Research Letter

Photo- and Electrochromic Properties of Activated Reactive Evaporated MoO₃ Thin Films Grown on Flexible Substrates

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The molybdenum trioxide (MoO₃) thin films were grown onto ITO-coated flexible Kapton substrates using plasma assisted activated reactive evaporation technique. The film depositions were carried out at constant glow power and oxygen partial pressures of 8 W and 1×10^{-3} Torr, respectively. The influence of substrate temperature on the microstructural and optical properties was investigated. The MoO₃ thin films prepared at a substrate temperature of 523 K were found to be composed of uniformly distributed nanosized grains with an orthorhombic structure of α -MoO₃. These nanocrystalline MoO₃ thin films exhibited higher optical transmittance of about 80% in the visible region with an evaluated optical band gap of 3.29 eV. With the insertion of 12.5 mC/cm², the films exhibited an optical modulation of 40% in the visible region with coloration efficiency of 22 cm²/C at the wavelength of 550 nm. The MoO₃ films deposited at 523 K demonstrated better photochromic properties and showed highest color center concentration for the irradiation time of 30 minutes at 100 mW/cm².

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1. INTRODUCTION

In the current nanoscience and technology era, the transition metal oxides (TMOs) constitute a fascinating and promising class of inorganic solids that have received substantial attention of solid state/materials chemists, due to their novel material characteristics. Among the various transition metal oxides, molybdenum trioxide (MoO₃) has been recognized as a promising and persistent wide band gap material owing to its quite motivating structural, chemical, chromogenic, catalytic, and optical properties. In particular, the orthorhombic layered α -MoO₃ structure with high electrochemical activity, high stability, and good coloration efficiencies of MoO₃ makes it useful for electro-, photo- and gasochromic industrial applications. Recently, nanocrystalline molybdenum trioxide in thin film configuration is considered as prospective chromogenic material to adapt it as active layers in the field of advanced electrochromic windows [1, 2]. Most of the researchers investigated extensively about the microstructural and electro-photochromic properties of MoO₃ thin films grown onto various solid substrates using various physical/chemical vapor thin films deposition

techniques and ensure their efficiency and durability in a device level [3, 4]. Nevertheless, at present the designing and fabrication of thin film coatings on flexible substrates have grown worldwide into a major challenging and novel research area for cutting-edge future-based technologies. These flexible substrates are unique than solid glass substrates due to the following reasons: (i) they are flexible, so they can bent and stick to any curved shape objects without altering their basic properties, (ii) they are weight less, and (iii) they are easy to carry and can be folded. Hence, deposition of thin film coatings on flexible substrates goes hand-in-hand with the explosion of scientific and technological breakthrough in microelectronics, electronic information displays, optical memory devices, and nanotechnology. To the best of our knowledge, reports are not available on the growth and chromic application of MoO₃ thin films on flexible substrates. In addition, despite various physical vapor deposition techniques, activated reactive evaporation (ARE) is one of the plasma-assisted physical vapor thin-film deposition techniques to grow nearly stoichiometric thin films with better uniformity at relatively lower substrate temperatures with higher deposition rates. In this deposition

technique, the reaction occurs predominantly in plasma; as a result, chemical composition of the films can be controlled by changing the ratio of reacting species. Hence, the present investigations aimed at growing molybdenum trioxide thin films onto ITO-coated flexible Kapton substrates using home-built activated reactive evaporation technique and explicated their microstructural and optical properties as a function of substrate temperature (T_s). The electrochromic and photochromic properties of the nanocrystalline MoO_3 thinfilms were investigated for their effective utilization in electrochromic windows.

2. EXPERIMENTAL DETAILS

The plasma assisted home built activated reactive evaporation technique is adapted to prepare molybdenum trioxide thin films onto ITO-coated flexible Kapton substrates. The ITO transparent conducting coating was deposited using sputtering technique on polyimide flexible substrate which can be used up to 673 K as substrates in the present investigation [5]. A constant and high density of plasma was established between two electrodes at the glow power and oxygen partial pressures of 8 W and 1×10^{-3} Torr, respectively. The film depositions were carried out at various substrate temperatures ranging from 300 K to 600 K. The structural characteristics of the as-deposited MoO_3 thin films were investigated using grazing incidence X-ray diffraction (GIXRD) technique (Seifert computerized X-ray diffractometer, model 3003 TT) with a grazing incidence of angle 3° . Atomic force microscopy (AFM) (Digital Instrument: Dimension 3100 series) was used to study the surface morphology of the films in a simple contact mode of operation. The optical measurements were carried out by Hitachi U-3400 UV-Vis-NIR double beam spectrophotometer in the wave length range of 300–1500 nm. The electrochromic studies were investigated by a dry lithiation method, and the photochromic behavior is studied by illuminating the specimens with a 100 W tungsten lamp. The intensity of radiation during illumination at the surface of the film is kept at about 100 mW/cm².

3. RESULTS AND DISCUSSION

3.1. Structural studies

Figure 1 shows the X-ray diffraction pattern of MoO_3 thin films grown at various substrate temperatures by maintaining constant glow power and oxygen partial pressures of 8 W and 1×10^{-3} Torr, respectively. The films deposited at room temperature were found to be amorphous, and the onset of crystallization in MoO_3 films is observed at around 473 K. This may be due to increased kinetic energy of the ionized species in presence of plasma (which is higher than the kinetic energy of evaporated species in the thermal evaporation), which enhances ad-atom mobility on the substrate surface. The enhancement of crystallinity in the films is observed with the augmentation of substrate temperature to the higher value of 523 K. As a result, the respective GIXRD pattern of the films exhibited (020), (110),

FIGURE 1: The X-ray diffraction patterns of MoO_3 thin films.

(040), and (060) Bragg reflections, and the evaluated lattice parameters which are $a = 0.395$ nm, $b = 1.384$ nm, and $c = 0.368$ nm are in good agreement with powder diffraction data and attributed to the orthorhombic structure of $\alpha\text{-MoO}_3$ (JCPDS card no. 05-0508). The crystallite size was estimated using Scherer's formula and found to be about 65 nm for the films deposited at 523 K.

3.2. Surface studies

The surface topographical investigations of tungsten trioxide thin films were carried out as a function of substrate temperature using atomic force microscopy (AFM). The smooth and featureless AFM surface morphological image of the films grown at $T_s < 423$ K supports the amorphous nature of the films. The films deposited at substrate temperature of 523 K (see Figure 2) are observed to be composed of needle-like morphology and nanosized grains of about 60 nm which are fused compactly together, and the root-mean-square surface roughness of the films is 3 nm. The temperature dependence of surface morphological features of the films can be explained as follows. The evaporated species interact with the established plasma and reach the surface of the substrates maintained at higher substrate temperature ($T_s = 523$ K) and acquire larger thermal energy and mobility. This process leads to the enhancement of the diffusion distance, initiates the nucleation, and increases the island formation in order to grow continuous film.

3.3. Optical and electrochromic properties

The optical transmittance characteristics of activated reactive evaporated molybdenum trioxide thin films are investigated as a function of substrate temperature. The fundamental absorption corresponding to the sharp decrease in transmittance is noticed in the wavelength range 300–400 nm. The MoO_3 films grown at lower substrate temperatures were observed to be light bluish in color indicating the presence of oxygen deficiency in the films. The increase in optical transmittance of the films is noticed with the increase of substrate temperature to the higher values, and the observed

FIGURE 2: The AFM picture of the MoO_3 thin film grown at the substrate temperature of 523 K.

FIGURE 3: The optical transmittance spectra of MoO_3 thin films.

fundamental absorption edge shifted towards lower wavelength side, by indicating the increase in optical band gap values. The nanocrystalline molybdenum trioxide thin films grown at $T_s = 523$ K exhibited higher optical transmittance of 80% in the visible region as shown in Figure 3. The estimated optical band gap value increased from 3.18 eV to 3.29 eV with the increase of substrate temperature to the higher values from 300 K to 523 K, respectively. The increase of optical band gap values as a function of substrate temperature can be explained as follows. The MoO_3 films prepared at lower substrate temperatures (< 423 K) may contain reduced oxidation states of "Mo" such as Mo^{5+} and Mo^{4+} states which are closely related to oxygen vacancies formed in the films during deposition. These oxygen ion vacancies present in the films are able to capture one or two electrons and as a result excited states of electrons trapped at Mo^{5+} sites commence to overlap with the empty "4d" states on the neighboring Mo^{6+} sites. Resultantly, the oxygen vacancies occupied by the electrons act as donor centers and form a narrow donor band in the forbidden gap at about 0.3 eV below the conduction band. This donor band deeply extends into the main band gap and causes lower optical band gap value of the amorphous MoO_3 films grown at lower substrate temperatures. With the increase of substrate temperature to the higher values, the oxygen deficiency in the films decreases and was responsible for the degradation of Mo^{5+} states in the films [6].

The electrochromic studies were carried out for the nanocrystalline MoO_3 thin films deposited at $T_s = 523$ K on

ITO-coated flexible substrates using dry lithiation method [7]. In this method, LiNbO_3 powder was heat treated in vacuum to expel lithium atoms, which inserts into MoO_3 thin films kept at temperature of 373 K, to give coloration for the films. The respective optical modulation in optical transmittance of the films in colored state is shown in Figure 3. When lithium atoms reach the exposed MoO_3 thin films surface, they diffuse into the films and become responsible for the following reaction:

No change in thickness of the films after Li-ion intercalation into the film confirms the diffusion of Li^+ ions into the films. However, the color of the film appeared blue with the insertion of Li^+ ions which just similar to the MoO_3 films lithiated using wet method. The quartz monitor is used for the measurement of the film thickness and lithiation process control. The thickness of the films and the quantity of the lithium intercalated into the film are measured by monitoring the frequency change of the quartz crystal as the mass of MoO_3 , and Li layers are deposited, respectively. The degree of such lithiation was measured by noting the change in the quartz crystal thickness (the effective mass) and calibrated against the electrochemical insertion. The maximum coloration studied here is for 20 nm effective mass thickness of lithium which corresponds to approximately 12.5 mC/cm^2 as varied from the electrochemical method. These films showed an average optical modulation (40%) in the visible region, and the coloration efficiency (CE) of MoO_3 films was evaluated by using relation $\text{CE} = \text{OD}/Q_{\text{in}}$, where OD is the optical density and Q_{in} (mC cm^{-2}) is the charge injected during the coloration cycle. The MoO_3 films grown at $T_s = 523$ K demonstrated maximum CE value of $22 \text{ cm}^2/\text{C}$ at the wavelength of (λ) 550 nm than the conventional MoO_3 films. Hsu et al. [8] reported 45% of optical modulation with coloration efficiency of $23.7 \text{ cm}^2/\text{C}$ at the wavelength of 550 nm for the sol-gel spin-coated MoO_3 thin films annealed at 573 K and Sivakumar et al. [9] reported maximum coloration efficiency of $30 \text{ cm}^2/\text{C}$ at the wavelength of 633 nm for e-beam evaporated MoO_3 thin films grown onto FTO-coated glass substrates at room temperature. During intercalation process, the injected electrons into nanocrystalline MoO_3 films are localized at Mo atom thus creating the Mo^{5+} sites and polarize their surrounding lattice to form small polarons. As a result, small overlap occurs between the wave functions corresponding to adjacent sites which are conducive for polaron formation. The incident photons are absorbed by these small polarons and can hop from an Mo^{5+} site to a neighboring Mo^{6+} (intervalence charge transformation) by the absorption of incident photon energy. Therefore, electrochromism of nanocrystalline MoO_3 thin films is attributed to the small polaron absorption.

3.4. Photochromic properties

The photochromic properties of ARE deposited nanocrystalline MoO_3 thin films were performed as a function of

irradiation time interval from 10 minutes to 150 minutes. Figure 4 indicates the optical absorption spectra of as-deposited and irradiated ITO-coated Kapton/MoO₃ samples. The broad faint absorption band near 850 nm is observed for as-deposited films. The observed intensity of broadband absorption increased with the increase of irradiation time. The irradiation of these films tends to increase anion vacancies (V_o^+) owing to the capture of released electrons by the oxygen vacancies. The absorption band with a peak at 850 nm (G-band at 1.46 eV) may be attributed to the V_o^+ type whose level lies close to the bottom of the conduction band. The color of the films after irradiation arises from the transfer of electrons from valence 2p oxygen orbital to empty Mo⁶⁺ (4d) level which gives rise to an incorporation of lower valence Mo⁵⁺ within the lattice. The color of the film changes from light blue to deep blue color with the increase of irradiation time. Hence, the illumination produces free electrons which are trapped by ion vacancies thereby forming color centers. The estimation of color center concentration was estimated by using Smakula's equation. The values of the refractive index and the oscillator strength for MoO₃ are taken as 1.9 and 0.18, respectively. The integral is evaluated in the spectral range 400–1200 nm, where color centers are generated by using the Gaussian approximation as shown in Figure 4. The absorption G-band whose maximum is located in the near infrared region (≈ 1.46 eV) is considered to originate from the intervalence transfer of electrons localized on transition metal ions. The shape of this absorption band is expected to be Gaussian from the intervalence transfer model. The asymmetric shape in the spectra is interpreted as the presence of random potential fluctuations in the films. Figure 5 shows the variation of color center concentration with irradiation time in MoO₃ film. The concentration of color centers is shown to vary nonlinearly with irradiation time. For flexible Kapton/MoO₃, samples irradiated for 30 minutes exhibited highest color center concentration of $1.3 \times 10^{17} \text{ cm}^{-3}$. From Figure 5, it is evident that there is a threshold time for which the concentration reaches its maximum value. When films irradiated beyond the threshold time, the color center concentration notably decreases due to the destruction of color centers.

4. CONCLUSIONS

The nanocrystalline MoO₃ thin films were deposited by using home built activated reactive evaporation technique. The films grown at substrate temperature of 523 K demonstrated orthorhombic structure of α -MoO₃, and the grain growth was observed to be needle-like morphology with 3 nm rms roughness, which might have slightly decreased the electrochromic properties. The as-deposited MoO₃ films at substrate temperature of 523 K were showed nearly 80% of optical transmittance in the visible region and demonstrated 40% of optical modulation during electrochromic studies with coloration efficiency of 22 cm²/C at the wavelength of 550 nm. The nanocrystalline MoO₃ films prepared onto flexible Kapton substrates demonstrated better photochromic properties with maximum color center concentration of

FIGURE 4: The optical absorption spectra at various irradiation times.

FIGURE 5: The variation of color center concentration as a function of irradiation time.

$1.3 \times 10^{17} \text{ cm}^{-3}$ when exposed for 30 minutes at an intensity of radiation 100 mW/cm².

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