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Theoretical Consideration on Photochromism of an Oxide Doped with Transition-Metal Ions in Strong Electric Field

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We propose a new principle of an optical memory using photoionization of transition-metal ions doped into an oxide which is kept in strong electric field. Several conditions required to realize an optical memory are present.

Photochromism of oxides doped with transition-metal ions has been studied from theoretical and practical viewpoints.[1,2] In an application of the photochromism to an optical memory, there was a substantial problem that the change in optical absorption induced by light irradiation was degraded with time. This degradation results from thermal reverse reaction.[2] We have preliminary considered various methods to suppress the thermal reverse reaction, and recently we found that the presence of strong electric field is effective to suppress the thermal reverse reaction. In the present letter, we describe a principle of field-assisted photochromism and propose preferable transition-metal ions and host materials.

The principle of the field-assisted photochromism is illustrated in Fig. 1. A photochromic material is interposed between two thin electrodes such that strong electric field is applied to the photochromic material. One of two electrodes should be blocking electrode for electron injection into the photochromic material. We assume that the charge of doped transition-metal ions, M^{n+}, is identical with the charge of metal ions of a host metal oxide, and M^{n+} ions form an impurity level with the state density of N_d at E_d below the bottom of the conduction band (the depth energy E_d is less than one-half of the band gap energy E_g).

Figure 1(a) shows the band diagram when a voltage, V, is applied such that the blocking electrode (right) is negatively charged with respect to the ohmic electrode (left). In the presence of strong electric field, electrons in a shallow impurity level of M^{n+} ions can be thermally emitted into the conduction band. The thermal emission of electrons results in the variation of the concentration of M^{n+} ions with time. Consequently, the formation of a deep impurity level of M^{n+} ions is an important condition required to realize an optical memory. If the condition is satisfied, the

positive space charges due to M^{n+1} ions are not formed in the photochromic material, and thus the band of the photochromic material is straight as shown in Fig. 1(a).

Under the light irradiation with photon energy $h\nu$, such as $E_d < h\nu < E_g - E_d$, electrons in M^{n+} ions can be optically transferred to the conduction band, and subsequently electrons in the conduction band are drifted toward the left electrode along an applied electric field. This process is called photoionization of doped transition-metal ions: $M^{n+} \rightarrow M^{n+1} + e^-$. Even if light irradiation is turned off, M^{n+1} ions lying above the Fermi level of the ohmic electrode remain unchanged. In weak electric field, the band bending Φ at a distance x is approximately given by,

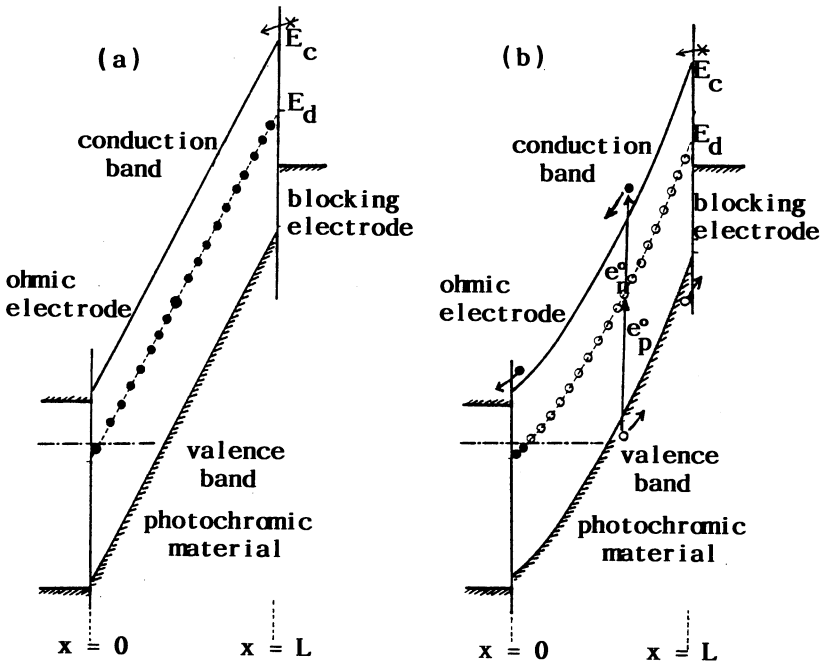

Fig. 1. Schematic illustration of field-assisted photochromism. Figs. 1(a) and 1(b) are the band diagrams of a film consisting of ohmic electrode (left), photochromic material, and blocking electrode (right) before and after light irradiation, respectively.

$$\Phi(x) = (2\varepsilon)^{-1} e N_0 (x - L + (2\varepsilon V/e N_0)^{1/2})^2 , \quad (1)$$

where ε is the dielectric constant of the photochromic material, N_0 is the concentration of M^{n+1} ions, and L is the thickness of photochromic material. In strong electric field, space charge is formed in the range of x = 0 to x= L. Thus, the band bending is the sum of linear potential and potential of space charge:

$$\Phi(x) = (2\varepsilon)^{-1} e N_0 x^2 + L^{-1} (V - (2\varepsilon)^{-1} e N_0 L^2) x . \quad (2)$$

Marked change in optical absorption will be obtained in the latter case. As seen in Fig. 1(b), the presence of the electric filed is effective for the charge separation of electron-hole pairs generated by light irradiation and for suppressing the thermal reverse reaction from the ohmic electrode.

In an optical memory, the concentration of M^{n+} ions must be optically monitored without modifying its concentration. For this purpose, d-d absorption of M^{n+} ions is most useful because d-d absorption within the band gap results in no free carriers in the conduction (valence) band. The

oscillation strength of d-d absorption of transition-metal ions is dependent on symmetry of the crystal field. It was reported that some d-d absorptions of transition metal ions doped into oxides with no inversion symmetry were the electric-dipole transition.[3-5] For instance, the oscillation strength of 0.01 was obtained for d-d absorption at 650 nm for Co-doped ZnO.[3] When 1 mol% Co-doped ZnO film with 1000 nm in thickness is used as a photochromic material, the change in optical density of d-d absorption at 650 nm is estimated to be of 6×10^{-3} at a voltage of 1000 V.

In an application of an optical memory, the M^{n+1} ions are should be reduced optically to M^{n+} ions. This requirement can be fulfilled by the photon-induced charge transfer from the valence band to vacant impurity level originating from M^{n+1} ions, as shown in Fig. 1(b). Under the light irradiation with a photon energy larger than $E_g - E_d$, M^{n+} ions are generated and successively the photoionization of M^{n+} ions takes place. The equilibrium concentration of M^{n+} ions, n_d, is calculated as follows:[6]

$$n_d = N_d(c_n n + e_p/(c_n n+c_p p+e_n+e_p)), \quad (3)$$

where n and p are the electron and hole concentrations in the conduction and valence bands, respectively. The emission rate for an electron, e_n, is the sum of the thermal emission rate, e_n^t, and the optical one, e_n^o. Similarly, the emission rate for a hole is: $e_p = e_p^t + e_p^o$. The capture probability, $c_{n,p}$, is also the sum of nonradiative capture and radiative one. Under the intense light irradiation and in the presence of strong electric field, the optical emission rates of e_n^o and e_p^o are predominant in Eq. 3. Thus, the concentration n_d is simplified to N_d ($e_p^o/(e_n^o + e_p^o)$). The optical emission rates of e_n^o and e_p^o are correlated to the photoionization cross section σ_n^o and to the charge-transfer cross-section σ_p^o such as $e_n^o = I\sigma_n^o$ and $e_p^o = I\sigma_p^o$ where I is photon flux. The optical cross section for photoionization is given by[6]

$$\sigma_n^o = \frac{\text{constant}}{h\nu} \sum | \langle \Psi_i | \mathbf{r} | \Psi_k \rangle |^2 J_k , \quad (4)$$

where Ψ_i and Ψ_k are wave functions of a M^{n+} ion and of a conducting electron, and the function J_k carries the information about the vibrational states. The optical cross section for charge transfer has an analogous formula.

On the basis of group theory, we consider the matrix element for the photoionization and charge transfer of Co-, Ni-, and Cu-doped ZnO. In a host material of ZnO, the bottom of the conduction band and the top of the valence band exist at the Γ point of the Brillouin zone.[7] In ZnO, Co^{2+}, Ni^{2+} and Cu^{2+} ions substituted for Zn sites undergo strong trigonal distortion, so that electronic states of these ions can be characterized by the irreducible representation in the double group $\overline{C_{3v}}$ including the spin-orbit interaction.[3-5] The irreducible representations of the conduction band minimum and valence band maximum are $E_{1/2}$ in $\overline{C_{3v}}$. For the electric

dipole transition, the electric dipole operator, er, is transformed as A_1 for the electric field parallel to c axis ($\mathbf{E}||c$), and as E for $\mathbf{E}\perp c$.

For the photoionization processes, $Co^{2+}(Ni^{2+}, Cu^{2+}) \dashrightarrow Co^{3+}(Ni^{3+}, Cu^{3+}) + e^-(c.b.)$, an electron at the initial state is localized in the ground state of Co^{2+} (Ni^{2+} and Cu^{2+}) ions, while an electron at the final state is delocalized in the conduction band. The ground states of Co^{2+}, Ni^{2+} and Cu^{2+} are $E_{1/2}$, A_1, and $E_{1/2}$, respectively. The allowed final states for the photoionization are written as:

$Co^{2+}(Cu^{2+})$; $E_{1/2}\times A_1 = E_{1/2}$ for $\mathbf{E}||c$, $E_{1/2}\times E = E_{1/2} + E_{3/2}$ for $\mathbf{E}\perp c$.

Ni^{2+}; $A_1 \times A_1 = A_1$ for $\mathbf{E}||c$, $A_1 \times E = E$ for $\mathbf{E}\perp c$.

Accordingly, the oscillation strength for the photoionization of Co^{2+} and Cu^{2+} ions is expected to be fairly large, whereas the photoionization of Ni^{2+} ions is forbidden. For the charge transfer of $Co^{3+}(Ni^{3+}, Cu^{3+}) + e^-(v.b.) \rightarrow Co^{2+}(Ni^{2+}, Cu^{2+})$, a transferring electron is in the valence band at the initial state and in $Co^{2+}(Ni^{2+}, Cu^{2+})$ ions at the final state. The irreducible representations of the allowed final states are

$E_{1/2} \times A_1 = E_{1/2}$ for $\mathbf{E}||c$, $E_{1/2} \times E = E_{1/2} + E_{3/2}$ for $\mathbf{E}\perp c$.

All of states of Co^{2+} (Cu^{2+}) consist of $E_{1/2}$ and $E_{3/2}$, whereas states of Ni^{2+} consist of A_1, A_2, and E.[3-5] Thus, the charge transfer is allowed for Co^{2+} and Cu^{2+} ions, but is forbidden for Ni^{2+} ions.

The selection rules for the photoionization and charge transfer at an arbitrary k vector in the Brillouin zone can be obtained by considering time inversion.[8] Non-zero matrix element is obtained for the initial state of a M^{n+} ion containing odd number of d electrons in the photoionization, and for the final state of a M^{n+} ion containing even number of d electrons in the charge transfer: $d^{2m+1} \dashrightarrow d^{2m} + e^1(c.b)$, and $d^{2m} + e^1(v.b) \dashrightarrow d^{2m+1}$. Using this selection rule, one can choose transition metal ions to be employed as a photochromic material.

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