Islamic Azad University

Journal of

Optoelectronical Nanostructures

Autumn 2018 / Vol. 3, No. 4

Growth and Characterization of Thin MoS2 Films by Low-Temperature Chemical Bath Deposition Method

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(Received 23 Sep. 2018; Revised 20 Oct. 2018; Accepted 22 Nov. 2018; Published 15 Dec. 2018)

Abstract: Transition metal dichalcogenide (TMDC) materials are very important in electronic and optical integrated circuits and their growth is of great importance in this field. In this paper we present growth and fabrication of MoS2 (Molibdan DiSulfide) thin films by chemical bath method (CBD). The CBD method of growth makes it possible to simply grow large area scale of the thin layers of this material in lower temperatures (near room temperature) and atmosphere pressure in comparison to costly complicated growth methods. The results show the effect of growth temperature and time on the quality of layers and XRD measurements were performed for analysis of crystalline structure of layers. The results show that for the bath temperature of 60oC and for 75 min growth time, better quality of layers can be obtained with low intensity. The low intensity of XRD peaks belongs to poor crystalline structure of layers. For higher bath temperatures, the films lose their uniformity. The results were confirmed by SEM images.

Keywords: Transition Metal Dichacogenide, Growth, Chemical Bath Deposition, Molybdenum Disulfide.

1. INTRODUCTION

In recent years transition metal dichalcogenide (TMDC) materials have attracted much interest because of their characteristics and applications in electronic and optoelectronic devices [1-3]. Most of these advantages arises from their 2D lattice structure which makes it possible to be utilized in ultra-integrated devices. The growing rate of studies over the application of these type of materials, predicts their potential applications especially in semiconductor devices. Among these materials, metal sulfides are known and extensively studied but very few metal sulfides such as WS2, MoS2, CoS, NiS, SnS and ZnS, have been employed to be fabricated [4-7]. Among the metal

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sulfides, molybdenum disulfide (MoS2) has a layered structure like graphite with strong interlayer covalent bonds separated by weak van der Waals forces [6]. Recently different studies demonstrated applications of MoS2 as the active channel region of a transistor [8, 9].

It was also shown that beside the exclusive electronic properties, MoS2 exhibits good optical properties which makes it a candidate to be replaced in optical integrated circuits.

Liu et al. studied refractive index and absorption properties of TMDCs in visible range and its potential applications in spintronics and optoelectronics [10]. Cudazzo et al. showed plasmonic properties of TMDC materials and studied the role of the layer anisotropy in the dispersion of the plasmons [11]. McMenamin et al. demonstrated photoemission from MoS2 layered structures [12].

Different methods have been proposed for growth and fabrication of TMDC material layers [13, 14]. Commonly known method is chemical vapor deposition (CVD), but it requires a costly and high-temperature procedure [15, 16]. Chemical bath deposition (CBD) is a simple, low-cost and low-temperature method which is used to growth of thin metal-oxide layers such as CuO, ZnO, CdS, etc [17, 18]. In this method the glass substrate is placed in a chemical solution which is prepared for desired material and under specific time and temperature the film is deposited on the substrate. In this paper we try to growth MoS2 layers by CBD.

2. MATERIALS AND METHOD

In order to fabricate large area MoS2 films, a glass substrate is considered and cleaned by acetone for 15 min then ethanol for 15 min. The substrate can be chosen from steel or ITO depending on the application of layer. The required materials for this experiment are as follows: 1) Ammonium Molibdat ($(NH_4)_6Mo_7O_{24}$), 2) Sodium Sulfide (Na_2S) and 3) Sulfuric Acid. Since the reaction is performed in aqueous bath, all of the materials should be in solution phase. To do so, deionized water is used to solve the Ammonium Molibdat and Sodium Sulfide powders and change them from solid phase into solution. Our calculations show that in preparing the solution of each above materials, 0.132 mg of Ammonium Molibdat and 156 mg of Sodium Sulfide powders is needed to be added to 10 ml deionized water. After adding the powder to deionized water, we put them in a glass beaker and stir using magnet. The final required solution for growth of thin film can be obtained by combining the solutions with Sulfuric acid in a Pyrex glass beaker. After adding the Sulfuric acid the color of solution changes into brown. The progress of solution preparing is shown in Fig. 1. Formation of MoS_2 layer by CBD is as follows. Firstly Sulfuric acid reacts with Ammonium Molibdat which leads to formation of $(NH_4)_2MoO_4$ as:

$$(NH_4)_6Mo_7O_{24} + 4H_2SO_4 \rightarrow 7(NH_4)_2MoO_4 + 4(NH_4)_2SO_4 + 4H_2O \quad (1)$$

On the other hand, Na_2S is decomposed into H_2S in the presence of water:

$$Na_2S + 2H_2O \rightarrow 2NaOH + H_2S \quad (2)$$

The resulted H2S reacts with $(NH_4)_2MoO_4$ under acidic condition and MoS_2 with brown color is formed as:

$$4(NH_4)_2MoO_4 + 3H_2SO_4 + 9H_2S \rightarrow 4MoS_2 + 4(NH_4)_2SO_4 + 12H_2O \quad (3)$$

The prepared substrate which is a glass slide is vertically placed in the beaker which is located within the bath. The temperature of bath is adjusted and controlled by an electronic circuit. Since the formation of thin layers is dependent on the temperature of solution and the time at which the substrate is placed within it, we study the effect of these parameters on the growth and properties of deposited layers.

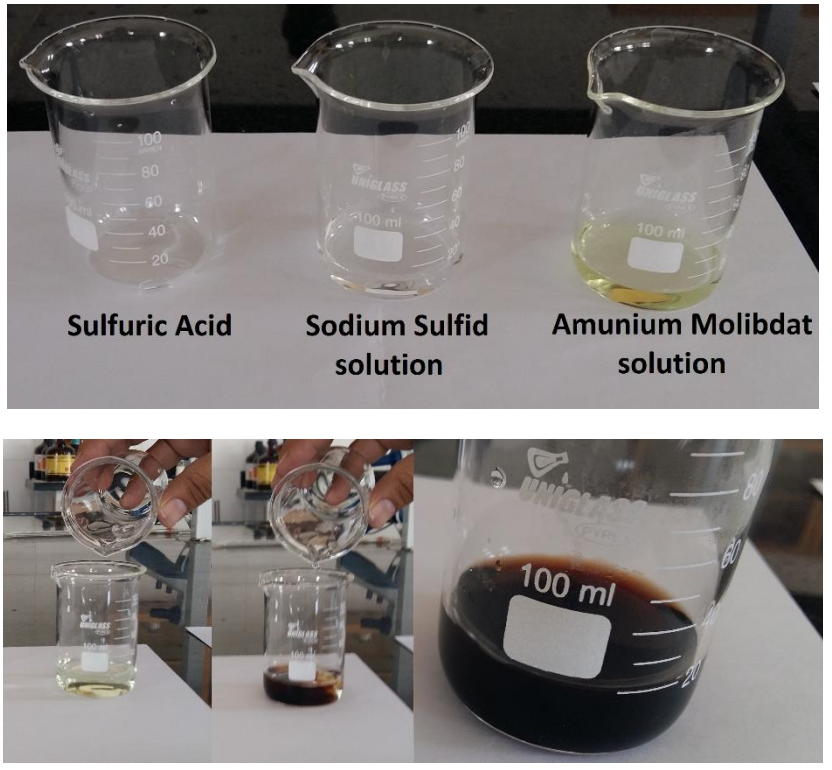


Fig.1. Progress of final solution production. Brown color of solution confirms presence of MoS_2.

Fig. 2 shows different samples which are deposited in different temperatures and times. According to the figure, at T=30^{o}C a very thin layer is formed which becomes thicker with increase in temperature. At T=60^{o}C some areas are formed with considerable thickness. However as the temperature reaches to T=90^{o}C, the layers are accumulated and the surface gets bulky structure. So it can be said that for increased temperatures the layer loses its uniformity and structure shape. So we continue the studies for T=30 and 60^{o}C.

More study is performed by XRD analysis of layers grown at different temperatures and in 60min. Growth time of 60min is chosen because according to the fig. 2 a proper surface morphology is achieved for this time. For T=30^{o}C no considerable peak is observed in XRD pattern. This is in agreement with what is seen from the very low thickness of layers grown at T=30^{o}C. So another analysis is performed for a sample grown at T=60^{o}C and the results are illustrated in Fig. 3(b). According to the pattern, two distinct peaks are evident in 12.49 and 50.45. The detailed specification of peaks are listed in Table 1. In

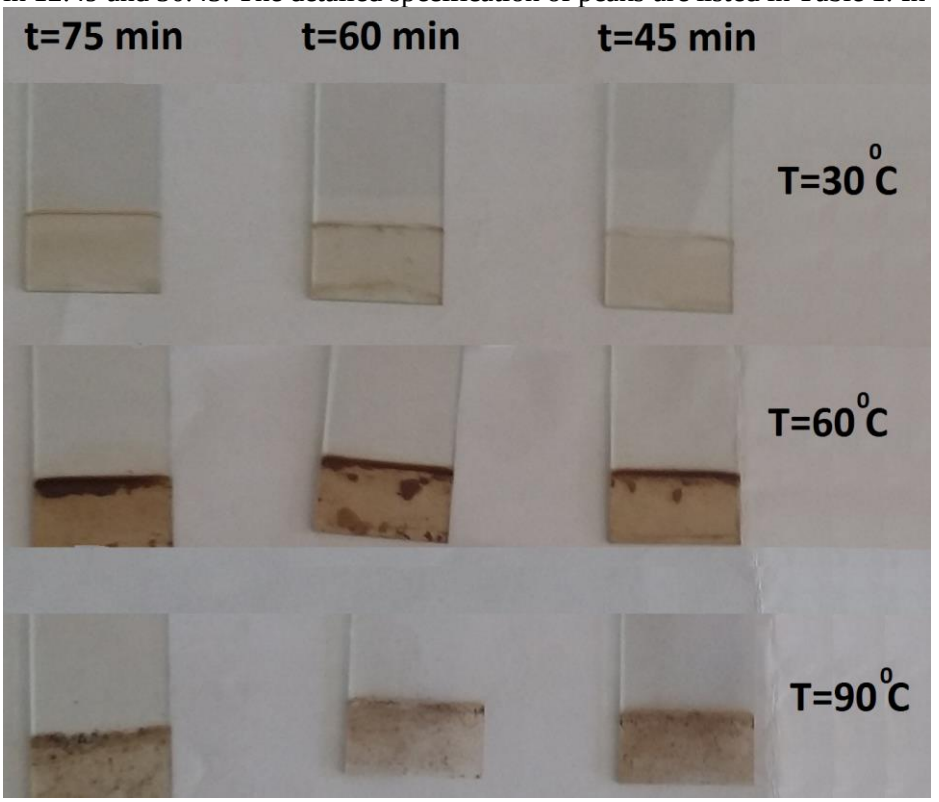


Fig. 2. Photograph of deposited layers at different growth time and temperatures.

comparison to the previously reported data, the peak of 50.45 is related to the (600) direction [19]. It is seen that increasing the temperature leads to observation of a standard peak in the XRD spectra. In order to investigate the effect of growth time, another sample is deposited at T=60°C and t=75min and the pattern is shown in Fig. 3(c). For this sample 4 peaks are observed at 12.60, 27.49, 31.07, and 50.42 with details listed in Table 1. Compared to the standard peaks reported for MoS_2, the peaks 31.07 and 50.42 are related to (100) and (600), respectively [19, 20]. So it can be concluded that increasing the growth time improves the quality and crystalline properties of layers.

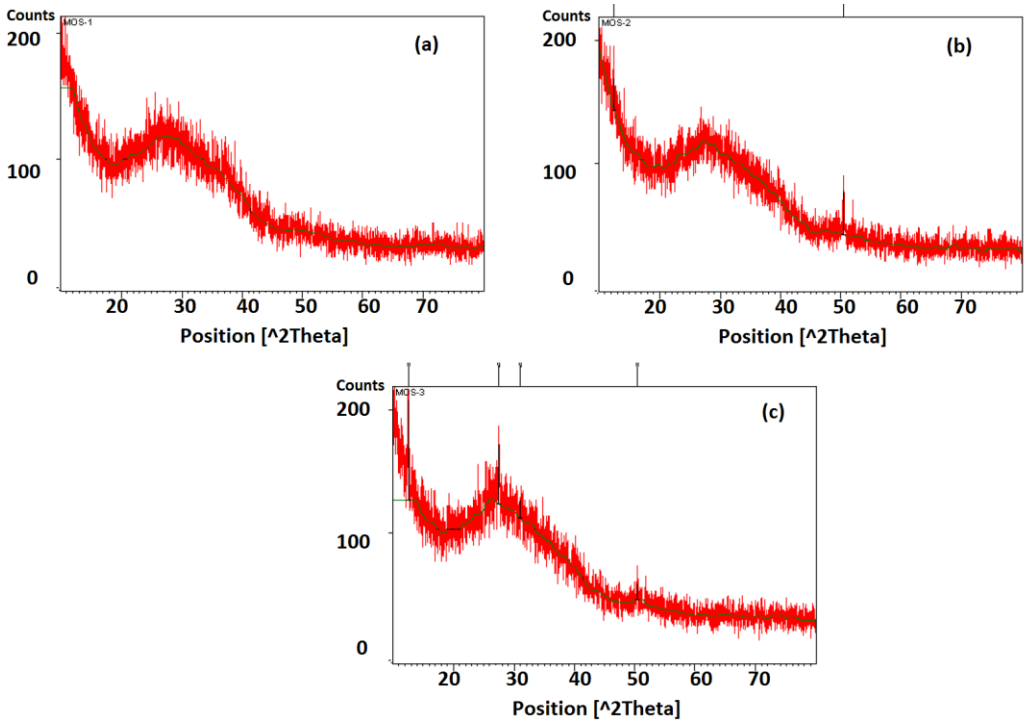


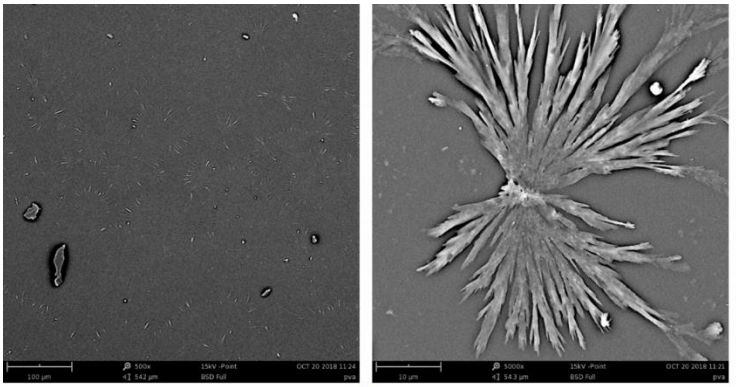
Fig. 3. XRD pattern for 3 samples grown in different conditions, (a) t=60 min, T=30°C, (b) t=60 min, T=60°C, (c) t=75 min, T=60°C.

Table.1.
Detailed specification of observed peaks for samples grown at different time and temperatures.

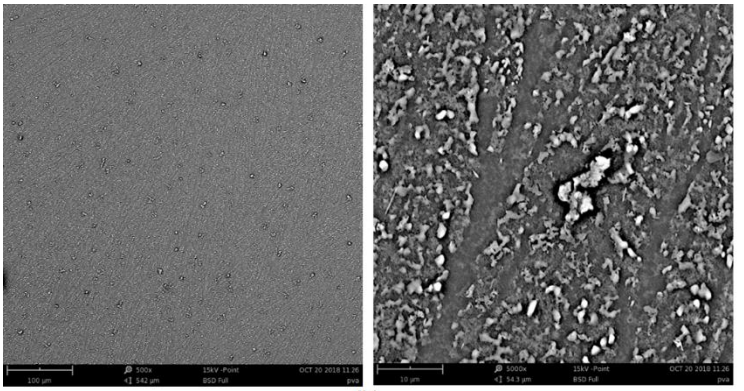
t=60 min, T=60°C				
Pos.[°2Th.]	d-spacing[Å]	Height[cts]	Rel.Int.[%]	Backgr.[cts]
12.4927	8.22129	25.20	70.98	144.00
50.4535	2.09878	35.50	100.00	43.00

t=75 min, T=60°C				
Pos.[°2Th.]	d-spacing[Å]	Height[cts]	Rel.Int.[%]	Backgr.[cts]
12.6058	8.15369	80.97	100.00	127.00
27.4950	3.76679	48.63	60.06	124.00
31.0772	3.34153	15.19	18.77	113.00
50.4262	2.09985	12.82	15.83	46.00

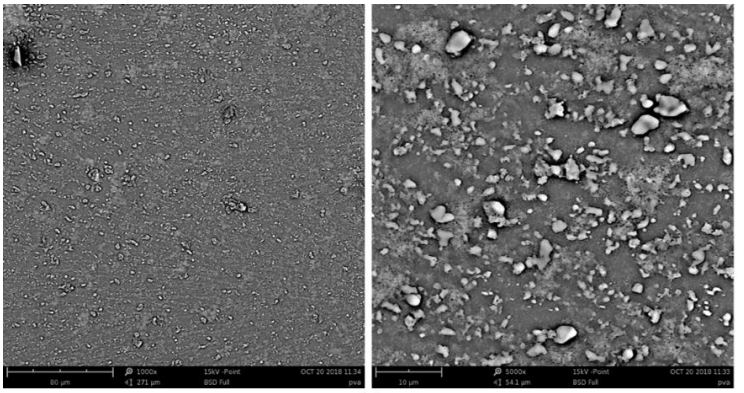
In order to study the morphology of deposited layers, scanning electron microscopy (SEM) images are prepared for samples and they are shown in Fig. 4. Fig.4(a) shows the layer formed in 30°C and 75 min. According to the figure some flower-like areas are formed as islands and no reasonable layer structure is formed. This is in agreement with predictions of Fig. 2 and XRD results. However by increasing the temperature a nearly uniform film is deposited as shown in Fig.4(b) in which the growth temperature and time are 60°C and 45 min, respectively. The figure reveals tendency of sub-micron particle to form a uniform layer in this condition and the film quality is improved when the growth time is increased to 75 min as shown in Fig.4(c). By more increase in growth temperature from 60°C to 90°C, the formation of microdomes occurs and this can be resulted from more accumulation of particles to individual islands. By comparing the SEM images at different temperatures, it can be deduced that in lower temperatures some slower-shape islands is formed and by increasing temperature they cover all the surface and a nearly uniform layer is deposited. For higher growth temperatures the layer accumulated to islands again and it loses uniformity. However the more growth time results in the more uniform layer.



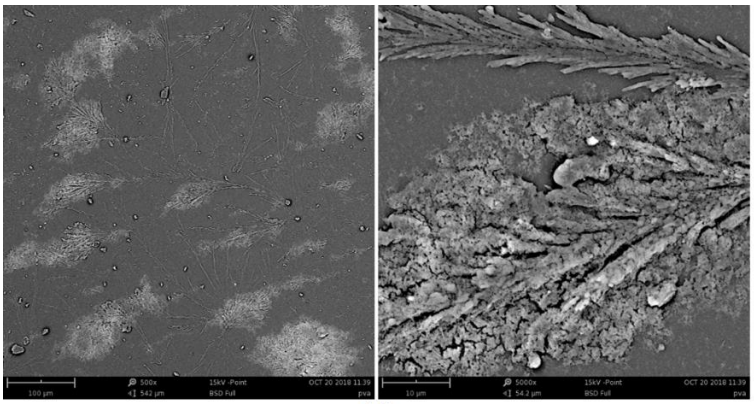
(a)



(b)



(c)



(d)

Fig.4. SEM images of samples grown at different conditions; (a) T= 30°C, t=75min, (b) T= 60°C, t=45min, (c) T= 60°C, t=75min, (d) T= 90°C, t=60min.

3. CONCLUSIONS

Growth of transition metal dichalcogenide material, MoS_2 was proposed based on chemical bath deposition method. Different growth conditions were studied and the effect of temperature and time were investigated simultaneously. Three different growth temperatures and deposition times were considered and the samples were grown. The results showed that by increasing the temperature more uniform layers are formed but for higher temperatures around T=90°C the structure loses its uniformity and changes into randomly distributed microdomes. We also found that higher growth times leads to more uniform layers. XRD analysis of some samples were performed and It was shown that for higher temperatures and growth times, some crystalline peaks were observed. The low intensity of XRD peaks shows the poor crystalline structure. The layers were also studied by SEM images and it was found that at low growth temperatures no layer is formed but for higher temperatures and higher growth time formation of a uniform layer is evident. By more increasing the temperature the film lose their uniformity.

ACKNOWLEDGE:
This work is supported by Islamic Azad University, Urmia Branch.

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