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Plasma Assisted Growth of MoO₃ Films on Different Substrate Locations Relative to Sublimation Source

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Abstract. In the present paper, we reported the role of substrate locations relative to source on the growth of MoO₃ films deposited on Ni coated glass substrates using plasma assisted sublimation process (PASP). According to the XRD and SEM results, substrate location is very crucial factor to control the morphology of MoO₃ films and the best nanostructure growth (in terms of alignments and features) is obtained in case of Sample B (in which substrate is placed on source). The structural results point out that all films exhibit only orthorhombic phase of molybdenum oxide (i.e. α -MoO₃) but the most preferential growth is recorded in Sample B due to the presence of intense peaks corresponding to only (0 k 0) family of crystal planes ($k = 2, 4, 6, \dots$). The Raman analysis again confirms the orthorhombic nature of MoO₃ NFs and details of vibrational bonds in Sample B have been given in the present report. The MoO₃ NFs show intense PL emission in wavelength range of 300-700 nm with three peaks located at 415, 490, and 523 nm in accordance to the improved crystallinity in Sample B.

INTRODUCTION

In recent years, solid state nanostructures with reduced dimensionality such as, nanowires, nanotubes, nanorods, nanobelts, nanoplates, nanoflakes, and nano/microspheres have considerable interest for scientific research owing to their importance in microscopic physics studies and their potential applications in electronics, photonics, mobile miniaturized devices, portable rechargeable batteries data recording media, and gas sensing[1]. As a layered metal oxide, orthorhombic molybdenum trioxide (α -MoO₃) is one of the most versatile transition metal oxides, because of its potential applications in different emerging research areas like in solar cells, gas sensing, catalysis, thermo and electro-chromic devices, and Li⁺-ion batteries[2]. Depending on deposition techniques, MoO₃ can be synthesized in different nano-micro structural morphologies (i.e. 1D, 2D, and 3D nanostructures) as mentioned above. So far, different number of techniques have been reported to synthesize MoO₃ nanostructures including RF-sputtering, thermal evaporation, sol-gel, hydrothermal, spray pyrolysis, chemical vapor deposition, and electro-deposition[2-3]. In the present paper, we reported that how the substrate locations relative to sublimation source (Mo-strip) effect the growth of MoO₃ nanostructures using PASP. Substrates are located at three different locations and each sample is characterized systematically.

EXPERIMENTAL

Plasma assisted sublimation process[4] (PASP) is employed for the growth of different types of MoO₃ nanostructures by subliming the source material in the form of Mo-metal strip in oxygen plasma and subsequently depositing the vapor onto substrates placed on different locations. In the present work, Ni coated glass slides are used as substrate in all experiments. Nickel films (~ 100 nm) is deposited on glass substrates by thermal evaporation of Ni powder (99.9% pure) at the base pressure of the order of 10⁻⁶ Torr. After that substrates are used to deposit MoO₃ films over them. During deposition all plasma parameters like plasma voltage, electrode separation, and

oxygen partial pressure are kept constant at 2500 Volts, 7.5 cm and 7.5×10^{-2} Torr, respectively. In order to study the effect of substrate locations on film growth, three different substrate locations have been chosen, as shown in Fig 1. The locations of substrates are determined in terms of angle, on first location substrate is placed at 90° by keeping its separation of $\frac{1}{2}$ cm from source (**Sample A**) and in second case, substrate is located at 0° . Furthermore, at 0° , two locations are possible, either substrate is placed on source (**Sample B**) or substrate is placed parallelly to source at $\frac{1}{2}$ cm (**Sample C**). The surface morphologies of samples are recorded with scanning electron microscope ZEISS-EVO series scanning electron microscope model EVO-50. Structural analysis of samples are performed using Philips X-ray diffractometer using Cu-K α radiation ($\lambda \sim 1.54 \text{ \AA}$) with glancing angle 1° . The vibrational study was carried out by micro-Raman spectroscopy of Renishaw-in Via (excited with Ar $^+$ line at 514.5 nm). The PL spectrum was recorded using Xe-lamp (excitation wavelength 250 nm).

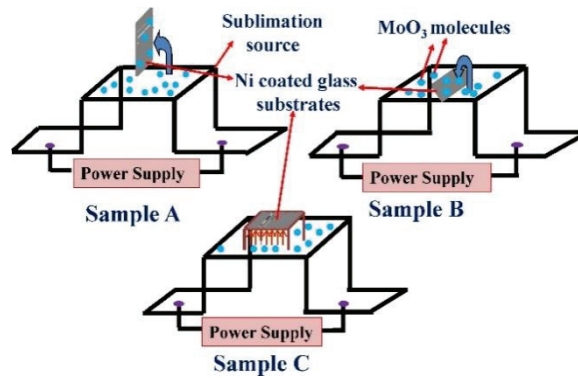


FIGURE 1. Schematic diagram of substrate locations relative to sublimation source (i.e. Mo-strip)

RESULTS AND DISCUSSION

XRD Analysis

To study structural properties of molybdenum oxide films deposited on different substrate locations, the X-ray diffractograms of films are recorded, as shown in Fig. 2. The XRD results show the presence of only orthorhombic phase of molybdenum oxide (i.e. α -MoO $_3$) on all samples, according to the standard peaks indexing as mentioned in JCPDS card no. (Ref. Code: 00-005-508).

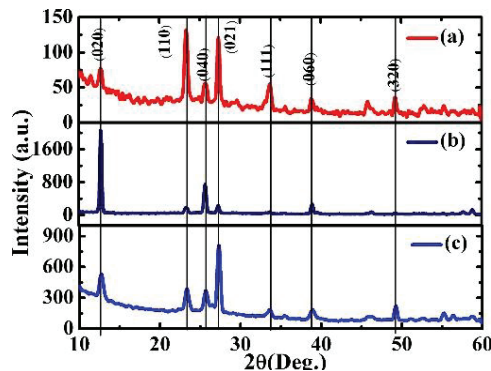


FIGURE 2. X-ray diffractograms of: (a) Sample A (b) Sample B (c) Sample C

The recorded intensity pattern of XRD peaks indicates that all films have nanostructures, but one of the best growth in terms of features and alignments would be found in Sample B. It can be noted that in Sample B the most intense peaks are belong to (0 k 0) family of crystal planes, which strongly evidenced that the most aligned growth of nanostructures will exist in Sample B. Further, on the basis of peak intensities and their sharpness it can also be stated that the best crystallinity is present in Sample B.

Surface Morphological Results

Figure 3 represents the surface morphological changes in MoO₃ films deposited on Ni coated glass substrates at different locations. The results show the remarkable surface changes in MoO₃ films deposited at different locations. In Sample A (substrate is kept at 90° and ½ cm above to sublimation source) a porous film is deposited with undefined (dimensionally) nanostructures. The surface morphology in Sample A seems like as bunched nanoplates (NPs). The accumulation/bunching of nanoplates is not only because of low substrate temperature but also due to the direction of oxide molecules impingement on substrate. Due to low substrate temperature the proper re-crystallization and the nucleation process in film do not take place. Since, due to the molecular gravity most of the oxide molecules approach and accumulate at the lowest edge of substrate. In contrast, on Sample B the uniform growth of vertically aligned MoO₃ nanoflakes (NFs) with excellent coverage on entire substrate is recorded. The role and the function of nickel buffer layer on glass substrate has been reported our earlier work [4]. The presence of Ni buffer layer on glass not only improves the alignments of nanostructure but also facilitates to grow nanostructure with better features. The estimated average width and thickness of NFs are recorded to be nearly 1 μm and 100nm, respectively. In Sample B, the substrate is placed onto source so the source and substrate will be on the same temperature (~ 500°C). Because of high temperature the impinging MoO₃ molecules are easily achieve proper nucleation sites on buffer layer, as a results the vertically aligned growth of 2D nanostructure (i.e. nanoflakes) is formed. In Sample C, nearly similar surface morphology to that recorded in Sample A is observed with relatively more areal coverage. In this case the substrate is placed parallel to the source. So, most of the emerging vapor from source directly strike on substrate and condensed there. This is the main cause of more areal density in Sample C.

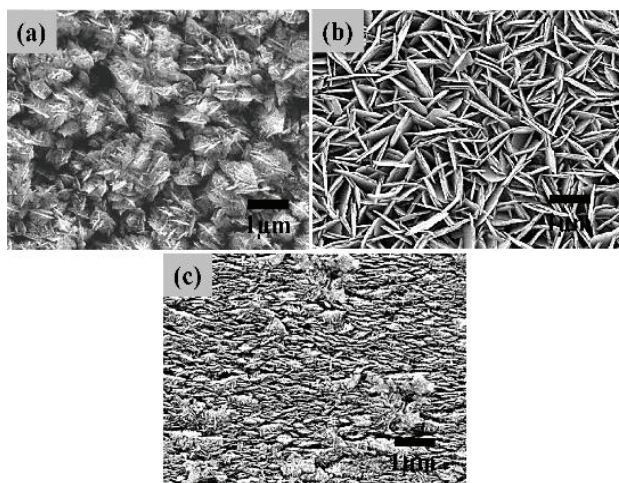


FIGURE 3. SEM micrographs of MoO₃ films at different substrate locations: (a) Sample A (b) Sample B (c) Sample C

Raman Analysis

From the above experimental results, it is concluded that Sample B has the best nanostructure growth in terms of features as well as alignments. So, in the further sections only Sample B is characterized and discussed. To study the vibrational properties, the Raman spectrum of NFs grown in Sample B is recorded and shown in Fig. 4.

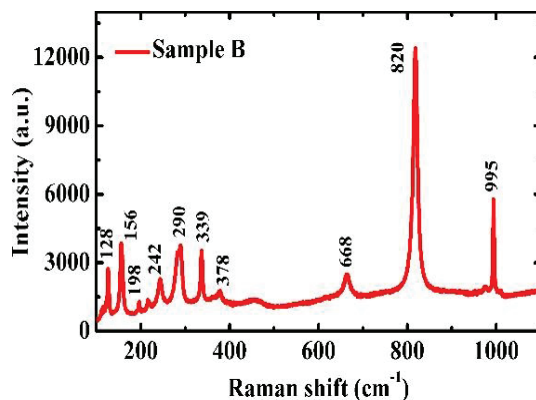


FIGURE 4. Raman spectrum of MoO₃ film deposited on Sample B

All the recorded peaks in Raman spectrum confirm the presence of only orthorhombic phase of molybdenum oxide (α -MoO₃). All the recorded peaks are well in agreement to those reported in literature by Pyet *et al.* [5]. The intense Raman peak positioned at 995 cm⁻¹ is correspond to the vibrational bond of Mo=O and confirms the presence of the characteristic layered structure in orthorhombic MoO₃. The intense Raman peak at 820 cm⁻¹ is attributed to stretching mode of doubly connected oxygen in Mo–O–Mo unit, which formed as a results of corner-shared oxygen between two octahedra. The peak at 668 cm⁻¹ is assigned to the triply coordinated oxygen (Mo₃–O) stretching mode, which formed from the edge-shared oxygen common in three octahedra [6]. Most of the low intense Raman peaks positioned in the range 100-400 cm⁻¹ are because of Mo–O₂ scissoring and O=Mo=O wagging modes[5].

Photoluminescence Study

Figure 5 shows the room temperature photoluminescence (PL) spectrum of MoO₃ film deposited on Sample B in the wavelength range from 300 to 700 nm with the excitation energy (4.97 eV) more than the band gap of MoO₃ (~ 2.9 eV)[1].The broad PL emission, as recorded in Fig. 4is the signature of the size distribution of NFs with improved crystallinityand alsoagreed withSEM results.

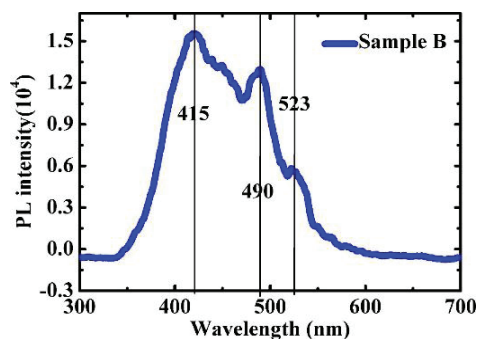


FIGURE 5. Photoluminescence spectrum of MoO₃ film deposited on Sample B

There are three PL peaks positioned at 415, 490, and 523 nm can be seen in PL spectrum. The PL peak positioned at 415 nm confirms the transition close to the near band edge emission, which is assigned to the free excitons recombination according to reported results[7]. The other two PL peaks are correspond to the transitions among defect levels, those formed in between the band gap of MoO₃. It is reported that oxygen vacancies are the most dominant defects in MoO₃ films deposited using PVD routes[8]. The PL emission peaks observed at 490 and 523 nm are attributed to the deep level Mo⁵⁺ (3d) transitions among defect states[9]. The intense PL emission of MoO₃ NFs, indicates that the MoO₃ NFs might be a potential photonic candidate for technical applications.

CONCLUSIONS

In this communication, we have reported the effect of substrate locations on the growth of MoO₃ films on Ni coated glass substrate using PASP. The results reveal that substrate locations relative to sublimation source is very important parameter for the controlled growth of MoO₃ nanostructures with excellent coverage. The XRD results endorse the presence of only orthorhombic phase of molybdenum oxide (i.e. α -MoO₃) in all samples and the most preferential growth is recorded in Sample B. The Raman analysis of Sample B further indicates the presence of α -MoO₃ on it and also justify the XRD results. The MoO₃ NFs grown in Sample B show the intense and broad PL emission at room temperature, which is the signature of size distribution of NFs and the presence of oxygen defects on their surfaces.

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REFERENCES

1. Xiaohui Chen, Weiwei Lei, Dan Liu, Jain Hao, Qiliang Cui, and Guangtian Zou, *J. Phys. Chem.* **113**, 21582 (2009).
2. Rabindar K. Sharma and G. B. Reddy *J. Phys. D: Appl. Phys.* **47**, 065305 (2014).
3. T. Siciliano, A. Tepore, E. Filippo, G. Micocci, M. Tepore, *Materials Chemistry and Physics* **114**, 687 (2009)
4. Rabindar K. Sharma and G. B. Reddy, *J. Appl. Phys.* **114**, 184310 (2013).
5. M. A. Py and K. Maschke, *Physica B+C* **105**, 370 (1981).
6. Rabindar K. Sharma and G. B. Reddy, *Physica B* **456**, 197–205 (2015).
7. Arrak Klinbumrung, Titipun Thongtem, and Somchai Thongtem, *J. of Materials* **1155**, 930763 (2012).
8. Tarsame S. Sian and G. B. Reddy, *Solar Energy Materials & Solar Cells* **82**, 375 (2004).
9. I. Navas, R. Vinodkumar, K. J. Lethy, A. P. Detty, V. Ganesan, V. Sathe, and V. P. Mahadevan Pillai, *J. Phys. D: Appl. Phys.* **42**, 175305 (2009).