity. As noted earlier, self-limiting growth seemed to occur between 250°C and 325°C. The crystallinity of the deposited films seemed to improve with increasing deposition temperature.

V. Weiss et al [9] were prepared MoS$_2$ thin films by reactive magnetron sputtering from a molybdenum target and textured structure (001) orientation occurs at high substrate temperatures. Zhan et al. [10] used lower temperatures of up to 750°C to grow MoS$_2$ on the SiO$_2$ substrate. The grain sizes were found to be 10-30 nm, and the devices fabricated with this grown MoS$_2$ displayed p-type behaviour with field-effect mobilities between 0.004 and 0.04 cm$^2$/Vs.

2.2. Optical properties

For optoelectronic device applications of MoS$_2$ to be fully understood, it is necessary to know the refractive index (n) and the absorption coefficient (α). The change in the absorption coefficient will change the reflectance of the films. Its complex refractive index in visible range is important, because many of its novel properties are closely related to this wavelength range. Beal et al. [11] measured the complex refractive index of bulk MoS$_2$ in 1979. Spectrophotometer is a powerful technique to measure the optical properties of thin films.

R Bichsel et al. [12] have been investigated as influence of process conditions on the electrical and optical properties of RF magnetron sputtered MoS$_2$ films and has been determined that the optical properties were weakly influenced by substrate temperature. Another report [13] of Mo films on soda lime glass substrates deposited by magnetron sputtering have been investigated the effect of sputtering parameters on the film properties and found coefficient of reflectance were weakly influenced by substrate temperature and demonstrated that the working pressure has a significant affect. In 2007, Blake et al. [14] successfully visualized graphene under an optical microscope by utilizing the contrast of graphene on a SiO$_2$/Si substrate. Given the refractive index of graphene, the contrast can further be calculated based on the Fresnel law.

We have analyzed the pronounced difference between the obtained complex reflectance of MoS$_2$ film at the different substrate temperatures. Furthermore, we have calculated bandgap of MoS$_2$ as a function incident light wavelength for using the obtained number of reflectance.
3. Experimental

Molybdenum disulphide films were prepared by magnetron sputtering MoS$_2$ (98% purity) target on silicon substrates at different substrate temperature (at 200 °C, 250 °C and 300 °C) and different deposition time (2 minutes and 60 minutes). Before the deposition, substrates were chemically cleaned, consisting of two stages: stage one – the substrates were cleaned in an ultrasonic bath in sequence: in alkaline solution and in ethanol for 2 minutes; the stage two is the treatment of the substrate surface by the flow of argon ions from an independent ion source in a vacuum, immediately before sputtering of the target material. The distance between the target and substrate was maintained at 50 mm for all the depositions. The different deposition parameters that are used for growing MoS$_2$ films on various parameters are listed in Table 1.

| Sample code | Substrate temperature, °C | Deposition time, min |
|-------------|---------------------------|----------------------|
| A           | 200                       | 60                   |
| B           | 250                       | 60                   |
| C           | 300                       | 60                   |
| D           | 300                       | 2                    |
| E           | 200                       | 3                    |
| F           | 300                       | 3                    |

4. Results and discussion

Surface morphology and roughness of MoS$_2$ thin film grown on Si were examined through AFM. The three-dimensional AFM images (30×30μm) of samples are shown in Fig.1.

![AFM images](Image)

**Figure 1(a, b, c).** AFM images 3D (30×30μm) of MoS$_2$ films deposited using various substrate temperatures: (a) experimental conditions of sample A: $Ra = 4.85$ nm; (b) sample B: $Ra = 3.68$ nm caption; (c) sample C: $Ra = 2.79$ nm.

So, the measured average surface roughness of these samples A, B, C was 4.85 nm, 3.68 nm and 2.79 nm. This verified the surface roughness of MoS$_2$ film is smoothly with the increase of substrate temperature and the grain size increases at a higher of substrate temperature.

Samples A, B and C are deposited 60 minutes for thick coating about 500 nm and samples D, E and F are deposited during 2 and 3 minutes for thin films MoS$_2$ on Si with a thickness 15 nm and 20 nm respectively. Fig.2 shows 3D AFM image and profile of sample E that used for films thickness determinate.
Figure 2(a, b). (a) 3D AFM image for film edge; (b) film edge profile for sample E (20nm).

For example, in Fig. 2 show the height of the step thin film MoS$_2$ on Si substrate formed by layering the growth planes with a clear outline of the island boundaries gives characteristic values of their thickness on the order of 20 nm.

We measured reflectance five samples MoS$_2$ thin films on Si substrate with the differing in substrate temperature and thickness. Fig. 3 represents the variation of reflectance of all samples with respect to wavelength from 378 to 800 nm.

Figure 3 shows that the thinner films MoS$_2$ ($\approx 20$nm) deposited at lower deposition time (samples D, E and F) demonstrate better reflectivity than thick films MoS$_2$ ($\approx 500$ nm) deposited at higher deposition time (samples A, B and C). Figure 3 shows that the MoS$_2$ films deposited 60 min at different substrate temperature 200 °C, 250 °C and 300 °C is nearly equally 30% reflectance.

The absorption coefficient has been determined using the equation from the Kubelka-Munk (K-M) model [15] to solve the relation of reflectance and absorption coefficients of the sample. Band gap energies of the MoS$_2$ samples (Fig. 4) were estimated from their diffuse reflectance spectra utilizing Kubelka-Munk treatment:

$$\frac{\alpha}{S} = \frac{(1 - R)^2}{2R}$$

(1)

Where $\alpha$ is the absorption coefficient of the sample. $R$ is reflectance. The scattering coefficient, $S$ is, in fact, dominated by particle size and refractive index of the sample. It is not a strong function of the wavelength or the absorption coefficient, so the K-M model considers it a constant. From Fig. 3,
the band gap energies of films can be determined using absorption coefficient $\alpha$ and then to solve the following equation:

$$(\alpha h v)^{1/2} \approx (h v - E_g) \quad \text{(for indirect band gap)} \quad (2)$$

Where $E_g$ is the optical band gap and $h v$ is the photon energy. So we can take the variation of the optical absorption coefficient, $(\alpha h v)^{1/2}$ to zero, then will be allowed us to determine the energy gap. If $(\alpha h v)^{1/2}$ equal to zero in the following equation 2, will be equally the photon energy and band gap of films MoS$_2$. The spectral dependence of absorption coefficient sputtered MoS$_2$ film of sample C at thickness 510 nm is shown in figure 4.

**Figure 4.** The graphs of absorption coefficient on wavelength (inset) and shows $(\alpha h v)^{1/2}$ vs the photon energy (Kubelka-Munk) plots of the sample C (thickness 510 nm).

Figure 4 presents the Kubelka-Munk plots for sample used to determine their band gap energy associated with an indirect transition. By extrapolating the different plots to zero absorption, the obtained energy gap is 1.31 eV for MoS$_2$ of sample C on Si substrate.

Using a Kubelka-Munk plot we obtained an indirect band gap for all samples MoS$_2$ on Si substrate, produced at different substrate temperatures and various deposition times. It can be observed that the indirect band gap increases gradually with the decrease of thickness. Therefore, the estimated indirect band gap values (1.38 eV) for sample D was very closely to the reported indirect band gap value of MoS$_2$ [16]. The effect of substrate temperature were weakly influenced on optical properties of MoS$_2$ films and the band gap ($E_g$) depends on thickness of the MoS$_2$ films. Consolidated experimental results included in table 2.

**Table 2.** Variation of energy band gap for samples prepared with different substrate temperatures and deposition times.

| Sample code | Substrate temperature, $^\circ$C | Deposition time, min | Thickness, nm | Roughness, nm | Bandgap, eV |
|-------------|-------------------------------|------------------------|---------------|--------------|------------|
| A           | 200                           | 60                     | 505            | 4.85         | 1.29       |
| B           | 250                           | 60                     | 500            | 3.68         | 1.30       |
| C           | 300                           | 60                     | 510            | 2.79         | 1.31       |
| D           | 300                           | 2                      | 15             | 0.465        | 1.38       |
| E           | 200                           | 3                      | 20             | 1.201        | 1.37       |
| F           | 300                           | 3                      | 20             | 0.974        | 1.37       |
As it can be seen from the Table 2, the optical band gap energy of samples A, B and C are 1.3eV ± 0.01eV that the same value as it for bulk MoS₂ and samples E and F are 1.37eV with the different substrate temperatures at the same deposition time. It can be seen band gap energy of samples increase with the decreasing thin films thicknesses. In can also be seen roughness of MoS₂ depend on thickness of thin films.

5. Conclusions
Molybdenum disulfide (MoS₂) films were grown on silicon substrate using a direct current (dc) magnetron sputtering system. MoS₂ films were deposited at different substrate temperatures and different deposition times by keeping other experimental parameters such as working pressure, target to substrate distance. Received samples were studied and compared for various characteristics using different techniques AFM and spectrophotometry. AFM results reveal that lower roughness can be observed on the surface of the deposited MoS₂ films for higher substrate temperatures. On the other hand, the band gap energy were weakly changed at the different substrate temperature. The band gap values of the MoS₂ films show a clear dependence on the MoS₂ film thickness, indicating that thinner MoS₂ films have a larger Eg.

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