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Electrical properties of N-doped ZnO grown on sapphire by P-MBE

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Abstract
N-doped ZnO samples were grown on sapphire substrate by plasma-assisted molecular beam epitaxy (P-MBE) method. The electrical properties of the samples were investigated by temperature-dependent Hall measurement. It was found that the carrier concentration and mobility of the samples showed some unstable characteristics under different magnetic fields at a certain temperature. However, the conductivity was a much more stable parameter. By fitting the dependence of conductivity on temperature and theoretical calculating, it was believed that the conduction mechanism was possibly the mix of band and hopping conduction mechanisms. The coexistence of a huge density of donor and acceptor defects was considered to cause the instability of some electrical properties (carrier concentration and mobility) and the appearance of the hopping conduction mechanism in N-doped ZnO samples.

1. Introduction

Recently, ZnO has attracted considerable attention as a potential candidate material for ultraviolet and blue light-emitting diodes (LEDs) [1, 2]. However, similar to many other wide band gap semiconductors, ZnO has the 'asymmetric doping' limitation and it is difficult to achieve p-type conduction by doping impurities. Thus recent works have been focused on the fabrication and characterization of p-type ZnO. So far p-type conductivity of ZnO could be achieved by doping with N, As, P or by codoping N with Al or Ga. Among them, N-doped ZnO is most promising due to the little mismatch in ionic radii between the N atom and O atom [3–5]. Our groups also have reported the results of N-doped p-type ZnO and the corresponding p–n homojunction LED [6, 7]. However, similar to other groups, we also met with the common problems faced to p-type ZnO: poor reproducibility of conductivity type and the instability of electrical properties. Thus many efforts were made to investigate the electrical properties of p-type ZnO. To our knowledge, although some groups have reported some electrical properties for p-type ZnO [8, 9], there were no reports available on the possible conduction mechanism in the samples.

In this paper, temperature-dependent Hall measurement was conducted to investigate the electrical properties of N-doped ZnO samples. It was found that the conduction mechanism was possibly the mix of band and hopping conduction mechanisms. The inhomogeneous distribution of a huge density of donor and acceptor defects was believed to cause the great fluctuation and instability of electrical properties in the Hall measurement.

2. Experiment

The N-doped ZnO samples in the experiment were grown by plasma-assisted molecular beam epitaxy (MBE) on *c*-face sapphire substrate. The zinc (Zn) source was supplied by evaporated metal zinc with 99.9999% through a Knudsen

Table 1. Hall measurement results of undoped and N-doped ZnO samples at room temperature with applied different magnetic fields.

Sample	Magnetic field (kG)	Carrier type	Hall coefficient ($cm^3\ C^{-1}$)	Resistivity (Ω cm)	Mobility ($cm\ V^{-1}\ s^{-1}$)	Carrier concentration (cm^{-3})
Undoped	3	n	−3.0187	0.196 71	15.344	2.0678×10^{18}
	6	n	−2.9680	0.196 70	15.087	2.1031×10^{18}
	9	n	−3.0651	0.196 71	15.580	2.0366×10^{18}
N-doped	3	p	31.370	120.50	5.9483	8.8133×10^{15}
	6	p	40.568	120.21	3.4070×10^{-1}	1.5387×10^{17}
	9	p	18.459	120.04	1.5503×10^{-1}	3.3816×10^{17}

effusion cell. NO gas activated by an Oxford Applied Research r.f. (13.56 MHz) plasma source with a power of 300 W was used as both N and O sources. An electrostatic ion trap was operated at 500 V during the growth process to suppress interference of ion in the plasma [6, 7]. The electrical properties of the as-grown samples were measured by Lake Shore's 7707 Hall Effect measurement system (made in the USA) in the Der Pauw configuration. This Hall measurement system is an automatic system with high accuracy and it is applicable to high resistance materials including semi-insulating materials. For this system, the resistances can be measured from 40 mΩ to 10 MΩ with less than 2% uncertainty. The output stability (per day) and the uniformity are ±0.05% and ±0.1%, respectively. Model 220 current source was equipped on Lake Shore's 7707 Hall measurement system to give a current supply. Under our measurement current (6 μA), the accuracy for the current source was 0.05%+1 nA and the noise was 100 ppm. In our Hall measurement, both positive and negative currents and magnetic fields were applied to the sample; the results were averaged automatically by the Hall software in order to compensate for various electromagnetic effects. The ZnO sample is 10 mm square and the thickness is 1532 nm. In order to minimize the contact noise, Ni/Au contacts (about 1 mm in diameter) which have commonly been used as ohmic contact material to p-type GaN and p-type ZnO were first evaporated on the four corners of the sample, then a rapid thermal annealing was conducted under nitrogen gas at 300 °C for 5 min. In order to obtain a tight contact, a small metal In dot together with a thin Au wire was soldered on the surface of Ni/Au contact under vacuum conduction at about 200 °C. Lastly, the Au wire was soldered on the Hall measurement system and the *I–V* curve for the contacts showed a linear relationship. In order to avoid the influence of sunlight (especially of UV light), the sample was kept in the dark for more than 1 week before the measurement.

3. Results and discussion

In order to investigate the crystal quality, x-ray diffraction (XRD) was conducted and the result is shown in figure 1. From this figure, it can be seen that besides the (0 0 6) diffraction peak of sapphire, only one peak related to ZnO was obtained. It proved that we obtained *c*-axis preferred ZnO thin films.

In order to investigate the electrical properties of N-doped ZnO, table 1 gives the Hall measurement results of the undoped and N-doped ZnO samples at room temperature with applied different magnetic fields. It was found that the undoped ZnO sample showed n-type conductivity, while the N-doped sample showed p-type conductivity. From table 1, it can also be seen that the conductivity, carrier concentration and mobility were all quite stable for undoped ZnO under different magnetic fields. However, the resistivity was stable, the mobility and carrier concentration showed some fluctuation for the N-doped sample. Here, it was necessary to emphasize that the N-doped ZnO sample showed p-type conductivity under most magnetic fields and temperatures, while it occasionally showed n-type conductivity under some magnet fields and temperatures in the temperature-dependent Hall measurement. Furthermore, the conductivity was quite stable; the mobility and carrier concentration showed great fluctuation under different magnetic fields, which was similar to the Hall measurement results at room temperature. In order to understand the reason for unstable electrical properties with varying magnetic fields and temperatures in the N-doped ZnO sample, we would discuss these electrical parameters in what follows.

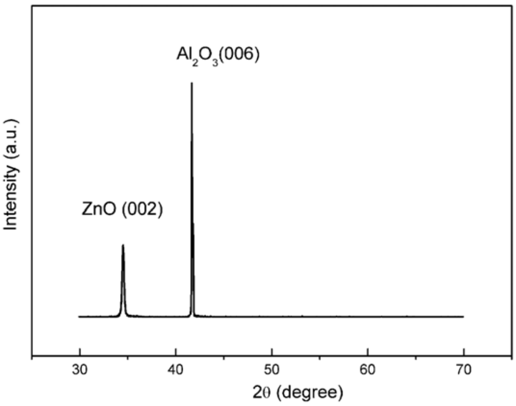

Figure 1. XRD result for the N-doped ZnO sample.

3.1. The conductivity

As the conductivity, which is a most important parameter for most semiconductors, was much more stable in our N-doped ZnO sample, the conductivity as a function of temperature for the sample was shown in figure 2(■). We found that the conductivity increased with increasing temperature; it seemed to indicate that the transport mechanism in the sample was by holes in valence band. The conductivity (σ) from holes in valence band can be described by the following equation [10, 11]:

$$\sigma_{\mathrm{band}} = A\exp(-E_A/kT) \qquad (1)$$

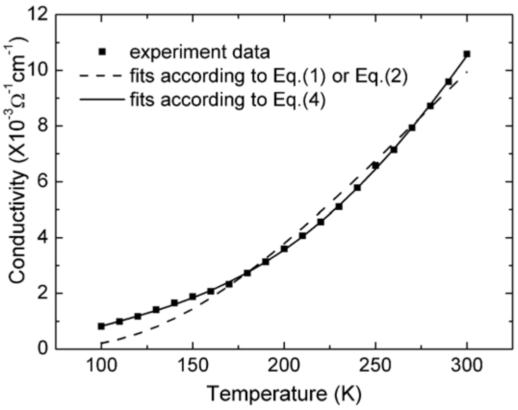

Figure 2. The dependence of conductivity on temperature for the N-doped ZnO sample. The dot line is the experiment data, the dash line is a fit according to equation (1) (or equation (2)), and the solid line is a fit according to equation (4).

where A is a temperature-independent constant, E_A is the acceptor activation energy, k is the Boltzmann constant and T is the thermodynamic temperature. The dash line in figure 2 is a fit to σ versus T data by equation (1). It can be seen that the experiment data cannot be fitted well according to equation (1), especially in the low-temperature region. Furthermore, the obtained acceptor activation energy of $E_A = 49$ meV was not in agreement with the reported value by Look *et al*, in which the acceptor activation energy was about 90 meV according to their Hall measurement results [9]. A better explanation for this phenomenon was that the transport mechanism in the sample was not due to holes conduction in valence band. It was noted that a recent investigation on GaN material which has similar properties as ZnO material showed that the conduction mechanism in a high resistivity GaN sample did not consist of carrier transport in the band but of hopping among localized defects [12]. As our N-doped ZnO sample also had a high resistivity, in the following we would discuss the conductivity according to the hopping conduction mechanism. Basically, the hopping conduction involves two limiting factors [12]: (1) the energy (E) necessary to hop from an occupied defect to one which is unoccupied, this unoccupied state is often provided by compensation between donors and acceptors; and (2) wavefunction overlap. If the temperature is not very low, the hopping conduction is usually dominant by the nearest-neighbour hopping mechanism (at an extremely low temperature, it is usually dominant by variable rang hopping conduction), and the dependence of conductivity on temperature for the nearest-neighbour hopping conduction can be expressed as [13]:

$$\sigma_{nn} = B\exp(-E_{nn}/kT), \tag{2}$$

where B is a constant independent of temperature, E_{nn} is the hopping activation energy and it can be further expressed as follows:

$$E_{nn} \cong e^2 N_A/4\pi\varepsilon\varepsilon_0 \tag{3}$$

where N_A is the acceptor concentration, ε_0 and ε are the vacuum dielectric constant and relative dielectric constant, respectively.

Similar to equation (1), the conductivity for the nearest-neighbour hopping should be proportional to $\exp(-E/kT)$. However we did not find this relationship as seen in figure 2 (dash line). So the nearest-neighbour hopping mechanism in the N-doped ZnO sample was not reasonable. Consider that there would simultaneously exist free carriers (hole) and defects in N-doped ZnO. The temperature dependence of conductivity was fitted by the mix of band and nearest-neighbour hopping conduction mechanisms. In such a case, the relationship between the total conductivity and temperature can be expressed as [10, 11]

$$\sigma_{\text{total}} = \sigma_{\text{band}} + \sigma_{nn} = A\exp(-E_{\text{A}}/kT) + B\exp(-E_{nn}/kT). \tag{4}$$

Obviously, the experiment data can be fitted well according to equation (4) as seen in figure 2 (the solid line). Furthermore, the acceptor activation energy ($E_{\text{A}} = 89$ meV) obtained by the fitting result was close to the reported value ($E_{\text{A}} = 90$ meV) [9]. Using equation (3) and the hopping energy of 17 meV obtained from the fitting result, the calculated acceptor concentration (N_{A}) is about 9×10^{17} cm^{-3}; this value is close to the experimental result from the Hall measurement.

In the following, we further prove this mixed conduction mechanism by comparing the average distance (R) between acceptors with the effective Bohr radius (a^*). The average distance between acceptors and the effective Bohr radius can be defined as [14]:

$$R \approx (3/4\pi N_{\text{A}})^{1/3} \tag{5}$$

$$a^* = 0.53\varepsilon\frac{m}{m^*} \tag{6}$$

where N_{A} is the acceptor concentration, m and m^* are the static mass for electron and hole effective mass for ZnO. According to equations (5) and (6), the average distance between the acceptor ($R = 6.4$ nm) and the effective Bohr radius ($a^* = 0.73$ nm) in our N-doped ZnO sample could be calculated.

If $R/a^* > 5$, it had been pointed out that the conduction mechanism in a semiconductor was band conduction plus nearest-neighbour hopping mechanism [14]. Thus, our fitting result was closely consistent with this conclusion.

3.2. The carrier concentration, mobility and conduction type

As mentioned above, the carrier concentration, mobility and conduction type for our N-doped ZnO sample showed unstable characteristics under different magnetic fields. This phenomenon was usually considered to relate to the accuracy of the measurement system, the influence of sunlight and the contact noise. However, Lake Shore's 7707 Hall measurement system with high accuracy was used in our experiment. The resistance and conductivity for our sample are about 1 MΩ and 10^{-2}–10^{-3} Ω^{-1} cm^{-1} respectively; the measurement system is obviously applicable to our sample. If the fluctuation in the electrical properties for N-doped ZnO was caused by the intrinsic error sources from the system such as Voltmeter offset, the offset can affect both n-type and p-type ZnO samples. However, we did not find great fluctuation in the electrical properties for the n-type sample. Furthermore, we roughly estimate that the accuracy of the system is about 20%. From the Hall data for n-type ZnO (table 1 in our paper), it can be seen that the fluctuation for the n-type sample is within our estimated limit. So we considered that

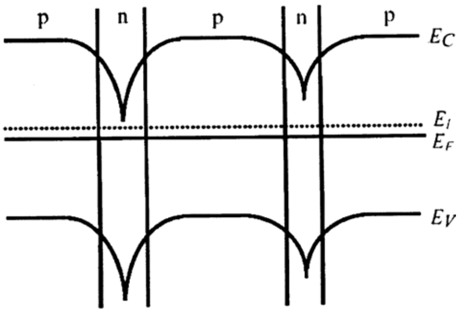

Figure 3. Contours of conduction and valence band in N-doped ZnO with different types of conductivities due to inhomogeneous distribution of defects.

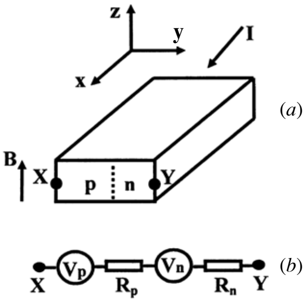

Figure 4. Simple model (*a*) and equivalent circuit (*b*) for the Hall measurement for N-doped ZnO samples.

the unstable characteristics of ZnO sample were not caused by the measurement system. As our sample was kept in the dark for more than 1 week before the measurement, the influence by sunlight was also ruled out. As for the contact noise, we have taken many measures to minimize it, which have been mentioned in the experiment. However, considering the existence of hopping conduction mechanism in our sample, we thought that the great fluctuation of carrier concentration and mobility was possibly related to this hopping conduction mechanism. Because the hopping distance and energy were uncertain at a given temperature and (or) magnetic field, it was this uncertainty that led to the great fluctuation of mobility and carrier concentration for N-doped ZnO samples in the Hall measurement. We considered that the hopping conduction mechanism and the fluctuation of electrical properties were possibly due to the inhomogeneous distribution of huge density of donor and acceptor defects in the N-doped ZnO sample. In the past, when considering the effect of impurity on the electrical properties of semiconductor, it has usually been assumed that the impurities were distributed uniformly; insufficient attention has been paid to the electrical properties of semiconductor material with a large inhomogeneous region. In fact, there existed a huge density of localized donor and acceptor defects in N-doped ZnO samples [15]. Furthermore, in our x-ray photoelectron spectrum (XPS) measurement (not shown), we found that this spectrum is slightly dependent on the thickness and position of the sample. With the difference in the thickness and position, the concentrations of N, Zn and O atoms have slight fluctuation. As our N-doped sample was grown under Zn-rich condition, many interstitial Zn atoms can exist in our sample. The interstitial Zn atom is a donor-defect and the N atom is an acceptor-defect. Thus the slight fluctuation of concentration for N, Zn and O atoms in the XPS result was possible due to the inhomogeneity of donors and acceptors. If the distribution of donors and acceptors was inhomogeneous, a space–charge region will be formed around the local inhomogeneous region to provide electrical neutrality. It resulted in the contortion of conduction and valence as shown in figure 3. A detailed description of the effects of the inhomogeneous region upon the electrical properties in the Hall measurement would be complicated by the necessity of taking into account abnormal current flow about the inhomogeneities, dislocation orientations and distributions, impurity distributions, and the temperature dependence of electron and hole mobilities. These features of the problem were difficult to describe analytically and prevented us from constructing a detailed model of the phenomena involved. For simplicity, a model for the Hall Effect measurement was shown in figure 4(*a*). According to the model, large quantities of n-type impurities are surrounded about the p-type region in the N-doped ZnO sample, thus producing p-type and n-type inhomogeneous regions. For an idealized p-type semiconductor with a homogeneous distribution of defects, when the electrical and magnet fields are applied along x- and z-directions (as shown in figure 4(*b*)), respectively, a positive Hall voltage along the y-direction will appear at the two sides of the sample. While for N-doped ZnO with an inhomogeneous distribution of donor and acceptor defects, the total Hall voltage was dependent on the Hall generator voltages associated with the n-type and p-type regions. A corresponding approximate equivalent circuit was also drawn in figure 4(*b*); V_n and V_p were the Hall generator voltages associated with the n-type and p-type regions, respectively. V_n and V_p are the internal resistances. In such a case, the total Hall voltage (V_{total}) should be given as

$$V_{\mathrm{total}} = V_n + V_p. \tag{7}$$

If the absolute value of V_n was larger than that of V_p, it would obtain an ‘n-type’ result. If the absolute value of V_n was smaller than that of V_p, it would obtain a ‘p-type’ result. As the mobility of the electron was larger than that of the hole, small quality of the inhomogeneous local n-type impurity region would possibly cause the ‘n-type’ result at a certain magnetic field and (or) electrical field.

According to the above analysis, it is believed that the inhomogeneous distribution of the huge density of donor and acceptors defects possibly caused the electrical instability of N-doped ZnO sample in the Hall measurement. At the same time, the compensation between the donors and acceptors provided lots of unoccupied states; thus it satisfied the two limitation factors for the hopping conduction mechanism, and caused the appearance of the nearest-neighbour hopping mechanism in the N-doped ZnO sample.

4. Conclusion

N-doped ZnO samples grown on sapphire substrate by a plasma-assisted molecular beam epitaxy (P-MBE) method were reported. According to the temperature-dependent Hall measurement, it was found that the carrier concentration and mobility in the samples showed unstable characteristics. By investigating the conductivity which was a stable parameter on temperature, it was found that the conduction mechanism in N-doped ZnO samples was possibly the mix of band conduction and nearest-neighbour hopping conduction mechanisms. The inhomogeneous distribution of donor and acceptor defects was believed to cause the unstable electrical properties and this conduction mechanism.

Acknowledgments

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