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A novel phenomenon: p-Type ZnO:Al films deposited on n-Si substrate

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ABSTRACT

Al-doped p-type ZnO thin films were fabricated by RF magnetron sputtering on n-Si (1 0 0) and homo-buffer layers in pure ambient oxygen. ZnO ceramic mixed with 2 wt% Al_2O_3 was selected as a sputtering target. XRD spectra show that the Al-doped ZnO thin films have a ZnO crystal structure. Hall Effect experiments with Van der Pauw configuration show that p-type carrier concentrations are arranged from 1.66×10^{16} to $4.04\times10^{18}\,cm^{-3}$, mobilities from 0.194 to $11.1\,cm^2\,V^{-1}\,s^{-1}$ and resistivities from 0.999 to 18.4 Ωcm. Field emission scanning electron microscopy (FESEM) cross-section images of different parts of a p-type ZnO:Al thin film annealed at 800 °C show a compact structure. Measurement of the same sample shows that density is $5.40\,cm^{-3}$, smaller than the theoretically calculated value of $5.67\,cm^{-3}$. Photoluminescence (PL) spectra at 10 K show a shoulder peak of p-type ZnO film at about 3.117 eV ascribed to electron transition from donor level to acceptor level (DAP).

1. Introduction

ZnO is a promising candidate for photoelectronic devices due to its direct wide electron energy bandgap of 3.37 eV at room temperature (RT) and large exciton binding energy of 60 meV. Its electron energy band structure is very similar to that of GaN and has advantages over GaN for light emitting devices: larger exciton binding energy, lower refraction index, shallower acceptor levels and so forth. Recent investigations on this material have made important progress in implementation of ZnO light emitting diodes (LEDs) [1–4], implying that the feasibility of ZnO for light emitting devices is proved, not only theoretically, but also experimentally. Despite these achievements, light emitting devices based on ZnO have not been commercialized due to their low efficiency. A tough bottleneck to obtain high-quality p-type ZnO hinders the development of LEDs based on this material. In doping ZnO p-type, many dopants and methods have been used. Usually group I and V elements are used as acceptors to dope p-type in ZnO [5–10], and especially, group V elements are extensively investigated. Nitrogen seems to be the best acceptor of group V elements, since nitrogen has nearly the same radius as oxygen and is the shallowest acceptor in ZnO [11]. However, it is hard to dope ZnO p-type with nitrogen. To solve hard p-type doping with a single element of group V, co-doping group V and III elements with a ratio of 2:1 was proposed to make deep acceptor levels shallower and to make acceptors more soluble in ZnO [12]. Though the methods mentioned above can dope p-type in ZnO, practically, it is hard to get satisfactory high quality p-type. The large radius elements in group V, such as As and Sb, show unexpectedly reasonable effects of p-type dopants in ZnO [13,14]; theoretically it was explained as a complex acceptor model of X_{Zn}–$2V_{Zn}$ (X = As, Sb) [15] or a cluster model of X_{Zn}–$4V_{Zn}$ [16], X with large radius occupying O site and repelling Zn to escape. An attempt to find other appropriate elements to act as complex acceptors like the models above should be studied, even group III elements should not be excluded. It is easy to dope n-type in ZnO with aluminum under the condition of oxygen-deficient growth. Heavily Al-doped ZnO films (AZO) usually show high electron concentration with low resistivity [17] and are employed as a transparent conduction oxide electrode (TCO). Heavily Al-doped ZnO films deposited in oxygen-rich condition, i.e., in pure oxygen ambient, have not been investigated to date. Aluminum can be bound tightly with oxygen, implying that tight bond strength of Al–O can be expected to attract O to Al and repel Zn to escape from ZnO in the growth procedure. This will produce many zinc vacancies (V_{Zn}) in ZnO:Al films and will make the films p-type. In this study, heavily Al-doped ZnO thin films were grown on n-Si substrate under the condition of pure ambient oxygen and the feasibility of Al-doped p-type ZnO films was investigated.

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2. Experiment

Heavily Al-doped ZnO films were deposited in pure oxygen gas (5N) by RF magnetron sputtering. To confirm the p-type conductivity of Al-doped ZnO, a little high resistivity n-type Si (1 0 0) (1~30 Ωcm) wafer was used as a substrate. Usually, homo-buffer layers are shown its benefit to improve the crystallinity of ZnO films. Therefore, homo-buffer layer was also selected as a substrate. Si is extensively used in semiconductor industry and much cheaper than sapphire. If LEDs are fabricated on Si, photoelectronic technology can be incorporated with present IT technology, which is a cause of selection Si as substrate in this study. The buffer layers were fabricated on n-(1 0 0) Si in the mixture of O_2 and Ar with a ratio of 1:4 at 100 °C and 15 mTorr with ZnO ceramic (5N) as the target by RF magnetron sputtering. RF power was set at 150 W for 25 min to obtain 70 nm thickness ZnO layers. Subsequently the buffer layers were in-situ annealed at 800 °C and 15 mTorr in O_2 for 20 min. The Al-doped ZnO thin films were realized in pure O_2 by RF magnetron sputtering. ZnO ceramic (5N) mixed with 2 wt% Al_2O_3 (5N) was selected as the sputtering target. The diameter of target is 5 cm and the distance of target and substrate is 7 cm. RF power and growth temperature were set at 180–210 W and 450 °C, respectively, for 180 min to obtain Al-doped ZnO thin films of 400–900 nm thickness. Some films were in situ annealed at 600 and 800 °C at 10 Torr pressure in pure O_2 for 5 min, respectively. The film microstructures were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM). Electrical, chemical and optical properties of the films were evaluated by Hall Effect measurements with Van der Pauw configuration, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL), respectively.

3. Result and discussion

Fig. 1 shows the XRD spectra of the buffer layer and the ZnO:Al thin films grown at 450 °C and 15 mTorr. All films exhibit (0 0 2) peak of two theta diffraction angle at about 34.44°, the value of the corresponding peak of bulk ZnO, implying all films do not have obvious internal stress. The films also show (1 0 0) and (1 0 1) peaks. It can be concluded, from the comparison of the changes of the intensities of (1 0 0), (1 0 1) and (0 0 2) peaks, that buffer layers and high annealing temperatures are beneficial to ZnO:Al film growth along the *c*-axis.

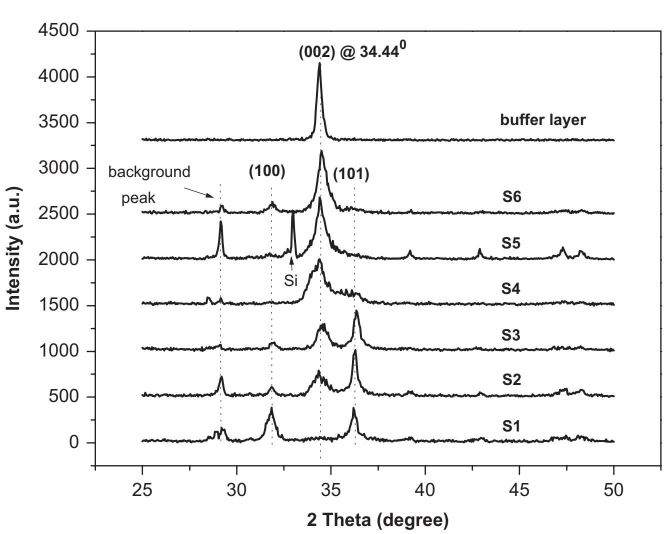

Fig. 1. XRD patterns of homo-buffer layer and ZnO:Al films grown on Si (S1: as-grown; S2: annealed at 600 °C; S3: annealed at 800 °C) and buffer layer (S4: as-grown; S5: annealed at 600 °C; S6: annealed at 800 °C).

Fig. 2 shows FESEM cross-section images of the different parts of a ZnO:Al film on Si (S7) grown at 6 mTorr and then annealed at 800 °C for 120 min. The images show compact microstructure. Weighting measurement reveals sample density of 5.40 g cm^{-3}, much less than the theoretically calculated value of 5.67 g cm^{-3} for bulk ZnO that has the crystal lattice constants of $a = 0.325$ and $c = 0.5207$ nm, and also less then practically measured value of 5.72 g cm^{-3} for n-type ZnO:Al (AZO) grown in a Zn-rich condition [17]. It can be inferred indirectly from the density of S7 that many Zn vacancies were formed, because the mass of atom Zn is much heavier than that of atom O, and the low film density is attributed to Zn scarcity.

Table 1 presents the conduction types, carrier concentrations, mobilities and resistivities of samples measured by Hall Effect with Van der Pauw configuration. The as-grown film on Si (S1) shows p-type conduction with low carrier concentration of 1.66×10^{16} cm^{-3} while 600- and 800 °C-annealed ones (S2, S3) show n-type with carrier concentrations of 8.99×10^{18} and 2.45×10^{18} cm^{-3}, respectively. As the annealing process is implemented at 600 and 800 °C, the conduction type converts to n-type with reduction of resistivity from 18.4 to 4.32 then to 1.29 Ωcm. Hall mobility decreases from 2.03 cm^2 V^{-1} s^{-1} for as-grown film (S1) to 0.161 cm^2 V^{-1} s^{-1} for 600 °C-annealed film, then increases to 1.98 cm^2 V^{-1} s^{-1} for 800 °C-annealed film. The conversion of conduction type from as-grown to 600 °C-annealing is due to the change of electrical property of films. The as-grown film on the buffer layer (S4) has high resistivity so that its electric property cannot be measured. The film annealed at 600 °C (S5) shows p-type conduction and high carrier concentration of 4.04×10^{18} cm^{-3} with resistivity of 7.97 Ωcm. As annealing temperature increases to 800 °C, the conduction type of the film (S6) converts to n-type with resistivity reducing to 1.35 Ωcm. This shows that the film on the buffer layer has higher type conversion temperature than that on Si. A ZnO:Al film (S7) was fabricated on Si at 6 mTorr and 450 °C with a consequent in situ annealing process at 800 °C for 2 h to investigate influence of pressure on conduction type. The film (S7) shows p-type conduction with mid carrier concentration of 5.64×10^{17} cm^{-3}, mobility of 11.1 cm^2 V^{-1} s^{-1} and resistivity of 0.999 Ωcm. Aluminum has very low diffusion coefficient in silicon crystal, especially below 700 °C [18]; this indicates that aluminum in ZnO:Al films cannot diffuse into Si substrate and is not able to make the substrates p-type. At high temperature, aluminum has a higher diffusion coefficient than at low temperature, indicating that at high annealing temperature, such as 800 °C in this study, aluminum may be diffused into Si substrates and may make Si substrates accumulate more p-type carrier. However, as in the case of the films above grown at 15 mTorr, higher annealing temperatures make films convert from p-type at low growth temperature to n-type at high annealing temperature. The p-type conduction shown by the Hall Effect measurement should be attributed to the property of ZnO:Al films, not to the property of n-Si substrate. It also indirectly confirms the density of sample S7 is 5.40 g cm^{-3}, smaller than the theoretical calculation of 5.67 g cm^{-3}. That is, many Zn vacancies are formed and this makes the film p-type.

Fig. 3 shows XPS spectra of O1s and surveys after plasma etching for 30 s. From the spectra of O1s (Fig. 3(a) and (b)) it can be seen that O1s peak appears at about 530.7 eV. This is attributed to O^{2-} ion on Wurtzite structure of ZnO, surrounded by Zn atoms, and shoulders appears at about 532.4 eV, attributed to O^{2-} ion of loosely bound oxygen on the surface of ZnO [19] and inner O^{2-} that also can be assigned to Zn-deficient state around O, indicating presence of Zn vacancies. It can be demonstrated, by Gaussian fitting, that the area ratio under the shoulder and peak of