



Title	Ultraviolet-induced erasable photochromism in bilayer metal oxide films
Author(s)	Terakado, Nobuaki; Tanaka, Keiji; Nakazawa, Akira
Citation	Solid State Communications, 151(18), 1285-1287 https://doi.org/10.1016/j.ssc.2011.05.037
Issue Date	2011-09
Doc URL	http://hdl.handle.net/2115/47300
Type	article (author version)
File Information	SSC151-18_1285-1287.pdf



[Instructions for use](#)

Ultraviolet-induced erasable photochromism in bilayer metal-oxide films

Nobuaki Terakado^a, Keiji Tanaka^a, Akira Nakazawa^b

^a *Department of Applied Physics, Graduate School of Engineering, Hokkaido University, Kita-ku, Sapporo 060-8628, Japan*

^b *Guala Technology Co., Ltd.*

Yokohama Kanazawa High-Tech Center, Technocore 4-D 1-1-1 Fukuura, Kanazawa-ku, Yokohama 236-0004, Japan

ABSTRACT

We demonstrate that optical transmittance of bilayer samples consisting of pyrolytically-coated amorphous Mg-Sn-O and metal-oxide films as In_2O_3 and SnO_2 decreases upon ultraviolet illumination, which can be recovered by annealing in air at $\sim 300^\circ\text{C}$. Spectral, structural, and compositional studies suggest that this photochromic phenomenon is induced by photoelectronic excitation in the Mg-Sn-O film, electron injection into the metal oxide, which becomes negatively charged, and subsequent formation of metallic particles, which absorb and/or scatter visible light.

Keywords:

A. Oxide film;

A. Wide-gap semiconductor;

D. Photochromism.

1. Introduction

It is known that a variety of materials exhibit photoinduced decreases in optical transmittance, which are temporary, permanent, or erasable. The most known may be the print-out effect in Ag-halide crystals in photographic films, in which Ag micro-crystals emerge following photoelectronic excitation [1]. Many similar or novel Ag-related phenomena have been discovered in amorphous and crystalline oxides [2-4]. Photo-reduction and oxidation in Ag-free inorganic materials can also exhibit several kinds of photochromisms [5-7]. It is also known that the chalcogenide glass exhibits a photoinduced red-shift of optical absorption edges, which can be recovered by annealing [8]. On the other hand, organic films present a variety of photochromism or coloration phenomena, which may be triggered by photoinduced isomerization of dye molecules [9]. These photochromic phenomena can be applied to smart windows, displays, and optical memories,

for which high performance and stable materials have been required. We here underline that the known phenomena appear in single materials.

By contrast, Nakazawa and Shinoda have discovered an erasable photochromic phenomenon in a new system, a *bilayer* sample consisting of Mg-Sn-O (MSO) and transparent electrically-conducting In-Sn-O (ITO) films [10]. This bilayer film has an initial transmittance of ~80% at visible wavelengths, which decreases to ~5% after an ultraviolet exposure with an intensity of 200 mW/cm² for 40 min. The darkened state is retained, at least, for one year, which can be recovered by annealing at 300°C. They found that the use of MgO or SnO₂ films, instead of the ternary MSO film, does not afford the darkening phenomenon [11]. They also confirmed that single layers of MSO and ITO undergo no photoinduced changes [11], the result suggesting the importance of MSO-ITO hetero-junctions.

However, the photochromic mechanism in the bilayer system remains speculative. In addition, since the structure, which is robust and stable, can be prepared relatively easily, some applications are also promising. We therefore investigate the mechanism through spectral, structural, and compositional experiments, demonstrating an important role of electron injection at the hetero-junction.

2. Experimental

Several kinds of bilayer samples were prepared in the present work. For the bottom layer, in addition to ITO films, which were sputtered to silicate-glass substrates, we also employed semi-transparent (~30 nm in thickness) films of In, Al, Sn, Sb, Bi, Cu, Te, Ge, and Au, which were evaporated in vacuum. Onto these films, MSO films were overlaid through spin-coating of organic metallic compounds and subsequent baking at ~300°C in air. The thickness of the MSO films was ~200 nm. X-ray photoelectron spectroscopy of the film suggested that the atomic ratio of Mg, Sn, and O was approximately 1:1:3, implying a chemical composition of MgO-SnO₂. In addition to these bilayer films, we also prepared single-layer samples of MSO and ITO films on silicate substrates for comparative measurements.

Optical transmittance at a wavelength region of 200 – 2500 nm and X-ray diffraction patterns were inspected for as-prepared, illuminated, and annealed samples. The optical transmittance was taken using a conventional spectrometer (JASCO, V570). The diffraction pattern was taken using a rotating Cu target (Rigaku, Ru-300) and a proportional counter fitted with a graphite monochromator. An X-ray beam was incident upon the MSO film with a grazing angle of $\theta = 2^\circ$, for enhancing and suppressing diffraction intensities from the thin-film samples and from the glass substrate. Slit widths were set sufficiently sharp, so that the peak width could be evaluated.

3. Results

Figure 1 shows transmittance spectra of (a) an MSO and (b) an ITO film on silicate substrates. The transmittance spectra of these samples are governed by the MSO and the ITO film, not the substrate, from which we estimate the optical gaps of these films at 3.6 and 4.6 eV, the results being consistent with those previously reported [10,12]. In addition, the ITO film possesses a transmittance reduction at near infrared, which has been ascribed to free-carrier absorption [12].

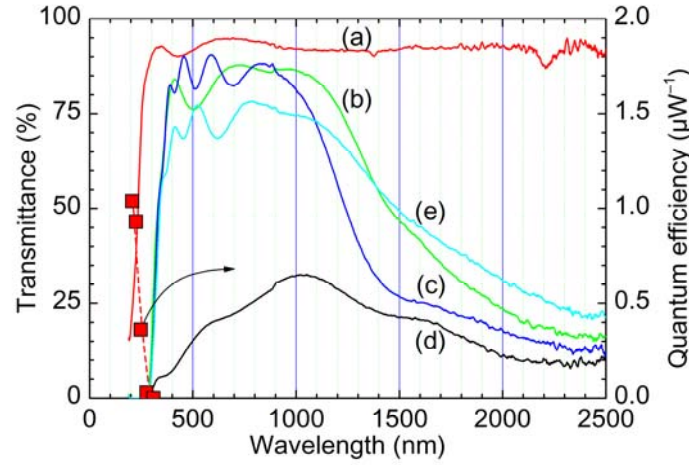


Fig. 1. Transmittance spectra of (a) an MSO, (b) an ITO, and an MSO/ITO film in (c) as-prepared, (d) illuminated, and (e) annealed states. Solid squares with the right-hand side scale show a quantum efficiency of the transmittance decrease.

Figure 2(a,b) shows the x-ray pattern of an MSO film and an ITO sample. The MSO film (a), which is thicker (~500 nm) a little than others, manifests a low-angle tail at $5 - 10^\circ$ and a broad halo centered at $\sim 26^\circ$. (Note that halo peaks arising from the substrate are completely suppressed in all the x-ray patterns.) These signatures indicate that the MSO film is heterogeneous and amorphous. In detail, the low-angle tail when analyzed using the Guinier's formula suggests electron-density fluctuation with a scale of ~ 20 nm. On the other hand, the halo position, combined with the Debye's formula, gives a pair distance of ~ 0.4 nm, which can be ascribed to the first-nearest Sn-Sn distance [13], since Sn has the greatest atomic scattering factor in Mg, Sn, and O. By contrast, the ITO sample in Fig.2(b) gives several sharp peaks, which can be identified to crystalline $\text{SnO}_2\text{-In}_2\text{O}_3$ [14], as expected.

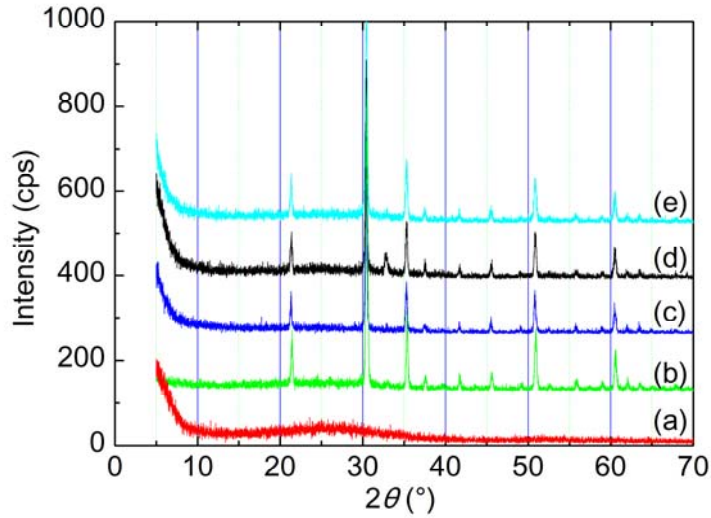


Fig. 2. X-ray diffraction patterns of (a) an MSO, (b) an ITO, and an MSO/ITO film in (c) as-prepared, (d) illuminated, and (e) annealed states.

Figures 1 and 2 also contain optical and x-ray changes in an MSO/ITO bilayer sample upon light exposure and subsequent annealing. Note that the optical change is qualitatively consistent with that [10] previously reported for a visible region. The as-prepared MSO/ITO film (c) contains three features; the optical gap of 3.6 eV, which is governed by ITO, interference fringes determined by an optical path length of the bilayer structure, and free-carrier absorption at the infrared. The corresponding x-ray pattern (c), consisting of a low-angle tail, a weak halo, and crystalline peaks, can be regarded as a superposition of amorphous MSO and crystalline ITO films. An exposure of ultraviolet light with intensity of 20 mW/cm² for 1 h, using a low-pressure Hg lamp, darkens the bilayer film as shown in Fig. 1(d), with a reduced transmittance possessing a broad peak at ~1000 nm. The corresponding x-ray pattern, Fig. 2(d), manifests a clear peak at 32.8°, which can be identified to the (101) plane of tetragonal In, the strongest peak in a common form of crystalline In [15]. Through applying the Scherrer's equation, we estimate the crystallite size at ~20 nm. Finally, as shown in Figs. 1 and 2 (e), an annealing treatment at 300 °C in air almost recovers the initial transmittance (~70%) and erases the In peak. (Such illumination-annealing cycles, though the reversibility gradually degrades, can be repeated 2 – 3 times.) We have also examined dependence of the crystalline-peak intensity and optical transmittance upon the annealing temperature. The temperature dependence demonstrates that the recovery starts from ~160 °C, which is nearly the same with the melting temperature of metallic In, 157°C. These facts suggest that the formation of In particles causes the photochromism in the MSO/ITO system.

Behaviors in the bilayer systems having the semi-transparent metal films provide additional

insight into the mechanism. The behaviors can be divided into the two, one containing In and Sn. For instance, an Sn film with a thickness of ~30 nm, when evaporated, had an optical transmittance of ~10 %. However, the coating of MSO films increased the transmittance to ~70%, and the bilayer sample exhibited crystalline x-ray peaks, which can be identified to related oxides as tetragonal SnO₂ (rutile-type). It seems that the pyrolytic coating and baking at 300°C converts, e.g. Sn to SnO₂, from a metal to a wide-gap semiconductor, which causes the transmittance increase. Then, ultraviolet illumination decreased the transmittance and produces x-ray peaks identifiable to orthorhombic γ -Sn, a relatively uncommon polymorph of Sn [16]. Successive annealing recovers these changes. These photo and annealing effects are qualitatively the same with those in the ITO system. Bi and Cu seemed to possess similar, but less marked, features. By contrast, the other metals were fairly intact. When covered by MSO films, Al, Te, Ge, and Au produced neither x-ray peaks of their oxides nor photo-effects. Incidentally, Ag films were likely to be peeled off upon the MSO coating, and accordingly, the characteristic could not be inspected.

4. Discussion

These results strongly suggest that the photo-generated metal particles as In and Sn give rise to the photochromism. The transmittance decrease can be attributed to light absorption and/or scattering, the relative roles, which may vary with the materials and exposure conditions, being unknown at present. We then focus upon the mechanism why the metallic particle is produced by the ultraviolet illumination. To understand the process, we need to know the location of photo-electronic excitation.

Figure 1 includes spectral dependence of a quantum efficiency of the photoinduced transmittance reduction. Here, the efficiency is defined as $-\ln(T_1/T_0)/I$, where T_0 and T_1 are transmittances at a wavelength of 500 nm before and after 5-hour exposure of monochromatic light with incident intensities of I . The efficiency shows a sharp change at ~250 nm, the photon energy being ~5.0 eV, which is nearly equal to the optical gap (~4.6 eV) of the MSO film and appreciably greater than that (3.6 eV) of ITO. In addition, it has also been confirmed that ultraviolet illumination from the ITO side cannot induce the darkening. These two observations strongly suggest that the photoelectronic excitation in the MSO film triggers this chromic phenomenon.

The band diagram illustrated in Fig. 3 provides a plausible idea. The diagram is illustrated for the simplest material combination, MSO on SnO₂, while qualitatively the same interpretations will apply to other bilayer structures of interest. Here, electronic properties of SnO₂ are fairly known. Crystalline SnO₂ has an energy gap of ~3.6 eV and a work function of ~5 eV [17]. The valence (VB) and the conduction band (CB) are formed by the 2*p* electron state of O and by the 5*s* electron state of Sn⁴⁺ ions [18]. The film exhibits an n⁺-type conduction due to oxygen deficiencies [19], which implies that the Fermi level, E_F , is located slightly above the bottom of the conduction band. On the

other hand, electronic properties of amorphous MSO have been little known, except the optical gap of 4.6 eV, presently evaluated. However, crystalline MgO has been studied more-or-less deeply [20], which is an insulator having an energy gap of ~ 8 eV [21] and a work function of 4.2 – 5.1 eV [22]. The top of the valence band and the bottom of the conduction band consist of O 2*p* and Mg 3*s* states [23]. Accordingly, it is highly plausible that the valence-band top in the MSO is produced also from the O 2*p* electron state. We thus assume in Fig. 3 a flat valence-band top throughout the bilayer structure. In addition, since the work functions of SnO₂ and MgO are comparable, the Fermi level can be fitted [22,24], so that a possible conduction-band barrier at the hetero-junction can be neglected for simplicity. We also know that, in general, electrons are more mobile than holes in the oxide [25].

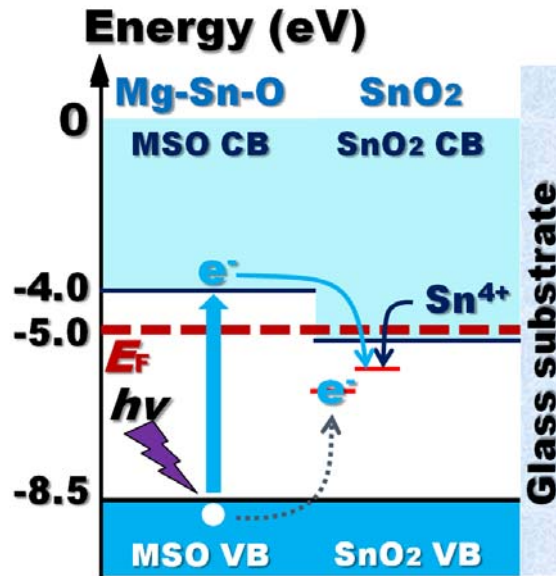


Fig. 3. A band diagram at around the hetero-junction of amorphous Mg-Sn-O and crystalline SnO₂. e^- and a white circle indicate a photo-excited electron and a hole.

Using the band diagram, we can envisage the following photo-electro-atomic process. Photons incident upon the SMO excite electrons and holes, and the electrons diffuse towards SnO₂, being trapped there, while the holes may be relatively immobile. The electrons negatively charge SnO₂, or neutralize Sn⁴⁺ ions near the MSO/SnO₂ interface to Sn⁰, which will work as an embryo of metallic Sn particles. This process, which can be regarded as a kind of photo-reduction, appears to resemble the photographic Ag clustering in Ag-halide crystals [1]. The annealing will dissolve and disperse the Sn particles into the original lattice.

The present idea can also provide an interpretation of the behavior in different bottom materials. A necessary condition of the darkening is that the conduction-band bottom of MSO is higher than that of the metal oxide. This condition seems to be satisfied in In₂O₃ and SnO₂ [12,17],

being consistent with the appearance of the photochromic effect.

5. Summary

We have examined optical, structural, and material properties of the thermally-erasable photochromic effect, originally discovered for the MSO/ITO bilayer structure [10]. The transmittance decrease seems to be induced by photoelectronic excitation in the MSO film, electron injection to the base transparent oxide film, and formation of metallic particles there.

We here underline that, in this bilayer system, the two functions of the photoelectronic excitation and transmittance reduction are taken by the two materials of MSO and metallic oxides. This principle will motivate further exploration of new bilayer combinations, which may have different spectral responses and temperature dependence. In addition, the proposed mechanism straightforwardly suggests that the electron injection by electric fields is able to induce a similar effect, i.e. electrochromism, as demonstrated in a preliminary experiment [10]. Photo-electric control of the darkening process will also be promising.

References

- [1] T. Tani, *Photographic Sensitivity* (Oxford University Press, Oxford, 1995).
- [2] Y. Kondo, H. Inouye, S. Fujiwara, T. Suzuki, T. Mitsuya, J. Appl. Phys. 88 (2000) 1244.
- [3] Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota, and A. Fujishima, Nature Mater. 2 (2002) 29.
- [4] S. Wang, Y. Zhang, X. Ma, W. Wang, X. Li, Z. Zhang, Y. Qian, Solid State Commun. 136 (2005) 283.
- [5] J. Liu, M. Li, J. Zhou, Ch. Ye, J. Wang, L. Jiang, Y. Song, Appl. Phys. Lett. 98 (2011) 023110.
- [6] N. Asakuma, H. Hirashima, T. Fukui, M. Toki, K. Awazu, H. Imai, Jpn. J. Appl. Phys. 41 (2002) 3909.
- [7] R. Ramirez, M. Tardio, R. Gonzalez, Appl. Phys. Lett. **86**, 081914 (2005).
- [8] A. V. Kolobov, *Photo-induced Metastability in Amorphous Semiconductors* (WILEY-VHC, Weinheim, 2003).
- [9] M. Irie, Chem. Rev. 100 (2000) 1683.
- [10] A. Nakazawa, T. Shinoda, ITE Tech. Rept. 31 (2007) 13, in Japanese.
- [11] A. Nakazawa (private communications in 2010).
- [12] Y. Sato, T. Ashida, N. Oka, Y. Shigesato, Appl. Phys. Express 3 (2010) 061101.
- [13] A. A. Bolzan, C. Fong, B. J. Kennedy, C. J. Howard, Acta Cryst. B53 (1997) 373.
- [14] A. E. Solov'eva, V. A. Zhdanov, Inorg. Mater. 21 (1985) 828.
- [15] P. Villars, K. Girgis, Z. Metallkd. 73 (1982) 169.

- [16] R. Kubiak, J. Less-Common Met., 116 (1986) 307.
- [17] M. Batzill, U. Diebold, Prog. Sur. Sci. 79 (2005) 47.
- [18] Z. Q. Li, Y. L. Yin, X. D. Liu, L. Y. Li, H. Liu, Q. G. Song, J. Appl. Phys. 106 (2009) 083701.
- [19] Ç. Kılıç, A. Zunger, Phys. Rev. Lett. 88 (2002) 095501.
- [20] K. Uetani, H. Kajiyama, A. Kato, A. Takagi, T. Hori, I. Tokomoto, Y. Koizumi, K. Nose, Y. Ihara, K. Onisawa, T. Minemura, Mater. Trans. 42 (2001) 1870.
- [21] U. Schönberger, F. Aryasetiawan, Phys. Rev. B52 (1995) 8788.
- [22] J. Y. Lim, J. S. Oh, B. D. Ko, J. W. Cho, S. O. Kang, G. Cho, H. S. Uhm, E. H. Choi, J. Appl. Phys. 94 (2003) 764.
- [23] A. Schleife, F. Fuchs, J. Furthmüller, F. Bechstedt, Phys. Rev. B73 (2006) 245212.
- [24] Y. Sato, R. Tokumaru, E. Nishimura, P.-K. Song, Y. Shigesato, K. Utsumi, H. Iigusa, J. Vac. Sci. Technol. A23 (2005) 1167.
- [25] H. Mizoguchi, P. M. Woodward, Chem. Mater. 16 (2004) 5233.