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Effect of Si substrate on the properties of p-type ZnO:Ag films

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p-type ZnO:Ag (SZO) films were deposited on Si (100) and glass substrates using RF magnetron sputtering. We observed the hole concentration and the solid solubility of Ag in SZO on Si are both higher than those in SZO on glass. Secondary ion mass spectroscopy (SIMS) measurement indicates the improvements were likely to be attributed to the lattice mismatch between Si and SZO. Furthermore, current-voltage (I-V) measurement shows the electrical characteristic of ZnO/SZO homojunction prepared on Si substrate is influenced by the deposition sequence. These results imply Si is a promising substrate material for SZO-based optoelectronic devices.

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Keywords: ZnO, Ag doping, P-type, Si substrate

1. Introduction

ZnO is a promising semiconductor material for short wavelength optoelectronic applications due to its wide band gap and large exciton binding energy [1-5]. Preparation of p-type ZnO is one of the key points for the realization of ZnO based devices. Group Ia elements (such as Li and Na) are possible p-type doping candidates but they tend to occupy interstitial sites rather than substitutional sites, thereby serve mainly as donors [6, 7]. Recently, Ag has been receiving attention as a good acceptor candidate for p-type ZnO [8-14]. Intuitively, Ag^+ is hardly to be an interstitial ion because its ionic radius is larger than that of Zn^{2+}. Yan et al. indicated the formation energy for Ag_{Zn} is lower than that for Ag_i, based on first-principles calculations [8]. Similarly results were also obtained by Wan et al. [9]. Moreover, p-type SZO films were successfully fabricated by sputtering, pulsed laser deposition or E-beam evaporation [10-14]. These works showed SZO is a promising p-type material.

In many studies, pure or doped ZnO films are grown on sapphire substrates. However, sapphire is an electrically insulating material, so it introduces complexity to device fabrication processes when grown crystals are applied to light-emitting devices. Silicon has been widely used as a substrate for ZnO deposition due to many advantages such as low cost, large wafer size, and easy transformation into electronic device [15-19]. In this study, we observed the hole concentration and the solid solubility of Ag in SZO on Si are both higher than those in SZO on glass. ZnO/SZO homojunctions prepared on Si substrates were also studied. These results imply Si may be a more valuable substrate material candidate for p-type SZO films.

2. Experimental

ZnO/SZO films were grown on Si or glass substrates by RF magnetron sputtering. The Si substrates were n-Si (100) with resistivity of 80-120 Ωcm. The sputtering targets for SZO films were disks of ceramic ZnO (99.99% purity) dispersed by silver dots (99.999% purity). For pure ZnO film, a disk of pure ceramic ZnO target was used. The base pressure in the deposition chamber was 1.4×10^{-5} Torr. Ar and O_2 with the volume ratio of 1:2 were used as the working gas at a total pressure of 3.0×10^{-2} Torr. The sputtering power was 100 W and the film thickness of samples was about 1000 nm. After growth, the samples were annealed at 600 °C in pure O_2 ambience for 2 hours. The crystal structure of the films was characterized by X-ray diffraction (XRD). Electrical properties of films were measured by a Hall automatic measuring system using the Van Der Pauw technique. The elemental distribution of Ag was obtained by performing SIMS measurements.

3. Results and discussion

Fig. 1 shows XRD patterns of SZO and pure ZnO films. Only ZnO (002) diffraction peak is observed in each film, indicating a strong preferential c-axis orientation. The ZnO (002) peaks of both pure ZnO films are at 34.40°. The two SZO films were deposited on Si and glass substrates respectively using the same ZnO target (dispersed by 0.1% area silver dots). The angle shift of ZnO (002) peak of each SZO film is caused by the increase of lattice constant due to the substitution of Zn^{2+} ions by Ag^+ ions.[10-12] It is noteworthy the diffraction angle of ZnO (002) peak in Fig. 1(a) is a little lower than that in Fig. 1(b), which implies there were more Ag_{Zn} defects in

SZO film on Si substrate. For comparison, the full-width at half-maximum (FWHM) values of ZnO (002) peaks for films before and after annealing are listed in Table 1. It indicates the annealing process effectively improved the crystallinity of all the films. Electrical properties of films were also measured. The as-grown SZO films do not show any conductivity. However, annealed SZO films show p-type conductivity.

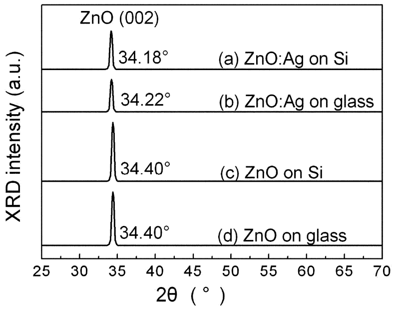

Fig. 1. X-ray diffraction patterns of Ag-doped/pure ZnO films.

Table 1. FWHM values of ZnO (002) peaks for films before and after annealing.

	as-grown (°)	annealed (°)
ZnO on Si	0.50	0.31
ZnO on glass	0.49	0.29
SZO on Si	0.52	0.33
SZO on glass	0.56	0.35

Table 2 lists the electrical properties of SZO films on Si and glass substrates. The two films have similar hall mobilities. However, the carrier concentration of SZO on Si is much higher than that of SZO on glass, which indicates there were more Ag_{Zn} acceptors in SZO film on Si substrate.

Table 2. Electrical properties of the SZO films.

	resistivity (Ωcm)	mobility (cm^2/Vs)	carrier concentration (cm^{-3})	carrier type
SZO on Si	9.87	2.11	3.0×10^{17}	p
SZO on glass	15.97	2.06	1.9×10^{17}	p

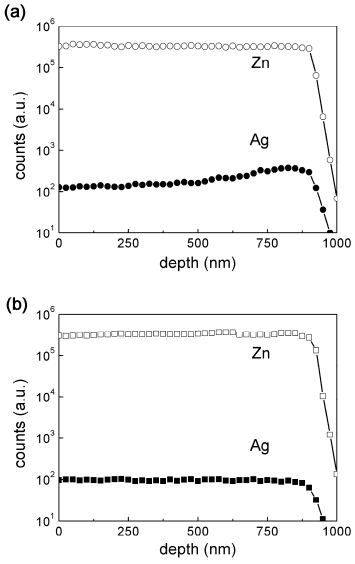

Fig. 2. SIMS depth profile for SZO films on different substrates: (a) Si, and (b) glass.

The results of XRD and Hall Effect measurement show that the p-type SZO film on Si substrate has higher hole concentration. We suppose the improvements are caused by the lattice mismatch between SZO and Si (100). As we know, the lattice constant (for the “a” parameter) of wurtzite ZnO is smaller than that of Si (100). It means tensile strains exist in the ZnO films on Si (100) substrates. Generally, tensile strains in film raise the system energy. So the tensile strains could be relaxed by substituting larger ions for smaller ones [20]. Thus, Ag_{Zn} defects form easily for improving the system stability because the ionic radius of Ag^+ is larger than that of Zn^{2+}. In order to test this deduction, the elemental distribution of Ag was obtained by performing SIMS measurements. It is clearly the thickness of SZO films was about 1000 nm. Fig. 2 (a) shows the Ag count of SZO films on Si considerably increases from the surface of SZO to the SZO/Si interface. On the other hand, Ag profile extends uniformly in the SZO film on glass substrate, as shown in Fig. 2 (b). It is completely consistent with our deduction.

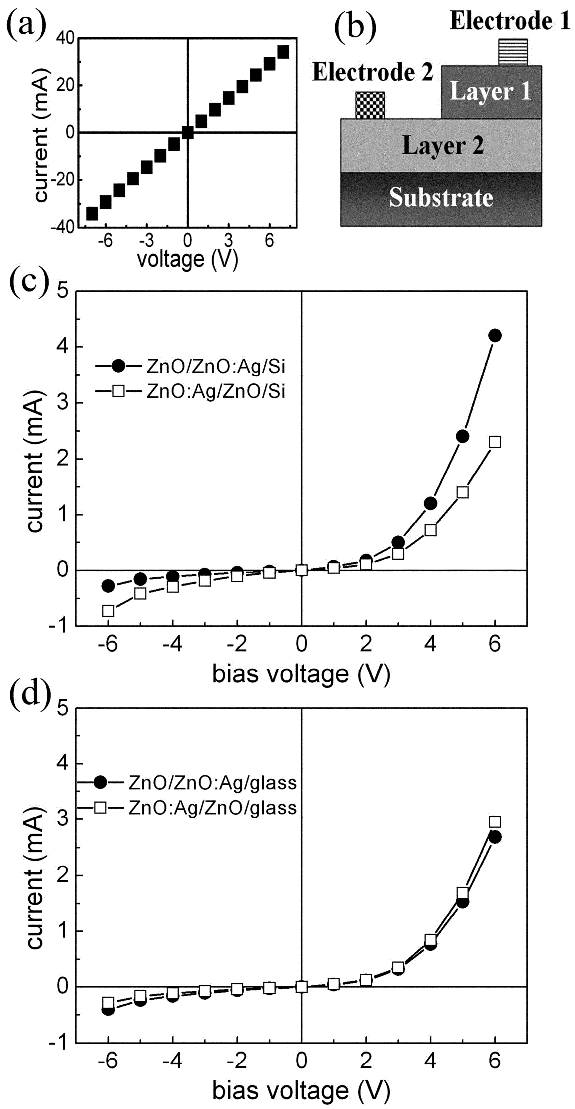

Fig. 3. (a) Ohmic contact between Ag electrode and SZO, (b) schematic structure, (c) I-V curves of ZnO junctions on Si, and (d) on glass.

ZnO homojunctions were fabricated on Si or glass substrates. The electrodes of SZO and pure ZnO were silver and indium, respectively [21]. Fig. 3 (a) gives the Ohmic contact between Ag and SZO. The schematic structure of junctions is shown in Fig. 3 (b). The SZO layer and pure ZnO layer were deposited in various sequences. Fig. 3 (c) gives the I-V curves of ZnO junctions on Si. Compared with the SZO/ZnO/Si structure, the ZnO/SZO/Si structure shows a better rectifying behavior. It implies the Si substrate can hardly improve the electrical properties of p-type SZO film on pure ZnO "buffer layer". As shown in Fig. 3 (d), the two I-V curves of ZnO junctions on glass are almost overlapping as expected. These results shows the ZnO/SZO/Si is a potential structure for ZnO based p-n junction device.

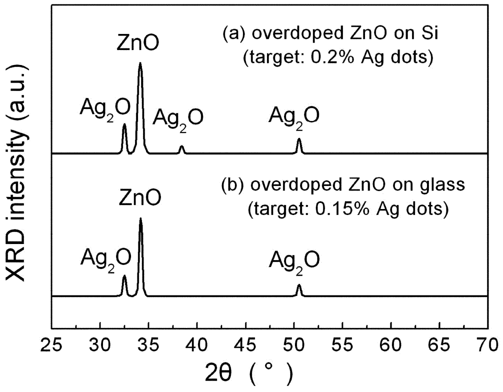

Fig. 4. X-ray diffraction patterns of overdoped ZnO films.

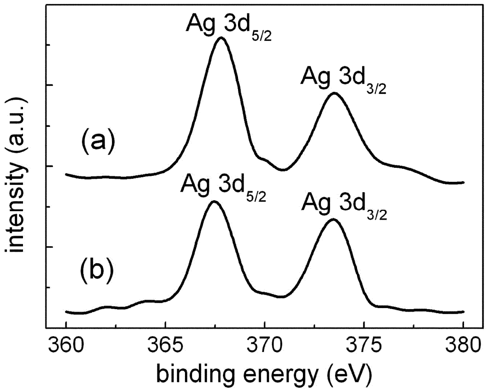

Fig. 5. XPS spectra of overdoped ZnO films on different substrates: (a) Si, and (b) glass.

The solid solubility of acceptor element is another important issue for p-type ZnO fabrication. Overdoping generally does not increase the acceptor concentration but causes new defects. It is adverse to the electrical properties of p-type ZnO. So the maximal hole concentration of ZnO is limited by the solid solubility of acceptor element. Higher solid solubility of Ag in SZO is valuable especially for heavy doped ZnO based device. The solid solubility of Ag in SZO is studied using XRD. SZO films were deposited on Si and glass substrates using ZnO targets dispersed by 0.1%, 0.15% and 0.2% area silver dots, respectively. Fig. 4 (a) shows the Ag_2O peaks in overdoped SZO film on Si substrate, which means Ag supersaturation appeared. Ag supersaturation in SZO on Si was not observed until the Ag area of target was expanded to 0.2%. On the other hand, Ag supersaturation was observed in SZO deposited on glass using ZnO target dispersed by 0.15% area silver dots, as shown in Fig. 4 (b). These results indicate the solid solubility of Ag in SZO is also improved by Si substrate addition. XPS measurement was used for characterization of the overdoped ZnO films as shown in Fig. 5. The Ag $3d_{5/2}$ peaks at 367.7eV and Ag $3d_{3/2}$ peaks at 373.7 eV were observed in each sample, indicating the existence of Ag_2O [10, 22, 23].

4. Conclusions

In summary, the effect of Si and glass substrates on structural and electrical properties of p-type SZO films is investigated. Results show the hole concentration and the solid solubility of Ag in SZO on Si are both higher than those in SZO on glass. The valuable improvement is likely caused by the lattice mismatch between SZO and Si (100). I-V measurements show the ZnO/SZO/Si has better junction characteristic than other three SZO/ZnO homostructures. These results indicate Si may be a promising substrate material for SZO based devices.

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