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E. E. Haller

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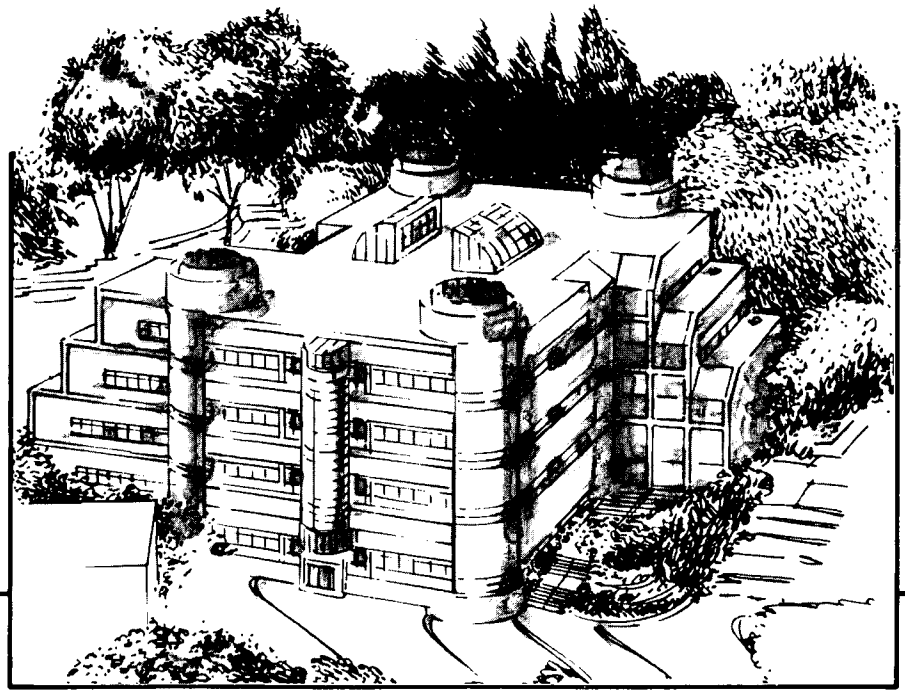

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SEMICONDUCTOR ISOTOPE ENGINEERING

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Semiconductor Isotope Engineering

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ABSTRACT

Isotopic control of semiconductor crystals offers a wide range of scientific and technical opportunities. We review neutron transmutation doping of natural and isotopically controlled semiconductor structures, special properties of isotope superlattices, the effect of host isotopes on local vibrational modes of low mass impurities, and intrinsic properties which depend on isotope mass and isotopic composition of single crystals.

I. INTRODUCTION

Two of the great achievements of modern semiconductor research and technology are ultra-purification and control of single crystal growth down to the atomic level. The control of impurities has reached an extreme for ultra-pure Ge [1] which is used for the fabrication of p-i-n diodes with fully depleted volumes of up to several hundred cubic centimeters. Such diodes are widely used in high resolution, high sensitivity gamma ray and particle spectrometers. Net-dopant levels of $\sim 10^{10}$ cm^{-3} (or less than 1 net-impurity in 10^{12} Ge atoms!) can be routinely achieved in crystals of up to 8 cm diameter and 30 cm length grown for such detector applications. Another extreme in dopant impurity control is the δ-doping technique in which a fraction of one monolayer of dopant atoms can be formed in a molecular beam epitaxy (MBE) machine. This deliberate introduction of dopants in one dimension can be extended to two and three dimensions with today's most advanced lithography tools. Indeed, the presence or absence of a single dopant atom in a zero dimensional quantum box can be determined.

We may call dopant impurity control the control of the atomic number Z in a semiconductor. What about controlling the atomic mass A, i.e., the isotopic composition of a semiconductor? One may call this semiconductor "Isotope Engineering" [2].

In this paper we will discuss the use of particular isotopes in neutron transmutation doping (NTD), the study of atomic interdiffusion with isotopically controlled superlattices, the effects of isotope control on local vibrational mode (LVM) spectra of impurities and finally, the relatively subtle but fundamentally interesting effects of isotopic composition on a number of intrinsic semiconductor properties.

II. NEUTRON TRANSMUTATION DOPING

Stable atomic nuclei have a finite absorption cross section for thermal neutrons σ_n. After capturing a thermal neutron the nucleus may undergo a number of reactions or may simply turn into another stable isotope of the particular element. Using the semiconductor Ge we can illustrate a number of cases. Natural Ge is composed of five stable isotopes. Table I shows the reactions after neutron capture. The final stable nuclei are shown in bold letters.

$$^{70}_{32}\mathrm{Ge}\ (20.5\%) + n \rightarrow {}^{71}_{32}\mathrm{Ge} \xrightarrow[T_{1/2} = 11.2\ \mathrm{d}]{\mathrm{EC}} {}^{71}_{31}\mathrm{Ga} \tag{1}$$

$$^{72}_{32}\mathrm{Ge}\ (27.4\%) + n \rightarrow {}^{73}_{32}\mathrm{Ge} \tag{2}$$

$$^{73}_{32}\mathrm{Ge}\ (7.8\%) + n \rightarrow {}^{74}_{32}\mathrm{Ge} \tag{3}$$

$$^{74}_{32}\mathrm{Ge}\ (36.5\%) + n \rightarrow {}^{75}_{32}\mathrm{Ge} \xrightarrow[T_{1/2} = 82.8\ \mathrm{min}]{\beta^-} {}^{75}_{32}\mathrm{As} \tag{4}$$

$$^{76}_{32}\mathrm{Ge}\ (7.8\%) + n \rightarrow {}^{77}_{32}\mathrm{Ge} \xrightarrow[T_{1/2} = 11.3\ \mathrm{hrs}]{\beta^-} {}^{77}_{34}\mathrm{As} \xrightarrow[T_{1/2} = 38.8\ \mathrm{hrs}]{\beta^-} {}^{77}_{34}\mathrm{Se} \tag{5}$$

Ge is especially interesting because of the rich variety of NTD products. The shallow acceptor Ga, the shallow donor As and the double donor Se form. Two Ge isotopes simply become stable, heavier Ge isotopes.

The isotopic abundances in natural Ge and the neutron capture cross sections yield p-type Ge crystals after NTD. The concentrations of Ga, As and Se are, respectively:

$$[\mathrm{Ga}] = N \cdot \sigma_n \cdot \left[{}^{70}_{32}\mathrm{Ge}\right] = N \cdot 2.94 \cdot 10^{-2}\ \mathrm{cm}^{-3} \tag{6}$$

$$[\mathrm{As}] = N \cdot \sigma_n \cdot \left[{}^{74}_{32}\mathrm{Ge}\right] = N \cdot 8.37 \cdot 10^{-3}\ \mathrm{cm}^{-3} \tag{7}$$

$$[\mathrm{Se}] = N \cdot \sigma_n \cdot \left[{}^{76}_{32}\mathrm{Ge}\right] = N \cdot 5.50 \cdot 10^{-4}\ \mathrm{cm}^{-3} \tag{8}$$

with N = neutron fluence (n/cm^2) and σ_n = thermal neutron cross section for the appropriate Ge isotope.

The compensation ratio K is:

$$K = \frac{[\mathrm{As}] + 2[\mathrm{Se}]}{[\mathrm{Ga}]} = 0.32 \tag{9}$$

The Se concentration is doubled because Se is a double donor. The value of K can vary depending on the neutron velocity distribution to which the crystal is exposed. If the same irradiation site and the same power of a nuclear reactor are chosen for NTD one can expect highly reproducible results. Ge has been doped with thermal neutrons already some thirty years ago by Fritzsche [3] who recognized the advantages of the inherent homogeneity of the dopant distribution generated by NTD. The large neutron field produced by a nuclear reactor, the small absorption cross section for neutrons minimizing "self-shadowing" and the perfect random distribution of the stable isotopes lead to a truly random dopant distribution.

In recent years we have used extensively the NTD technique to obtain Ge crystals with a wide range of doping concentrations. Small chips of these crystals (typically ~(0.5 mm)^3) are

used as thermistors for bolometric detection of far infrared and submillimeter radiation [4]. Astronomy, astrophysics and dark matter search experiments currently under construction are the biggest users of these low temperature sensors. Figure 1 shows the logarithm of the resistivity ρ of ten selected NTD Ge crystals as a function of $T^{-1/2}$. Table I contains information on each of the NTD Ge samples. The linear dependence is characteristic for the variable range hopping conduction regime. Note that practically any value of resistivity between a few Ωcm and

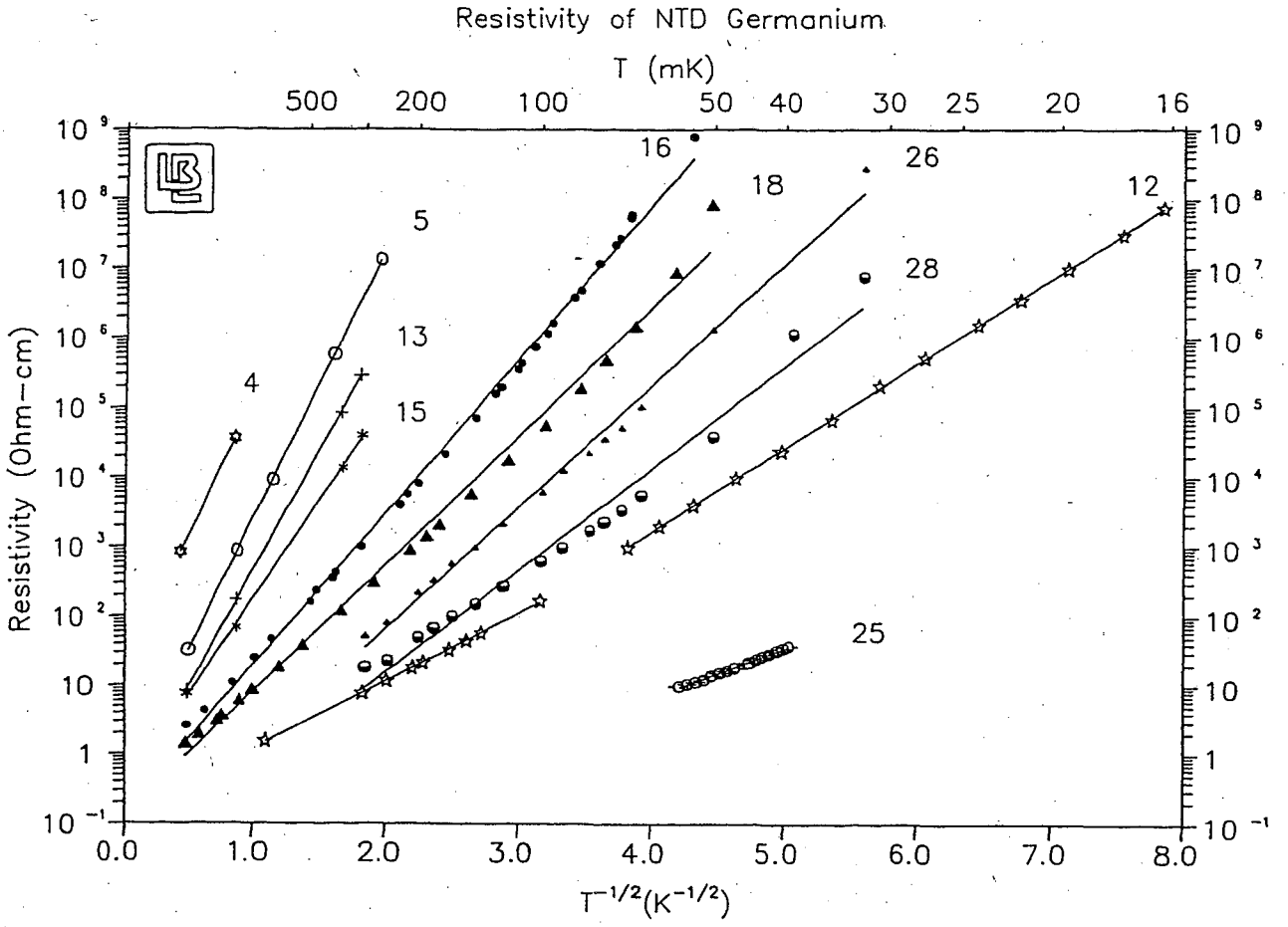


Figure 1. A plot of the logarithm of ten selected NTG Ge samples as a function of $T^{-1/2}$. The linear dependence indicates variable range hopping conduction.Table I contains the neutron fluence and the various dopant concentrations for each sample (compiled by J. Beeman, Lawrence Berkeley Laboratory).

Table I. NTD Ge thermistor data

NTD#	n Dose (cm^{-2})	N_{Ga} (cm^{-3})	N_{As} (cm^{-3})	N_{Se} (cm^{-3})	$N_{Ga} - \Sigma N_D$ (cm^{-3})
4	3.38E+17	9.94E+15	2.83E+15	1.86E+14	6.74E+15
5	7.50E+17	2.21E+16	6.29E+15	4.13E+14	1.50E+16
13	1.24E+18	3.65E+16	1.04E+16	6.83E+14	2.47E+16
15	1.54E+18	4.53E+16	1.29E+16	8.49E+14	3.07E+16
16	2.07E+18	6.09E+16	1.73E+16	1.14E+15	4.13E+16
18	2.61E+18	7.67E+16	2.19E+16	1.44E+15	5.20E+16
26	2.82E+18	8.29E+16	2.36E+16	1.55E+15	5.62E+16
28	3.07E+18	9.03E+16	2.57E+16	1.69E+15	6.11E+16
12	3.33E+18	9.79E+16	2.79E+16	1.83E+15	6.64E+16
25	4.20E+18	1.23E+17	3.52E+16	2.31E+15	8.37E+16

10^9 Ωcm at any temperature between 15 mK and 4K can be engineered with NTD. Shklovskii and Efros [5] have developed a theory for this kind of carrier transport which leads to

$$\rho = \rho_o \exp\left(\Delta/T\right)^{1/2}. \tag{10}$$

ρ_o and Δ are constants.

Equation (10) differs from Mott's earlier equation only in the exponent. Mott obtained $T^{-1/4}$ instead of $T^{-1/2}$ for the temperature exponent with his simple and elegant deviation of hopping conduction. Shklovskii and Efros introduced the density of states gap at the Fermi level which in turn led to the new exponent of $-1/2$.

With natural Ge the compensation K is fixed to the value given in equation (9). Only changing the isotopic composition allows a change in K. Using Ge single crystals of pure and deliberately mixed isotopes we have started a systematic study of the dependence of the constants ρ_o and Δ on K. We can investigate n- and p-type crystals with K ranging from 0.01 to 0.95. The temperature exponent may change from $-1/2$ to -1 below a certain temperature for very heavily doped crystals as it was observed in Si:B [6]. An interesting experiment with ^{76}Ge crystals doped with Se by NTD has been proposed by Grimmeiss [7]. The study of the double donor Se in Ge is of importance for the broader understanding of chalcogenide donors in Si and Ge. Conventional doping techniques during crystal growth and with diffusion have encountered difficulties insofar as only a small fraction of the Se introduced in the crystal is electrically active. Using NTD and isotopically pure Ge one can introduce a precise concentration of Se. During the short annealing cycle at moderate temperature the Se is not expected to move more than by a few lattice constants. Preliminary data show several Se related peaks in deep level transient spectroscopy (DLTS) measurements [8].

Technically the most important application of NTD is found for Si. Most high power, high voltage rectifiers are fabricated with NTD Si [9]. Natural Si consists of three isotopes: $^{28}_{14}$Si (92.3%), $^{29}_{14}$Si (4.7%), and $^{30}_{14}$Si (3.1%). The heaviest Si isotopes transmutes into P via β^- decay:

$$^{30}_{14}\mathrm{Si} + n \rightarrow {}^{31}_{14}\mathrm{Si} \xrightarrow[T_{1/2} = 2.62\ \mathrm{hrs}]{\beta^-} {}^{31}_{15}\mathrm{P} \tag{11}$$

The small isotopic abundance of $^{30}_{14}$Si and secondary NTD transmuting $^{31}_{15}$P into $^{32}_{16}$Se limit practical P doping levels to a few times 10^{15} cm^{-3}. Enrichment of natural Si with $^{30}_{14}$Si would allow an increase in this limit. Unfortunately, the costs for implementing this on a technical production scale is still prohibitive.

Not only Si and Ge but practically every semiconductor can be doped with neutron transmutation. For example, all three isotopes in GaAs $\left(^{69}_{31}\mathrm{Ga}, {}^{71}_{31}\mathrm{Ga}\right.$ and $\left.^{75}_{33}\mathrm{As}\right)$ transmute into shallow donor dopants. The neutron capture cross sections for the two Ga isotopes differ by a factor of close to three. The donor concentrations in a GaAs isotope superlattice $\left(^{69}_{31}\mathrm{GaAs} : {}^{71}_{31}\mathrm{GaAs}\right)$ doped by NTD would differ by this same factor. Another example is the wide bandgap ZnSe which is attracting a lot of interest in the context of the worldwide effort to develop a reliable blue light emitting diode or laser. The isotopes of Zn form Cu and Ga while the isotopes of Se lead to As and Br. We foresee interesting NTD studies of this semiconductor, especially when the isotopic composition is controlled such that only a limited number of transmutation products are generated.

These four examples of semiconductor NTD serve to illustrate the almost unlimited possibilities offered by this doping technique when combined with isotope control. Table II lists a few of the isotopes of interest for semiconductors with their thermal neutron capture cross sections and their neutron transmutation products.

Table II. (All data are from Ref. 10)

Isotope	Abundance (%)	Thermal neutron capture Cross section (10^{-24} cm^2)	Neutron transmutation product
$^{10}_{5}B$	19.8	3838 (n,α) 0.52	$^{7}_{3}Li + ^{4}_{2}He$ $^{11}_{5}B$
$^{11}_{5}B$	80.2	0.005	$^{12}_{6}C$
$^{12}_{6}B$	98.89	0.0034	$^{13}_{6}C$
$^{13}_{6}C$	1.11	9×10^{-4}	$^{14}_{7}N$
$^{14}_{7}N$	99.63	0.076	$^{15}_{7}N$
$^{15}_{7}N$	0.37	4×10^{-5}	$^{16}_{8}O$
$^{16}_{8}O$	99.76	1.78×10^{-4}	$^{17}_{8}O$
$^{17}_{8}O$	0.038	0.235 (n,α)	$^{14}_{6}C + ^{4}_{2}He \rightarrow ^{14}_{7}N$
$^{18}_{8}O$	0.204	1.58×10^{-4}	$^{19}_{9}F$
$^{27}_{13}Al$	100	0.231	$^{28}_{14}Si$
$^{28}_{14}Si$	92.23	0.17	$^{29}_{14}Si$
$^{29}_{14}Si$	4.67	0.10	$^{30}_{14}Si$
$^{30}_{14}Si$	3.10	0.11	$^{31}_{15}P$
$^{31}_{15}P$	100	0.18	$^{32}_{16}S$
$^{32}_{16}S$	95.02	0.53	$^{33}_{16}S$
$^{33}_{16}S$	0.75	0.095 (n,α)	$^{30}_{14}Si + ^{4}_{2}He$
$^{34}_{16}S$	4.21	0.24	$^{35}_{17}Cl$
$^{36}_{16}S$	0.017	0.15	$^{37}_{17}Cl$
$^{64}_{30}Zn$	48.6	0.78	$^{65}_{29}Cu$
$^{66}_{30}Zn$	29.7	1.0	$^{67}_{30}Zn$
$^{67}_{30}Zn$	4.1	7.0	$^{68}_{30}Zn$
$^{68}_{30}Zn$	18.8	0.88	$^{69}_{31}Ga$
$^{70}_{30}Zn$	0.62	0.098	$^{71}_{31}Ga$
$^{69}_{31}Ga$	60.1	1.7	$^{70}_{30}Zn$ (0.2%) $^{70}_{32}Ge$ (99.8%)
$^{71}_{31}Ga$	39.9	4.7	$^{72}_{32}Ge$
$^{70}_{32}Ge$	20.5	3.25	$^{71}_{31}Ga$
$^{72}_{32}Ge$	27.4	1.0	$^{73}_{32}Ge$

$^{73}_{32}Ge$	7.8	15.0	$^{74}_{32}Ge$
$^{74}_{32}Ge$	36.5	0.36	$^{75}_{33}As$
$^{76}_{32}Ge$	7.8	0.16	$^{76}_{34}Se$

III. ISOTOPE SUPERLATTICES

The growth of Ge isotope superlattices has been proposed recently [11]. Superlattices consisting of pure, undoped $^{70}_{32}Ge$ and $^{74}_{32}Ge$ layers can be doped with NTD yielding p-n-p-n structures. Insertion of $^{72}_{32}Ge$ or $^{73}_{32}Ge$ layers which do not get doped by neutron capture would produce n-i-p-i structures. The separation of the growth process from the doping process offers a number of advantages. First, the growth of pure undoped layers will not be affected by dopant promoted interdiffusion. Second, the dopant concentration can be chosen very precisely with NTD and the same sample can, in principle, be doped several times to ever higher concentrations. Undoped short period isotope superlattices offer interesting phonon physics. Brillouin zone folding is expected to modify significantly the phonon dispersion relationships. An interesting diffusion study has recently been conducted with $^{69}_{31}Ga^{75}_{33}As : ^{71}_{31}Ga^{75}_{33}As$ superlattices [12]. The aim was to determine the Ga self-diffusion coefficient in GaAs through isotope disordering reactions. The MBE grown structure was analyzed with secondary ion mass spectrometry (SIMS). Figure 2 shows the normalized $^{69}_{31}Ga$ and $^{71}_{31}Ga$ profiles for the as-grown structure and after annealing for 10 hrs at 900°C. Interdiffusion is evident from the strongly rounded profile contours. It is unfortunate that the results of this study were apparently strongly affected by the heavily Si-doped substrate on which the isotope layers were grown. Donor promoted out-diffusion of Ga vacancies form the substrate into the superlattice led to a Ga self-diffusion enthalpy of 4 eV, which seems to be too low by ~2 eV when compared to earlier studies.

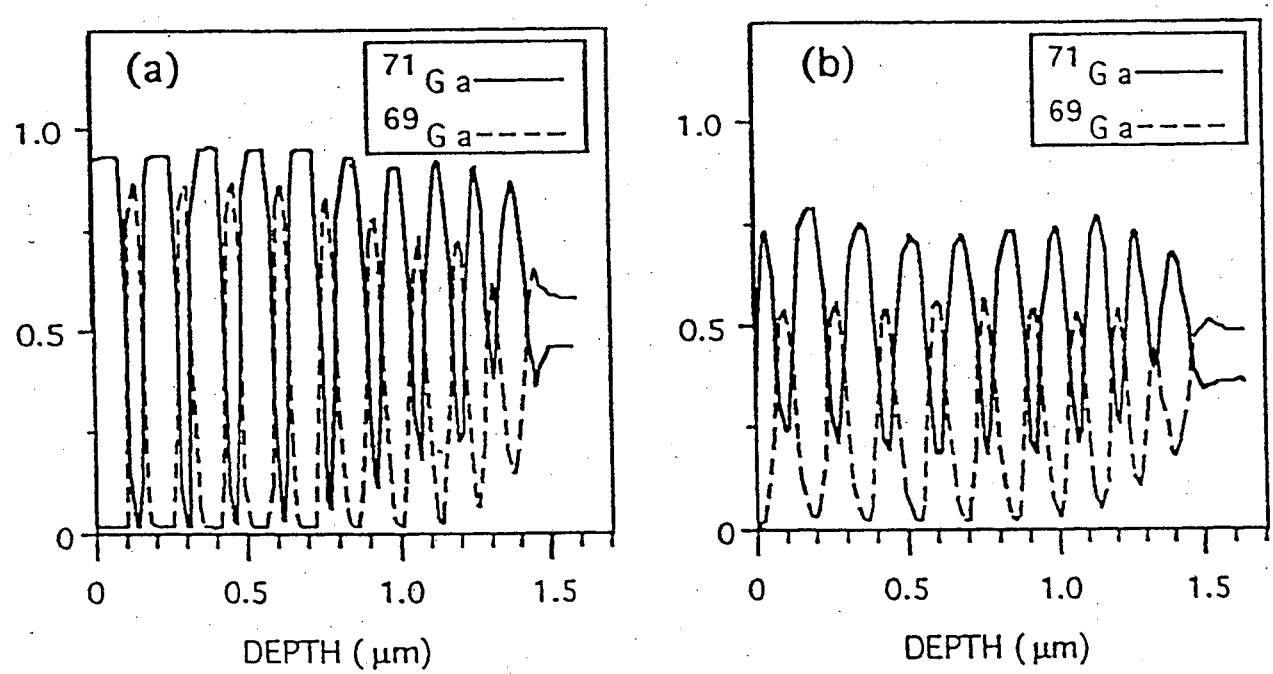


Fig. 2. Normalized $^{69}_{31}Ga$ and $^{71}_{31}Ga$ profiles measured by SIMS. (a) An as-grown sample, and (b) a sample annealed at 900°C for 10 hrs. Vertical axes denote relative fractions. (Courtesy Tan *et al.*, Ref. 12)

Isotope superlattices hold promise for a large variety of studies. Because of the very small quantities of isotopes used for the growth of such structures, the rather large costs of pure stable isotopes will not be a severe handicap for these kinds of experiments. MBE effusion cells with small volumes in the cm^3 range are already commercially available.

IV. LOCAL VIBRATIONAL MODE SPECTROSCOPY (LVM)

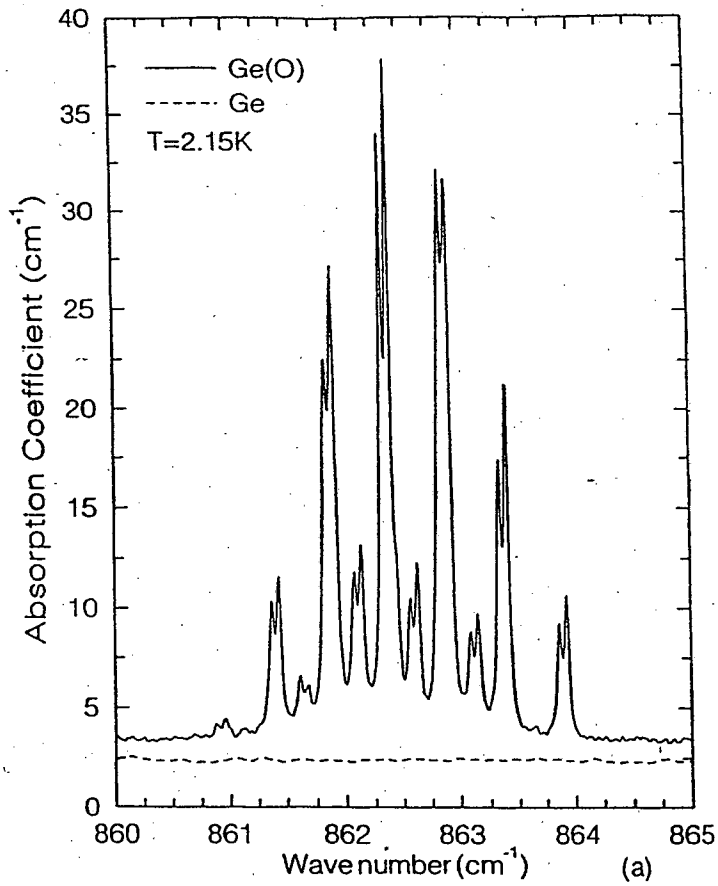
The vibrational frequency of a light impurity in a semiconductor host lattice is affected by the masses of the atoms to which it is bound. High resolution infrared spectroscopy, conducted with samples cooled to low temperatures, has generated ample data of many different impurities in various crystals showing this mass dependence. Typical examples are the LVM studies of oxygen in silicon [13] and germanium [14], and carbon in GaAs [15]. The latter case is especially noteworthy since it offered unambiguous proof of the lattice location of substitutional carbon. Since As is monoisotopic, one would expect no isotope related multiple lines if carbon sat on a Ga site (C_{Ga}) surrounded by four As atoms. The multicomponent carbon LVM line clearly showed that C does not occupy a Ga site. There are five distinctly different isotope mass combinations of $^{69}_{31}Ga$ and $^{71}_{31}Ga$ for C_{As}. Together with the different vibrational modes of a XY_4-like molecule one expects a maximum of 9 lines [16]. So far, five closely spaced lines have been resolved. It would be of great interest to study the LVM spectrum of C_{As} in GaAs with only one Ga isotope. This would allow the clear separation of the isotope effects from the fundamental vibrational mode spectrum of the C Ga_4 pseudo molecule.

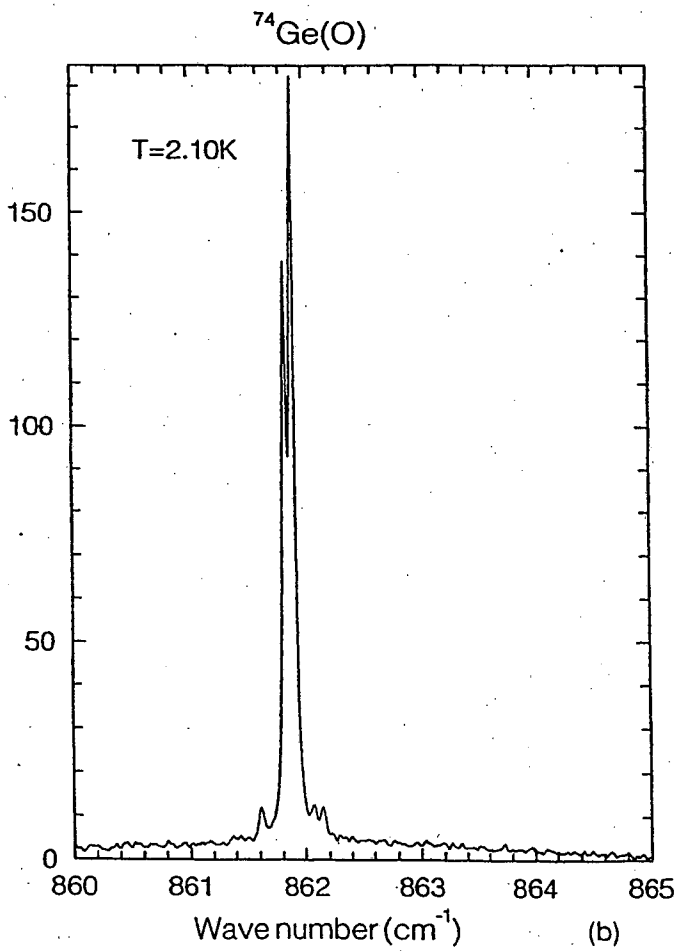
The effect of isotope control on LVM spectra has been demonstrated very effectively with oxygen in germanium [17]. Oxygen occupies a bond centered interstitial position and is bound to two neighbors. In natural germanium, with five different isotopes, one finds eleven relevant different mass combinations taking into account that only different mass averages of the two Ge neighbors lead to different LVM frequencies of the oxygen (i.e., the combinations ^{76}Ge-O-^{70}Ge, ^{74}Ge-O-^{72}Ge and ^{73}Ge-O-^{73}Ge give identical LVM frequencies). Figure 3 shows the LVM spectrum of oxygen in a natural and in a highly enriched ^{74}Ge single crystal. The simplification of the spectrum in the isotopically controlled crystal is most remarkable and it allows for an unambiguous assignment of the lines in the crystal of natural isotope composition. This is especially useful for the line components created by isotope combinations which are rare because of low isotopic abundance (e.g. ^{76}Ge-O-^{76}Ge). Detailed studies of the temperature dependence of the oxygen LVM spectra in isotopically pure Ge crystals of four of the five stable isotopes are currently in progress [18] at our laboratory in collaboration with Professor A.K. Ramdas' group at Purdue University.

It is worthwhile to point out the difference in using different pure isotopes of a particular impurity which should be studied by LVM spectroscopy versus controlling the isotopic composition of the host crystal. The former allows the unambiguous assignment of LVM lines to a specific impurity via the isotope shift in the LVM frequency ω which is inversely proportional to the square root of the impurity mass ($\omega \propto 1/\sqrt{A}$). The latter allows the identification of the impurity lattice location, of course only if there is more than one stable isotope of the host lattice available for such a study.

V. ISOTOPE MASS DEPENDENT INTRINSIC PROPERTIES OF SEMICONDUCTORS

One of the most important properties of a semiconductor is the energy of the bandgap. Recently Davies *et al.* [19] used photoluminescence to determine the indirect gap energy E_I in natural and four isotopically enriched, chemically pure Ge crystals. The deliberate introduction of small concentrations of copper led to strong no-phonon (NP) lines of copper bound excitons (figure 4). This in turn allowed a phonon independent, direct determination of the change in bandgap energy with the host isotope mass. In these studies it was assumed that the exciton binding energy was not Ge isotope dependent. This assumption is strongly supported by the following experimental findings: the energy of the NP lines of excitons bound to different dopant impurities show exactly the same Ge isotope mass dependence and the hydrogenic energy state series of bound exciton states tracked for different host isotopes. This latter finding indicates that the effective mass is not measurably affected by the host isotope mass.





The indirect gap E_I was found to move linearly to higher energy with increasing isotope mass:

$$dE_I/dA = 0.35 \pm 0.02 \text{ meV} \quad (12)$$

Electron-phonon coupling and, to a lesser degree, the isotope dependence of the lattice constant cause the bandgap increase. Accurate experimental data exist for Ge which allow a good estimate of both contributions. The lattice constant dependent term or volume term, is found to be $(dE_I/dA)_V = 0.044$ meV. The electron-phonon term is estimated by using a simple harmonic oscillator to find the mean-square displacement $\langle u^2 \rangle$ of each atom. At low temperatures

$$\langle u^2 \rangle \propto 1/\sqrt{A} \quad (13)$$

Together with the experimentally determined temperature dependence of the bandgap energy one finds:

$$0.22 \text{ meV} < (dE/dA)_{e\text{-}ph} < 0.30 \text{ meV} \quad (14)$$

The total isotope induced shift is

$$0.26 \text{ meV} < (dE/dA)_{total} < 0.34 \text{ meV} \quad (15)$$

in rather good agreement with the experimental value. A recent first principle calculation predicts $(dE/dA)_{e\text{-}ph} = 0.42$ meV [20].

Phonon energies depend directly on the isotope mass of a crystal. Besides the obvious dependence on $1/\sqrt{A}$, one expects isotope disorder related effects. In order to maximize such effects, we have grown single crystals of pure isotopes of Ge and of isotope mixtures containing equal concentrations of ^{70}Ge and ^{76}Ge [21]. Fuchs *et al.* [22] studied these crystals with Raman spectroscopy. In the isotopically pure ^{70}Ge crystal a single line due to the TO phonon at k=0 appears. In a natural Ge crystal and more strongly in the isotopically mixed crystal band modes appear at energies below E_{T0} with k>0 (figure 5). The spectra are well described by calculations based on coherent potential approximation.

Figure 3. a) LVM spectrum of oxygen in natural Ge; b) as in a) but in a ^{74}Ge crystal enriched to 96%.

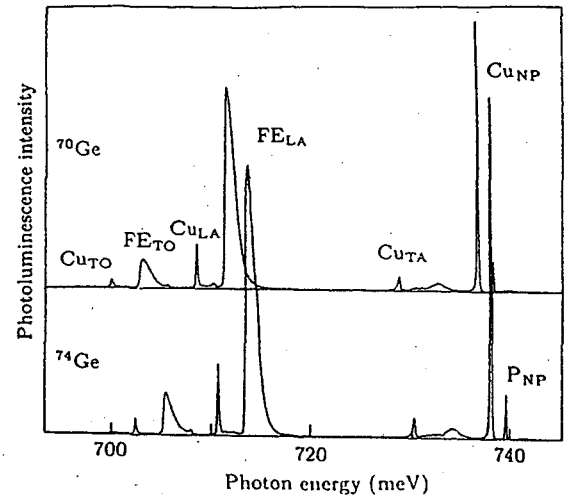


Figure 4. Luminescence from the decay of free excitons (FE) and excitons bound to Cu triple acceptors and P donors in ^{70}Ge and ^{74}Ge at 4.2 K. The subscripts indicate the L-point phonons involved in each transition. (Courtesy Gordon Davies *et al.*, Ref. 19)

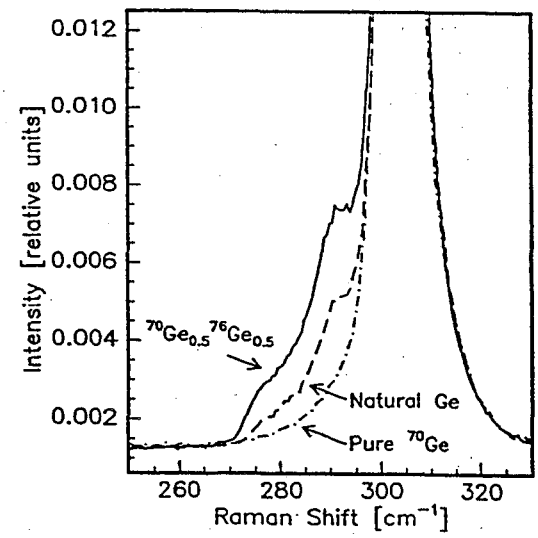


Figure 5. Raman spectra of isotopically pure ^{70}Ge, natural Ge, and $^{70}Ge_{0.5}$ showing the main Raman line at 304.5 cm^{-1} (off scale) and the isotopic disorder-induced band modes at 80 K. The spectrum of ^{70}Ge is shifted in energy for comparison. (Courtesy Fuchs *et al.* [22])

VI. SUMMARY AND OUTLOOK

Whereas the control of impurities (Z control) has been developed and practiced from the earliest beginnings of systematic semiconductor studies, very little attention has been given to controlling the isotopic composition (A control). In part this may be due to the difficulties and costs involved in obtaining sizable quantities of pure, stable isotopes. This situation appears to change rapidly with the opening of markets in the former Soviet Union. There may exist an interest to devote a part of the existing isotope separation capabilities to semiconductors if a real need for separated stable isotopes develops.

The experiments and data described in this paper show the broad range of possibilities offered by semiconductor isotope engineering. It is now up to researchers and technologists to make use of the vast opportunities. We expect to see a steadily increasing interest in isotopically engineered semiconductor structures and we hope that new and exciting semiconductor physics and technology (i.e., devices) will emerge.

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have grown most of the isotopically controlled Ge single crystals. The experiments described in section V were made possible through collaborations with G. Davies and E. Lightowlers at King's College, London, and M. Cardona and his group at the Max-Planck-Institute in Stuttgart. The isotope related work was supported in part by the Laboratory Directed Research and Development Program of the Lawrence Berkeley Laboratory, in part by NASA contract W17605 through interagency agreement with the US Department of Energy Contract DE-AC03-76SF00098, and by the US National Science Foundation through the Center for Particle Astrophysics at UC Berkeley under contract ADT-8809616.

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