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# CHROMIC MECHANISM IN AMORPHOUS WO<sub>3</sub> FILMS

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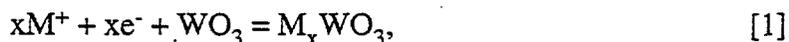
## ABSTRACT

We propose a new model for the chromic mechanism in amorphous tungsten oxide films (WO<sub>3-y</sub>·nH<sub>2</sub>O). This model not only explains a variety of seemingly conflicting experimental results reported in the literature that cannot be explained by existing models, it also has practical implications with respect to improving the coloring efficiency and durability of electrochromic devices. According to this model, a typical as-deposited tungsten oxide film has tungsten mainly in W<sup>6+</sup> and W<sup>4+</sup> states and can be represented as W<sup>6+</sup><sub>1-y</sub> W<sup>4+</sup><sub>y</sub> O<sub>3-y</sub> · nH<sub>2</sub>O. The proposed chromic mechanism is based on the small polaron transition between the charge-induced W<sup>5+</sup> state and the original W<sup>4+</sup> state instead of the W<sup>5+</sup> and W<sup>6+</sup> states as suggested in previous models. The correlation between the electrochromic and photochromic behavior in amorphous tungsten oxide films is also discussed.

## 1. INTRODUCTION

Since the discovery of the solid-state, thin film electrochromic (EC) phenomena in WO<sub>3</sub> by Deb<sup>1</sup> more than twenty years ago, various models have been proposed to explain the electrochromic mechanism in this material (see recent review by Granqvist<sup>2</sup>). It is well

known that crystalline tungsten oxide films may have a different coloring mechanism than those of amorphous tungsten oxide films. Deneuille et al.<sup>3</sup> measured colored  $WO_{3-y}$  films after they were annealed at temperatures from 25 to 500°C in both vacuum and oxygen environments. They found that the absorption peaks of the films were centered at ~ 1.38 eV at annealing temperatures below 350°C, but shifted abruptly to 0.72 eV at annealing temperatures above 400°C. The basic coloration mechanism in crystallized  $WO_{3-y}$  films is believed to be Drude-like free electron absorption<sup>4</sup>. Svensson and Granqvist<sup>5</sup> have developed a more detailed theory for the optical properties of crystalline electrochromic materials based on free electron scattering in heavily doped semiconductors with ionized impurities<sup>6</sup>. On the other hand, there are still some controversies about the coloration mechanism in amorphous  $WO_3$  films. It is widely believed that optical modulation in the films is directly related to the double injection/extraction of electrons and ions in the films as indicated by the following reaction<sup>7</sup>:



where  $M^+ = H^+, Li^+$ , etc. This process increases the number of  $W^{5+}$  ions and hence the number of color centers. Schirmer et al.<sup>8</sup> proposed that the optical absorption of the films is caused by the small polaron (SP) transitions between two nonequivalent sites of tungsten ( $W^{5+}$  and  $W^{6+}$ ):



According to this model, inserted electrons are localized in  $W^{5+}$  sites and polarize their surrounding lattice to form small polarons. Incident photons are absorbed by these small polarons which hop from one site to another. The intervalence transition model proposed by Faughnan and Crandall<sup>7</sup> has a similar physical explanation for this process. Although these models are consistent with many experimental observations, they cannot explain the

following experimental results:

a. The oxygen deficiency ( $y$ ) in evaporated tungsten oxide films ( $\text{WO}_{3-y}$ ) may vary from 0 to 0.4 depending on the deposition environment and temperature<sup>3,9,10</sup>, but the films all appear transparent. If we assume  $\text{W}^{5+}$  is the main low-valence tungsten ion and the optical transition can be represented by eq. [2], then we cannot explain the colorless appearance of these oxygen-deficient, as-deposited  $\text{WO}_{3-y}$  films.

b. Several experiments indicate that the coloring efficiency ( $\eta$ ) of tungsten oxide films ( $\text{WO}_{3-y}$ ) increases with increasing oxygen deficiency ( $y < 0.4$ )<sup>10-12</sup>. In a reactive evaporation process, increasing the oxygen partial pressure ( $P_{\text{O}_2}$ ) by two orders of magnitudes results in a decrease in  $\eta$  to about one-half the initial values. Rutherford Backscattering Spectroscopy (RBS) was used to verify that the decrease in  $\eta$  is associated with a decrease in the oxygen deficiency<sup>12</sup>.

c. When a tungsten oxide film was colored by lithium injection, the  $\text{Li}^+$  content in the film increases with increasing coloration as proved conclusively by nuclear reaction analysis (NRA)<sup>13</sup>. This is consistent with eq. [1]. On the other hand, when a tungsten oxide film was colored by proton injection, the  $\text{H}^+$  content in the film does not increase with increasing coloration as found by the same technique<sup>14,15</sup>. This contradicts the prediction of eq. [1].

We propose a new model for chromism in amorphous tungsten oxide ( $\alpha\text{-WO}_3$ ) films. We will use this model to explain seemingly-conflicting experimental results discussed above. The practical implications of this model with respect to improving the coloring efficiency and durability of EC devices are also discussed. A unified explanation for both electrochromic and photochromic behavior in  $\alpha\text{-WO}_3$  films will be presented.

## 2. ORIGIN OF ELECTROCHROMISM

Most  $\alpha$ - $\text{WO}_3$  films used in the electrochromic process possess both an oxygen deficiency ( $y$ ) and a certain amount of water. Therefore, its molecular formula should be expressed as  $\text{WO}_{3-y} \cdot n\text{H}_2\text{O}$ , where  $n$  is the amount of water bonded in the film structure. On the other hand, mass-spectroscopic studies during the sputtering of  $\text{WO}_3$  films showed the presence of O, WO,  $\text{WO}_2$ ,  $\text{WO}_3$ ,  $\text{W}_2\text{O}_6$ , and  $\text{W}_3\text{O}_9$  with proportions that depend on the sputtering condition<sup>16-19</sup>. This indicates that  $\text{W}^{6+}$  and  $\text{W}^{4+}$  states are much more easy to form than the  $\text{W}^{5+}$  state in a physical deposition process. Therefore, we propose that as-deposited  $\alpha$ - $\text{WO}_3$  films include mainly  $\text{W}^{6+}$  and  $\text{W}^{4+}$  states, and their chemical formula can be written as  $\text{W}_{1-y}^{6+} \text{W}_y^{4+} \text{O}_{3-y} \cdot n\text{H}_2\text{O}$ .

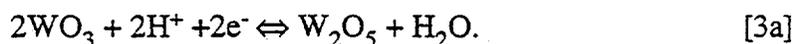
The experimental identification of  $\text{W}^{5+}$  and  $\text{W}^{4+}$  states in as-deposited  $\alpha$ - $\text{WO}_{3-y}$  films is quite controversial. Among the vast amount of data reported to date, one has to distinguish the following differences: (a) The original oxygen deficiency and charge-induced oxygen deficiency and (b) the original lower-valence tungsten state and charge-induced lower-valence tungsten state.

Angelis et al.<sup>20</sup> and Salje et al.<sup>21</sup> observed  $\text{W}^{4+}$  in  $c$ - $\text{WO}_{3-y}$  films, but conjectured that this species does not contribute to the optical absorption. Although several groups<sup>22,23</sup> have reported the existence of  $\text{W}^{5+}$  in the tungsten oxide films, most of these data are for the films colored by various post-treatment methods. Salje et al.<sup>24,25</sup> used optical spectroscopy (diffuse scattering) and X-ray photoelectron spectroscopy (XPS) to investigate concentration of color centers ( $\text{W}^{5+}$ ) in crystalline  $\text{WO}_{2.72}$ . According to previous theory,  $\text{WO}_{2.72}$  corresponds to the chemical formula  $\text{W}_{0.44}^{6+} \text{W}_{0.56}^{5+} \text{O}_{2.72}$ , but the observed concentration of color centers by both methods was only half as much as expected from this chemical formula. In other words, only 28% of all tungsten positions

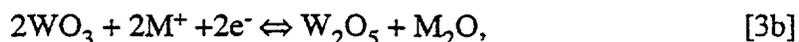
(W<sup>5+</sup> and W<sup>6+</sup>) are occupied by W<sup>5+</sup>, instead of 56% as given by the chemical formula. Their explanation is that approximately half of the carriers (W<sup>5+</sup>) appear as polarons (or color centers) and the other half appear as free carriers in WO<sub>2.72</sub>. In the electron paramagnetic resonance (EPR) measurement<sup>14,26</sup>, no W<sup>5+</sup> signal was found in either c-WO<sub>3</sub> or as-evaporated α-WO<sub>3-y</sub> (0 > y > 0.4) films, although the W<sup>5+</sup> signal was found to increase with increasing coloration in the post-treated films. Gerard et al.<sup>14</sup> used the pairing of W<sup>5+</sup> polarons to explain this discrepancy.

From our point of view, it is not a coincidence that the carrier concentration of the film is only half that expected from the theory based on polaron transitions between W<sup>5+</sup> and W<sup>6+</sup>. If we assume that W<sup>4+</sup> is the main low-valence species in virgin tungsten oxide, then WO<sub>2.72</sub> can be written as W<sup>6+</sup><sub>0.72</sub>W<sup>4+</sup><sub>0.28</sub>O<sub>2.72</sub>. Apparently, the carrier concentration measured by both optical absorption spectra and XPS is just what we expect for the concentration of W<sup>4+</sup>. The absence of a W<sup>5+</sup> signal measured by EPR in as-deposited α-WO<sub>3-y</sub> films is also predicted by our model.

Although the presence of W<sup>5+</sup> state is not favored in physical deposition processes, this state or color center can be formed in a film by various post-treatment processes. These chromic processes include those such as electrochemical coloration (electrochromic), UV illumination, H exposure, ionbeam and electron beam irradiation, etc.<sup>27</sup>. In the case of electrochemical coloration, part of WO<sub>3</sub> film (the amount is proportional to the concentration of the injected charges) will undergo the following reaction<sup>28</sup>:



or more generally:



where  $M = H, Li, Na, \text{ etc.}$  Eq. [3b] indicates that an electrical field will help injected ions ( $M^+$ ) break some of the  $W=O$  bonds and combine with  $O^{2-}$  to form  $M_2O$ . Consequently, this will induce  $W^{5+}$  states. A reversed electrical field will break the  $M-O$  bond and extract the  $M^+$  ions from the film. Then the  $W^{5+}$  state will release an electron and return to the  $W^{6+}$  state. This process can be described more clearly as shown in Fig. 1.

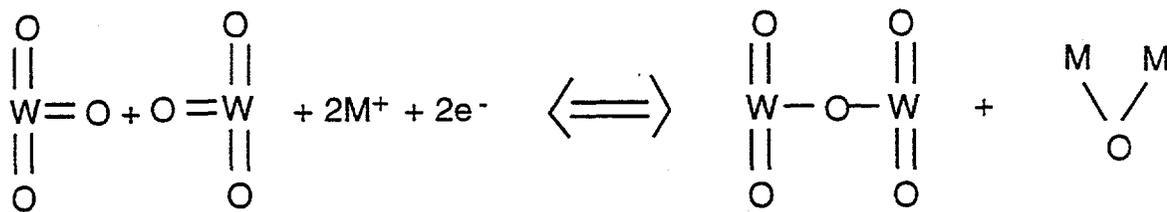
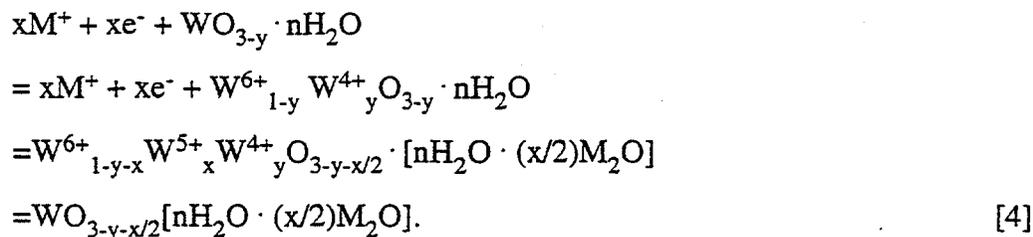


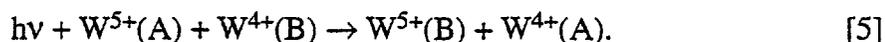
Fig. 1. Schematic of the reduction of  $W^{6+}$  in  $WO_3$  to a  $W^{5+}$  state and the oxidation of  $M^+$  to form  $M_2O$ .

We notice that only part of the film will undergo the reaction depicted in Fig. 1. More realistically, the electrochromic process in  $WO_{3-y} \cdot nH_2O$  films can be written as the following:



We propose that the chromic mechanism is originated from the small polaron (or

intervalence) transition between  $W^{5+}$  and  $W^{4+}$  states instead of  $W^{5+}$  and  $W^{6+}$  states as suggested by previous models. This process can be expressed as



Usually, a virgin film ( $y < 0.4$ ) consists mainly of  $W^{6+}$  and  $W^{4+}$  and looks transparent because there is no polaron available in the as-deposited films. According to the small polaron theory<sup>29</sup>, the electrochromic absorption peak can be expressed by the following formula:

$$\alpha = A \hbar \omega \exp\left(\frac{(\hbar \omega - \varepsilon - 4U)^2}{8U \hbar \omega_0}\right), \quad [6]$$

where  $\hbar\omega_0$  is the energy of the scattered phonon,  $U$  is the activation energy, and  $\varepsilon$  is the difference between the initial and final energy levels. This formula can still be used to express the small polaron absorption in our model. The only difference is that  $\varepsilon$  represents the difference between the local  $W^{5+}$  and  $W^{4+}$  levels instead of the difference between the local  $W^{5+}$  and  $W^{6+}$  levels as proposed in the previous models.

### 3. EXPLANATION OF EXPERIMENTAL RESULTS

#### a. Relation Between Coloration Efficiency and Ion Concentration

The coloring efficiency in an electrochromic film is defined as  $\eta = \Delta O.D./jt = \Delta O.D./Q = \log_{10}(T_b/T_c)/Q$ , where  $T_b$  and  $T_c$  are the transmittances of the film in the bleached and colored states, respectively, and  $Q$  is the charge injection per unit area

corresponding to the optical density change  $\Delta O.D.$ . The optical transmittance of the film can be expressed as a function of the absorption coefficient  $\alpha$  and the film thickness  $L$ , i.e.,  $T = T_0 \exp(-\alpha L)$ . Combining the above formulas, we have:

$$\eta = (\alpha_c - \alpha_b)(L/Q)/2.3. \quad [7]$$

where  $\alpha_c$  and  $\alpha_b$  are the absorption coefficients in the colored and bleached states, respectively. Because  $\alpha_b \ll \alpha_c$  for films with various oxygen deficiencies ( $y < 0.4$ )<sup>30,31</sup> we have

$$\eta \approx \frac{\alpha_c}{Q} \frac{L}{2.3} = \frac{\alpha_c}{x} \left[ \frac{M}{Fm} \frac{L}{2.3} \right], \quad [8]$$

where  $F$  is the Faraday constant,  $m$  and  $M$  are the mass and molar weight of the film, and  $x$  is the ion concentration in the film. The optical absorption of a solid film depends on the transition probability ( $P$ ) between the initial and final states. According to our model, optical absorption is caused by the transition between the metastable state  $W^{5+}$  and the stable state  $W^{4+}$ . The number of available sites in the  $W^{5+}$  and  $W^{4+}$  states is  $N_{5+} = x$  and  $N_{4+} = y$ , respectively. Therefore we have

$$\begin{aligned} \alpha_c &\propto P \propto (N_{5+})q(N_{4+}) \\ &\propto x y, \end{aligned} \quad [9]$$

where  $q$  is the coordinate difference between the transition sites. Combining eqs. [8] and [9] we have

$$\eta \sim y, \quad [10]$$

i.e., for a film with a specific oxygen deficiency  $y$ ,  $\eta$  is a constant. On the other hand,  $\eta$  increases with increasing oxygen deficiency ( $y$ ). These predictions are consistent with previous experimental results cited in section 1(a)<sup>3,9,10</sup> and give a reasonable explanation where other models have failed.

Yoshimura et al.<sup>32</sup> reported that tungsten oxide films had increased coloration efficiency if they were evaporated from a  $WO_2$  powder rather than from the conventional  $WO_3$  powder. Apparently, this increase is because the  $WO_2$  source can easily generate more  $W^{4+}$  states in the film than those of  $WO_3$  source. According to eq. [10], an increase in the number of  $W^{4+}$  state ( $y$ ) increases the coloring efficiency. On the other hand, if we assume the optical absorption is caused by the transition between the  $W^{5+}$  and  $W^{6+}$  states, then we should have

$$\eta \propto \frac{\alpha_c}{x} \propto \frac{(N_{6+})q(N_{5+})}{x} \propto \frac{(1-y-x)x}{x} = (1-y-x). \quad [11]$$

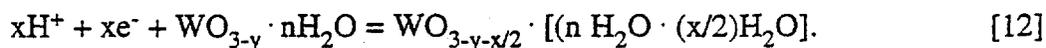
Eq. [11] is not consistent with the previous observation that  $\eta$  is independent of the ion concentration  $x$  in tungsten oxide films. Similarly, if we assume the optical absorption is caused by the transition between  $W^{6+}$  and  $W^{4+}$  states, we should have

$$\eta \propto \frac{\alpha_c}{x} \propto \frac{(N_{6+})q(N_{4+})}{x} \propto \frac{(1-y-x)y}{x}. \quad [11']$$

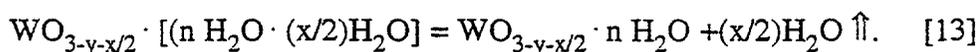
Therefore, this transition can also be eliminated because it results in a coloring efficiency that contradicts the known experimental observations.

#### b. Hydrogen Concentration in Tungsten Oxide Films During Electrochromic Reactions

In the case of proton (H<sup>+</sup>) injection, eq. [4] becomes:



The number of water molecules that can be incorporated into a tungsten oxide film depends on the dynamic balance of the film and its surrounding environment. If a WO<sub>3-y</sub> film can only absorb n water molecules per unit formula in a given environment, then the extra (x/2)H<sub>2</sub>O in the film generated during the ion injection process will escape into the surrounding environment, i.e.,



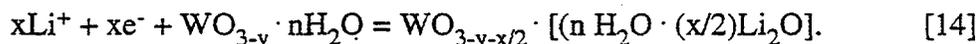
Therefore, the hydrogen content of the film (see left side of eq. [12] and right side of eq. [13]) will be a constant before and after proton injection. This result can explain the puzzling phenomena reported in the literature<sup>14,15,33</sup> that showed that the hydrogen content of the film was a constant before and after ion injection. Rauch and Wagner<sup>33</sup> used NRA to measure the hydrogen concentration profile before and after a tungsten oxide film was colored in a high-vacuum chamber. The WO<sub>3-y</sub> · nH<sub>2</sub>O film was covered with Rh film (50 nm) and exposed to hydrogen gas for coloration. This coloring process can be expressed by eq. [12]. Because the film was exposed to the same vacuum environment before and after the coloration, the extra (x/2)H<sub>2</sub>O was released to the surrounding environment and the film became WO<sub>3-y-x/2</sub> · nH<sub>2</sub>O. Therefore, the measured H concentration (c<sub>H</sub>) should be a constant before and after the coloration. The only difference in the film is the increased oxygen deficiency or W<sup>5+</sup> state after coloration.

In a separate experiment<sup>15</sup>, Rauch and Wagner measured hydrogen concentration in a solid state device with a structure of Al/NiO<sub>x</sub>/Ta<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/ITO/glass. When this device was colored at +1.8 V, c<sub>H</sub> in the NiO<sub>x</sub> layer decreased drastically to about half the value at

0 V. Unexpectedly,  $c_H$  in the  $WO_3$  layer did not increase, but  $c_H$  increased at the  $WO_3/ITO$  and  $WO_3/Ta_2O_5$  interfaces. They concluded that the assumed reaction of eq. [1] was not adequate for explaining the electrochromism of  $WO_3$ . According to our model, lost  $c_H$  in the  $NiO_x$  layer has been relocated to the  $WO_{3-y}$  layer and induces coloration in the film. These hydrogen atoms combine with  $x/2$  moles of oxygen in the film to form  $(x/2)H_2O$  and is then released to the surrounding environment ( $Ta_2O_5$  and ITO). The increase in the total amount of hydrogen in  $Ta_2O_5/WO_3/ITO$  is just equal to the decreased hydrogen concentration in  $NiO_x$  and the integer amount of hydrogen in the whole device has not changed.

#### c. Lithium Concentration in Tungsten Oxide Films During Electrochromic Reactions

In the case of lithium ion injection, eq. [4] becomes:



Because  $Li_2O$  cannot escape easily from the film into the surrounding environment, the accumulation of lithium in the tungsten oxide film will be observed after lithium ion injection. This is consistent with the result reported by Goldner et al.<sup>13</sup>.

#### d. Self-Bleaching Behavior in Tungsten Oxide Films

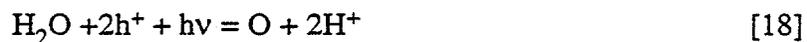
The above model can be used to explain the self-bleaching behavior of tungsten oxide films<sup>34</sup>. A colored tungsten oxide film may remain in the colored state for a long time if it is stored in an oxygen-free environment, but it will bleach soon after exposure to an oxygen environment. This is because the oxygen in the surrounding environment can diffuse into the film and oxidize the  $W^{5+}$  sites. For a lithium colored film, this reaction can be expressed as the following:



achieved by heating them in an oxidizing atmosphere at a temperature near 300°C. This phenomenon can be explained if the as-deposited  $WO_{3-y}$  film is mainly composed of  $W^{6+}$  and  $W^{4+}$  as we proposed here. When the film is exposed to the surrounding environment, two processes compete with each other: the first is the reduction of  $W^{6+}$  to  $W^{5+}$  and the second is the oxidization of  $W^{5+}$  to  $W^{6+}$ . In an inert environment or vacuum, the first process is favored and heating may reduce some of  $W^{6+}$  to  $W^{5+}$  and form color centers. This reduction process is the origin of the thermochroism in  $WO_{3-y}$  films. In an oxygen environment, heating will enhance the opposite process (i.e., oxidization of  $W^{5+}$  into  $W^{6+}$ ) and bleach a colored film. A  $WO_{3-y}$  film heated at 300°C in an oxygen environment does not lend itself to further UV coloration because it has lost residual water that provided the compensating ions for the photochromic process. Its electrochromic coloring efficiency is also reduced because of the reduction of its porous structure.

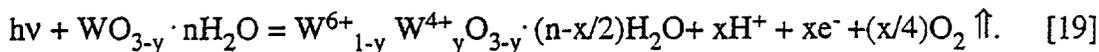
#### 4. CORRELATION BETWEEN PHOTOCROMISM AND ELECTROCHROMISM

The above model can also be used to explain photochromism in tungsten oxide films. In a photocoloration process, incident photons can separate part of the  $H_2O$  adsorbed in a  $WO_{3-y}$  film as suggested by Bechinger et al.<sup>37</sup>. A water-based electrolyte that is in contact with  $WO_3$  can be decomposed by irradiation into hydrogen and oxygen (photolysis). The photogenerated holes ( $h^+$ ) can weaken the H-O bond of water molecules and cause these water molecular to decompose into protons and highly reactive oxygen atoms according to:

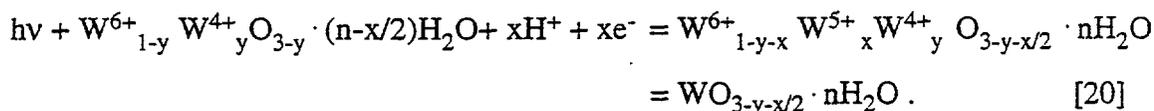


Therefore, the first step in a photochromic reaction in a  $WO_{3-y} \cdot nH_2O$  film can be expressed

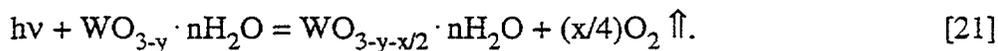
as:



After oxygen escapes from the film, separated protons will combine with some  $\text{O}^{2-}$  in the film to form more  $\text{H}_2\text{O}$  with the help of photon energy. This step is exactly the same as in the case of electrochemical coloration (eqs. [4] and [12]):



By combining reactions [19] and [20], the net reaction is



Eq.[21] indicates that the photochromic coloration of a tungsten oxide film is accompanied by the release of oxygen<sup>34</sup>. This means that the photochromic reaction will be faster in an oxygen-free environment (vacuum) and slower in an oxygen-rich environment. This has been observed by Bechinger et al.<sup>37</sup>. Eq. [21] also indicates that the number of water molecules in a tungsten oxide film is unchanged during the photochromic reaction but that the oxygen deficiency in the film is increased.

The self-bleaching behavior of a photocolored film has been reported by Bechinger et al.<sup>37</sup> and is very similar to that of an electrochemically colored film, i.e., exposure to oxygen will largely accelerate the self-bleaching process as indicated by eq. [17]. We notice that the initial electrochromic phenomenon in a tungsten oxide film, as reported by Deb<sup>1</sup>, was found in a film with the two gold electrodes deposited on the same surface. The coloration of Deb's film can also be expressed by eq. [19] if we simply replace  $hv$  by electric field  $E$ . For a film stored in a dry environment, the equilibrium value of  $n$  is much

smaller than for those stored in a humid environment, therefore the final coloration of the film will be much less in a dry environment.

In order to distinguish the coloring efficiency in electrochromic and photochromic processes, we express the electrochromic-coloring efficiency as  $\eta_{EC}$  in the following discussion.  $\eta_{EC}$  is defined as

$$\eta_{EC} = \Delta O.D./jt . \quad [22]$$

where  $j$  is the current density ( $A/cm^2$ ), and  $t$  is the coloring time (sec) corresponding to the optical density change  $\Delta O.D.$ . Considering the fact that the elementary charge =  $1.6 \cdot 10^{-19}$  A sec, we have  $jt = 1.6 \cdot 10^{-19} \cdot (\# \text{ of electrons}/cm^2)$ . Therefore,

$$\begin{aligned} \eta_c &= 6.25 \cdot 10^{18} [\Delta O.D./(\# \text{ of electrons}/cm^2)]. \\ &= \Delta O.D. [6.25 \cdot 10^{18} /(\# \text{ of color centers}/cm^2)], \end{aligned} \quad [23]$$

Similar to eq. [22], we define the photochromic-coloring efficiency ( $\eta_{PC}$ ) as:

$$\eta_{PC} = \Delta O.D./It, \quad [24]$$

where  $I$  is the light intensity. For simplification, we consider here only the case of photochromic coloration by a monochromic light ( $h\nu$ ) source, then we have

$$It = n_1 h\nu, \quad [25]$$

where  $n_1$  is the number of photons (with energy  $h\nu$  in eV) falling on a unit area in time  $t$

(sec). Considering the relation that  $1 \text{ eV} = \text{Joule}/6.25 \times 10^{18}$ , we have

$$n_i = \# \text{ of photons/cm}^2 = I t * 6.25 \times 10^{18}/h\nu, \quad [26]$$

where the unit of  $h\nu$  is in Joules.

In a photochromic-coloring process, suppose the proton generation efficiency (corresponding to the forward reaction shown in eq. [19]) of a photon (with energy  $h\nu$ ) is  $\beta$  and the ion injection efficiency (the possibility of forward reaction shown in eq.[20]) is  $\gamma$ , then every photon can induce  $\alpha = \beta\gamma$  color centers (or  $W^{5+}$ ) during the combined process shown in eq. [21]. Therefore we have:

$$\# \text{ of color centers/cm}^2 = \alpha n_i = \alpha I t * 6.25 \times 10^{18}/h\nu. \quad [27]$$

or

$$I t = \# \text{ of color centers/cm}^2 / [\alpha * 6.25 \times 10^{18}/h\nu]. \quad [28]$$

By inserting eq. [28] into the definition of the  $\eta_p$  (eq.[24]) we have:

$$\eta_{PC} = [\alpha/h\nu] \Delta O.D [6.25 \times 10^{18} / \# \text{ of color centers/cm}^2]. \quad [29]$$

By combining the eq. [23] and [29], we obtain a relation between  $\eta_{EC}$  and  $\eta_{PC}$  as:

$$\eta_{PC} = [\alpha/h\nu] \eta_{EC}. \quad [30]$$

We notice that the forward reaction efficiency  $\alpha$  for eq. [14] depends not only on the photon energy, but also on the oxygen release rate (or surrounding environment), which affects the equilibrium conditions in [19].

## 5. SUMMARY

Electrochromism in  $\alpha$ - $\text{WO}_{3-y}$  films has been investigated for more than twenty years and a variety of models have been developed to explain this phenomenon. Although these models are consistent with many experimental observations, they cannot explain several important experimental results reported in the literature. We propose a new model to describe the chromic mechanism in  $\alpha$ - $\text{WO}_3$  films ( $\text{WO}_{3-y} \cdot n\text{H}_2\text{O}$ ). It not only explains several seemingly-conflicting experimental results reported to date, but also has practical implications with respect to improving the coloring efficiency and durability of EC devices. The model indicates that as-deposited tungsten oxide film ( $\alpha$ - $\text{WO}_3$ ) should include mainly  $\text{W}^{6+}$  and  $\text{W}^{4+}$  states and can be expressed as  $\text{W}^{6+}_{1-y} \text{W}^{4+}_y \text{O}_{3-y} \cdot n\text{H}_2\text{O}$ . In this model, the chromic mechanism is based on the small polaron transition between the  $\text{W}^{5+}$  and  $\text{W}^{4+}$  states instead of  $\text{W}^{5+}$  and  $\text{W}^{6+}$  states as suggested by previous models. This model predicts an increased coloring efficiency for  $\alpha$ - $\text{WO}_3$  films with increasing oxygen deficiency and a constant coloring efficiency for  $\alpha$ - $\text{WO}_3$  films with a specific oxygen deficiency. It reveals that a lithium-colored film will undergo an irreversible degradation during the self-bleaching (or oxidation) process. The model also explains the fact that the  $\text{H}^+$  content in an  $\alpha$ - $\text{WO}_{3-y}$  film remains constant when the film is colored by injecting protons, but the  $\text{Li}^+$  content in the film increases when the film is colored by injecting lithium ions. The model predicts that a well-controlled oxygen deficiency level can enhance the coloring efficiency of the EC devices. On the other hand, hermetic sealing of a lithium-based electrochromic device can minimize the irreversible degradation that appears during the self-bleaching process. Finally, a unified theory for both electrochromic and photochromic behavior in amorphous  $\text{WO}_{3-y}$  films has also been presented.

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