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Highly Conductive and Transparent Silicon Doped Zinc Oxide Thin Films Prepared by RF Magnetron Sputtering

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Highly conductive and transparent films of Si-doped ZnO have been prepared by rf magnetron sputtering of a ZnO target with SiO_2 or SiO dopant added. Films with resistivity as low as $3.8\times10^{-4}\,\Omega$ cm and average transmittance above 85% in the visible region can be produced on low temperture substrates at below 250°C. Great improvement in the stability of the resistivity for use at high temperatures was obtained for Si-doped ZnO films in comparison with undoped films.

§1. Introduction

Recently zinc oxide (ZnO) has attracted interest as a transparent and conductive coating material because of its low cost for large scale coating applications. In undoped ZnO and impurity doped ZnO, highly transparent films with a low resistivity of the order of $10^{-4}\,\Omega$ cm have been achieved.[1-5] We have reported in recent years that the resistivity is lowered by doping of group III elements such as B, Al, Ga and In into ZnO films, and also that a more stable resistivity for use at high temperature can be attained for these films in comparison with undoped ZnO films.[4,5] These doping effects were though to be obtained from each group III element which acts as effective donors in ZnO.

At present, indium tin oxide (ITO) films are generally used for practical applications such as display and photovoltaic devices, although ITO is a relatively expensive material because indium is in rather limited supply. In the practical use of ITO films for amorphous silicon (a-Si) solar cells, however, it has been pointed out that the characteristics of these devices are degraded by the diffusion of indium from the films into the a-Si layer.[6-9] It has been believed that a group III element such as In doped into a-Si acts as an acceptor impurity and introduces further disorder in a-Si. If group III element doped ZnO films are used for such devices, the effect described above may also be caused by the diffusion of the group III element, although the impurity content introduced into ZnO is one order of magnitude less than that of In in ITO.[5] If a group IV element doped into ZnO films acts as an effective donor, it may be possible to avoid the degradation of the device characteristics. In this letter, we report on properties as transparent conductors of ZnO thin films doped with silicon (Si), prepared by rf magnetron sputtering. This is the first report of the fact that a group IV element acts as an effective donor in ZnO of II-VI compound semiconductors.

§2. Experimental Procedure

Films were prepared by rf magnetron sputtering in a plasma focusing magnetic field of 5×10^{-3} T using an external solenoid coil. Details of the sputtering system have been described elsewhere.[10] A powder mixture of ZnO with a purity of 99.9% and dopant SiO_2 or SiO with a purity of 99.99% was used as the target (diameter, 80 mm) using a stainless steel holder. Substrates of Corning 7059 glass were suspended perpendicular to the target surface. The substrate temperature was varied in the range from room temperature to 400°C. The deposition rate depended on the content of SiO_2 or SiO added to the ZnO powder target and a typical value under a SiO_2 content of 2 wt% was about 12 nm/min at an rf power of 50 W. Film thickness was measured by a conventional surface roughness detector with a stylus. The electrical resistivity and Hall mobility were measured at room temperature by the van der Pauw method. In order to evaluate the stability of the resistivity for heat treatment at high temperatures, the change in electrical resistance with temperature was measured in various ambients. The temperature in heat treatments was changed at a heating rate of 2°C/min maintained at 300, 400 or 500°C for 1 hour and then was gradually lowered to room temperature. The optical transmission through films was measured in the wavelength range 300–800 nm.

§3. Results and Discussion

The electrical properties of the sputtered ZnO films doped with Si are quite dependent on sputtering conditions such as gas pressure, external magnetic field and the position and temperture of the substrates. The following deposition conditions have to be fulfilled simultaneously in order to obtain highly conductive films: 1) The films are deposited onto substrates placed perpendicular to the target surface. 2) The pure argon gas pressure during the sputter deposition is about 0.8 Pa. 3) The external plasma focusing dc magnetic field is about 5×10^{-3} T. 4) The substrate temperature is between room temperature and 250°C. Figure 1 shows the SiO_2 content dependence of the electrical resistivity ρ, Hall mobility μ and carrier concentration n of Si-doped ZnO (SZO) films prepared with such conditions as described above. The SiO_2 content shown is the content of SiO_2 powder added to the ZnO powder target. The results for the undoped powder target are also plotted at the left in Fig. 1. It can be seen that the SZO films exhibit a high carrier concentration

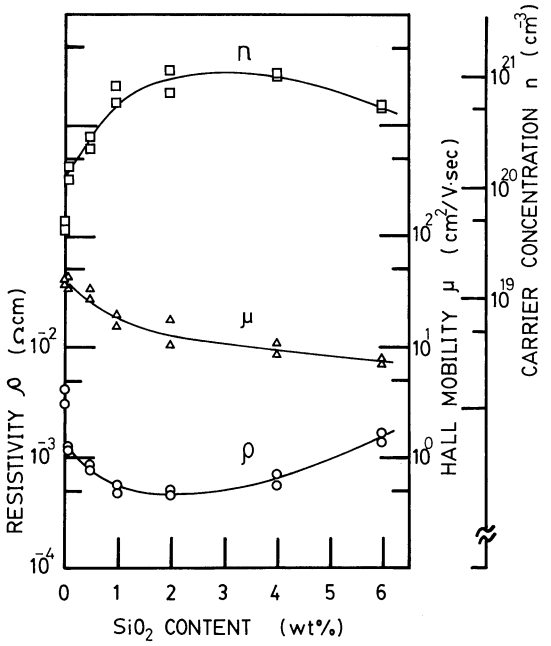

Fig. 1. Dependence of resistivity ρ, Hall mobility μ and carrier concentration n of sputtered ZnO films on SiO_2 content.

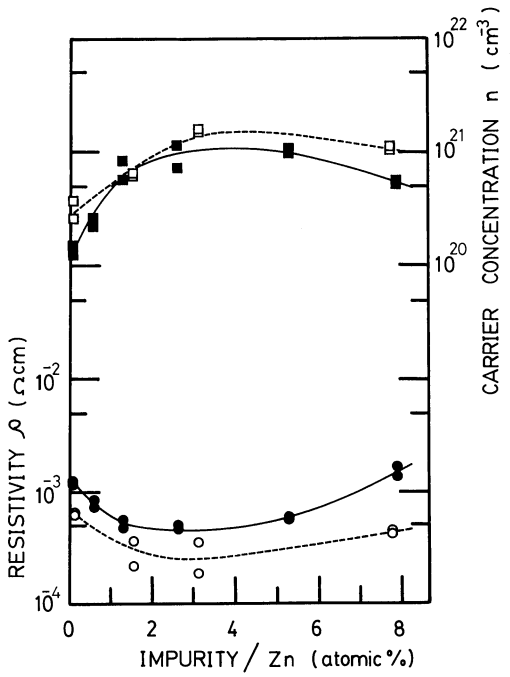

Fig. 2. Dependence of carrier concentration n and resistivity ρ of ZnO films doped with Si (●, ■) and Al(○, □) on atomic ratio of impurity/Zn.

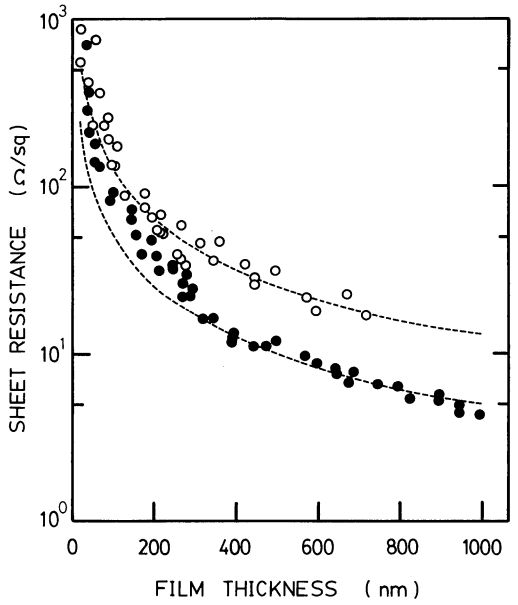

Fig. 3. Sheet resistance of undoped ZnO (○) and SZO (●) films as a function of the film thickness.

and a low mobility in comparison with those of undoped films and that the films with the lowest value of resistivity are obtained with SiO_2 contents of 1–3 wt%. We found that the doping effects shown in Fig. 1 can also be obtained by using the SiO dopant.

It can be generally predicted that a group IV impurity will act as either a donor or acceptor in II–VI compound semiconductors, as well as in the case of a group IV impurity in III–V compound semiconductors such as a Si-doped GaAs.[11] On the other hand, we reported that the Al impurity doped in ZnO acts as an effective donor because a single free electron is caused from an Al^{3+} ion on a substitutional site of a Zn^{2+} ion.[4] The dependences of the carrier concentration on the Si impurity content and the Al impurity content were compared as indicated for doped ZnO films in Fig. 2. The impurity/Zn ratio shown is the quantity calculated from the content of those oxide powders added to the ZnO powder target. It can be seen that the obtained carrier concentration of the Si-doped films is comparable to that of the Al-doped films. Thus, we can suggest that the Si impurity acts as an effective donor in ZnO because it may be substitutionally placed on a Zn site and will then cause a single free electron.

The resistivity of the SZO films prepared under conditions of sputtering gas pressures both lower and higher than about 0.8 Pa was always increased. These resistivity increases are due to the decrease in carrier concentration. It was found that the resistivity of the SZO films is almost independent of the change in substrate temperature in the range from room temperature to 250°C, if the substrate is kept at a constant temperature during the sputter deposition. The increase in the mobility and the decrease in carrier concentration were, however, observed as a substrate temperature increase in the range from room temperature to about 140°C. But the resistivity of the SZO films was increased with increasing substrate temperature above 250°C, and was due to the decrease in both the mobility and carrier concentrations. It was found that the mobility of all films doped with SiO_2 content up to about 4 wt% varies approximately as $n^{-2/3}$ with the carrier concentration n, if the film thickness is larger than about 300 nm. This dependence suggests that the mobility of the SZO films is limited by ionized impurity scattering. On the other hand, the mobility of doped films was dependent on the film thickness below about 300 nm. The thickness dependence of the sheet resistance for the SZO (SiO_2 content of 2 wt%) films is compared in Fig. 3 with that for undoped

films. Broken lines are the theoretically calculated sheet resistance when the resistivity is independent of the film thickness d. It can be seen that the resistivity of the SZO films is dependent on the films thickness below 300 nm, although that of undoped films is independent of the d. The increase in resistivity with decreasing thickness is due to the decreases in both μ and n, which are related with the lowered crystallinity of doped films as evidenced by X-ray diffraction analysis. Thus, the sheet resistance below 10 Ω/sq can be achieved for a film thickness above 500 nm. A minimum resistivity of 3.8×10^{-4} Ω cm in a ZnO film doped with SiO_2 content of 2 wt% can be obtained for the preparation under the best conditions.

Figure 4 shows the transmission spectra of ZnO films doped with the various SiO_2 contents shown in Table I. In all films with a thickness below 600 nm, the average transmittance in the visible region is approximately above 85%. The absorption edge is blue-shifted with increasing SiO_2 content up to about 4 wt%, which is related with the increase in carier concentration. This blue-shift in the SZO films can be interpreted as the result of competition between many body effects and Burstein-Moss effect.[12-14]

We have reported that a stable resistivity for use in various ambients at high tempeatures of below 400°C is attained as one of the doping effects of Al introduced into ZnO films. In the SZO films, we also evaluated the stability of the resistivity for heat treatments in various ambients. The resistance changes of Si-doped (SiO_2 content of 2 wt%) and undoped films in a vacuum of 0.8 Pa were compared in the range from room temperature to 500°C as indicated for the typical films in Fig. 5. In all

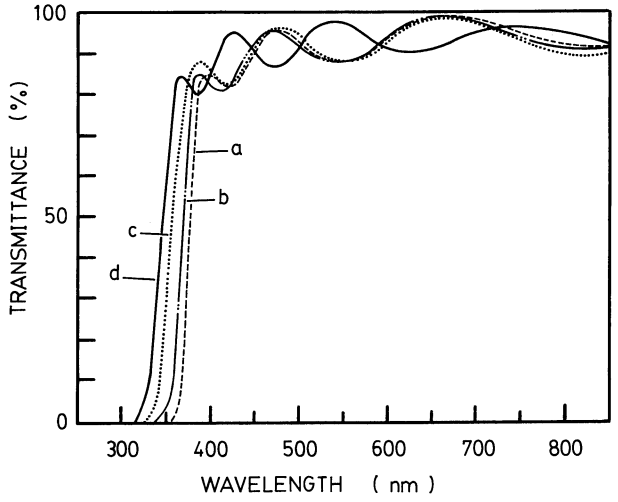

Fig. 4. Optical transmission spectra for SZO films doped with SiO_2 content of 0.1, 0.5, 1.0 and 2.0 wt%.

Table I. SiO_2 content, carrier concentration and film thickness for each film.

Sample No.	SiO_2 content (wt%)	Carrier concentration (cm^{-3})	Film thickness (nm)
a	0.1	1.4×10^{20}	400
b	0.5	2.8×10^{20}	350
c	1.0	5.4×10^{20}	450
d	2.0	1.2×10^{21}	445

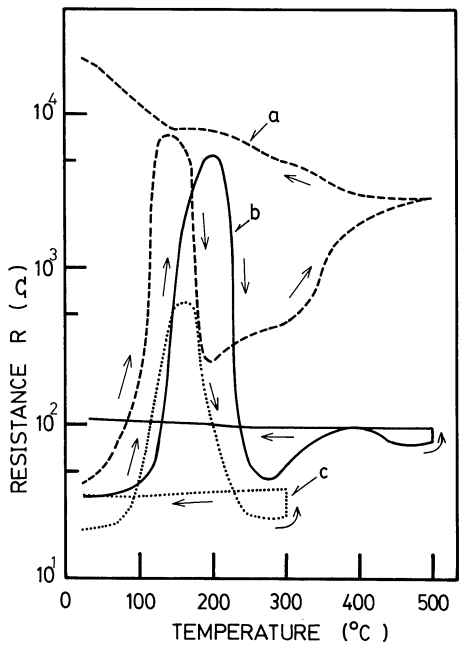

Fig. 5. Resistance as a function of temperature for undoped film (curve a) and SZO films (curves b and c) doped with SiO_2 content of 2 wt%.

our sputtered ZnO films, a peak in resistance changes in the temperature range from 100 to 200°C was always observed only during the first heating run, which may be ascribed to the water adsorbed on the surface of film and the grain boundary.[15] If these samples were heated again, the resistance versus temperature curves were similar to those obtained in the cooling cycle in the first heat treatment. It can be seen that the improvement of resistance change with temperature is also obtained by doping of Si, although the resistance after heat treatments is slightly increased. This resistance increase is mainly due to the decrease in carrier concentration, which is ascribed to the chemisorption of oxygen in the films.[15,16] It was also found that the changes in resistance with temperature in inert and nitrogen gases (purity, 99.99%) at atmospheric pressure are similar to those in a vacuum as shown in Fig. 5. It can be concluded that the properties of undoped ZnO transparent conducting film, which are unstable for use at high temperatures, can be improved by doping with Si impurity. No cracking or peeling of SZO films from the substrate was observed nor was there any change of the transmittance in the visible region after heat treatments. The Si-doped films presented a very stable resistivity when the films were exposed to the atmosphere for 10 months after deposition. It was confirmed that doping effects of Si impurity for ZnO films as descrived above are obtained by using the SiO dopant. We further found that these impurity doping effects in Si-doped ZnO films can be obtained by doping with other group IV elements such as Ge, Hf, Ti and Zr. However, we believe that the Si is the best dopant, as evidenced by its properties as transparent conductor and its stable resistivity for use at high temperatures.

§4. Summary

Highly conductive and transparent films of Si-doped

ZnO were prepared by rf magnetron sputtering of the ZnO target with SiO_2 or SiO dopant added. Films with resistivity as low as $3.8\times10^{-4}\,\Omega$ cm and transmittance in the visible region above 85% were obtained with a SiO_2 content of 2 wt%. A sheet resistance below $10\,\Omega/sq$ can be realized with a thickness above 500 nm on the substrate between room temprature and 250°C. A high carrier concentration of the order of $10^{21}\,cm^{-3}$ was obtained for SZO films. Great improvement in the stability of the resistivity for use at high temperatures was obtained for SZO films in comparison with undoped films. The Si-doped ZnO films should be useful as inexpensive transparent electrodes for a-Si solar cells because they do not require the use of group III elements.

Acknowledgements

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