Effect of annealing temperature on the microstructure and optical properties of MoS$_2$ films

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Abstract. In this paper, MoS$_2$ films were prepared on silicon and glass substrates by RF magnetron sputtering. The surface morphology, structure and transmission and reflectivity of MoS$_2$ films were characterized by SEM, XRD and spectrometer. The effect of annealing temperature on the properties of MoS$_2$ films was analyzed. The results show that the annealing temperature has an obvious effect on the surface morphology of MoS$_2$ thin films, and different annealing temperature can change the position of XRD diffraction peak of MoS$_2$ thin films. The higher the annealing temperature, the better the growth quality and the higher the transmission and reflectivity of MoS$_2$ film.

1. Introduction
MoS$_2$ is a layered, band gap adjustable semiconductor material. Its main component is molybdenite, which belongs to brownish black solid, melting point of 1185 °C, density of 4.8g/cm$^3$, insoluble in water. In recent years, some research results show that MoS$_2$ has many similar but better properties than graphene. For example, the single-layer MoS$_2$ is a semiconductor with direct energy band gap and its energy band gap is adjustable, resulting in great changes in its optical and electrical properties, thus expanding the application of MoS$_2$ in electronic devices, catalysis and solid lubrication [1-3]. There are many preparation methods of molybdenum disulfide film, including physical method, chemical method and biological method. The commonly used preparation methods are chemical vapor deposition (CVD), mechanical stripping, hydrothermal and RF magnetron sputtering. In 1991, Bijan K. miremad and others in Canada prepared MoS$_2$ films by lithium ion intercalation. In 1993, S. D. walck et al. prepared porous MoS$_2$ film by laser pulse [4-16]. Shao Honghong et al. prepared MoS$_2$ thin films on GCr15 steel by magnetron sputtering and obtained better tribological properties [11]. The RF magnetron sputtering method is used in this investigation. The magnetron sputtering is a high vacuum device used to deposit thin films or coatings. In high vacuum, a certain proportion of Ar is filled into the device, and molybdenum disulfide is sputtered on the substrate at a specific power. Magnetron sputtering is a kind of physical vapor deposition (PVD), which can be used to prepare different semiconductors, insulators, metals and other materials. It has the advantages of simple equipment, simple operation and easy control. It can greatly improve the coating area and film adhesion. The disadvantage is that the coating period is long. Under the premise of coating technology, single and multi-layer films can be prepared by using target baffle and sample turntable controlled by
microcomputer, which is another new research method in the research direction of films and new materials.

2. Experimental parameters
MoS$_2$ thin films were prepared on glass substrates by RF magnetron sputtering using JPG450 type ultra-high vacuum magnetron sputtering equipment. The morphology, structure and reflective properties of MoS$_2$ thin films at different annealing temperatures and substrates were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and spectrometer.

The substrate used in the experiment is p-type silicon. Before sputtering, the substrate is ultrasonic cleaned by acetone, anhydrous ethanol and deionized water. The target material is MoS$_2$ ceramic target, and the purity of the target material reaches 99.99%. The target base distance is 70 mm. The MoS$_2$ film is prepared by RF magnetron sputtering. A series of MoS$_2$ films are prepared by changing the annealing temperature. Other process parameters are as follows: the sputtering temperature is room temperature. The substrate power is 80W, the background vacuum is $4.4 \times 10^{-4}$ Pa, the gas flow of argon is 90 sccm, the sputtering time is 4 h, and the sputtering pressure is 3Pa.

3. Result and discussion

3.1. SEM (scanning electron microscope) surface morphology analysis of MoS$_2$ thin film
Scanning electron microscope (SEM) is to study the surface morphology by using the secondary imaging of electronic signals. It uses electron beam to scan the surface of the object to be studied repeatedly. It can produce different effects through the multiple interactions between the electron beam and the material on the surface of the object for feedback. The feedback secondary electron makes the surface of the object to be studied produce magnified morphology image, which is called scanning electron microscope. SEM can be used to observe and analyze the structure and morphology of the surface of the object as well as the composition of the material elements, which is helpful to study the microstructure of the material. Figure 1 shows the SEM image of MoS$_2$ film at the same magnification.

![SEM images of MoS$_2$ films on silicon substrate at different annealing temperatures.](image)

(a) 25$^\circ$C  (b) 100$^\circ$C  (c) 300$^\circ$C

It can be seen from Figure 1 that when the sputtering power of the same substrate material is maintained at 80 W, different annealing temperatures will have a greater impact on the surface structure of the nano film. When the annealing temperature is 25 $^\circ$C and 100 $^\circ$C, the surface of the film presents a round particle shape. When the annealing temperature rises to 300 $^\circ$C, it appears a needle like shape. The shape change of the film particles should be due to the regeneration length of the
material at high temperature, from nanoparticles to nanowires [11]. Table 1 lists atomic composition of MoS$_2$ film on silicon substrate annealed at 25 °C.

Table 1. Atomic composition of MoS$_2$ film on silicon substrate annealed at 25 °C.

| Element | Mass% | Error% | Atom% |
|---------|-------|--------|-------|
| S K     | 23.38 | 1.06   | 47.73 |
| Mo L    | 76.62 | 3.48   | 52.27 |
| Total   | 100.00|        | 100.00|

By comparing the composition table and the atomic mass spectrum, we can find that the atomic percentage of Mo and S atoms is 52.27:47.73, which is different from the molecular formula of molybdenum disulfide. The possible reason is that the coating is not uniform.

3.2. XRD analysis of MoS$_2$ film

The working principle of XRD is diffraction phenomenon. The processed diffraction pattern of X-ray signal is obtained by X-ray diffraction on the object surface. The main purpose of XRD is to get the basic information of the structure, composition and morphological structure of the material, and finally determine the molecular and atomic structure of the material. Figure 2 shows the X-ray diffraction patterns of MoS$_2$ films on silicon substrate with different annealing temperatures.

![XRD patterns](image)

**Figure 2.** XRD patterns of MoS$_2$ films on silicon substrate at different annealing temperatures (a)25°C (b)100°C (c)300°C.

It can be seen from Figure 2 that there are diffraction peaks at 26.5 °, 27.5 °, 24.6 °, 35.3 ° and 40.12 ° positions of MoS$_2$ films at different annealing temperatures, and the corresponding growth directions are (004), (102) and (103), indicating that the film shows preferred growth in (004) direction. Through the analysis and comparison of the different annealing temperature of the molybdenum disulfide nano film, it is found that when the annealing temperature changes for the same
substrate material, the diffraction peak intensity, position and quantity of the molybdenum disulfide nano film are changed, which indicates that different annealing temperature will change the crystallinity and crystal index of the same material. The data are processed by fitting, and the experimental data are analyzed and calculated by using Scheler formula, and Table 2 is obtained.

**Table 2. Grain size of MoS2 film on silicon substrate at different annealing temperatures.**

| Annealing temperature /℃ | Diffraction peaks /° | Full width at half maximum | Diffraction intensity | Grain size /nm |
|--------------------------|----------------------|---------------------------|----------------------|----------------|
| 25℃                     | 24.61398             | 0.60565                   | 40.04209             | 17.7181        |
| 100℃                    | 26.58491             | 0.54597                   | 39.01239             | 25.7689        |
| 300℃                    | 27.49275             | 0.5249                    | 38.06759             | 54.1953        |

**Figure 3.** Full width of half peak and grain size of MoS2 film on silicon substrate at different annealing temperatures.

It can be seen from Figure 2, Table 1 and Figure 3 that although changing the annealing temperature will not have a significant impact on the growth direction of MoS2 film, when the annealing temperature increases from 25 °C to 300 °C, the growth intensity of the film in the (004) direction will gradually weaken, the diffraction peak position will shift to the right, and the grain size of the film will gradually increase.

### 3.3. Analysis of the reflection properties of MoS2 films

Figure 4 shows the reflectivity of MoS2 films on silicon substrate at different annealing temperatures. The reflectivity of MoS2 thin films on silicon substrates annealed at 25 °C and 100 °C has no obvious change, both of which are very low. The reflectivity between 200nm and 1000nm is about 5%; the reflectivity from annealed at 300 °C is also very low, but there are some obvious fluctuations. The highest reflectivity peaks are 10% and 15% respectively at 245nm and 700nm. The reflection properties of MoS2 films annealed at 25 °C and 100 °C have no obvious change, they are very low, basically kept at about 5%; the reflection properties of MoS2 films annealed at 300 °C have obvious fluctuation, up to 30%.
3.4. Study and analysis of transmission properties of MoS$_2$ film

Figure 5 shows transmittance of MoS$_2$ film on glass substrate at different annealing temperatures. The annealing temperature is 25 $^\circ$C, 100 $^\circ$C and 300 $^\circ$C, respectively. The transmission properties of MoS$_2$ thin films on silicon substrates annealed at 25 $^\circ$C and 100 $^\circ$C are very low, and the reflectivity between
200nm and 1000nm is kept at about 0-10%; when annealed at 300 °C, the transmission changes obviously from 500nm to 1000nm, and the highest transmission peaks are above 50%.

4. Conclusion
MoS$_2$ thin films were prepared on silicon and glass substrates by RF magnetron sputtering at different annealing temperatures. The morphology, structure and reflective properties of MoS$_2$ thin films were studied by SEM, XRD and spectrometer. The following conclusions were obtained: 1) Dense and flat MoS$_2$ thin films can be prepared on silicon substrate by RF magnetron sputtering. 2) The change of annealing temperature has no significant effect on the growth direction of the film, and the film mainly grows along the (004) direction. 3) With the increase of annealing temperature, the crystalline state of the film improved and the grain size increased. 4) The reflective properties of MoS$_2$ films increase with the increasing annealing temperature. 5) The transmission properties of MoS$_2$ films increase with the elevated annealing temperature.

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