Effect of plasma voltage on sulfurization of α-MoO3 nanostructured thin films

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Effect of Plasma Voltage on Sulfurization of α-MoO_3 Nanostructured Thin Films

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Abstract. In this report, the effect of plasma voltage on plasma assisted sulfurization (PAS) of vertically aligned molybdenum trioxide (α- MoO_3) nanoflakes (NFs) on glass substrates has been studied systematically. MoO_3 NFs were deposited using plasma assisted sublimation process. These nanoflakes were subjected to H_2S/Ar plasma at two different plasma voltages 600 and 1000 volts; to study the effect of plasma ionization on degree of sulfurization of MoO_3 into MoS_2. XRD and Raman analysis show that film sulfurized at 1000 volts have relatively higher degree of conversion into MoS_2, as more intense peaks of MoS_2 and MoO_2 are obtained than that sulfurized at 600 volts. HRTEM of sulfurized film shows that outer surface of nanoflake has been converted into MoS_2 (4-5 monolayers). Meanwhile, MoO_3 was reduced into MoO_2 as confirmed by XRD and Raman results. All the observed results are well in consonance with each other.

INTRODUCTION

Recently, researchers have been focusing on transition metal disulfides (TMDs) materials, aiming to overcome the shortage of graphene and widening its scope of applications. These layered structured materials have unique physical and chemical properties, making them highly interesting to study these materials theoretically as well as experimentally. MoS_2 is a layered material, where in single layer of MoS_2, Mo and S are arranged to a sandwich structure by covalent bonds. Due to distinctive electronic, optical and catalytic properties, MoS_2 have attracted great interest among other TMDs. These properties enable the use of MoS_2 in industrial applications such as catalysis, nanotribology, lithium batteries, optoelectronic devices, microelectronics, hydrogen storage, etc. [1] Many methods for MoS_2 thin film synthesis have been investigated such as micromechanical exfoliation, intercalation assisted exfoliation, hydrothermal synthesis and physical vapour deposition [2]. 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. Here, we present sulfurization of MoO_3 NFs using novel plasma assisted sulfurization (PAS) process. In this process, sulfurization is carried out by treating MoO_3 NTFs with H_2S/Ar plasma in a vacuum chamber. Since this is a newer technique, there are very few studies based on the effect of plasma voltage on sulfurization of MoO_3 nanostructured thin films using plasma assisted sulfurization process have been reported. Here, we report, sulfurization of MoO_3 NFs as a function of plasma voltage.

EXPERIMENTAL

Nanostructured MoO_3 thin films have been deposited on glass substrate using PASP route [3]. The experimental setup of PAS process have two cup-shaped Al–electrodes facing each other and are placed at an optimum distance of 7.5 cm. Plasma assisted sulfurization of MoO_3 NTFs is attained by treatment with H_2S/Ar plasma. The prepared MoO_3 NTFs sample (B1) are then placed in vacuum chamber over molybdenum metal strip. The chamber is evacuated till the pressure inside drops down to 8.5×10^{-6} Torr. Afterward, Mo-strip is gradually heated by passing controlled current, till it reaches 450 °C. The temperature is monitored by thermocouple arrangement as shown in schematic diagram (Fig. 1). Afterwards gas mixture of H_2S (10%) and Ar (90%) is introduced into chamber at a

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constant partial pressure of 6.5×10^{-1} Torr. The MoO_3 NFs are sulfurized in H_2S/Ar plasma at plasma voltages of 600 and 1000 volts are simply named as B2 and B3 respectively. The process continues for 60 minutes. Samples are allowed to cool in Ar ambient at pressure of 9.0 × 10^{-1} Torr. Structural studies are carried out using Rigaku Ultima IV model X-ray diffractometer equipped with Cu-Kα radiation (λ ~ 1.54Å) source keeping the glancing angle constant at 1º. The 2θ range used in measurement was from 10° to 70° with steps of 0.05°.

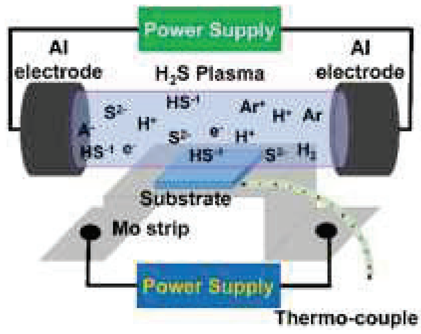

FIGURE 1: Schematic diagram of plasma assisted sulfurization process setup

Vibrational studies of sulfurized films were carried out by Raman spectroscopy (Horiba Lab RAM HR Evolution) equipped with Ar ion 514 nm laser at 20 mW power. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) studies were made using Tecnai F30, FE operated at 200 kV. All the measurements are performed at room temperature.

RESULTS AND DISCUSSION

X-Ray Diffraction

Figure 2 shows the X-ray diffractogram of MoO_3 film deposited on glass substrate at temperature of 500 ºC. We obtained sharp and intense peaks corresponding to (110), (120) and (021) crystallographic planes. The clear and sharp peak indicates that MoO_3 NTFs has high degree of crystallinity. The calculated average value of lattice parameter are a=3.952 Å, b=13.869 Å and c=3.692 Å, which are in good accordance with those reported earlier in JCPDS card no. 05-0508 (a=3.962 Å, b=13.858 Å, c=3.697 Å) for orthorhombic α- MoO_3 [4].

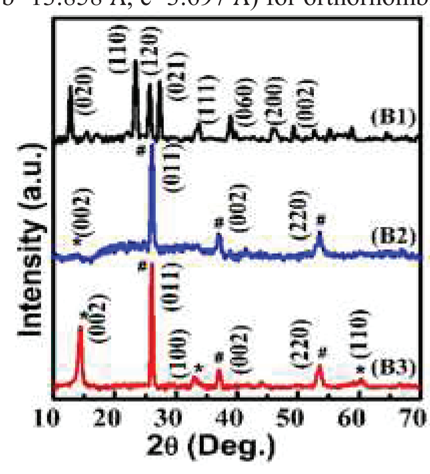

FIGURE 2: XRD diffractogram of MoO_3 NTFs (B1); and sulfurization of MoO_3 film at: 600 volts (B2), 1000 volts (B3).

Figure 2 (B2 and B3) shows X-ray diffraction pattern of sulfurized MoO_3 thin film at different plasma voltages. It can be clearly seen that all peaks of α-MoO_3 have disappeared and new peaks correspond to monoclinic phase of MoO_2 (JCPDS card no. 78-1073) are obtained at 2θ values of 26.00°, 37.05°, and 53.54°, along with hexagonal phase of MoS_2 (*) peaks (JCPDS card no.37- 1492) at 14.34°, 33.54°, and 60.45°. This indicates that MoO_3 nanoflakes were initially reduced in presence of reducing environment provided by H_2S reactive ionic species (mainly H^+) to form suboxide MoO_2, which then reacted with species of sulfur (S*, HS^{-1} and, S^{2-}) to form MoS_2. In sample B3 the peak intensity of (002) crystal plane corresponding to MoS_2 having relatively higher intensity as compared to sample sulfurized at lower plasma voltage (600 volts). It is due to the reason that at higher plasma voltage degree of ionization of H_2S gas is relatively higher, which in turn leads to higher sulfurization rate of MoO_3 nanostructures film.

Raman Spectroscopy

Raman spectra are recorded to investigate vibrational modes of MoO_3, MoO_2 and MoS_2 coordinated in distinct fashion for all samples (B1-B3) in the spectral range from 200 to 1020 cm^{-1}, can be seen in Fig. 3. The Raman spectrum of sample B1 reveal prominent peaks positioned at 242, 287, 339, 667, 818, and 997 cm^{-1}, attributed to different vibrational modes and are in good agreement with those reported for α-MoO_3 [4]. The strong peak at 818 $cm^{-1}$and 997 cm^{-1} are contributed by doubly coordinated oxygen (Mo-O_2), and the terminal oxygen (Mo-O_1), respectively. The Raman spectrum of sample B2 shows peaks corresponding to MoO_2 positioned at 223 and 740 cm^{-1} (marked by #) [5] with MoS_2 hexagonal phase (marked by *)peaks at 382 and 407 cm^{-1}[6].

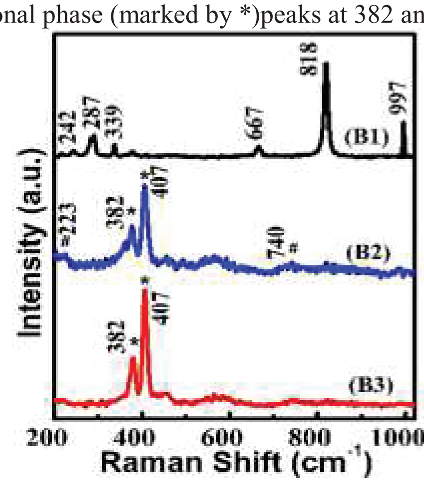

FIGURE 3: Raman spectrum of MoO_3 NTFs (B1); and sulfurization of MoO_3 film at: 600 volts (B2), 1000 volts (B3).

Whereas at higher plasma voltage, no peak other than MoS_2 is obtained. It confirms that surface of nanoflakes have been converted into MoS_2 and which is also supported in HRTEM results. The relatively intense and sharp Raman peaks in B3 further confirmed the increament in degree of crystallinity and also strongly support XRD outcomes.

HR-TEM analysis

For further analysis of sulfurized MoO_3 NFs, HRTEM analysis of sample B3 has been carried out to obtain more insight information of sulfurized MoO_3 nanoflake.

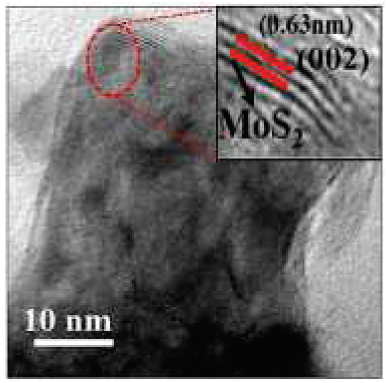

FIGURE 4: HRTEM image of MoO_3 film sulfurized at 1000 volts (inset: fringe pattern recorded from the encircled region of nanoflakes showing d-spacing between adjacent layers is ~ 0.63 nm).

The fringe pattern is recorded by HRTEM analysis form the encircled region marked on NFs point out that, the single crystalline nature of NFs as viewed in the inset of Fig. 4. Fringe pattern from outer surface of NFs shows the d-spacing between two adjacent layers is 0.63 nm, which is in good agreement with the d-spacing of MoS_2 (002) crystal plane as reported in literature [7]. Figure 4 inset shows 4-5 monolayers of MoS_2.

CONCLUSIONS

In conclusion, nanostructured thin films of MoO_3 were deposited prior to sulfurization, then subjected to sulfurization under the reducing atmosphere provided by H_2S/Ar plasma. The effect of plasma voltage on sulfurization of MoO_3 NTFs has been studied systematically. Results from XRD analysis show disappearance of MoO_3 peaks, while all the peaks corresponding to MoO_2 and MoS_2 in sulfurized films were detected. As plasma voltage is increased from 600 to 1000 volts, MoS_2 phase gets strengthened. Similarly, the Raman analysis confirms that after sulfurization, surface of MoO_3 film is completely converted into MoO_2 and MoS_2. Further, more insight characterization of sulfurized film is performed using HRTEM, which exhibits 4-5 monolayers of MoS_2 on outer surface of nanoflakes. Thus, results obtained in HRTEM analysis justify the XRD and Raman results. Therefore, it is concluded that plasma voltage affects the degree of sulfurization of MoO_3 to form MoS_2 with best results obtained at higher plasma voltage of 1000 volts.

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