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

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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'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 $1.7 \times 10^{18}$ cm$^{-2}$ 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. However, it is well known that the fabrication of p-type ZnO is rather difficult due to the self-compensating effect from native defects ($V_0$ and $Zn_i$) and/or H incorporation. 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:$N^-$, 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, As, and Sb, which have much larger ionic radii than the oxygen atom. Surprisingly, good p-type conductivities were observed from these films, indicating the feasibility of p-type doping with large-size-mismatched impurities. Recently, Limpijumnon et al. 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 $As_{Zn}\cdot V_{Zn}(Sb_{Zn}\cdot V_{Zn})$ complex. However, few Sb-doped ZnO studies were reported in the literature. Only Aoki et al. 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 $5 \times 10^{20}$ cm$^{-3}$, a mobility of 1.5 cm$^2$/V s and a resistivity of $8 \times 10^{-3}$ 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 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 $5.0 \times 10^{18}$ 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 $6.0 \times 10^{17}$ cm$^{-3}$ and a mobility of 25.9 cm$^2$/V s. By increasing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sb cell temp. (°C)</th>
<th>Type</th>
<th>Mobility (cm$^2$/V s)</th>
<th>Resistivity (Ω cm)</th>
<th>Carrier density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Undoped</td>
<td>n</td>
<td>95.6</td>
<td>0.01</td>
<td>$5.0 \times 10^{18}$</td>
</tr>
<tr>
<td>B</td>
<td>330</td>
<td>p</td>
<td>25.9</td>
<td>0.3</td>
<td>$6.0 \times 10^{17}$</td>
</tr>
<tr>
<td>C</td>
<td>350</td>
<td>p</td>
<td>20.0</td>
<td>0.2</td>
<td>$1.7 \times 10^{18}$</td>
</tr>
</tbody>
</table>

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the cell temperature to 350 °C (sample C), the carrier concentration increases to $1.7 \times 10^{18}$ 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, which may imply the similar doping mechanisms, as predicted by Limpijumnong et al.

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 $R_{\text{Hall}}$ 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. 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 $\Omega$ cm was obtained for sample C, in comparison to a reported value of 0.4 $\Omega$ cm for ZnO:As. 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 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 ($D^0 X$) is observed at 3.346 eV. By doping ZnO with Sb, however, the $D^0 X$ emission completely vanishes and new near-band-edge emissions were observed at 3.358 and 3.360 eV. These emissions are attributed to the acceptor-donor-acceptor (ADA) transition, which is characteristic of Sb-doped ZnO films.
p-type conductivity with a very low resistivity of 0.2 Ω cm, a high carrier concentration of $1.7 \times 10^{18}$ 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.

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