Effects of Hydrogen Introduction on Electrical and Optical Properties of Cd-doped Ge Oxide and Zn Oxide Thin Films

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Cadmium-doped Ge oxide and Zn oxide thin films were deposited by RF magnetron sputtering. The electrical and optical properties of these films were investigated. All deposited films except for highly Cd-doped Ge oxide were transparent to visible light. Hydrogen introduction reduced the resistivity of the films, although the optical transmittance for visible light did not change significantly. The enhancement of conductivity could be attributed to the increase in carrier density by the hydrogen introduction.

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1. Introduction

There are some oxides which possess both high conductivity and transparency, though most oxides are optically transparent but are electrically insulating. They are called transparent conductive oxides (TCOs). Recently TCO thin films have been used for the transparent electrodes in liquid crystal displays or solar cell panels. Indium-tin oxide (ITO) and SnO₂ are used mainly in these applications. It is, however, still required to have higher conductivity and more stability in various environments. On the other hand, induction of electric conductance of other transparent oxides by a new technique might widen the choice of TCOs for various applications.

One of the crucial parameters that governs the conductivity is carrier density of oxides. The carrier density would be controlled by impurity doping. For example, ITO is a material of tin-doped indium oxide. It has been reported that the electrical conductivities of SnO₂ and ZnO were improved by the doping of F, Sb¹⁻⁴⁾ and Al⁵⁻⁷⁾ respectively. Generally, to make the conductivity of oxides better, hydrogen introduction will be a good candidate. It is considered that the introduced hydrogen behaves as a donor or an acceptor in the materials and makes the density of electrical charge carrier high. The hydrogen introduced into the oxides, however, sometimes gives coloration to the oxides. So the change of the optical properties by hydrogen introduction must be considered when TCO materials are studied.

In this work, optical and electrical properties of two types of oxides deposited by RF sputtering were investigated and the effect of hydrogen introduction on them was examined. We used hydrogen gas exposure as well as hydrogen ion implantation to introduce hydrogen into the oxides. The oxide films examined in this study were Cd-doped Ge oxides (Ge–Cd oxide) and Zn oxides. Ge–Cd oxides have been studied by some researchers.^{8,9)} There are some reports on TCO of Zn oxide films also. Aranovich *et al.*¹⁰⁾ and Bahadur *et al.*¹¹⁾

investigated the optical and electrical properties of ZnO films prepared by spray pyrolysis and with annealing in hydrogen atmosphere. However, no study on hydrogen ion implantation into Zn oxide films has been performed yet.

2. Experimental Procedure

All oxide films were deposited on fused silica glass with an RF sputtering apparatus ULVAC BC2227. The deposited area was 12 × 12 mm². The base pressure of the chamber was 1.3 × 10⁻³ Pa, and the distance between the substrate and the target was 60 mm. For deposition of Ge–Cd oxide films, we used a commercial sintered CdO disk (99.99%) as the sputtering target with Ge (99.999%) tips on it occupying 20% of the CdO surface area. The Ge/Cd ratio of the deposited films was varied by the configuration of the Ge tips on the CdO disk surface. The sputtering gas was the mixture of O₂ and Ar. The fraction of O₂ ranged from 20 to 80%, and the total pressure was 2.7–11 Pa. The RF power of 50 W was applied. For deposition of Zn oxide film, a commercial sintered ZnO disk (99.99%) was used as a target. The sputtering gas was Ar and the total pressure was 6.7 × 10⁻¹–2.7 Pa. The RF power of 100 W was applied.

To characterize the structure of deposited films XRD measurements were performed with Cu K α radiation. The transmittance spectra of the oxide films were measured in the range from 200 to 1100 nm using Shimadzu UV160A UV-visible spectrophotometer. The resistivity of the films was estimated by Van der Pauw method with four probes at a constant current of 5 nA–0.1 mA. For the Zn oxide films the Hall measurement was performed and the carrier density was estimated.

H₂⁺ ions were implanted into the oxides using an ion gun with the acceleration voltage of 4.8 kV for Ge–Cd oxides and 1 kV for Zn oxides, respectively. The ion current was about 2 μ A and the implanted hydrogen dose was 0.4–1.2 × 10¹⁷ ions/cm². We have performed the hydrogen exposure experiment for Zn oxide films. A chamber contained the sample was first evacuated by a turbo molecular pump and a rotary

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pump, then filled with hydrogen gas of 1×10^5 Pa and retained 7 days. In order to enhance the hydrogen introduction on the hydrogen gas exposure test, a very thin Pd layer was deposited on the Zn oxide surface by RF sputtering. For Pd layer deposition, a Pd disk was used as a target and the sputtering gas was Ar. The RF power of 10 W was applied for 2 sec.

3. Results and Discussion

3.1 Ge–Cd oxide films

With the fraction of 50% O_2 , total pressure of 2.7 Pa, and the sputtering time of 1.5 h, a Ge–Cd oxide film was deposited. The ratio of Ge/Cd was about 0.7 and the thickness was about 750 nm (Cd-rich film). While with another configuration of Ge tips on the CdO target, total pressure of 11 Pa, and the 1.5 h deposition, an oxide film having the Ge/Cd ratio of 1.8 was formed (Ge-rich film). The thickness of this film was about 200 nm. Figure 1 shows the XRD profiles for these two films. For the Cd-rich film diffraction peaks were observed between 30° and 40° in 2θ indicating a crystalline structure. While the Ge-rich film showed no diffraction peak but a very broad one around 30° suggests amorphous structure, where the broad peak around 20° is due to the diffraction from the silica substrate. The transmittance spectrum for the Ge-rich film is shown in Fig. 2. The spectrum for the Ge-rich film displays the fundamental absorption edge at about 300 nm and the transparency for the visible light was over 90%. The band gap energy of 5.3×10^{-19} J (3.3 eV) was estimated from Tauc plot eq. (1) of the transmittance spectrum.

$$\alpha \propto (h\nu - E_g)^2 / h\nu \quad (1)$$

Fig. 1 XRD profiles for Cd–Ge oxide films.

Fig. 2 Transmittance spectra for the Ge-rich Ge–Cd oxide film.

Here, α is the absorption coefficient calculated from the transmittance, $h\nu$ the photon energy, and E_g the band gap energy of the oxide. Figure 3 shows the transmittance spectrum of the Cd-rich film. The fundamental absorption edge lies between 400 and 500 nm corresponding to the band gap energy of 3.5×10^{-19} J (2.2 eV). This film showed yellow color. The transmittance spectra for the oxide films showed oscillations in the high transmittance region, which were attributed to the interference of light in the oxide layer. Table 1 summarizes the electrical resistivity of these two films. The Cd-rich film showed $1 \times 10^{-1} \Omega m$, while the Ge-rich film showed considerably high resistivity ($> 10^4 \Omega m$) so that the exact value could not be evaluated by the apparatus.

Using an ion gun, H_2^+ ions were implanted into the films. The ion energy was 4.8 keV and the implanted dose was 4×10^{16} ions/cm². After the implantation, the Cd-rich film showed a small decrease in transmittance below the absorption edge but there was no significant change in the fundamental absorption edge and the band gap energy. In contrast with the optical properties, the electric conductivities of both the films were considerably improved by the hydrogen ion implantation. After the ion implantation the resistivities of both the films were reduced over 2 orders of magnitude as shown in Table 1. Kikuchi *et al.*⁹⁾ studied the effect of hydrogen ion implantation on the electrical properties of Cd–Ge amorphous films and reported that the films of the Ge/Cd ratio of which was smaller than 0.25 showed over 10 orders of magnitude of decrease in resistivity by H^+ implantation with the acceleration voltage of 80–140 kV. They suggested that improvement of conductivity of the oxides is due to the increase in carrier density. The mechanism of the decrease in resistivity in our study would be also attributed to the increase in carrier density. Kikuchi *et al.* also reported that there was no effect on resistivity of the oxides with the Ge content over 56%. In our study, the effect of hydrogen implantation on the Ge-rich oxide film was observed. So the effects of hydrogen introduction would depend on various implantation conditions and structures of oxide films.

Fig. 3 Transmittance spectra for the Cd-rich Ge–Cd oxide film.

Table 1 Resistivities of Cd–Ge oxide films.

	Ge/Cd = 0.7	Ge/Cd = 1.8
as-deposited	$1 \times 10^{-1} \Omega m$	$> 10^4 \Omega m$
$4 \times 10^{16} H_2^+$ implanted	$6 \times 10^{-4} \Omega m$	$3 \times 10^2 \Omega m$

Fig. 4 XRD profiles for Zn oxide films.

Fig. 5 Transmittance spectra for the Zn oxide film deposited at 6.7×10^{-1} Pa of Ar pressure.Table 2 Resistivities and carrier densities of the Zn oxide films deposited at 6.7×10^{-1} Pa of Ar pressure.

	Resistivity	Carrier density
as-deposited	$9.9 \times 10^1 \Omega\text{m}$	$3.6 \times 10^{18} \text{m}^{-3}$
$1.2 \times 10^{17} \text{H}_2^+$ implanted	$1.1 \times 10^{-4} \Omega\text{m}$	$3.6 \times 10^{23} \text{m}^{-3}$

3.2 Zn oxide films

The XRD profiles of Zn oxide films deposited at 2.7 Pa and 6.7×10^{-1} Pa of Ar pressure are shown in Fig. 4. The thicknesses of the two films were about 150 nm. Diffraction peaks of wulzite ZnO (002) appear at about 33° in 2θ . Figure 5 shows the transmittance spectra for the Zn oxide film deposited at 6.7×10^{-1} Pa of Ar pressure after and before the hydrogen implantation. The fundamental absorption edge lies around 400 nm. The band gap energy values were estimated for direct optical transition by the eq. (2), and were 5.1×10^{-19} J (3.2 eV) for both films.

$$\alpha \propto (h\nu - E_g)^{0.5} / h\nu \quad (2)$$

Hydrogen ions were implanted into the film with the acceleration voltage of 1 kV and the implanted dose of 1.2×10^{17} ions/cm². After the implantation the absorption edge and the band gap energy did not change. Table 2 shows the resistivities and carrier densities of the film after and before the hydrogen ion implantation. From the Hall measurement it is confirmed that the conduction type of the Zn oxide films was n-type. The resistivity of the as-deposited film was $9.9 \times 10^1 \Omega\text{m}$. After the implantation the value reduced to $1.1 \times 10^{-4} \Omega\text{m}$. Corresponding to the resistivity the carrier

Fig. 6 Transmittance spectra for the Zn oxide film deposited at 2.7 Pa of Ar pressure.

Table 3 Resistivities and carrier densities of the Zn oxide film deposited at 2.7 Pa of Ar pressure.

	Resistivity	Carrier density
as-deposited	$1.9 \times 10^2 \Omega\text{m}$	$1.2 \times 10^{18} \text{m}^{-3}$
7 day H ₂ exposure	$2.5 \times 10^2 \Omega\text{m}$	$9.1 \times 10^{17} \text{m}^{-3}$

Table 4 Resistivities and carrier densities of the Zn oxide film deposited at 2.7 Pa of Ar pressure with Pd coating on the surface.

	Resistivity	Carrier density
as-deposited	$6.6 \times 10^1 \Omega\text{m}$	$5.1 \times 10^{17} \text{m}^{-3}$
7 day H ₂ exposure	$2.5 \times 10^{-1} \Omega\text{m}$	$1.9 \times 10^{20} \text{m}^{-3}$

density increased several orders of magnitude. This indicates the improvement of the conductivity of the Zn oxide film is due to the increase in carrier density induced by hydrogen ion implantation.

Figure 6 shows the transmittance spectra for the films deposited at 2.7 Pa of Ar pressure. The spectrum for the as-deposited film had the absorption edge at 400 nm and showed the transparency of around 80% in the visible region. By the eq. (2), the calculated E_g value was 5.1×10^{-19} J (3.2 eV). For this film the hydrogen gas exposure test was performed. After the exposure for 7 days there was no significant change observed. The resistivity of this Zn oxide film is summarized in Table 3. The resistivity of the as-deposited film was about $2 \times 10^2 \Omega\text{m}$ then the value remained constant or slightly increased with the exposure to hydrogen gas. The carrier density also showed no significant variation after and before the exposure.

To enhance hydrogen introduction, a very thin Pd layer was deposited on the surface of some of the samples by RF sputtering. The spectrum for the Pd-coated Zn oxide sample is also shown in Fig. 6 and the resistivity of the film are listed in Table 4. With the Pd coating the absorption edge of the sample did not change, but the transmittance decreased from 80 to 60% in the visible range of wavelength. The hydrogen gas exposure test did not affect on the transmittance spectrum of the Pd-coated sample. While the Pd coated sample showed a decrease in the resistivity and an increase in the carrier density of two orders of magnitude. Similar to the case of the hydrogen ion implantation the improvement of the conductivity is due to the increase in the carrier density induced by the exposure to hydrogen gas. It is confirmed that the surface

Pd layer activates hydrogen incorporation. Palladium has a high permeability and solubility for hydrogen therefore hydrogen is easily introduced from gas phase into oxide films. It is considered that the introduced hydrogen by gas exposure as well as ion implantation behaves as a donor and makes the density of charge carrier high.

4. Summary

Cadmium-doped Ge oxide and Zn oxide thin films were deposited by RF magnetron sputtering. The electrical and optical properties of these films were investigated and the effect of hydrogen introduction on them was examined. All deposited films except for highly Cd-doped Ge oxide were transparent to visible light. Hydrogen ion implantation reduced the resistivity of the films. Hydrogen gas exposure also enhanced the conductivity of the Zn oxide film with the help of a Pd coating on the surface. The optical transmittance for visible light wasn't changed significantly by both the hydrogen ion implantation and the gas exposure. The enhancement of conductivity could be attributed to the increase in carrier density by the hydrogen introduction.

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