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Study of Photo-Conductivity in MoS_2 Thin Films Grown in Low-Temperature Aqueous Solution Bath

Mahdi Zavvari*,1, Yashar Zehforoosh[1]

[1] Department of Electrical Engineering, Urmia branch, Islamic Azad University, Urmia, Iran.

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Abstract: An experimental study over the optical response of thin MoS_2 films grown by chemical bath deposition (CBD) method is presented. As two important factors, the effect of bath temperature and growth time are considered on the photocurrent generation in the grown samples. The results show that increasing the growth time leads to better optical response and higher difference between dark and photocurrent. For higher bath temperatures the layer loses its uniformity and the current reduces. Better performance of optical response is obtained for t=90min and T=70°C. We also studied the effect of post-annealing on the performance and quality of thin films. The I-V measurements show no current flow for annealed films because of rupture of the film structure. Temporal response of the films to light source ON and OFF states is also studied and the results showed relaxation of photocurrent after about several seconds. The importance of the MoS_2 thin films obtained by CBD method is low-temperature process and large area of fabricated layers which can be used in many applications.

Keywords: Transition Metal Dichalcogenide, Molybdenum Disulfide, Chemical Bath Deposition, Photocurrent.

1. INTRODUCTION

By increasing the demand for high capacity optical communication systems, it is necessary to design and fabricate more reliable and high performance optoelectronic and photonic devices [1]. Recently highly integrated optical systems have been proposed as solution to overcome the speed limitations and enhance the transmission characteristics. Different integrated devices have been presented such as light emitters and detectors, modulators/demodulators, multiplexers/demultiplexers, amplifiers, and etc [2, 3]. However photodetectors are essential block in a transmission system and they play an important role in a typical system since some of their performance characteristics can restrict the

* Corresponding author. Email: **m.zavvari@iaurmia.ac.ir**

system operation [4]. In past years many different types have been proposed for photodetectors based on different mechanisms of operation and structure. PIN detectors, avalanche photodiodes (APD), quantum confined photodetectors such as quantum well and quantum dot photodetectors (QWIP and QDIP) are the most known structures with high capability which can be designed for a wide range of wavelengths and to promote performance characteristics [5-7]. The most common issue in these above mentioned structures is the high cost of fabrication which limits their utilization for some special projects. It is well-known that photodetectors have wide variety of applications in optical communication systems, chemical detection, medicine, etc [8]. The costly process of fabrication leads to some limitations in these applications. On the other hand, photoconductive effect in which the absorption of optical radiation leads to generation of photo-carriers has been reported for many of applications [9]. In this method of detection, any absorbed amount of light changes the conductivity of the layer and hence by sensing the electrical current variations, the power of incoming light can be estimated [10]. The process is usually performed on a thin film of a semiconductor. That, how the semiconductor film is deposited, determines the quality of absorption and the cost of fabrication.

Normally some high temperature chemical reactions from vapor phase of materials is implemented to deposit the thin films of semiconductor such as chemical vapor deposition (CVD) or some other high temperature processes like physical vapor deposition [11-14]. Because of dependence of the layer quality on the growth temperature and difficult control of high temperatures, these methods are costly and difficult to fabricate [15]. A simple, low-temperature, and low-cost method is the production of thin layers from an aqueous solution of chemical compounds which is called chemical bath deposition (CBD) [16]. In this method the required compounds are inserted within a bath and react and then under a given temperature and growth time, the film is deposited on the substrate [17].

On the other hand transition metal dichalcogenide materials (TMDC) have been proposed as interesting materials in the field of electronics and optical devices [18-20]. Two-dimensional layers of these materials exhibit carrier mobility in the order of silicon and high on/off ratio and small thickness are high potential properties of devices based on 2D TDMC [21, 22]. Recently some groups have reported photo-response of TMDC based detectors which shows values similar to graphene [23]. The first TMDC based photo-transistor with a MoS_2 monolayer active region showed a photo-responsivity of 7.5 mA W^{-1} which is similar to graphene devices that reach 6.1 mAW^{-1}. Multilayer MoS_2 show higher photo-responsivities, about 100 mAW^{-1}, which is similar to silicon devices [24].

In this paper we are going to fabricate the thin films of MoS_2 material and study the effect of different growth mechanism on its photoconductivity. Although other growth mechanisms have been presented for MoS_2 deposition, however our aim is to study the optical properties of low-cost CBD grown thin films of MoS_2 to compare the results with other presented methods.

2. EXPERIMENTAL SETUP

CBD method is based on a chemical reaction in the aqueous phase of some chemical compounds to achieve a final solution which is used for deposition. We used glass substrate to proceed the growth procedure. Previously we reported our experiment in preparation of MoS_2 thin films by CBD [25]. Here and to do so, first the substrate is carefully cleaned by acetone for 15 min then ethanol for 15 min. This helps to achieve a nearly uniform and impurity-less thin film. 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, all of them in solution phase. The solution phase of powder materials is achieved using deionized water. This requirement is necessary to be utilized in an aqueous bath. It should be noted that 0.132 mg of Ammonium Molibdat and 156 mg of Sodium Sulfide powders is needed to be added to 10 ml deionized water for preparation of solution phase. The final required solution for growth of thin film can be obtained by combining all of the three solutions in a Pyrex glass beaker. The progress of the final solution preparation is as follows. Firstly Sulfuric acid reacts with Ammonium Molibdat which leads to formation of $(NH_4)_2MoO_4$ as:

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

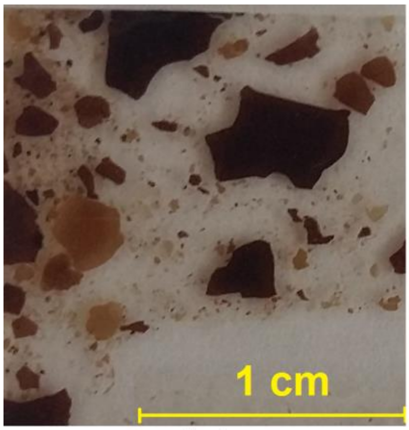
On the other hand, Na_2S is decomposed into H_2S in the presence of water:

$$Na_2S + 2H_2O \rightarrow 2NaOH + H_2S \tag{2}$$

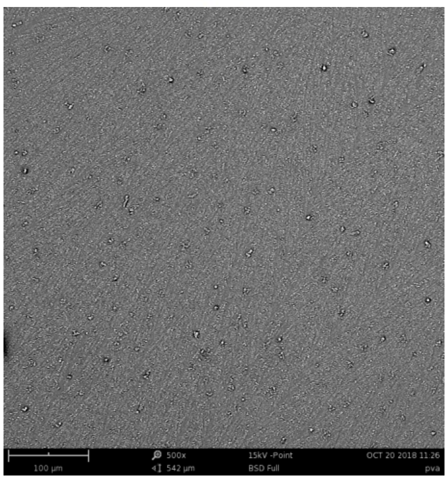
The resulted H_2S reacts with $(NH_4)_2MoO_4$ under acidic condition and MoS_2 with brown color is formed as:

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

The solution within beaker is stirred using a magnet and its temperature is precisely controlled using an electronic circuit. The substrates are vertically inserted within solution and the thin film growth is followed and studied for different time lapse. In CBD process two different parameters affecting the quality of grown layers are growth time and bath temperature. In many cases the deposition is followed by a post-annealing process to activate dopants, change film to film or film to wafer substrate interfaces, densify deposited films, change states of grown films, repair damage from implants, move dopants or drive dopants from one film into another or from a film into the wafer substrate.



(a)



(b)

Fig. 1. The photograph of grown MoS_2 layer and (b) its SEM image.

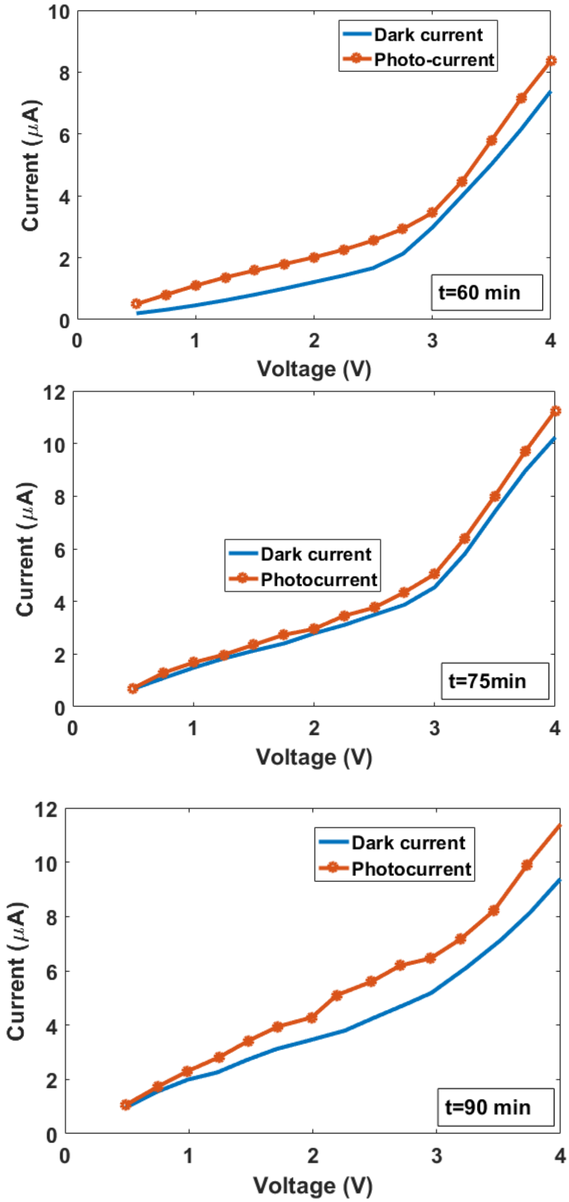


Fig. 2. I-V characteristics of thin MoS_2 films grown at different times for dark and illumination conditions. The bath temperature is held on T=60 °C.

3. RESULTS AND DISCUSSIONS

In this paper we study the effect of annealing on the electrical and optical obtained samples. Previously we reported CBD growth of MoS_2 thin films and based on the obtained results it was concluded that the growth temperature of about 60°C and growth time about 75min are nearly suitable for better quality of grown layers [25]. Here we try to obtain the photoconductive behavior of grown layers for different growth conditions. Fig. 1 shows the photograph and SEM image of the MoS_2 thin film. According to the SEM results the surface of the film is nearly uniform and this makes it a reliable way to extend the growth of such layers.

In order to study the effect of different growth conditions, three different growth time and temperatures are studied. Fig. 2 illustrates the measured I-V characteristics in both dark and illuminated conditions. For measuring the photocurrent, all the samples are excited by a high power white light. The source is an array of white LEDs which is illuminated near the surface of thin film.

According to the results shown in the figure, one can deduce that for increased growth time, the order of current gets higher values. For example in applied bias of 4V, the dark current stays around 8uA in t=60 min, while it reaches to about 10uA for the samples with higher growth times. This can be attributed to the thickness increase of the films as a function of growth time. In the other words, the conductivity of layer is dependent on the cross section of current path and since thicker layers are obtained by time duration, its conductivity is reduced and hence the current increases. Another important result from the figures is the difference between dark and photocurrent. It is evident that this difference is decreased for t=75 min in comparison to the t=60min. One reason to this reduction can also be due to the increased thickness of layers. This means that although the dark current increases with thickness, however the incident light is absorbed in top of layer surface and it doesn’t reaches to the entire of the layer. For t= 90min the difference increased again. By comparison of the results, it is seen that for higher applied bias the slope of dark current is reduced and it gets lower values than that of the sample of t=75min. However it can be deduced that t=90 min is suitable because of higher difference between dark and photo-current which leads to increased values of detectivity.

For deposition of thin films by CBD method, there are three affecting mechanisms; growth time, bath temperature and annealing. We proceed our study by considering the effect of bath temperature on the photo-conductivity of grown layers. To do so, three bath temperatures are applied and the samples are measured and analyzed. Fig. 3 shows the obtained results for bath temperature of 70 ° and 80° C and the results for T=60° C are in Fig. 2(a). The reason for choosing these temperatures is related to the results reported in our previous work where it was demonstrated that the suitable range for achieving uniform layers is around 60^{o}C. In this case the growth time is fixed at t=60 min for all of the samples.

Fig. 3 shows the I-V characteristics of the samples grown at different bath temperatures. According to the figures and in comparison to the results of Fig. 2, by increasing the bath temperature form 60^o to 70^o C the currents are very slightly changed and enhanced. But for more increase in the bath temperature, both the currents are considerably drop to lower levels.

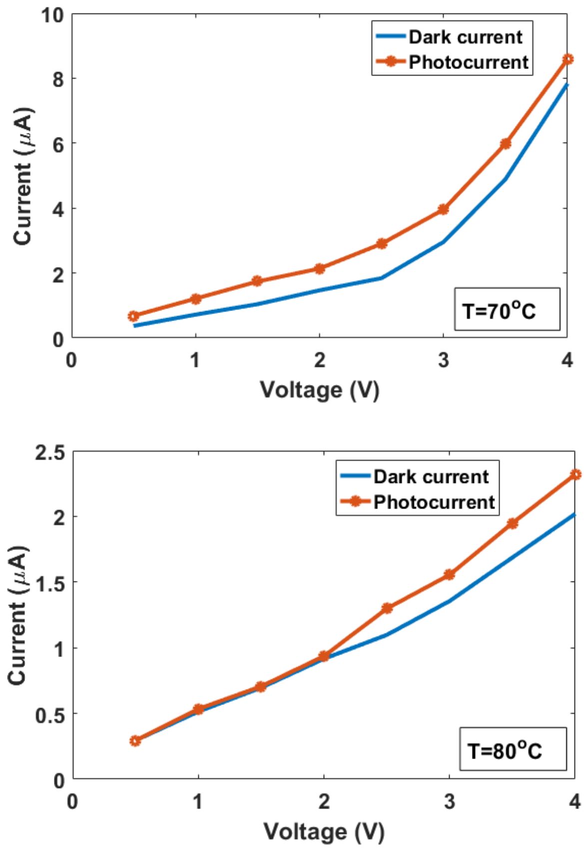


Fig. 3. I-V characteristics of thin MoS_2 films grown at different bath temperatures for dark and illumination conditions. The growth time is held on t=60min.

We believe that this is related to the structure changes of the films for increased temperatures. In the other words and using the reported results of

[25], the uniform layer changes into microdomes and consequently a nonuniform area is created in which the flow of current is influenced by the morphology of the film surface. That's why a sudden decrease in the transmitted current occurs. So there is an optimum bath temperature around T=70^o C at which a high photo-conductivity is expected from the sample. However in all of the cases the absorption of illuminated light leads to generation of carriers and hence increasing the flowing current.

In order to study the effect of annealing on the performance of deposited layers, they were subjected to a 400^{o}C furnace for 10 min and the I-V measurement showed no current flowing. This can be attributed to physically rupture of layer structure and hence pinching the channel off.

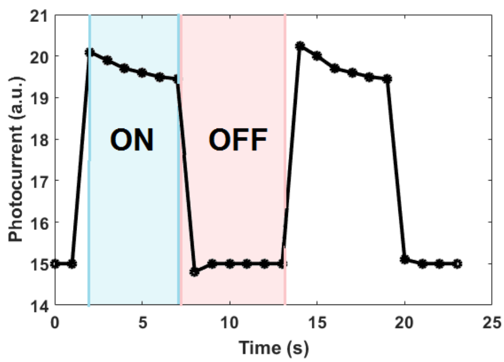


Fig. 4. Time response of grown MoS_2 thin film to light source ON/OFF.

We also study the time response of the films to turning a light source on/off. The results are shown in Fig. 4. According to the figure, the current responds to the variations of source illumination such that by exposing the light, it gets higher levels. However the photocurrent has a decaying behavior by time before it gets stable. The reason can be related to the thermal recombination response of the layer where it takes a while to respond the excess photo-generated carriers and being stable in thermal equilibrium.

4. CONCLUSION

Photoconductive response of thin MoS_2 films grown by using CBD method as a low-cost, low-temperature method was studied. Three different growth times and temperatures were considered and analyzed. Results showed that increasing the bath temperature and growth time leads to better optical response of the layers. However at higher temperatures because of non-uniformity of layers the current level decreases. We also studied the effect of annealing and no current were flowed for annealed samples. Time response of the samples to switching source was also studied and the results showed a deep in photocurrent before being stable.

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REFERENCES

[1] H. Kalt and C. F. Klingshirn, *Semiconductor Optics 1: Linear Optical Properties of Semiconductors* Switzerland AG; Springer, 2019.

[2] S. L. Chuang, *Physics of Photonic Devices*, Wiley, 2012.

[3] V. Fallahi, M. Seifouri, *Novel structure of optical add/drop filters and multi-channel filter based on photonic crystal for using in optical telecommunication devices.* J. Optoelectron. Nanostruct. 4(3) (2019) 53-68.

[4] C. E. Png, S. Sun, B. Ping, *State-of-the-art photodetectors for optoelectronic integration at telecommunication wavelength.* Nanophoton. 4 (2015) 277-302.

[5] D. J. Norris, *Multispectral quantum-dot photodetectors*. Nat. Photon. 13 (2019) 230-232.

[6] M. Zavvari and V. Ahmadi, *Dynamics of avalanche quantum dot infrared photodetectors*. Mod. Phys. Lett. B. 26 (2012) 1250216.

[7] E. Rodriguez, A. Mottaghizadeh, D. Gacemi, et al., *Room-Temperature, Wide-Band, Quantum Well Infrared Photodetector for Microwave Optical Links at 4.9 μm Wavelength.* ACS Photon. 5 (2018) 3689-3694.

[8] M. Karimi, K. Abedi, and M. Zavvari, *Resonant cavity enhanced quantum ring photodetector at 20μm wavelength.* Opt. Quant. Electron. 45 (2013) 1249–1258.

[9] A. Gazman, Z. Zhu, M. Bahadori, K. Bergman, *Wavelength Locking of Multicast Signals Using Photo-Conductive Effect in Silicon Photonic Platform.* Presented at IEEE Optical Interconnects Conference (OI), (2018).

[10] Q. Guo, A. Pospischil, M. Bhuiyan, *Black Phosphorus Mid-Infrared Photodetectors with High Gain*. Nano Lett. 16 (2016) 4648-4655.

[11] S. Liang, W. H. Liu, D. Chi, *Recent progress in chemical vapor deposition growth of two-dimensional transition metal dichalcogenides.* Prog. Cryst. Growth Charact. Materials. 62 (2016) 9-28.

[12] M. Amani, M. L. Chin, A. G. Birdwell, T. P. O'Regan, S. Najmaei, Z. Liu, P. M. Ajayan, J. Lou, M. Dubey, *Electrical performance of monolayer MoS2 field-effect transistors prepared by chemical vapor deposition.* Appl. Phys. Lett. 102 (2013) 193107.

[13] M. Gholampour, A. Abdollah-zadeh, L. Shekari, R. Poursalehi, M. Soltanzadeh, *Green Method for Synthesizing Gallium Nitride Nanostructures at Low Temperature.* J. Optoelectron. Nanostruct. 3(1) (2018) 51-64.

[14] B. B. Nasab, A. Kosarian, N. A. Sheini, *Effect Of Zinc Oxide RF Sputtering Pressure on the Structural and Optical Properties of ZnO/PEDOT:PSS Inorganic/Organic Heterojunction.* J. Optoelectron. Nanostruct. 4(3) (2019) 33-46.

[15] J. D. Cain, F. Shi, J. Wu, V. P. Dravid, *Growth Mechanism of Transition Metal Dichalcogenide Monolayers: The Role of Self-Seeding Fullerene Nuclei.* ACS Nano 10 (2016) 5440–5445.

[16] K. Taneja, A. M. Madiraju, M. Kumar, R. Seelaboyina, A. K. Keshri, S. Mahajan, *Substrate Rotation Chemical Bath Deposition of Cadmium Sulfide Buffer Layers for Thin Film Solar Cell Application.* Presented at International Conference on Solar Energy Photovoltaics, (India, 2012).

[17] M. Husham, Z. Hassan, A. M. Selman, N. K. Allam, *Microwave-assisted chemical bath deposition of nanocrystalline CdS thin films with superior photodetection characteristics.* Sens. Actuat. A. Phys. 230 (2015) 9-16.

[18] X. Duan, C. Wang, A. Pan, R. Yu, X. Duan, *Two-dimensional transition metal dichalcogenides as atomically thin semiconductors: opportunities and challenges.* Chem. Soc. Rev. 44 (2015) 8859-8876.

[19] W. Choi, N. Choudhary G. H. Han, J. Park. D. Akinwande, Y. H. Lee, *Recent development of two-dimensional transition metal dichalcogenides and their applications.* Materialstoday 20 (2017) 116-130.

[20] S. Manouchehri, J. Zahmatkesh, M. H. Yousefi, *Substrate Effects on the Structural Properties of Thin Films of Lead Sulfide.* J. Optoelectron. Nanostruct. 3(2) (2018) 1-18.

[21] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, *2D transition metal dichalcogenides.* Nat. Rev. Mater. 2 (2017) 17033.

[22] V. B. Miandoab, E. S. Iranizad, H. Kahrade, *The effect of concentration and time of hydrothermal process on the fluorescent property of Molybdenum Diselenide nano-layers.* J. Optoelectron. Nanostruct. 1(3) (2016) 35-42.

[23] S. Ahmed, J. Yi, *Two-Dimensional Transition Metal Dichalcogenides and Their Charge Carrier Mobilities in Field-Effect Transistors.* Nano-Micro Lett. 9 (2017) 50.

[24] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, *Ultrasensitive photodetectors based on monolayer MoS2* Nat. Nanotech. 8 (2013) 497–501.

[25] M. Zavvari, Y. Zehforoosh, *Growth and Characterization of Thin MoS2 Films by Low- Temperature Chemical Bath Deposition Method.* J. Optoelectron. Nanostruct. 3(4) (2018) 35-44.