Effect of UV light irradiation in SnO₂ thin film

Naoko Takubo¹, Yuji Muraoka² and Zenji Hiroi¹

¹The Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan
²Department of Physics, Okayama University, Tsushima-ku, Okayama 700-8530, Japan

E-mail: takubo@riken.jp

Abstract. We observed a drastic increase in conductivity up to three orders of magnitude as a result of a photo-induced effect at the surface in a tin dioxide (SnO₂) thin film. The oxygen-atmosphere effect and the light-intensity dependence of conductivity change were also experimentally studied. The experimental results indicate that the conductivity increase was caused by photo-induced oxygen desorption at the surface of the thin film.

1. Introduction

Photo-induced effect at the surface of oxide has been widely studied. Photocatalyst in TiO₂ is a typical example of the photo-induced effect. In addition, spectral changes in Eu₂O₃ and SrTiO₃ as a result of photo-induced effect have been reported in terms of control of solid state [1, 2]. The spectral changes are mainly caused by oxygen desorption from the surface of oxide after light irradiation. Such photo-induced oxygen desorption from the surface has been generally observed in oxide.

In this study, we focused on the photo-induced effect at the surface to achieve novel approach and drastic effect of solid-state control. We used SnO₂ for this study because it is an n-type semiconductor with a wide band gap about 3.6 eV and high mobility of carrier (150 cm²/Vs at room temperature in single crystal [3]). Moreover, SnO₂ has been applied to gas sensor at a high working temperature up to about 400 °C, where its conductivity changes due to electron transfer between adsorbed gas and solid [4]. Therefore, it is expected that the conductivity of SnO₂ can drastically change as a result of photo-induced gas adsorption at the surface.

Photoconductivity of SnO₂, which is caused by UV light irradiation, has been previously reported [5, 6]. Specifically, we have observed a persistent photoconductivity SnO₂ with drastic resistance change by several orders of magnitude in vacuum [6]. It has been also suggested that the persistent photoconductivity is mainly caused by the photo-induced mobility increase as a result of oxygen desorption from the surface. Here, we will describe the oxygen-atmosphere effect and the light-intensity dependence of conductivity change in the photo-induced effect in a SnO₂ thin film.
2. Method

We have grown a SnO$_2$ thin film on Al$_2$O$_3$ (0001) substrate by pulsed-laser deposition (PLD) method. The resistivity drastically decreases as oxygen pressure (PO$_2$) during the film growth decreases because oxygen vacancy acts as donor and provides electron career. The thin film was prepared at PO$_2 = 6$ Pa. The resistivity of the thin film at room temperature is about $10^{-1}$ Ωcm in the presence of a certain amount of oxygen vacancy. Grain structure was observed in the thin film by using an atomic force microscope (AFM). Resistivity of the thin film was also measured by using a four-point probe method with indium electrodes on the film. Light from a Xe lamp at a wavelength of 300-400 nm was used for excitation. The irradiated light was absorbed in the film because it has large energy than the band gap of SnO$_2$. However, there was no absorption in substrate because it is less than band gap of Al$_2$O$_3$ about 8 eV. Therefore, photo-induced effect from the Al$_2$O$_3$ substrate was negligible for conductivity change in the SnO$_2$ thin film on the substrate.

3. Results and discussion

3-1. Atmosphere effect

Figure 1 shows the ratio of resistance change ($\Delta R = R / R_{\text{initial}}$) of coated and uncoated at the surface films under the light irradiation for various atmospheres. The light intensity $I$ was 0.3 W/cm$^2$. The Al$_2$O$_3$ coating was prepared on SnO$_2$ film by PLD method. The property of conductivity for the coated film did not change from it for uncoated sample. Under the light irradiation, the resistance of the coated film does not change, while it of the uncoated films changes. In vacuum, the resistance decreases during measurement time. In oxygen atmosphere, the film initially shows drastic decrease of the resistance same as in vacuum and it does not change about ten seconds later.

These results indicate that the difference of $\Delta R$ for various atmospheres is due to efficiency of oxygen desorption by light irradiation. The conductivity of the film increases as follows: 1. Electron-hole pairs are generated by light absorption in thin film. 2. Hole near the surface react oxygen, which adsorb as negative ion and disturb conduction. 3. The adsorbed oxygen desorbs and electron career can move with high mobility [6, 7]. As for the coated film, oxygen is unable to desorb from the surface, and the resistance does not change. In oxygen atmosphere, the resistance keeps equilibrium value, when the ratio of desorption by irradiation equilibrate its re-adsorption. In vacuum, oxygen continues to desorb and $\Delta R$ is large in the measurement time because there is not re-adsorbed oxygen.

![Figure 1. Change of $\Delta R$ under light irradiation for various atmospheres ($\Delta R = R(s)/R(0)$). Red line, blue line and black line denote for Al$_2$O$_3$ coated at the surface film in vacuum, uncoated film in oxygen atmosphere and uncoated film in vacuum, respectively.](image)
3.2. Light intensity dependence

Figure 2 shows $\Delta R$ under irradiation with different light intensity in vacuum. $I = 0.5 \text{ W/cm}^2$ was defined as 100 %. According to the experimental results, $\Delta R$ increases as the light intensity increases. These results indicate that the oxygen desorption decreases as photocarrier in thin film decreases. In addition, for large excitation, the resistance closes to constant value. This may be because almost all the adsorbed oxygen have desorbed from the surface of thin film.

![Figure 2](image)

Figure 2. Change of $\Delta R$ under irradiation for each light intensity in vacuum. ($I = 0.5 \text{ W/cm}^2$ is defined as 100 %)

4. Conclusion

In conclusion, a drastic photo-induced conductivity increase was observed as a result of a photo-induced effect at the surface of SnO$_2$ thin film. It was experimentally found that the $\Delta R$ of SnO$_2$ thin film depends on both oxygen atmosphere and light intensity. These results indicate that the photo-induced effect is caused by oxygen desorption from the surface of SnO$_2$ thin film.

References

[1] Mochizuki S, Nakanishi T, Suzuki Y and Ishi K 2001 Appl. Phy. Lett. 79 3785
[2] Mochizuki S, Fujishiro F and Minami S 2005 J. Physics.: Condens. Matter 17 923
[3] Jarzebski Z M and Marton J P 1976 J. Electrochem. Soc. 123 199C
[4] Watson J, Ihokura K and Coles G S V 1993 Meas. Sci. Technol., 4, 719
[5] Messias F R, Vega B A V, Scalvi L V A, Siu Li M, Santilli C V and Pulcinelli S H 1999 J. Non-Crystalline Solids, 247, 171
[6] Takubo N, Muraoka Y and Hiroi Z, in preparation.
[7] Morrison S R, 1990 The Chemical Physics of Surfaces, Plenum, New York, p142