

TEMPERATURE DEPENDENT HALL MEASUREMENTS MADE ON CdGeAs₂

A.J. Ptak^{*}, S. Jain^{*}, K.T Stevens^{*} and T.H. Myers^{*,†}, P.G. Schunemann^{**}, S.D. Setzler^{**} and T.M. Pollak^{**},

^{*}Department of Physics, West Virginia University, Morgantown, WV

^{**}Sanders, A Lockheed Martin Company, Nashua, NH; [†]tmyers@wvu.edu

ABSTRACT

Seventeen samples of CdGeAs₂ have been extensively characterized by temperature-dependent Hall effect and resistivity measurements. Due to the anisotropic nature of the electrical properties, carefully matched sample sets were fabricated with the c-axis either in or out of the plane of the sample. The matched samples allowed determination of carrier concentration and both in-plane and out-of-plane mobilities as a function of temperature. The electrical properties of both undoped and lightly doped samples were dominated by either native defects or residual growth impurities, leading to compensated p-type material. N-type doped material was obtained only with heavy doping. An apparent variation in acceptor activation energy between 110 and 165 meV could be best explained in terms of two deep acceptor levels and at least one shallow donor. Room temperature absorption coefficient data and the relation to background doping is also reported.

INTRODUCTION

CdGeAs₂ has attracted much attention in recent years for its potential as a frequency conversion material operating in the infrared. It has the highest nonlinear optical coefficient of any known phase-matchable compound (236 pm/V). CdGeAs₂ has shown promise for the second harmonic generation of a CO₂ laser to produce a tunable infrared source for the mid-infrared wavelengths [1] which are potentially useful for the monitoring of many atmospheric pollutants. Unfortunately, this material has suffered from several problems that have limited its usefulness, although some success has been achieved. [1,2] These drawbacks include a high background of p-type carriers from native acceptors and residual impurities, and a large anisotropy in the coefficient of thermal expansion. This latter problem has made it very difficult to grow large, crack-free crystals.

A range of acceptor activation energies have been reported for CdGeAs₂. Fischer *et al.* [3] have reported values for E_a ranging between 100 and 150 meV in undoped material. Bairamov *et al.* [4] have studied both undoped as well as Cu- and Ga-doped material. In their study, undoped samples indicated an intrinsic, or native, defect possibly related to cadmium vacancies with an acceptor level around 150 to 160 meV. The Cu and Ga produced acceptor levels about 120 to 130 meV above the valence band. Our study indicates that both native levels and extrinsic impurities both continue to play an important role in unintentionally doped CdGeAs₂.

EXPERIMENTAL

The CdGeAs₂ samples were grown at Sanders, A Lockheed Martin Company (Nashua, NH) and were both intentionally and unintentionally doped. Two different growth methods were employed, horizontal gradient freeze (HGF) and travelling heater (THM) with both techniques producing similar material. Temperature dependent Hall effect measurements were

performed at West Virginia University using a system based on a typical Keithley Instruments Hall effect set-up. Indium contacts were soldered to the samples using the standard Van der Pauw geometry.

Since CdGeAs₂ is a highly anisotropic crystal, specially matched sets of samples were fabricated from each boule for Hall analysis. Hall measurements performed on the sample that had the c-axis perpendicular to the plane of the sample (c_{\perp}) allowed measurement of the carrier concentration, the mobility and the resistivity along the a-axis. The other sample had the c-axis in the plane of the sample, parallel to one edge (c_{\parallel}), allowing the resistivity of both the a- and c-axes to be determined directly. For each matched set, the a-axis resistivities agreed reasonably well, with the worse case differing by a factor of two. It is reasonable to assume this variation is due primarily to carrier concentration variations within a boule, and thus the resistivity ratio coupled with the a-axis mobility determines the c-axis mobility, giving a complete set of electrical properties for each direction in the crystal. In addition to the electrical data, infrared absorption measurements were performed at room temperature from 2-20 μm using a Nicolet Magna-IR 550 FTIR spectrometer.

SAMPLE CHARACTERIZATION AND ANALYSIS

Representative data from the temperature dependent Hall measurements made on the c_{\perp} samples of CdGeAs₂ are plotted in Figure 1. Hall effect measurements of this type indicated p-type material in all but one case. Shown in Figure 1 are the carrier concentration and mobility measured for sample 49. The room temperature carrier concentration for this particular sample was $\sim 1 \times 10^{15} \text{ cm}^{-3}$ with the effect of carrier “freeze-out” easily seen. The maximum hole mobility was seen to be $\sim 225 \text{ cm}^2/\text{V}\cdot\text{sec}$ occurring $\sim 190 \text{ K}$. Also of note, the Hall coefficient changes signs, from positive to negative, at about 350 K, indicating that intrinsic carrier

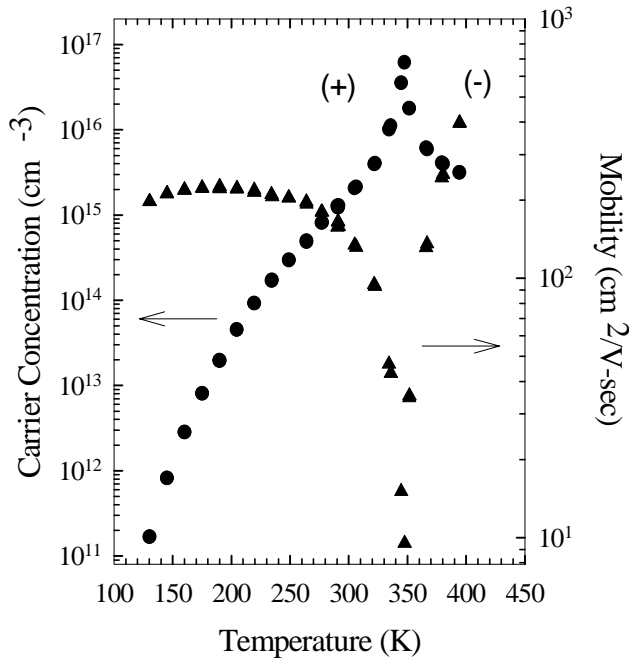


Figure 1. Typical electrical properties of cadmium germanium arsenide.

concentration effects are becoming important near this temperature. The activation energy of the acceptors can be determined from the low-temperature carrier concentration data, where the intrinsic electrons have not yet become important. The data was fit to the full charge balance equation, based on one acceptor level and a fully ionized shallow donor with no assumptions about the relative concentrations of impurities. [5] Due to the large activation energy of the acceptors, complete ionization would only occur at temperatures where conduction is dominated by intrinsic electrons. With the constraint of incomplete ionization, the fitting procedure could only determine the compensation of the material, i.e. the ratio of the number of donors to the number of acceptors.

Table I contains information on all of

the samples that were measured, including the compensation ratio and the activation energy of

Table I. Selected material parameters.

Sample	Dopant	RT Carrier Concentration (10^{16} cm^{-3})	Activation Energy (meV)	Compensation Ratio	p-to-n Transition Temp. (K)	RT Absorption Coefficient at $5.75 \mu\text{m}$ (cm^{-1})
29	Cr	0.21	141	0.71	377	1.1
30	Ag	0.20	131	0.77	417	1.9
31	Undoped	1.8	110	0.26	--	11.0
34	Se	-8.8	<20	--	--	0.9
37 "dark"	Undoped	3.1	109	0.25	--	18.4
37 "light"	Undoped	0.089	125	0.95	329	1.8
49	Se	0.12	154	0.69	346	1.3
50	Undoped	(a)	153	0.83	259	3.5
51	Te	0.2	164	0.50	336	0.4

(a) Not reliable due to proximity to Hall coefficient transition

the acceptors.

If the extrinsic p-type doping is sufficiently low, or the sample is highly compensated, intrinsic conduction effects become important. Ambipolar conduction effects can result in the Hall coefficient changing from positive to negative since the electron mobility in CdGeAs_2 is at least 10 times that of the hole mobility. [6] The square of the mobility ratio determines this effect, allowing the switch to occur while the electron concentration is still one to two orders of magnitude less than the hole concentration. When this effect is observed, the following equation relates the total concentrations of acceptor impurities (N_a) in the material to the carrier density:

$$N_a = \frac{p}{1 - R - \frac{1}{\frac{1}{2} \exp\left(\frac{E_F - E_a}{k_B T}\right) + 1}} \quad (1)$$

where R is the compensation ratio listed in Table I, and the Fermi level, E_F , is determined from the mobility ratio and effective masses through the standard formula for the intrinsic carrier concentration. [7] Since there is uncertainty in the material parameters necessary for this calculation, particularly in the band gap and the effective masses of holes and electrons, the values of N_a determined in this way must be viewed as approximate. Values of N_a are listed in Table II, determined when the transition in conductivity was observed. These calculations have assumed a ratio for the electron-to-hole mobility of 12, [4] and effective masses based on the theoretical work of Borisenko *et al.* [8]

Four point resistivity measurements were performed for each sample set on the $c_{||}$ sample, allowing the resistivity anisotropy to be directly measured. Representative temperature-dependent resistivity measurements (for sample 49) are shown in Figure 2. The resistivity anisotropy is also summarized in Table II. If we assume that the a-axis mobilities of the two matched samples are the same, reasonable since they were cut from the same area in the boule, then the anisotropy in resistivity determines the mobility parallel to the c-axis. The highest a-axis p-type mobility directly measured in these samples was $\sim 260 \text{ cm}^2/\text{V}\cdot\text{sec}$, and the highest measured a-axis n-type mobility was $\sim 1500 \text{ cm}^2/\text{V}\cdot\text{sec}$. For samples exhibiting type conversion, the n-type mobility had not yet saturated within the limits of our measurements. It

should also be noted that the electrical contacts became blocking for the less conductive

Table II. Selected material parameters.

Sample	RT ρ Anisotropy	a-axis Mobility ($\text{cm}^2/\text{V}\cdot\text{sec}$)	c-axis Mobility ($\text{cm}^2/\text{V}\cdot\text{sec}$)	N_a Estimate (cm^{-3})	Maximum Mobility ($\text{cm}^2/\text{V}\cdot\text{sec}$)	Temperature for Maximum Mobility (K)
29	340	178	60520	3×10^{16}	245	170
30	14.7	210	3087	1×10^{17}	245	170
31	2.7	140	378	-	146	250
34	4	910	3640	-	1500(μ_e)	400
37 "dark"	3.6	124	446	$>10^{18}$	120	250
37 "light"	4	155	620	2×10^{17}	210	185
49	40	165	6600	3×10^{16}	225	190
50	(a)	(b)	(a)	5×10^{15}	150, 1500(μ_e)	185, 400
51	2.2	149	328	1×10^{17}	240	180

(a) Not measured (b) Not reliable due to proximity to Hall coefficient transition

samples at lower temperatures, limiting the temperature range of the Hall measurements.

DISCUSSION OF RESULTS

Both doped and undoped sample sets were characterized. Early in this study it was recognized at Sanders that the infrared absorption varied strongly from place to place within a given boule, occasionally with a sharp transition zone. Two sample sets (labeled 37) were cut for Hall analysis on either side of one such transition, one termed the "light" set due to its relative lack of absorption, and the other termed the "dark" set for its higher level of absorption. Electrically, as well as optically, the two sets were quite different. The "light" set was much less conductive due to a mixture of higher compensation and lower N_a , with the measured acceptor energy level somewhat larger than its "dark" counterpart, 125 vs. 109 meV. This trend in electrical properties is consistent with the results of absorption coefficient measurements for

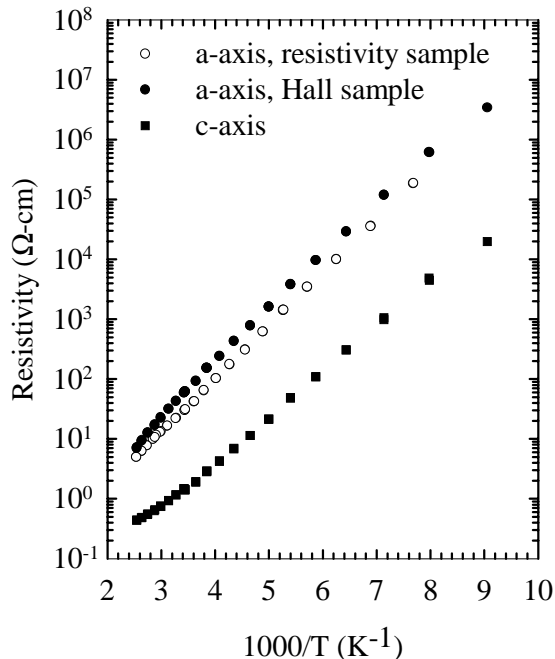


Figure 2. Resistivity anisotropy for sample set 49.

the four undoped sample sets measured, as indicated by the data in Table I. In order to learn more about the origin of this difference in electrical and optical properties, more must be known about the impurities in the material. Seven of the nine sample sets investigated were pre-selected based on optical absorption measurements.

Of particular interest are the high values for the c-axis mobility, with one reaching above 60,000 $\text{cm}^2/\text{V}\cdot\text{sec}$. These are not artificial values as the error involved in measuring the a-axis resistivity ratio of these sets cannot account for the high mobilities. The ratio is roughly constant over all temperatures

investigated, even though each resistivity varied by five orders of magnitude, and the measurements have been carefully repeated. Work is underway to directly measure the c-axis mobility of material from these boules by using a standard Hall bar geometry.

Samples that were intentionally doped were done so with the n-type dopants selenium, tellurium and silver, and chromium which is expected to be a deep acceptor. The Cr, Ag, Te and lightly Se-doped samples all exhibited few differences. They were all p-type with carrier densities of $\sim 1-2 \times 10^{15} \text{ cm}^{-3}$ at room temperature, and appeared to be dominated by the background p-type doping. The doped samples had acceptor activation energies that ranged from 130 to 150 meV and were more likely due to native defects and residual impurities than to intentional dopants. The only real distinction between these samples was in the ratio of the c- and a-axis resistivities, which also may be coincidental. This ratio ranged from ~ 2 for the Te-doped set to ~ 340 for the Cr doped samples. The higher conductivity for the c-axis is related to the smaller effective mass, and thus higher mobility, along this direction. The mobility is related to the scattering lifetime as well as the effective mass. Any isotropic scattering process, such as ionized impurity scattering, will tend to “homogenize” the mobility thereby lowering the anisotropy. It is interesting that the samples with the larger resistivity anisotropy also had the lowest estimated concentrations of background acceptors.

Sample set 34 was highly doped with Se, and was n-type at room temperature with an electron density of $\sim 9 \times 10^{16} \text{ cm}^{-3}$ which did not change appreciably over the temperature range measured, ~ 200 to 400 K . It proved difficult to make contacts with indium to the n-type samples that performed below $\sim 220 \text{ K}$. The carrier concentration over this temperature range showed no evidence of carrier “freeze-out” resulting in an upper limit for the donor activation energy of $\sim 20 \text{ meV}$ below the conduction band. It is likely that this sample was highly

compensated assuming the sample had the same background acceptor levels as the others measured. This was consistent with the steadily decreasing electron mobility measured with decreasing temperature at all temperatures investigated, indicating significant ionized impurity scattering.

Previous studies [3,4] indicate a clear demarcation between activation energies for extrinsic acceptors (120 to 130 meV) vs. native defects (150 to 160 meV) in CdGeAs_2 . The differences in the activation energies from sample to sample can be understood by considering the possibility of two separate acceptor levels. Predicted carrier concentrations were generated using the appropriate charge-balance models [9] with known parameters for two acceptors, then fit with the single acceptor model used for all of the above samples in order to test the validity of this assumption. The data was generated assuming that there were two acceptor levels, one lying at 120 meV (N_{a120}) and the other at 160 meV (N_{a160}), completely

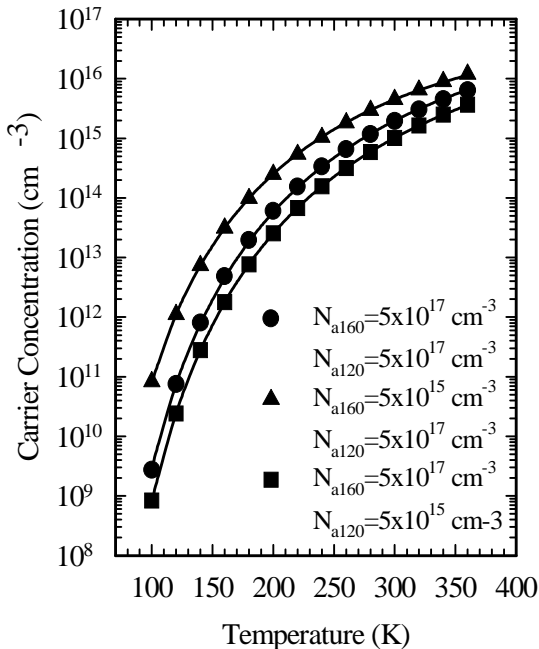


Figure 3. Generated data based on a two acceptor level, one shallow donor model and their corresponding one acceptor level fits.

ionized donors, and a total compensation ratio of 0.70. The data generated in this way can be fit quite well by the single acceptor model as seen in Figure 3. For the two cases where the concentration of one level is 100 times larger than the other, the fit using the single acceptor model returns the values attributed to that level ($N_d/N_a \sim 0.70$ and $E_a \sim 0.160\text{meV}$ for the squares and $N_d/N_a \sim 0.69$ and $E_a \sim 0.121\text{meV}$ for the triangles.) When the levels are equally abundant, the fit is dominated by the deeper level ($N_d/N_a \sim 0.61$ and $E_a \sim 0.152\text{meV}$ for the circles). If the more shallow level is associated with extrinsic impurities, then we should measure the smaller activation energy only for those samples with a high concentration of impurities that greatly exceed intrinsic acceptors. As can be seen by comparing Table I and Table II, samples with a shallower acceptor level tend to have a significantly higher total concentration of impurities. Thus, it can be seen that the wide range of acceptor energies often observed is consistent with the presence of at least two distinct acceptor energy levels.

CONCLUSIONS

Several sets of CdGeAs₂ samples have been measured and analyzed by temperature-dependent Hall effect. N-type conduction was only obtained with high levels of doping, with electrical measurements indicating that Se is a shallow donor. Both undoped and less heavily-doped samples grown with the deliberate introduction of Se, Te, Cr and Ag show similar electrical properties dominated by the background p-type doping, with a wide range of acceptor energies observed. All of the p-type results are consistent with a model employing a single shallow donor and at least two separate acceptor levels. An intriguing mobility has been observed along the c-axis that is still under investigation.

ACKNOWLEDGEMENTS

The work performed at West Virginia University was supported by the Air Force Office of Scientific Research through Grant No. F49620-96-1-0452 and by funding from Sanders, A Lockheed-Martin Company. Crystal growth and analysis at Sanders, A Lockheed Martin Company was supported by the Air Force Research Labs Materials and Manufacturing Directorate under contract F33615-94C-5415.

REFERENCES

1. P.G. Schunemann in *Conf. on Lasers and Electro-Optics*, 1996 OSA Technical Digest Ser., vol. 9 (Optical Society of America, Washington, DC, 1996) p. 230.
2. G.W. Iseler, H. Kildal, and N. Menyuk, *J. Electron. Mater.* **7**, 737 (1978).
3. D.W. Fischer, M.C. Ohmer, and J.E. McCrae, *J. Appl. Phys.* **81**, 3579 (1997).
4. B.H. Bairamov, V.Yu. Rud', and Yu.V. Rud', in *MRS Bulletin* vol. 23(7) (Mater. Res. Soc., Pittsburgh, PA, 1998) p.41.
5. See, for example, N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders College Publishers, New York, 1976), p. 586.
6. See, for example, R.H. Bube, *Electronic Properties of Crystalline Solids* (Academic Press, New York, 1974), p.364.
7. See, for example, J.P. McKelvey, *Solid State Physics for Engineering and Materials Science* (Krieger Publishing Company, Malabar, Florida, 1993), p. 388.
8. S.I. Borisenko and G.F. Karavaev, *Izv. Vyssh. Uchebn. Zaved., Fiz.* **1**, 68 (1982). IssN0021-3411.

9. See, for example, R.H. Bube, *Electronic Properties of Crystalline Solids* (Academic Press, New York, 1974), p.311.