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Optical properties of thin films of WO₃, MoO₃ and mixed oxides WO₃/MoO₃

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Abstract. Optical properties of thin films prepared by thermal evaporation of WO₃, MoO₃, and mixed oxides WO₃/MoO₃, have been studied. Satisfactory derivation of the refractive and absorption indices from the measured normal incidence transmittance of the films was achieved for the films of WO₃ and MoO₃. However, for films of the mixed oxides this was not possible, especially for the spectral region in which these films were absorbing. Rutherford backscattering spectrometry (RBS) measurements on the films revealed that the films of WO₃ and MoO₃ were fairly uniform but the films prepared from the mixed oxides were chemically inhomogeneous. In fact, we were able to fit the RBS data for the mixed-oxide films by assuming that the Mo content in the film decreased (while the W increased) along the direction of growth of the film (i.e. from the substrate side of the film to its surface).

1. Introduction

Tungsten oxide is probably the most thoroughly investigated representative of a group of materials that are known as chromogenic. Their most distinct feature is that they can be continuously switched between two different optical states. This property is quite interesting, for example, for 'smart window' or display applications, and has been studied extensively [1–4]. Films of molybdenum oxide and mixed oxides such as WO₃ and MoO₃ are known for their chromogenic behaviour [4–7]; however, there are only a few published reports on these materials.

The purpose of this study is to determine the optical properties of thin films of WO₃, MoO₃, and mixed oxides WO₃/MoO₃. The starting materials used in the preparation of mixed-oxide films were hot-pressed pellets of mixtures of WO₃ and MoO₃ powders with composition $(1 - x) \text{WO}_3 - x \text{MoO}_3$, where $x = 0.05, 0.10, 0.15, 0.20, 0.25,$ and 0.30 . Chemical analysis were performed using RBS. The method [8] used in determining the optical constants (refractive and absorption indices) of thin dielectric films requires measurements at normal incidence of the transmission from two films of different thicknesses, for a given material. The transmission data on a film, measured in the spectral region in which the film was nonabsorbing, were used in determining the thickness of the film [9]. Hence, the properties of the films in the two spectral regions (in which the films are absorbing and nonabsorbing) are reported under two different sections.

2. Experiment

Thin films were deposited simultaneously on fused silica and carbon substrates in a Leybold model L560 box coater pumped by a turbomolecular pump. The system was pumped to

a base pressure of less than 10^{-6} mbar. Oxygen was readmitted to raise the pressure to 1×10^{-4} mbar which was kept constant during film deposition. Molybdenum boats were used to evaporate MoO_3 and tungsten boats were used for WO_3 and the mixed oxides. Substrates were rotated while deposition took place. The rate of evaporation (0.4 nm s^{-1}) was controlled by a quartz crystal thickness monitor and rate controller. The source to substrate distance was about 40 cm. Films which varied in thickness from about 200 to 600 nm were deposited under similar evaporation conditions. All the films were deposited on substrates that were maintained at ambient temperature in the vacuum chamber. These films are expected to be amorphous in nature [1–7].

After the films were deposited, they were removed from the coating chamber and exposed to the ambient atmosphere, prior to measurement of optical properties and RBS. Transmission measurements on the films were made over the 300–850 nm wavelength range using a double-beam Bausch and Lomb spectrophotometer, model Spectronic 2000. The optical constants were determined from the transmission spectra. The RBS was used with 2 MeV He^{2+} , which measured the stoichiometry of the films with an accuracy greater than $\pm 3\%$, as a large beam spot (diameter > 2 mm) was used. A gold film deposited on a silicon substrate was used in calibrating the channel-energy scale of the detection system. The system has been described elsewhere [10]. The system resolution for the used He^{2+} beam, including detector resolution, straggling, and electronic setup was 17 keV. The collected RBS spectra were then fitted by a code RUMP [11] to find the relative concentrations of various elements in the samples.

3. Results

3.1. Refractive indices of the films in the nonabsorbing region

A method [9] for determining both refractive index and the thickness of a transparent film on a transparent substrate from measurement of transmittance, T , at normal incidence was used in the present work for the spectral region in which the films were nonabsorbing. Figure 1 is an example of the transmittance curves for a film of MoO_3 on a fused silica substrate of thickness 433 nm. The transmission spectrum of an uncoated fused silica substrate is also shown in figure 1. The maxima and minima in the transmission spectrum of the film arise due to multiple reflection in the film. For a perfectly nonabsorbing film on a transparent substrate, the maximum transmittance value would correspond to the transmittance of the uncoated substrate. According to the above, it appears from figure 1 that the MoO_3 film is nearly transparent for the spectral region above 450 nm. The method [9] used in determining the refractive index of a film is valid for the spectral region in which the films are transparent. Therefore, for the films of MoO_3 the spectral region covered ranges from 450 nm to 850 nm. Similarly, the spectral region covered ranges from 400 to 850 nm for the WO_3 films and 450 to 850 nm for the mixed-oxide WO_3/MoO_3 films.

From the measured T (figure 1), the dispersion curve (represented by dots) shown in figure 2 was obtained using the formula for T for a single transparent film on a transparent substrate [9], beginning with an approximate film thickness estimated from the positions of the consecutive minima and maxima of the T curve and then adjusting this value in an attempt to obtain a closed dispersion curve [9]. Figure 2 is typical of the results for ten different MoO_3 films of different thicknesses. Figure 2 shows the multiple solutions and proper closure of the curve. The average dispersion is shown by the solid line in figure 2.

Similar results were obtained for the films of WO_3 and the mixed oxides. Transmission and dispersion curves, for a film of mixed oxides of thickness 322 nm, are shown in figures 3

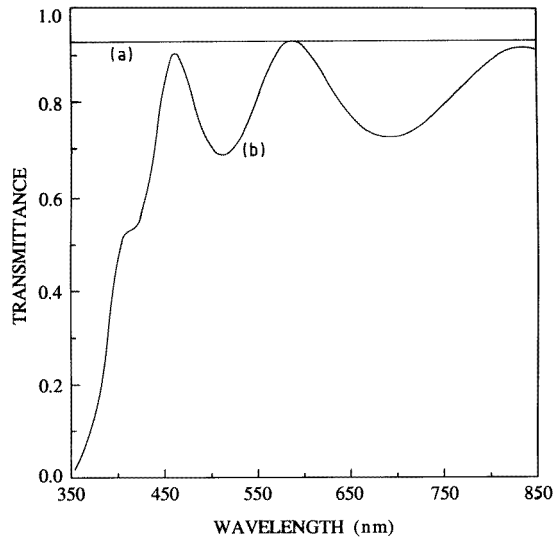


Figure 1. Measured normal incidence transmittance from (a) an uncoated fused silica substrate and (b) an MoO₃ film of thickness 433 nm, on a fused silica substrate.

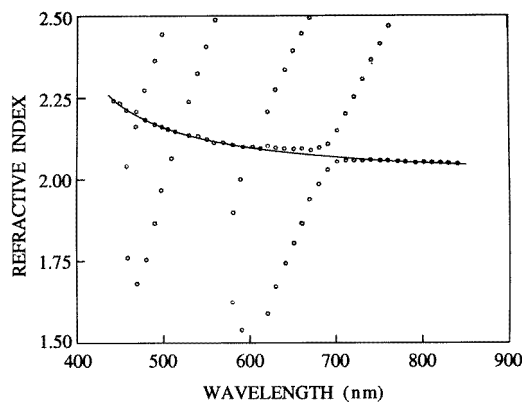


Figure 2. Dispersion curve (shown by dots) for an MoO₃ film showing multiple solutions and proper continuity [13], derived from the data of figure 1. The solid line is the average dispersion obtained from ten different films of MoO₃ of different thicknesses.

and 4, respectively. In the spectral regions in which the films are nonabsorbing, satisfactory results could be obtained for all the films by treating each of the films as a single uniform film with nearly parallel faces.

3.2. Optical constants of the films in the absorbing region

A method for the determination of the refractive (n) and absorption (k) indices of thin dielectric films on transparent substrates (with refractive index n_s) was reported earlier [8]. It requires measurement at normal incidence of the transmittance (T_1 and T_2) from two films of a given dielectric of different thicknesses (d_1 and d_2) as a function of wavelength (λ).

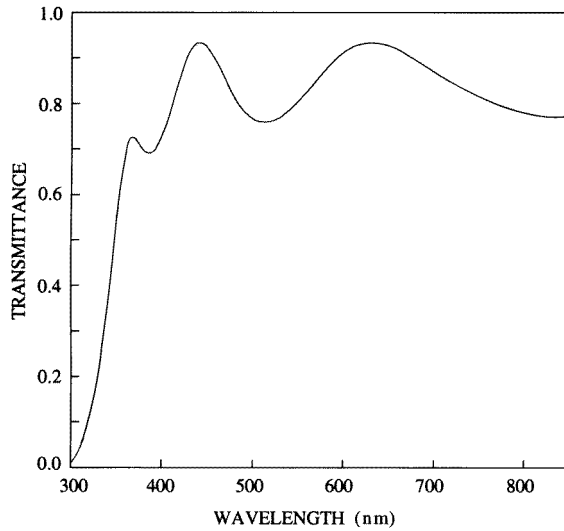


Figure 3. Normal incidence transmittance from a mixed-oxide film of thickness 322 nm, on a fused silica substrate, prepared from initial composition of 0.75 WO₃-0.25 MoO₃.

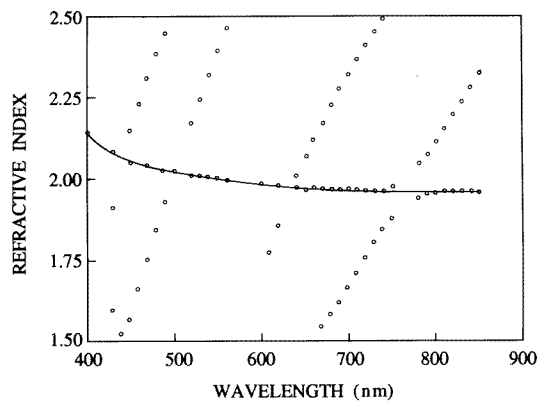


Figure 4. Dispersion curve (shown by dots) for a mixed-oxide film showing multiple solutions and proper continuity [13], derived from the data of figure 3. The solid line is the average dispersion obtained from four different films of mixed oxides of different thicknesses and prepared from 0.75 WO₃-0.25 MoO₃.

Then, T_1 and T_2 may be written in function form as

$$T_1 = F_1(n, k, n_s, \lambda, d_1)$$

and

$$T_2 = F_2(n, k, n_s, \lambda, d_2).$$

If T_1 and T_2 from two films of given material of thicknesses d_1 and d_2 are measured as a function of λ , d_1 , d_2 , and n_s are known, then, in principle, n and k can be determined from the above relations for T_1 and T_2 . An expression giving an explicit value of n and k cannot be obtained [8]. However, the equations for T_1 and T_2 can be solved by a numerical method [8].

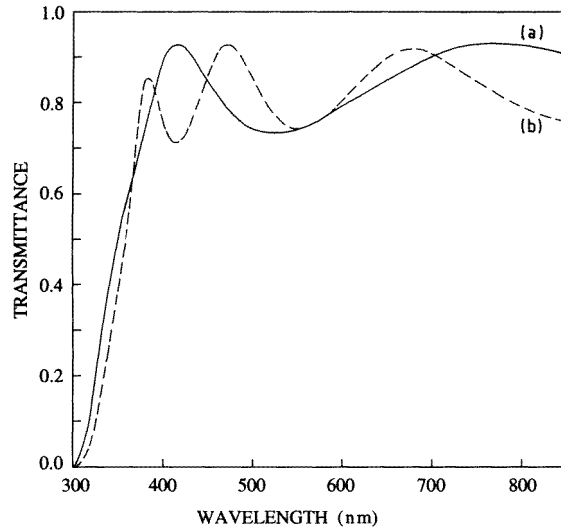


Figure 5. Measured spectral transmittance curves for a set of WO₃ films deposited on fused silica substrates of thickness about 192 nm (curve a) and 337 nm (curve b).

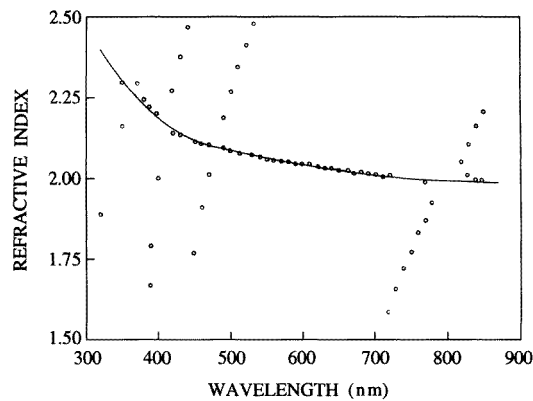


Figure 6. Dispersion curve for WO₃ films showing multiple solutions and proper continuity, derived from the data of figure 5.

This method was used in the present work. Figure 5 is an example of the transmittance curves for two films of WO₃ of thicknesses 192 nm (curve a) and 337 nm (curve b). From the measured transmittance curves (figure 5) the dispersion curve ($n-\lambda$) shown in figure 6 was obtained. Figure 6 is typical of the results for a different set of two films of WO₃ of different thicknesses. Figure 6 shows multiple solutions and proper closure of the curve and suggests that the films are uniform with smooth surfaces [12, 13]. Average dispersion is shown by the solid line in figure 6. The average absorption curve ($k-\lambda$) for the films of different thicknesses is shown in figure 7.

Similar results were obtained for the films of MoO₃. These are presented in figures 7 and 8. Satisfactory results could not be obtained for films of the mixed oxides. The mixed-oxide films were prepared from WO₃ and MoO₃ powders with composition $(1-x)$ WO₃- x

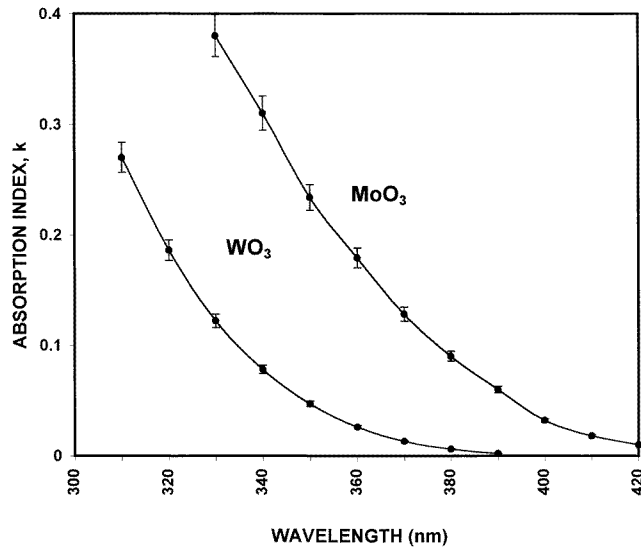


Figure 7. Average absorption curves for different films of WO_3 and MoO_3 . The vertical bars show the range within which the individual curves fell.

MoO_3 , where $x = 0.05, 0.10, 0.15, 0.20, 0.25,$ and 0.30 . Four films were prepared with different thicknesses for each value of x . For a given x , transmission data from different sets (each of two films, as required by the above method) were used in an attempt to extract n and k . However, for all the sets we were unable to obtain acceptable solutions for the n and k . This holds true for all the values of x stated above. A basic requirement of the method used in determining the optical constants is that two films of different thickness should have identical optical properties. The RBS results (discussed later) suggest that the above requirement may not have been met in the case of the mixed-oxide films, and thus proper solutions for the n and k may not be possible.

For comparison the n - λ curves for the films of WO_3 , MoO_3 , and mixed oxides WO_3/MoO_3 (for $x = 0.10$ and 0.30) are shown in figure 8. The curves for the other values of x are not shown in figure 8. However, a general trend, in which the refractive index decreases with an increase in the value of x , was observed.

Data on absorption in the films were analysed in view of the theory developed for amorphous materials by Davis and Mott [14]

$$n\alpha h\nu = B(h\nu - E_0)^m$$

where $\alpha = 4\pi k/\lambda$ is the absorption coefficient at the wavelength λ , $h\nu$ is the corresponding photon energy, E_0 is the optical energy gap, B is a constant, and $m = 2$ or 3 . It is reported that a cubic relation gives the best fit to data on some amorphous semiconductors and multicomponent oxide glasses [15–17]. In the present case $m = 3$ gives a better fit to the data as compared with $m = 2$. Therefore the cubic fits alone (with the data based on figures 7 and 8) are shown in figure 9, with $B = 1.16 \times 10^6 \text{ cm}^{-1} \text{ eV}^{-2}$ and $E_0 = 3.04 \text{ eV}$ for the films of WO_3 , and $B = 1.25 \times 10^6 \text{ cm}^{-1} \text{ eV}^{-2}$ and $E_0 = 2.70 \text{ eV}$ for the films of MoO_3 . The values of B are within the range that is predicted by the theory [14].

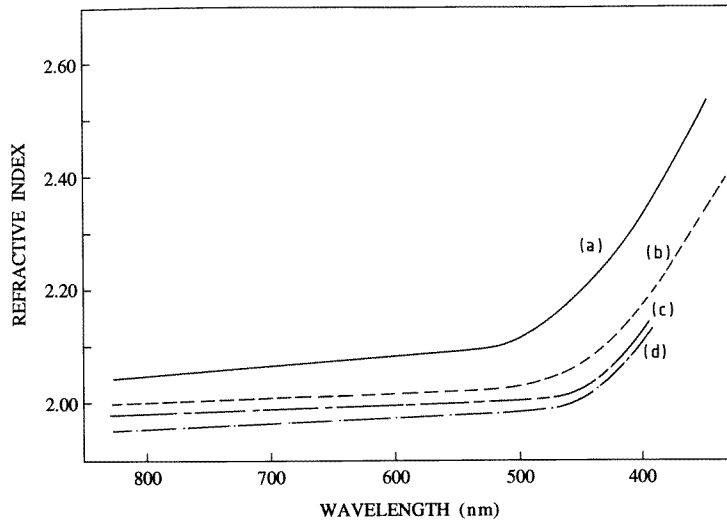


Figure 8. Comparison of dispersion curves for films of (a) WO₃, (b) MoO₃ and mixed oxides with (c) $x = 0.10$ and (d) $x = 0.30$.

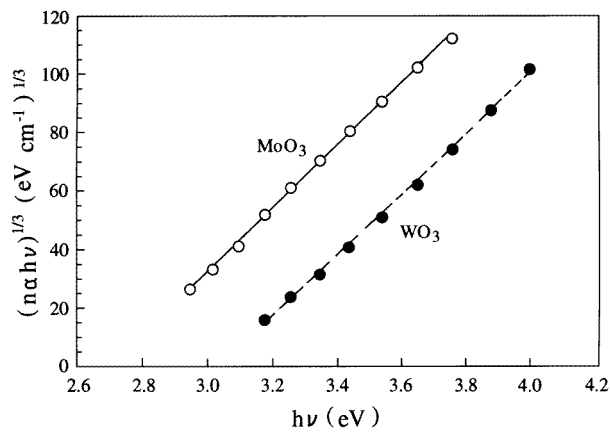


Figure 9. Plots of $(n\alpha h\nu)^{1/3}$ against $h\nu$ for the data based on figures 7 and 8 for films of WO₃ and MoO₃.

3.3. Rutherford backscattering spectrometry

A typical spectrum from a film of WO₃ deposited on a carbon substrate is shown in figure 10, where the backscattering yield of 2 MeV He²⁺ ions is plotted as a function of the energy of the scattered ions (\propto channel number). The data represented by dots are overlaid with a corresponding theoretical fit as generated by the code RUMP [11]. A single homogeneous film on a substrate is assumed for the generation of the theoretical fit. Similar spectra for films of the molybdenum oxide and mixed oxides are shown in figures 11 and 12, respectively. It is clear from figures 10 and 11 that good fits to the data are obtained for the films of WO₃ and MoO₃. However, for all the films of the mixed oxides, it has

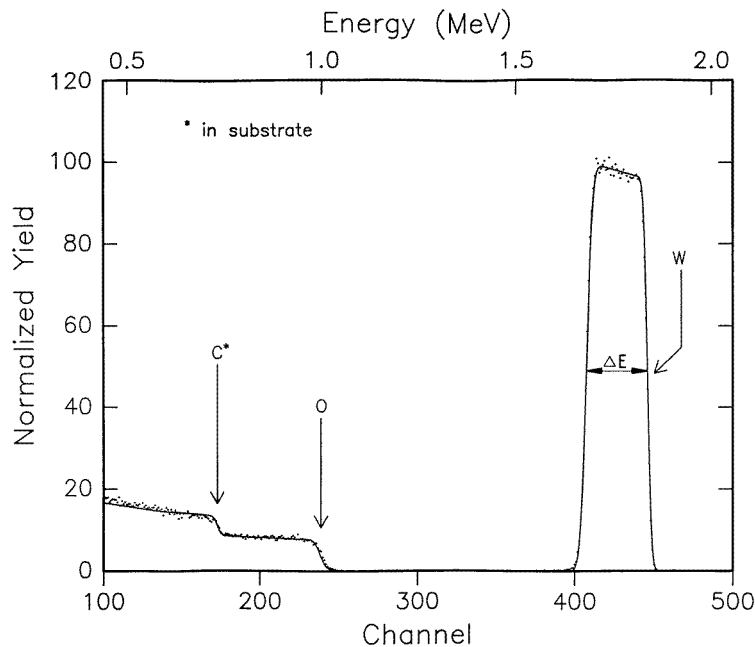


Figure 10. Rutherford backscattering spectrum (2 MeV He^{2+} analysis) of a WO_3 film on carbon substrate (\cdots) overlaid with the corresponding theoretical fit (—) as generated by the code RUMP [11], assuming a uniform single film.

been found impossible to fit the results using the single-homogeneous-layer model (see for example figure 12). This suggests that the films of the mixed oxides may be chemically inhomogeneous. In fact, we were able to obtain a good fit to the data (figure 13) by assuming that Mo content in the film decreased (while the W content increased) across the film from substrate to its surface. Details of the generation of the theoretical fit (figure 13) are briefly described below. An inhomogeneous layer (or film) was considered as an ensemble of P sublayers of different composition with thicknesses equal to d/P , where d is the film thickness. $P = 5$ was used for the results shown in figure 13. The atomic concentrations of the sublayers used in the generation of the fit (by the code RUMP [11]) shown in figure 13 are given in table 1. In order to obtain a smoother curve than the one shown in figure 13, one needs to use a value of P that is much higher than 5.

4. Discussion

Films of the mixed oxides were found to be chemically inhomogeneous. This inhomogeneity may arise because of the differences in the vapour pressure of the MoO_3 and WO_3 , at a given temperature. The vapour pressure MoO_3 is much higher than that of WO_3 [18]. Therefore, the ratio Mo:W for the material left in the evaporation boat is expected to decrease with time and hence this will result in a decrease in the ratio across the film from the substrate to its surface (see table 1). Moreover, the relative atomic concentration of Mo in the films was found to be much smaller than the same in the starting material from which the film was prepared (table 1). This may perhaps be due to a loss of Mo at the time the

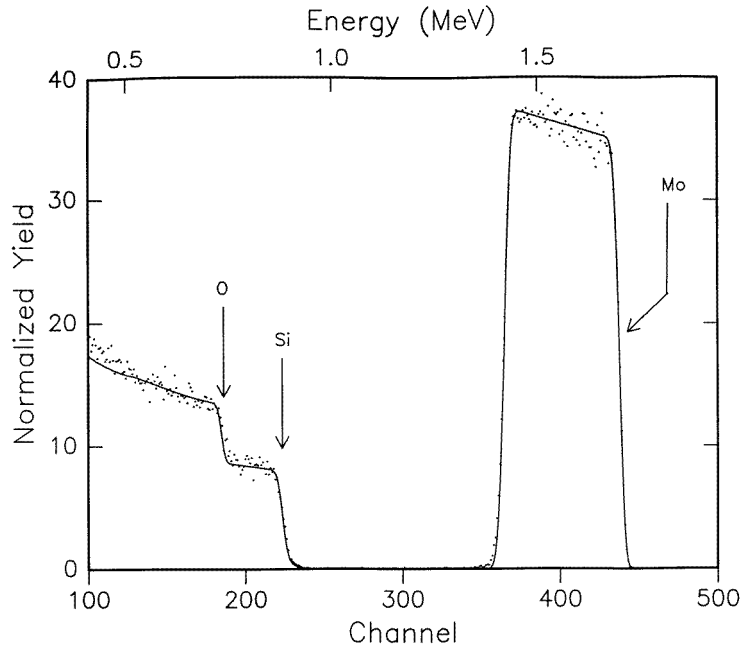


Figure 11. Rutherford backscattering spectrum (2 MeV He²⁺ analysis) of an MoO₃ film on fused silica substrate (· · · · ·) overlaid with the corresponding theoretical fit (—) as generated by the code RUMP [11], assuming a uniform single film.

Table 1. Relative atomic concentrations of the five sublayers (sublayer 1 is the one adjacent to the substrate and sublayer 5 is the outermost layer) for a film of mixed oxides prepared from an initial composition of 0.75 WO₃–0.25 MoO₃ (that is, relative atomic concentration of W—0.188, Mo—0.063 and O—0.75), used in the code RUMP [11] for generation of the fit given in figure 13.

Sublayer number	Tungsten	Molybdenum	Oxygen
1	0.182	0.040	0.778
2	0.204	0.021	0.775
3	0.221	0.014	0.765
4	0.227	0.008	0.765
5	0.229	0.005	0.766

source material was being degassed. During degassing a shutter between the source and the substrate prevented deposition on the substrate.

In spite of the observations that the films of the mixed oxides were chemically inhomogeneous, the optical measurements made in the spectral region in which the films are nonabsorbing suggest that these films could be treated as uniform single films on substrates. Effects due to the presence of inhomogeneities in these films on the optical properties (in the nonabsorbing region) may not be pronounced because MoO₃ and WO₃, the two components of the mixed oxides, have refractive indices that are close to each other (within 5%, see figure 8).

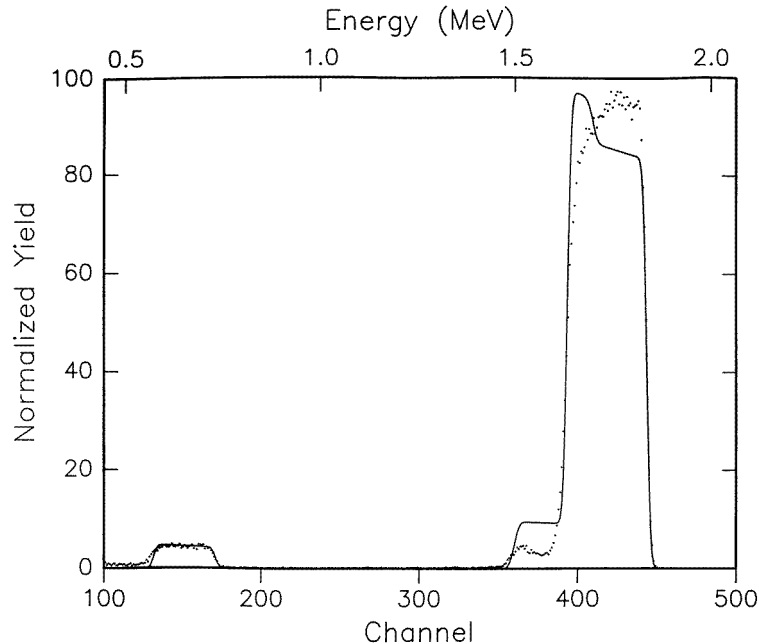


Figure 12. Rutherford backscattering spectrum (2 MeV He^{2+} analysis) of a mixed-oxide film (prepared from 0.75 WO_3 -0.25 MoO_3) on carbon substrate (\cdots) overlaid with a curve (—) as generated by the code RUMP [11] based on the assumption of a uniform single film. The assumption of a homogeneous layer seems insufficient to correctly explain the measured spectrum.

Similar optical measurements on films with structural inhomogeneities (e.g., films of ZrO_2 [19]) in a previous study suggest that these could not be treated as single uniform films on substrates. Thermally evaporated ZrO_2 films are known to be inhomogeneous [19]. This results from the fact that the films have a columnar structure. The columnar diameters tend to increase or decrease with distance from the substrate side of the film. The voids existing between columns tend to adsorb moisture from the atmosphere. An immediate prediction of these inhomogeneities is that there will be a variation in film properties (such as refractive index and density, in a way similar to those observed in films of the mixed oxides) along the direction of growth in such films. In this case much larger differences exist between the refractive indices (n) of the component materials, ZrO_2 ($n \sim 2.2$) and moisture ($n \sim 1.3$), compared with those found for the component materials of the mixed-oxide films.

The absence of any meaningful solutions for n and k in the absorbing region for the mixed-oxide films can again be explained in terms of large differences in n (and k) for the two components, WO_3 and MoO_3 , seen in figures 7 and 8.

Moreover, the refractive index of a mixed-oxide film decreases with an increase in x and is observed to be less than that for films of either WO_3 or MoO_3 (figure 8). One would have expected this value to lie in between the corresponding values for the WO_3 and MoO_3 films, provided that there were no major changes in the packing densities of the films. However, some changes in the packing densities of the films were detected by RBS, as discussed below. The energy width, i.e. energy loss ΔE of the He^{2+} beam between the

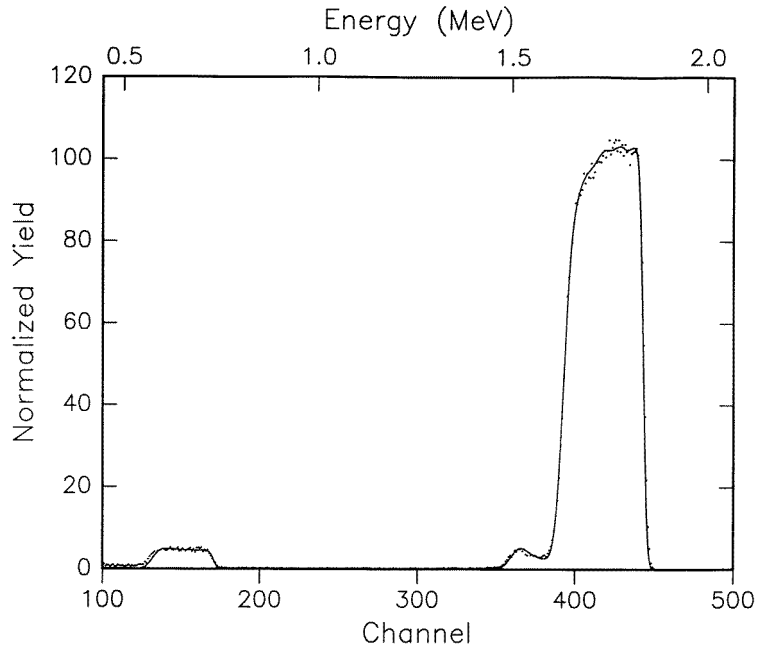


Figure 13. Rutherford backscattering spectrum (same as figure 2) of a mixed-oxide film (prepared from 0.75 WO₃-0.25 MoO₃) on carbon substrate (·····) overlaid with a curve (—) as generated by the code RUMP [11] based on the assumption that the film is an ensemble of five sublayers of equal thicknesses and of different composition (given in table 1).

surface and interface (film-substrate) as shown in figure 10, is related to the film thickness, t , through [20]

$$\Delta E = St \quad (1)$$

where S is the backscattering energy loss factor. The factor S is given by [20]

$$S = (N_A \rho / M) [K \varepsilon(E_0) + \varepsilon(K E_0) / |\cos \theta|] \quad (2)$$

where N_A is Avogadro's number, ρ is the film density, M is the molecular mass, K is the ratio of the projectile energy after and before scattering, ε is the molecular stopping cross section, $E_0 = 2.0$ MeV (incident beam energy), and $\theta = 164^\circ$ is the scattering angle. From the measured ΔE (figure 10) and t (section 3.1) we can obtain S using (1). It was found that $S = 710$ eV nm⁻¹ for WO₃, $S = 667$ eV nm⁻¹ for MoO₃, and $S = 680$ eV nm⁻¹ for the mixed oxides. The values given above are the average values obtained for films of different thicknesses (in case of WO₃ and MoO₃) and different compositions for the mixed oxides. The spread in the value of S , from film to film, for each of the three materials, was found to be well within the uncertainty of 6% that is associated with the measurement of S in the present work. About 1% arises from t and 5% from ΔE due to the energy resolution of the RBS system. Since the uncertainty in the measurement of the S factor of a material is quite high, the present discussion is only intended to provide approximate results. For a mixed-oxide sample if we assume that additivity of S factor values of WO₃ and MoO₃ to obtain an S factor value for the mixed oxides is valid, then for the mixed

oxides of composition $0.7 \text{ WO}_3\text{-}0.3 \text{ MoO}_3$ (i.e. $x = 0.3$) we have

$$S = 0.7 \times 710 + 0.3 \times 667 = 697 \text{ eV nm}^{-1}.$$

It follows from above that for all the other values of x , the S factor should have values that are higher than 697 eV nm^{-1} . In the actual films the ratio of W:Mo was found to be even higher than that in the starting material (table 1), therefore S factor values higher than 697 eV nm^{-1} are expected. However, the measured average value of 680 eV nm^{-1} is less than this. It follows from above and (2) that the lower values of S factor may be due to lower values of the densities of the mixed oxide films. Hence, this may lead to lower values of the refractive indices of the mixed-oxide film compared to those for the WO_3 films.

5. Conclusion

Refractive and absorption indices of thin films of WO_3 and MoO_3 have been determined. These films were found to be homogeneous, while films prepared from the mixed oxides were chemically inhomogeneous. We were able to determine average refractive indices for the mixed-oxide films in the spectral region in which these were nonabsorbing. However, in the absorbing region the optical constants (n and k) could not be determined for the mixed-oxide films, as we were unable to prepare a set of two films of different thicknesses which have the same optical properties.

Acknowledgment

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