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Growth of MoO_3 Nanostructured Thin films as a function of O_2-partial pressure

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Abstract. In this report, we synthesized molybdenum trioxide (α-MoO_3) nanostructured thin films (NST_s) with nanoflakes (NF_s) on the Ni-coated glass substrates employing plasma assisted sublimation process (PASP) as a function of oxygen partial pressure (PO_2). The effect of oxygen partial pressure on structural, morphological, and vibrational properties have been investigated systematically. The structural analysis divulged that all films deposited at different PO_2 have pure orthorhombic phase, no impurity phase is detected under the limit of resolution. The morphological studies of samples is carried out by SEM, revealed that features as well as alignment of MoO_3 NST_s can be monitored by PO_2 and the sample having best features is obtained at 7.5×10^{-2} Torr. In addition, the more insight information is accomplished by TEM/HRTEM on the best featured sample, which confirmed the single crystalline nature of nanoflakes. The vibrational study of all samples are performed by FTIR, and strongly supports the XRD observations. All the results are in consonance with each other.

Keywords: Molybdenum oxide, Oxygen partial pressure, Plasma assisted sublimation process
PACS: 68.55.-a, 81.07.-b, 78.67.-n

INTRODUCTION

Being a smart functional material, molybdenum trioxide (MoO_3) is one of the well-known n-type semiconductors and attractive due to its various potential applications in many fields, such as photochromic and electrochromic devices, gas sensors, and catalysts. For these applications, large aspect and surface-to-volume ratio are found to be very crucial factors that greatly influence the efficient parameters, particularly when the size of the material approaches toward nano dimensions. The larger surface to volume ratio at nano level ensure a high percentage of surface atoms and the great level of crystallinity, which reduce possible instabilities and make MoO_3 favorable from chemical applications prospectives. Till date, different techniques including physical vapor deposition (PVD) and chemical vapor deposition (CVD) with or without post treatments have been developed to explore novel architectures and morphological patterns of MoO_3. M. B. Rehmani et al. [1] have been reported the formation of lamellar structure of MoO_3 onto gold inter digital fingers on quartz substrates using thermal evaporation. S. Hu et al. [2] have been prepared single walled nano tubes (SWNT) by thiol-assisted hydrothermal method. Recently K. Krishnamoorthy et al. [3] have yielded MoO_3 2D nanoplates by a simple wet chemical approach. They investigated the antibacterial efficiency of MoO_3 nanoplates against pathogenic bacteria and they identify MoO_3 as a new functional material in the biomedical applications. In this report, we have prepared MoO_3 NST_s via. PASP on Ni/glass substrate as a function of oxygen partial pressure. The structural, morphological, and vibrational studies of these samples are discussed in this paper briefly.

EXPERIMENTAL SETUP

The basic experimental setup of PASP consists of two cup-shaped Al–electrodes confronting each other and kept at an optimum distance of 7.5 cm. First, nearly 100 nm 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. After that Ni-coated glass substrates are placed on Mo-strip, maintained at 500°C. The strip temperature is suitably control by adjusting the current flowing across it. At the time of deposition Ni-coated face of substrate is placed above and expose directly in O_2-plasma, whereas the other face will be in contact of heated Mo-strip. In order to synthesize MoO_3 NST_s at distinct value of PO_2, first the chamber is evacuated to 7.5×10^{-6} Torr after that, high purity oxygen gas is inserted into the chamber and maintain the value of oxygen partial pressure at three distinct levels of 6.5×10^{-2}, 7.5×10^{-2}, and 8.5×10^{-2} Torr with the help of gas flow controller. The samples

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deposited corresponding to these values of oxygen partial pressure are named as P_1, P_2, and P_3 respectively. Thermocouple arrangement is adjusted inside vacuum chamber to record the substrate/growth temperature during the growth of MoO_3 films. It is observed that thermal gradient between base and the upper surface of substrate (where the deposition is taking place) is found nearly of 50°C. The surface microstructure of all the deposited samples is studied with scanning electron microscope ZEISS EVO series scanning electron microscope model EVO-50. Structural studies are carried out using Philips X-ray diffractometer equipped with Cu-K_α radiation (λ~1.54 Å) source keeping the glancing angle constant at 1°. Infrared (IR) measurements are performed to study the different vibrational modes of Mo and O atoms in all samples by employing Perkin Elmer make (Model BX2) spectrophotometer. Transmission Electron Microscopy (TEM) study of MoO_3 NST_s is carried out with Philips Model CM12 operated at 120 kV with HRTEM analysis. All the measurements are performed at room temperature.

RESULTS AND DISCUSSION

In order to investigate the crystal structure and purity of the MoO_3 NST_s, X-ray diffraction pattern have been recorded, can be seen in Fig. 1(P_1-P_3). The sharp diffraction peaks in the diffractograms of sample P_1 to P_3 are endorsed the polycrystalline nature of films and assured the fabrication of nanostructures on films as well. The observed XRD results divulge the single orthorhombic nature of all the MoO_3 NST_s deposited at different value of PO_2 and no impurity phase is detected under the resolution limit of XRD. The obtained average values of lattice parameters from XRD analysis are a = 3.85 Å, b = 13.849Å and c = 3.691 Å, which are in good agreement with the reported values as given in JCPDS (Ref. Code: 00-005-508) a = 3.962 Å, b = 13.858Å and c = 3.697 Å for α-MoO_3. It can be noted that X-ray pattern of sample P_2 among all, shows the highly preferred orientational growth along [110] crystallographic direction.

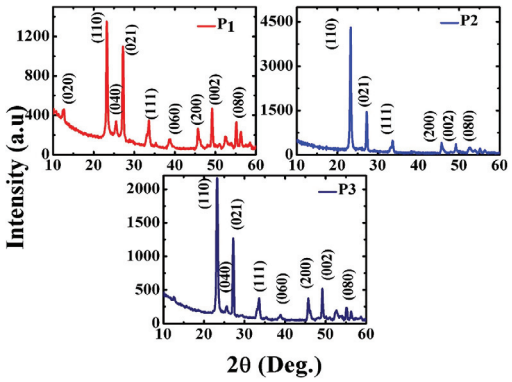

Figure 1. XRD of MoO_3 NST_s deposited at different value of PO_2: 6.5×10^{-2} (P_1), 7.5×10^{-2} (P_2), and 8.5×10^{-2} (P_3) Torr.

The average crystallite size of samples P_1, P_2, and P_3 is calculated corresponding to the diffraction peak having maximum intensity using the Debye-Scherrer formula can be seen in Table 1. According to our observations the larger crystallite size is obtained in case of P_2 which indicate its relatively better crystallinity.

Figure 2 depicts the surface microstructure of MoO_3 NST_s corresponding to samples P_1, P_2, and P_3. The obtained results indicate that in sample P_1 nanoflakes (NF_s) are formed having small dimensions with incomplete features owing to the lack of oxygen ionic species at smaller value of PO_2, which leads to formation of lesser amount of MoO_3 on Mo-strip during oxidation in O_2-plasma. On increasing oxygen partial pressure upto 7.5×10^{-2} (P_2) completely developed NF_s is formed with vertical alignment. The well-established feature in case of P_2 (at 7.5×10^{-2}) mainly because of better rate of oxidation as well as volatilization of MoO_3 from Mo-strip during deposition. Further increase in PO_2 upto 8.5×10^{-2} (P_3) furnishes more and more oxide content on substrate due to the enhancement of oxidation (volatilization) rate of Mo (MoO_3) [4-5]. The continuous and relatively more than enough supply of MoO_3 on growth in P_3 considerably affect the features as well as alignment of grown MoO_3 NF_s as can be seen in Fig. 2 (P_3). Therefore, it can be concluded that proper equilibrium should be upheld between oxidation of Mo metal strip as well as volatilization of their oxide to obtain better features and alignment of NST_s.

TABLE 1. Shows the dimensional analysis of samples P_1, P_2, and P_3

Oxygen partial pressure (PO_2) in Torr	Average length (nm)	Average Thickness (nm)	Crystalline Size
6.5×10^{-2}	200	50	18.2
7.5×10^{-2}	1000	40	42.8
8.5×10^{-2}	800	40	32.6

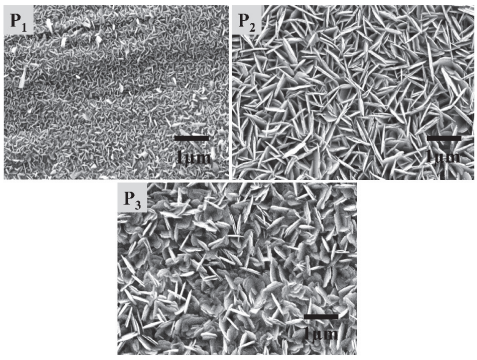

Figure 2. SEM images MoO_3 nanostructured thin films: deposited at different value of PO_2: 6.5×10^{-2} (P_1), 7.5×10^{-2} (P_2), and 8.5×10^{-2} (P_3) Torr.

The observed SEM result are verify the XRD outcomes. In further analysis, we selected the best sample (which is P_2 in this case) in order to obtain more insight information of grown nanostructure through TEM in bright field mode accompanied with HRTEM, can be seen in Fig. 3. Here TEM image is primarily focused on a single flake, which is nearly matched with SEM observations from dimensional prospectives. In addition, the fringe pattern is recoreded by HRTEM analysis form the encircled region marked on NF_s that corroborated the single crystalline nature of NF_s can be viewed in the inset of Fig. 3.

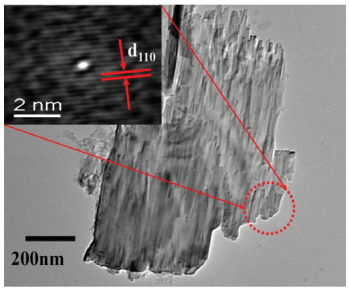

Figure 3. Bright field TEM image of sample P_2 along with the fringe pattern recorded using HRTEM in the inset

FTIR spectra are recorded in order to investigate the modes of chemical bonding between molybdenum and oxygen atoms of all samples (P_1-P_3) in the spectral regime from 400 cm^{-1} to 1800 cm^{-1} depicted in Fig. 4.

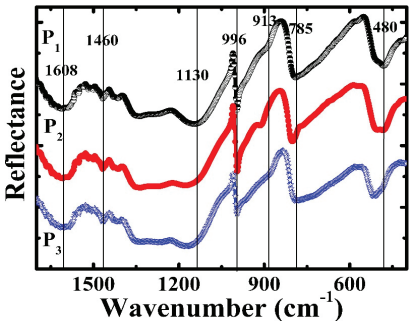

FIGURE 4. FTIR spectra of MoO_3 NST_s: (P_1) 6.5×10^{-2}, (P_2) 7.5×10^{-2}, and (P_3) 8.5×10^{-2} (P_3) Torr.

The recorded FTIR reflectance spectra of samples endorsed several prominent absorption peaks positioned at 1608, 1460 1130, 996, 785, 480 cm^{-1}, attributed to different vibrational modes. The strong absorption peak at 997 cm^{-1} indicates the presence of Mo=O stretch mode of vibration, which represents the the basic characteristic of layered structure in α-MoO_3. The comparatively weak IR-peak corresponding to 913 cm^{-1} represents the asymmetric vibration of Mo-O bond relative to oxygen in same Mo_2-O entity. Whereas, the peak positioned at 778 cm^{-1} is due to the stretching mode of triply coordinated bridge-oxygen, caused by edge-shared oxygen atoms in common to three octahedrons. Peak present at 480 cm^{-1} is due to the bending mode of O-Mo-O, shifted towards lower wavenumber, may be owing to the dominance of Vander wall interaction among NF_s situating very close among each other. The relatively intense and sharp IR peaks in P_2 further assured the betterment in crystallinity and support XRD results as well. Three additional intense peaks located at 1608, 1130, and 1460 cm^{-1} are corresponding to the bending mode of Mo-OH bond in all samples owing to the hydroxylation of film when taking these out of the vacuum chamber.

CONCLUSIONS

In summary, molybdenum oxide NST_s having vertically aligned nanoflakes with very high exposer/surface area are synthesized on Ni coated glass substrates using plasma assisted sublimation process (PASP). The obtained structural and morphology outcomes endorsed that the growth of single crystalline MoO_3 nanoflakes of better coverage density as well as alignment on large area scale took place only when oxygen partial pressure (PO_2) is upheld at 7.5×10^{-2} Torr. Both the features and alignment of grown nanostructure are found to be strongly dependent on the value of oxygen partial pressure. In addition, the TEM/HRTEM results divulged that MoO_3 nanoflakes (in sample P_2) are single crystalline in nature and well matched with the

SEM observations from dimensional point of view. These grown novel architectures by PASP might be better candidate in variety of applications such as energy storage devices (Li^+-ion batteries), display devices, and gas sensor devices etc.

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