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Delayed onset of photochromism in molybdenum oxide films caused by photoinduced defect formation

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Abstract
We report the photochromic properties of amorphous MoO$_3$ films deposited by dc sputtering with different O$_2$ flow rates. The kinetics of film coloration under UV light irradiation is determined using optical transmission spectroscopy. Changes in the absorbance and refractive index were derived from the analysis of transmittance spectra. The absorbance spectra exhibited a growing broad peak centered around 830 nm, which was induced by the UV irradiation. In the early stages of irradiation, the absorbance of the films did not change but their refractive indices did change. This induction time was correlated with the O$_2$ partial pressure during the film deposition, which was controlled by the O$_2$ flow rate. The origins of this observation are discussed.

Keywords: photochromism, molybdenum oxide, oxygen vacancy, thin film, absorption coefficient, refractive index

1. Introduction

Molybdenum trioxide (MoO$_3$) is a wide-band-gap n-type material, which is interesting because of its ability to form several nonstoichiometric phases containing oxygen vacancies. The optical and electronic properties of MoO$_3$ can be altered by varying the concentration of oxygen vacancies [1–6]. Amorphous films of MoO$_3$ can be prepared by a variety of methods and the exact properties of the films vary with the preparation method [3–8]. Thin amorphous films of MoO$_3$ absorb light with wavelengths longer than 400 nm and are thus transparent in the visible range. Irradiation by UV light induces an absorption band centered around 830 nm, thereby turning the films blue [8, 9]. Such photochromic behavior of amorphous MoO$_3$ and other transition metal oxide films might be interesting for a range of applications such as information displays, sensors, high-density memory devices [6, 10] and energy-conserving smart windows [11].

A few models exist to explain the mechanism of photochromism in amorphous films of transition metal oxides such as WO$_3$ and MoO$_3$. However, there are some contradictions among these models. In early studies, Deb and Chopoorian suggested that the photoinduced color in MoO$_3$ films was due to the generation of color centers and was closely related to the formation of Mo$^{5+}$ ions and the presence of oxygen ion vacancies in the lattice [12, 13]. According to this model, oxygen vacancies play an important role in coloration. This model has been criticized for a few reasons. Firstly, in some films the density of color centers appears to be much higher than the expected density of oxygen vacancies [14]. Secondly, conclusive evidence for color centers is lacking in the spectra of these oxides. Thirdly, the photochromism of MoO$_3$ films is inhibited by lowering the temperature [8, 14–16]. This has led to other models being proposed.

An alternative mechanism for the photochromic phenomena in molybdenum oxide is the double insertion/ extraction of ions and electrons. In this model, it is assumed that the films initially always contain some water [14, 17–20]. In the presence of photogenerated holes, water
is split into oxygen and protons. These protons can diffuse into the MoO₃ lattice and react with photogenerated electrons and MoO₃ to form H₂[Mo⁵⁺O₃] (molybdenum bronze). The film turns blue because there is now the possibility of intervalence charge-transfer absorption from Mo⁵⁺ to Mo⁶⁺ sites.

The next proposed coloration mechanism is a small 'correction' or refinement to the above described intervalence charge-transfer. In this model, the intervalence charge-transfer absorption band appears due to electron self-trapping, alone, and the subsequent polaron formation. This polaron model is considered by some scientists as being the most accurate [8, 21, 22]. Although the last two described models have been widely accepted, they ignore the role of oxygen vacancies and therefore cannot account for the lack of coloration in films with a low density of oxygen vacancies (MoO₃₋ₓ when x < 0.3) [23]. They also cannot explain why coloration is faster in an oxygen atmosphere or why the coloration efficiency increases with increasing oxygen deficiency in the film.

Additionally, it is suggested from Raman data that the number of defects in the lattice increases with the progress of the photochromic reaction [24]. Since crystalline films are much less photochromic than amorphous films, one may expect that the photochromic response would increase with greater photoinduced disorder in the lattice.

As stated by Deb in [23], one of the key challenges in transition metal oxide systems is to fully understand the mechanism of photocoloration. The goal of the current work is therefore to investigate the role of oxygen vacancies in the coloration reaction of MoO₃₋ₓ films.

We fabricated a series of thin amorphous films of MoO₃₋ₓ under different deposition conditions: we varied the oxygen partial pressure by changing the ratio of oxygen flow rate to argon flow rate then investigated the photochromic parameters of the films such as the coloration rate and the maximum coloration achieved.

2. Experimental details
Thin films of MoO₃₋ₓ were deposited by dc reactive sputtering using an ion beam assisted sputtering/thermal system (KVIBAD-T15080, T5036). A 7.6 cm diameter Mo target (99.95% purity, SCI Engineered Materials) was sputtered in an atmosphere of Ar and O₂. The sample was set at zero bias so that the resulting films were amorphous. This is because additional bias can result in the films becoming polycrystalline [25]. The chamber was first evacuated to a base pressure of 1 × 10⁻⁷ torr before the deposition was started. To remove the surface oxide layers, the target was presputtered in an Ar atmosphere. For the deposition of MoO₃₋ₓ films, the total chamber pressure was maintained at 6 × 10⁻⁷ torr. Different flow rates of O₂ (3, 4, 5, 6, 7 and 12 sccm) were used while the flow rate of Ar was kept constant at 5 standard cubic centimeters (sccm) for all samples. The dc sputtering power was 100 W for all depositions and the process was carried out at room temperature. The distance between the sample and target was 10 cm for all samples.

| Sample | 1  | 2  | 3  | 4  | 5  | 6  |
|--------|----|----|----|----|----|----|
| [O₂/Ar] | 3/5| 4/5| 5/5| 6/5| 7/5| 12/5|
| P₉₃ (mTorr) | 2.25 | 2.66 | 3 | 3.27 | 3.5 | 4.23 |

Figure 1. Thickness of films deposited with different oxygen flow rates during dc sputtering of MoO₃₋ₓ films (deposition time for all samples: 240 min).

Microscope slides (soda-lime float glass, Sail brand, Cat. No. 7101, manufactured by Yancheng Huida medical instruments Co.) cut to 25.4 × 36 × 1 mm were used as substrates. The substrates were degreased by immersion in acetone at 50°C for 10 min then washed by ethanol and rinsed in deionized water before deposition. The cleaned substrates were then dried in air. Table 1 shows the different ratios of O₂ to Ar flows used and their corresponding O₂ partial pressures based on the assumption that O₂ and Ar obey ideal gas behavior.

The thickness and refractive index of the films were measured using a variable-angle spectroscopic ellipsometer (VASE, J.A. Woollam Co. model HS-190). The transmittance spectra were measured using an absorption spectrometer (UV-2450, Shimadzu) in the range from 300 to 1200 nm (∼8300–33 000 cm⁻¹). The spectral resolution was 0.2 nm. Samples were irradiated with a 400 W UV lamp (DYMAX light curing system, Model 2000 Flood, with the range from 220 to 590 nm and maximum intensity peaks at 370, 380 and 390 nm). The irradiation was carried out in air at a sample distance of 13 cm, for periods varying from 0 to 360 min. The transmission spectra of the films were measured off-line at various times during the irradiation procedure.

3. Results and discussion
Figure 1 shows the thickness of films deposited with different O₂ flow rates and for the same deposition time (240 min). The deposition rate is lower at a higher partial pressure of O₂, and thus thinner films are formed for the same deposition time by increasing the O₂ flow rate. This reduction in deposition rate may be related to the lower density of plasma in an
Figure 2. Refractive index, \( n \), at 589.3 nm and thickness, \( d \), for as-deposited films with \( O_2 \) partial pressures (mTorr) and deposition times (minutes) of (a) \( P_{O_2} = 2.25 \) and \( t = 120 \), (b) \( P_{O_2} = 2.66 \) and \( t = 150 \), (c) \( P_{O_2} = 3 \) and \( t = 180 \), (d) \( P_{O_2} = 3.27 \) and \( t = 180 \), (e) \( P_{O_2} = 3.5 \) and \( t = 240 \), and (f) \( P_{O_2} = 4.2 \) and \( t = 240 \).

Figure 3. Transmittance spectrum for the as-deposited film denoted by sample \( e \) in figure 2 (before irradiation).

The atmosphere with a higher oxygen content since the ionization energy of \( O_2 \) is higher than that of \( Ar \).

On the other hand, the lower atomic weight of \( O \) (16) compared with \( Ar \) (40) gives it less momentum, therefore less mass is transported. It is possible that an increase in the flow rate of \( O_2 \) with a constant flow rate for \( Ar \) will lead to a reduction in the number of \( Ar \) ions colliding with the Mo target. Therefore, less Mo will be ejected from the target.

Figure 2 shows the refractive index, \( n \), at 589.3 nm and film thickness, \( d \), of films deposited with different oxygen flow rates, measured by ellipsometry. Different deposition times were used to maintain a similar thickness for all samples. One can see that when the \( O_2 \) flow rate increases, \( n \) increases slightly. The small increase in \( n \) may imply that the density of the films is slightly higher at a higher \( P_{O_2} \) and therefore the \( MoO_3-x \) stoichiometry may be more complete. Also, there is no apparent direct correlation between thickness and refractive index.

Figure 3 shows the evolution of transmittance spectra with UV irradiation time for a virgin film deposited with \( P_{O_2} = 3.5 \) mTorr (corresponding to sample \( e \) in figure 2). The transmittance spectra contain oscillations due to the interference between reflections from the interfaces of the film. The period of oscillations \( \Delta \nu \) is related to the product \( nd \) by the expression \( \Delta \nu = (2nd)^{-1} \). Here \( n \) is the average refractive index in the wavelength range spanned by the oscillations.

From table 2, we can compare values of \( \Delta \nu \) obtained from transmittance spectra with values of \((2nd)^{-1}\) derived from ellipsometry. The agreement between the two methods is satisfactory, although the dependence of \( n \) on wavenumber was disregarded.

Figure 4 shows the transmittance spectrum for the UV-irradiated film (sample \( e \)). The absorption in the visible range increases and the oscillations in the transmittance spectra shift significantly in the first 60 min, but little change is observed for longer irradiation. As the oscillation amplitudes for the film thicknesses used are comparable to the changes in absorbance, these two contributions need to be separated before the analysis. This can be achieved using Fresnel equations for thin-film transmittance [26]; however, this procedure requires modeling of the shape and position of the absorption spectrum as well as the refractive index spectrum. Instead, we used a simplified deconvolution approach which relied on two assumptions. The first is that the spectral shape and the position of the absorption spectrum are constant with UV irradiation time.

The second is that the absorption spectrum does not contain oscillations of the same frequency as the interference effect. Both of these assumptions are validated below. Then it is possible to use Fourier filtering to separate the higher-frequency interference component from the lower-frequency absorption spectrum. Fourier filtering has previously been successfully employed [27]. However, in our case the amplitude of the oscillation is larger than that in [27] and comparable with the change in absorbance. Additionally, because our films are thinner, the period of oscillations is longer and closer to the absorption spectrum width. Thus, our approach is somewhat more involved, as described next.

Firstly, we obtain a pure difference spectrum between the initial and final spectra in the visible region. We do this by first selecting a film with the maximum number of oscillations—it will be easier to apply Fourier filtering to this film as the period of oscillation will have the greatest difference from the width of the absorption component. Hence we selected sample \( e \), which incidentally is the thickest film. Next we minimize the contribution of the oscillations to the absorbance by taking the spectrum with maximum absorbance (360 min) and subtracting a spectrum obtained with a shorter irradiation time to generate a difference spectrum. Subtracting the spectrum for 0 min is obviously not appropriate as the shift of oscillations between 0 and 60 min is too great. We therefore choose a spectrum obtained with a longer irradiation time as the shift of oscillations is relatively small after 60 min of irradiation, and we subtract the spectrum at 120 min from that at 360 min (figure 5(a)). Note that this spectrum also gave the maximum ratio of absorbance amplitude to oscillation amplitude after deconvolution (figure 5(b), solid line).

The resulting difference spectrum now mainly contains the absorption component with a smaller residual oscillation,
which remains because the exact amplitude of the oscillation is not the same for the two spectra. In fact, the oscillations are somewhat over-subtracted since the contribution of interference to the spectrum is naturally larger when there is less absorbance. Next, Fourier filtering is applied to the subtracted spectrum to smooth out the residual oscillation. This yields a ‘model’ spectral envelope in terms of shape and position for the absorption component in the visible range (figure 5(b), dotted line).

Next, we use this model spectral envelope to extract kinetic data as follows. The spectrum for each irradiation time contains a mixture of absorbance and interference components. To separate these we subtract the model spectral envelope from the mixed spectrum until the resulting spectrum contains an oscillation about a flat baseline at longer wavelengths (lower wavenumbers in the range 8300–20 000 cm⁻¹). If we oversubtract, the oscillation will bend downwards at the maximum of the model spectrum. If we undersubtract, the oscillation will bend upwards. For each irradiation time contains a mixture of absorbance and interference to the spectrum is naturally larger when there is less absorbance. Next, Fourier filtering is applied to the subtracted spectrum to smooth out the residual oscillation. This yields a ‘model’ spectral envelope in terms of shape and position for the absorption component in the visible range (figure 5(b), dotted line).

After the ‘induction’, the absorption coefficients for most of the films in figure 8 start increasing steeply and then the

Table 2. Comparison between data derived from ellipsometry and transmittance measurements. \( v_1 \) to \( v_3 \) correspond to the peaks shown in figure 3. Sample notation is as in figure 2.

| Sample | \((2nd)^{-1} \text{cm}^{-1}\) (from ellipsometry, \( n \) at 589.3 nm) | \( \Delta \nu_1 = (v_2 - v_1) \) (\( v \) = wavenumber at peak) | \( \Delta \nu_2 = (v_3 - v_2) \) |
|--------|-----------------|-----------------|-----------------|
| a      | 7291            | 6900            | –               |
| b      | 7508            | 7520            | –               |
| c      | 6617            | 6425            | –               |
| d      | 6948            | 6570            | –               |
| e      | 5384            | 5660            | 5200            |
| f      | 6788            | 6600            | –               |

Table 3. Oxygen partial pressures and corresponding thicknesses for the second set of samples.

| Sample | \( P_{O_2} \) (mTorr) | Thickness (nm) |
|--------|------------------------|----------------|
| g      | 2.25                   | 405            |
| h      | 2.66                   | 465            |
| i      | 3                      | 555            |
| j      | 3.27                   | 565            |
| k      | 3.5                    | 475            |
| l      | 4.23                   | 309            |

Figure 6 shows the residual oscillation spectra and the initial spectrum for sample \( e \) after subtraction of the model spectrum. As noted above, the oscillation shifted very little during the coloration reaction at later times. However, as we demonstrate below, this was not the case at earlier times.

Figure 7 shows the resulting absorption coefficient, \( \alpha \), as a function of the irradiation time for different samples. The absorption coefficient increases with irradiation time and begins to plateau as the absorption becomes saturated. As a general trend, the initial rate of the change of absorption is greater for films deposited with a lower \( P_{O_2} \), although the plateau value may be similar at longer times than those considered here. This can be attributed to the lower stoichiometry of MoO\(_{3-x}\) at a reduced \( P_{O_2} \).

In figure 7 there is an indication of a delay in the onset of the change in the absorbance of the film deposited with the highest \( P_{O_2} \). To investigate the rate of color change in the early stages of irradiation a second series of experiments was conducted on a second series of films. \( P_{O_2} \) during deposition and corresponding thicknesses for the second set of samples are given in table 3.

Figure 8 shows the absorption coefficients for these films as a function of irradiation time, deduced using the deconvolution procedure described above. It is clear from figure 8 that all films exhibited an induction time before the onset of the maximum rate of change of absorbance.

Figure 9(a) shows the dependence of the induction time on \( P_{O_2} \). Although the trend is not perfect, the longest induction times tended to be for the films deposited with the highest \( P_{O_2} \). We interpret this as the films deposited with the highest \( P_{O_2} \) will initially be the most stoichiometrically complete and will have the fewest defect sites. For these films the UV irradiation itself might cause photochemical damage that increases disorder and the number of defects such as oxygen vacancies. These defects can contribute to the color change by trapping free charges as suggested by Deb and Chopoorian [12, 13, 23].

After the ‘induction’, the absorption coefficients for most of the films in figure 8 start increasing steeply and then the
rate of increase becomes lower. The highest rates of increase in absorbance obtained from the dependences in figure 8, measured immediately after the induction, are plotted against the oxygen partial pressure in figure 9(b). Again, the trend is not perfect, but the steepest slopes tended to be for the films deposited with the lowest $P_{O_2}$. The above arguments can again be used to conclude that a lower oxygen pressure will lead to more defects and more efficient photochromism.

To investigate changes in the refractive index of the films during irradiation we analyzed the residual oscillation spectra. Figure 10 shows transmittance spectra for film $i$ deposited with $P_{O_2} = 3$ mTorr before and after UV irradiation. It is clear that in the very early stages there is a large horizontal shift in the oscillation of the spectra due to interference when...
Figure 9. (a) Induction time before coloration versus $P_{O_2}$ during deposition, (b) slope of the absorption coefficient dependence on UV irradiation time (immediately after induction) for films deposited with different $P_{O_2}$. Samples are from table 3.

Figure 10. Transmittance spectra for the film deposited with $P_{O_2} = 3$ mTorr before UV irradiation and after 5, 10, 15, 20, 30, 40, 60, 90, 120 and 180 min of UV irradiation (sample i in table 3); $v_1$ and $v_2$ denote the approximate positions of maximum oscillation used in figure 11.

there is very little vertical shift due to absorption. This initial horizontal shift becomes less prominent when the vertical shift due to absorbance begins.

The peak position difference, $\Delta v_{12} = v_2 - v_1$, in the residual oscillations for the data in figure 10 (sample i) is plotted against the UV irradiation time in figure 11. The change in the absorption coefficient with irradiation time for the same sample is also shown.

One can see from figure 11 that the main increase in $\Delta v_{12}$ occurs during the initial 30 min of irradiation. This roughly corresponds to the induction period for the change in absorption, when the absorption coefficient is still very low. Both oscillation peaks, $v_1$ and $v_2$, in figure 10 are positioned within the rising absorption envelope. Only during this induction time can we safely ignore the abnormal change in the refractive index caused by absorption since the absorbance is low at this time. The product $nd$ decreases by up to 15% with irradiation time since it is inversely proportional to $\Delta v_{12}$. This may be due to the decrease in $n$ or film thickness, either from chemical changes or changes in density. If the film is damaged by UV irradiation, as we have speculated previously, then this could cause a chemical or structural change, such as a loss of oxygen which may affect $n$. Alternatively, the film could lose thickness due to chemical or structural changes, such as a loss of oxygen. Either way the film becomes optically thinner with increasing irradiation time during the induction period.

In our separation of changes in absorbance and changes in $nd$ from the transmission data we make two assumptions. The first is that the spectral shape and position of the signals related to color centers are constant with time. The second is that the spectra do not contain higher frequency oscillation with a similar frequency to the interference effect. From our analysis, we found that in general the spectra obtained from many Fourier filtering procedures gave similar spectral shapes and peak maxima. We are therefore confident that small variations in the spectra will not add a significant error to the derived kinetics. Although it has been reported that there are some small band structures in MoO$_3$ films, we did not see any such structures remaining in the residual oscillation after Fourier filtering. We can therefore assume that their contribution would be much less than that of oscillation and be confident that it will not affect the derived kinetics. In any case, even when reported, the amplitude of band structures was much less than the amplitude of the overall absorption envelope.
4. Conclusions

The kinetics of the coloration of MoO$_{3-x}$ films, dc sputtered with different oxygen partial pressures under UV irradiation, was studied to determine the role of oxygen vacancies in photochromism. The contributions of absorbance and interference in the transmittance spectra were separated using a simplified approach based on Fourier filtering of the spectra and thus the evolutions of absorbance and refractive index of the films were assessed independently. For all oxygen pressures used for the deposition of the films, a broad absorbance peak centered around 830 nm appears and rises with UV irradiation time. For the UV lamp intensities and oxygen pressures used in this study, the change in absorbance decreases upon UV irradiation. In the early stages of UV irradiation the absorption starts to increase after about 6 h of irradiation to approximately the same value of absorption coefficient (6000–7000 cm$^{-1}$, corresponding to an absorbance of ~0.3 for the film thicknesses used here). The difference in oxygen pressure during the deposition mainly affects the initial stages of UV irradiation. By increasing the oxygen partial pressure during sputtering, the initial rate of change in absorbance decreases upon UV irradiation. In the early stages of UV irradiation the absorption starts to increase after a certain delay or induction time. This induction time depends on the oxygen pressure during the film deposition, and the higher the pressure, the longer the induction time. The product of the refractive index and film thickness varies during this induction time, indicating structural or chemical changes within the film. This change in $n_d$ occurs before the change in absorption and is thus unrelated to it. The induction time was attributed to formation of oxygen vacancies or other defects.

The results reported here demonstrate the importance of the initial stoichiometry in the photochromism of MoO$_{3-x}$ amorphous films, particularly in the initial stages of UV irradiation. In future, it would be interesting to study the early stages of UV irradiation more accurately to understand why an induction time and structural changes of the film were observed during the initial stages of UV irradiation for MoO$_{3-x}$ films with different densities of oxygen vacancies.

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References

[1] Pichat P and Mozzanega M N 1988 Phys. Chem. 92 467
[2] Hussain O M and Rao K S 2003 Mater. Chem. Phys. 80 638
[3] Rao K S, Madhuri K V, Uthanna S, Hussain O M and Julien C 2003 Mater. Sci. Eng. B 100 79
[4] Okumu J, Koerfer F and Salinka C 2006 Thin Solid Films 515 1327
[5] Scarminio J, Louremo A and Gorenstein A 1997 Thin Solid Films 32 66
[6] Yao J N, Yang Y A and Loo B H 1998 J. Phys. Chem. B 102 1856
[7] He T and Yao J 2006 Prog. Mater. Sci. 51 810
[8] He T and Yao J 2003 Photochem. Photobiol. C: Photochem. Rev. 4 125
[9] Tubbs M R 1974 Phys. Status Solidi a 21 253
[10] Yang Y A, Cao Y W, Loo B H and Yao J N 1998 J. Phys. Chem. B 102 9392
[11] Baetens R, Jelle B P and Gustavsen A 2010 Solar Energy Mater. Solar Cells 94 87
[12] Deb S K and Chopoorian J A 1966 J. Appl. Phys. 37 4818
[13] Deb S K 1968 Proc. R. Soc. A 304 211
[14] Faughnan B W, Crandall R S and Heyman P M 1975 RCA Rev. 36 177
[15] Hughes A E, Henderson B J H, Crawford L M and Slifkin 1972 Point Defects in Solids vol. 1 ed J H Crawford and L M Slifkin (New York: Plenum) p 435
[16] Wagner H J, Driessen P and Schwardtfeiger C 1979 J. Non-Cryst. Solids 34 335
[17] Faughnan B W, Staebler D L and Kiss Z J 1971 Applied Solid State Science vol. 2 (New York: Academic) p 107
[18] Bange K 1999 Solar Energy Mater. Solar Cells 58 1
[19] Beydaghyan G, Doiron S, Haché A and Ashrit P V 2009 Appl. Phys. Lett. 95 0519171
[20] He T and Yao J 2007 J. Mater. Chem. 17 4547
[21] Schirmer O F, Wittwer V, Baur G and Brandt G 1977 J. Electrochem. Soc. 124 749
[22] Lehan J P, Yu P C, Backfisch D L and Chambers J P 2002 J. Appl. Phys. 92 3608
[23] Deb S K 2008 Solar Energy Mater. Solar Cells 92 245
[24] Ajito K, Nagahara L A, Tryk D A, Hashimoto K and Fujishima A 1995 J. Phys. Chem. 99 16383
[25] Babu P M, Radhakrishna B, Rao G V, Reddy P S and Uthanna S 2004 J. Optoelectron. Adv. Mater. 6 205
[26] Abdellaloua A, Leveque G, Donnadieu A, Bath A and Bouchikhi B 1997 Thin Solid Films 304 39
[27] Trithart U, Gey W and Gavrilyuk A 1998 Ionics 4 299