

COLORATION AND BLEACHING PHENOMENA OF AMORPHOUS WO₃ FILMS DUE TO THE ELECTROCHEMICAL INSERTION OF DIVALENT CATIONS

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ABSTRACT

It was confirmed that the divalent cations, Zn²⁺ and Cu²⁺ were electrochemically inserted into amorphous WO₃ films prepared by r.f.-magnetron sputtering method. Coloration of the films was also observed, and the films were, however, bleached gradually. The bleaching mechanism was discussed based on the ab-initio molecular orbital calculations, in which Li⁺ or Zn²⁺ ions were introduced into the WO₃ frameworks. In the case of Zn insertion, electrons were trapped in a non-bonding Zn 4s orbital just below the conduction band. It was finally concluded that in the films with distorted WO₃ frameworks, Zn 4s orbital was mingled in the conduction band and electrons were free to be transferred between W⁶⁺ and W⁵⁺. As the structural relaxation progressed, electrons were gradually trapped in Zn 4s orbital, and the films were finally bleached.

INTRODUCTION

Amorphous WO₃ thin films have been extensively studied because of their reversible electrochromic (EC) property, being applied to EC display and smart windows. Electrochromism of WO₃ is due to the formation of tungsten bronze according to the following reaction.¹



Where small-polaron² is formed by insertion of electron, and a part of W⁶⁺ changes into W⁵⁺. A wide absorption peak ranging from visible to infrared region is caused by the transfer of an electron between W⁵⁺ and W⁶⁺. In the previous researches, monovalent cations such as H⁺ and Li⁺ have been inserted to the films. Recently, it was found that the divalent cations, Zn²⁺ and Cu²⁺ were also inserted by means of the conventional electrochemical method.³ After the coloration, gradual bleaching was observed in the case of the insertion of the divalent cations, whereas such the bleaching has not been observed in the monovalent cation insertion. According to the theoretical calculations, Nanba et al.⁴ showed that the electron insertion brought about the distortion of WO₆ unit, which was consistent with the small-polaron absorption model.² In the case of insertion of divalent cations, two electrons are simultaneously inserted per one divalent cation. Furthermore, the divalent cations, Zn²⁺ and Cu²⁺ are quite different in the chemical bonding character with the monovalent cation, H⁺ and Li⁺. Then, in the present study, the coloration and bleaching phenomena due to the insertion of divalent cations were investigated

under the various conditions, and the bleaching mechanism was discussed based on the ab-initio molecular orbital calculations.

EXPERIMENTAL

WO₃ films were prepared by an r.f. magnetron sputtering method on the indium tin oxide (ITO) coated glass substrates. According to Nanba et al.,⁵ the hexagonal-WO₃ like structure is formed in the films prepared under a low O₂ partial pressure (Ar/O₂ = 4/1), and the tetragonal-WO₃ like framework is produced at a high O₂ pressure (Ar/O₂ = 1/1) (Fig.1). The electrochemical insertions of Li⁺ or Zn²⁺ ions were performed using a conventional electrochemical cell; 1M LiClO₄/propylene carbonate solution (PC) or ZnCl₂/PC was used as the electrolyte. The amount of ions inserted into the films was estimated by the coulomb meter. X-ray photoelectron spectroscopic (XPS) measurements were carried out to obtain valence band spectra. Transmittance spectra were measured for the colored and bleached films.

(a) Tetragonal-WO₃

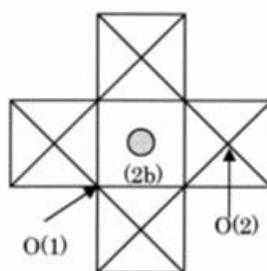
P4/nmm(No.129)

a₀=0.527nm

c₀=0.392nm

(2b)-O(1) = 0.27nm

(2b)-O(2) = 0.26nm



(b) Hexagonal-WO₃

P63/mcm(No.193)

a₀=0.73nm

c₀=0.78nm

(2b)-O(1) = 0.33nm

(2b)-O(2) = 0.37nm

(4d)-O(1) = 0.25nm

(4d)-O(2) = 0.21nm

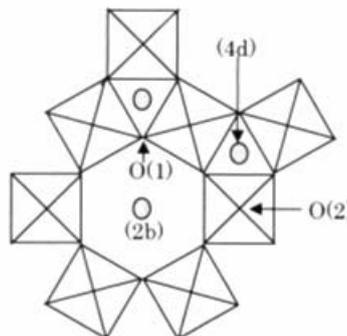


Fig. 1. Framework structures of (a) tetragonal- and (b) hexagonal-WO₃ crystals and the vacant sites for the cation insertion.⁴

The electronic states of WO₆ unit were examined by using the discrete variational X α (DV-X α) molecular orbital (MO) method.⁶ The atomic orbitals used in the MO calculations were W 1s-6s, O 1s-2p, Li 1s-2p, and Zn 1s-4p. Cluster models were constructed according to the previous study,⁴ which were embedded in Madelung potentials generated by point charges outside the clusters to reduce the termination effects. In the previous study, only electrons were introduced to the vacant W 5d orbital, and in the present study, however, Li⁺ and Zn²⁺ cations were also introduced to the vacant sites; 2b site in tetragonal-WO₃ and 4d site in hexagonal-WO₃ (Fig.1).

RESULTS AND DISCUSSION

Coloration and bleaching phenomena in WO_3 films

Films were amorphous even after the Zn insertion, which was confirmed by X-ray diffraction measurements. Fig. 2 shows the valence band XPS spectra.⁷ Zn 3d peak at 10 eV increases in intensity with increasing the amount of Zn ions inserted to the films. Therefore, it is confirmed that Zn ions are successfully inserted. A small peak appears commonly at 0 eV in the Zn-inserted films, which is identified as the reduction of W ions; $\text{W}^{6+}(5d^0) \rightarrow \text{W}^{5+}(5d^1)$.

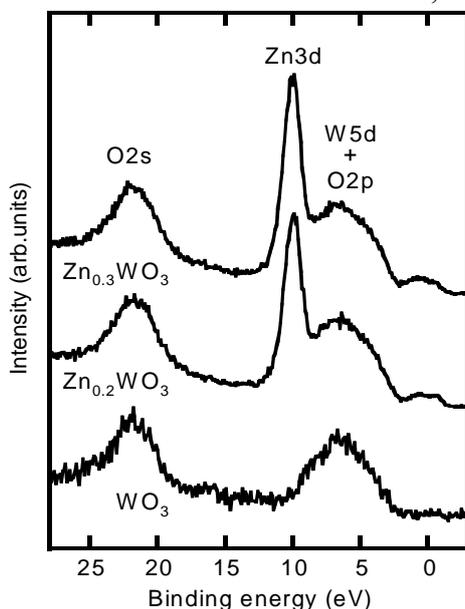


Fig. 2. Valence band spectra of the WO_3 films before and after Zn insertion.⁷

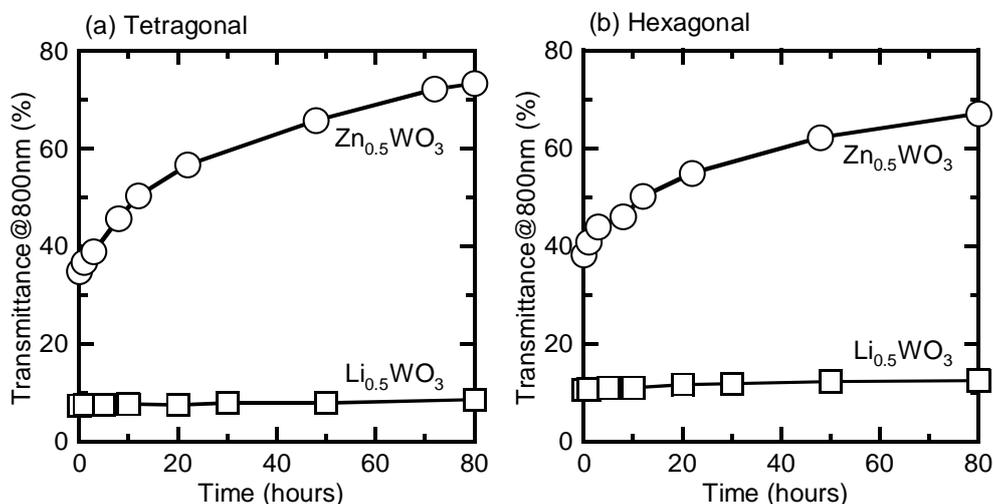


Fig. 3. Time dependence of the optical transmittance at 800 nm after the Li and Zn insertions into WO_3 films with (a) hexagonal- and (b) tetragonal-frameworks.⁷

WO_3 films were colored by the insertion of Zn ions as well as Li ions, in the case of Zn insertion, however, the films were gradually bleached. Fig. 3 shows the time dependence of the transmittance at 800 nm after the ionic insertions.⁷ In the case of Li insertion, the transmittance is

kept at almost constant. In the Zn insertion, however, the transmittance gradually increases and is restored to the initial state after 80 h.

Consideration on the bleaching mechanism

The ionic radii of Li^+ and Zn^{2+} are very close ($\text{Li}^+ = 0.090$ nm, $\text{Zn}^{2+} = 0.088$ in 6-coordination). The difference between Li and Zn ions is not only the charge but also the chemical bonding character. It is therefore supposed that the difference in chemical bonding character is the reason for the bleaching phenomena in the WO_3 films. Then, molecular orbital calculations were performed to examine the bonding character and electronic states in the WO_3 films. Fig. 4 shows the bond overlap population (BOP) of the W-O bonds in the central WO_6 units in the cluster models. BOP was estimated from the Mulliken population analysis of the results of MO calculations. It indicates the electronic population shared between two atoms, and is used as a measure of bond covalency and bond strength. In the MO calculation for the cluster model constructed from hexagonal- WO_3 , when one Li or Zn ion was introduced to the cluster, the MO calculation did not reach to a convergence. The results shown in Fig. 4 were obtained by introducing two Li or Zn ions into the cluster.

In Fig. 4, “none” means the results without introducing the ions into $(\text{WO}_6)_7$ clusters, and “ $7e^-$ ” indicates the results after introducing seven electrons into the clusters which simulates the reduction of all W ions in the clusters from $6+$ to $5+$ states. These results were given in Ref. 4. “O1-6” means oxygen in the central WO_6 units in the cluster models. After the insertions of ions and electrons, BOP decreases in most W-O bonds. As for Li and Zn insertions, larger change in BOP is commonly observed after Zn insertion.

Before the MO calculations, it was expected that Zn-O bonds showed much higher BOP than Li-O, because Zn has much higher electronegativity than Li (Zn = 1.65, Li = 0.98 in Pauling scale). Contrary to the expectation, Zn-O bonds in the WO_3 frameworks showed smaller BOP than Li-O bonds (Zn-O = 0.021, Li-O = 0.036 in tetragonal- WO_3 , Zn-O = 0.130, Li-O = 0.226 in hexagonal- WO_3). This result is quite remarkable.

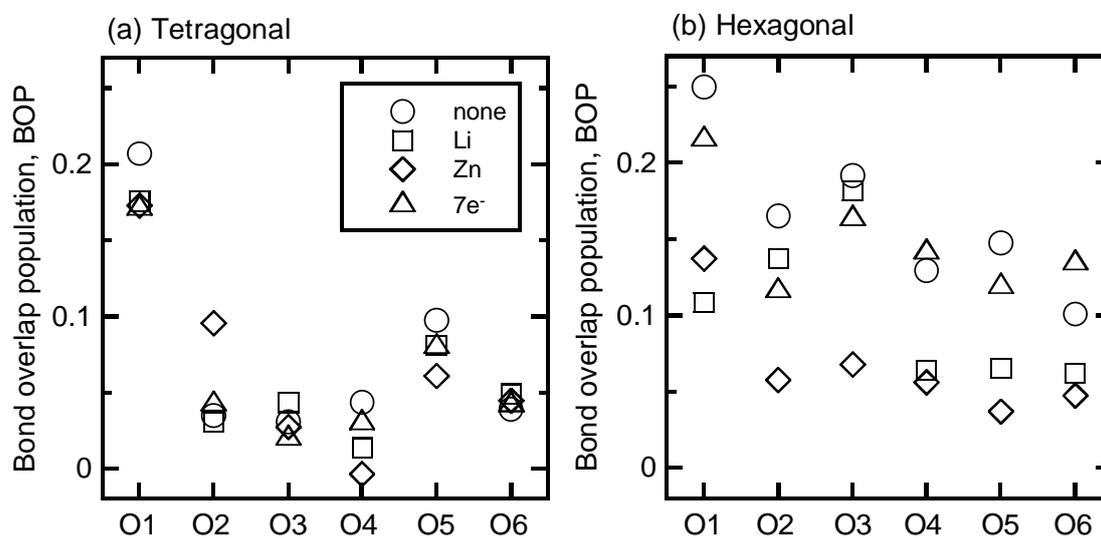


Fig. 4. Effect of cation and electron insertion on the bond overlap population of W-O bonds in the central WO_6 units in the cluster models constructed from (a) tetragonal- and (b) hexagonal- WO_3 frameworks.

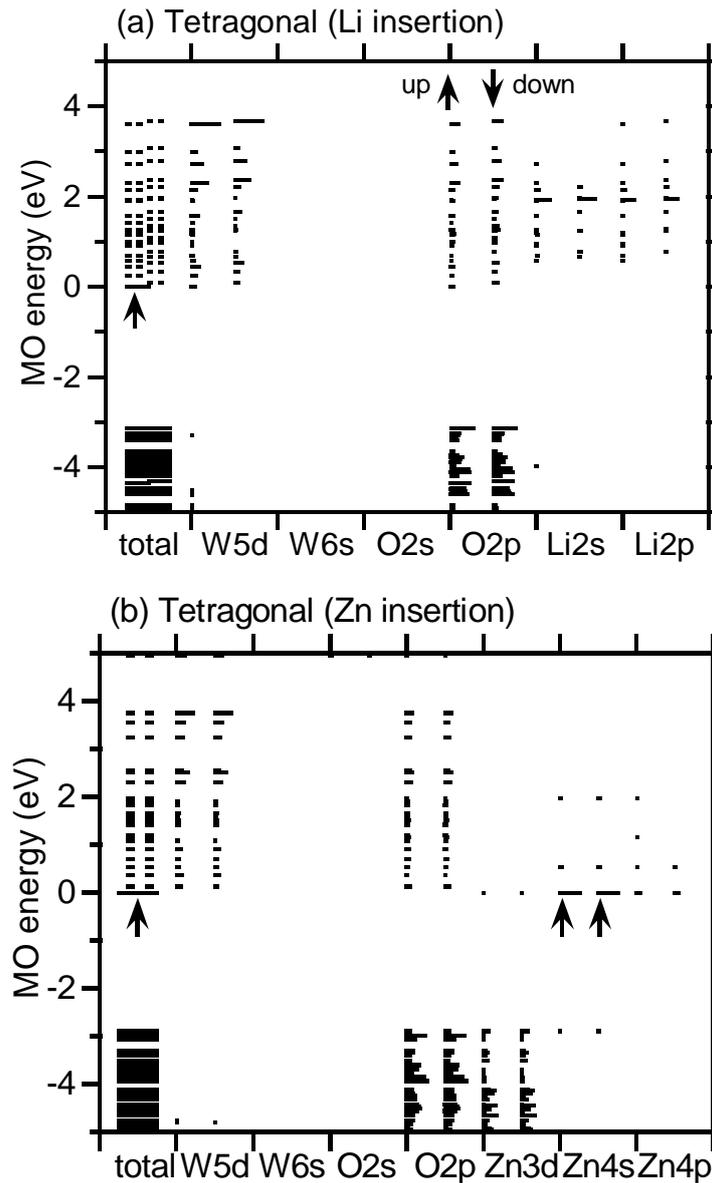


Fig. 5. Energy level diagrams for the cluster models constructed from the tetragonal- WO_3 framework associated with (a) Li and (b) Zn ions. On the extreme left, the MO levels occupied by electrons are drawn by continuous lines, and the vacant levels are by dotted lines. The contributions of atomic orbitals in each MO level are also shown.

Fig. 5 shows the energy level diagrams, in which the contributions of up spin and down spin are separately shown. As shown in Fig. 5a, Li insertion into the tetragonal- WO_3 framework introduces an electron into the bottom of the conduction band (0 eV), which is formed by W 5d and O 2p orbitals, and is in a conventional notation, anti-bonding t_{2g}^* level. Moreover, an energy splitting due to the spin polarization is also reproduced. It is noted that there is no contribution of Li in the t_{2g}^* level. As for the Zn insertion (Fig. 5b), the contribution of Zn is clearly observed in the MO level at the bottom of the conduction band. The level is located just below t_{2g}^* level. It is noted that there is no contribution of O 2p in this level, that is, this level is non-bonding Zn4s

orbital. It is therefore indicated that due to the non-bonding Zn 4s orbital, BOP of Zn-O bonds in WO₃ frameworks is reduced. Moreover, it is identified as an “electron-trapped state.” In such the state, electrons are not transferred to the surrounding W⁶⁺ ions through oxide ions, and the electron transfer between W⁶⁺ and W⁵⁺ must be restricted. The electronic states reproduced in Fig. 5b are the final states, that is, the bleached states. It may take a long time for Zn ions to settle into the stable sites because it must be accompanied by the relaxation of WO₃ frameworks and the migration of Zn ions within the WO₃ frameworks.

CONCLUSION

Coloration of WO₃ films was confirmed due to the electrochemical insertion of the divalent cations. But the films were gradually bleached only in the insertion of the divalent cations. The bleaching mechanism was theoretically interpreted. The molecular orbital calculations were performed by introducing Li and Zn ions into the WO₃ frameworks. In the case of Zn insertion, it was reproduced that electrons were trapped in a non-bonding Zn 4s orbital. The trapped level was located just below the conduction band. The following mechanism was finally proposed; if the WO₃ frameworks were distorted, electrons were transferred from Zn to W ions via neighboring O ions. As the structural relaxation progressed, electrons formerly transferred between W⁶⁺ and W⁵⁺ were gradually trapped in Zn 4s orbital, and the films were finally bleached.

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