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Fabrication of Sb-doped p-type ZnO Thin Films by Pulsed Laser Deposition

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Abstract

In this work, antimony (Sb)-doped p-type ZnO thin films on c-plane sapphire substrates have been fabricated by pulsed laser deposition, with Sb_2O_3 used as the dopant source. The effects of ambient gas or growth temperature on the fabrication process were investigated. The nitrogen ambient was found to be essential to achieve the p-type conduction. The Hall-effect measurements at room temperature indicated that the ZnO thin films doped with 3 at.% Sb and grown at 600 °C under N_2 atmosphere exhibited p-type behavior with a hole concentration of 1.17×10^{17} cm^{-3}, hole mobility of 0.63 $cm^2/V\cdot s$, and resistivity of 84.51 Ω·cm. X-ray diffraction and scanning electron microscopy revealed good crystallization and homogenous surface morphology of the ZnO:Sb thin films. The optical transmission spectrum of the ZnO:Sb thin films indicated that the energy band gap value was around 2.9 eV. Post-growth annealing at 650 °C converted the p-type conduction to n-type. This result implied that Sb-doping and annealing treatment were dominant factors determining native and extrinsic defects in the ZnO thin films, and thus controlling their electrical conductivity properties.

Keywords: Antimony doping; P-type ZnO; Pulsed laser deposition; Thin film.

Introduction

Zinc Oxide (ZnO) has been considered as one of the most promising materials for optoelectronic applications due to its wide energy band gap of 3.37 eV, large exciton binding energy of 60 meV, high optical gain, high radiation and temperature stability (Klingshirn, 1975; Pandey et al., 2013). In order to develop the ZnO-based optoelectronic devices, the first step is the fabrication process of high-quality n- or p- type ZnO thin films. It is easy to grow good-quality n-type ZnO with resistivity of 1–2 orders of magnitude higher than metals, because of intrinsic non-stoichiometric growth of ZnO (Yamamoto et al., 2001). However, one of the current challenges in the fabrication process is to prepare p-type ZnO. The p-type conduction has been realized by doping with elements of N (Guo et al., 2003), As (Look et al., 2004), P (Kim et al., 2003), Li (Zeng et al., 2006), Li/N co-doping (Zhang et al., 2010), and so on. However, indistinct doping mechanism and reliable p-type conduction are still the essential issues that hinder the development of all ZnO-based optoelectronic devices. A model has been proposed for group-V dopants, such as As and Sb, to achieve reliable p-type conduction in ZnO (Limpijumnong et al., 2004). In this model, a Sb_{Zn}-$2V_{Zn}$ complex was considered to primarily cause the acceptor-like behavior in the Sb-doped ZnO (SZO) films (Limpijumnong et al., 2004). According to their theory, the Sb atom occupying Zn side (Sb_{Zn}) in ZnO has sufficient energy to spontaneously induce two zinc vacancies (V_{Zn}), forming a shallow acceptor complex (Sb_{Zn}-$2V_{Zn}$) with a formation energy (ΔH_f) of 2.0 eV and an acceptor ionization energy of 0.16 eV. In addition, controversial results on oxygen-rich growth condition or annealing processes have been reported for achieving p-type conductivity in this system.

SZO films have been grown by various deposition techniques,

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such as molecular beam epitaxy (Xiu et al., 2005), pulsed laser deposition (PLD) (Guo et al., 2007), radio-frequency sputtering (Wanga et al., 2006), and dual ion beam sputtering deposition (Pandey et al., 2013). However, the prepared p-type ZnO thin films exhibited diverse characteristics and properties with poor stabilities. In this work, we study the p-type behavior in Sb-doped ZnO thin films fabricated by PLD. The effects of ambient and growth temperature are investigated for further exploration.

Materials and Methods

The ZnO:Sb films were deposited on c-plane sapphire substrates by PLD. The targets were high-purity ZnO–Sb_2O_3 ceramic disks with various Sb contents. The Nd:YAG Q-switched laser with 266 nm wavelength and a pulsed duration less than 10 ns was adopted as the ablation source. The sapphire substrates were rinsed thoroughly with acetone, alcohol, and de-ionized water; and were subsequently purged by pure nitrogen gas in order to remove dust particles and various organic contaminants before being loaded into the chamber. The sapphire substrates were baked at 600 °C for 40 min in vacuum inside the deposition chamber before the growth process.

The vacuum chamber was pumped to a base pressure of 3×10^{-6} torr. The growth temperature varied from 450 to 650 °C. Oxygen, nitrogen, and argon were used as the ambient gases at the flow rate of 5 sccm (standard cubic centimeters per minute). The working pressure was kept at 1×10^{-2} torr during the growth process. The laser repetition rate was 10 Hz and the energy per pulse was 1.5 J/cm^2. All the films were deposited for duration of 12,000 laser pulses in this work.

Results and Discussion

The average thickness of the Sb-doped ZnO thin films was approximately 200 nm, as measured by cross-sectional scanning electron microscopy (SEM). Room-temperature Hall effect measurements were carried out using van der Pauw configuration. The ZnO–Sb_2O_3 targets with Sb contents of 1, 3, 5, and 7 at.% were used to make sure the suitable atomic weight percentage of Sb.

Fig. 1 shows X-ray diffraction (XRD) patterns of the Sb-doped ZnO films grown with different atomic weight percentage of antimony. Only one peak corresponding to ZnO (002) plane is observed because that all the fabricated films were at (002) highly preferential orientation, while no any other secondary phases, such as Sb_2O_3, are detected in the patterns. The angle position of the (002) peak shifts evidently with the target Sb content, indicating the incorporation of Sb into the ZnO lattice. The incorporation of Sb into the ZnO host lattice leads to the change in the lattice constant, which in turn leads to the diffraction angle shift, according to the Bragg's law.

Table 1 summarizes the electrical properties of Sb doped ZnO thin films grown with targets composed of Sb in different atomic weight percentages. The insulating sapphire substrates as adopted here can assure that any conduction type must come from the ZnO films rather than from the substrates. It seems that

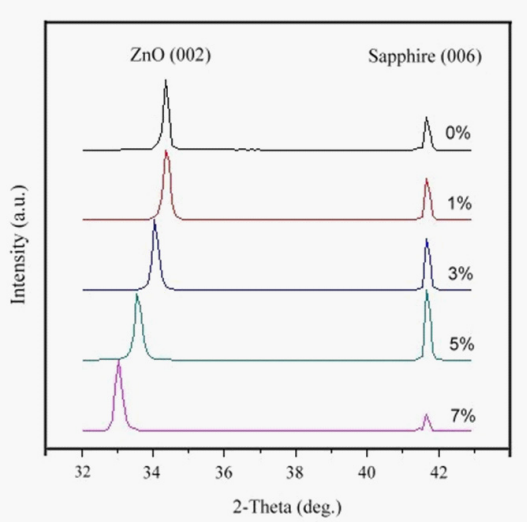

Fig. 1. X-ray diffraction patterns of Sb-doped ZnO thin films grown with different Sb at %. The angle of ZnO (002) peak shifts to lower angles as Sb at % increases.

Table 1. Electrical properties of Sb-doped ZnO thin films grown by using targets with different Sb at %.

Sb at %	Resistivity (Ω-cm)	Hall mobility (cm^2/V·s)	Carrier Conc. (cm^{-3})	Conduction Type
0%	0.5	40.7	$3.08X10^{17}$	n
1%	1968	71.97	$4.41X10^{13}$	n
3%	>1GΩ	---	---	---
5%	>1GΩ	---	---	---
7%	>1GΩ	---	---	---

p-type conduction cannot be achieved in the range of 1-7 at %.

The film grown with 1 at % Sb presents a n-type conduction. This is probably associated with the formation of oxygen vacancy because the Sb-related acceptor is not enough to compensate the background electrons from the native defects. When the atomic weight percentage of antimony is higher than 3 at.%, the sample shows relatively high resistivity (the resistance is higher than 1 Giga Ohms), which may be caused by the reduction of hole concentration that is due to the formation of native defects at high oxygen working pressure, according to Samanta's research (Samanta et al., 2012). These native defects normally give n-type background carriers and act as a trap for non-equilibrium holes in the ZnO:Sb thin film. Thus, the doped Sb atom cannot create strong discrepancy of conduction type. It seems better to choose the 3% target as the starting point, based on the observation that the electron concentration decreases with increasing Sb content. In order to achieve the p-type doping, it needs to adjust growth parameters, such as ambient and temperature, to compensate the intrinsic n-type doping.

The ZnO–Sb_2O_3 target with Sb content of 3 at.% was used to grow p-type ZnO:Sb thin films under the ambient oxygen, nitrogen, or argon gases, respectively, according to Table 2. The other growth parameters were held the same as described above. The electrical properties of three samples are summarized in Table 2. It seems that p-type conduction can be achieved in either nitrogen or argon ambient gases. However, the hole concentration in the sample produced in nitrogen is 1.17×10^{17} cm^{-3}, which is much higher than the one grown in argon atmosphere.

Table 2. Electrical properties of 3at % Sb-doped ZnO thin films grown in different ambient gases.

Ambient Gas	Resistivity (Ω·cm)	Hall Mobility ($cm^2/V·s$)	Carrier Conc. (cm^{-3})	Conduction Type
5 sccm O_2	>1GΩ	---	---	---
5 sccm N_2	84.51	0.63	$1.17x10^{17}$	P
5 sccm Ar	273.45	18.28	$1.25x10^{15}$	P

The reason may be that the p-type conduction has been realized by doping nitrogen atom, and therefore it is a reasonable assumption that the nitrogen gas helps to increase the hole concentration. In addition, there is no publication on adopting Ar as ambient gas in ZnO:Sb thin film, whereas there are many papers evaluated the Ar as ambient gas for ZnO thin film (Igasaki et al., 2004; Park et al., 2007.) Apparently, Ar ambient gas affects the characteristic of ZnO thin film and the correlated features of Sb-doped ZnO thin films. The p-type conduction can be reasonably achieved in Ar ambient gas.

Fig. 2 shows XRD patterns of the Sb-doped ZnO films grown in different ambient gases. Only one diffraction peak corresponding to ZnO (002) plane is observed, and no secondary phase is detected. It is suggested that all the films are at (002) high preferential orientation. The full width half maximum (FWHM) of the (002) diffraction peak is 0.195°, 0.21°, and 0.29° for the samples grown in the N_2, O_2, and Ar ambient gases, respectively, suggesting that the crystallinity of the sample grown in ambient nitrogen gas is superior to others. The same XRD angle as depicted in Fig. 2 implies the same amount of Sb atoms doped into the ZnO thin films. Nevertheless, the thin film deposited in the N_2 atmosphere reaches higher hole concentration under same amount of doped Sb atoms, according to Table 2.

In an attempt to reduce the high resistivity and to crystallize the grown film, an in-situ post-growth annealing was processed at 650 °C for 30 min. Under this condition, the resistivity is comparatively low, however, the conduction type converts back to n-type. This was probably associated with the Sb-related acceptor being not enough to compensate the background electrons from the native defects. Increasing of native donors results in a decrease of hole concentration via electron-hole recombination (Samanta et al, 2012). It is easy to observe the specific phenomenon at a high temperature growth. However, better understanding of this origin is in progress.

To optimize the electrical properties and crystallization of the Sb-doped p-type ZnO thin films in ambient nitrogen gas, a high-purity ZnO–Sb_2O_3 ceramic disk with Sb content of 3 at.% was used as the target and nitrogen gas was applied for the ambient gas. The growth temperature varied from 450 to 650 °C. Fig. 3 shows XRD patterns of the Sb-doped ZnO films grown at different temperatures. Only one diffraction peak corresponding to ZnO (002) plane is observed, and no secondary phase is detected in this patterns. It suggests that all the films are highly (002) oriented. The FWHM of the (002) peak decreases evidently as the temperature increases, indicating that the crystallinity is improved at a high growth temperature. However, the conduction type is n-type at 450 °C and 650 °C. The growth temperature of 600 °C is one of the dominant parameters in this study. The provided energy may be insufficient if the growth temperature set at 450 °C is not high enough. Therefore, the amount of active donors is less, in spite of the fact that doping more Sb atoms into ZnO might cause strong deformation of the original lattice. The native defect behavior at the same growth temperature may be similar while annealing temperature is set at 650 °C. Therefore, when the growth temperature remains at 650 °C, the hole concentration is reduced due to the increase of native donors. A decrease of hole concentration via electron-hole recombination is thus sustained (Samanta et al., 2012). Therefore, it is reasonable that the conduction type remains in n-type due to the increased native donors of ZnO:Sb thin film at 650 °C growth temperature

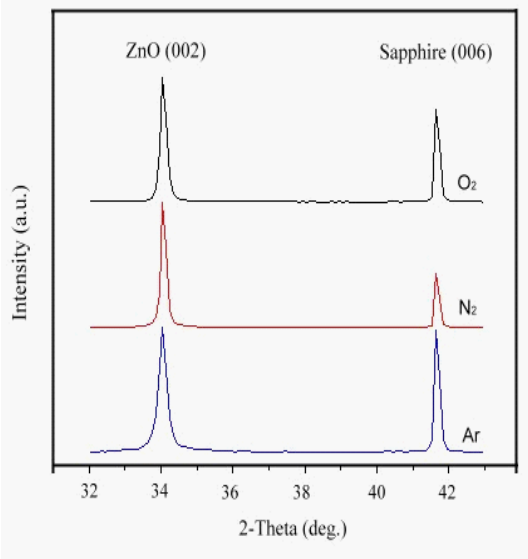

Fig. 2. X-ray diffraction patterns of Sb-doped ZnO thin films grown in different ambient gases. The ZnO (002) peak angle remains the same angle position without any shift.

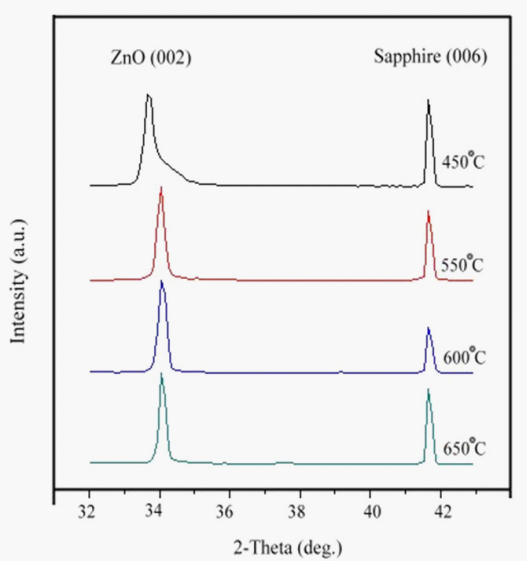

Fig. 3. X-ray diffraction patterns of Sb-doped ZnO thin films grown at different temperatures. The p-type behavior of Sb-doped ZnO thin films was observed at 550 °C and 600 °C; however, the Sb-doped ZnO exhibited n-type behavior at 450 °C and 650 °C.

as presented in this work. Further investigations of SZO homojunction with similar growth condition despite the growth temperature is suggested in the future.

The surface morphology of the Sb-doped ZnO thin film grown at 600 °C was observed by SEM. As shown in Fig. 4, the surface is composed of dense grains with a similar size, which is consistent with the XRD result. This result suggested that the Sb-doped ZnO films seemed to reach acceptable crystallinity.

The optical transmission spectrum of the ZnO:Sb thin film is shown in Fig. 5. The value of transmittance of thin films in the visible range is about 65-85%, which rises with increasing wavelength while becomes fixed near the UV band. The value of band gap is estimated from fundamental absorption edge of the films. For the direct transitions, the absorption coefficient is expressed as follows:

$$\alpha^2 (h\nu) = A (h\nu - E_g) \qquad (1)$$

where A is the constant, E_g is the energy gap, ν is the frequency of the incident radiation and h is Planck's constant.

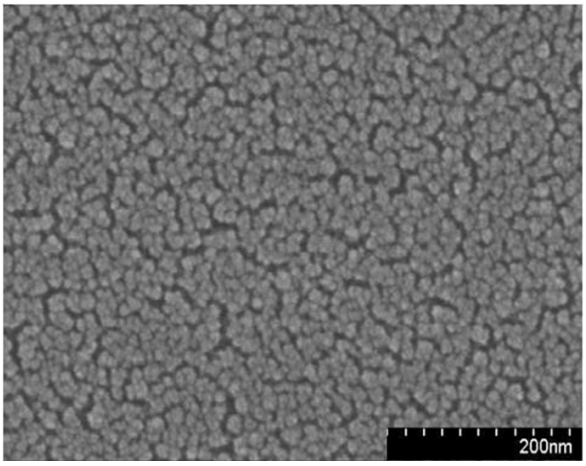

Fig. 4. SEM morphology of Sb-doped ZnO thin film grown at 600 °C.

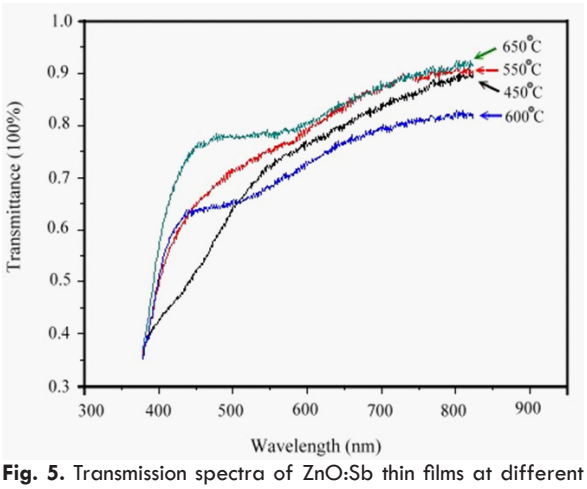

Fig. 5. Transmission spectra of ZnO:Sb thin films at different growth temperatures. The transmittance rises as the wavelength increases, while the are almost the same near the UV range.

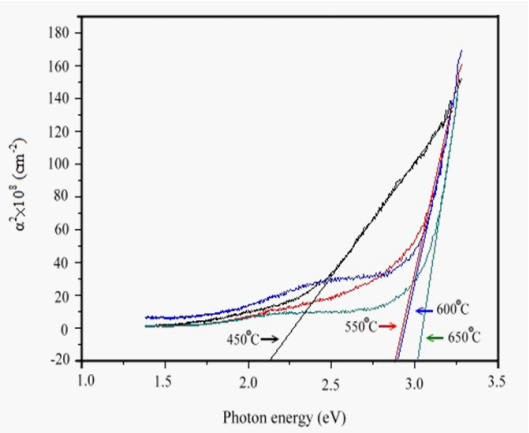

Fig. 6. Plot of α^2 vs. $h\nu$ for the ZnO:Sb thin films at different temperatures. The band gap values are almost the same at 550 °C and 600 °C, while it is less at 650 °C. There exists an extra low band gap value below growth temperature 450 °C.

Fig. 6 shows the plot α^2 vs. $h\nu$ for the ZnO:Sb thin films. The band gap value of each thin film is calculated from this plot. The X-interceptions are 2.26, 2.90, 2.91, 3.02 eV for 450, 550, 600, 650 °C, respectively. The presence of a single slope in the plot suggests that the films have direct and allowed transition. The band gap energy is obtained by extrapolating the regressed straight line to the zero absorption coefficient. The band gap value (photon, eV) of ZnO:Sb thin film is found to be around 3 eV except at 450 °C growth temperature. The band gap value at growth temperature 550 °C is similar to that at 600 °C, but is ~0.1 eV less than that at 650 °C which may be due to the acceptor levels of thin films. The band gap is just around 2.25 eV at 450 °C growth temperature, due to the impurity level that may result from the defects.

Conclusions

In summary, Sb-doped p-type ZnO thin films have been grown on c-plane sapphire substrates by using pulsed laser deposition method. The optimal p-type conduction was achieved at the growth temperature of 600 °C, resulting a resistivity of 84.51 Ω·cm, carrier concentration of 1.17×10^{17} cm^{-3} and Hall mobility of 0.63 $cm^2/V{\cdot}s$. No p-type conduction was found in Sb-doped ZnO films upon post-growth annealing treatment. Furthermore, the incorporation of Sb into the ZnO thin films was identified and confirmed by XRD analysis. SEM image and XRD pattern showed that the Sb-doped ZnO films seemed to have acceptable crystallinity. The optical transmission spectrum of the ZnO:Sb thin film indicated that the band gap value was around 2.9 eV.

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