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A STUDY OF THE OPTICAL BAND GAP OF LITHIUM TUNGSTEN TRIOXIDE THIN FILMS

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ABSTRACT

The insertion of lithium (lithiation) into tungsten trioxide results in the formation of the tungsten bronze Li_xWO_3. Polycrystalline, rf sputter deposited thin films of Li_xWO_3 were investigated for their application in Smart Window Devices. The optical band gap studies of these films revealed the narrowing of the intrinsic band gap as a consequence of lithium insertion. The results suggest that the rigid band model, which is generally adopted in interpreting the electronic structure of the tungsten bronzes may not be applicable in Li_xWO_3.

INTRODUCTION

Thin films of tungsten trioxide (WO_3) have been extensively researched for their potential applications in electrochromic devices [1,2]. Our attention was drawn to this material for it showed promise as the principal electrochromic layer in an electrochromic "Smart Window" device [3], useful for energy conservation purposes. When alkali metal atoms are incorporated into tungsten trioxide it results in the formation of tungsten bronzes and the optical state changes from a transparent to a reflective state. High reflectivities, approximately 80% in the near infrared (NIR) region, has been reported [4] for rf sputtered polycrystalline WO_3 films when inserted with lithium atoms resulting in the formation of lithium tungsten bronze (Li_xWO_3).

The electronic, optical and structural properties of the tungsten bronzes, mainly the sodium bronzes (Na_xWO_3) have been investigated in depth. The band structure of the bronzes has been qualitatively explained in terms of a model developed by Goodenough [5]. In short, the conduction band in WO_3 is derived from the three t_{2g} (5d) tungsten orbitals and the valence band from the oxygen 2p atomic orbitals. The inserted alkali metal atom merely contributes one electron into the otherwise empty conduction band of WO_3 suggesting a rigid band model for these bronzes. The band structure calculations of WO_3 and Na_xWO_3 [6,7] as well as the data on the optical constants of Na_xWO_3 [8] is supportive of this model. However the validity of this theory has been questioned by several authors based on XPS studies [9,10].

In this paper we would like to report that our results from optical band gap studies of polycrystalline thin films of Li_xWO_3 suggests the narrowing of the optical band gap as a function of lithium content [Li] and would like to show that the rigid band model may not be applicable in Li_xWO_3.

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EXPERIMENTAL

Tungsten trioxide films in the present study were prepared by an rf sputter deposition technique. The target was a 5-inch diameter partially reduced WO_3 - obtained from Cerac, Inc. The deposition parameters were the following: 200 Watts of power (13.5 MHz), an atmosphere of 10 mT of oxygen and a substrate temperature of approximately 430°C to 440°C. The film thicknesses were 0.2 ± 0.02 μm for film 5-804, and 0.19 ± 0.02 μm for films 5-875 B2, C2, A1 and 0.21 ± 0.02 μm for film 5-875 B1. The polycrystalline nature of these films were confirmed by transmission electron microscopy (JEOL 200CX) and X-ray Diffraction (Nicolet I2) studies. The crystallite sizes, as determined by TEM measurements, varied from 50 to 300Å with a larger percentage of 300 Å crystallites. The lithiation of the film 5-804 was achieved by rf sputtering a lithium aluminum borate (LABO) compound. The LABO deposition was performed for 15, 30 and 50 minutes representing three different lithium concentrations, using an rf power of < 50 watts, at ambient temperature, and

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5 to 6 mT of argon. The samples 5-875 (B2, C2, B1, A1) were lithium carbonate (LCO) deposited for 5 minutes (B2), 8 minutes (C2), 15 minutes (B1), and 20 minutes (A1) at 100 watts, ambient temperature and 10 to 11 mT of argon. A qualitative measure of lithium content was obtained from an atomic absorption measurement.

The reflection and transmission spectra of these films were measured using a Beckman DK-2 spectrophotometer. The optical band gap as a function of lithiation was obtained from the measured transmission spectra for the two sets of films. The open circuit voltage measurements of the samples 5-875 after lithiation were measured in an electrochemical cell as described elsewhere [11].

RESULTS

Figures 1a and 1b represent the optical reflectivity R(λ) modulation for various lithiation states in films 5-804 and 5-875 respectively.

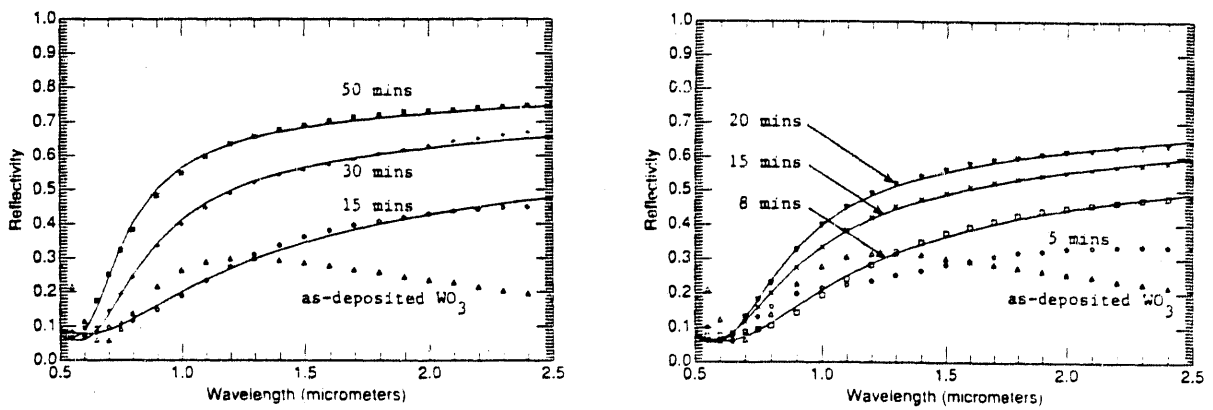

Figure 1. Reflectivity vs. wavelength for films (a) 5-804 (LABO deposited) and (b) 5-875 (LCO deposited), as a function of lithiation. (Symbols: measured data, Lines: Drude model fit).

The near infrared (NIR) reflectivity, R (λ), is observed to increase with the lithium content. The spectra exhibits a typical Drude free electron like [12] behavior with the plasma edge (ω_p) shifting to higher frequencies in accordance with the equation,

$$\omega_p^2 = \frac{[n]e^2}{m_c^* e_0} \tag{1}$$

where [n] is the carrier density (number of electrons per unit volume) and m_c^* is the conduction band effective mass. A good fit is obtained between the measured R (λ) and the R (λ) calculated using the Drude equations,

$$e_1 = e_b - \frac{E_p^2}{E^2+E_T^2} \tag{2}$$

and

$$e_2 = \frac{E_T}{E}\frac{E_p^2}{E^2+E_T^2} \tag{3}$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric constants, ε_b is the contribution to the dielectric constant from the bound electrons, E_T is the scattering parameter, which is inversely proportional to the relaxation time. E_p is the plasma energy ($E_p = \hbar\,\omega_p$).

A best fit was obtained for the parameters as tabulated in Table 1 below.

Sample	[Li]	E_T (ev)	E_p (ev)	ε_b
5-804	15 mins	1.92	3.50	4.0
	30	0.96	3.99	4.75
	50	0.75	4.78	6.0
5-875				
C2	8	1.56	3.28	4.0
B1	15	1.21	3.80	4.25
A1	20	1.10	3.95	4.75

Table 1. Drude parameters that give a best fit for measured R (λ).

It is apparent from Table 1 that E_T decreases as [Li] increases. This suggests that the scattering due to impurities (lithium ions in this case) may not a play a dominant role. Furthermore, ε_b increases with [Li]. According to the Lorentz oscillator model [12] for bound electrons in a solid, this would imply that the intrinsic band gap decreases with [Li].

Optical transmission T (λ) modulation as a function of lithiation presented in Figures 2a and 2b displays the shift in the optical band gap towards higher energies.

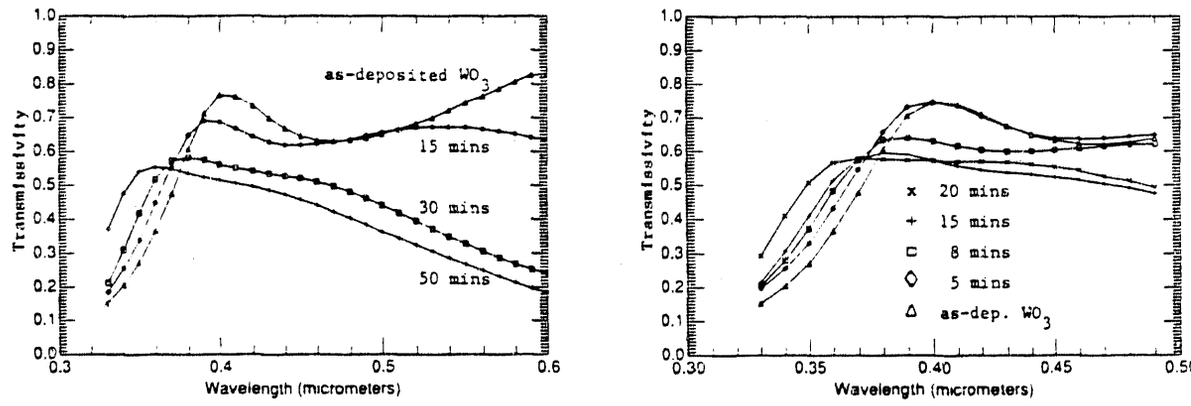

Figure 2. Transmission vs. wavelength for films (a) 5-804 (LABO deposited) and (b) 5-875 (LCO deposited), as a function of lithiation.

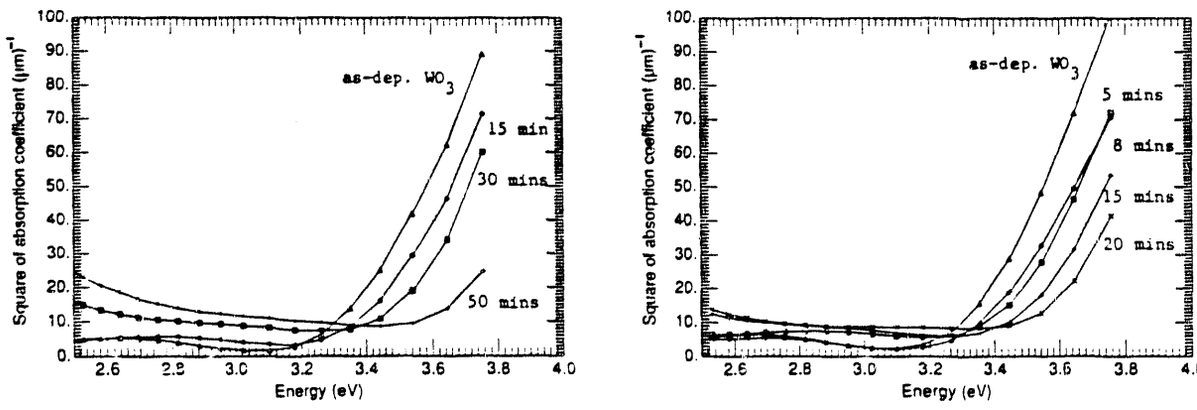

Figure 3. Square of the absorption coefficient vs. energy for films (a) 5-804 (LABO deposited) and (b) 5-875 (LCO deposited), as a function of lithiation.

The absorption coefficient (α) is calculated using the relation

$$\alpha = \frac{1}{d} \ln T(\lambda) \tag{4}$$

where d is the thickness of the film. A plot of α^2 versus energy ($h\nu$) as shown in Figures 3a and 3b yields the (direct) optical band gap, when the curves are extrapolated to zero absorption coefficient. The values are presented in Table 2.

Sample #	Reference	$[n]\times10^{27}$ m^{-3}	E_F (ev)	E_{opt} (ev)
5-804	WO_3			3.39
	15 mins	4.45	0.95	3.47
	30 mins	5.78	1.13	3.52
	50 mins	8.29	1.43	3.66
5-875	WO_3			3.38
	5 mins			3.48
	8 mins	3.91	0.87	3.48
	15 mins	5.24	1.06	3.55
	20 mins	5.66	1.1	3.60

Table 2. Electron density [n], Fermi energy E_F, and optical band gap E_{opt} for films 5-804, 5-875 as a function of [Li].

[n] is calculated from Eq. 1, assuming an effective mass of $0.5m_0$ [13] and the Fermi energy E_F is calculated using the relation,

$$E_F = \frac{\hbar^2}{2m_c^*}\left[\frac{1}{3}\,3\pi^2[n]\right]^{\frac{2}{3}} \tag{5}$$

taking into account the orbital degeneracy of the conduction band.

From Table 2 it is clear that as [n] increases the Fermi level increases and the optical band gap shifts to higher energies due to the filling up of the conduction band. The optical band gap is related to the carrier concentration according to the Burstein-Moss [BM] effect [14] as shown in Figure 4a and is represented by Equation 6.

$$E_{opt} = E_g + \Delta E_g^{BM}\ ; \qquad \Delta E_g^{BM} = \frac{\hbar^2}{2m_r}\left[3\pi^2[n]\right]^{\frac{2}{3}} \tag{6}$$

where E_g is the intrinsic band gap, ΔE_g is the MB shift, m_r is the reduced effective mass such that,

$$\frac{1}{m_r} = \frac{1}{m_c^*} + \frac{1}{m_v^*}$$

where m_c^* and m_v^* are the conduction and valence band masses respectively. Assuming an infinite mass for the valence band,

$$\Delta E_g = E_F = \frac{\hbar^2}{2m_c^*}\left[3\pi^2[n]\right]^{\frac{2}{3}} \tag{7}$$

A rigid band structure in which there is no change in E_g would then imply that the change in the optical band gap must equal the change in the Fermi energies between two states of lithiation ($\Delta E_{opt} = \Delta E_F$) as shown in Figures 4a and 4b.

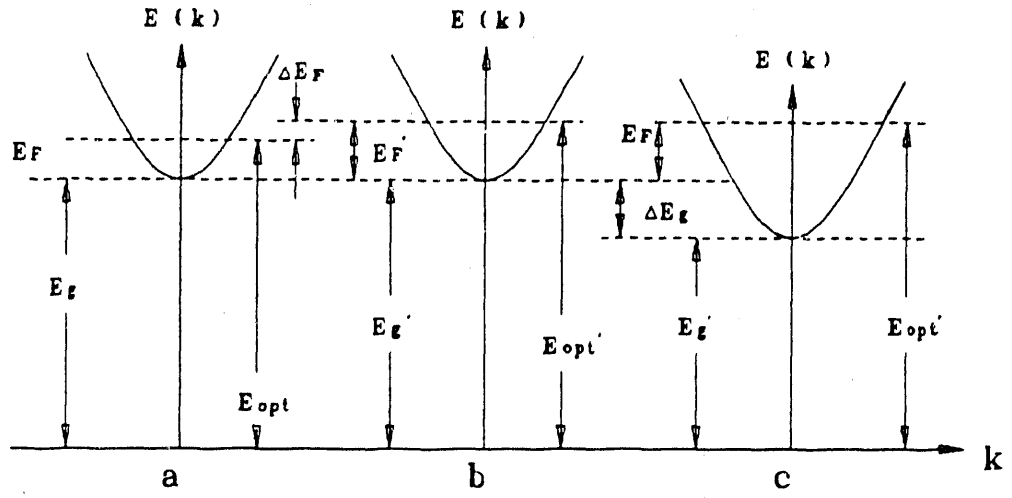

Figure 4. Simple band structure illustrating the band gap narrowing. (a) Lower [Li], (b) Higher [Li], $\Delta E_{opt} = \Delta E_F$, (c) Higher [Li], $\Delta E_{opt} = \Delta E_g + \Delta E_F$.

[Li] (Mins)	ΔE_{opt} (ev)	ΔE_F (ev)	$\Delta E_F = \Delta V_{OC}$ (ev)
(5-804)			
15-30	0.05	0.18	
15-50	0.14	0.30	
30-50	0.19	0.48	
(5-875)			
8-15	0.07	0.19	0.15
8-20	0.12	0.23	0.25
15-20	0.05(*)	0.04(*)	0.10

Table 3. Values of the optical band gap shifts and Fermi level shifts between various lithiation states [Li] is represented here in terms of deposition times. ΔV_{OC} is the difference in the open circuit voltages of the lithiated samples (measured only for 5-875).

However, the values tabulated for the differences in E_{opt} and E_F in Table 3 reflect that $\Delta E_F > \Delta E_{opt}$. From Figures 4a and 4c this would be true if the intrinsic band gap in Figure 4c corresponding to a higher lithiation state decreased, in going from state 4a to state 4c.

It should be noted that there is some uncertainty in the data marked (*) in Table 3. At present it is not clear whether this is due to non uniform thickness or due to a non uniform distribution of lithium in the film. Also, the values of ΔE_F are in good agreement with the values obtained from the open circuit voltage measurements for these films.

CONCLUSIONS

Based on our results for the optical band gap and the dielectric constant of the bound electrons it may be concluded that the intrinsic band gap in Li_xWO_3 polycrystalline thin films decreases as the lithium concentration increases. Furthermore, this band gap narrowing with lithium insertion suggests that the rigid band model may not be applicable for interpreting the electronic structure of lithium tungsten bronzes.

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