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Effect of Different Substrate Temperature on Sb-Doped ZnO Thin Films Prepared by Pulsed Laser Deposition on Sapphire Substrates *

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Sb-doped ZnO thin films are deposited on c-plane sapphire substrates by pulsed laser deposition. Hall results indicate that the conductivity of the Sb-doped ZnO thin films is strongly dependent on the substrate temperature. The sample deposited at the temperature of 550°C exhibits p-type conductivity. It gives a resistivity of 15.25 Ω·*cm, with a Hall mobility of* 1.79 $cm^2V^{-1}s^{-1}$ *and a carrier concentration of* 2.290×10^{17} cm^{-3} *at room temperature. The x-ray diffraction indicates that the Sb-doped ZnO thin films deposited in the range of 450–650° C are high c-axis oriented. Low-temperature photoluminescence spectra indicate that the sample deposited at 550° C shows the strong acceptor-bound exciton* (A^0X) *emission.*

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ZnO has been of great interest recently because of its 3.37 eV band gap and relatively high exciton binding energy (60 meV) at room temperature (RT), which make this material a promising candidate for the next generation of short-wavelength light emitting diodes (LED) and lasing devices (LD).[1,2] However, the fabrication of the p-type ZnO, which is indispensable to the practical application of ZnO-based optoelectronic devices, is difficult because of the influence of native defects in ZnO. Many different dopants have been tried for obtaining p-type ZnO and some progress has been made. Recently, Limpijumnong proposed a new model for large scale elements doping in ZnO. A Sb dopant was predicted to substitute a Zn atom and simultaneously connect two Zn vacancies to form a Sb_{Zn}–$2V_{Zn}$ complex, which is a shallow acceptor,[3] Xiu *et al.*[4] have doped p-type ZnO:Sb film and produced ZnO based homojunction LED by molecular beam epitaxy (MBE), indicating that Sb is a promising dopant for realizing p-type ZnO. It is very necessary to study the properties of Sb-doped ZnO thin films.

To date, many growth techniques, such as pulsed laser deposition (PLD),[5] molecular beam epitaxy (MBE),[6] spray pyrolysis,[7] metal organic chemical-vapor deposition (MOCVD),[8] and rf magnetron sputtering,[9] have been widely applied to prepare high quality ZnO films. Among these methods, the PLD technique has some distinctive advantages, it can preserve the stoichiometry during the mass transfer from the target to the substrate and the deposition can be carried out at very low temperature. However, the fabrication of Sb-doped p-type ZnO films by PLD is seldom reported. In this study, the Sb-doped ZnO thin films are prepared on sapphire substrates by PLD then annealed in oxygen. The effect of substrate temperature on optical, structural and electrical properties of the Sb-doped ZnO thin films is mainly investigated to obtain high-quality p-type ZnO thin films fitting for device applications.

Sb-doped ZnO thin films were prepared by PLD on c-plane sapphire substrates using a ZnO target mixed with 1 mol% Sb_2O_3. The target was ablated 10 min by laser to clean its surface. The background pressure of the chamber was 10^{-3} Pa. A KrF excimer laser (248 nm, 5 Hz) was used to ablate ceramic Sb-doped ZnO target for the deposition of Sb-doped ZnO thin films. The sapphire substrates were cleaned by toluene, acetone and ethanol in ultrasonic baths in sequence. The energy density of laser was 2.5 J/cm^2, the distance between target and substrate was 5 cm and the target holder was rotated at the rate of 5 rpm. The growth oxygen pressure was 50 Pa. The substrate temperature is kept at 350, 450, 550 and 650°C, respectively. All the films were deposited for 90 min. Finally, all the samples were annealed at 950° in oxygen ambient with a pressure of 1×10^5 Pa for 40 min.

The electrical properties of the ZnO:Sb samples were examined by the four-probe van-der-Pauw method at room temperature using a Hall-effect-measurement system (HL5500PC) in a magnetic field strength of 0.5 T. The crystal structure of the ZnO:Sb samples was investigated by x-ray diffraction (XRD) with a Cu radiation (λ = 1.5418 Å). Low temperature photoluminescence (PL) spectra (He-Cd laser, 325 nm, 30 mW) were used to examine the optical properties of the samples.

For convenience, the sample deposited at 350°C

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is called sample 1, and the samples deposited at 450, 550, 650°C are called samples 2, 3 and 4, respectively.

Hall-effect measurements were carried out to investigate the electrical properties of the samples and the results are listed in Table 1. The insulating sapphire substrates used here can ensure that the electrical signal originates from the ZnO film rather than the substrate. The samples grown at the substrate temperatures 350 and 450°C exhibit n-type conductivity. When the substrate temperature was increased to 550°C, the conductive type converted from n-type to p-type, it gave resistivity of 15.25 Ω·cm, with Hall mobility of 1.79 $cm^2V^{-1}s^{-1}$ and carrier concentration of 2.290×10^{17} cm^{-3} at room temperature. The film deposited at 650°C exhibited n-type conductivity. From the changes of the carrier concentrations, it can be concluded that for samples 1, 2 and 3, compared with the concentration of the donor, the concentration of Sb-related acceptor was significantly enhanced with the substrate temperature increasing.

Table 1. Electrical properties of Sb-doped ZnO thin films deposited on sapphire substrates.

Sample	Carrier type	Resistivity (Ω·cm)	Hall mobility ($cm^2V^{-1}s^{-1}$)	Carrier concentration (cm^{-3})
1	n	0.53	1.33	8.825×10^{18}
2	n	57.95	2.05	5.247×10^{16}
3	p	15.25	1.79	2.290×10^{17}
4	n	1018	1.89	3.236×10^{15}

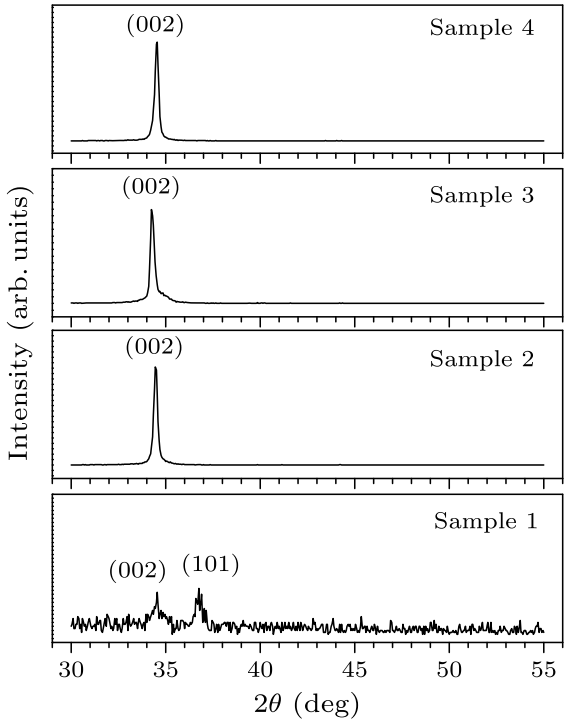


Fig. 1. XRD patterns of Sb-doped ZnO thin films grown at different substrate temperatures.

Figure 1 shows the XRD patterns of the samples. It can be seen that sample 1 exhibits peaks at 34.5° and 37.8° corresponding to ZnO (002) plane and (101) plane respectively. This is because the atoms do not have enough energy to locate their right position at low substrate temperature. However, when the substrate temperature increases to 450°C, only the (002) peak of ZnO could be observed, in samples 2, 3 and 4 the similar phenomenon appears, which indicates that high *c*-axis oriented Sb-doped ZnO films can be obtained by PLD method. Generally, the full wide half maximum (FWHM) of the (002) peak can reveal the crystal quality of the ZnO thin film to a certain extent. The FWHM values of samples 2, 3 and 4 are shown in Fig. 2. It can be seen that the FWHM value of the film deposited at 550°C is slightly larger than the FWHM values of samples 2 and 4, indicating that its cystallinity is slightly worse. This may be because the formation of the Sb-related acceptors destroys the crystallinity of the ZnO thin films.

We took a measurement of PL spectra at 11 K to investigate the optical properties of the samples. The low-temperature PL performances of the samples are shown in Fig. 3. First, for sample 1, a clear feature is the emission at 3.361 eV, which is related to the neutral donor-bound exciton (D^0X).[10] For sample 2, it can be seen that the peak around at 3.3664 eV is related to D^0X [11] and the peak around at 3.355 eV should be related to A^0X. Further raising the substrate temperature to 550°C, sample 3 showes a strong A^0X peak and a peak nearly at 3.09 eV, which should be related to donor-acceptor pair (DAP). When the substrate temperature reaches 650°C, the sample shows a strong D^0X peak nearly at 3.365 eV, which should be related to D^0X.[11] For the four samples, compared with the emission of D^0X, the intensity of A^0X emission increases with the increasing substrate temperature until 550°C, and then decreases after the substrate above 550°C. This may be because when the substrate temperature increases below 550°C, more oxygen atoms are introduced into the film, so the amount of V_{Zn} increases, this is in favor of forming the Sb_{Zn}–$2V_{Zn}$, and when the substrate temperature further increases, the amount of oxygen atoms introduced into the film begins to decrease, this is not in favor of forming V_{Zn}, and of forming Sb_{Zn}–$2V_{Zn}$ that is embarrassed. This result is in good agreement with the Hall-effect measurement. The peaks around at 3.310 eV and 3.381 eV should be related to the free electrons to acceptor level (FA) and free exciton (FX), respectively.

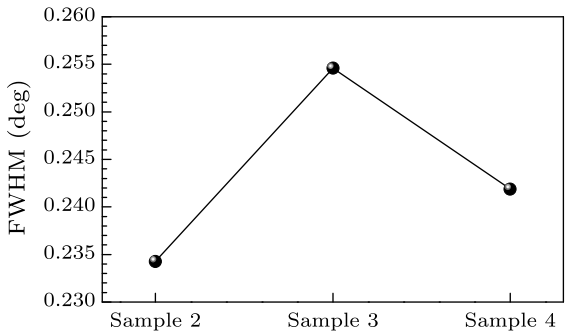


Fig. 2. FWHM of (002) peaks of XRD patterns of Sb-doped ZnO thin films deposited at the substrate temperatures of 450, 550 and 650°C.

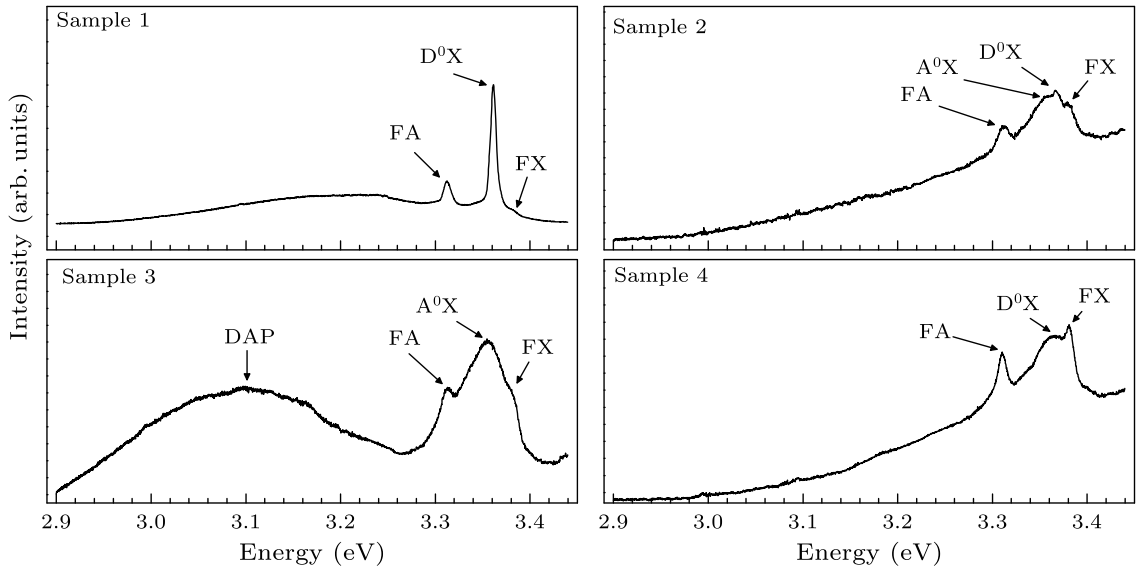


Fig. 3. Low-temperature PL spectra for Sb-doped ZnO thin films grown at different substrate temperatures.

In summary, Sb-doped ZnO thin films have been deposited on c-plane sapphire substrates by PLD. The influences of substrate temperature on the electrical, structural and optical properties of the samples are studied. We have obtained the p-type Sb-doped ZnO thin film possessing resistivity of 15.25 Ω·cm, Hall mobility of 1.79 $cm^2V^{-1}s^{-1}$ and relatively high carrier concentration of 2.290×10^{17} cm^{-3} at room temperature. The XRD results indicate that the Sb-doped ZnO thin films deposited at the substrate temperature from 450°C to 650°C are high *c*-axis oriented. For the sample prepared at the substrate temperature of 550°C, the low-temperature PL spectrum reveals a strong A^0X emission. Further investigations on the Sb-doped ZnO thin films are in progress.

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