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Temperature dependence of electrical properties of Ga-doped ZnO films deposited by ion plating with DC arc discharge

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ABSTRACT

Ga-doped ZnO (GZO) films with carrier concentration n ranging from 3×10^{18} to 1.04×10^{21} cm^{-3} were deposited by ion plating with DC arc discharge. The results of Hall effect measurements of the GZO films revealed that the gradients of Hall mobility (μ)-temperature (T) curves (denoted by $\Delta\mu/\Delta T$) plotted as a function of n can be divided into three regions: (1) Region I ($3\times10^{18}<n<4\times10^{19}$ cm^{-3}); $\Delta\mu/\Delta T>0$ and μ decreasing with increasing n, (2) Region II ($4\times10^{19}<n<3\times10^{20}$ cm^{-3}); μ independent of T ($\Delta\mu/\Delta T=0$) and (3) Region III ($n>3\times10^{20}$ cm^{-3}); $\Delta\mu/\Delta T<0$. For all GZO films, the activation energies extracted from the 1000/T–ln (μT) curves were lower than the thermal energy k_BT at 300 K, indicating that the carrier electrons can overcome the potential barriers at grain boundaries. Moreover, comparison of the calculated mean free path l of the carrier electrons and the depletion layer width at the grain boundaries showed that the grain boundary scattering mechanism plays a minor role in the carrier transport compared with the intra-grain scattering mechanism for GZO films with n higher than 3×10^{18} cm^{-3}. The dependence of $\Delta\mu/\Delta T$ on n demonstrates the continuous transformation of the dominant intra-grain scattering mechanism from the ionized impurity scattering mechanism to the phonon scattering mechanism with increasing n.

1. Introduction

Tin-doped indium (In) oxide (ITO) films are widely used as transparent conducting oxide (TCO) films in the electrodes of flat display panels and in the window layers of thin-film solar cells. The need for an alternative TCO is growing because of the limited availability of In, a rare metal. One of the most promising candidates for use as an alternative TCO is gallium (Ga)-doped zinc oxide (GZO) films, which are inexpensive and have low electrical resistivity and high optical transmittance in the visible to near-infrared ranges. Moreover, GZO films can be deposited at low temperatures (typically <200 °C) and are stable under the hydrogen plasma processes commonly used for the production of a-Si based solar cells [1].

A variety of deposition methods, such as sputtering [2,3], ion plating (IP) [4,5], molecular beam epitaxy [6,7], chemical vapor deposition [1,8,9], sol–gel [10], chemical spray pyrolysis [11,12], and pulsed laser deposition [13,14], have been used for the preparation of GZO films. Among these methods, the IP method with a high-density plasma beam generated by DC arc discharge has attracted considerable attention because of its higher growth rate, typically 170 nm/min [4,5], than that of DC magnetron sputtering [15]. Furthermore, IP can be easily adapted to production using large-area substrates of more than 1 m^2 required for the manufacture of displays. The successful fabrication of 3-in. thin-film-transistor liquid crystal display panels (TFT LCDPs) and 20-in. TFT LCD TVs utilizing GZO-based highly transparent common electrodes on RGB-color-filter substrates on a commercially compatible mass production line was reported recently [16]. Note that the variation in the electrical resistivity of 200-nm-thick GZO films before and after reliability tests for 500 h under damp heat conditions (60 °C and a relative humidity of 95%) was found to be less than 10% [17].

Understanding of the carrier transport mechanisms in GZO films is a key issue in improving the performance of GZO-based transparent electrodes and their widespread applications. Very few studies have been reported on the temperature dependence of the electrical properties of GZO films such as resistivity ρ, carrier concentration n and Hall mobility μ. To clarify the carrier transport characteristics, we have investigated the temperature dependence of the electrical properties of GZO films with different carrier concentrations deposited by IP as reported in the present paper.

2. Experimental

Polycrystalline GZO films with a thickness of 200 nm were deposited on alkali-free glass substrates (100×100 mm^2) at 200 °C by IP with DC arc discharge. Details of the deposition system are given in ref. [18]. Sintered ZnO tablets with different Ga_2O_3 content ranging from 0.003 to 4 wt.% were used as resources. During the growth process, O_2 gas was introduced into the deposition chamber to compensate for the oxygen

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deficiency. The O_2 flow rate was varied from 0 to 30 SCCM as a deposition parameter.

Hall effect measurements were carried out using the van der Pauw method at 83–343 K under a magnetic field of 0.47 T. The samples were cut into squares with dimensions of 5×5 mm^2. Indium dot electrodes were formed at the four corners on the surface of each sample.

For optical transmittance measurements, a double-beam spectrometer (Hitachi, U-4000) was used. The value of the transmittance used in the present paper was that measured with a reference alkali-free glass substrate. The optical gap energy E_{opt} of the films was determined using Tauc's model for a direct-bandgap semiconductor given by

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right), \tag{1}$$

where α is the optical absorption coefficient, $h\nu$ is the photon energy and A is a constant [19]. α was evaluated using

$$\alpha = \left(\frac{1}{d}\right)\ln\left(\frac{1}{T_r}\right), \tag{2}$$

where d is the film thickness and T_r is the transmittance.

3. Results and discussion

Fig. 1 shows the variations of n and E_{opt} of GZO films deposited at different O_2 flow rates as a function of Ga_2O_3 content. We found that n decreases with increasing O_2 flow rate for any given Ga_2O_3 content in the resources. This is probably due to an increase in the density of n-type killer defects, such as Zn vacancies, compensating for donors (Ga atoms substituting at Zn sites) [20]. With increasing Ga_2O_3 content in the resources from 0.003 to 0.03 wt.%, n hardly changes regardless of the O_2 flow rate. In such films, the n values are close to or lower than the Mott density of 3.7×10^{19} cm^{-3} [21]. Above a Ga_2O_3 content of 0.03 wt.%, n increases markedly. The value of n at a Ga_2O_3 content of 4 wt.% is 10 to 15 times larger than that at a Ga_2O_3 content of 0.03 wt.%. E_{opt} remains almost constant at ~3.3 eV up to a Ga_2O_3 content of 0.03 wt.%. When the Ga_2O_3 content increases from 0.03 to 0.3 wt.%, E_{opt} increases slightly from ~3.3 to 3.4 eV. With further increasing Ga_2O_3 content from 0.3 to 4 wt.%, there is a marked increase in E_{opt} from ~3.34 to ~3.9 eV. The above findings, i.e., similar dependences of E_{opt} and n on the Ga_2O_3 content, indicate that the increase in E_{opt} is closely related to the increase in n, which will be discussed below.

Fig. 2 shows the relationship between n and E_{opt}. The solid line indicates the calculated bandgap energy based on both bandgap widening caused by filling of the lowest states of the conduction band, the so-called Burstein–Moss shift [22–24], and bandgap narrowing caused by the electron–electron and electron-impurity interactions [25]. Fig. 2 demonstrates that the E_{opt} values for the films with $n>3\times10^{19}$ cm^{-3} are well fitted by the calculated curve, suggesting that these films are n-type degenerate semiconductors. On the other hand, the E_{opt} values for the films with $n<3\times10^{19}$ cm^{-3} are slightly lower than the calculated values. This may be due to the effect of the tail states introduced by the presence of external and/or intrinsic defects.

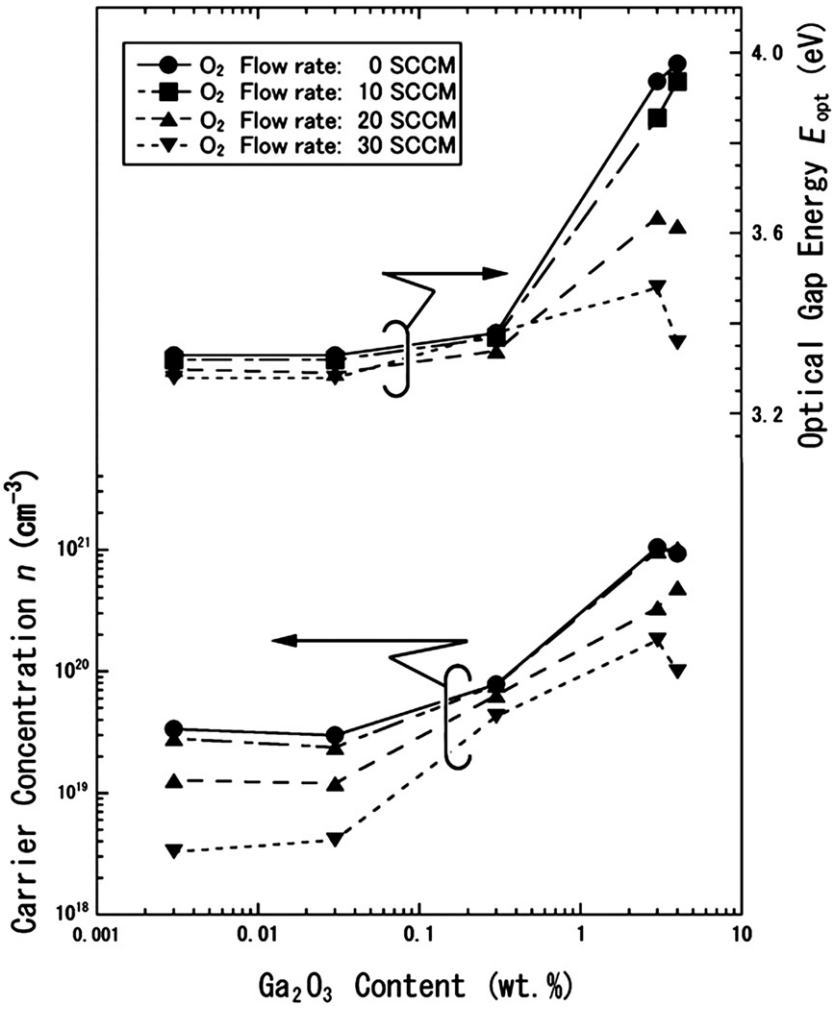

Fig. 1. Variations of carrier concentration n and optical gap energy E_{opt} as a function of Ga_2O_3 content.