Research of the influence of vacuum deposition on the growth rate of MoS$_2$ films

A I Belikov$^1$, V N Kalinin$^1$ and A V Sikov$^1$

$^1$Department of Electronic Technologies in Mechanical Engineering, Bauman Moscow State Technical University “BMSTU”, 105005, Moscow, Russia

Email: belikov@bmstu.ru

Abstract. The research results of the working pressure and discharge power influence on the growth rate of molybdenum disulfide thin films on silicon substrates during magnetron sputtering of the target in vacuum are presented. Based on experimental data, an empirical model has been developed that relates the film growth rate to argon pressure and discharge power on a magnetron sputtering system.

1. Introduction

The magnetron deposition of thin films method is one of the widely used methods in production. This is explained by its capabilities: versatility with respect to the materials used in the process (conductors, semiconductors and dielectrics), coating intricate surfaces of products, depositing high-quality multicomponent coatings at relatively high deposition rates [1].

Thin-film coatings based on molybdenum disulfide (MoS$_2$) are widely used as antifriction coatings in mechanical engineering, and in recent years they have been actively studied in the field of nanoelectronics, where they can be used as a two-dimensional semiconductor. The film-forming particles deposition rate on the substrate affected onto the film structure formation peculiarities and ultimately at the thin films properties. The molybdenum disulfide thin films properties substantially depends on the thickness [2]. Ultrathin MoS$_2$ films (from monolayer and up to several nanometers thick) can be used in nanoelectronics (transistors, various sensors, etc.) [3]. In this regard, it is necessary to ensure the coating growth at a certain rate to obtain the desired thickness and film structure. In order to refine the technological process parameters for a new thin-film coatings formation and to efficiently choosing the technological regimes of magnetron deposition, it is necessary to take into account the influence of the main process parameters (Figure 1), such as the pressure of the working gas in the vacuum chamber, the distance between the magnetron and the substrate, and the target material, its size, and etc., on the MoS$_2$ films growth rate. The working gas type and its flow rate, the temperature of the substrate heating and the bias potential supplied to substrate, the substrate surface ion pretreatment presence and its parameters can also determines thin films quality. In addition, modern power supplies for sputtering systems provide stabilized sputtering modes of targets with various parameters. The gas discharge during sputtering can be maintained in constant current (DC) mode and in pulsed mode at medium frequencies (MF), with providing by the power source a frequency rate and pulse duty rate. In DC mode, the key parameters are the current and discharge power, the supplied voltage and the type of stabilized parameter (stabilization by current/voltage/power). And in the pulse mode, these parameters are supplemented with the...
characteristics of the pulses: frequency rate repetition, duty cycle and power in the pulse. The energy and the flow of film-forming particles reaching the substrate surface are significantly depending from the working gas pressure and the sputtering modes of the target, and the discharge power acts as the most frequently used parameter of the sputtering process. Therefore, in this work, the problem of studying and evaluating the argon pressure degree and magnetron sputtering system discharge power influence on the molybdenum disulfide thin films growth rate on silicon substrates was solved.

![Diagram of technological parameters](image)

**Figure 1. Scheme of technological parameters**

### 2. Research methods

In this work, MoS₂ thin films were deposited on polished silicon substrates with a surface roughness of less than 3 nm. The thickness of the deposited films was measured by the height difference «film-substrate». For these purposes, a TR220 model profilometer was used.

After preliminary preparation of the substrate surfaces, immediately before their placement in the technological equipment chamber, masks were fixed on the substrate surfaces, which were removed after films deposition. It ensured a "film-substrate" step profile formation. By using the surface profile obtained with the profilometer, the thickness value was measured by the height difference on the prepared step. In addition, for samples with the films that were previously examined on a tribometer test, as a result of which after complete wear of the coating layer wear tracks were formed on their surfaces, from which it is also, was possible to evaluate the film thickness. The scheme of the sample with the wear tracks and the prepared line of the «step», includes plan of the points, starting from which the profilometry and the measurements were carried out, is presented in Figure 2.

At the initial measurements stage, the probe of the profilometer passed through the center line (from points 1-3) of the silicon substrate with the deposited molybdenum disulfide film (Figure 2).
The first three scans directions were carried out along the center line of the samples with the initial location of the probe at points 1, 2, and 3 and its movement to the substrate center, which made it possible with the more accuracy, constructs and estimates the complete surface profile, taking into account the profiles of wear tracks. The subsequent construction of profiles for two additional measurement areas with the scanning start from points 4 and 5 at the direction parallelly to the center line, that makes it possible to receive information of the film thickness along the «step» line. To increase the reliability 10 measurements were performed for each sample.

The thickness estimate results was carried out using both types of the results of the measurements as at the «step» lines areas and so on the obtained wear tracks profiles.

![Figure 2. Scheme of the sample with the initial points for profilometry displacement](image)

3. Results and discussion
To improve films to substrates adhesion, immediately before the molybdenum disulfide films deposition, the silicon substrates surfaces was etched throw an autonomous ion source. Ion treatment was carried out at an ion current density on the substrate of approximately 1.5 A/m²; the treatment time was 30 minutes.

Prior to the technological processes of the molybdenum disulfide films deposition on silicon substrates, the etching depth of silicon after ion treatment was initially determined. Since the «step» was formed as a result of the overlapping of one area of the substrate with a mask (Figure 3), and the film was deposited on the area that was previously exposed with ion treatment, film growth was starting out from the surface which was formed as a result of layer etching (Figure 4).

![Figure 3. Scheme of the mask layout on the substrate](image)

![Figure 4. The substrate surface line after ion treatment](image)

The presence of the etching effect must be taken into account when the deposited on the substrate film thickness determines since the measured value of the step profile corresponds to the measured
value of $h_1$ (Figure 5), which does not an actual film thickness ($h_2$). To obtain the real film thickness $h_2$, the value of the etching depth must be added to the obtained value of $h_1$. For ion treatment that was used in this work, the measured with the profilometer etching depth value was 0.3 μm. Taking into account the obtained etching depth value, the measured values $h_1$ were corrected up to the film thickness values $h_2$.

![Figure 5. The film on the substrate location after removing the mask](image)

Before loading into a vacuum chamber, the samples were pretreated in organic solvents. To degrease the surface and remove large contaminants, the silicon wafers were cleaned in an ultrasonic bath for 2 minutes at a frequency of 50 kHz. The substrates were firstly cleaned in acetone and then in isopropyl alcohol. The temperature of the solutions was 20 °C. Further, the substrates were dried, after which they were placed on a substrate holder and loaded into a vacuum chamber.

Samples with molybdenum disulfide films were prepared on a vacuum unit equipped with a magnetron sputtering system with planar targets. In this work, produced by pressing powder of DMI-7 MoS$_2$ powder targets were used. The diameter of the target was 75 mm, and the thickness was 5 mm.

The limiting residual pressure in the vacuum chamber of the equipment was $10^{-3}$ Pa. The working gas was argon. The variable process parameters were the discharge power $P$, (factor 1) and the argon pressure $p$, (factor 2).

The output parameter was the average film growth rate $V$, [nm/min].

The controlled and stabilized factors were: the operation mode of the power source – constant current mode, discharge current stabilization, substrate heating temperature – 250 °C, the bias potential on the substrate – the earth potential, the film deposition time – 60 minutes, the distance between the magnetron and the substrate – 100 mm.

The measurements results of the average films thickness for three series of measurements performed at different times are presented in Table 1.

**Table 1 – MoS$_2$ thin films average thickness experimental values**

| $P$, W | $p = 1$ Pa | $p = 0.4$ Pa |
|-------|------------|-------------|
| 20    | 0.17 μm    | 0.14 μm     | 0.11 μm     | 0.62 μm | 0.67 μm | 0.74 μm |
| 40    | 0.27 μm    | 0.24 μm     | 0.25 μm     | 0.92 μm | 0.95 μm | 1.00 μm |
| 60    | 0.23 μm    | 0.27 μm     | 0.28 μm     | 1.71 μm | 1.78 μm | 1.83 μm |
| 80    | 0.47 μm    | 0.45 μm     | 0.50 μm     | 2.56 μm | 2.62 μm | 2.67 μm |

The pressure in the vacuum chamber was monitored using the AP6100 XM sensors (Pirani thermal sensor, error 15%) and AIM-X Edwards (inverse magnetron sensor, error 30%).

The operation modes of the magnetron sputtering system (power, current and discharge voltage) were set using the APEL-M-3 power supply, the values were controlled by a measurement system built into the unit with a microcontroller (error 3%).

The distance between the magnetron and the substrate was controlled by a vernier caliper (error 0.05 mm).

The deposition process time was controlled by a stopwatch (0.1 s error).

The working gas flow was installed and controlled using gas flow controllers (error 0.5%) with computer control.

The substrate temperature was maintained by a temperature controller based on feedback, the temperature sensor was a thermocouple (error 0.5 °C).
The film thickness was measured with a TR220 profilometer (error ≤10%). For the films deposition process time (60 minutes), the average values of the film growth rate were determined (Table 2).

| P, W | p = 1 Pa | p = 0.4 Pa |
|------|----------|------------|
| 20   | 7.3 nm/min | 16.3 nm/min |
| 40   | 9.2 nm/min | 20.9 nm/min |
| 60   | 9.3 nm/min | 34.6 nm/min |
| 80   | 12.9 nm/min | 48.6 nm/min |

As a result of regression analysis, based on experimental data, the following mathematical model was obtained (1):

\[
y = 21.3 + 9.5X_1 + 11.2X_2 + 6.7X_1X_2
\]  

(1)

As follows from model (1), the coefficient \(b_2\) of factor \(X_2\) turned out to be 15.2% higher than the coefficient \(b_1\) of factor \(X_1\), therefore, factor \(X_2\) (pressure) has a greater effect on the film growth rate than factor \(X_1\) (discharge power). The combined effect of these two factors is less than the influence of only one factor \(X_1\) by 41.8%, and less than factor \(X_2\) by 67.2%.

Obtained results indicate the presence of a nonlinear dependence of the MoS\(_2\) films growth rate on the power supplied to the magnetron during sputtering. Nonlinearity is observed for each of the two experimental series, in which different working gas pressure values were used. Such deviations from linearity may be explained by the formation and deepening of the sputtered region (erosion zone) on the target surface, with an increase in the time of its use, which leads to a changes in the electric fields configuration at the target surface and a changes in the trajectories of the bombarding ions relative to the target original nominal plane. Due to the presence of anisotropy in the structure of the MoS\(_2\) crystals, a change in the angle of ions relative incidence to the axis of the crystal can lead to a change in the sputtering coefficient. Therefore, under the same sputtering conditions, by the presence of different erosion zones on the target surface, different streams of atomized material can forms.

4. Conclusion
As a result of the studies, the influence of the magnetron discharge power and argon pressure in the chamber on the growth rate of molybdenum disulfide films was established. According to the obtained mathematical model, with decreasing pressure, the film growth rate increases. An increase in discharge power also leads to an increase in the film growth rate. The influence of the pressure factor on the film growth rate was more significant.

The obtained empirical model can be used to determine the deposition modes of thin MoS\(_2\) films with a given growth rate and obtain coatings of the required thickness by calculating the required discharge power for a specific argon operating pressure.

During the work, the etched depth of the silicon substrate after ion treatment was established, the value was 0.3 μm. This value is significant when applying thin films of molybdenum disulfide with a thickness of less than a micrometer; therefore, to increase the accuracy of measurements by profilometry methods, it is necessary to correct results by this value.

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