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Electron beam evaporated molybdenum oxide films: a study of elemental and surface morphological properties

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Abstract
Thin films of transition metal oxides are very important in electrochromic applications. Molybdenum oxide (MoO_3) thin films were prepared by using one of the physical vapour depositions of the electron beam evaporation technique in a vacuum of the order of 10^{-6} mbar. The detailed elemental analysis of the films was performed by a particle-induced x-ray emission (PIXE) study and the nanosurface nature of the films was studied by using an atomic force microscopy (AFM) analysis. To the best of our knowledge this is the first time PIXE analysis has been used for the elemental studies of electron beam evaporated MoO_3 films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nowadays, a large amount of extensive research has been focused in the field of electrochromic oxide thin films due to their wide applications in gas sensors, elements for information display, electrochromic devices and the major advance in energy-efficient window technology [1, 2]. The intrinsic property of electrochromic materials is the electrochromism, i.e., change in optical properties under the influence of the external voltage pulse. Due to this unique property of electrochromism, the materials are largely considered as transforming windows and skylights from an energy liability in buildings to an energy source. The glazing can be reversibly switched from clear to a transparent, coloured state by applying a low voltage, resulting in dynamically controllable thermal and optical properties, i.e., 'smart windows'. Among the electrochromic materials, in the present case, we have discussed molybdenum oxide (MoO_3) thin films. In recent years, orthorhombic molybdenum (α-MoO_3) and its derivatives have attracted attention for their use as cathodes of lithium-containing microbatteries [3, 4], and as working electrodes of electrochromic devices [5].

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In response to this wide range of applications, various preparation techniques have been developed and investigated for the host material MoO_3 [6, 7]. Recently, we have reported the preparation of MoO_3 films by an electron beam evaporation technique; the films have been subjected to systematic characterization studies and the results have been discussed in detail [8, 9]. Indeed, the systematic characterization of the structure of the films is of great interest and is necessary for understanding the electrochromic properties of the films. The present work describes the nanosurface nature of the films and elemental concentration of the constituent element in the films using atomic force microscopy (AFM) and particle-induced x-ray emission (PIXE) studies, respectively. The effect of substrate temperature and annealing temperature (post-heat treatment) on the films was studied simultaneously.

2. Experimental details

2.1. Film preparation

Thin films of molybdenum oxide (MoO_3) were prepared by the electron beam evaporation technique using a HINDHIVAC vacuum coating unit model 12A4D with electron beam

power supply model EBG-PS-3K. The detailed procedure for the preparation of MoO_3 films was presented in our earlier articles [8, 9]. The films were deposited both on microscopic glass and fluorine-doped tin oxide (FTO) coated glass substrates. The ablated material of molybdenum oxide pellets was evaporated by the resultant electron beam with an accelerating voltage of 5 kV and a power density of about 1.5 kW cm^{-2} in a vacuum of the order of 1×10^{-5} mbar. The films were prepared at different substrate temperatures (T_{sub}), such as room temperature (RT), 100 and 200 °C. The room-temperature prepared films were further annealed (post-heat treatment) (T_{anne}) at 200 and 300 °C in the vacuum environment.

2.2. PIXE studies

Particle-induced x-ray emission, commonly abbreviated to PIXE, is a technique for multi-elemental analysis. A beam of protons or, on occasion, heavier ions accelerated to energy of a few MeV excites a characteristic x-ray spectrum which is recorded in energy-dispersive mode by a semiconductor x-ray detector. With highly focused proton beams, there is the additional option of both one- and two-dimensional imaging of element distributions in a specimen [10]. The advantages of the PIXE technique are its nondestructive, rapid quantitative estimation and high sensitivity for various elements detectable, in principle, in a single irradiation, with relatively uniform sensitivity from element to element. Nowadays, the PIXE technique has been used to analyse trace elements in the gel, in neo-formed bone and in bone [11] and fly ash and pond ash samples [12]. To the best of our knowledge this is the first time a PIXE analysis has been used to estimate the elemental concentration of the constituent element (Mo) present in the electron beam evaporated MoO_3 thin films.

The PIXE measurements were carried out by using the Tandem Pelletron Accelerator (9SDH-2, NEC, USA) facility at Ion Beam Laboratory, Institute of Physics, Bhubaneswar, India. The samples of MoO_3 thin films on glass and FTO substrates were fixed on the sample holder and then loaded into the PIXE chamber. A collimated proton beam of 3 MeV (obtained from a 3 MV Tandem pelletron accelerator) energy was used to irradiate the samples. The chamber pressure during the irradiation measurements was maintained at about 10^{-6} Torr. Each sample was irradiated for about 1 h with a beam spot of 2 mm diameter. The PIXE measurements were performed with a maximum beam current of ~6 nA. A liquid nitrogen cooled energy dispersive Si (Li) detector (Canberra) with full-width at half-maximum (FWHM) of 170 eV at 5.9 keV (active area of 30 mm^2, beryllium window thickness of 8 μm) was used to detect characteristic x-rays emitted from the targets. The detector was kept at 90° with respect to the incident beam direction. Characteristic x-rays emitted from the samples exit the PIXE chamber through a 50 μm Mylar window and traverse an approximately 1 cm air gap, before entering the detector. A 25 μm thick aluminium absorber was kept in front of the detector to attenuate the bremsstrahlung background and dominant low-energy x-ray peaks. Spectra were recorded by using a PC-based multichannel analyser (MCA). The thick-target PIXE spectra were analysed by the simulation software 'GUPIX-2000' [12–14]. The GUPIX-2000 software package provides nonlinear least-squares fittings of the spectrum, together with subsequent conversion of the x-ray peak intensities to elemental concentrations via a defined standardization technique involving fundamental parameters and a user-defined instrument constant. Full account was taken of matrix effects and secondary fluorescence contributions in both the spectrum-fitting portion and the calculation of concentrations.

2.3. AFM studies

The development of the AFM technique for surface analysis has led to a detailed study of the surface of materials down to atomic scale because of its exceptionally high vertical resolution [15, 16]. In this work AFM was used to monitor the morphological change of MoO_3 films with substrates, substrate temperatures and annealing temperatures. The variation of morphological change of the molybdenum oxide film is used to establish a quantitative correlation with the corresponding charge state. This would benefit our understanding of the electrochemical behaviour of the film, such as unidirectional current flow phenomena [17] and electrochromism. In this regard, the AFM study of nanostructured substoichiometric oxides can provide vital information about the high surface-to-volume ratio and the semiconducting behaviour which are the combined properties prerequisite for technological applications.

The film surfaces were analysed using a Nanoscope-III atomic force microscope with STM attachment. The analyses were carried out at UGC-DAE Consortium for Scientific Research, Indore, India. The technique is based on the electron tunnelling between a sharp metal tip and the surface of a conducting/semiconducting solid surface. A map of the film/solid surface is generated by scanning the tip over the surface from side to side in parallel lines. The AFM studies are usually carried out to study the surface morphology, detect any damages, crack on the surface, surface homogeneity, uniformity, nanostructure, nature of grains, and any other special features, that are in the nanometre regime. Also AFM is the basic confirmation tool and it plays an important role in nanotechnology.

3. Results and discussion

3.1. Elemental analysis

The principle of PIXE is that an electron in an inner shell jumps and undergoes an interaction with a particle beam. Another electron in the shell moves to an inner orbit. A characteristic x-ray, which has particular energy, is emitted. Consequently, the quantity of an element in a sample can be measured by counting the number of characteristic x-rays. The obtained collimated proton beam of 3 MeV energy from 3 MV Tandem pelletron accelerator was used to irradiate the MoO_3 films, which emit the characteristic x-ray for molybdenum (Mo). The spectra give the intensity of the characteristic x-rays of the molybdenum emitted from the sample as a function of channel number. The intensities of these characteristic x-rays can be converted into the concentration of element present in the samples using the 'GUPIX-2000' software package [13]. The prepared MoO_3 films on glass and FTO substrates at different conditions were labelled as A, B, C, D, E and F, G,

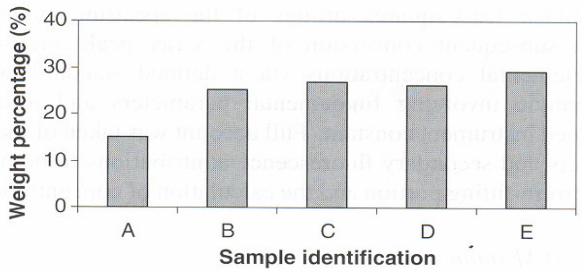

Figure 1. Evaluated Mo wt% of MoO_3 films on glass substrates.

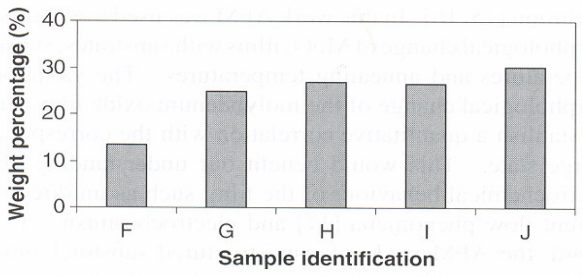

Figure 2. Evaluated Mo wt% of MoO_3 films on FTO substrates.

H, I, J, respectively, as indicated in table 1. In the present case, the molybdenum oxide films were prepared by evaporating stoichiometric MoO_3 pellets. Hence the deposited films have both the elements molybdenum (Mo) and oxygen (O). Moreover, the PIXE technique can detect and identify elements with atomic number in the range $Z = 11$–92 [10]. Light atoms such as oxygen ($Z < 11$) cannot be detected. Hence, the characteristic x-rays for molybdenum (Mo) ($Z = 42$) have been observed from the PIXE spectra. The graphical representation of various Mo content in MoO_3 films on glass and FTO substrates is shown in figures 1 and 2, respectively. Evidence of the presence of Mo in the films regardless of substrate and deposition conditions has been confirmed from the PIXE analysis.

In our earlier work [8, 9], we reported the structural and optical properties of electron-beam evaporated MoO_3 films. The x-ray diffraction pattern shows well-resolved and sharp peaks for MoO_3 films, which showed evidence of the stoichiometric nature of the films. Also the results showed an improvement in film crystallinity with increasing substrate temperature and post-annealing temperature. Figures 1 and 2 show the increase in Mo concentration with increasing substrate temperatures as well as annealing temperatures. This indicates that the level of oxygen is decreasing with increasing substrate and annealing temperatures with its respective stoichiometric formulation. The optical properties of MoO_3 films studied by UV–vis–NIR spectra [8, 9] showed the decreasing transmission range of the films with increasing substrate and annealing temperatures, which may be due to the formation of more oxygen-ion vacancies in the films at higher temperatures. These observations of our earlier work provide supportive evidence for, and correlate well with, the results obtained in the present work.

Table 1. Sample identifications for MoO_3 films prepared from different conditions.

Sample identification	Sample details
A	MoO_3/glass/RT
B	MoO_3/glass/RT annealed at 200 °C
C	MoO_3/glass/RT annealed at 300 °C
D	MoO_3/glass/100 °C
E	MoO_3/glass/200 °C
F	MoO_3/SnO_2/glass/RT
G	MoO_3/SnO_2/glass/RT annealed at 200 °C
H	MoO_3/SnO_2/glass/RT annealed at 300 °C
I	MoO_3/SnO_2/glass/100 °C
J	MoO_3/SnO_2/glass/200 °C

3.2. Surface morphological studies

The detailed morphological studies of the electron beam evaporated MoO_3 films were carried out by AFM. The surface nature of the films was analysed with regard to different substrates (glass and FTO substrates), deposition temperatures (RT and 200 °C) and annealing temperature (300 °C). Figures 3(a)–(c) show the AFM images of MoO_3 films prepared on glass substrates at T_{sub} = RT, T_{sub} = 200 °C and T_{anne} = 300 °C, respectively. The respective AFM microstructures of the films on FTO substrates prepared in the above conditions are shown in figures 4(a)–(c). A systematic scanning analysis was carried out at different locations of thin films with different resolutions and magnifications. The images are illustrated in figures 3 and 4. The images demonstrate that the electron-beam evaporated MoO_3 films are homogeneous and uniform. The AFM micrograph of MoO_3 films deposited on glass substrate at T_{sub} = RT (figure 3(a)) shows that the material appears to be uniform, grainy and composed of spherical nanoparticles of various sizes. Also, well-resolved spherical grains with uniform size and homogeneity throughout the film are observed for the films on FTO substrates prepared at room temperature. The crystalline FTO substrate yielded an ordered and repetitive arrangement for the evaporated species. Hence, the morphology contains well-defined and highly aligned spherical grains on all sides of its growth front. The calculated crystallite size using Scherrer's formula is of the order of 70 nm [9]. This also suggests the nanocrystalline nature of the MoO_3 film. The AFM nanostructures of figures 3(a) and 4(a) show the optimization of MoO_3 films at lower substrate temperature (T_{sub} = RT) and the images having uniform nanospherical grains without any post-heat treatment.

When the substrate temperature was increased further, i.e., T_{sub} = 200 °C, the morphology of the films on glass substrates (figure 3(b)) shows spherical wrinkled mountains originating from the columnar growth of the films combined with the small needle-like grains. Figure 4(b) reveals pyramidal-like morphology, which may exist by the accumulation of the needle-like crystallites. Such needle-like crystallites of MoO_3 films on glass and FTO substrates at T_{sub} = 200 °C were observed by the authors [9] using scanning electron microscopy (SEM), which enumerated the layered nature of the films. Figures 3(c) and 4(c) are AFM micrographs of MoO_3 films prepared at room temperature, further annealed at 300 °C (T_{anne}) on glass and FTO substrates, respectively.

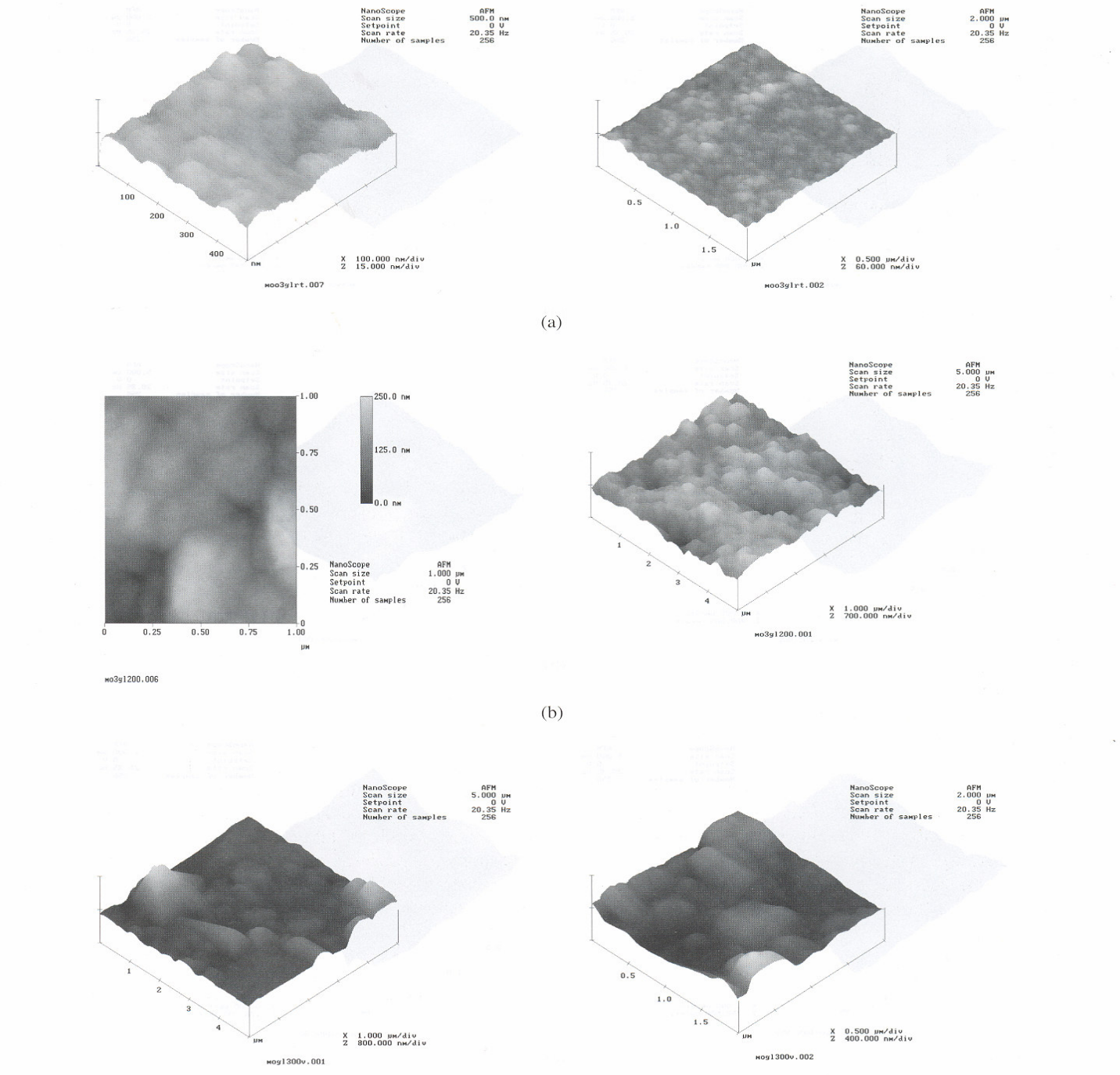

Figure 3. AFM images of MoO_3 films on glass substrates at different preparative conditions: (a) T_{sub} = RT, (b) T_{sub} = 200 °C and (c) T_{anne} = 300 °C.

Figure 3(c) reveals the stacking of platelet crystallites and also some needle-like grain morphology, identified from various scanning locations on the films. These microstructures may be characterized by a high and dense columnar structure. The AFM morphology (figure 4(c)) of MoO_3 films on FTO substrates at T_{sub} = RT, T_{anne} = 300 °C shows uniform grains and the formation of cauliflower-like morphology by the coalescence of needle-like grains. The SEM analysis also revealed the same morphology [8] for films deposited in the above conditions. The identical morphological nature of MoO_3 films has been reported by others: Sunu *et al* [1] observed spherical granular morphology for pulsed laser-deposited MoO_3 films, and layered-like crystallites were observed by Hussain and Rao [18]. There are no cracks and morphological disturbances and/or defects observed in the films due to the higher substrate temperature and annealing temperature. From the AFM analysis, the uniform crystallinity, surface homogeneity, and nanocrystal grain

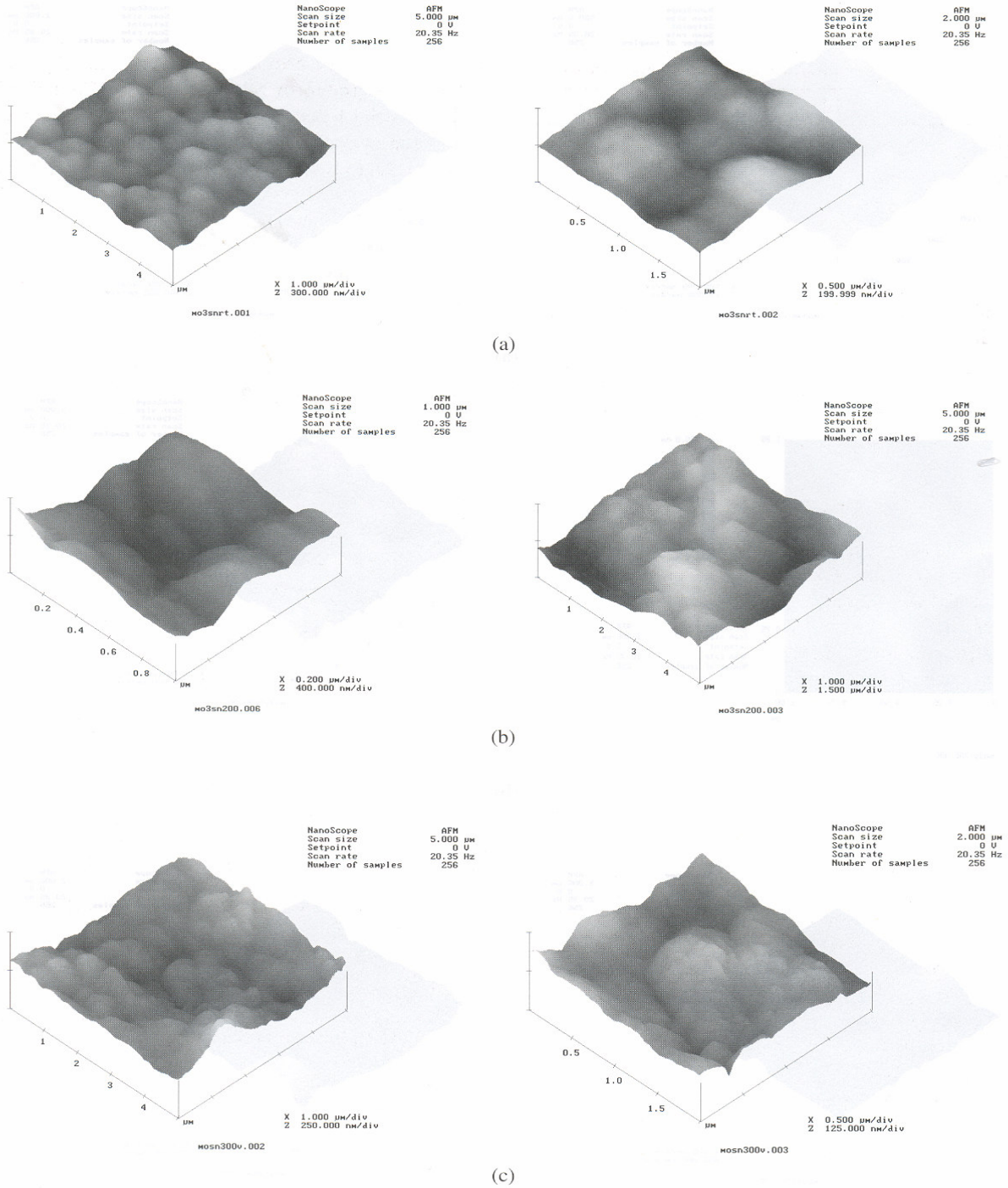

Figure 4. AFM images of MoO_3 films on FTO substrates with different preparative conditions: (a) T_{sub} = RT, (b) T_{sub} = 200 °C and (c) T_{anne} = 300 °C.

nature is clearly identified for the MoO_3 films prepared in the present work. Also, the AFM was used to measure the root-mean square roughness (R_{rms}) of thin films. Surface roughness is calculated as the standard deviation of the mean height of surface structures [19]. The evaluated R_{rms} values of MoO_3 films from the AFM images (figures 3 and 4) are shown in table 2. It is observed that the roughness of the films increased with increasing substrate and annealing temperatures; the values of roughness are in the range 0.21 to 0.52 μm.

However, the MoO_3 film deposited on glass and FTO substrates exhibited $\langle 110 \rangle$ preferred crystalline orientation along with $\langle 0k0 \rangle$ orientations (where k = 2, 4 and 6), observed in x-ray diffraction patterns [8, 9]. The results are not shown here. The formation of such $\langle 0k0 \rangle$ growth orientations confirms the layered nature of the films reported by Julien *et al* [20]. A sharp absorption edge was observed in the visible region of the optical transmittance spectrum [8, 9], which confirms the nanostructured nature of the MoO_3 films that was

Table 2. Root-mean square surface roughness (R_{rms}) of MoO_3 films.

Sample	Surface roughness (R_{rms}) (μm)	
	Glass substrates	FTO substrates
MoO_3/RT	0.21	0.22
MoO_3/200 °C	0.50	0.52
MoO_3/RT/T_{anne}: 300 °C	0.23	0.24

seen from the AFM structures (shown in figures 3 and 4). The change in surface morphology (AFM features) with substrates, different substrate temperatures and annealing temperature is mainly due to the realization of different surface energy leading to crystallites of varying crystalline nature and size. Lower substrate temperature results in low surface migration of adatoms while too high a substrate temperature causes the adatoms to re-evaporate from the film surface.

4. Conclusions

This paper has reported systematic investigations of elemental and surface morphological studies of electron-beam evaporated molybdenum oxide thin films by PIXE and AFM analyses, for different substrates and temperatures. The PIXE studies confirm the presence of Mo element in the films. The AFM morphological images reveal that the electron-beam evaporated MoO_3 films are crystalline, have uniform surface homogeneity, crack-free surface, nanocrystal grain structure and good architectural nature. The needle-like morphology and platelet stacking layers confirm the layered nature of the films in the present work.

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