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STRUCTURAL, OPTICAL AND ELECTROCHROMIC PROPERTY OF WO_3: MoO_3 THIN FILM PREPARED BY RF MAGNETRON SPUTTERING TECHNIQUE

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ABSTRACT

Tungsten oxide (WO_3) films have been deposited on glass substrates by RF magnetron sputtering method for different MoO_3 concentration. During experiment consternation of MoO3 was varied from 5%, 10% and 15%. We examined the effect of various MoO_3 concentration on structural, optical and electrochromic properties of WO_3 films. To study, crystal structure and other properties XRD analysis carried out, and we found that the deposited films shows amorphous feature. The optical properties were examined using UV–Visible spectrophotometer using wavelength range 300-900 nm. From the transmittance spectra we found that as the concentration of MoO_3 increases the band gap and transmittance value decreases. The electrochromic properties were examined using three electrode electrochemical cell and the potential applied between ±2.2 V. After studying electrochromic property we observed that WO_3:MoO_3 the films have good coloration and bleaching properties and the maximum value for coloration efficiency was 2.303 mm^2/C for 15% MoO_3 concentration.

Contribution/ Originality: This study is one of the very few studies which have investigated structural, optical and electrochromic property of WO_3: MoO_3 thin film by varying concentration of MoO3 to understand the behavior of WO3 thin film.

1. INTRODUCTION

Transition metal oxide thin films are of great technological importance due to their applications in electrochromic devices. Among the transition metal oxides, tungsten oxide (WO_3) is categorized as an n-type semiconductor and it shows good electrochromic properties in both visible and infrared regions, In addition, it has high coloration efficiency with low power consumption and excellent memory effects under open circuit conditions. Electrochromic materials have been studied over four decades after the original work on WO_3 films by Deb [1]; Deb [2]. Electrochromic materials are capable of charging their optical properties when the voltage is applied. Electrochromic of the transitional metal oxides has been widely researched due to their potential applications in smart windows, displays, gas sensors and electro-optic device. In addition, the electrochromic devices are considered as another low-carbon green material. Syrrakou, et al. [3]; Granqvist, et al. [4]; Yang, et al. [5]. A quite rare research has been carried out by changing the concentration of MoO_3 material for electrochromic application. After MoO_3 is introduced into WO_3, the electrochromic effect will be more pronounced. Buch, et al. [6],

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[7]. Electrochromic devices can be classified based on the electrolyte (liquid, organic or organic- inorganic gel electrolyte) [8-10]. In this research paper, we analyse the effect of MoO_3 concentration (5%, 10% and 15%) on structural, optical and electrochromic properties WO_3 films.

2. EXPERIMENTAL

The WO_3 films were deposited on Corning glass substrate by radio frequency magnetron sputtering using WO_3:MoO_3 target in argon atmosphere at the temperature of 100℃. The concentration of MoO_3 varies from 5% to 15%. Initially the chamber was evacuated to a base pressure of 200×10^{-2} Pa. The chamber gas pressure was carefully monitored and kept at 0.0422 Pa m^3/s. During deposition, all the other parameters were kept constant as shown in Table 1.

Table-1. Deposition parameters for preparing WO_3:MoO_3.

Sputter target	**:**	**WO_3:MoO_3**
Target to substrate distance	:	60 mm
Base pressure	:	200×10^{-2} Pa
Chamber pressure	:	0.0422 Pa
Sputter power	:	150 W
Substrate temperature	:	100℃
Time for deposition	:	30 min

Source: Author's experiment data from survey.

Structural properties of WO_3 films were investigated using X-ray diffractometer (Bruker, Model D2 phase) with Cu-Kα radiation having wavelength 1.54 Å. The transmittance and absorption properties of the films were studied in the wavelength range of 300-900 nm using UV-Vis-NIR spectrophotometer (Shimadzu, Model UV-3600 plus). To study the electrochromic property of the film, three electrode electrochemical cell was used. The cyclic voltammetry (CV) measurements were performed for variable scan rates with potential applied between ±2.2 V.

3. RESULTS AND DISCUSSION

3.1. Structural Property

X-ray diffractometer study indicates that all deposited films shows amorphous nature as shown in Figure 1. One of the reasons for this may be low activation energy of sputtering atoms at low substrate temperature. The crystallization of the films cannot occur at a low temperature [11-15]. For electrochromic device applications, Sivakumar, et al. [16] also reported that amorphous nature is preferable.

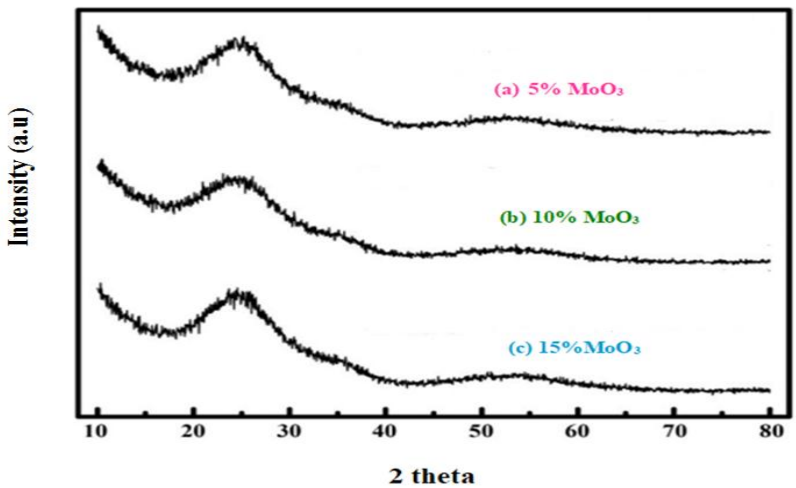

Figure-1. XRD Pattern of WO_3 based film deposited with different concentration of MoO_3.

Source: Author's experiment's result.

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3.2. Optical Property

Transmittance *vs* wavelength curve is one of the most important parts for electrochromic thin films studies. Figure 2 shows the transmittance spectra for the WO_3: MoO_3 film. Due to interference effect, the deposited film shows homogeneous feature and good optical transparency. When the ratio of MoO_3 increases, the transmittance of the film starts to decrease slightly (from 67 to 65%) due to rough surface morphology. By using Tauc [17] the energy band gap calculated from transmittance spectra. From the plot for (αhυ) *vs.* hυ is (not shown over here), it was found that the values of optical band gap decrease as the Mo content increases. The calculated band gap values are listed in Table 2.

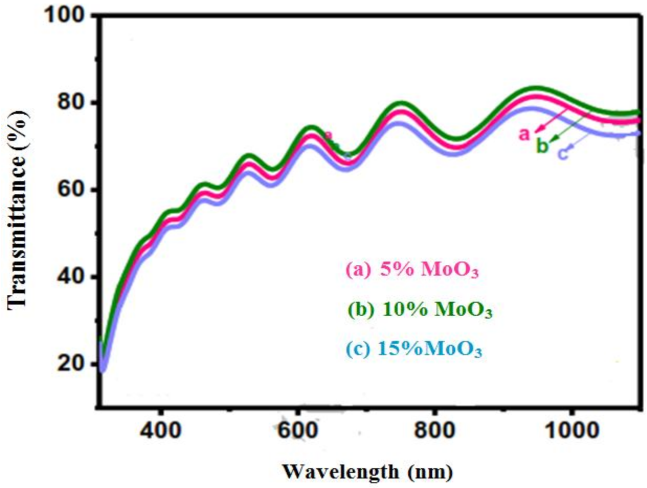

Figure-2. Optical transmittance spectra for WO_3: MoO_3 film.
Source: Author's experiment's result.

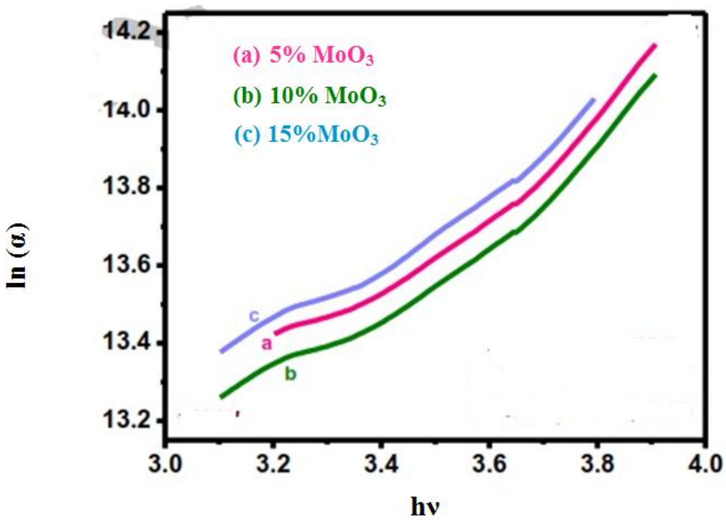

Figure-3. Urbach energy plot spectra for WO_3: MoO_3 film.
Source: Author's experiment's result.

Table-2. Band gap of WO_3:MoO_3 films.

Sample	Band Gap Eg (eV)	Urbach energy Eu (eV)
5% MoO_3	3.14	0.981
10% MoO_3	2.97	1.058
15% MoO_3	2.84	1.161

Source: Author's experiment's result.

Plots of lnα vs. hυ for Nb2O5:MoO3 films are shown in Figure 1. The Eu values were calculated from the slopes of the curves. It is observed that Eu values increases (0.981 eV for 5% MoO3, 1.058 eV for 10% MoO3, 1.161

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eV for 15% MoO3) with increasing MoO3 concentration. The mixing of MoO3 into WO3 matrix results in the rise of additional band tail states, leading to shrinkage of the band gap and the increase of the Urbach energy.

3.3. Electrochromic Property

To study electrochromic properties, the three electrode electrochemical cell was used with 0.5 M $LiClO_4$ into PC (propylene carbonate) as electrolyte, tungsten as working electrode, a platinum wire as a counter electrode and Ag/Agcl as reference electrode. By varying the scan rates (25, 50,100, 150 mV/s), the coloration and bleaching effect observed. Figure 4 shows the cyclic voltammograms when the voltage is applied between ± 2.2 V. When negative potential is applied, the film shows brown color, which is indicative of the intercalation of Li^+ ion. Reversely, when the positive potential is applied, the film exhibits bleached state, indicating the deintercalation process. The cathodic peak is observed when the negative potential is applied and anodic peak is observed upon applying the positive potential. Based on Randles–Servcik equation, we can calculate the diffusion coefficient shown in Table 3. It is observed that the value of D increase with increasing MoO_3 concentration.

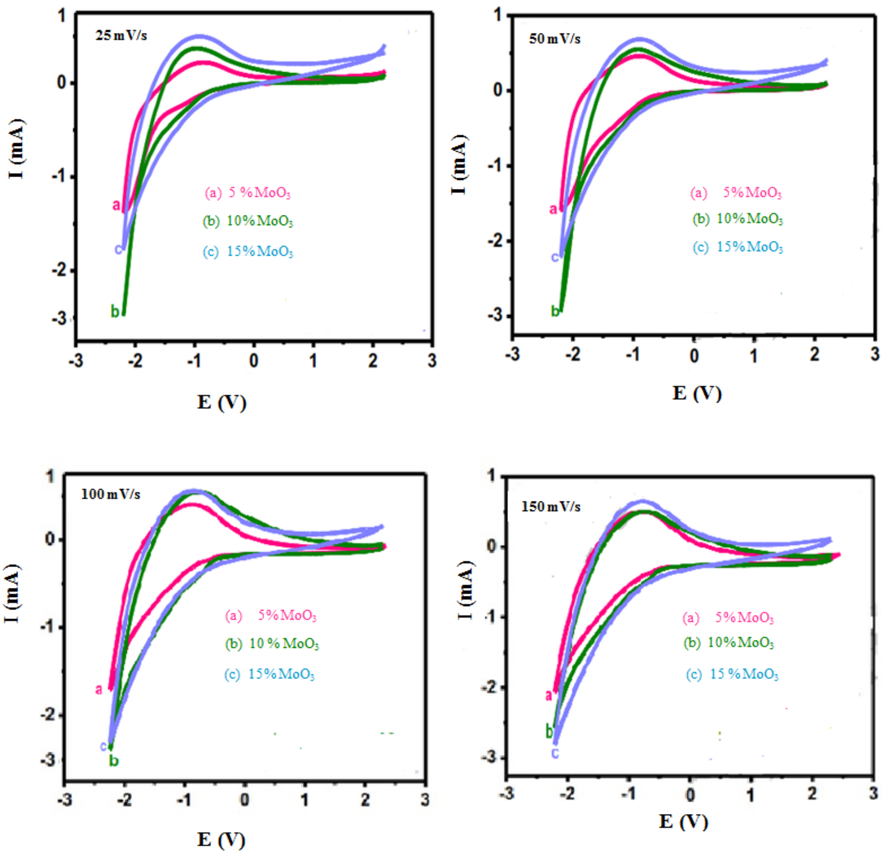

Figure-4. Cyclic voltammograms of films at different scan rates.
Source: Author's experiment's result.

From the transmission data, the OD (optical density) of film is calculated based on the equation $OD = \ln {T_b}/{T_c}$, where, T_b is the transmittance in bleached state and T_c is the transmittance in colored state. It is noted that the optical density increases with increasing MoO_3 concentration at 633nm.

The chronocoulometry was carried out to study the intercalation-deintercalation process of Li^+ ion. For performing chronocoulometry, 10 s was taken as time interval. In this process, the intercalation takes place by a

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diffusion process. Coloration efficiency was calculated using the equation, $CE = \Delta OD / Q_{in}$. Table 4 shows the values of CE for WO_3:MoO_3 films. It was found that as the MoO_3 concentration increases, CE is also increasing.

Table-3. Electrochemical parameters i_{pa}, i_{pc} and D of WO_3:MoO_3 films related with Li^+ ions.

Scan rate (mV/s)	Sample	Anodic peak current i_{pa} (mA)	Diffusion coefficient (D) for i_{pa} [× 10^{-20} (m^2/s)]	Cathodic spike current i_{pc} (mA)	Diffusion coefficient (D) for i_{pc} [× 10^{-19} (m^2/s)]
25	5% MoO_3	0.215	1.001	1.393	4.200
	90:10	0.318	3.141	2.848	13.353
	85:15	0.491	5.230	1.806	7.058
50	95:5	0.460	2.290	1.587	2.725
	90:10	0.544	3.206	2.963	9.498
	85:15	0.686	5.094	2.199	5.230
100	95:5	0.752	3.059	2.024	2.216
	90:10	0.934	4.725	2.963	4.344
	85:15	0.949	4.874	2.834	4.344
150	95:5	0.937	3.169	2.295	1.898
	90:10	0.952	3.266	2.963	3.166
	85:15	1.147	4.746	3.251	3.810

Source: Author's experiment's result.

Table-4. Coloration efficiency of WO_3:MoO_3 films.

Sample	Optical Density (ΔOD)	Amount of charge intercalated Q_{in} (mC/mm^2)	Coloration efficiency CE (mm^2/C)
5% MoO_3	0.052	1.023	0.505
10% MoO_3	0.374	1.922	0.938
15% MoO_3	0.444	3.912	2.303

Source: Author's experiment's result.

4. CONCLUSIONS

In summary, we studied structural, optical and electrochromic properties of WO_3:MoO_3 films. The conclusions are as follows:

1. XRD analysis shows that the deposited film was amorphous in nature.
2. Transmittance study we found that as the concentration of MoO_3 increases the band gap and transmittance value start decreases.
3. After electrochromic study it was observed that the deposited films shows good reproducibility and better reversibility. The maximum coloration efficiency observed for 15% concentration.
4. From all of the above results, we can conclude that the deposited film suitable for electrochromic device applications.

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