Conference Paper

Structural, Optical, and Electrochromic Properties of Pure and Mo-Doped WO_3 Films by RF Magnetron Sputtering

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Pure and Mo-doped WO_3 films were formed on ITO-coated glass substrate held at 473 K by RF magnetron sputtering technique. The structural, morphological, and optical properties of pure and Mo-doped WO_3 thin films have been systematically studied. The structural properties revealed that the pure WO_3 films exhibited a (020) reflection related to the orthorhombic phase of WO_3 , whereas Mo-doped films showed (200) reflection. The surface morphology revealed that pure WO_3 films showed the dense surface and Mo-doped films contained agglomerated grains which were uniformly distributed on the surface of the substrate. The optical transmittance decreased from 85% to 75% for pure and Mo-doped WO_3 films, respectively. The electrochromic properties of the films were measured by cyclic voltametry in 1 M Li_2SO_4 electrolyte solution. The optical modulation of pure WO_3 films at near IR was 50%, and the calculated color efficiency was $33.8 \text{ cm}^2/\text{C}$, while in Mo-doped WO_3 the efficiency improved to $42.5 \text{ cm}^2/\text{C}$.

1. Introduction

Tungsten oxide (WO_3) is the most widely used electrochromic material because of easiness in synthesis and favorable electrical and optical properties. The application of electrochromic materials for smart windows, displays, and antiglare mirrors and several applications have been developed such as control of incoming daylight into buildings, smart windows, rearview mirrors, and photochromic and electrochromic devices [1–3]. Tungsten oxide is the extensively studied electrochromic material [4, 5]. Doping of vanadium, niobium, nitrogen, titanium, or nickel to WO_3 enhances in the electrochromic properties. Muthu Karuppasamy and Subramanyam [6] reported that the color efficiency decreased from 121 to $13 \text{ cm}^2/\text{C}$ with increase of vanadium doping of 9 at. % in tungsten oxide films deposited by DC magnetron sputtering. Bathe and Patil [7] studied the electrochromic properties of niobium-doped WO_3 films, and the coloration efficiency decreased with the increase

of niobium doping. Sun et al. [8] studied the nitrogen-doped WO_3 films formed by reactive DC pulsed sputtering and the color efficiency achieved to $45 \text{ cm}^2/\text{C}$ at 5 at. % nitrogen doped films. Karuppasamy and Subrahmanyam [9] studied the electrochromic properties of titanium doped tungsten oxide films and realized the improvement in the electrochromic properties with the increase of titanium doping. Gesheva et al. [10] studied MoO_3 - WO_3 films formed by chemical vapour deposition method and showed the color efficiency of $141 \text{ cm}^2/\text{C}$ when compared to $84 \text{ cm}^2/\text{C}$ for WO_3 and $39 \text{ cm}^2/\text{C}$ for MoO_3 films. Valyukh et al. [11] reported on the optical properties of Ni-doped tungsten oxide films formed by DC magnetron sputtering.

In mixed metal oxide films optical absorption was induced by intense electron transitions between the electronic states like W^{5+} and W^{6+} and the corresponding lower energy electronic states of Mo (Mo^{5+} , Mo^{6+}) thus resulted in improved electrochromic effect. Various thin film deposition

FIGURE 1: EDAX spectra of Mo-doped WO_3 films and pure WO_3 films (inset).

techniques such as spray pyrolysis [12, 13], sol-gel process [14–16], electrodeposition [1, 17], thermal oxidation [4], atmospheric pressure chemical vapour deposition [10], plasma assisted evaporation [18], and DC and magnetron sputtering [5–9, 11, 18, 19] were employed for the growth of pure and doped WO_3 films. Among the physical methods, magnetron sputtering has the advantage for the growth of films on large area substrates and industrially practiced technique. In the present investigation, RF magnetron sputtering technique was employed for deposition of pure and molybdenum-doped WO_3 films on corning glass and ITO coated glass substrates held at temperature of 473 K. The deposited films were characterized for their chemical composition, crystallographic structure, surface morphology, and optical and electrochromic properties.

2. Experimental

Pure and molybdenum-doped tungsten oxide thin films were deposited onto corning glass and ITO-coated glass substrates held at a temperature of 473 K by RF magnetron sputtering of mosaic target of Mo-W at sputtering power of 150 W and at oxygen partial pressures of 6×10^{-2} Pa and sputter pressure of 4 Pa. The films were deposited for a duration of 120 min. The films deposited on corning glass substrates were used for structural and morphological and optical characterization, and the films formed on ITO-coated glass substrates were used for electrochromic characterization. The chemical composition of the films was determined by energy dispersive X-ray analysis (EDAX) attached to scanning electron microscope. The structural analysis of the deposited films was studied by X-ray diffraction technique. The surface morphology of the films was examined by using scanning

FIGURE 2: XRD patterns of pure and Mo-doped WO_3 films.

electron microscope, and the optical properties were carried out by UV-Vis-NIR double-beam spectrophotometer. RF-sputtered WO_3 films coated on ITO substrate was used as working electrode; platinum and Ag/AgCl were used as counter and reference electrodes, respectively. 1 M Li_2SO_4 aqueous solution was taken as electrolyte. Electrochemical treatment was carried out using three-electrode cells (Pt/Ag/AgCl/ WO_3 /ITO).

3. Results and Discussion

3.1. Chemical Composition. The chemical composition of pure and molybdenum-doped WO_3 films was determined by EDAX analysis. Figure 1 shows the EDAX spectra of pure WO_3 (inset) and Mo-doped WO_3 films. Figure 1 (inset) clearly shows that the oxygen and tungsten peaks are present in the films. The atomic ratio of oxygen to tungsten was 2.97 in pure WO_3 films which revealed that the films were of nearly stoichiometric. For Mo-doped WO_3 films, EDAX spectrum shows the intensity of the tungsten peak is decreased due to the substitution of molybdenum to the tungsten in the Mo-doped WO_3 films, while the content of oxygen remains almost constant as shown in Figure 1. The content of molybdenum present in the Mo-doped WO_3 films was 1.2 at. %.

3.2. Structural Properties. Figure 2 shows the XRD patterns of pure and Mo-doped WO_3 thin films. It is observed that the pure WO_3 films exhibit a diffraction peak at $2\theta = 23.6^\circ$ related to the (020) reflection of orthorhombic phase of WO_3 where these were embedded in the amorphous matrix. The films WO_3 formed with Mo doping showed the predominant peak at $2\theta = 24.2^\circ$ related to the (200) orientation corresponding to the orthorhombic phase of WO_3 . The diffraction peaks related to the MoO_3 were not observed in Mo doped WO_3 films since the molybdenum substituted into the tungsten in WO_3 . The full width at half maximum (FWHM) of the diffraction peak of the films decreased in Mo-doped WO_3 films. The decrease of peak width indicated

FIGURE 3: Scanning electron microscopic images of (a) pure and (b) Mo-doped WO_3 films.

FIGURE 4: Optical transmittance spectra of virgin and colored states of pure and Mo-doped WO_3 films.

the increase in the crystallinity of the films by doping of Mo in WO_3 films. The crystallite size (D) of the films was calculated by using Debye-Scherrer's relation:

$$D = \frac{0.89\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the full width at half maximum, λ is the X-ray wavelength (0.15406 nm), and θ is the diffraction angle. The crystallite size of the pure WO_3 films was 14 nm while those in Mo-doped film increased to 20 nm. The XRD studies revealed that the pure WO_3 films are of nanocrystalline and the crystallinity increased in Mo-doped WO_3 films.

3.3. Surface Morphology. Figure 3 shows the scanning electron microscope images of pure and Mo doped WO_3 films.

Doping of Mo in WO_3 exhibited a significant surface morphological change in the films. In Figure 3(a), the pure WO_3 films surface seen to be dense with fine grain surface, where as Mo doped films contains nanograins and the coarseness of morphology are observed as shown in Figure 3(b). This type of morphological films are very useful for electrochromic properties. The average grain size of the Mo doped WO_3 films is about 300 nm. Weng et al. [20] noticed the similar nature of morphology in titanium-tungsten oxide films formed by co-sputtered targets titanium and tungsten by pulsed sputtering deposition which exhibited good electrochromic properties.

3.4. Optical Properties. There is a significant dependence of optical transmittance and the absorption edge of the films on the doping of Mo in WO_3 . Figure 4 shows the optical transmittance spectra of pure and Mo-doped WO_3 films in its virgin. It shows that the average transmittance above wavelength of 600 nm decreased from 85 to 75% for pure and Mo-doped WO_3 films. The transmittance of the colored WO_3 films is lower than the bleached transmission spectrum of the films, which is attributed to the volume scattering in the film due to the microstructure. De León et al. [12] also noticed that the optical transmittance decreased in Mo-doped WO_3 films formed by spray pyrolysis. The optical absorption coefficient (α) of the films was calculated from the optical transmittance (T) data using the following relation:

$$\alpha = -\left(\frac{1}{t}\right) \ln T, \quad (2)$$

where t is the thickness of the film.

In order to determine the optical band gap of the films, we assume that the direct transition takes place in these films. The fundamental absorption corresponds to the electron excitation from the valance band to the conduction band, and the absorption coefficient was fitted to the Tauc's relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (3)$$

where A is the absorption edge width parameter, and $h\nu$ is the incident photon energy. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for

FIGURE 5: The plots of $(\alpha h\nu)^2$ versus photon energy for the pure and Mo-doped WO_3 films.

the virgin state of the films are illustrated in Figure 5. The optical band gaps of the pure and Mo-doped WO_3 films are 2.89 and 2.78 eV, respectively. It is to be noted that the optical band gap of the molybdenum-doped WO_3 films formed by spray pyrolysis [12] decreased from 3.49 to 3.38 eV with increase of molybdenum content from 2 to 10 at. % in WO_3 films. Such an optical band gap reduction was also noticed in vanadium-doped WO_3 films due to creation of defect levels below the conduction band of WO_3 [6]. P. R. Patil and P. S. Patil [21] showed a band gap of 2.76 eV in spray deposited MoO_3 - WO_3 films. The decrease in the band gap for Mo-doped WO_3 films is due to the doping of molybdenum which creates impurity levels below the conduction band of WO_3 . Figure 6 shows the variation of refractive index with wavelength of pure and Mo-doped WO_3 films. It is seen from the figure that the refractive index of pure WO_3 films decreased from 2.45 to 2.15, and, in Mo-doped films it decreased from 2.39 to 2.08 with increase of wavelength from 400 to 800 nm, respectively. The refractive index of the films at 550 nm decreased from 2.23 to 2.16 in pure and Mo-doped WO_3 films, respectively. The decrease in the refractive index in Mo-doped WO_3 films was due to the lower density.

3.5. Electrochromic Properties. The optical transmittance spectra of the pure and Mo-doped WO_3 films in their colored and along with virgin states are also in Figure 4. The optical modulation is achieved about 50% in the near infrared (>600 nm) in pure WO_3 films. The Mo-doped WO_3 films exhibited the optical modulation of about 40% at near infrared region. High optical modulation in the wavelength >600 nm is desired for efficient electrochromic (EC) smart windows. In electrochromism experiments, the transport of Li ions is a major factor that affects the electrochromic behaviour. The mobility of intercalated Li^+ ions in the films

FIGURE 6: Wavelength dependence of refractive index of pure and Mo-doped WO_3 films.

depends strongly on the microstructure, density, and porosity of the films. Scanning electron microscopic images show the coarseness of morphology in Mo-doped film. This type of morphology exhibits the good electrochromic behaviour.

The color efficiency (CE) which is relevant parameter to describe the electrochromic performance of the films. Coloration efficiency is defined as the change of optical density (ΔOD) per unit of charge of insertion or extraction and is given by the following relation:

$$\text{CE} = \frac{\Delta\text{OD}}{\Delta Q} = \frac{\log(T_a/T_b)}{\Delta Q}, \quad (4)$$

where $\Delta(\text{OD})$ is the variation in optical density, Q is the charge density (C/cm^2), and T_b and T_c are the optical transmittance in the bleached and colored states, respectively. The color efficiency of the both pure and Mo-doped WO_3 films is calculated by using (4). The calculated color efficiency was about $33.8 \text{ cm}^2/\text{C}$ for pure WO_3 films, and it increased to $42.5 \text{ cm}^2/\text{C}$ for Mo-doped WO_3 films. Zhang et al. [4] reported the tunnel structure of hexagonal and highly porous surface morphology, a large optical modulation of WO_3 nanotree films up to 30% and coloration efficiency of $43.6 \text{ cm}^2/\text{C}$ at 400°C for 2 h. Granqvist [22] reported that the electrochromic effect is highly influenced by the Mo content 6 and 8 at. % in WO_3 and the color efficiency and the optical modulation are greater. A high value of colouration efficiency indicates that the electrochromic film exhibits large optical modulation with small charge inserted (or extracted). Comparatively high color efficiency is attributed to the structure and large porous of the WO_3 film, which provides more surface area and direct paths for the process of Li^+ ion intercalation.

4. Conclusions

The pure and Mo-doped nanocrystalline WO_3 thin films were deposited on corning glass and ITO-coated glass by RF magnetron sputtering technique in an oxygen partial pressure of 6×10^{-2} Pa, sputter power of 150 W, and at substrate temperature of 473 K. The structural and morphological and optical and electrochromic properties of pure and Mo-doped WO_3 thin films have been systematically studied. The structural properties revealed that the pure WO_3 films exhibits the predominant peak of (020) reflection of orthorhombic phase of WO_3 , while Mo-doped films exhibited the (200) reflection. The crystallite size of the films increased with doping of molybdenum in WO_3 . Mo doped WO_3 films were of coarseness in the morphology which exhibits good electrochromic properties. The optical transmittance spectra revealed that the transmittance decreased from 85% to 75% for pure and Mo doped WO_3 films. The optical band gap of pure WO_3 films was 2.89 eV and it decreased to 2.78 eV in Mo-doped WO_3 films. The color efficiency is $33.8 \text{ cm}^2/\text{C}$ for pure WO_3 films and improved to $42.5 \text{ cm}^2/\text{C}$ in molybdenum-doped WO_3 films.

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