

Isotopically Controlled Germanium: A New Medium for the Study of Carrier Scattering by Neutral Impurities

Kohei M. Itoh

Department of Materials Science and Mineral Engineering,
University of California at Berkeley
and
Lawrence Berkeley Laboratory

Abstract

Isotopically enriched, high purity ^{70}Ge and ^{74}Ge single crystals were grown and subsequently doped by the neutron transmutation doping method for the optimum control of shallow impurities. The crystals had isotopic enrichments of over 96% and a net residual impurity concentration of $\sim 2 \times 10^{12} \text{ cm}^{-3}$ prior to the NTD process. As a result of thermal neutron irradiation, a series of $^{70}\text{Ge}:\text{Ga}$ and $^{74}\text{Ge}:\text{As}$ wafers with carrier concentrations in the range $10^{14} \sim 10^{16} \text{ cm}^{-3}$ were produced. The samples were characterized by variable temperature Hall effect. Low temperature mobilities were measured in order to investigate the effect of neutral impurity scattering. We find excellent agreement between the low temperature experimental mobility and phase shift calculations for the hydrogen atom scaled to the impurity atoms in semiconductors.

1. Introduction

With very few exceptions most materials science research and technology is completely oblivious to the composition of stable isotopes in the material. The available types of stable isotopes and their abundances in all elements are pre-determined by nature, i.e., the isotopic composition of a certain element (or material) does not depend on the source of the sample that is measured. Therefore, scientists and engineers usually assume a given isotopic composition of the material and never intend to control it, partly because most effects caused by differences in isotope nuclear masses are negligibly small, and partly because it is very complicated and costly to separate isotopes.

However, not all isotope effects are negligibly small as I will show now with diamond as an example. A naturally available diamond (NatC) consists of 98.89% ^{12}C and 1.11% ^{13}C isotopes. It has been recently shown that the elimination of 1.11% ^{13}C leads to more than 150% increase in the room temperature thermal conductivity ¹. This diamond was found to be the "*world's most efficient heat conductor*" and has been used very recently as monochromators for synchrotron radiation, where the heating (and the subsequent broadening of the spectrum) is a persistent problem due to high incident radiation density ². The isotopically enriched diamond (^{13}C) also holds other world records: it is the "*hardest known terrestrial material*" ³ having the "*largest atomic density of any known solid*" ⁴. The ^{13}C diamonds, therefore, are very interesting from a material engineer's point of view and they may become useful tool materials for mechanical processing of natural diamonds in the near future.

In order to clearly discern the isotope effect from other existing effects, it is ideal to use a material which is structurally perfect and chemically pure. Elemental semiconductors (Si and Ge) are the natural choice for this purpose because of their unrivaled structural perfection and high chemical purity (electrically active impurity concentration less than 10^{-5} ppm). Then the question is how does one obtain isotopically separated semiconductor

materials? For experimentalists in western countries separated isotopes of many elements have been available from the Oakridge National Laboratory and other suppliers for a few decades. However, due to the extremely high price of separated semiconductor isotopes (greater than a few US\$ per milligram!), they have been practically inaccessible. Up to now only one group ⁵ has been able to obtain a large enough quantity of isotopically enriched semiconductor material (96% ⁷⁴Ge) from the Oakridge National Laboratory in order to grow a single crystal. The semiconductor isotope supply situation changed dramatically (at least for Professor Eugene Haller's group at Berkeley) when the US-Soviet cold war ended. The Former Soviet Union's massive isotope separation facilities that had been developed in previous years for the isotope separation of uranium and plutonium under the atomic weapon development program were turned into "isotope separators for scientific research". As a result, it became possible for us to obtain a variety of enriched Ge isotopes by establishing scientific collaborations with scientists in Russia.

Incidentally I happened to start my graduate career when the first Isotopically enriched Ge materials arrived at Berkeley from Kurchatov Institute of Atomic Energy, Russia. Thus I became responsible for this project. It is impossible to cover the whole spectrum of what has been done using the materials in this paper. Instead I am going to describe the projects which I consider my own. They are (1) development of a small high purity Ge crystal growth system for growing isotopically controlled Ge, (2) neutron transmutation doping of isotopically controlled Ge, and (3) neutral impurity scattering studies using isotopically engineered Ge. The projects I am not going to discuss in this paper include isotope effects on phonon frequencies ⁶⁻¹⁴, energy gaps ¹⁵⁻¹⁸, oxygen impurity local vibrational mode frequency ¹⁹, and other transport studies ²⁰. References 6-20 involved isotopically engineered Ge crystals that were grown using the method described in this paper.

2. Crystal Growth of Isotopically Engineered Ge

We started from 100g each of isotopically enriched ⁷⁰Ge and ⁷⁴Ge powders. Even though the powders were isotopically enriched, they contained more than 10^{17}cm^{-3} aluminum and other impurities when we received them from Russia. We first designed a zone refining system which allowed us to purify these powders. Using the zone refiner we obtained ⁷⁰Ge and ⁷⁴Ge polycrystalline bars of $\sim 10^{11}\text{cm}^{-3}$ electrically active impurity concentration. We then developed a growth system which could produce high quality Ge crystals in small size in order to grow Ge crystals containing mixed isotopes in controlled ratios. Consumption of separated Ge isotopes for this purpose must be minimized because mixing reverses the isotope separation, an extremely elaborate and costly process. The elimination of the use of a seed crystal is also important in order to conserve the high isotopic purity of the starting material. Small pieces from each bar ($\sim 4\text{g}$) were then grown into high purity ⁷⁰Ge and ⁷⁴Ge single crystals using our modified vertical Bridgman system shown in Fig.1. Prior to crystal growth, the interior of a specially designed graphite crucible (Fig.2) is coated with a $\sim 20\mu\text{m}$ thick carbon soot formed by an oxygen starved high purity butane (C_4H_{10}) flame. The soft carbon layer acts as a cushion which provides the extra space of expansion when the molten Ge solidifies. Carbon is of no concern regarding purity because it is a neutral impurity in Ge and its solubility is $\sim 10^{14}\text{cm}^{-3}$ near the melting point ²¹. The pure graphite crucible containing Ge starting material is placed inside the double-wall quartz tube. The crucible rests on the inner quartz support and the quartz tube is positioned inside a vertical furnace. A N_2 gas flows along the path shown by arrows and exits through the gas outlet valve during the heating process. Having melted the germanium inside the crucible completely, the furnace temperature is lowered slowly, and the cold gas arriving first at the bottom of the crucible creates an appropriate temperature gradient for upward single crystal growth. Again, no seed

crystal is used in order to conserve the isotopic composition of the starting materials. With this relatively simple method isotopically enriched ^{70}Ge and ^{74}Ge crystals shown in Fig.3 (~4g, 4cm in length) were grown. Both crystals contain a net residual impurity concentration of $\sim 2 \times 10^{12} \text{ cm}^{-3}$ and have a dislocation density of $10^2 \sim 10^3 \text{ cm}^{-2}$. The isotopic composition of the ^{70}Ge and ^{74}Ge enriched crystals measured by secondary ion mass spectroscopy (SIMS) is shown in Table 1. Isotopic enrichment of over 96% was found for both crystals.

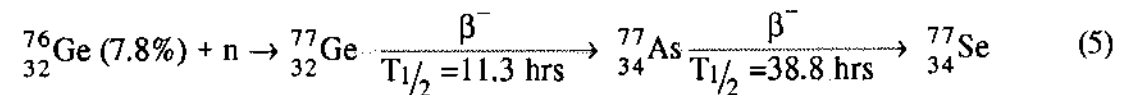
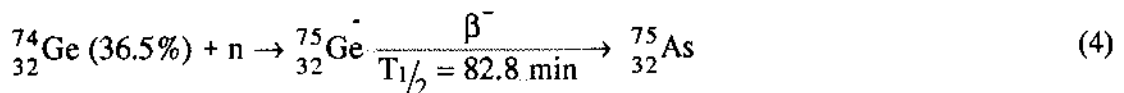
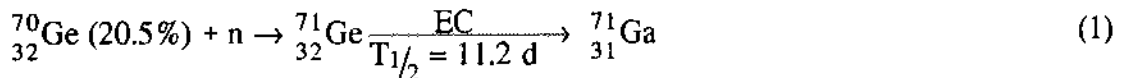
Table 1 Isotopic composition of the isotopically enriched Ge crystals

Isotopic product \ Isotope	^{70}Ge	^{72}Ge	^{73}Ge	^{74}Ge	^{76}Ge
Natural Ge	20.5%	27.4%	7.8%	36.5%	7.8%
^{74}Ge	0.5%	0.17%	2.2%	96.8%	0.33%
^{70}Ge	96.3%	2.1%	0.1%	1.2%	0.3%

3. Neutron Transmutation Doping of Isotopically Ge

Obtaining a crystal with highly uniform majority and minority impurity distributions using one of the conventional bulk doping technique is impossible. During Czochralski growth, for example, one cannot maintain a fixed concentration ratio of two or more impurities along the growth axes because of their different distribution coefficients. In addition non-uniform concentration fluctuations (called impurity striations) are caused by natural and forced convection of the melt during growth. Since crystal growth from the melt is a high temperature process during which impurities remain mobile for prolonged time, it is possible that two types of impurities with opposite charge attract each other causing further microscopic inhomogeneities.

In order to obtain semiconductor materials with extremely homogeneous dopant impurity distribution, we have developed a new technique "*neutron transmutation doping (NTD) of Isotopically engineered Ge*". We may say by far the largest affect due to isotopic composition occur in this process. Exposure of semiconductor materials to a flux of thermal neutrons may result in the transmutation of certain isotopes of the host semiconductor to other chemical species. Using the semiconductor Ge we can illustrate a number of cases. Natural Ge is composed of five stable isotopes as shown in Table 1. The reactions after neutron capture are:



Therefore, one can create random distribution of Ga, As, and Se atoms in natural Ge by irradiating thermal neutrons. This NTD technique is known to produce the most homogeneous, perfectly random dopant distribution down to the atomic level due to very small neutron capture cross sections ($\sim 10^{-24} \text{ cm}^2$) of typical semiconductor isotopes. This means most neutrons go through a sample without having any interactions, i.e., the probability for the above nuclear reactions to occur is essentially same for every lattice site in the sample. This perfectly random impurity distribution is very important for many applications and basic studies as I will show in section 4.

Ge is especially interesting semiconductor from NTD's point of view because of the rich variety of resulting transmutation products. The shallow acceptor Ga, the shallow donor As and the double donor Se form. (Two Ge isotopes simply become stable, heavier Ge isotopes.) However, if Ge containing only Ga impurities is desired then one can not apply NTD to ^{70}Ge . For this purpose one has to grow an isotopically enriched ^{70}Ge single crystal first so NTD leads to a reaction which only produces Ga (Eq.1). Similarly one has to grow a ^{74}Ge crystal for As doped Ge. Fig.4.a and b shows the Hall effect electrical characterization results performed on four NTD $^{74}\text{Ge:As}$ and two $^{70}\text{Ge:Ga}$ samples of various As and Ga concentrations, respectively^{*1}. A free carrier concentration $n(T)$ is plotted as a function of reciprocal temperatures. From this measurement, we obtain the majority concentrations N_{MJ} (i.e., [As] in $^{74}\text{Ge:As}$ and [Ga] in $^{70}\text{Ge:Ga}$) and minority impurity concentration N_{MN} (i.e., concentration of impurities whose type (p or n) is opposite to that of majority impurities) in each sample. This was done using a standard semiconductor statistics equation for Hall effect curve fitting²². The result is shown in Table 2.

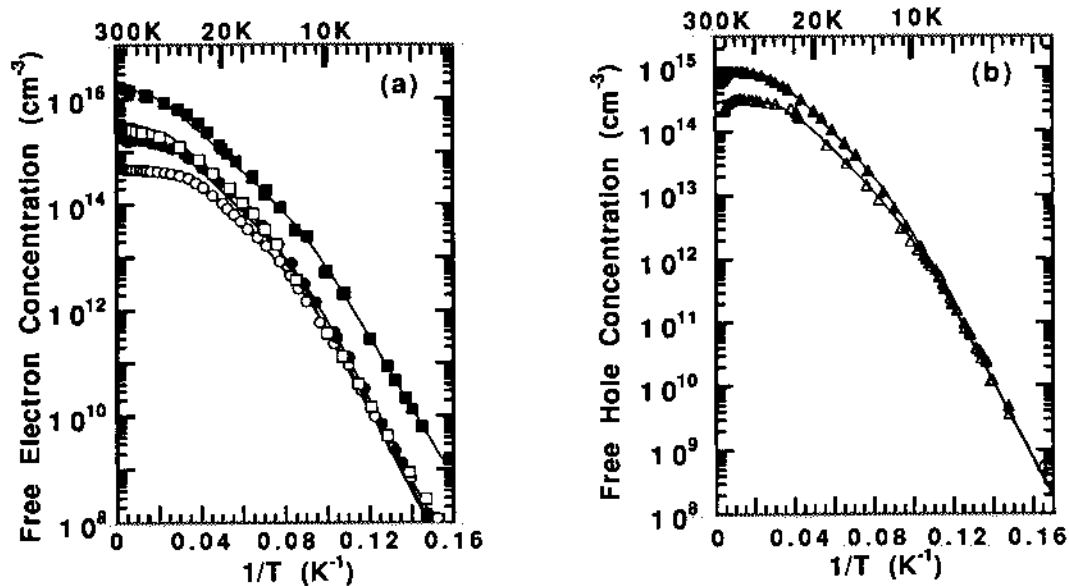


Fig.4 Temperature dependence of free carrier concentration in (a) four $^{74}\text{Ge:As}$ and (b) two $^{70}\text{Ge:Ga}$ samples: $^{74}\text{Ge:As-1}$ (O), $^{74}\text{Ge:As-2}$ (●), $^{74}\text{Ge:As-3}$ (□), $^{74}\text{Ge:As-4}$ (■), $^{70}\text{Ge:Ga-1}$ (Δ), and $^{70}\text{Ge:Ga-2}$ (▲). Solid curves are the best fits.

^{*1} The notations Ge:As and Ge:Ga are used for As and Ga doped Ge semiconductors, respectively.

Table 2 N_{MJ} and N_{MN} obtained from the Hall curve fittings

Sample	$N_{MJ} (cm^{-3})$	$N_{MN} (cm^{-3})$
$^{74}Ge:As-1$	4.5×10^{14}	2.5×10^{12}
$^{74}Ge:As-2$	1.8×10^{15}	6.0×10^{12}
$^{74}Ge:As-3$	2.9×10^{15}	2.1×10^{13}
$^{74}Ge:As-4$	1.5×10^{16}	4.2×10^{13}
$^{70}Ge:Ga-1$	3.2×10^{14}	1.0×10^{12}
$^{70}Ge:Ga-2$	8.8×10^{14}	5.1×10^{12}

Before we go on to the next section let me point out that a series of both p and n-type Ge samples with well defined compensation ([Ga] to [As] ratio) can also be generated by applying NTD to a crystal of controlled ^{70}Ge and ^{74}Ge isotopic composition (from pure ^{70}Ge to pure ^{74}Ge). This was experimentally demonstrated by us recently ²³.

4. Neutral Impurity Scattering

The neutral impurity scattering mechanism becomes important in extrinsic infrared photoconductors (Ge:Ga, Ge:Zn, Ge:Be, Ge:Cu, Si:B, etc. ^{24, 25}) that are widely used by astrophysicists ²⁶ for observation of the "infrared universe". With the ability to observe long infrared wavelengths, one can perform a detail probing of the structure and history of the universe. Because semiconductor photoconductor materials are typically nominally uncompensated and run at low temperatures ($T < 10K$), electrons moving, for example in Ge:As, are scattered by collision with an As impurity which has one loosely bound electron (just like a hydrogen atom) with the Bohr radius of 80Å. This 80Å corresponds to about 40 Ge lattice spacings so that one can imagine the high scattering efficiency of neutral As impurities. The size of the photoconductor signal is directly proportional to the electron (hole) mobility μ in Ge:As (Ge:Ga) materials ^{*2}. μ is determined by the rate of the neutral impurity scattering. Therefore, a proper understanding of neutral impurity scattering is very important for development and modeling of semiconductor photoconductors.

Theoretical research on neutral impurity scattering has been active since 1950 ²⁷⁻³¹. Following the progress of the theory, a few experimental studies probing the nature of neutral impurity scattering were published ³²⁻³⁵. However, for these experiments it was necessary to introduce adjustable parameters to obtain good agreement between the experimental results and theory. Consequently, there still exists no solid experimental verification for the theoretical models of the neutral impurity scattering rate. In the past the main experimental limitation has been the difficulty of producing appropriate samples. Reduction of the much more efficient ionized impurity scattering by minimizing the compensation is one issue. However, the most important requirement is the uniform distribution of neutral impurities (As in $^{74}Ge:As$ and Ga in $^{70}Ge:Ga$) since the standard scattering models assume a random distribution of scattering centers. These conditions are not easily achievable with standard doping techniques as I discussed in the previous section. It is obvious by now that in this work the previous difficulties in fabricating appropriate samples for such a study were overcome by using isotopically enriched germanium and the neutron transmutation doping technique. This combination guarantees

^{*2} The velocity v of electrons (holes) is given by $v = \mu E$ where E is the applied electric field. Thus μ is the measure of how fast electrons (holes) can move in n- (p-) type semiconductors.

unprecedented doping uniformity. I will show later that samples prepared in this manner are indeed necessary for the rigorous study of neutral impurity scattering.

The same samples shown in Fig.4 were used for this study. Using $n(T)$, N_{MJ} , and N_{MN} shown in Table 2, we calculate the total mobility as a function of temperature for each sample using *no adjustable parameters*. A detailed description of our calculation as well as values of non-adjustable parameters are given elsewhere³⁶. Three scattering mechanisms are included: neutral impurity, ionized impurity, and acoustic phonon deformation potential scattering. The optical phonon deformation potential scattering can be neglected since $T < 25K$. We assume that the charge transport can be described in terms of average isotropic electron (hole) effective masses.

In general the scattering rate τ^{-1} for neutral impurity scattering is given by: 27, 31

$$\tau_{\text{neutral}}^{-1} = \frac{A \kappa N_N \hbar^3}{m_H^{*2} e^2} \quad (6)$$

where κ is the dielectric constant, e is the electron charge, $N_N = N_{MJ} - N_{MN} - n(T)$ is the neutral impurity concentration, and m_H^* is the hydrogenic model effective mass scaled to the value of the shallow hydrogenic binding energy $E_B = E_{B0}(m_H^*/m_0)/\kappa^2$ where $E_{B0} = 13.6\text{eV}$ is the binding energy of hydrogen and m_0 is the electron rest mass. A theoretically calculated E_B of a perfect hydrogenic impurity without any central cell corrections should be used in this case. The differences between various models of neutral impurity scattering lie in the dependence of the function A on energy. Erginsoy proposed an energy independent $A=20$ by considering only s-wave scattering²⁷. Higher order partial wave calculations have predicted an energy dependent A ^{30, 31}. In this work the expression of A given by Meyer and Bartoli (Eq. 3.28 in Ref.31) is used to calculate the neutral impurity scattering rate.

Contributions of ionized impurity and lattice scattering are calculated with well known Brooks-Herring and deformational acoustic phonon scattering expression, respectively. The average $\langle \tau \rangle$ considering three scattering mechanisms is given by:

$$\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} \int_0^\infty x^{3/2} \exp(-x) (\tau_{\text{ac}}^{-1} + \tau_{\text{ion}}^{-1} + \tau_{\text{neutral}}^{-1})^{-1} dx, \quad (7)$$

where $x = E/k_B T$ and E is the incident electron energy. The total mobility μ_{total} is finally calculated using:

$$\mu_{\text{total}} = e \langle \tau \rangle / m_{\text{con}}^* \quad (8)$$

Fig.5 (a) and (b) show a direct comparison of our experimental results with two theoretical total mobility curves calculated from (i) Erginsoy's and (ii) Meyer and Bartoli's (MB) theories. A strikingly good agreement was obtained between the experimental and theoretical mobilities calculated with the MB model for all samples. Again our calculation uses no adjustable parameters, i.e., a direct quantitative comparison is possible. The Hall factor r_H is unity for every experimental point in Fig.5 since $\mu_B > 1$. Thus our data points should represent the drift mobility μ_d . The contribution of hopping conduction to the measured mobility is negligible because, as seen in Fig.4, there is no deviation between the experimental points and the fitted curves for all samples even at the lowest T . Also shown in Fig.5 (b) is the contribution of different scattering mechanisms to the total mobility in the $^{70}\text{Ge}:\text{Ga}$ sample with smaller Ga concentration. Mobilities in other samples with higher dopant concentration are dominated by neutral impurity scattering up to higher temperatures.

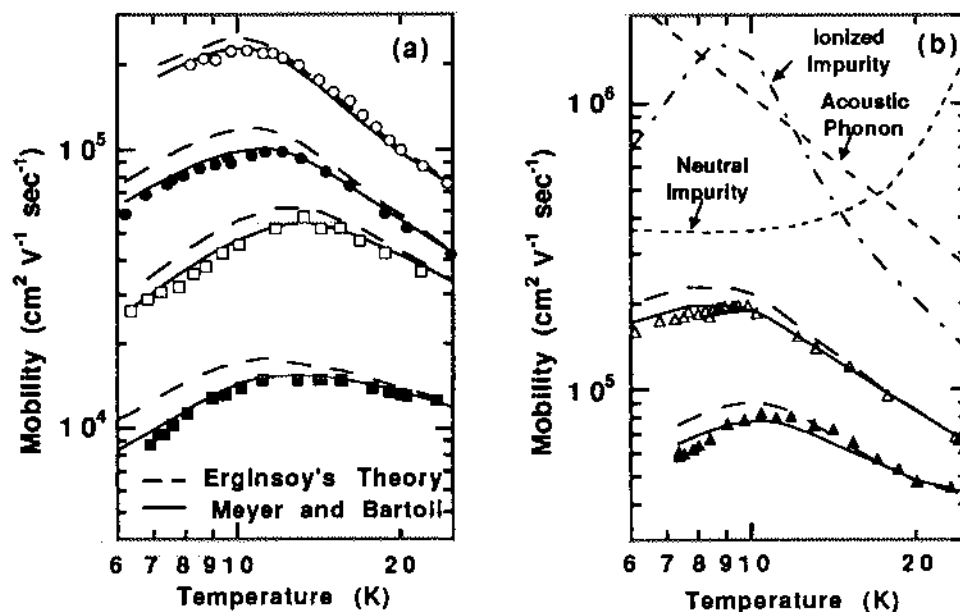


Fig. 5 Data points represent experimentally measured carrier mobility in (a) four ⁷⁴Ge:As and (b) two ⁷⁰Ge:Ga samples. Also shown are theoretically calculated mobility using Erginsoy's theory (broken line) and Meyer and Bartoli's theory (solid line). The contributions of the different scattering mechanisms to the total mobility of the high-mobility ⁷⁰Ge:Ga sample are also shown in Fig.5.(b).

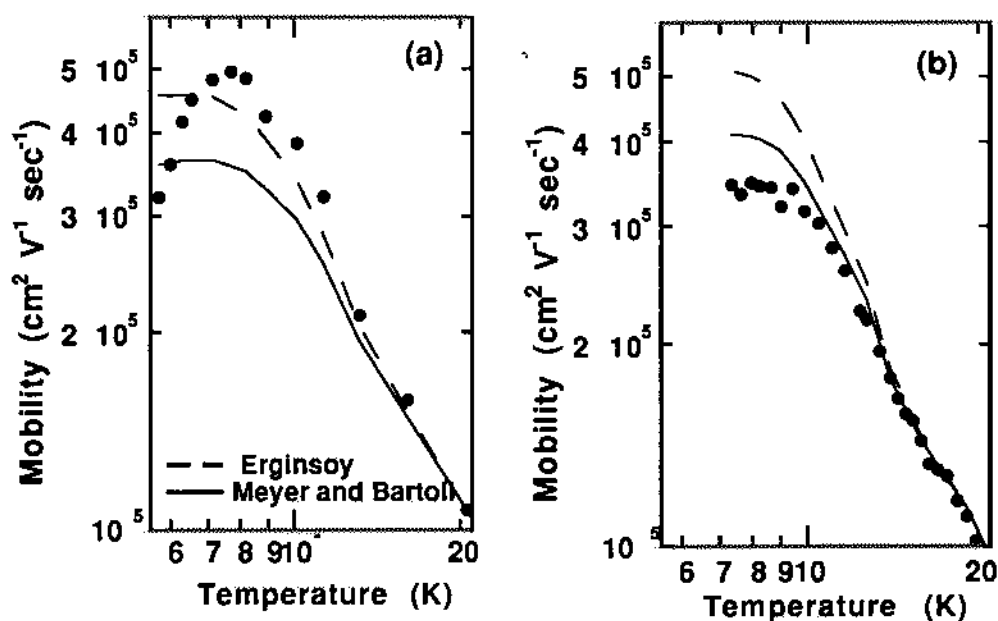


Fig.6 (a) and (b) A direct comparison of theoretically calculated mobilities to experimentally measured mobilities in two conventional Ge:Ga samples.

In order to demonstrate the importance of the homogeneous dopant distribution, we have performed the same study on samples cut from Ge:Ga crystals grown by the conventional Czochralski (Cz) method. Compared to our NTD $^{74}\text{Ge}:\text{As}$ and NTD $^{70}\text{Ge}:\text{Ga}$, we expect these samples to have less homogeneous Ga impurity distributions since Ga impurities were introduced to Ge melt during the crystal growth. We have measured four Cz-Ge:Ga samples cut from four different ingots. All samples had $[\text{Ga}] \sim 1.5 \times 10^{14} \text{cm}^{-3}$ and $N_{\text{MN}} \sim 2 \times 10^{11} \text{cm}^{-3}$. Among these four samples, mobilities of only two samples had a fair agreement with the theoretically calculated mobility. However mobilities in two other samples as shown in Fig. 6 (a) and (b) substantially deviate from the theory. These observed deviations of the measured mobility from the theoretical calculations are most likely due to inhomogeneous Ga impurity distributions in melt doped Ge. Only the use of the neutron transmutation doped semiconductors with randomly distributed dopants allows for an accurate test of the neutral impurity scattering models.

5. Conclusions

We have shown that high purity ^{70}Ge and ^{74}Ge crystals can be grown and selectively doped by NTD to form Ga and As, respectively. Using these crystals the effect of neutral impurity scattering at low temperatures was studied. Use of the Neutron Transmutation Doping technique provided the necessary dopant uniformity. We have shown that the low temperature mobility is accurately described by the phase shift based electron scattering model by the hydrogen atom scaled to hydrogenic impurities in semiconductors. Using this scattering model it is now possible to calculate the infrared detector responsivity for any semiconductor photoconductors in general.

6. Acknowledgment

This work was performed under the guidance of Professor E. E. Haller of UC Berkeley and Lawrence Berkeley Laboratory, and in collaboration with Dr. W. Walukiewicz, Dr. H. D. Fuchs, and J. W. Beeman of Lawrence Berkeley Laboratory. Professor V. I. Ozhogin of Kurchatov Institute in Russia kindly provided the isotopically enriched Ge materials. The neutron irradiation was performed by Dr. J. W. Farmer at University of Missouri Research Reactor. I would like to thank O. Dubon for many stimulating discussions. This work was supported in part by the Lawrence Berkeley Laboratory Director's Research and Development program, and in part by US NASA contract W17605 through interagency agreement with the US DOE contract DE-AC03-76SF00098. The author was supported by the US NSF Center for Particle Astrophysics ADT-8809616.

7. References

1. L. Wei, P. K. Kuo, R. L. Thomas, T. R. Anthony, and W. F. Banholzer, *Phys. Rev. Lett.* **70**, 3764 (1993).
2. L. E. Berman, J. B. Hatings, D. P. Siddons, M. Koike, V. Stojanoff, and S. Sharma, *Synchr. Rad. News.* **6**, 21 (1993).
3. A. K. Ramdas, S. Rodriguez, M. Grimsditch, T. R. Anthony, and W. F. Banholzer, *Phys. Rev. Lett.* **71**, 189 (1993).
4. H. Holloway, K. C. Hass, M. A. Tamor, and T. R. Anthony, *Phys. Rev. B*, **7123** (1991).
5. T. H. Geballe, and G. W. Hull, *Phys. Rev.* **110**, 773 (1958).
6. H. D. Fuchs, C. H. Grein, C. Thomson, M. Cardona, W. L. Hansen, K. Itoh, and E. E. Haller, *Phys. Rev. B* **43**, 4835 (1991).

7. H. D. Fuchs, C. H. Grein, R. I. Devlen, and J. Kuhl, *Phys. Rev. B* **44**, 8633 (1991).
8. H. D. Fuchs, C. H. Grein, M. Cardona, W. L. Hansen, K. Itoh, and E. E. Haller, *Sol. State Comm.* **82**, 225 (1992).
9. H. D. Fuchs, P. Etchegoin, M. Cardona, K. Itoh, and E. E. Haller, *Phys. Rev. Lett.* **70**, 1715 (1993).
10. P. Etchegoin, J. Weber, M. Cardona, W. L. Hansen, K. Itoh, and E. E. Haller, *Sol. State. Comm.* **83**, 843 (1992).
11. P. Etchegoin, H. D. Fuchs, H. Weber, M. Cardona, L. Pintschovius, K. Itoh, and E. E. Haller, *Phys. Rev. B* **48**, 12661 (1993).
12. M. Cardona, C. H. Grein, H. D. Fuchs, and S. Zollner, *J. Non-Cryst. Solid* **141**, 257 (1993).
13. M. Cardona, P. Etchegoin, H. D. Fuchs, and P. Molinas-Mata, *J. Phys. Condens. Matter* **5**, A61 (1993).
14. G. Davies, J. Hartung, V. Ozhogin, K. Itoh, W. L. Hansen, and E. E. Haller, *Semic. Sci. and Technol.* **8**, 127 (1993).
15. G. Davies, E. C. Lightowers, K. Itoh, W. L. Hansen, E. E. Haller, and V. Ozhogin, *Semic. Sci. and Technol.* **7**, 1271 (1992).
16. G. Davies, E. C. Lightowers, T. S. v. Hui, V. Ozhogin, K. M. Itoh, W. L. Hansen, and E. E. Haller, *Semic. Sci. and Technol.* **8**, 2201 (1993).
17. G. Davies, E. C. Lightowers, V. Ozhogin, K. Itoh, W. L. Hansen, and E. E. Haller, in Proc. of "The 5th Intl. Conf. on Shallow Impurities in Semiconductors", Ed. by T. Taguchis, **117 & 118** (Trans Tech Publications, Kobe, Japan, 1993), pp. 111.
18. C. Parks, A. K. Ramdas, S. Rodriguez, K. M. Itoh, and E. E. Haler, *Phys. Rev. B* **49**, 14244 (1994).
19. A. J. Mayur, M. Dean Sciacca, M. K. Udo, A. K. Ramdas, K. M. Itoh, J. Wolk, and E. E. Haler, *Phys. Rev. B* **49**, 16293 (1994).
20. K. M. Itoh, W. L. Hansen, J. W. Beeman, E. E. Haller, J. W. Farmer, and V. I. Ozhogin, *J. Low Temp. Physics* **93**, 307 (1993).
21. E. E. Haller, W. L. Hansen, P. N. Luke, R. McMurray, and B. Jarrett, *IEEE Trans. Nucl. Sci.* **NS-29**, 745 (1982).
22. J. S. Blakemore, in "Semiconductor Statistics". (Dover, New York, 1987).
23. K. M. Itoh, W. L. Hansen, J. W. Beeman, E. E. Haller, J. W. Farmer, A. Rudnev, A. Tikhomirov, and V. I. Ozhogin, *Appl. Phys. Lett.* **64**, 2121 (1994).
24. P. R. Bratt, in "Semiconductors and Semimetals", edited by R. K. Willardson, A. C. Beer, (Academic Press, New York, 1977) pp. 67.
25. E. E. Haller, *Infrared Phys. Technol.* **35**, 127 (1994).
26. S. E. Church, M. J. Griffin, P. A. R. Ade, M. C. Price, P. J. Emery, and B. M. Swinyard, *Infrared Phys.* **34**, 389 (1993).
27. C. Erginsoy, *Phys. Rev.* **79**, 1013 (1950).
28. A. L. Anselm, *Zh. Eksp. Teor. Fiz.* **24**, 85 (1953).
29. L. E. Blagosklonskaya, E. M. Gershenson, Y. P. Ladyzhinskii, and A. P. Popova, *Sov. Phys. Solid State* **11**, 2402 (1970).
30. T. C. McGill, and R. Baron, *Phys. Rev. B* **11**, 5208 (1975).
31. J. R. Meyer, and F. J. Bartoli, *Phys. Rev. B* **24**, 2089 (1981).
32. P. Norton, T. Braggins, and H. Levinstein, *Phys. Rev. B* **8**, 5632 (1973).
33. R. Baron, M. H. Young, and T. C. McGill, in Proc. of "The 13th Intl. Conf. on Physics of Semiconductors", Ed. by F. G. Fumis, (North-Holland, Rome, 1976), pp. 1158.
34. J. S. Blakemore, *Phys. Rev. B* **22**, 743 (1980).
35. J. R. Meyer, and F. J. Bartoli, *Solid State Commun.* **41**, 19 (1982).
36. K. M. Itoh, W. Walukiewicz, H. D. Fuchs, J. W. Beeman, E. E. Haller, J. W. Farmer, and V. I. Ozhogin, to be published in *Phys. Rev. B*,