DISTRIBUTION OF DONORS AND ACCEPTORS IN HIGH-PURITY GERMANIUM CRYSTALS*

Eugene E. Haller⁺, William L. Hansen and Fred S. Goulding

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

SUMMARY

The axial and radial dependence of the net-concentrations of donors and acceptors in high-purity germanium has been investigated. The methods include dc-conductivity measurements on Czochralski grown crystals, Hall effect experiments on full area slices, collimated alpha particle probing on detectors, and C-V measurements on detector arrays. Some quantitative correlations between the results of the different methods are presented. Many of the crystals exhibit internal junctions, whose influence on the properties of high-purity germanium detectors will be discussed.

INTRODUCTION

Apart from crystallographic examination, the first observations made on our high-purity germanium crystals concern the distribution and concentration of impurities. Since conventional methods of measuring hole and electron concentrations are not reliable in the concentration range below $10^{10}/\text{cm}^3$, it has been necessary to develop new techniques that provide unambiguous results. We report here the most useful measurement techniques and present data on three representative crystals. Some of the methods used for these measurements were developed by R. N. Hall--in these cases, only a brief description of the method is given and any changes we have made to improve results are discussed.

Use of these methods has led to a better understanding of the role of chemical impurities and structural defects in determining the net-acceptor and -donor concentrations of these high-purity materials. The results also explain some aspects of detector behavior, such as the very thin windows observed on the p-side of many high-purity germanium detectors.

EXPERIMENTAL METHODS AND RESULTS

Conductivity Test

The first measurement on a new crystal is designed to establish the gross impurity concentration distribution by a simple dc-conductivity measurement. This method is well established.^{1,2} After breaking the crystal from its seed, notches 1 cm apart along the length of the surface are made with a diamond file. After etching* and rinsing the crystal with methanol, In-contacts (current contacts) are soldered to the head and tail and InGa eutectic is rubbed into the notches (voltage contacts). The soldered contacts are ohmic on both p- and n-material. It is important that the current contacts be made to the very ends of the original crystal as this makes it possible to extend the conductivity measurements to the regions where impurities tend to congregate. This provides some information on the nature of donors and acceptors.

After application of the contacts to the crystal it is immersed in liquid nitrogen, and a constant current of 100 μA is passed through it. As the crystal cools, a drop in conductivity is observed due to the exponential decrease of the intrinsic carrier concentration. At some temperature ($\sim 190^\circ\text{K}$) the material becomes extrinsic and the increase in mobility at lower temperatures produces an increase in conductivity. Deep-lying donors or acceptors disturb this simple picture. After the crystal achieves liquid nitrogen temperature, measurement of the voltage differences between the 1 cm marks on the surface, and of the corresponding crystal diameters yield average values of the conductivity and of the axial net-carrier concentration along the crystal length. As previously reported² all our crystals grown in pure H_2 exhibit a p-type region near the head. When measured to the far ends, all crystals change to n-type somewhere in the lower half. This observation complements those reported by us earlier.

Metal Point Probing

The existence of radial impurity concentration variations in crystals reduces the value of these gross conductivity measurements. As nearly all crystals exhibit such radial variations this simple measurement can be used only as a rough guide in evaluating the crystal. More detailed information must be obtained by studying the radial distribution of impurities at several points along a crystal. To

* This work was done under the auspices of the U. S. Atomic Energy Commission.

+ Presently working with a grant from the Schweizerischen Nationalfonds.

* Etch solution: $\text{HNO}_3(70\%) : \text{HNO}_2(\text{red fuming}) :$
 $\text{HF}(49\%) = 5:1:2$

MASTER

do this, one or more slices of suitable thickness for planar high-purity germanium detectors (0.5 to 1.5 cm) are cut perpendicular to the crystal-growth axis. The slices are lapped and polish etched and a preferential etch* is used to reveal the dislocation distribution. Polish etching and rinsing in methanol* is then used to prepare the samples for metal point probing as described by Hall, et.al.¹ After blowing dry with nitrogen, one flat side is covered completely with a thin InGa eutectic film which is rubbed into the surface to break through any oxide layer. Each sample is placed on a metal plate covered with In foil and is immersed in liquid nitrogen. Using a tin and an iron probe (or In/Pt) the typeness is determined. Our Hall-effect experiments show that this method determines typeness correctly on p-type material at net acceptor concentrations over $2 \times 10^{10}/\text{cm}^3$. On n-type material problems arise at net donor concentrations below $2 \times 10^{10}/\text{cm}^3$. Probing experiments on more than 150 samples from about 50 crystals show that the head end of our crystals is invariably p-type with a radial concentration variation. At a few centimeters from the head end, the central region becomes either very high-purity p- or n-type, while the periphery clearly remains p-type. This behavior extends over several centimeters until the p-skin disappears. Hall-effect measurements described in the next paragraph show that the central region is high-purity n-type at this point.

The results given so far concern only well dislocated crystals. Where dislocations are absent the probing tests clearly indicate p-typeness even if the surrounding dislocated material is n-type. This observation is in agreement with results on dislocation free crystals,³ where a constant net-acceptor concentration of 2 to $4 \times 10^{11}/\text{cm}^3$ was found and where the net-concentration of chemical impurities was below $5 \times 10^{10}/\text{cm}^3$. The transition from n- to p-material as the boundary of dislocation-free regions is surprisingly sharp and extends over less than 1 mm. This must represent a maximum value for the radius of the region cleared of vacancies by a dislocation. More detailed measurements are required to better define this radius.

Hall-Effect Measurement

More quantitative results on radial concentration variations can be obtained from Hall-effect measurements using the Van der Pauw arrangement.^{1,4} Figure 1 shows the arrangement used in our experiments. After warming up the probed sample and removing the InGa eutectic, it is re-etched and rinsed with methanol only. Four InGa eutectic contact strips 2 to 4 mm wide are rubbed on the circumference of the sample spaced at 90°. The Ge piece is held in a styrofoam cryostat by the teflon ring shown in Fig. 1 which contains four stainless steel screws, each covered with an Al-cap and In foil providing good contacts and avoiding mechanical damage to the material. A

Helmholtz-coil arrangement is used to produce a magnetic induction of about 100 Gauss along the axis of the sample. Only non-magnetic materials are used to assure zero field at zero current. Sample currents ranging from 1 μA to 10 mA are employed depending on the net carrier concentration to determine the resistivity, typeness, concentration and mobility.⁴ The results are usually independent of sample current over three decades for both polarities, which indicates the excellent ohmic properties of the contacts. In making comparisons of the Hall-effect results with conductivity experiments, we use the following mobility ratios.^{5,6}

$$\text{Electrons: } \frac{\mu_{\text{Hall}}}{\mu_{\text{Drift}}} = 0.83$$

$$\text{Holes: } \frac{\mu_{\text{Hall}}}{\mu_{\text{Drift}}} = 1.30$$

At 77°K high-purity germanium with a uniform concentration of impurities should therefore exhibit the following Hall mobilities which can be regarded as reference values:

$$\mu_{\text{Holes}} = \mu_{\text{Electrons}} = 45,000 \text{ cm}^2/\text{Vs}$$

In many of the samples tested the current distribution is disturbed by impurity concentration variations, and the measured mobility deviates from its reference value. An apparent mobility is then observed, its value providing an indication of the non-uniformity of impurity concentration. Our crystals exhibit concentration variations with cylindrical symmetry--in this case, we find that a relatively simple interpretation can be given to Hall-mobility results. If the central region of a sample has a lower concentration than at its periphery, the apparent mobility is smaller than the reference value. The Hall signal remains representative of concentration down to apparent mobilities of $10,000 \text{ cm}^2/\text{Vs}$ which corresponds approximately to a slow variation in concentration across the radius with the central region concentration five times smaller than at the outside. For higher concentration ratios, and also in the case where the typeness changes from the center to the periphery, the Hall signal decreases rapidly. The apparent mobility becomes very small and the derived concentration values are useless. This is a common problem in crystals with a high concentration skin of either type. Removing the skin by lapping or grinding, or extending the contact strips away from the surface may make Hall-effect measurements possible in these cases.

Figures 2 through 4 show conductivity, metal-point probing and Hall-effect data on three crystals. Figure 2 shows the classical example of a crystal exhibiting little or no radial concentration variation. Nearly all the crystal is p-type changing to n-type very near the tail. In this case, excellent agreement is seen between conductivity, probing and Hall-effect measurements of typeness and concentration. The Hall mobility essentially has its reference value. Figure 3 shows a somewhat more complex case where the crystal changes typeness about half way along its length, but where a p-type skin extends down somewhat past half way. At the two ends the conductivity and Hall-effect measurements of concentration agree well and the Hall mobility also approaches its reference value. Near the middle of the crystal the apparent Hall mobility drops radically and the

* Etchant for <1,1,1> planes: KOH(6g):K₂Fe(CN)₆(4g):H₂O(50g)

for <1,0,0> planes: HNO₃(70%):HF(49%):Cu(NO₃)₂(10%/weight) = 1:2:1.

+ No water is used in this process.

and the concentration data becomes unreliable. The final example in Fig. 4 is the extreme case of a crystal whose central region changes from p- to n-type near the middle, but with a p-type skin extending all down the length of the crystal. In this case, values of the apparent Hall mobility indicate the problem, and the metal-point probing confirms it. The concentration measurements are very doubtful.

Alpha-Particle Scanning--Depletion Voltage Determination

Possibly the best method for measuring the concentration of impurities uses an alpha source to scan the metal barrier side of a detector made from the material. By measuring the applied detector bias at which full depletion occurs in the different regions--and therefore where the full amplitude alpha signal is produced--the impurity concentration profile is determined. Unfortunately all metals tested by us* can replace only p⁺ contacts which restricts the use of this method to testing p-type material. The use of "regrowth" n-type contacts of the type studied by Ottaviani, et. al.,⁷ and Marrello, et. al.,⁸ may extend the use of this technique to testing n-type material.

Precise determination of the full depletion voltage is made difficult by the fact that charge produced by alpha particles diffuses from undepleted material into the depletion layer when that layer does not extend fully to the metal barrier. A convenient way to handle this problem is illustrated in Fig. 5 where the alpha pulse-height is plotted as a function of voltage for three different amplifier pulse-shaping time-constants. The charge diffusing slowly from undepleted material is largely lost when a short shaping time is employed, so the apparent depletion voltage is higher than when longer times are used. By extrapolating the linear rising portion of the amplitude plot to the full amplitude level an "extrapolated depletion voltage" is obtained for each time constant. It is convenient to regard this as the voltage required to deplete the full detector thickness (1 cm in this case) minus a diffusion length Δ related to the amplifier time constant τ by the equation.

$$\Delta = \sqrt{\mu \frac{KT}{q}} \tau = 173 \sqrt{\tau} \text{ mm}$$

where τ is in μ s and a temperature of 77°K is assumed. The results shown in Fig. 5 support this conclusion since the calculated concentrations were virtually independent of τ .

The results given in Fig. 5 were for the central region of detector #220-13.0 (the same piece as shown in Fig. 2, 13 cm from the head end of the crystal). Measurements near the periphery yielded almost the same concentration. The perfect agreement in the concentration determined by conductivity measurements, by Hall-effect determination and by alpha-probing gives high confidence in these methods. An example where much lower concentration and a radial variation are both present is illustrated by Figs. 6 and 7. Detector #212-4.5 (4.5 mm thick) was probed with alpha particles at the center, at medium radius and near the periphery. Full rotational symmetry was found.

Because of the very high-purity the electric field at full depletion is small. The resulting collection times (> 200 ns) lead to errors in the determination of the depletion voltage if short filter time constants ($\tau = 0.5 \mu$ s) are used. These values are presented only for information but are not used. The result shows that the concentration increases rapidly near the edge. This is the classical case of a p-type skin surrounding a lower-concentration p-type core.

Detector Arrays

The most elaborate method for determining the radial distribution involves slicing a detector into an array of small diodes. After probing and Hall-effect measurements, a detector is made with a Li-diffused n⁺ contact and with a Pd-metal Schottky barrier on the reverse side. The capacity voltage relationship is plotted, and the detection properties are checked. A pattern of 0.7 mm wide grooves are cut into the n⁺ contact side for p-material, or through the Pd contact for n-material. We use a groove depth approximately 1.5 to 2 mm smaller than the detector thickness. The capacity-voltage curve is determined for all the detectors using a pulser and standard detector electronics. By plotting $1/C^2$ - V relationship the concentration is determined for each device. We have:

$$\text{Conc.} = 8.86 \times \frac{10^6}{A^2 (\text{cm}^4)} \times \frac{\Delta V (\text{V})}{\Delta C^{-2} (\text{pF}^{-2})}$$

A = area of device
V = reverse bias
C = capacity

The full depletion voltage may also be determined to provide a check on the concentration value determined by capacity measurement. Results on two detector arrays made of the crystal slices #212-3.0 and #212-10.0 are presented in Fig. 8. Good agreement with the previous results is again observed.

DISCUSSION AND CONCLUSIONS

Our experimental results show that most of our high-purity germanium crystals exhibit three characteristic regions. Near the head end the crystals are uniformly p-type. A transitional region then occurs where the typeness changes, first near the axis and more slowly at the periphery. In the tail-end region, the crystal is mostly n-type with the possibility of a p-type skin. This situation may be explained by observing first only the donor distribution. Examination of the lower half of many crystals shows that the net-donor profile can be explained by the segregation of a chemical impurity with a coefficient of approximately 0.1. Low temperature measurements show that the donor level is very shallow. These two experimental facts, together with the pervasive nature of phosphorous in the environment support the assumption that phosphorous is the observed donor. Phosphorous has been identified in high-purity germanium made by General Electric Company.⁹ Our

* Al, Mg, Cr, Ca, Zr, Hf, Gd, Dy and Yb.

measurements on the tail-ends of some crystals are consistent with between 10^{11} and 10^{12} donor atoms in the starting melt (approximately 200 cm^3).

Consideration of the behavior of the acceptor distribution is more complicated and is hardly explainable in terms of only chemical impurity segregation. A segregation coefficient > 0.1 and N_A total $> N_D$ total are both necessary to make the crystal p-type near the head end. Only boron has such a segregation coefficient, but the acceptor concentration does not decrease fast enough to be consistent with boron doping.* The radial concentration variation could be explained as the natural consequence of the known liquid flow patterns in rotated Czochralski growth. We have observed that crystals grown with very slow relative rotation of crystal and crucible (1 rpm) exhibit little or no radial variation. This observation is also evidence that the p-skin is not due to diffusion from the hydrogen ambient.

Observations made on partially and totally undislocated crystals indicate that structural defects play a dominant role as acceptors.³ Near the tail end of a half dislocated crystal, the dislocated part is n-type and the undislocated region is strongly p-type. The detection of p-spots in n-type samples, and their correlation with low dislocation-density regions, fit in this picture perfectly. Experiments for the determination of the acceptor and donor distribution in the neighborhood of a dislocation with good spatial resolution are planned to throw further light on the role of the dislocations. At the present time from our experiments we conclude only that the origin and the distribution of acceptors in our high-purity germanium is strongly dependent on structural defects, including dislocations, vacancies and vacancy clusters. Although the radial concentration variations may appear undesirable to the purist in semiconductor technology we must observe that certain advantages in practical detectors do result.

In our work the n^+ contact of these detectors is exclusively made by lithium-diffusion. The p-n junctions fabricated by this process have proven to yield very good leakage current characteristics. Especially critical is the region where the junction comes to the surface where it is desirable to have p-material to reduce the effect of surface channels. For thin-window detectors it is preferable to have n-material because the detector then starts to deplete from the thin-window side (Pd-Schottky barrier). This is an important parameter for charged particle and low-energy X- and gamma-ray detector applications. It is likely that detectors with n-type bulk material and an p-type skin, such as we commonly observe in our tests, are ideal for these detector applications. If so we have a fortuitous combination!

ACKNOWLEDGEMENTS

Discussions with R. H. Pehl, and the experimental work of M. Roach have been very valuable in this program. We also thank R. C. Davis for constructing much of the apparatus used in our crystal-growing program. We have profitted from discussions with R. N. Hall on many aspects of the work.

REFERENCES

1. R. N. Hall, R. D. Baertsch, T. J. Soltys and L. J. Petrucco, Annual Reports: Nos. 1,2,3,4 and 5 (1968-1972), General Electric Research and Development Center, Contract No. AT(30-1), 3870.
2. W. L. Hansen and E. E. Haller, IEEE Trans. Nucl. Sci. NS-19, No. 3, 260 (1972).
3. E. E. Haller, W. L. Hansen and F. S. Goulding, IEEE Trans. Nucl. Sci. NS-19, No. 3 271 (1972).
4. L. J. Van der Pauw, Philips Res. Reports 13, No. 1, 1-9 (1958).
5. A. C. Beer and R. K. Willardson, Phys. Rev. 110, 1286 (1958).
6. H. Miyazawa and H. Maeda, J. Phys. Soc. Japan, 15, 1924 (1960).
7. G. Ottaviani, V. Marrello, J. Mayer, M-A. Nicolet and J. Caywood, Appl. Phys. Lett., 20, No. 8, 323-325 (1972).
8. V. Marrello, T. A. McMath, J. W. Mayer and I. L. Fowler, "High-purity Germanium γ -ray Spectrometers with Al Regrowth p^+ Contacts", submitted to Nucl. Inst. and Methods.
9. S. D. Seccombe and D. M. Korn, Solid State Research Lincoln Lab., No. 1, 43 (1972).

* The effective segregation coefficients are closer to one than their equilibrium values, which means impurities other than boron would probably segregate more slowly than phosphorous!

XBL 7211-7436

Fig. 1. Mount for Hall-effect measurements.

1. High-purity germanium slice with four InGa-contact strips.
2. Teflon ring.
3. Four stainless steel screws each one covered with an Al-cap and In-foil.

A,B,C,D: current/voltage contacts.

$\vec{B}$ = magnetic induction (106 Gauss).

CRYSTAL 220

Fig. 2. Combined net-concentration results on crystal #220 from conductivity test, metal point probing and Hall-effect measurements. π and ν indicate very low net-acceptor and net-donor concentrations respectively.

XBL 7211-7442

CRYSTAL 212

Metal Point Probing

Typeness	
Center	Periphery
p	p
p	p
π	p
π	p
π	p
π/U	p
n	n

Hall-Effect

Van der Pauw

Typeness	Concentr. ($\times 10^9 / \text{cm}^3$)	Mobility (cm^2 / Vs)
p	11.8	44,500
p	10.3	41,000
p	6.6	37,800
p	5.9	33,600
p	4.2	25,400
p	6.0	3,500
n	11.2	18,300

XBL 7211-7443

Fig. 3. Combined net-concentration results on crystal #212 from conductivity test, metal point probing and Hall-effect measurements. π and ν indicate very low net-acceptor and net-donor concentrations respectively.

CRYSTAL 151

XBL 7211-7441

Fig. 4. Combined net-concentration results on crystal #151 from conductivity test, metal point probing and Hall-effect measurements. π and ν indicate very low net-acceptor and net-donor concentrations respectively.

XBL 7211-7438

Fig. 5. Alpha particle amplitude--bias relationship for detector #220-13.0. The same concentration was obtained from measurement at five different points.

XBL 7211-7440

Fig. 6. Alpha particle amplitude--bias relationship for detector #212-4.5. The alpha particles were collimated into the peripheral region.

XBL 7211-7439

Fig. 7. Alpha particle amplitude--bias relationship for detector #212-4.5. The alpha particles were collimated into the central region.

XBL 7211-7437

Fig. 8. Radial net-concentration variation for two slices of crystal #212 obtained from the $I/C^2 - V$ relationship of the individual detectors. Good rotational symmetry was observed.