Hole Transport in p-Type ZnO

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A two-band model involving the A- and B-valence bands was adopted to analyze the temperature-dependent Hall effect measured on p-type ZnO. The hole transport characteristics (mobilities and effective Hall factor) are calculated using the “relaxation time approximation” as a function of temperature. It is shown that the lattice scattering by the acoustic deformation potential is predominant. In the calculation of the scattering rate for ionized impurity mechanism, an activation energy of 100 or 170 meV is used at different compensation ratios between donor and acceptor concentrations. The theoretical Hall mobility at an acceptor concentration of $7 \times 10^{19}$ cm$^{-3}$ is about 70 cm$^2$ V$^{-1}$ s$^{-1}$ with the activation energy of 100 meV and the compensation ratio of 0.8 at 300 K. We also found that the compensation ratios conspicuously affected the Hall mobilities.

KEYWORDS: zinc oxide, hole, donor doping, mobility, nitrogen

1. Introduction

Recently, ZnO has received much attention because of its potential applications in ultraviolet (UV) and blue optoelectronic devices and its unique material properties such as a large direct band gap of $\pm 3.3$ eV at room temperature, high transparency for visible light, mixability with Mg and Cd to form the quaternary system (Zn, Mg, Cd)O with a tunable band gap between 3.0 and 4.0 eV. Nominally, ZnO is grown under fairly residual n-type. It is not difficult to achieve higher electron concentrations with excess zinc or by doping with Al, Ga, or In.

On the other hand, it is necessary to obtain p-type layers for light-emitter application and continuously develop them for its reliable technology. However, this has not been solved up to now and remains the major bottleneck for ZnO-based optoelectronics.

Because of the difficulties in growing p-type ZnO films as mentioned earlier, very little is known about the material and its physical properties. Fortunately, the situation is now improving and several groups have reported the growth of p-type ZnO films with valid and reasonable sets of experimental data. Among them, Look and coworkers have reported on the temperature dependence of the Hall-effect measurement. Tsukazaki and coworkers have fabricated the first ZnO-based light emitters in which they also reported a temperature-dependent Hall-effect (T-Hall). In this work, we report mainly on the theoretical aspects of the T-Hall results and the comparison of those results with the experimental data.

Several groups have already reported the electron transport characteristics of n-ZnO both experimentally and theoretically. On one hand, there are few theoretical investigations of the hole transport characteristics of p-ZnO. In this paper, the Hall coefficient anisotropy factors for ZnO are determined and theoretical hole transport characteristics (Hall and drift mobilities, and effective Hall factor) are calculated. The calculated hole transport characteristics, with changing compensation ratio over a wide range of temperatures ($T = 50$ to $400$ K), assume transport in both A-valence-hole and B-valence-hole bands (a two-band model) with scattering allowed between these bands.

2. Calculation Procedures

The analysis follows essentially the same method used for representative cubic semiconductors (GaAs, c-GaN), but the calculation was modified to fit the valence band structures of wurtzitic ZnO. In addition, we take the effects of the warping of surfaces into account for the hole transport studied here. The Hall coefficient factor, which generally links the experimentally measured Hall mobility with the drift mobility can be written as

$$r_i = \left(\frac{\tau^2_i}{\tau^0_i}\right)^2,$$  \hspace{1cm} (2.1)

where $\tau$ is the carrier scattering time, $(\cdots)$ indicates a thermal average over the distribution of carrier energy and the index $i$ runs over A- ($i = 1$) and B-valence ($i = 2$) holes.

The Hall coefficient factor depends on the degree of warping at the warped bands as well as the scattering mechanism, and can be written as:

$$r_i = r_{Ai} \left(\frac{\tau^2_i}{\tau^0_i}\right)^2,$$  \hspace{1cm} (2.2)

where $r_{Ai}$ is the anisotropy factor for the $i$-th hole band.

For their evaluation, one should determine the valence band parameters $L$, $M$, and $N$ defined in terms of the interband matrix element, as well as $A$, $B$, and $C$ parameters (which are different from the notation related to the split valence bands of wurtzitic semiconductors), which have been used in an approximate expression for the B-valence- and A-valence-hole energy surfaces. We use here the cubic approximation. These valence band parameters were calculated from those of effective mass parameters ($A_1$ to $A_6$) that have been recently reported by Fan et al., which are shown in Table I. The cubic approximation yielded the linkage of $A_1$ to $A_6$ with the parameters of $L$, $M$, and $N$, whose relations are given by
Table I. Valence band parameters for ZnO. The notations of parameters used here are the same as those in ref. 14.

| A_1 | A_2 | A_3 | A_4 | A_5 | A_6 | -A | -B | C^2 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| -6.680 | -0.454 | 6.128 | -2.703 | -2.767 | -6.462 | 1.41 | 1.95 | 0.796 |

\[ L_1 = A_2 + A_4 + A_5, \]
\[ L_2 = A_1, \]
\[ M_1 = A_2 + A_4 - A_5, \]
\[ M_2 = A_1 + A_3, \]
\[ M_3 = A_2, \]
\[ N_1 = 2 \times A_3, \]
\[ N_2 = \sqrt{2} \times A_6, \]

where the notations introduced above are
\[ L = (L_1 + L_2)/2, \]
\[ M = (M_1 + M_2 + M_3)/3, \]
\[ N = (N_1 + N_2)/2. \]

The relationships between the parameters \( L, M, \) and \( N \) and the well-known notations of \( A, B, \) and \( C \) are given in ref. 14.

Here, we used the formulae expressed in ref. 15 to calculate \( r_\lambda, \) the detailed descriptions of which are given in eq. (B.2) of ref. 14.

The scattering mechanisms due to (1) deformation potential caused by acoustic (dp) and optical phonons (nopp), polar optical phonon (pop), piezoelectric (pe), ionized impurity (imp), and interband deformation potentials are taken into account in the two-band analysis involving both kinds of hole scatterings. All scattering rates have been derived assuming a nonparabolic band, which is given below, and spherical bands, and band warping is accounted for.

The dispersion relation of energy band is represented for the nonparabolic band picture as
\[ \frac{\hbar^2 k_i^2}{2m^*} = E(1 + \xi E), \]
where all the notations used take their conventional meanings. The detailed explanation for the description can be found elsewhere.\(^{14}\)

The approximated expressions for the “overlap function” describing the hole scattering from the initial state \( k \) in band \( i(k_i) \) to the final state \( k' \) in band \( f(k'_f) \) are given by
\[ G(k_i, k'_f) = \begin{cases} 
(1 + 3 \cos^2 \theta)/4 & \text{for } i = f \text{ intraband} \\
3(1 - \cos^2 \theta)/4 & \text{for } i \neq f \text{ interband}
\end{cases} \]
where \( \theta \) is the angle between the wavenumbers of these relevant two states.

We summarize the relevant equations related to the scattering mechanisms treated in this study. The screening effects for the phonon scattering mechanism can be neglected as far as the regime of low-impurity concentrations is concerned here.

The ionized impurity scattering mechanism was treated using the Brooks–Herring approximation, where particles interact via the screened Coulombic potential.\(^{16,17}\) The inverse of screening length, \( \lambda_0, \) can be written for a low hole concentration
\[ \frac{1}{\lambda_0^2} = \frac{e^2}{\epsilon_s k_B T} [p/(p + N_D)][1 - (N_D + p)/N_A], \]
where \( p \) is the total hole concentration, and \( \epsilon_s \) is the static dielectric constant. The other notations have their usual meanings. The free-hole concentration \( p \) can be calculated using eq. (3.3) of ref. 14.

In the Hall-effect measurement, we evaluated \( E_s \) to be approximately 100 meV, whereas the spectroscopic studies experimentally yielded \( E_s \approx 170 \text{ meV} \).\(^{8,18}\) Therefore, \( E_s \) used in this work is 100 or 170 meV.

The scattering rate due to the density of ionized impurities \( N_i \) \((N_i = p + 2N_D)\) and the level of ionization of the impurity atom \( Z_i \) is given by:
\[ S_{\text{con}}(k_i, k'_f) = \frac{Z_i^2 N_i \epsilon_s m^*_f}{8\pi \epsilon_s \hbar^2 k'_f} \left[ \int_{-1}^{1} \frac{(1 - y)G(y)}{[1 - y + 1/2k'_f^2\lambda_0^2]^2} dy \right], \]
where \( y \equiv \cos \theta \) and \( G(y) = G(\cos \theta) \) are the overlap functions in eq. (2.14). Also, \( m^*_f \) is the effective mass of the relevant band into which the holes are being scattered, \( k_i \) is the magnitude of the initial-state wave vector and the other notations take their conventional meanings.

The scattering rate for the nonpolar optical scattering is given elsewhere.\(^{14}\) The quantity of \( D_{\text{opt}} \) is found to be about \( 3.9 \times 10^{-11} \text{ eV/m} \). We list here the scattering rate for the polar optical scattering mechanism because of some possible typographical errors appearing in ref. 14.
\[ S_{\text{po}}(k_i, k'_f) = \frac{e^2 m^*_f \epsilon_\infty}{4\pi \hbar^2} \left[ \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right] \times \frac{1}{k'_{f}} \times \left[ \sum_{\pm} k_{\pm} \left( n_0 + \frac{1}{2} \right) + \frac{1}{2} \right] \times \int_{-1}^{1} \frac{G(y)}{[1 - 2(k_{\pm}/k_i) + (k_{\pm}/k_i)^2]^{1/2}} \ dy \]
Here, \( \epsilon_\infty \) is the high-frequency dielectric constant. The wavevectors \( k_{\pm} \) correspond to energies \( E_{\pm} \pm \hbar \omega_0 \). The equations in regard to the scatterings by acoustic deformation potential and piezo-scattering have been enumerated in ref. 14 as eqs. (c.2) and (c.3).

To determine drift and Hall mobilities from the above-mentioned scattering mechanisms, we have determined the effective Hall factor using the “relaxation time approximation” or otherwise known as “Mathiessen’s rule”. The effective Hall factor \( r_{\text{eff}} \) is
\[ r_{\text{eff}} = \frac{(1 + \alpha^2/3)(r_1 \alpha^2/3 + \beta^2 r_2)}{(1 + \alpha^2/3)^2}, \]
with \( \alpha = m_1 = m_2, \beta = \mu_1/\mu_2, \mu_1 = \epsilon(E_i)/m^*_f, \) and \( r_1 = r_A/(\tau_i)^2. \) Quantities \( m_1, \mu_1, \) and \( \tau_i \) are the effective masses, drift mobilities and the relaxation times for the \( i \)-th hole band, respectively. (The index \( i = 1 \) always refers to A-valence, and the index \( i = 2 \) to B-valence holes.)

The drift mobility \( \mu \) is determined from relationships between drift and Hall mobilities given by
$$\mu = \frac{\mu_{H}}{r_{\text{eff}}},$$  \hspace{1cm} (2.19)

where $\mu_{H}$ is the Hall mobility and $r_{\text{eff}}$ is the effective Hall factor given by eq. (2.18).

The Hall mobility $\mu_{H}$ is determined to be

$$\mu_{H} = \frac{e}{m_{l}^{*}} \left( \frac{\tau_{1}}{\alpha_{1}} + \frac{\alpha_{1}}{\tau_{2}} \right),$$  \hspace{1cm} (2.20)

where $m_{l}^{*}$ is the effective A-valence-hole mass, and $r_{A1}$ and $r_{A2}$ are given in eq. (B.2) of ref. 14.

The material parameters used in the calculations on ZnO are shown in Table II. Rode$^{9}$ suggests a theoretical value of 3.8 eV for deformation potential $E_{1}$, but later studies resulted in a better agreement with the experimental data if a larger value was used.

### Table II. Material parameters of ZnO used in calculation.

| Property                  | Units | Value |
|---------------------------|-------|-------|
| $E_{g}$ Energy gap for A-valence hole | eV    | 3.445 |
| $E_{g}$ Energy gap for B-valence hole | eV    | 3.455 |
| $m_{1}/m_{0}$ Effective A-valence hole mass ratio |      | 0.59  |
| $m_{2}/m_{0}$ Effective B-valence hole mass ratio |      | 0.59  |
| $\rho$ Density             | kg/m$^3$ | 5.67526 |
| $s$ Sound velocity         | m/s   | $6.09 \times 10^5$ |
| $E_{1}$ Acoustic deformation potential | eV    | 15.0  |
| $D_{\text{ipo}}$ Optical coupling constant | eV/m  | $3.9 \times 10^{11}$ |
| $\epsilon_{s}$ Static dielectric constant |     | 8.2   |
| $\epsilon_{\infty}$ High-frequency dielectric constant | | 3.7   |
| $\hbar\omega_{0}$ Polar optical phonon energy | eV    | 0.072 |
| $\hbar\omega_{p}$ Piezoelectric constant | C/m$^2$ | 0.89  |

### 3. Results and Discussion

We determined the valence band parameters $L$, $M$, $N$, $A$, $B$, and $C$ using Luttinger parameters. The results are shown in Table I. The evaluated anisotropy factors $r_{A1}$ and $r_{A2}$ both yielded values very close to unity, which is significantly different from the situation observed in GaN. This difference may be due to the isotropic nature of the hole masses in ZnO.$^{19}$

The partial “scattering time versus temperature” curves are shown in Fig. 1. The interband scattering characteristic caused by nonpolar optical phonons shown in Fig. 1(a) is different from that caused by other scattering mechanisms shown in Figs. 1(b)–1(d). This is because the scattering relaxation time caused by nonpolar optical phonon scattering is determined by the final-state effective hole mass ($m_{2}^{*}$), whereas that caused by other scattering mechanisms is determined by both $m_{1}^{*}$ and the magnitude of the initial state of the wave vector $k_{i}$ in which nonparabolicity is considered.

![Fig. 1. Variations in calculated scattering relaxation time with temperature corresponding to nonpolar optical phonon mode (a), polar optical phonon mode (b), acoustic deformation potential mode (c) and piezoelectric mode (d). Many traces are almost overlapped to each other because the two hole masses are the same in ZnO. (h $\rightarrow$ h — scattering from A-valence-to-A-valence-hole band, h $\rightarrow$ l — scattering from A-valence-to-B-valence-hole band, l $\rightarrow$ l — scattering from B-valence-to-B-valence-hole band, and l $\rightarrow$ h — scattering from B-valence-to-A-valence-hole band.)](image-url)
Note that the relative importance of the various scattering mechanisms mimics that found in ZnSe.\(^2\) For example, at temperatures below 300 K, the acoustic deformation potential scattering plays the most important role.

Figure 2 shows the average scattering time \(\tau_{av}\) by ionized impurities calculated for two activation energies \((E_a = 100 \text{ and } 170 \text{ meV})\) with compensation ratios \((K = N_D/N_A)\) between 0.1 and 0.8. \(\tau_{av}\) is calculated with \(\tau_{av} = \tau_{av}(170)/\tau_{av}(100) \approx 1\) at 300 K, whereas the corresponding effect for a low compensation ratio \((K = 0.1)\) is appreciable \(\tau_{av}(170)/\tau_{av}(100) \approx 2\) at 300 K.

The temperature dependences of the Hall factors for the four different scattering mechanisms are shown in Fig. 3. The Hall factors for A-valence-hole and B-valence-hole bands of nonpolar and polar optical scatterings vary with temperature, whereas those for the acoustic deformation potential and piezoelectric scattering remained nearly unchanged. These different observations may be attributed to the temperature dependence of the scattering relaxation time of respective participating phonons. The values of the Hall factor both for A-valence-hole bands and for B-valence-hole bands varied from 1.0 to 1.5.

The partial Hall and drift mobilities, and the effective Hall factor that we calculated against temperature are shown in Fig. 4. The acoustic phonon scattering is the most important mechanism limiting hole mobility over a wide range of temperature. For temperatures above 300 K, the polar optical phonon scattering mechanism is the predominant factor.

The obtained effective Hall factors vary from 1.1 to 1.7 with changing temperature, as shown in Fig. 4(b), indicating the importance of proper considerations of the Hall factors at high temperatures when comparing drift mobility with \(\mu_{H1}\).

Finally, Fig. 5 corresponds similarly to the plot in Fig. 4, including the ionized impurity scattering with four different compensation ratios \((K)\) between 0.0 and 0.8. The acceptor concentration is \(N_A = 7 \times 10^{19} \text{ cm}^{-3}\) and \(E_a = 100 \text{ meV}\). We also plotted the experimental data of \(p\)-ZnO with a nitrogen concentration of \(2 \times 10^{20} \text{ cm}^{-3}\) (different from the acceptor concentration \(N_A\)) for comparison. The compensation ratio and free hole concentration at 330 K of this sample are \(p \approx 8 \times 10^{16} \text{ cm}^{-3}\) and approximately \(K = 0.8\), respectively.\(^2\)

Unfortunately, the calculated Hall mobility in this study is still higher than that in experimental reports. We considered only dp, npop, pop, and imp scattering mechanisms in our modeling, which may have resulted in this poor agreement. A dislocation scattering and the space-charge effect probably also contribute as a scattering mechanism of holes to the mobility determination. Actually, it is known that the former mechanism has an influence on relatively poor-quality n-
type ZnO epitaxial layers. We propose that more experiments using further-optimized samples be performed in the future.

With an increase in compensation ratio ($K$), the peaking temperature at maximum mobility also increases. The effective Hall factor $r_{\text{eff}}$ increases as $K$ decreases with increasing temperature. From Figs. 5(a) and 5(b), it is observed that the maximum value of the Hall and drift mobilities are in the temperature range of 50 to 100 K for all values of $K$ between 0.1 and 0.8. In comparison with Figs. 4(b) and 5(b) shows that the inclusion of scattering by ionized impurities into the Hall factor calculation is important at high compensation ratios ($K = 0.1$ to 0.8), exhibiting wavy behavior with a change in temperature. The obtained effective Hall factors vary from 1.1 to 1.5 with changing temperature ($K \geq 0.1$). The temperature at which the effective Hall factor is minimized and the effective Hall factor are affected by the ionized impurity scattering mechanism.

4. Conclusions

In this study, a two-band model analysis was carried out in detail on p-doped ZnO epitaxial layers. The theoretical Hall
and drift mobilities, and the effective Hall factor were calculated at temperatures of 50 to 400 K. The hole transport is characterized by scattering of the acoustic deformation potentials at temperatures below 330 K. The theoretical Hall mobility at an acceptor concentration $N_A = 7 \times 10^{18} \text{ cm}^{-3}$ is about 70 cm$^2$ V$^{-1}$ s$^{-1}$ with the activation energy of 100 meV and the compensation ratio of 0.8 at 300 K. The compensation ratio strongly affected the hole transport characteristics.

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1) D. C. Look: Semicond. Sci. Technol. 20 (2005) S55.
2) A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki: Nat. Mater. 4 (2005) 42.
3) T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, R. Shiroki, K. Tamura, T. Yasuda and H. Koinuma: Appl. Phys. Lett. 78 (2001) 1237.
4) T. Makino, K. Tamura, C. H. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo and H. Koinuma: Phys. Rev. B 65 (2002) 121201(R).
5) T. Makino, Y. Segawa, A. Tsukazaki, A. Ohtomo, S. Yoshida and M. Kawasaki: Appl. Phys. Lett. 85 (2004) 759.
6) K. J. Kim and Y. R. Park: Appl. Phys. Lett. 78 (2001) 475.
7) K. Ellmeier: J. Phys. D 34 (2001) 3097.
8) D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason and G. Cantwell: Appl. Phys. Lett. 81 (2002) 1830.
9) D. L. Rode: Semiconductors and Semimetals (Academic, New York, 1975) Vol. 10, p. 1.
10) D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell and W. C. Harsch: Solid State Commun. 105 (1998) 399.
11) J. D. Albrecht, P. P. Ruden, S. Limpijumnong, W. R. L. Lambrecht and K. F. Brennan: J. Appl. Phys. 86 (1999) 6864.
12) T. Makino, Y. Segawa, A. Tsukazaki, A. Ohtomo and M. Kawasaki: Appl. Phys. Lett. 87 (2005) 022101.
13) W. Fan, J. Xia, P. A. Agas, S. Tan, S. Yu and X. Sun: J. Appl. Phys. 99 (2006) 013702.
14) Y. Hayashi, K. Watanabe, T. Jimbo and M. Umemo: Jpn. J. Appl. Phys. 37 (1999) 622.
15) J. D. Wiley: Semiconductors and Semimetals (Academic, New York, 1975) Vol. 10, Chap. 2.
16) G. B. Benedek, W. Paul and H. Brooks: Phys. Rev. 100 (1955) 1129.
17) C. Herring: Bell Syst. Tech. J. 34 (1955) 1.
18) B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann and M. Strassburg: Phys. Status Solidi B 241 (2004) 231.
19) E. Mollwo: in Semiconductors: Physics of II–VI and I–VII Compounds, Semimagnetic Semiconductors, ed. O. Madelung, M. Schulz and H. Weiss (Springer, Berlin, 1982) Landolt-Börnstein New Series, Vol. 17, p. 35.
20) H. E. Ruda and B. Lai: J. Appl. Phys. 68 (1990) 1714.
21) T. Makino, Y. Segawa, A. Tsukazaki, A. Ohtomo and M. Kawasaki: Phys. Status Solidi C 3 (2006) 956.