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Rabindar K. Sharma and G. B. Reddy

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Growth of Vertically Aligned α-MoO_3 Nanoflakes by Using a Facile PVD Route

Rabindar K. Sharma* and G. B. Reddy

Thin Film Laboratory, Physics Department, Indian Institute of Technology Delhi, New Delhi-110016, India
**E-mail: rkrksharma6@gmail.com*

Abstract. In this report, we synthesize vertically aligned molybdenum trioxide (α-MoO_3) nanoflakes (NFs) with high aspect ratio (height/thickness >15) on the cobalt coated glass substrates by the plasma assisted sublimation process, employing Mo metal strip as a sublimation source. The effect of substrate temperature, nature of substrate as well as the geometry of the sublimation source (Mo-strip) have been investigated on the morphological, structural and optical properties of the grown NFs, keeping plasma parameters as fixed. The surface morphology, crystalline structure and optical properties of MoO_3 NFs have been studied systematically by using scanning electron microscope (SEM), transmission electron microscope (TEM) with selected area electron diffraction (SAED), X-ray diffractometer, and IR- spectroscopy. The experimental observations endorse that the characteristics of MoO_3 NFs are strongly depend on substrate temperature, substrate nature as well as geometry of Mo-strip. All the observed results are well in consonance with each other.

Keywords: Molybdenum oxide (MoO_3), Plasma assisted sublimation process, Nanoflakes (NFs), Substrate temperature.
PACS: 81.07.-b, 78.67.-n

INTRODUCTION

In recent years, molybdenum oxide (MoO_3) has received considerable attention of the researchers across the world because of its diverse applications as in smart windows[1], ion storage layer in high energy density secondary lithium ion batteries[2], gas sensors[3], and field emission source[4]. The new class of nanostructures possess novel characteristics due to the large surface to volume ratio that ensure a high percentage of surface atoms and the great level of crystallinity which reduce possible instabilities. Molybdenum oxide thin films with variety of nanostructures have been reported. Li et al.[5] have formed nanoflowers of MoO_3 by chemical route. Ban et al.[6] have synthesized large area films of MoO_3 micro belts on silicon substrate by thermal evaporation. Yang et al.[7] have reported Tremllela-like structures of MoO_3. Khedemi et al.[8] have prepared molybdenum oxide film with nanostars and studied their field emission property. In the present paper the authors have reported the growth of NFs with very large (1:15) thickness versus height ratio. Experimental results of successfully grown of MoO_3 nanoflakes by oxygen plasma assisted sublimation route are reported and discussed systematically in the present paper.

EXPERIMENTAL DETAILS

The setup consists of two cup-shaped Al -electrodes facing each other at a distance of 7.5 cm. First, nearly 100 nm thick Co-film is deposited on a glass substrate by thermal evaporation of 99.99 % pure Co powder keeping the base vacuum of 7.5×10^{-6} torr. After that the cobalt coated glass substrate is mounted on Mo strip (glass side touching the strip) and its temperature raised gradually up to desired value (250, 350 or 450°C) by suitably control the current, passing through the Mo-strip and studied its effect on the growth of nanostructures. Beside that the effect of substrate nature and the source geometry are also investigated.

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The temperature of sublimation source and substrates are monitored by thermocouple arrangement independently. First, the chamber is evacuated to 7.5×10^{-6} torr and then high purity oxygen is inserted into the chamber to maintain the base vacuum level at 2×10^{-3} torr. In this experiment the Mo strip surface temperature is higher nearly 50°C, when substrate is maintained at 450°C. The entire heating cum sublimation source is placed inside the oxygen plasma. The surface microstructure of deposited nanostructured thin films 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-Kα radiation (λ~1.540Å) source keeping the glancing angle constant at 1°. Infrared measurements are carried out with Perkin Elmer make (Model BX2) spectrophotometer. Transmission Electron Microscopy (TEM) study of MoO_3 NFs is carried out with Philips Model CM12 operated at 120 KV with selected area electron diffraction analysis.

RESULTS AND DISCUSSION

The surface morphology of films deposited keeping the substrate temperature at 250, 350 and 450°C are shown in figure 1(a), 1(b) and 1(c) respectively. These micrographs reveal the formation of well aligned MoO_3 NFs when the substrate temperature is ≥ 350°C. The onset of particle formation can be seen at temperature 250°C (see in figure 1a). As the temperature increases from 250 to 450°C particles convert in NFs with uniform distribution on large area substrate. The SEM micrographs show the average length and thickness of vertically aligned nanoflakes vary from 200 to 800 nm and from 25 to 100 nm respectively with temperature.

TableI. The dimensional detail of MoO_3 NFs grown at different substrate temperature.

Substrate temperature (°C)	Average length (nm)	Average thickness (nm)
250	200	100
350	500	50
450	800	25

It is appeared that MoO_3 NFs with the maximum aspect ratio are obtained when the substrate temperature is kept at 450°C (figure 1c), which confirms from the cross-sectional view of same film is shown in figure 1(d). The microstructure of the films, deposited on cobalt coated ITO glass and Si substrates by using circular shape sublimation source at strip temperature 450°C, are shown in figures 1(e) and 1(f) respectively. These experiment results suggest that theshape and size of grown nanostructures not only depend on the nature of substrate but also on sublimation source geometry. It is noticed that in case of ITO substrate few numbers of flakes get start to fused together resulting to the formation of multipods like morphology and also enhanced the sharpness of flake edges for circular geometry. This is due to the curvature effect of circular source shown in figure 1e. For the cobalt coated Si substrate vertically aligned nanoplates are formed owing to its crystalline nature may help to grow nanoplates like morphology (see in fig. 1f). It is supposed that the sublimated MoO_3 transporting onto the substrates in larger amounts from circular source geometry compared to that in case of flat source geometry and that would also assist to increase number of flakes/plates per unit area.

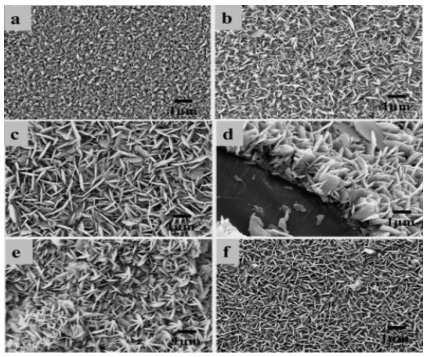

FIGURE 1. SEM micrographs of MoO_3 nanostructured thin films deposited at substrate temperatures (a) 250°C (b) 350°C (c) 450°C (d) Cross–section view with 45° tilt angle. (e) Film deposited using circular shape sublimation source on ITO coated glass at 450°C (f). Film on cobalt coated Si substrate at 450°C.

Further characterization of MoO_3 NFs grown at 450°C was performed by transmission electron microscopy (TEM) with the corresponding selected area electron diffraction (SAED) pattern is divulged in figure 2.

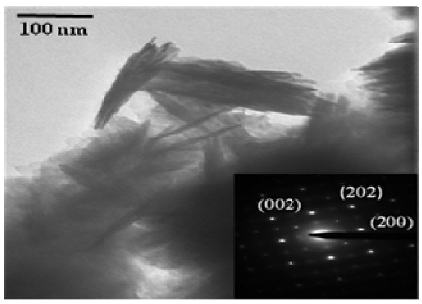

FIGURE 2. Bright field TEM micrograph of film deposited at 450°C with SAED pattern

The SAED pattern in the inset image, clearly exhibited diffraction spots with d spacing that could be indexed according to the orthorhombic crystal structure recorded from individual flake.

The observed pattern confirms single crystalline nature of MoO_3 nanoflakes.

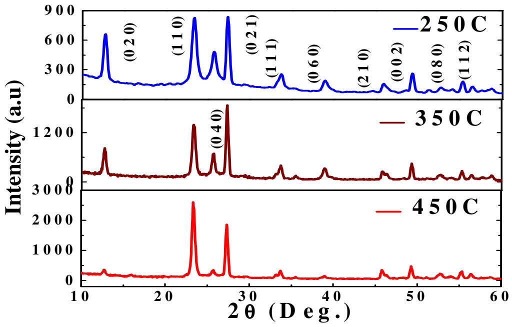

FIGURE 3. XRD pattern of MoO_3 nanoflakes deposited at 250°C, 350°C, and 450°C.

X-ray diffractrograms of MoO_3 thin films deposited at different substrate temperatures are shown in figure 3. These results reveal the single phase of orthorhombic structure. The sharp changes in crystallographic orientation along (110) and (020) are occurred in MoO_3 thin films. The clear and sharp peaks indicate that MoO_3 NFs are having high degree of crystallinity and it increases with increasing substrate temperature. The SAED pattern of single NFs, shown in the inset of figure 2, also confirms the XRD findings. The obtained average value for lattice parameters are a= 3.962 Å, b= 13.849 Å, c= 3.691 Å which is in good agreement with those given in the JCPDC (a= 3.962 Å, b= 13.858 Å, c=3.697 Å) for α- MoO_3.

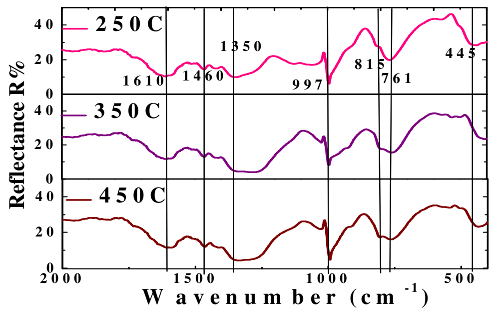

FIGURE 4. FTIR spectra of MoO_3 NFs prepared at 250°C, 350°C, and 450°C.

FTIR spectra are recorded to investigate the chemical bonding states between molybdenum and oxygen atoms of all samples in the spectral range from 400 cm^{-1} to 2000 cm^{-1} shown in figure 4. Measured IR reflectance spectra of NFs show several significant absorption peaks positioned at 1610, 1460 1350, 997, 815, 761, 445 cm^{-1}, which have attributed to different modes of vibrations. The strong absorption peak at 997 cm^{-1} indicates the presence of Mo=O stretch mode of vibration, confirms the basic characteristic of layered structure of MoO_3. The peak at 815 cm^{-1} is attributed to the doubly connected bridge-oxygen Mo-O-Mo stretching mode. The peak at 761 cm^{-1} is due to the stretching mode of triply coordinated bridge-oxygen. But IR peak presence at 450cm^{-1} is caused by edge-shared oxygen atoms in common to three octahedrons. The additional peaks at 1610, 1460, and 1350 cm^{-1} reveal the presence of adsorbed water [9]. IR analysis also assured the formation of pure α-MoO_3.

CONCLUSIONS

In summary, uniformly distributed and vertically aligned molybdenum oxide nanoflakes with large aspect ratio (1:15) are synthesized on cobalt coated glass substrates by plasma assisted sublimation process. The observed experimental result affirms the growth of single crystalline MoO_3 nanoflakes with the uniform distribution on large area scale is occurred when substrate temperature is maintained at 450°C. The features of grown nanostructure are found to be strongly dependent on the substrate temperature, nature of substrates as well as the geometry of sublimation source. All the obtained results are well and in consonance to each other. The morphology obtained by SEM measurements indicates that the NFs have large surface area and distributed uniformly on entire substrate with high aspect ratio may be better candidate for applications such as secondary batteries, display devices and gas sensor devices.

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