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Low Temperature Electrical Properties of Zn-Doped ZnO

P. W. LI AND K. I. HAGEMARK

3M Central Research Laboratories, P.O. Box 33221, St. Paul, Minnesota 55133

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The electrical resistivity, the Hall coefficient, and Hall mobility of Zn-doped ZnO single crystals have been measured from 4.2 to 300 K. Excess Zn has been introduced by controlled high temperature heat treatments in a Zn atmosphere. The donor levels and the concentration of donors and acceptors are calculated by a best fit to the data at the higher temperature range. Lattice scattering is the dominant mechanism at the upper temperature range of the measurements. At the intermediate temperature range the ionized and neutral defect scattering mechanisms dominate. Donor band conduction is observed at the lowest temperatures.

I. Introduction

Pure ZnO is an *n*-type semiconductor due to the incorporation of excess Zn. The physical properties of the crystals, particularly at low temperatures, depend strongly on the concentration of native defects caused by the deviation from the stoichiometric composition. As a result of the high concentration of shallow donors, a donor band conduction mechanism becomes evident at low temperatures. This has been demonstrated by Hausmann (*1*) (combined EPR and electrical resistivity studies), Hausmann and Teuerle (*2*), (Hall effect studies), and Wagner and Helbig (*3*) (Hall effect studies). All three studies have been on as-grown or high temperature vacuum treated ZnO crystals. Donor band conduction has also been observed in heavily Zn-doped ZnO by Muller and Schneider (*4*), Hausmann (*1*), and Van der Schroeff (*5*) all by EPR studies, and by Bogner (*6*) and Hausmann and Teuerle (*7*) by Hall effect studies.

In the present paper, we will discuss the low temperature electrical transport properties of Zn-doped ZnO. Of particular interest is the existence of the donor band conduction mechanism and its dependence on non-stoichiometric composition. A series of controlled Zn-doped ZnO crystals with a wide range of resistivity have been studied. In most cases the electrical resistivity, Hall coefficient and Hall mobility have been measured in the temperature range 4.2–300 K. The range was only limited by either too high sample resistance or too low Hall voltage.

The donor level E_D, and the concentrations of donors N_D and acceptors N_A have been calculated by a best fit to the data in the range where donor band conduction is negligible. The Hall mobility will be discussed and the donor band mobility will be estimated.

II. Experimental

A. Crystals

Vapor phase grown 3M ZnO crystals and in one case a ZnO crystal supplied by Heiland (*8*) have been investigated. Emission spectrographic and mass spectrographic analyses show that the 3M crystals have no major impurities above 1 ppm (4×10^{16} cm^{-3}) except for Si (approximately 10–20 ppm). The crystals supplied by Heiland had been intentionally doped with 10 ppm Cu (5×10^{17} cm^{-3}). The 3M crystals were cut into bars of typical size $2 \times 2 \times 12$ mm with a *c*-axis either parallel or perpendicular to the long dimension of the bars.

To obtain a wide range of electrical resistivity, the stoichiometric composition of some of the ZnO crystals was changed by controlled high temperature Zn doping in sealed silica ampoules (see Hagemark and Chacka (*9*)). To minimize the surface effects, the crystals were etched in 90°C concentrated H_3PO_4. About 50 μm of material was removed from the surface. Emission spectrographic and mass spectrographic analyses subsequent to the doping showed that the impurity content did not change significantly (less than 1 ppm) during the doping. The color of the crystals changed from light yellow for highly doped crystals ($N_D \sim 5 \times 10^{17}$ cm^{-3}) to deep red for heavily doped crystals ($N_D > 5 \times 10^{18}$ cm^{-3}).

B. Electrical Measurements

A conventional Hall method was used. The details of the technique and apparatus are described by McFadden and Hagemark (*10*). A Leeds and Northrup K-4 Potentiometer (low sample resistances) or a Keithley 610BR Electrometer (high sample resistances) were used for voltage readings. A constant current supply (*11*) stable to one part in 10^5 was used for the Hall coefficient measurements. A calibrated Au + 0.07 at.% Fe vs Cu thermocouple was used for temperature measurements in the range 4.2–77 K and a calibrated Cu vs constantan thermocouple from 77 to 300 K. The magnetic induction B was 10 kG in the earlier runs and 6.5 kG in the later ones with no difference in the results (weak field region). The orientation of the samples was either with current I parallel or perpendicular to the *c*-axis. Low resistance ohmic indium contacts were formed by capacitor discharge welding (*10*).

III. Results and Discussion

The results of the electrical resistivity ρ, the Hall coefficient R_H and the Hall mobility μ_H are shown in Figs. 1, 2, 3a, and 3b, respectively. The behavior at low temperatures is characteristic of a donor band conduction and will be discussed in more detail.

The shape for the log μ_H vs log T plots shown in Figs. 3a and 3b can be explained by a two-band conduction mechanism. The location of the maximum in these curves depends on the concentration of donors and the degree of compensation. For the three highly resistive samples ("Heiland," 146G and 507-B7), the maximum occurs at temperatures above 140 K with a very rapid decrease in the mobility on the low temperature side of the maximum. In these three compensated crystals a hopping mechanism probably accounts for the mobility behavior at lower temperatures.

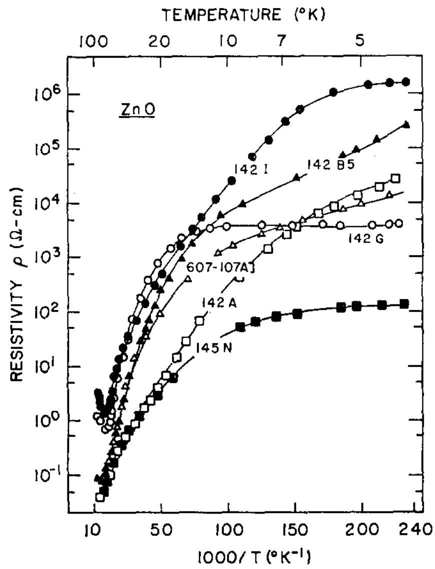

FIG. 1. The resistivity ρ is shown vs $10^3/T(K^{-1})$ from 4.2 to 300 K.

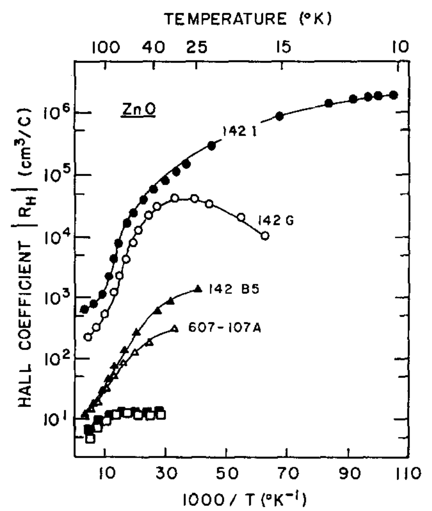

FIG. 2. Temperature dependence of Hall coefficient R_H from 10 to 300 K. An R_H maximum is clearly observed in sample 142G. □ 142A; ■ 145N.

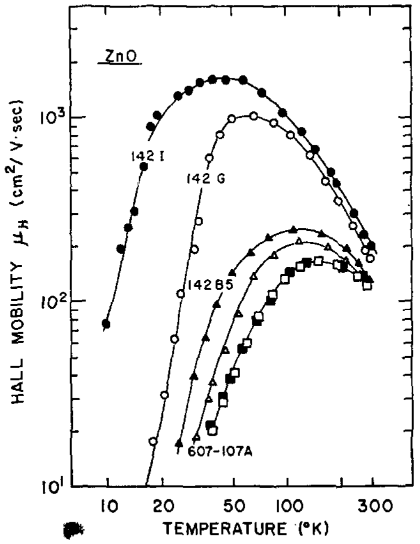

FIG. 3a. Temperature dependence of Hall mobility μ_H from 10 to 300 K. □ 142A; ■145N.

A. The Hall Coefficient

First we will discuss the temperature range where donor band conduction is negligible. The concentration of conduction band electrons is assumed to be

$$n_{\text{exp}} = 1/(eR_H).$$

From semiconductor statistics (*12*), considering a single type donor and a close to degeneracy case, we can calculate the electron concentration n using the expression

$$\frac{n(n+N_A)}{(N_D-N_A-n)(1-0.27(n/(N_c))} = 1/\beta\, N_c \times \exp(-E_D/kT).$$

N_D and N_A are the concentration of donors and acceptors, $N_c = 4.83 \times 10^{15}$ $(m^x/m)^{3/2} T^{3/2}$. The density-of-states mass m^x/m is assumed to be equal to 0.3, β is related to spin degeneracy of the donor: $\beta = 2$ for H-type donors and $\beta = 0.5$ for He-type donors, E_D is the donor level. The term $(1\text{–}0.27\ n/(N_c))$, suggested by Blakemore (*12*) as valid for $n/N_c < 1.3$.

The values for E_D, N_D, and N_A were obtained by minimizing the expression.

$$\sigma_N = [1/M \sum (1\, n/(n_{\text{exp}}))^2]^{1/2}$$

using a modified nonlinear least-squares fit computer program. Here M is the number of

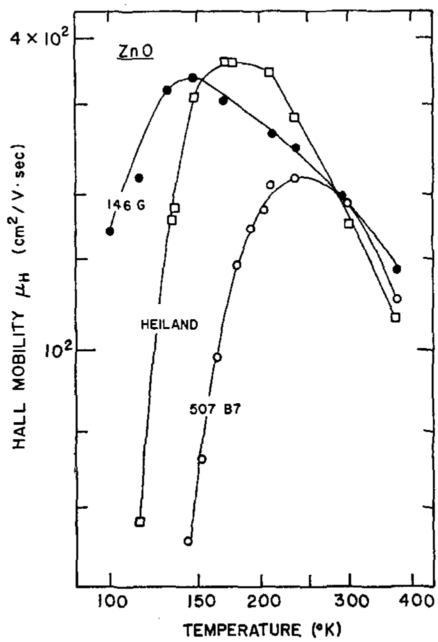

FIG. 3b. Temperature dependence of Hall mobility μ_H for three highly resistive samples.

observations. Both H-type donors, $\beta = 2$, and He-type donors, $\beta = 0.5$, were assumed. The results are given in Table I. The value of σ_N does not seem to depend too strongly on the choice of β. Thus, we might deal with an uncompensated crystal with a deeper donor or a close to compensated crystal with a shallower donor level (see for example 142A). As will be shown, and also discussed elsewhere (*9*), the fit to the mobility data requires a lower acceptor concentration favoring the uncompensated case. An example of a good fit is shown in Fig. 4 for crystal 142 G using the values listed in Table I ($\beta = 2$ and 0.5 give practically the same curve).

B. Hall Mobility

Based on a two-band conduction model suggested by Hung (*13*) we can express the Hall constant as

$$R_H = 1/e\,[((b^2-1)n + N_D - N_A)/(((b-1)n + N_D - N_A)^2)]$$

where

$$b = \mu_{HC}/\mu_{HDB},$$

the ratio between conduction band Hall

TABLE I

RESULTS OF CARRIER CONCENTRATION ANALYSIS

Crystal	c-axis	n_{RT} (cm^{-3})	β	E_D (meV)	N_D (cm^{-3})	N_A (cm^{-3})	σ_N
142I	$\parallel$	9.6×10^{15}	2	35	1.7×10^{16}	7.2×10^{15}	5.0×10^{-2}
			0.5	30	8.7×10^{16}	7.7×10^{16}	5.0×10^{-2}
142G	$\parallel$	3.1×10^{16}	2	22	9.9×10^{16}	6.5×10^{16}	2.3×10^{-2}
			0.5	19	4.2×10^{17}	3.8×10^{17}	2.1×10^{-2}
142B5	$\parallel$	5.9×10^{17}	2	14	1.2×10^{18}	1.8×10^{17}	5.2×10^{-2}
			0.5	16	1.3×10^{18}	5.7×10^{17}	3.6×10^{-2}
607–107A	$\perp$	6.5×10^{17}	2	13	1.4×10^{18}	1.8×10^{17}	3.7×10^{-2}
			0.5	11	2.1×10^{18}	1.2×10^{18}	2.6×10^{-2}
142A	$\parallel$	1.2×10^{18}	2	2	2.3×10^{18}	1.6×10^{16}	3.2×10^{-2}
			0.5	7	1.7×10^{18}	1.3×10^{17}	2.6×10^{-2}
			0.5	1	3.0×10^{18}	1.3×10^{18}	2.5×10^{-2}
145N	$\perp$	1.2×10^{18}	2	2	2.4×10^{18}	1.3×10^{17}	3.0×10^{-2}
			0.5	8	1.6×10^{18}	1.2×10^{17}	4.9×10^{-2}
507–B7	$\perp$	3.5×10^{15}					
Heiland	$\parallel$	4.7×10^{13}					
146G	$\perp$	3.6×10^{15}					

mobility μ_{HC} and donor band Hall mobility μ_{HDB}. From the maximum value of R_H with respect to n we can calculate b from

$$(b+1)^2/4b = (R_H)_{\max}/(R_H)_{\text{exh}},$$

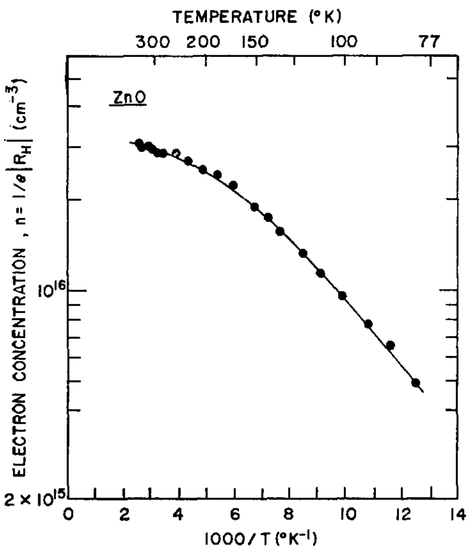

FIG. 4. Nonlinear least-square fit for sample 142G using values for E_D, N_D, and N_A given in Table II. ($\beta = 2$ or 0.5 give practically the same curve.) ● experimental; — nonlinear least-square fit.

where $(R_H)_{\text{exh}}$ is the value of R_H in the exhaustion range ($n = N_D - N_A$). From Fig. 2 a maximum in R_H is clearly observed in one case (142G). The b values for other crystals have also been estimated by using the largest values for R_H. The related μ_{HDB} values are given in Table II.

In the case of 142G we have also calculated the μ_H using the relation

$$\mu_H = \mu_{HDB}[((b^2-1)n + N_D - N_A)/((b-1)n + N_D - N_A)].$$

In calculating μ_{HC} both the lattice mode scatter-

TABLE II

RESULTS OF HALL MOBILITY ANALYSES

Crystal	μ_{HDB} cm^2 V^{-1} sec^{-1}
142I	0.5
142G	2.0
142B5	0.5
607–107A	1.8
142A	15
142N	15

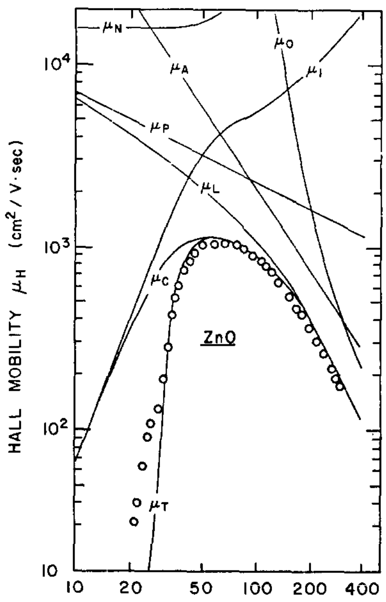

FIG. 5. Best fit to the Hall mobility data of sample 142G by using a two band model. μ_c is the conduction band mobility calculated from lattice and defect mode scatterings; and μ_T is the total mobility of the two band conduction model where $\mu_{HDB} = 2$ cm^2 V^{-1} sec^{-1}. o = experimental.

ing (optical μ_O, acoustical μ_A, and piezoelectric μ_P) and defect mode scattering (ionized μ_I and neutral μ_N) have been considered. The details are given by Wagner and Helbig (*3*) and Hagemark and Chacka (*9*). The results are shown in Fig. 5 using $E_D = 0.0255$ eV, $N_D = 4.1 \times 10^{16}$ cm^{-3}, $N_A = 6.8 \times 10^{15}$, $\beta = 2$ and $\mu_{HDB} = 2$ cm^2 V^{-1} sec^{-1}. The calculated mobility μ_T is in fair agreement with experimental data except at lower temperatures. A considerably lower acceptor concentration than the one given in Table I had to be assumed. Only a less satisfactory fit could be obtained in the other cases, particularly at the lower temperatures.

Summary

We have discussed the low temperature Hall coefficients and Hall mobilities of Zn-doped ZnO. The donor levels and the concentration of donors and acceptors have been calculated based on a H-type and a He-type donor. The Hall mobility at low temperatures have been calculated by assuming a two band conduction mechanism. A more consistent fit between carrier concentration analysis and mobility analysis was obtained by assuming an uncompensated crystal (low acceptor concentration) and a H-type donor.

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