Bull. Mater. Sci., Vol. 36, No. 1, February 2013, pp. 45–49. © Indian Academy of Sciences.

Synthesis and characterization of MoO_3–WO_3 composite thin films by liquid phase deposition technique: Investigation of its photochromic properties

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MS received 19 September 2011; revised 5 April 2012

Abstract. **In order to achieve high colouration efficiency, MoO_3–WO_3 composite thin films have been successfully deposited on sodium silicate glass and silicon wafer (111) at 30 °C by a very simple novel wet process known as liquid phase deposition. The deposited films were annealed at different temperatures and characterized by carrying out SEM, EDAX, UV-vis and XRD analyses. The EDAX and SEM analyses support the structure and existence of peaks corresponding to Mo, W and O. X-ray diffraction studies showed that MoO_3–WO_3 is amorphous at lower temperature and turns crystalline at higher annealing temperature and suggested the mixture of two crystalline phases such as orthorhombic–monoclinic. Photochromic properties of the MoO_3–WO_3 composite films were studied in the spectral region 400–1200 nm by illuminating them in polychromatic light. The photochromic behaviour is observed to be more effective in composites films in visible region.**

Keywords. **MoO_3–WO_3 thin films; composites; LPD technique; photochromism.**

1. Introduction

Among advanced materials, photochromic materials have generated considerable interest because of their potential application in fields such as information displays, chemical sensors, modified electrodes, holographic storage devices and others (Brown 1971; Yao *et al* 1992, 1996; Bechinger *et al* 1993; Katsoulis 1998). The interesting aspect of the present work is to prepare composite or mixed oxide materials based on transition-metal oxide compounds and study their photochromic nature. The properties of these materials depend not only on the chemical nature of each component, but also on the interface and synergy between them. Since the charge transfer plays a key role in the photochromism of these materials, it is very important to increase the charge (electrons, holes, and protons) interactions between the two components in either composites or mixed oxides. To realize this, an effort has been made to optimize the two components on a molecular or nanometer scale, which is closely relevant to the constituents, sample history (pre-treatment, preparation and post-treatment), environment (humidity, presence of reducible or oxidizable matters, light-irradiation wavelength, intensity, time, etc).

Based on these, many novel composite or mixed oxide materials with improved photochromism, visible-light colouration, reversible photochromism, multicolour photochromism or, possibly, fast photoresponse, have been prepared during the last two decades. This may underscore the opportunity of using these composite and mixed oxide materials in photonic applications. MoO_3 and WO_3 are well-known photochromic materials that exhibit photochromism under UV-light irradiation, whereas the composites of MoO_3–WO_3 show colouration under visible light (Tao and Jiannian 2006) and have more intense blue colour when compared to pure MoO_3 or WO_3 (Deb and Chopoorian 1966; Deb 1969; Zhang *et al* 1994). The fabrication of such materials may rely on the principles of molecular self-assembly and self-organization. Most likely, thin film technologies will play a major role in future applications. Although there have been some reports (Mirkin 1961; Sohn *et al* 2005) on photochromic composite films based on both inorganic components obtained by various physical and chemical methods, these techniques, however, have certain disadvantages, one of which, is the difficulty to obtain large-area films with highly ordered structures. Hence, a simple novel technique known as LPD (Nagayama *et al* 1988; Hashinuma *et al* 1991; Avellaneda César and Bulhões 2003; Begum and Ahmed 2008) has been used to develop homogeneous composite thin films with good mechanical and chemical stability. The LPD technique has proved to be a powerful and versatile means for assembling multicomposite supramolecular structures with good control over the layer composition and thickness.

2. Experimental

2.1 *Preparation of MoO_3–WO_3 thin films by LPD*

Mixed oxide films based on Mo and W (1·95 g each) were successfully deposited on glass and Si wafer by LPD

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technique. The precursor solution for deposition of MoO_3–WO_3 was prepared by dissolving Mo (99·9% pure, Fluka chemicals) and W (99·9%, Aldrich chemicals) powder separately in 30% ice-cold solution of H_2O_2 and acetic acid. The reaction mixtures were kept overnight at a temperature ranging from 0 to 12 °C. The solutions were then filtered and mixed with 0·5% aqueous solution of $NH_4F{\cdot}HF$ (ammonium bifluoride). These solutions were mixed together in desired proportion {Mo–W (90:10) and Mo–W (80:20) at %}. The sodium silicate glass and Si wafer after degreasing and washing with double-distilled water were immersed into the treatment solution and suspended vertically. Boric acid solution ($\sim$0·05 mol/dm^3) was added, to act as a free F^- scavenger and shift the equilibrium to one side. The solution was maintained at 30° for 40 h, after which the sample was taken out from the treatment solution, washed with distilled water and dried at room temperature. Annealing of deposited film was carried out at different temperatures.

3. Characterization of deposited films

The surface morphology, elemental analysis and X-ray diffraction studies were carried out on the mixed oxide films deposited over Si wafer. However, for optical and photochromic properties, the film deposited on glass substrate were used. The surface morphology and elemental analysis of deposited films were studied using scanning electron microscope and EDAX (type: Leica Cambridge Ltd./Leica S440i for SEM and Oxford link software for EDAX). X-ray diffraction analysis was obtained from an X-ray diffractometer (type: PW 3710 based tube anode: CuKα_1: 1·54056 and Kα_2: 1·54439). Optical and photochromic properties were studied by using UV-vis-NIR, scanning spectrophotometer (type: Shimadzu-2003, Japan) in the wavelength range 400–1200 nm.

4. Results and discussion

4.1 *EDAX analysis*

The elemental analysis of mixed MoO_3–WO_3 thin films (Mo–W20) was ascertained from EDAX spectra (figure 1). The EDAX data confirm existence of peaks corresponding to Mo, W and O atoms. This observation supports the existence of MoO_3 and WO_3 phases in mixed oxide thin films.

4.2 *Structure and morphology*

Figure 2 shows XRD patterns of as deposited and annealed films, annealed at 200 °C and 500 °C, respectively. XRD spectra presented in figures 2(b) and (c) manifest very weak and diffused peaks located at 2θ = 20–40° which is evidence for amorphous structure of MoO_3–WO_3 mixed films. But there are two major peaks observed (figure 2(b)) around 2θ = 7 and 26° at 200 °C which may be due to the substrate.

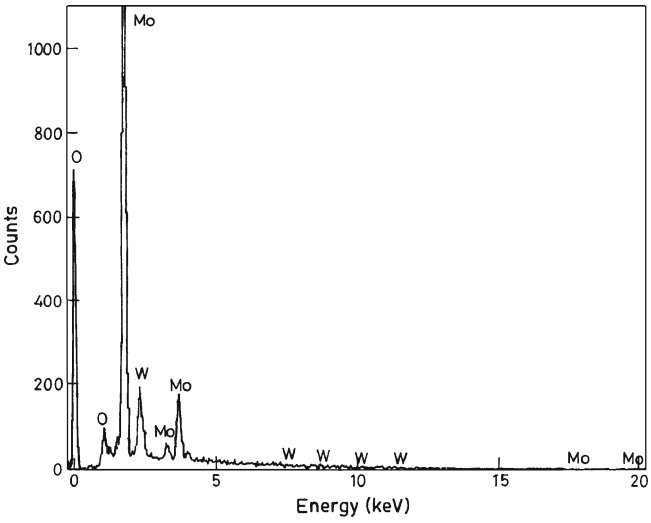

Figure 1. EDAX spectra of MoO_3–WO_3 (80:20 at%) composite film.

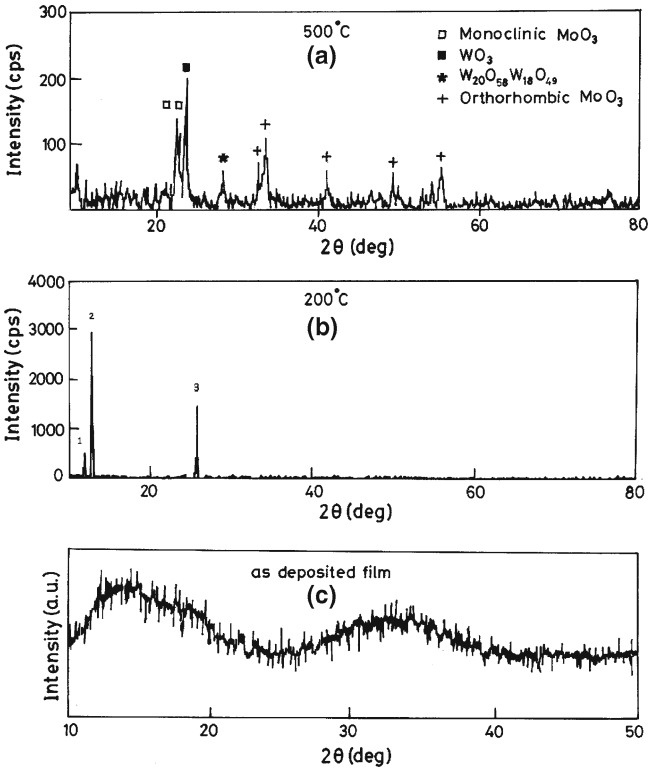

Figure 2. XRD pattern of MoO_3–WO_3 (80:20 at%) composite films; film annealed at **(a)** 500 °C, **(b)** 200 °C and **(c)** as deposited film.

After annealing the mixed films at 500 °C, three strong peaks are seen (figure 2a) in this range, at 2θ = 22·87, 23·306 and 24·110. XRD data and d-spacing values correspond to the observed peaks in the spectrum of mixed films annealed at 500 °C (table 1).

XRD data reveal that most of the peaks are assigned to molybdenum oxide and only two of them are attributed to

WO_3 or tungsten sub-oxides (Geshava *et al* 2007). This suggests that tungsten oxide fraction is still amorphous in mixed films. The two peaks at $2\theta = 22{\cdot}87$ and $23{\cdot}36°$ are attributed to monoclinic MoO_3 and about five lines at ($2\theta = 33{\cdot}060$, $33{\cdot}940$, $49{\cdot}690$, $55{\cdot}490$ and $55{\cdot}660$) are attributed to orthorhombic MoO_3. This suggests that molybdenum oxide fraction in the crystallized mixed oxide films represents a mixture of two crystalline phases—orthorhombic and monoclinic. XRD study shows that MoO_3–WO_3 films are amorphous at 200 °C and turn crystalline after annealing at 500 °C. Since WO_3 states have amorphous network, the molybdenum oxide transforms through crystallization into two crystalline phases.

To observe the surface morphology, scanning electron micrographs of the samples were recorded. Figures 3 and 4 show SEM of Mo–W10 (90:10 at%) sample before and after annealing at 500 °C. It is observed that the as-deposited film has non-uniformly covered the substrate. The excess solute gets deposited on some part of the substrate. The annealed film has rod-like morphology with partially an irregular agglomeration due to amorphous WO_3 fraction. The segregation of WO_3 in mixed oxide film is also confirmed through photochromic behaviour of the film annealed at 500 °C. The enclosed observation of the annealed film surface reveals that the grain size is not uniform with different contrasts. The diameter of the grain varies from 100–500 nm. Figures 5 and 6 show similar morphology for Mo–W (80:20 at%) sample before and after annealing at 500 °C.

Table 1. XRD data and d-spacing values of MoO_3–WO_3 (80:20 at %) composite film.

XRD line [2θ]	d-spacing	Attributed to
22·87	3·8852	Monoclinic MoO_3 (Geshava *et al* 2007)
23·36	3·8048	Monoclinic MoO_3 (Geshava *et al* 2007)
24·110	3·6881	WO_3 (Geshava *et al* 2007)
28·540	3·1249	$W_{20}O_{58}$ or $W_{18}O_{49}$ (Geshava *et al* 2007)
33·940	2·6390	Orthorhombic MoO_3 (Geshava *et al* 2007)
49·690	1·8332	
55·490	1·6546	
55·660	1·6449	

4.3 *Photochromic property*

The photochromic properties of thin films are confined to amorphous region. Therefore, pure MoO_3 or WO_3 films are less transparent at low annealing temperature and more transparent at higher temperature (Geshava *et al* 2003; Geshava and Ivanova 2006; Ahmed 2008). However, when the mixed oxide films are annealed up to 500 °C, MoO_3 becomes crystalline but WO_3 fraction still be amorphous in nature. The maximum transmittance value of mixed oxide films would correspond to the transmittance of MoO_3 but not WO_3 under visible light. The maxima and minima in the transmittance

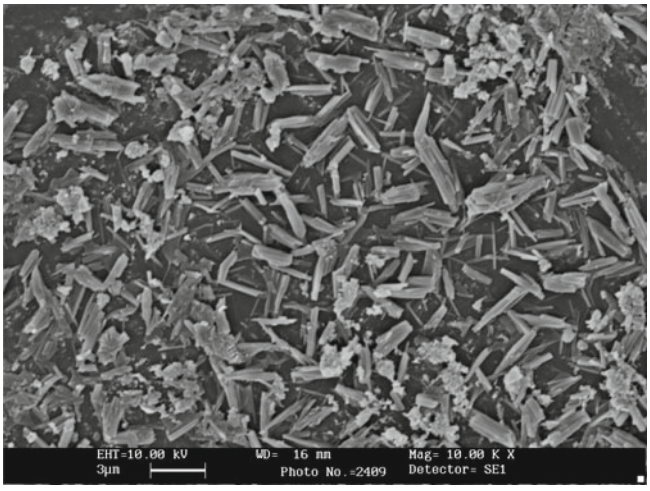

Figure 4. SEM of Mo–W10 (90:10) thin film annealed at 500 °C.

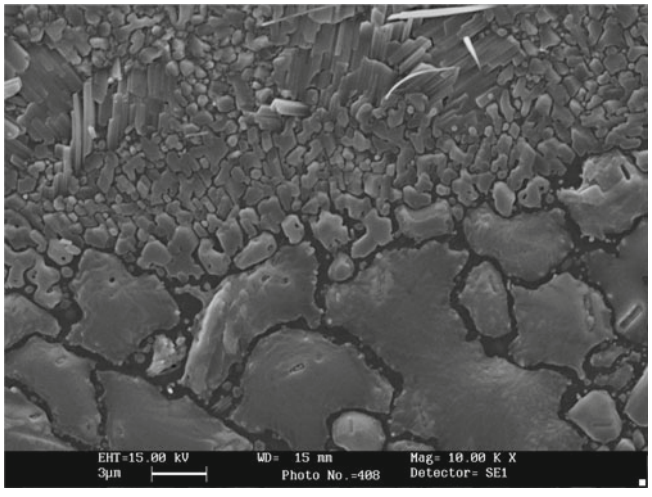

Figure 3. SEM of as-deposited Mo–W10 (90:10) thin film.

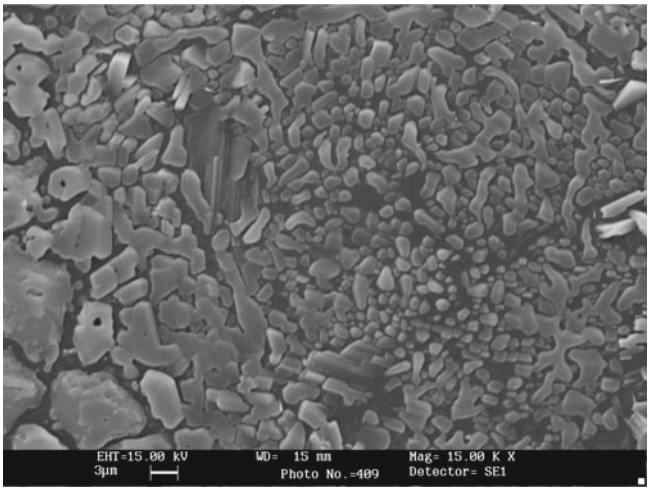

Figure 5. SEM of as-deposited Mo–W20 (80:20) thin film.

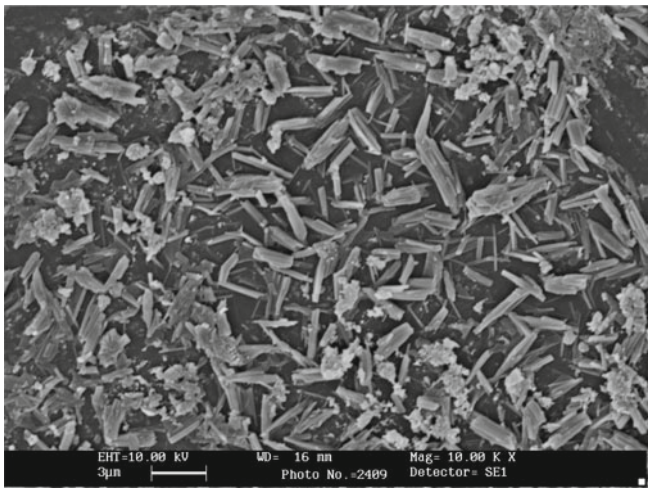

Figure 6. SEM of Mo–W20 (80:20) thin film annealed at 500 °C.

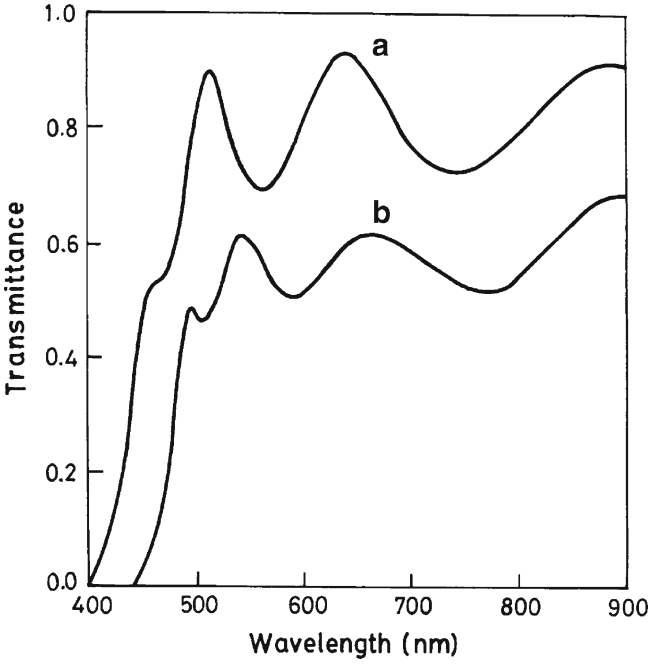

Figure 7. UV-vis transmittance spectra: **(a)** Mo–W10 and **(b)** Mo–W20 thin films.

spectra of the film arise due to multiple reflections in the film. The transmittance decrease with increasing concentration of WO_3 in mixed oxide films as shown in figure 7 clearly indicates that the pure MoO_3 film is more transparent for the spectral region above 450 nm.

Figure 8 shows UV-visible absorption spectra of mixed oxide thin films at different irradiation times under visible light. It was found that the intensity of blue colour increases with increasing irradiation time.

Photochromic effect can be considered as due to electron transitions between multivalent metallic states such as $Mo^{5+} \rightarrow Mo^{6+}$, $W^{5+} \rightarrow W^{6+}$ and $Mo^{5+} \rightarrow W^{5+}$, $Mo^{6+} \rightarrow W^{6+}$. Molybdenum multivalent states are situated at lower energy with respect to tungsten state; therefore, the transfer of electrons between these levels is likely probable. Summarizing, in the mixed oxides, electron transition takes place between two kinds of metal sites with different valences (W^{6+}, W^{5+}, W^{4+}, Mo^{6+}, Mo^{5+}, Mo^{4+}) or with different structural surroundings (Faughnan and Crandall 1977; Hiruta *et al* 1984; Ivanova *et al* 2005). In our present studies, electronic states like W^{6+}, W^{5+} and the corresponding lower energy Mo multivalent sites in the electronic structure of mixed oxide films were considered in order to study their photochromic properties. The presence of two types of metallic site assumes stronger absorption of light due to more intense electron transition not only between different valence metallic sites but also between the same metal sites. Increasing the ratio of MoO_3–WO_3 induces intensive electronic transition and results in good photochromic properties.

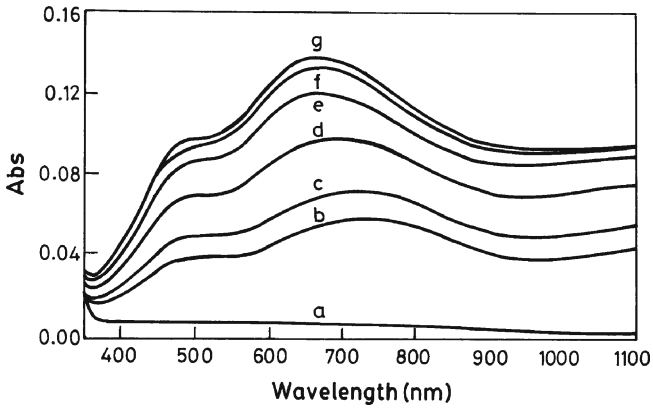

Figure 8. UV-vis absorption spectra at different irradiation times **(a)** before irradiation, **(b)** after 10, **(c)** 20, **(d)** 30, **(e)** 40, **(f)** 50 and **(g)** 60 min.

5. Conclusions

The MoO_3–WO_3 films at different compositions {Mo–W (90:10) and Mo–W (80:20) at%} were deposited on glass and Si wafer by LPD technique to optimize the two components on nanometer scale. The deposited films are annealed at different temperatures and characterized. The photochromic property of the films was studied.

EDAX spectra reveal elementary analysis of the films by exhibiting peaks corresponding to Mo, W and O atoms. XRD analysis supports crystallinity of the films at higher temperatures with the diffraction peaks corresponding to MoO_3 and WO_3. The major peaks were due to MoO_3. This finding suggests the amorphous nature of WO_3 in mixed films. The result also shows the two crystalline phases—orthorhombic and monoclinic of MoO_3 in mixed oxide films. SEM analysis reveals that the microstructure of as-deposited film is non-uniform and the film annealed at 500 °C has rod-like structure with the diameter of the grains ranging

from 100–500 nm. The UV-vis transmittance spectra reveal that the mixed oxide films are less transparent when compared to pure MoO_3 films. The maxima and minima in the transmission spectrum of the film arise due to multiple reflections in the film. The transmittance value decreases with increasing concentration of WO_3. Photochromic property of films was studied under visible light irradiation. The intensity of blue colour increases with increase in irradiation time. Photochromic effect is due to electron transitions between multivalent metallic states that are present in mixed oxides.

Acknowledgements

The authors are grateful to Dr K R Gunasekar, Department of Instrumentation, Indian Institute of Science, Bangalore and Dr Kannan, Materials Research Centre, Indian Institute of Science, Bangalore for XRD, SEM and EDAX data.

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