# High-mobility Sb-doped *p*-type ZnO by molecular-beam epitaxy

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(Received 7 June 2005; accepted 15 August 2005; published online 4 October 2005)

Reproducible Sb-doped *p*-type ZnO films were grown on *n*-Si (100) by electron-cyclotron-resonance-assisted molecular-beam epitaxy. The existence of Sb in ZnO:Sb films was confirmed by low-temperature photoluminescence measurements. An acceptor-bound exciton ($A^{\circ}X$) emission was observed at 3.358 eV at 8 K. The acceptor energy level of the Sb dopant is estimated to be 0.2 eV above the valence band. Temperature-dependent Hall measurements were performed on Sb-doped ZnO films. At room temperature, one Sb-doped ZnO sample exhibited a low resistivity of 0.2 Ω cm, high hole concentration of $1.7\times10^{18}$ cm$^{-3}$ and high mobility of 20.0 cm$^2$/V s. This study suggests that Sb is an excellent dopant for reliable and reproducible *p*-type ZnO fabrication. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2089183]

With a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has received considerable attention as a promising material for optoelectronic devices such as blue-light emitting and short-wavelength laser diodes with low thresholds in the UV region.[1–6] However, it is well known that the fabrication of *p*-type ZnO is rather difficult due to the self-compensating effect from native defects ($V_o$ and $Zn_i$)[7] and/or H incorporation.[8] Moreover, the low solubility and the deep acceptor levels of the dopants may yield low carrier concentrations, making *p*-ZnO even harder to fabricate.

Recently many groups tried to grow *p*-type ZnO. Some groups have reported successfully fabricating *p*-type ZnO:N,[9–15] which is reasonable because nitrogen has a similar ionic radius as oxygen and is easily substitutable. Unfortunately, reliably obtaining *p*-type ZnO:N is still problematic. To seek better *p*-type dopants, a few groups have tried other group-V elements, including P,[16–20] As,[21–25] and Sb,[26] which have much larger ionic radii than the oxygen atom. Surprisingly, good *p*-type conductivities were observed from these films,[18,22,24] indicating the feasibility of *p*-type doping with large-size-mismatched impurities. Recently, Limpijumnong *et al.*[27] proposed a new doping mechanism for As and Sb impurities in ZnO based on a first-principles calculation. They suggested that As (Sb) would substitute for Zn instead of oxygen and then produce two corresponding Zn vacancies, which is a $As_{Zn}$-$2V_{Zn}$($Sb_{Zn}$-$2V_{Zn}$) complex. However, few Sb-doped ZnO studies were reported in the literature. Only Aoki *et al.*[26] fabricated an Sb-doped ZnO film using an excimer laser doping technique. In their experiment, a layer of Sb was deposited on the intrinsic ZnO film. Then the excimer laser was used to drive Sb impurities into the ZnO film. A *p*-type Sb-doped ZnO film was obtained with a carrier concentration of $5\times10^{20}$ cm$^{-3}$, a mobility of 1.5 cm$^2$/V s and a resistivity of $8\times10^{-3}$ Ω cm. Nevertheless, the residual Sb metal film on top of the ZnO layer and the nonuniformity of Sb doping might be a potential problem for device performance.

In our study, *p*-type ZnO:Sb films were grown using a Perkin-Elmer molecular-beam epitaxy system. Elemental zinc (5N) and antimony (5N) were evaporated by low-temperature effusion cells. The oxygen (5N) plasma was generated by an electron-cyclotron-resonance source. The Si substrates are (100)-oriented, *n*-type wafers with the resistivity of 20–30 Ω cm. All substrates were cleaned by the Piranha-HF method and dried using nitrogen gas. During the growth, several steps were followed. In step I, the Si substrate was thermally cleaned at 650 °C for 10 min. In step II, a thin Zn metallic layer was deposited on the Si substrate for 10 seconds in order to minimize the formation of $SiO_2$ on the surface. In step III, a ZnO:Sb film was grown on top at 550 °C. In step IV, *in situ* annealing at 800 °C under vacuum was performed to activate the Sb dopants. The total thickness of the films was about 200 nm.

Hall effect and electrical resistivity measurements were conducted as a function of temperature to characterize the electrical properties of the undoped and ZnO:Sb films using a van der Pauw configuration[28] with a physical property measurement system by Quantum Design. The results are summarized in Table I. Undoped ZnO has an *n*-type conductivity with a carrier concentration of $5.0\times10^{18}$ cm$^{-3}$ and a mobility of 95.6 cm$^2$/V s at room temperature. The ZnO:Sb film, however, shows strong *p*-type conductivity. With a relatively low Sb cell temperature of 330 °C (sample B), the film exhibits a carrier concentration of $6.0\times10^{17}$ cm$^{-3}$ and a mobility of 25.9 cm$^2$/V s. By increasing

TABLE I. Electrical properties at room temperature of ZnO and ZnO:Sb films.

| Sample | Sb cell temp. (°C) | Type | Mobility (cm$^2$/V s) | Resistivity (Ω cm) | Carrier density (cm$^{-3}$) |
|---|---|---|---|---|---|
| A | Undoped | *n* | 95.6 | 0.01 | $5.0\times10^{18}$ |
| B | 330 | *p* | 25.9 | 0.3 | $6.0\times10^{17}$ |
| C | 350 | *p* | 20.0 | 0.2 | $1.7\times10^{18}$ |

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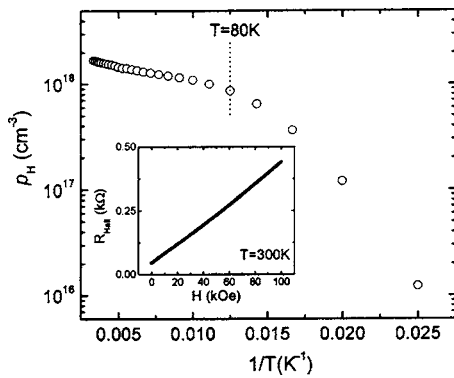


FIG. 1. Temperature dependence of the hole concentration for an Sb-doped ZnO film (sample C). The inset shows the Hall resistance as a function of applied magnetic field at $T=300$ K.

the cell temperature to 350 °C (sample C), the carrier concentration increases to $1.7\times10^{18}$ cm$^{-3}$ while the mobility decreases to 20.0 cm$^2$/V s. Interestingly, these results are quite close to what was reported for ZnO:As films,[21] which may imply the similar doping mechanisms, as predicted by Limpijumnong *et al.*[27]

Figure 1 shows the carrier concentration $p_H$, determined from the Hall coefficient, as a function of temperature for a $p$-type ZnO:Sb film (sample C). The inset of Fig. 1 shows the Hall resistance $R_{Hall}$ as a function of magnetic field at a temperature of 300 K; the positive slope (i.e., the Hall coefficient) indicates $p$-type conduction. The temperature range covered by Fig. 1 represents the extrinsic region. At high temperatures, the activation energy of the carriers is one half the acceptor ionization energy.[29] As the carriers freeze out at lower temperatures, the carrier concentration decreases more dramatically with an activation energy equal to the full value of the acceptor ionization energy.

Figure 2 shows the Hall mobility $\mu_H$ as a function of temperature. Values of 20.0 and 1900.0 cm$^2$/V s were measured at 300 and 40 K, respectively. Over this temperature range, $\mu_H \sim T^{-3/2}$, indicating acoustic phonon scattering dominates at these temperatures. The inset of Fig. 2 shows the electrical resistivity $\rho$ as a function of temperature. At room temperature, a reasonable value of 0.2 Ω cm was obtained for sample C, in comparison to a reported value of 0.4 Ω cm for ZnO:As.[22] It is also worth mentioning that in order to improve the performance of optoelectronic devices, such as light-emitting diodes and laser diodes, a highly conductive $p$-type layer with a decent mobility is needed. Based

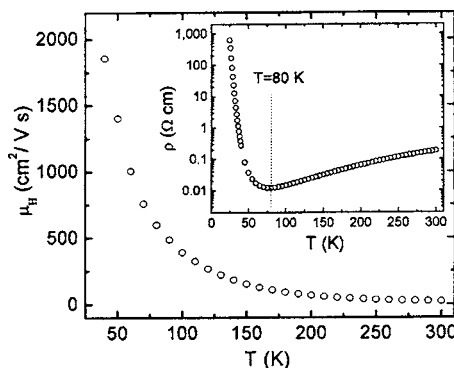


FIG. 2. Temperature dependence of the Hall mobility for an Sb-doped ZnO film (sample C). The inset shows the temperature dependence of electrical resistivity.

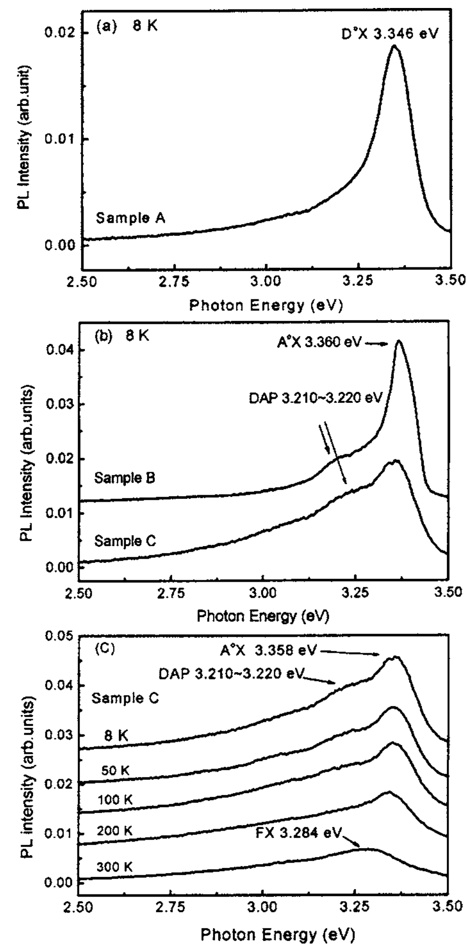


FIG. 3. PL spectra at $T=8$ K for (a) undoped ZnO film (sample A) and (b) ZnO:Sb films (samples B and C); (c) shows the PL spectra at several temperatures for a ZnO:Sb film (sample C). In (b) and (c), the spectra were shifted vertically for clarity.

on the electrical data for ZnO:Sb films, Sb dopants should be excellent candidates for fabricating these devices.

Consistent with the observed temperature variation of the carrier concentration, the resistivity increases with temperature above 80 K. As we may know, resistivity depends inversely on the hole concentration and the scattering time, which are both temperature dependent. At low temperatures, the number of carriers changes much more rapidly than the scattering time, and this dominates the temperature dependence of the resistivity. As the temperature is increased above 80 K, the temperature variation in the number of carriers is much less dramatic, as indicated in the Fig. 1, and the decreasing scattering time overcomes the increasing number of carriers, resulting in an increasing resistivity with temperature.

Low-temperature photoluminescence (PL) measurements were carried out to characterize the optical properties of undoped and Sb-doped ZnO films using a 5 mW He–Cd laser with an excitation wavelength of 325 nm. The laser beam was impinged on the sample surface with an angle of approximately 60°. The excited PL emission was measured with an Oriel monochromator, aligned normal to the sample surface. Figure 3(a) shows a spectrum for the undoped ZnO film (sample A). A strong near-band-edge emission associated with the neutral-donor-bound exciton ($D°X$) is observed at 3.346 eV. By doping ZnO with Sb, however, the $D°X$ emission completely vanishes and new near-band-edge emis-

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sions associated with acceptor-bound excitons ($A^\circ X$) were observed at 3.360 and 3.358 eV, for lightly (sample B) and heavily doped ZnO films (sample C), respectively; these data are shown in Fig. 3(b). Similarly, Ryu, Lee, and White[21] recently reported that the $A^\circ X$ emission was observed at 3.359 eV for As-doped *p*-type ZnO films. This similarity may also indicate that Sb has the same doping mechanism since the ionic radii are very similar (Sb 1.40 Å; As 1.20 Å). In fact, Limpijumnong *et al.*[27] developed a model for large-size-mismatched group-V dopants in ZnO and proved that $\mathrm{Sb}_{Zn}-2V_{Zn}$ and $\mathrm{As}_{Zn}-2V_{Zn}$ complexes may have lower formation energies, and they can serve as acceptors with ionization energies of 160 and 150 meV, respectively.

In comparison with undoped ZnO (sample A), another Sb-associated peak is found in the spectra between 3.210 and 3.220 eV both for lightly doped and heavily doped ZnO films, as shown in Fig. 3(b). Two attempts are made to identify this peak. First, according to the low-temperature PL spectra for Arsenic-[21,25] and phosphorus-doped[16] ZnO films, the emissions around 3.210 eV were identified as the transitions from donor-acceptor pairs (DAP). If this is also the case for ZnO:Sb films, the peak at 3.210–3.220 eV may be a DAP emission ($E_{\mathrm{DAP}}$). The binding energy of an acceptor $E_A$ can be calculated with the equation

$$E_A = E_{\mathrm{gap}} - E_D - E_{\mathrm{DAP}} + \frac{e^2}{4\pi\varepsilon_o \varepsilon r}. \quad (1)$$

The donor binding energy $E_D$ is reported to be 60 meV,[6,30] and the intrinsic band gap $E_{\mathrm{gap}}=3.437$ eV;[12,16,21,31] $r$ is the pair separation, which can be estimated by $(3/4\pi N_A)^{1/3}$; $\varepsilon$ is the dielectric constant of ZnO (8.6). With $N_A = 10^{18}-10^{19}$ cm$^{-3}$, the last term of Eq. (1) is 30–60 meV. Therefore, the value of $E_A$ is calculated to be 197–227 meV. This acceptor level is quite reasonable considering Limpijumnong's model, which predicts a level of 160 meV.[27]

In another scenario, the peak between 3.210 and 3.220 eV could be ascribed to the transition between free electrons and acceptors $E_{\mathrm{FA}}$. The $E_A$ can then be calculated with the relation

$$E_A = E_{\mathrm{gap}} - E_{\mathrm{FA}} + k_B T/2. \quad (2)$$

Using the same parameters as in the first scenario, a value of 217–227 meV is calculated, which is similar to the value estimated above. However, the assumption in the second scenario may be questionable since it is well known that the majority of *p*-type ZnO films doped by group-V elements have an $E_{\mathrm{FA}}$ emission around 3.310 eV and a DAP emission around 3.200 eV.[11,16,21–23,25]

To further confirm the assignment of PL peaks and the acceptor binding energy of ZnO:Sb films, a temperature-dependent PL measurement was performed on sample C over the temperature range from 8 to 300 K, as shown in Fig. 3(c). It is evident that at low temperatures (8–100 K), the spectrum is dominated by the $A^\circ X$ and DAP emissions. As the temperature rises above 100 K, the DAP emission disappears while the $A^\circ X$ emission gradually decays. When the temperature reaches 300 K, a free exciton emission ($FX$) at 3.284 eV dominates, which is also reported for ZnO by other groups.[11,18,32]

In summary, *p*-type Sb-doped ZnO thin films were achieved by MBE for the first time. Room temperature Hall measurements reveal that an Sb-doped ZnO film exhibits *p*-type conductivity with a very low resistivity of 0.2 Ω cm, a high carrier concentration of $1.7\times10^{18}$ cm$^{-3}$, and a high Hall mobility of 20.0 cm$^2$/V s. The temperature-dependent PL study shows that the acceptor energy level of the Sb dopant is about 0.2 eV above the valence band. These experimental results indicate that Sb should be an excellent candidate for *p*-type ZnO fabrication.

This work was supported by DARPA/DMEA through the center for NanoScience and Innovation for Defense (CNID) under the award No. H94003-04-2-0404.

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