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Abstract
Electrical transport properties of p-type ZnO:N films grown by thermal activation of the nitrogen dopant were investigated via the temperature-dependent Hall effect. The Hall mobility increases with decreasing temperature. Varied scattering mechanisms have been analysed including lattice vibration scattering, ionized impurity scattering and dislocation scattering. A fit of the theory to temperature-dependent hole mobility experimental data in p-type ZnO:N films gives dislocation densities in the order of 10^{12} cm^{-2}. The analysis shows dislocation scattering is indeed important for the p-type ZnO films grown on the mismatched substrate. The thermal ionization energy of the nitrogen acceptor is estimated to be 170 meV in terms of the temperature-dependent hole concentration. On the other hand, the emission related to the acceptors is observed in PL spectra.

1. Introduction

ZnO is a direct band-gap semiconductor suitable for the development of efficient blue and UV optoelectronic devices [1]. One of the key steps toward realization of ZnO potential was the achievement of controlled p-type doping. Theoretical calculation predicts that nitrogen is an outstanding acceptor candidate in the current research for p-type doping of ZnO [2], and a number of groups have successfully realized p-type ZnO employing nitrogen as a dopant source [3–7]. Kawasaki *et al* have recently observed electroluminescence from a ZnO homoepitaxial p–n junction structure [8]. Although many progresses have been made, one must be aware that some of the basic aspects of p-type ZnO, such as electrical transport properties and the properties of the acceptors, are still not well understood.

In this paper, the electrical transport properties of p-type ZnO thin film were investigated by the temperature-dependent Hall effect. Here, the hole Hall mobility was emphasized, particularly since mobility is considered to be an important characteristic parameter. The thermal ionization energy of the nitrogen acceptor (E_a) was obtained according to the temperature-dependent carrier concentration. Optical properties of p-type ZnO thin films are also investigated.

2. Experiment

The detailed experimental processes have been introduced in a previous paper [5]. The p-type ZnO:N thin films were prepared by a two-step experiment. First, the as-grown thin film was deposited on a fused silica substrate at a low temperature of 100 °C by employing the plasma enhanced chemical vapour deposition (PECVD) technique. Diethylzinc (DEZn) was used as the Zn source, and high-purity Ar (99.9993%) was used as the carrier gas. High purity NH$_3$ (99.999%) served as the nitrogen source and CO$_2$ (99.999%) as the oxygen source. The flux ratio of NH$_3$ to CO$_2$ is 4. The pressure of the growth chamber was maintained at 250 Pa and deposition lasted 3 h. Secondly, the samples were cut into several pieces after deposition and were transferred into a

Table 1. List of ZnO material parameters.

Parameter	Symbol	Literature value	Reference
Hole effective mass	m_p^*	$0.64 \times (9.1095 \times 10^{-31})$ kg	[12]
High-frequency dielectric constant	ε_∞	$3.72 \times (8.8542 \times 10^{-12})$ (F m^{-1})	[12]
Static dielectric constant	ε_0	$8.12 \times (8.8542 \times 10^{-12})$ (F m^{-1})	[12]
Longitudinal lattice constant	c	5.207 Å	[13]
Piezoelectric coefficient	P	0.21	[12]
Longitudinal optical phonon energy	$\omega\hbar$	72 meV	[12]
Acoustic deformation potential	Ec	15 eV	[12]
Debye temperature	T	837 K	[12]
Longitudinal elastic constant	c_l	1.6×10^{11} Pa	[13]

tube furnace and annealed at 500 °C, 600 °C and 700 °C for 1 h each in ultrapure oxygen (99.999%). Film thickness was measured using a field emission scanning electron microscope; it was 400–500 nm. The best quality p-type ZnO sample was obtained at an annealing temperature of 600 °C with a typical hole concentration of 2.7×10^{16} cm^{-3} and a mobility of 0.3 cm^2 V^{-1} s^{-1}. The sample, which was annealed at 700 °C, showed n-type conductivity.

The electrical measurements were conducted after the sample was kept in the dark for more than 15 h to avoid the effect of persistent photoconductivity [9]. The Hall coefficient was measured in the Van der Pauw configuration with indium ohmic electrodes using a Lakeshore's 7707 Hall system by using a direct current of 30 nA and a magnetic field of 0.9 Tesla. Data were compiled employing both positive and negative currents and magnetic fields, and the results were averaged in order to compensate for various electromagnetic effects. To examine the reliability and repeatability of the experimental results, Hall coefficient measurements were performed several times under the same condition. Significantly, the Hall coefficient was positive for all four current/field combinations, which gives confidence that the layer is truly p-type. At room temperature, the averaged hole concentration is 2.7×10^{16} cm^{-3}, with a mobility of 0.3 cm^2 V^{-1} s^{-1} and a resistivity of 946 Ω cm. For better understanding of the electrical properties of the sample, we recorded the Hall coefficient as a function of the temperature in the range from 180 K to 300 K. Below 180 K, the high sample resistance exceeded the measurement limit of the Hall effect equipment.

3. Results and discussions

3.1. Analysis of the Hall mobility of the hole

Figure 1 shows the temperature dependence of Hall mobility (μ_H) for p-type ZnO:N film by closed squares. The Hall mobility decreases with increase in temperature. The average values of Hall mobility μ_H are 0.3 cm^2 V^{-1} s^{-1} and 24 cm^2 V^{-1} s^{-1} measured at 300 K and 180 K, respectively.

The transport properties of a semiconductor depend strongly upon the types of scattering mechanisms involved. In general, they include ionized impurity scattering, lattice vibration scattering and charged dislocation scattering. Lattice vibration scattering consists of three parts: (a) due to a partial ionization of the atoms in crystals without inversion symmetry, the acoustic-mode phonon vibrations produce a piezoelectric potential scattering (μ_{pz}); (b) the changes in lattice-atom positions due to acoustic-mode phonon vibrations
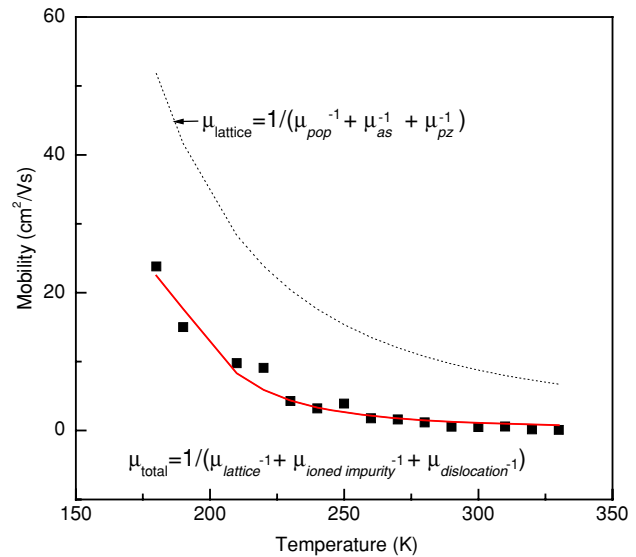

Figure 1. Comparison of calculated drift mobility of holes controlled by lattice vibration scattering (dashed curve) and measured Hall mobility (the closed squares) for a p-type ZnO thin film. The solid line is a least-squares fit to the experimental data considering lattice vibration scattering, ionized impurity scattering and dislocation scattering, which yields parameters $N_{dis} = (1.3 \pm 1.1) \times 10^{12}$ cm^{-2}.

produce a potential that scatters carriers (μ_{as}); (c) the optical-mode phonon vibrations produce a polarization of the ionic charges on neighbouring atoms, leading to dipole moments that can interact with the free holes (μ_{pop}). Each lattice scattering mechanism exhibits characteristic temperature dependence. According to the relaxation time approximation and perturbation modes, formulae for μ_{pz}, μ_{as} and μ_{pop} can be expressed, which are shown in the literature [10, 11]. Hutson *et al* have reported that only lattice scattering needs to be considered above 200 K for n-type ZnO crystals [11]. Here, the mobility determined by the lattice vibration scattering was calculated according to $\mu_{lattice} = 1/(1/\mu_{as} + 1/\mu_{pop} + 1/\mu_{pz})$, as shown in figure 1 with a dashed. The material parameters related to ZnO used in the calculation are listed in table 1 [12, 13].

It is clear that the experimental mobility data are not in good agreement with the calculated mobility controlled by the lattice vibration scattering. This indicates that the lattice scattering alone is not sufficient to explain the experimental behaviour in the present p-type ZnO thin films. For doping thin film, ionized impurity scattering through the Coulomb

potential should be considered. For a non-degenerate p-type material, the mobility involved ionized impurity scattering (μ_i) can be characterized by [14, 15]:

$$\mu_i = \frac{64\sqrt{\pi}\varepsilon_0^2 (2k_B T)^{3/2}}{N_I e^3 \sqrt{m_p^*} \ln \frac{12m_p^* k_B^2 T^2 \varepsilon_0}{e^2 \hbar^2 p'}} \quad (1)$$

where $p' = p + (N_A + N_D^+ - p)(N_D^+ + p)/N_A$ is the density of screening holes surrounding the ionized acceptors impurity. N_I is ionized acceptors impurity concentration. k_B is Boltzmann's constant and $\hbar$ is Planck's constant divided by 2π. Moreover, dislocation scattering should not be ignored for the present p-type ZnO films grown on the amorphous fused silica substrate. There is a large mismatch in the thermal expansion coefficient. Thus, it is not difficult to speculate high concentrations of threading edge and screw dislocations, which traverse from the ZnO/SiO$_2$ interface to the ZnO surface. Weimann *et al* employed Pődőr's relaxation rate to obtain an expression for the transverse mobility component due to Coulomb scattering at charged dislocation lines [16],

$$\mu_{dis} = \frac{\hbar^3 \varepsilon_0^3 c^2}{e^3 f^2 m_p^{*2} N_{dis} \lambda_D^4} \cdot (1 + \xi_\perp)^{3/2} \quad (2)$$

where f is the fraction of filled traps and it ranged form 0 to 1. $\lambda = (\varepsilon_0 kT/e^2 p)^{1/2}$ is the Debye length describing the screening and the radius r is measured from the centre of the dislocation line. The parameter $\xi_\perp = (2k_\perp \lambda_D)^2$ describes the transverse component of the kinetic energy of the holes; N_{dis} is the dislocation density. Thus, the total mobility in a semiconductor due to mixed scattering processes mentioned above can be calculated by using the expression

$$\frac{1}{\mu_{total}} = \frac{1}{\mu_i} + \frac{1}{\mu_{as}} + \frac{1}{\mu_{pop}} + \frac{1}{\mu_{pz}} + \frac{1}{\mu_{dis}}. \quad (3)$$

We attempt to fit the experimental mobility data with equation (3). And the fitting solid line showed in figure 1, which fitted well with the experimental data. The best fitting parameters for ionized acceptors impurities concentration $N_I = 10^{16}$ cm^{-3}, $N_{dis} = (1.3 \pm 1.1) \times 10^{12}$ cm^{-2} and the error come from the value of the fraction of filled traps f varying from 0 to 1. This result indicates ionized impurity scattering and dislocation scattering are as important as the lattice vibration scattering for p-type ZnO. Ionized impurity scattering is quite common in doping semiconductor. However, dislocation scattering in semiconductor materials is often ignored, because it becomes significant only for dislocation areal densities $N_{dis} > 10^8$ cm^{-2}. Such high densities are rare in most semiconductor devices, such as those fabricated from Si or GaAs, but are indeed quite common in devices based on ZnO and GaN materials, which involve mismatched substrates [12, 17]. In ZnO grown on Al$_2$O$_3$ (sapphire), the reported typical dislocation densities are 10^{10} cm^{-2} or higher [12]. For the present p-type ZnO grown on the amorphous silica substrate, there should be higher dislocation densities. Therefore, the fitted result of $N_{dis} = (1.3 \pm 1.1) \times 10^{12}$ cm^{-2} is reasonable. On the other hand, the hole Hall mobility is low for the present p-type ZnO film. The higher dislocation densities should be responsible for it. It has been reported that the mobility would drop to less than 100 cm^2 V^{-1} s^{-1}, a typical value found in many epitaxial ZnO layers, for the usual concentration of dislocations found in ZnO/Al$_2$O$_3$

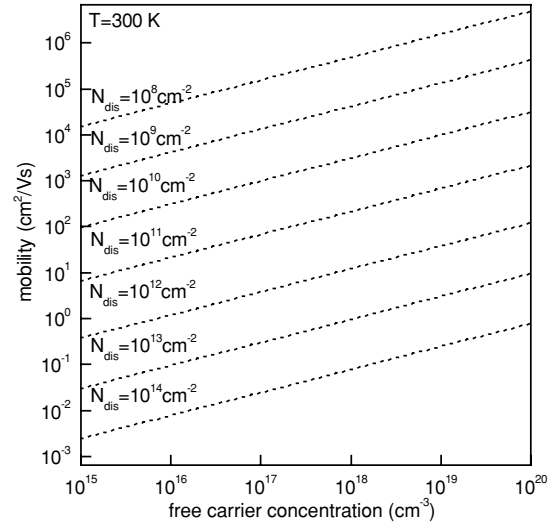**Figure 2.** Transverse mobility component due to dislocation scattering.

about $N_{dis} = 10^{10}$ cm^{-2} [12]. In research on n-type GaN, Weimann *et al* compared their results with detailed mobility versus carrier concentration at various values of N_{dis} [16]. The mobility has dropped to 1–10 cm^2 V^{-1} s^{-1} with $N_{dis} = 10^{11}$ cm^{-2} and the carriers concentration 10^{16} cm^{-3} at room temperature. Similarly, we calculated mobility versus hole carrier concentration at various values of N_{dis} in the present p-type ZnO film in terms of equation (2), where the fraction of filled traps f is assumed to 1 and the temperature is 300 K. The calculated results for μ_{dis} are shown in figure 2. As shown in the figure, the mobility controlled by dislocation scattering decreased with the increasing N_{dis}. And we can find the mobility dropped to <1 cm^2 V^{-1} s^{-1} with $N_{dis} = 10^{12}$ cm^{-2}, which matched the measured mobility 0.3 cm^2 V^{-1} s^{-1} at room temperature. From the above analysis, one can conclude that there do exist high dislocation densities of about 10^{12} cm^{-2} for the p-type ZnO grown on mismatched substrate. The scattering of holes at charged dislocation should not be ignored. It would drop drastically the carrier mobility. This is the possible reason for the reported mobility of p-type ZnO being low.

3.2. Thermal ionization energy of the nitrogen acceptor

As illustrated in figure 3, hole concentration increased with increasing the temperature. This is because the nitrogen acceptors can be gradually thermally ionized with the increasing temperature. For the acceptor dopant, one of the basic characteristics is its thermal ionization energy, because it controls the degree of ionization of the dopant centres, and in this way it determines the available free charge carrier density, dopant efficiency, etc. The thermal ionization energy of the nitrogen acceptor can be obtained roughly by the fitting of p versus T, which is derived from the charge-balance equation (CBE). For a p-type sample, the simple CBE in a nondegenerate, single-donor/single-acceptor, model will be given by [6, 12]:

$$p = \frac{1}{2}(\varphi_A + N_D)\left\{\left[1 + \frac{4\varphi_A(N_A - N_D)}{(\varphi_A + N_D)^2}\right]^{1/2} - 1\right\} \quad (4)$$
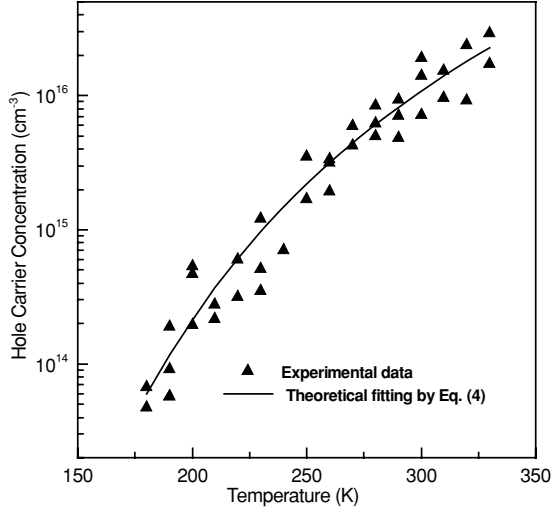
Figure 3. Hole carrier concentration as a function of temperature for the p-type ZnO thin film. The solid line is the least-squares fit to the experimental data with equation (4): $p = \frac{1}{2}(\varphi_A + N_D)\{[1 + \frac{4\varphi_A(N_A - N_D)}{(\varphi_A + N_D)^2}]^{1/2} - 1\}$. The fitted value of E_a, the thermal ionization energy of the nitrogen acceptor, is 170 meV.

where N_A and N_D are the acceptor and donor concentrations, respectively, and $\varphi_A = g_{A1}/g_{A0}N_V'T^{3/2}\exp(-E_a/kT)$, g_{A1} and g_{A0} are the occupied and unoccupied state degeneracies, respectively. For nitrogen on an oxygen site, the values of g_{A1}, g_{A0} are 1 and 4. N_V' is the effective density of states at 1 K, $N_V' = 2(2\pi m_p^* k)^{3/2}/h^3$. If an effective hole mass is assumed to be $m_p^* = 0.64m_0$, then $N_V' = 2.47 \times 10^{15}$ cm^{-3} K$^{-3/2}$. E_a is the acceptor ionization energy and T is the absolute temperature. By performing a least-squares fit to the experimental Hall hole concentration p as a function of the temperature according to equation (4), the fitted nitrogen acceptor activation energy E_a is about 170 meV. And the fitted parameters are: $N_A = 9.1 \times 10^{16}$ cm^{-3}, and $N_D = 2.5 \times 10^{16}$ cm^{-3}. According to the previous results of XPS [5], the physical nitrogen acceptor concentration approaches 10^{20} cm^{-3}, and the difference between the physical nitrogen acceptor concentration (10^{20} cm^{-3}) and the acceptor concentration determined from Hall measurements (10^{16} cm^{-3}) implies that not all nitrogen is electrically active on substitutional lattice sites.

3.3. The temperature variation of resistivity

Figure 4 shows the temperature variation of resistivity of p-type ZnO thin film. As a whole, the resistivity decreases exponentially with increasing temperature. It is well known that the resistivity depends inversely on the hole concentration and Hall mobility (that is the scattering time), which are both temperature dependent. At the whole measurement temperature, the increasing rate of carriers with the temperature rapidly increases. And the increasing number of carriers overcomes the decreasing scattering time, resulting in a decreasing resistivity with the temperature.

However, the plot of the resistivity does not monotonously decrease as temperature increased, but slows down in the temperature range 200 K to 220 K, labelled by the dashed
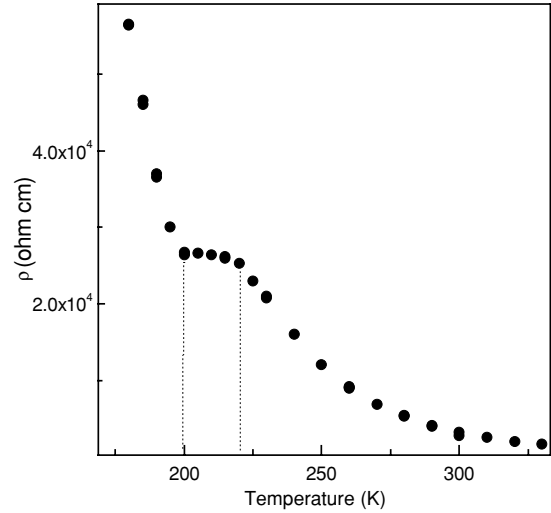

Figure 4. Temperature variation of resistivity of the p-type ZnO thin film in the temperature range from 180 K to room temperature.

lines shown in figure 4. Similar behaviour has been observed in the temperature dependence of photoluminescence-integrated intensity [18]. It might be caused by spatial localization of the defect states. When the temperature increases from 180 K to 200 K, it is only high enough to activate those defects located at the shallow energy level leading to the decreasing resistivity with temperature. While temperature is in the region of 200–220 K, defects at the shallow energy level left few and most of the defects at deeper energy level do not have enough thermal energy to be activated. The rate of carrier activation decreases and the decrease in resistivity slows down. A plateau is noted in the temperature range 200 K to 220 K. When the temperature is above 220 K, enough thermal energy can be provided to activate defects in the deep energy level, resulting in decreasing resistivity with the temperature.

3.4. Optical properties

Photoluminescence (PL) spectra of p-type ZnO film were observed in the temperature range of 77 K–300 K using a 5 mW He–Cd laser with an excitation wavelength of 325 nm. Figure 5 shows a free exciton emission peak at 3.28 eV at 300 K and acceptors bound exciton (A°X) peak at 3.350 eV at 77 K. This PL property is nearly the same as observed by others for the p-type ZnO film in comparison with that of undoped ZnO, which has the dominance of a donor bound exciton (D$_o$X) and an EX peak [19–21]. Besides the much broader A°X lines at 77 K, another peak is found in the spectra at about 3.313 eV. Some researchers have reported this line as arising from a deep acceptor bound exciton [6, 22]. However, some authors have suggested that the 3.313 eV line is a donor–acceptor pair transition, rather than an A°X transition [20, 21]. Fortunately, P-doped and As-doped p-type ZnO also displays this transition near 3.31 eV [23, 24]. Thus, this transition, whatever its identity, seems to be associated particularly with acceptors in p-type ZnO. These PL properties, in addition to Hall measurements, also confirm that the nitrogen-doped p-type ZnO thin film was obtained under optimum annealing conditions. Moreover, the electrical and optical properties of
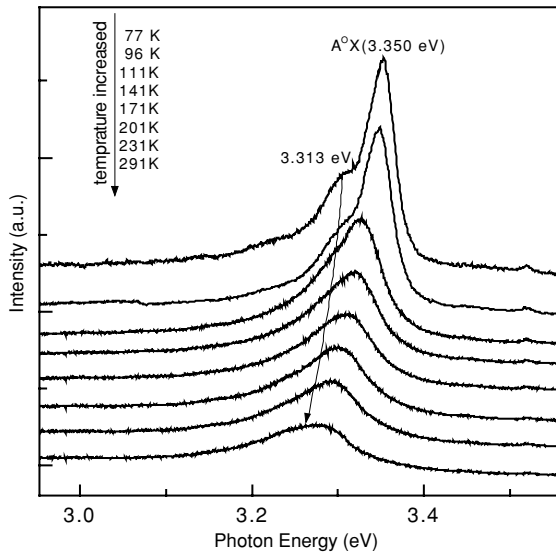
Figure 5. PL spectra of nitrogen-doped p-type ZnO thin film in the temperature range 77 K to 300 K.

p-type ZnO were stable, even after 10 months. Therefore, we believe this is a good method to prepare stable p-type ZnO by thermal activation of the nitrogen dopant.

4. Conclusions

In summary, electrical transport characteristics of p-type ZnO are experimentally studied. From the analysis of the p-type ZnO Hall mobility, it has been shown that the experimental Hall mobility cannot be explained solely by traditional lattice scattering mechanisms. Defects including ionized impurities and dislocation scatterings have also been considered for the present polycrystalline p-type ZnO:N film. The fitted results agree well with the experimental data, which indicates that the total carrier mobility is controlled by the above-mentioned scattering mechanisms. The thermal ionization energy of the nitrogen acceptor has been obtained to be 170 meV from the temperature dependence of the hole concentration. The mild variation in the resistivity in the range 200 K to 220 K is assumed to be related to the introduction of spatially localized defects. We also observe the bound exciton emission associated with nitrogen acceptors in the cryogenic photoluminescence.

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