***p*-type behavior in nominally undoped ZnO thin films by oxygen plasma growth**

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(Received 21 March 2006; accepted 13 May 2006; published online 28 June 2006)

We report on intrinsic *p*-type ZnO thin films by plasma-assisted metal-organic chemical vapor deposition. The optimal results give a resistivity of 12.7 Ω cm, a Hall mobility of 2.6 cm²/V s, and a hole concentration of 1.88×10^{17} cm⁻³. The oxygen concentration is increased in the intrinsic *p*-type ZnO, compared with the *n*-type layer. Two acceptor states, with the energy levels located at 160 and 270 meV above the valence band maximum, are identified by temperature-dependent photoluminescence. The origin of intrinsic *p*-type behavior has been ascribed to the formation of zinc vacancy and some complex acceptor center. © 2006 American Institute of Physics.
 [DOI: 10.1063/1.2217165]

With a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has become an attractive material for short-wavelength optoelectronic devices, such as light-emitting diodes and laser diodes.¹ Nominally undoped ZnO typically exhibits *n*-type conductivity, which has been ascribed to various mechanisms including interstitial hydrogen and native defects.^{2–4} The realization of *p*-type ZnO has proven difficult due to its asymmetric doping limitations.⁵ Fortunately, thanks to the considerable worldwide efforts, various elements have been used as *p*-type dopants for ZnO, such as N,^{6–8} P,⁹ As,¹⁰ and Li.¹¹ However, it is the inexplicit *p*-type doping mechanism as well as the stability and reproducibility problems that become the bottleneck in the development of ZnO devices. In addition, there are a few reports on intrinsic *p*-type behavior in intentionally undoped ZnO,^{12–14} in which the oxygen pressures were optimized. In this letter, we investigate *p*-type behavior in nominally undoped ZnO thin films by oxygen plasma growth. Two acceptor states are identified by temperature-dependent photoluminescence (PL).

Intentionally undoped ZnO thin films were grown on *a*-plane (11-20) sapphire substrates by plasma-assisted low-pressure metal-organic chemical vapor deposition (MOCVD). Diethyl zinc was used as the zinc source. Oxygen plasma, generated by a radio-frequency (rf) plasma source, was employed as the oxygen source. The growth temperature ranged from 250 to 400 °C and the chamber pressure was maintained at 5 Pa. The average thickness of the ZnO thin films was around 300 nm. Hall-effect measurements were carried out in the van der Pauw configuration (BIO-RAD HL5500PC) at room temperature. The insulating sapphire substrates assured that the measured electrical properties came from the ZnO thin films. Thus, necessary caution should be exercised in the previous reports on intrinsic

p-type ZnO on silicon substrates.^{12,14} Moreover, ZnO *p*-*n* homojunction was fabricated by deposition of an intrinsic *p*-type ZnO layer on an *n*-type layer. The depth profile of ZnO thin film was investigated by a Cameca IMS-3f secondary ion mass spectroscopy (SIMS). Finally, temperature-dependent PL measurements were performed using a He–Cd 325 nm laser as the excitation source.

The results of Hall-effect measurements are summarized in Table I. It shows that *p*-type conductivity with a hole concentration above 10^{17} cm⁻³ can be achieved at the growth temperatures of 250 and 300 °C. It is speculated that the oxygen chemical potential is enhanced by virtue of oxygen plasma, which can lower the formation energy of some acceptor defect, such as zinc vacancy,⁵ and thus accounts for the *p*-type conductivity. Increasing the growth temperature to 350 and 400 °C results in *n*-type conductivity with an electron concentration around 10^{17} cm⁻³. The inversion to *n*-type conductivity can be explained as the compensation effect by the ionized oxygen vacancy donor, which is ready to form at a high growth temperature.¹⁵ Note that this electron concentration is lower than 10^{18} – 10^{19} cm⁻³ typically grown in the same MOCVD system without a rf source, suggesting that the background electron concentration not only in *n* type but also in *p*-type ZnO could be suppressed by using a rf source. However, the sample grown at a moderate temperature of

TABLE I. Electrical properties of nominally undoped ZnO thin films grown at different substrate temperatures.

Substrate temperature (°C)	Resistivity (Ω cm)	Hall mobility (cm ² /V s)	Carrier concentration (cm ⁻³)	Carrier type
250	15.8	1.86	2.12×10^{17}	<i>p</i>
300	12.7	2.6	1.88×10^{17}	<i>p</i>
325	269.8	2.06	7.27×10^{15}	<i>p</i>
350	18.5	6.63	5.2×10^{16}	<i>n</i>
400	2.24	7.36	3.75×10^{17}	<i>n</i>

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FIG. 1. The variation of Hall voltage as a function of magnetic intensity for the *p*-type ZnO thin film grown at 300 °C.

325 °C gives a weak *p*-type signal with a low hole concentration of $7.27 \times 10^{15} \text{ cm}^{-3}$, indicating a carrier-type transition around this temperature. Furthermore, Hall voltage was measured as a function of magnetic intensity for the sample grown at 300 °C, as shown in Fig. 1. The definitive positive Hall voltages under all magnetic intensity and their quasilinear relation confirm the *p*-type conductivity in our sample.

ZnO *p-n* homojunction was prepared via a two-step process: an intrinsic *n*-type ZnO layer without a rf source was grown first, followed by an intrinsic *p*-type ZnO layer by using a rf source. In-Zn alloy was used as both *n*-side and *p*-side electrodes, showing linear *I-V* characteristics indicative of good Ohmic behavior, as illustrated in the inset in Fig. 2. Figure 2 shows *I-V* characteristics of the ZnO homojunction. The device exhibits rectification for repeated measurements, which is consistent with the formation of a *p-n* junction at the interface.

The depth profile of the ZnO homojunction was investigated by SIMS measurements. It can be seen from Fig. 3 that the two-layer structure is clearly identified. It is also found that the oxygen concentration increases evidently in the *p*-type layer whereas the zinc concentration shows no detectable difference in the two layers. Therefore, it is inferred that employing a rf source not only lowers the formation energy of some acceptor defects, as mentioned above, but also compensates for the oxygen vacancy donor, which are both favored towards *p*-type doping in ZnO. In addition, no unintentionally doped acceptor element, such as nitrogen, has been detected by SIMS, which confirms the intrinsic nature of the *p*-type ZnO.

FIG. 2. *I-V* characteristics of ZnO *p-n* homojunction measured at room temperature. The inset shows *I-V* characteristics of In/Zn alloy contacts on the ZnO thin films.

FIG. 3. SIMS depth profile of double-layer-structured ZnO *p-n* homojunction.

To better understand the intrinsic *p*-type behavior, temperature-dependent PL measurements were performed. Figure 4(a) illustrates 8 K PL spectrum for the *p*-type ZnO thin film grown at 300 °C. The strong UV emission with weak visible band indicates that the ZnO thin film is of high optical quality. The inset shows Gaussian fitting to the near-band-edge emission peak, consisting of three bands centered at 3.33, 3.27, and 3.16 eV, labeled as A, B, and C, respectively. From these peak positions, we tentatively assign band A to a neutral acceptor-bound exciton emission (A^0X) and the others to two free-to-neutral-acceptor (e, A^0) transitions.

To support our assignment, temperature-dependent peak positions of these three bands are plotted in Fig. 4(b). For band A, an obvious temperature-dependent blueshift from 3.33 eV at 8 K to 3.36 eV at 70 K is observed. We suggest that this PL peak gradually changes from (A^0X) emission to free exciton (FX) emission with increasing temperatures due

FIG. 4. (a) 8 K PL spectrum for the *p*-type ZnO thin film grown at 300 °C. The inset shows Gaussian fitting to the near-band-edge emission peak. (b) Temperature-dependent peak positions and their fitting curves for bands A, B, and C in (a).

to the thermal effect. The temperature-dependent band gap is described according to Ref. 16 as

$$E_g(T) = E_g(0) - \alpha T^2 / (T + \beta), \quad (1)$$

where $E_g(T)$ is the temperature-dependent band gap energy, α and β are constants, and T is the temperature. A fitting curve of E_g –60 meV, as illustrated in Fig. 4(b), confirms its typical FX characteristics above 70 K. A similar transition from bound exciton emission to FX emission has also been observed in GaN, with the same transition temperature at 70 K.¹⁷

For bands *B* and *C*, two acceptor energy levels, located at 160 and 270 meV above the valence band maximum, are obtained from

$$E_A = E_g - E_{eA} + k_B T / 2, \quad (2)$$

where E_{eA} is the temperature-dependent (e, A^0) transition, E_A is the acceptor energy level, and k_B represents Boltzmann constant. Furthermore, we fit the (e, A^0) peak positions with Eq. (2), as shown in Fig. 4(b). A perfect match between the experimental values and the fitting curves supports our assignment of the (e, A^0) transitions.

There are some intrinsic defects, such as zinc vacancy and oxygen antisite, behaving as acceptors in ZnO. Zinc vacancy has lower formation energy and may serve as the dominant acceptor in intrinsic ZnO.^{5,18,19} Moreover, there are several reports on zinc vacancy-related emission, such as 3.028 eV at 20 K,¹³ 3.1 eV at 80 K,²⁰ and 3.09 eV at 6 K.²¹ In particular, recent calculation suggests that the $\varepsilon(2-1-)$ transition level of zinc vacancy is located at 270 meV above the valence band maximum.²² With this available literature, we tentatively attribute our 3.16 eV (e, A^0) transition to zinc vacancy-related acceptor, with an energy level of 270 meV. It may be a simple zinc vacancy acceptor or binding to some unintentionally doped donor, such as hydrogen or aluminum. However, the origin of another 160 meV shallow acceptor has not been clear now. This acceptor should be a complex acceptor center because it seems too shallow for a simple, intrinsic acceptor.²³

In summary, we have demonstrated the reproducible growth of intrinsic *p*-type ZnO thin films by plasma-assisted MOCVD. The *p*-type behavior is temperature dependent. The increment of the oxygen concentration in the intrinsic *p*-type ZnO, compared with the intrinsic *n*-type layer, is well

confirmed by SIMS. The origin of intrinsic *p*-type behavior has been ascribed to the formation of zinc vacancy and some complex acceptor center. Understanding of these intrinsic acceptor states will help elucidate the extrinsic as well as intrinsic *p*-type doping mechanism in ZnO.

This work was supported by National Natural Science Foundation of China under Contract Nos. 50532060 and 50572095 and Zhejiang Provincial Natural Science Foundation of China Under Grant No. Y405126.

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