Sulfurization of α-MoO3 nanostructured thin film

Prabhat Kumar, Megha Singh, Rabindar K. Sharma, and G. B. Reddy

Citation: AIP Conference Proceedings **1675**, 030051 (2015); doi: 10.1063/1.4929267
View online: http://dx.doi.org/10.1063/1.4929267
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1675?ver=pdfcov
Published by the AIP Publishing

Sulfurization of α-MoO_3 Nanostructured Thin Film

Prabhat Kumar[1], Megha Singh[1], Rabindar K. Sharma*, [1] and G. B. Reddy[1]

[1]*Thin Film Laboratory, Physics Department, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India*

*E-mail: rkrksharma6@gmail.com

Abstract. In this report, the sulfurization of vertically aligned molybdenum trioxide (α- MoO_3) nanoflakes (NFs) with high aspect ratio (height/thickness >20) on the nickel coated glass substrates in a mixture of H_2S and argon gas at atmospheric pressure has been studied. The effect of sulfurization have been investigated to understand the basic reaction mechanism and the morphology, structural properties of grown nanoflakes. XPS and XRD indicate the formation of MoS_2 along with the other intermediate phase such as MoO_2 at temperature 200 ºC. The surface morphology of samples have been studied systematically by using scanning electron microscope (SEM). The results demonstrate partial conversion of MoO_3 NFs into MoS_2 along with the change in the morphology of nanoflakes. All the observed results are well in consonance with each other.

INTRODUCTION

Since the synthesis of graphene and subsequent noble prize, layered structured materials have grabbed the attention of whole scientific community. These layered materials have unique properties, which make it highly interesting to study these materials theoretically as well as experimentally. MoS_2 is a layered material which has graphene like structure, with a bandgap of 1.2-1.9 eV [2]. MoS_2 has distinctive electronic, optical and catalytic properties and hence has attracted great interest. These properties enable the use of MoS_2 in industrial applications such as lubricants, optoelectronic devices, sensors, etc. Many methods for synthesis of MoS_2 thin film have been investigated such as intercalation assisted thermal cleavage method, micromechanical exfoliation, liquid exfoliation and vapour deposition [1]. Recently, the sulfurization of MoO_3 has been one of the most attractive method for synthesizing MoS_2 nanostructured thin films (NSTs) with excellent aspect ratio. There are very few studies based on the effect of sulfurization mechanism on the features of grown nanostructure have been reported. Here, we report, sulfurization of MoO_3 nanoflakes.

EXPERIMENTAL

MoO_3 have been deposited by using PASP route [5]. The experimental setup of plasma assisted sublimation route essentially have two cup-shaped Al–electrodes confronting each other and placed at an optimum separation of 7.5 cm. First, about 100nm thick Ni-film is deposited on glass substrate using thermal evaporation of 99.99% pure Ni powder at base vacuum of 7.5×10^{-6} Torr. Later Ni/glass substrate is placed on Mo-strip, held at temperature 500 ºC. The strip temperature is appropriately control by adjust current flowing across it. In order to deposit MoO_3 NSTs at a plasma voltage of 2500 Volt, first the chamber is evacuated to 7.5×10^{-6} Torr, than high purity oxygen gas is inserted into the chamber and maintain the value of oxygen partial pressure at the level of 7.5×10^{-2} Torr to sustain stable plasma across electrodes. The growth process continues for 30 min. Nanostructured thin films of MoO_3 nanoflakes were obtained. Thermocouple arrangement is adjusted inside vacuum chamber to read the substrate/growth temperature. The sulfurization experiments were done in a glass tube reactor. Initially Ar gas passed into the tube to remove the residual gases. MoO_3 nanostructures thin film is heated at desired temperature of 200 ºC for 2 hr in presence of H_2S (generated by chemical reaction of FeS and HCl, separately) with Ar at a flow rate of 50 sccm. The surface microstructure of all the films is studied with scanning electron microscope ZEISS

Advanced Materials and Radiation Physics (AMRP-2015)
AIP Conf. Proc. 1675, 030051-1–030051-4; doi: 10.1063/1.4929267

EVO series model EVO-50. Structural studies are carried out using Philips X-ray diffractometer equipped with Cu-Kα radiation (λ ~ 1.54Å) source keeping the glancing angle constant at 1º. The 2θ range used in the measurement was from 10 to 70 in steps of 0.05°.

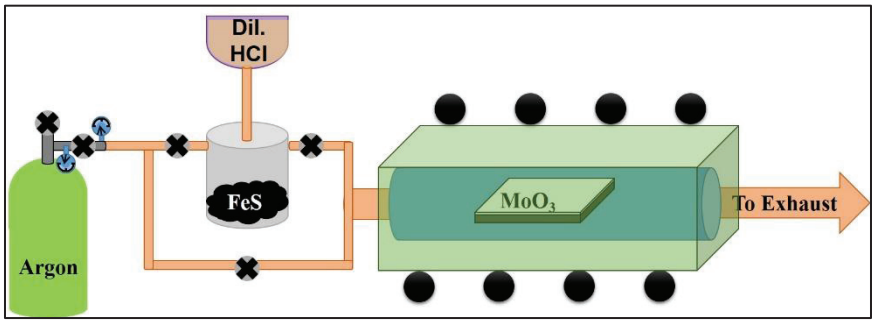


FIGURE 1: Schematic diagram of sulfurization experimental setup

Photoelectron spectroscopic studies is carried out by SPECS, with anode Mg/Al 25kV X-ray source and a hemispherical analyzer PHOIBOS HSA3500 150 R6 [HW Type 30:14] MCD-9. Measurements were done at 40 eV pass energy. Charging was corrected for by using the carbon peak at 284.6 eV as a reference.

RESULTS AND DISCUSSION

X-Ray Diffraction

X ray diffractogram of MoO_3 nanostructured thin film deposited in nickel/glass substrate at temperature of 500 ºC is shown in figure 2. The result shows single phase of orthorhombic structure. We got sharp peak along (020) and (021) crystallographic planes. The clear and sharp peak indicates that MoO_3 nanostructured thin film has high degree of crystallinity. The average value of lattice parameter obtained are a=3.962 Å, b=13.849 Å and c=3.691 Å, which are in good agreement with those reported earlier in JCPDS card no. 05-0508 (a=3.962 Å, b=13.858 Å, c=3.697 Å) for α- MoO_3 [4].

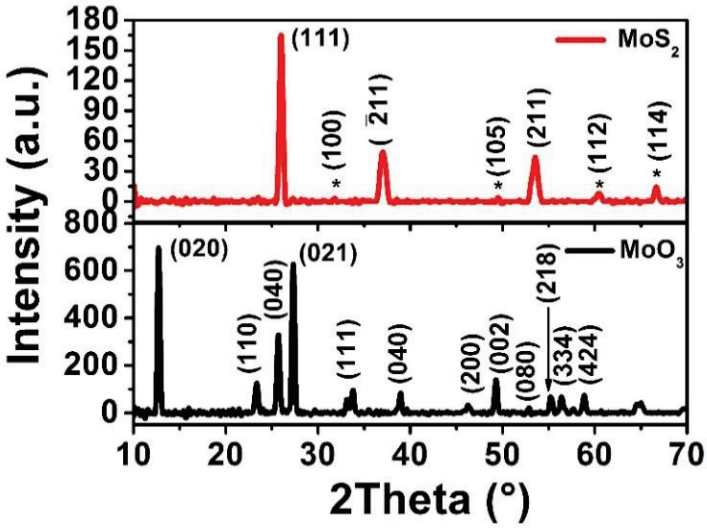


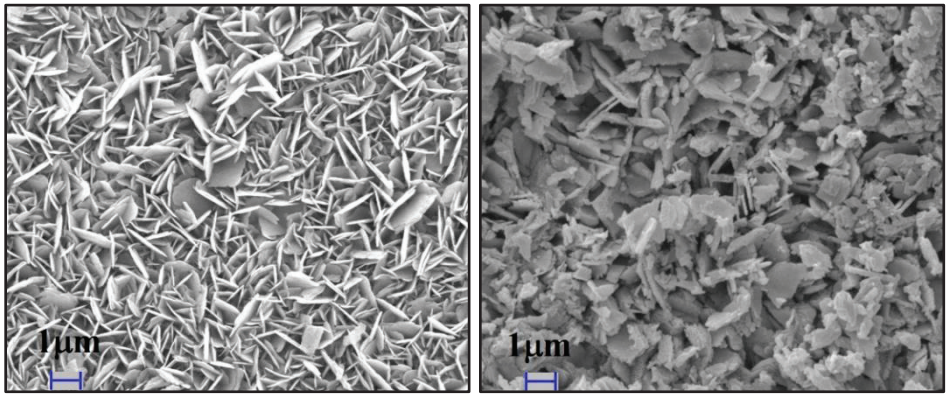
FIGURE 2: X-ray diffraction pattern of MoO_3 and MoS_2

Figure 2 shows x-ray diffraction pattern of sulfurized MoO_3 thin film. It can be seen clearly that all peaks corresponding to MoO_3 have disappeared and new peaks corresponding to monoclinic MoO_2 phase (JCPDS card no.65-5787) are obtained at position (2θ) of 26.00°, 37.05°, and 53.54°, along with hexagonal MoS_2 phase (*) peaks (JCPDS card no.37- 1492) at 31.92°, 49.63°, 60.45°, and 66.73°. This indicates that MoO_3 nanoflakes were initially

reduced due to presence of reducing environment of H_2S vapour to form suboxide MoO_2, which then reacted with species of sulfur to form MoS_2.

Scanning Electron Microscopy

Figures 3(a) and 3(b) show scanning electron micrograph of MoO_3 and MoS_2 nanostructures thin films respectively. As is seen in figure 3(a) vertically aligned MoO_3 nanoflakes with sharp edges are obtained. The orientation of nanoflakes with respect to substrate is random.



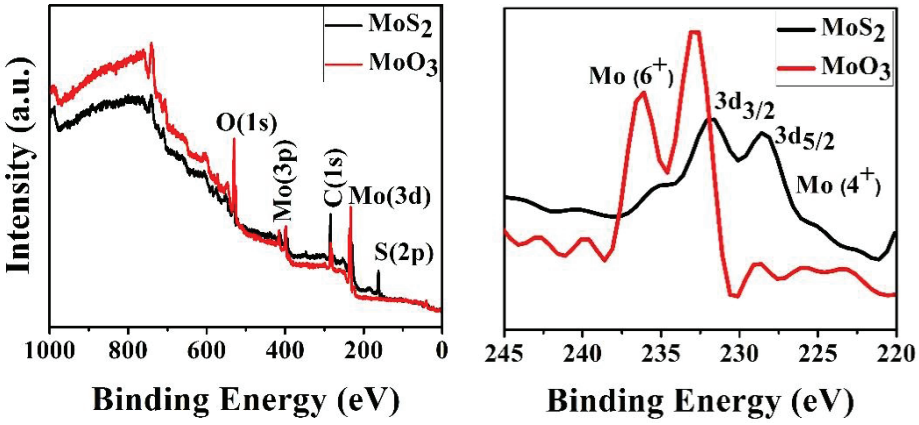
(a) (b)

FIGURE 3: SEM micrograph of (a) MoO_3 nanoflakes and (b) MoS_2 (after sulfurization of MoO_3)

As these nanoflakes undergo the process of sulfurization the sharp edges begins to soften and the thickness of nanoflakes increases may be due to some extent of mass transfer between the individual nanoflakes, leading to formation of thicker layer of MoS_2, which is confirmed by XPS and XRD data.

X-ray Photoelectron Spectroscopy

For further analysis of sulfurized MoO_3 nanostructured thin film XPS analysis of have been carried out to obtain the material quality and composition.



(a) (b)

FIGURE 4: (a) Survey scan of MoO_3 and MoS_2 displaying peaks of Mo (3d), Mo(2p), C(1s), O(1s) and S(2p); (b) Core level scan of MoO_3 and MoS_2 showing shift in Mo peaks due to change in oxidation state.

Figure 4(a) shows the XPS survey spectrum of MoO_3 NSTs which display only three intense peaks corresponding to molybdenum (3d), oxygen (1s) and carbon (1s), nearly matching to the reported value of core level binding energies, no any other element is detected, which show highly pure MoO_3 nanostructured thin film. The

core level scan shows single Mo (3d) doublet with Mo $3d_{5/2}$ binding energy 232.76 eV which is characteristic binding energy for Mo in a 6^{+} oxidation state. Figure 4(b) shows MoO_3 sulfurized thin film at 200 ºC. Peaks corresponding to molybdenum, oxygen, carbon as well as sulfur are observed. Mo Doublet peak broadened show presence of multiple oxidation state. We can also observe doublet with Mo $3d_{5/2}$ binding energy of 228.58 eV, which is expected value for Mo^{4+} centres in MoS_2. The corresponding S (2p) spectrum consist of a doublet with S $2p_{3/2}$ binding energy of 162.61 eV that indicates the presence of S^{2-} type ligands in MoS_2.

CONCLUSIONS

In conclusion, MoO_3 nanostructured thin films were deposited on Ni coated glass substrate. Nanoflakes obtained were highly uniform and vertically aligned. These samples were then subjected to sulfurization under the reducing atmosphere provided by H_2S gas in combination with argon at 200 ºC. The samples were then studied. Surface morphological study carried out by SEM shows noticeable differences in the external morphology after sulfurization of MoO_3 nanoflakes. In case of XRD all peaks associated with MoO_3 disappear, while all the peaks detected corresponding to MoO_2 and MoS_2 in sulfurized films. Further, more insight characterization of sulfurized film is performed using XPS, which shows a clear shift in the peak position of Mo doublet. Thus results obtained in XPS analysis endorse the XRD results.

REFERENCES

1. Bo Li, Shengxue Yang, Nengjie Huo, Yongtao Li, Juehan Yang, Renxiong Li, Chao Fan and Fangyuan Lu, RSC Adv., 4, 26407-26412 (2014).
2. Yumeng Shi, Jing-Kai Huang, Limin Jin, Yu-Te Hsu, Siu Fung Yu, Lain-Jong Li and Hui Ying Yang, Scientific Reports, 3:1839, 1-7(2013).
3. Th.Weber, J.C.Muijsers, J.H.M.C. van Wolput, C.P.J. Verhagen, and J.W. Niemantsverdriet, J.Phys. Chem. 100, 14144-14150 (1996).
4. Rabindar K. Sharma and G. B. Reddy, Journal of Applied Physics 114, 184310 (2013).
5. Rabindar K. Sharma and G. B. Reddy, J. Phys. D: Appl. Phys. 47, 065305 (2014).