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# Isotopically Controlled Semiconductors

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## Abstract

The following article is an edited transcript based on the Turnbull Lecture given by Eugene E. Haller at the 2005 Materials Research Society Fall Meeting in Boston on November 29, 2005. The David Turnbull Lectureship is awarded to recognize the career of a scientist who has made outstanding contributions to understanding materials phenomena and properties through research, writing, and lecturing, as exemplified by the life work of David Turnbull. Haller was named the 2005 David Turnbull Lecturer for his “pioneering achievements and leadership in establishing the field of isotopically engineered semiconductors; for outstanding contributions to materials growth, doping and diffusion; and for excellence in lecturing, writing, and fostering international collaborations.”

The scientific interest, increased availability, and technological promise of highly enriched isotopes have led to a sharp rise in the number of experimental and theoretical studies with isotopically controlled semiconductor crystals. This article reviews results obtained with isotopically controlled semiconductor bulk and thin-film heterostructures. Isotopic composition affects several properties such as phonon energies, band structure, and lattice constant in subtle, but, for their physical understanding, significant ways. Large isotope-related effects are observed for thermal conductivity in local vibrational modes of impurities and after neutron transmutation doping. Spectacularly sharp photoluminescence lines have been observed in ultrapure, isotopically enriched silicon crystals. Isotope multilayer structures are especially well suited for simultaneous self- and dopant-diffusion studies. The absence of any chemical, mechanical, or electrical driving forces makes possible the study of an ideal random-walk problem. Isotopically controlled semiconductors may find applications in quantum computing, nanoscience, and spintronics.

*Keywords: diffusion, dopant, Ge, semiconductor, Si, spintronic, thermal conductivity.*

## Introduction

I would like to thank the Materials Research Society for choosing me as the Turnbull Lecturer and for making this meeting a very special one for me. I would also like to thank my colleagues, who encouraged my choice of isotopically controlled semiconductors as the subject of this talk.

First, I will discuss stable isotopes, describing their discovery and history. Then I will talk about thermal conductivity and phonon physics. My next topic will be the selective neutron transmutation doping (NTD) of isotopes, which has always held a special interest for me. Next I will discuss self-diffusion in isotope multilayers and superlattices, and finally local vibrational mode spectroscopy of O in Ge.

I hope that this presentation will stimulate some of you to think about using isotopes in your research. I would like to communicate some of my interest in and enthusiasm for isotopes not only because they are available and have become relatively affordable, but also because they are eminently suitable for many types of research, especially for thin-film semiconductor studies.

Among the excellent researchers I have collaborated with on isotopically controlled semiconductors, I wish to point out one person in particular: Valerii Ozhogin of The Russian Research Centre Kurchatov Institute in Moscow. Ozhogin “primed the pump” for this critical research by providing me with 100 g each of isotopically enriched  $^{70}\text{Ge}$  and isotopically enriched  $^{74}\text{Ge}$ . The transfer of this material happened around 1990 through a colleague of mine who, before a visit to the Kurchatov, asked me how much Ge I would need to accomplish “something useful.” The colleague hesitated at asking for 100 g because just a milligram of this isotopically enriched material cost about \$5, making 100 g worth \$500,000! I encouraged him to ask anyway and, in return, received 100 g each of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  powder, which Ozhogin had measured into small brown glass bottles. When this material arrived at my office at the University of California at Berkeley—\$1,000,000 worth of isotopically enriched Ge—I was overwhelmed. That is what I call “priming the pump.”

## **Stable Isotopes**

My talk here will be limited to stable isotopes, not radioactive isotopes. Francis William Aston, won the Nobel Prize in Chemistry “for his discovery, by means of his mass spectrograph, of isotopes, in a large number of nonradioactive elements...” Aston, the discoverer of stable isotopes, identified about 200 of them.

## ***Isotope Separation***

Isotope separation is an expensive, high-tech process. One of the ways to separate isotopes is by a centrifuge-based technology. It was developed for the Soviet Union by German scientist Gernot Zippe. Zippe was captured by the Soviets during World War II and kept as a prisoner-of-war until the mid-1950s.

With a separation plant that contains enough centrifuges, researchers can enrich molecules that exist in a gaseous form at room temperatures. In other words, Ge isotopes can be separated from natural  $\text{GeF}_4$ , Si isotopes can be separated from  $\text{SiF}_4$ , and so forth. Whatever can be converted into gaseous form can be separated into its isotopes in a centrifuge. The major cost is essentially energy. In Russia, where centrifuge technology was preferred for isotope separation, energy is abundant in Siberia. A good article on centrifuge physics, by my colleague Don Olander, can be found in the August 1978 issue of *Scientific American* (*Sci. American* **239**, pp 37-43).

For Western science, an interesting facet of the Russian isotope separation story began right before the end of the Cold War. This story helps to explain how Valerii Ozhogin was able to supply us with isotopically enriched Ge. In the 1980s, the former Soviet Union produced great amounts of fissionable materials for making weapons. It is estimated that there were about 200,000 isotope separation experts active in the Soviet Union at that time. About then, however, they had begun to suspect that the Soviet empire would not last too much longer and were seeking ways to “capitalize on” some of their excess isotope separation activity. Since the Soviets were against laying off workers, as is done in the West, they needed to find a way to keep all of these experts busy. Based on the fact that separated isotopes are extremely expensive, they devised a plan to build up a large supply of these isotopes for later resale. Then, when the Cold War ended, they would have a valuable resource to market to the West. They began separating a large number of isotopes of the whole table of elements.

After the Cold War had ended and Ozhogin had primed the pump for our efforts with the initial supply of Ge, I approached him about obtaining a much larger quantity of isotopically enriched material. We spent some time negotiating a price, which even when deeply “discounted,” was in the millions of dollars and completely unrealistic for us. At that point, Ozhogin and I decided to strike a bargain. We would work together, using Western technology for purification, crystal growth, and characterization, and Soviet technology for isotope separation. In that way, Ozhogin was able to provide us with the Ge. I can clearly recall the day he walked into my office carrying two manila envelopes, one containing about 750 g of  $^{70}\text{Ge}$  and the other about 650 g of  $^{74}\text{Ge}$ , in oxide form. A little later, I will describe what we did with this material.

### *Stable Isotopes of Semiconductor Elements*

The isotope table shows that Si, still today the most important semiconductor, has three stable isotopes:  $^{28}\text{Si}$  at 92.2%,  $^{29}\text{Si}$  at 4.7%, and  $^{30}\text{Si}$  at 3.1%. An awareness of the existence of these isotopes can raise an interesting question—how will they affect future computers? For example, quantum computing could make good use of the nuclear spin of  $^{29}\text{Si}$ , and there are efforts underway to do exactly that—to embed  $^{29}\text{Si}$  in specific places in a  $^{28}\text{Si}$  matrix. The concept of using nuclear spins to enable quantum computing may be a good one (Ref. 1).

Bathing these isotopes in thermal neutrons, which are available in copious quantities in any nuclear reactor, results in these isotopes absorbing one neutron each and shifting one slot to the right in the table of isotopes.  $^{28}\text{Si}$  is transformed into  $^{29}\text{Si}$ ,  $^{29}\text{Si}$  becomes  $^{30}\text{Si}$ , and  $^{30}\text{Si}$  becomes  $^{31}\text{Si}$ .  $^{31}\text{Si}$  is not stable, so I must make an exception by discussing radioactivity for a moment.  $^{31}\text{Si}$  decays with a half-life of 2.6 hours, with  $\beta^-$  decay into  $^{31}\text{P}$ . Today several hundred tons of Si are doped with P by this neutron transmutation doping process for applications of high-voltage rectifiers and silicon controlled rectifiers (SCRs).

Another interesting fact is that the neighbor elements of Si—Al and P—have only one stable isotope. The isotope  $^{27}\text{Al}$  is nature’s only stable Al isotope. We seldom think about how much is accomplished with that one Al isotope—for example, as the primary construction material of the airplanes that brought us to Boston. About 20% of all the

elements in nature consist of only one stable isotope, including, for example, Au. The other 80% of elements have multi-isotopic compositions.

The next most important semiconductor element, Ge, has been rediscovered in recent years. Ge has five stable isotopes:  $^{70}\text{Ge}$ ,  $^{72}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$ , and  $^{76}\text{Ge}$ . GaAs, most important for optoelectronics, consists of two isotopes of Ga,  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  plus  $^{75}\text{As}$ , which is monoisotopic. All these isotopes can be separated in centrifuges after converting them into gaseous fluorides.

### *Single-Crystals of Ge and Si*

Using the supply of Ge given to us by Ozhogin, we grew one single crystal each of 95% enriched, ultrapure  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  (Fig. 1). As part of our agreement, I gave Ozhogin the top two-thirds of each crystal to use in the Soviet Union, while keeping the rest for our collaborative research. These crystals are worth about \$4 million and \$3.5 million respectively. They are probably the only crystals in the world that are composed of one isotopically enriched element and are ultrapure (Ref. 2).



Fig. 1. Photograph of 95% enriched, ultrapure Ge single crystals. The ruler is 150 mm long.

Producing crystals of Si was much more laborious and difficult. Si has a melting point of  $1420^{\circ}\text{C}$ , about  $500^{\circ}\text{C}$  higher than the melting point of Ge. Since we did not have a crystal growth system for bulk Si, we needed to seek help. We looked first to the Si industry, but were not successful there. Because we had only a few hundred grams of material and their machinery was scaled for handling much larger amounts—say, hundreds of kg—they were unable to process our Si.

We accomplished our task by securing  $^{28}\text{SiF}_4$ ,  $^{29}\text{SiF}_4$ , and  $^{30}\text{SiF}_4$  from the Electrochemical Plant in Zelenogorsk Siberia through a special grant from the U.S. Department of Energy (Initiative for the Prevention of Proliferation). We then had these gases shipped to the New Jersey company Voltaix, where they converted the  $\text{SiF}_4$  into silane ( $\text{SiH}_4$ ). Back at Berkeley, we performed silane decomposition in our own silane reactor, heating a graphite rod to  $730^\circ\text{C}$  in a recirculating flow of  $\text{H}_2$  and silane. After 14 h, this procedure had coated the graphite rod with 35 g of poly  $^{28}\text{Si}$  (Ref. 3).

Next, we sent the poly  $^{28}\text{Si}$  to Dr. Helge Riemann at the Institut für Kristallzüchtung in Berlin, where he grew for us several isotopically enriched ultrapure floating-zone single crystals of Si. This entire process took several years, much longer than it took us to produce the Ge crystals!

## Isotope Mass-Dependent Properties and Processes

### *Thermal Conductivity*

Once we had acquired the Ge (and later Si) single crystals, we began performing experimental studies with them. Thermal conductivity was one of the early topics we addressed.

In 1942, Pomeranchuk, a theorist in Moscow, published a paper in English in which he stated that the thermal conductivity of a perfect single crystal of an insulator would suffer reduction in conductivity due to the presence of isotopes of different masses. This theory was tested experimentally in 1958 by Theodore Geballe and G.W. Hull at Bell Labs (Ref. 4). Using 17 g of 96% enriched  $^{74}\text{Ge}$  from Oakridge National Laboratory, they performed the first thermal conductivity measurements. In these studies, natural Ge with its five isotopes showed a peak in conductivity of 10 watts per cm per degree, roughly at 18 K, while the enriched  $^{74}\text{Ge}$  showed an increase of about a factor of three.

This result leads to an interesting question. If we go from the isotope mixture of natural Ge—five isotopes present in tens of percents, representing a large disorder of isotopes—to 96% enriched  $^{70}\text{Ge}$ , we observe a factor 3 increase in peak thermal conductivity. If I went to 99.9% enriched  $^{70}\text{Ge}$ , by how much would the peak thermal conductivity increase? What actually happens is surprising.

In 1995, Ozhogin and his colleague Alexander Inyushkin repeated the Bell Labs measurements, using natural Ge and 96% enriched  $^{70}\text{Ge}$ , and obtained the same result as did the 1958 researchers. When they conducted these measurements with more highly enriched material, with 96% and 99.99%  $^{70}\text{Ge}$ , they observed another increase in the peak thermal conductivity of a factor of three (Figure 2, Ref. 5).

From that experiment we learned that even very small additions of isotopes of different mass have a large effect on thermal conductivity. That is observed most elegantly in diamond, as was demonstrated in 1993 by Lan-hua Wei and his colleagues in an experiment comparing thermal conductivities in natural and enriched diamond (Ref. 6). Diamond of natural composition has 1% of  $^{13}\text{C}$ , but if the  $^{13}\text{C}$  is reduced to 0.1%, the thermal conductivity increases substantially. It increases to values which are too high for measurement. Essentially a 1 cm size enriched diamond acts as a thermal short circuit.

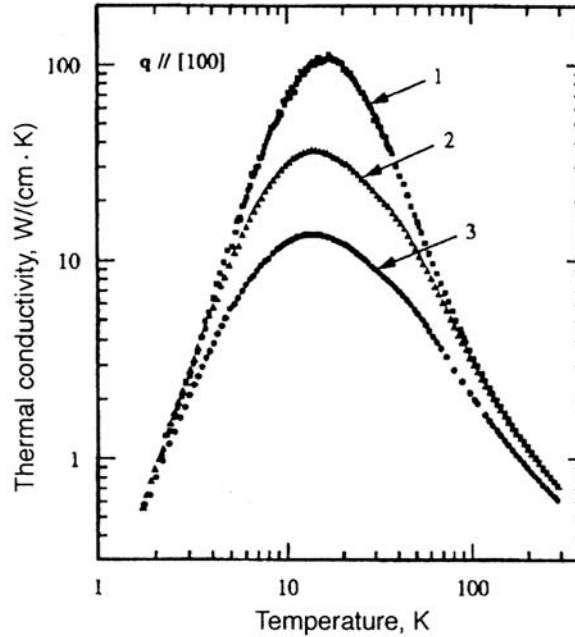


Fig. 2. Temperature dependence of the thermal conductivity along the [100] direction of germanium single crystals with different isotopic composition: Curve 1 – 99.99%  $^{70}\text{Ge}$ ; Curve 2 — 96.3%  $^{70}\text{Ge}$ ; Curve 3 — natural Ge. [Courtesy V.I. Ozhogin et al., (Ref. 5)]

### *Phonons in Bulk Crystals and Isotope Superlattices*

The crystal lattices we study are agitated by phonons, or lattice vibrations. The frequency (or energy) of a phonon depends on the inverse of the square root of the mass of the atoms ( $\omega \propto A^{-1/2}$ ). Phonons at  $k = 0$ , the center of the Brillouin Zone, can be observed by Raman spectroscopy. Phonons at  $k \neq 0$  can be observed by photoluminescence.

Let us first consider Ge, which has an indirect bandstructure with holes sitting at the center of the Brillouin Zone, at the top of the valence band, and electrons located at the L point, at the bottom of the conduction band. The recombination of an electron and a hole requires the assistance not only of a photon, but also of a phonon.

There are four different kinds of phonons that can assist in this recombination process: TO, LO, LA, and TA (see Ref. 7) resulting in four phonon energies, i.e., four discrete photoluminescence peaks.

The first PL spectra of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  were recorded by Gordon Davis of Kings College, London. Davis used the first Ge crystals grown from the 100 g of “priming” material given to us by Ozhogin. Figure 3 depicts two sets of photoluminescence lines from  $^{74}\text{Ge}$  and  $^{70}\text{Ge}$  single crystals and natural Ge. The set of low energy are TO phonon-assisted, while the higher energy lines are due to LA phonon-assisted recombination. The TA and LO-phonon-assisted PL regions lie outside the range of this spectrum.

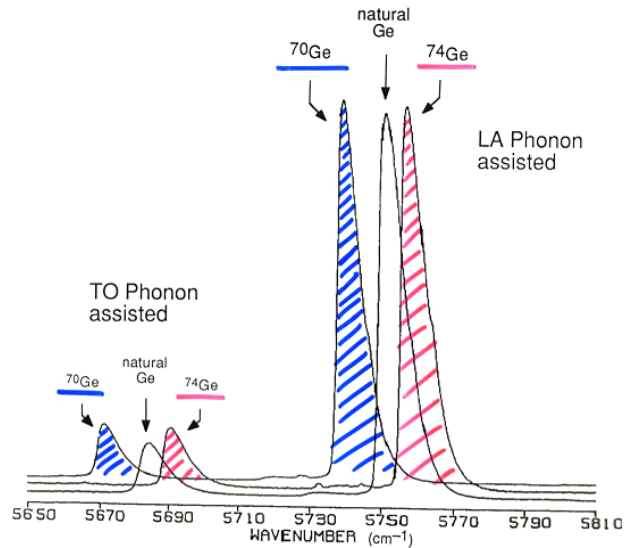


Fig 3. Free exciton emission from  $^{70}\text{Ge}$ ,  $^{74}\text{Ge}$  and natural Ge (Courtesy G. Davies, et al., King's College London, Oct. 20, 1991)

At roughly the same time, Manuel Cardona and his colleagues in Stuttgart, Germany recorded Raman spectra showing the Raman lines of  $^{76}\text{Ge}$ ,  $^{74}\text{Ge}$ , natural Ge, and  $^{70}\text{Ge}$  (Fig. 4). At first Cardona was surprised by the results. He had expected that natural Ge, with its large mixture of isotopes, would have a much broader line width than did the highly enriched isotopes. Instead, the natural Ge had a Raman line width of about  $1\text{ cm}^{-1}$  similar to those of the enriched Ge crystals.

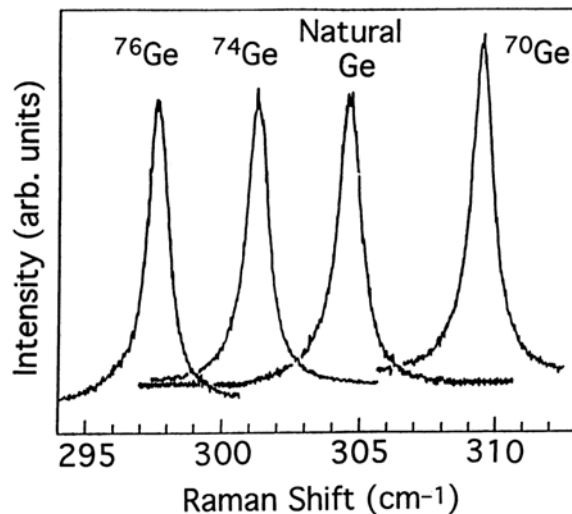


Fig. 4. First-order Raman spectra of isotopically enriched and natural Ge. The data were taken at 80 K with an excitation energy of  $E_L=2.41\text{eV}$ . High resolution ( $\pm 0.02\text{cm}^{-1}$ ) was achieved by measuring in tenth diffraction order of the grating (316 lines/mm) of a 2.12-m SOPRA double monochromator. (Courtesy H.D. Fuchs et al., (Ref. 8))



Cardona then showed that the phonons are delocalized and that their energy depends on the average atomic mass of the crystal. He further pointed out that the Raman linewidth is dominated by the phonon lifetime which in turn is given by the anharmonic decay of the optical phonons. The characteristic time constant for this process is close to 6 picoseconds at low temperature (Ref. 8).

The first set of Germanium isotope superlattices was grown in the laboratory of Prof. Gerhard Abstreiter at the Walter Schottky Institute in Munich. Abstreiter grew these superlattices ranging from alternating half a layer of  $^{70}\text{Ge}$  and half a layer of  $^{74}\text{Ge}$  to two and two layers each and so on up to 32 layers of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$ . He repeated these combinations up to over 100 times for each sample. How would the phonon spectra look? Raman spectroscopy was the method of study.

Using the planar bond charge model and the band polarizability approach, Cardona calculated the Raman spectra for the various multilayer structures shown in Fig. 5 on the right-hand side (Ref. 9). The agreement with the data shown on the left-hand side is outstanding. We see that the sequence of two layers of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  each leads to a single Raman line corresponding to  $^{72}\text{Ge}$ , the average of the two isotope masses. As the number of layers increases several features develop until at 32 layers each spectrum displays two lines corresponding to the Raman lines of bulk  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$ .

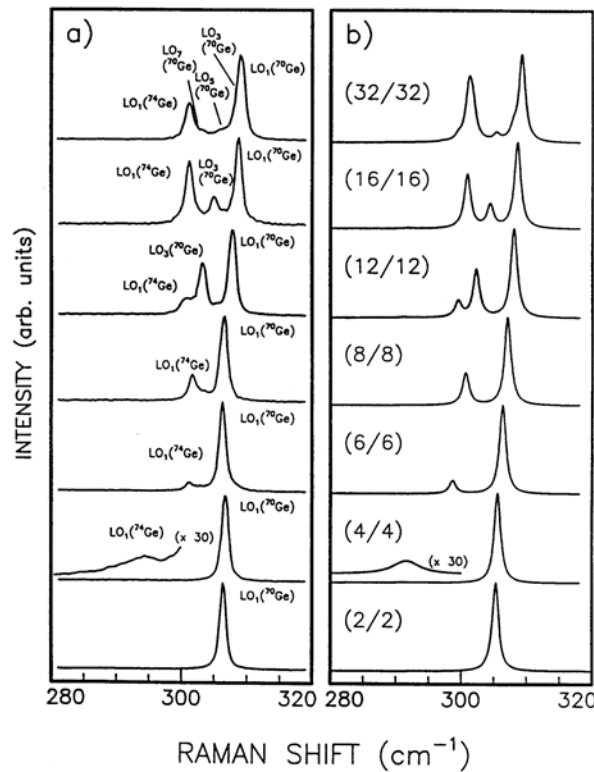


Fig. 5. (a) Measured at T=10K and (b) calculated Raman spectra for a series of isotope superlattices  $^{70}\text{Ge}_n/^{74}\text{Ge}_n$  grown along [001] with n = 2, 4, 6, 8, 12, 16, and 32. A number of modes confined to the  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  layers are evident. [Courtesy W. G. Spitzer et al., (Ref. 9)].

## Metal-Insulator Transition with NTD Ge

In discussing the metal-insulator transition with NTD Ge, let us go back to the table of isotopes to consider what happens when Germanium isotopes are exposed to thermal neutrons. Earlier I described the results of this process with Si. Exposing Ge to thermal neutrons is more complicated because there are 5 stable isotopes:  $^{70}\text{Ge}$ ,  $^{72}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$  and  $^{76}\text{Ge}$ .

Many research reactors have a special space in which you can place semiconductors to expose them to thermal neutrons. If you expose  $^{72}\text{Ge}$  to neutrons, it captures them with a cross-section of about 1 barn (with a barn being equal to  $10^{-24}\text{ cm}^2$ ) and forms the stable isotope  $^{73}\text{Ge}$ . Nothing dramatic has happened. Upon neutron capture  $^{73}\text{Ge}$  turns into  $^{74}\text{Ge}$ , again a stable isotope turning into another stable one. When  $^{74}\text{Ge}$  captures a neutron, however, it becomes  $^{75}\text{Ge}$  which is not stable.  $^{75}\text{Ge}$  decays with an 82 min. half-life into  $^{75}\text{As}$  emitting a  $\beta^-$ . If pure, highly enriched  $^{74}\text{Ge}$  were placed in a reactor, it would become *n*-type, because of the As production. Now let's look at  $^{70}\text{Ge}$ . This isotope becomes  $^{71}\text{Ge}$  upon capture of a neutron which in turn decays with electron capture into  $^{71}\text{Ga}$ . The result is Ga-doped Ge. If pure, enriched  $^{70}\text{Ge}$  is placed in a reactor, it turns *p*-type. Natural Ge, of course, produces both *p*-type and *n*-type dopants, in a ratio of about three to one, with more acceptors than donors.

My former student, Kohei M. Itoh, now a professor at Keio University in Yokohama, Japan, conducted a very clever experiment based on the above observations. He wanted to study the metal-insulator transition (MIT), which is the transition from semiconductor-like to metallic conduction that occurs when semiconductors are doped with increasingly higher amounts of acceptors or donors. At sufficiently high concentrations the dopants form their own band. Once this happens, there is no longer any thermal excitation required to bring the carriers into the conduction band or the valence band for conduction and one observes metallic conduction.

To set up the experiment, Itoh took a slice of our original ultrapure  $^{70}\text{Ge}$  and cut it up into many small pieces. He doped 14 of them from low acceptor concentrations to concentrations approaching the metal-insulator transition but not exceeding it. He then took 10 of the samples and doped all of them to different concentrations beyond the metal-insulator transition. He had 14 samples on the insulator side and 10 on the metal conduction side of the metal-insulator concentration. Itoh was able to structure the experiment in this way because the perfectly random impurity distribution reflects uniform neutron flux and uniform isotopic distribution. There is no more perfectly random way of doping than with neutron transmutation! This is the material of choice to study the metal-insulator transition in its really pure form, not affected by doping fluctuations or related problems.

On the insulator side, Itoh plotted a kind of activation energy (Fig. 6)  $T_0$  (K).  $T_0$  is decreasing in increasingly heavily doped  $^{70}\text{Ge}$  samples. Once the acceptor concentration of the samples approached the metal-insulator transition, the activation energy  $T_0$  dropped dramatically to very small values. On the metal side, Itoh used the zero temperature conductivity  $\sigma_0$  as a characteristic parameter that was plotted as a function of concentration. If things work out properly, these two branches of changing parameters, or different physics, should merge perfectly at the same value—the concentration corresponding to the metal-insulator transition and they did that within less than 0.1%.

The value of the critical Ga concentration at the metal-insulator transition was  $1.86 \times 10^{17} \text{ cm}^{-3}$ . This study led to many further measurements, e.g., the MIT in magnetic fields. It would be interesting to repeat this experiment with donors in  $^{74}\text{Ge}$  and with two-dimensional structures.

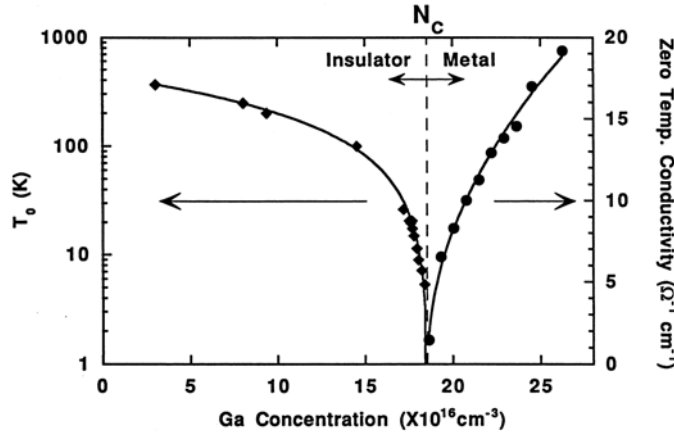


Fig. 6. Extrapolated zero temperature electrical conductivity (right axis) and characteristic temperature  $T_0$  (left axis) for variable range hopping for 14 samples with carefully controlled concentrations of  $^{71}\text{Ga}$ -doped  $^{70}\text{Ge}$  made with neutron transmutation doping. The metal insulator transition (MIT) is found to occur at an acceptor concentration of  $1.86 \times 10^{17} \text{ cm}^{-3}$ . [Courtesy K. M. Itoh et al., Phys. Rev. Lett. **77**, 4058 (1996)].

### Effect of Isotope Composition on Energy Gaps

A much more subtle effect than neutron transmutation doping (NTD) is the effect of isotope mass on energy gaps of semiconductors. High resolution spectroscopy can resolve this effect well and make it easily visible.

In a study done by the students of Professor Anant K. Ramdas at Purdue University, the direct gap and the indirect gap of several isotopes was measured with piezo- and photomodulated reflectivity. In Figure 7, we see how the direct gap increases from  $^{70}\text{Ge}$  to  $^{74}\text{Ge}$  and to  $^{76}\text{Ge}$ .

As part of the same experiment, data on the indirect bandgap were obtained. The experiment shows that the indirect bandgap changes with about one-third of a meV per atomic mass unit ( $\partial E_g / \partial A = 0.36 \text{ meV/amu}$ ) and that the direct gap changes with about one-half of an meV ( $\partial E_o / \partial M = 0.49 \text{ meV/amu}$ ). Photoluminescence experiments show in good agreement that the no-phonon excitons shift in energy with about .35 mV per atomic mass unit. We understand these theoretical isotope mass dependences quite well.

Two components contribute to this bandgap shift, or bandgap change with isotope mass. One of them originates in the lattice constant dependence, which is about 0.132 meV per atomic mass unit. The other one comes from the electron-phonon interaction and is between 0.22 meV and 0.30 meV per atomic mass unit. When these two components are added, the result comes close to the experimental ones just described. The effect is a subtle, but for the physical understanding an important one.

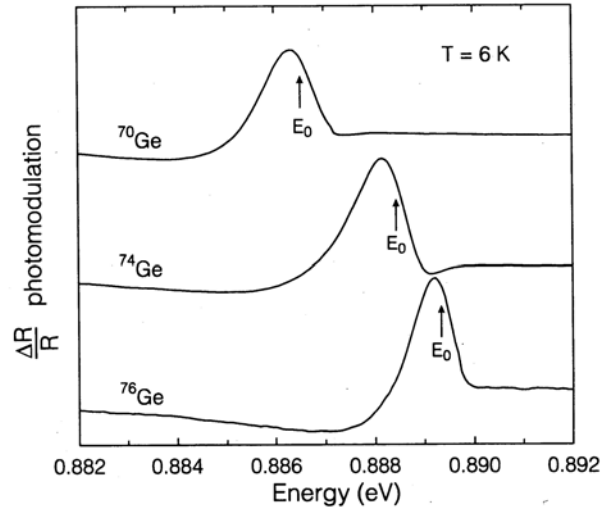


Fig. 7. Photomodulated reflectivity showing the  $E_0$  direct gap of single crystals of  $^{70}\text{Ge}$ ,  $^{74}\text{Ge}$ , and  $^{76}\text{Ge}$  at  $T = 6\text{K}$ . [Courtesy C. Parks et al., Phys. Rev. B **49**(20), 14244 (1994).]

## Self-Diffusion in Isotope Multilayers and Superlattices

The rationale for performing self- and dopant diffusion with isotope multilayers and superlattices is an issue that I raised with David Eaglesham many years ago when he was still working at the former Bell Labs. To demonstrate why such studies are valuable, I will discuss research that we did in Si and GaSb diffusion.

### *Si Self-Diffusion*

For this study, we started with a superlattice that consisted of layers of natural Si alternating with layers of Si that was depleted of  $^{29}\text{Si}$  and  $^{30}\text{Si}$ —in other words, enriched in  $^{28}\text{Si}$ . The  $^{28}\text{Si}$  layers had no measurable  $^{29}\text{Si}$  or  $^{30}\text{Si}$ . As the experiment proceeded, the secondary ion mass spectra (SIMS) of  $^{30}\text{Si}$  were recorded as a function of depth for multilayer structures annealed at different temperatures and times. Interdiffusion of  $^{30}\text{Si}$  occurred from the natural Si layers into the neighboring  $^{28}\text{Si}$  enriched layers. We were, of course, concerned about Transient Enhanced Diffusion (TED) extensively studied and published by David Eaglesham and his colleagues at Bell Labs (Ref. 10). Several critical tests showed that no TED occurred in our structures. This study led us to an activation energy for self-diffusion in Si of 4.75 eV (Ref. 11).

After completing the Si self-diffusion studies, we decided to conduct a similar study using dopants. Colleagues in Aarhus, Denmark added an amorphous layer of Si on the top of the  $^{nat}\text{Si}/^{28}\text{Si}$  multilayer structure. Into the amorphous layer we implanted dopants. In this way implantation effects would not influence diffusion processes farther down in the sample.

Perhaps the most elaborate of our diffusion experiments was the measurement of the simultaneous diffusion of As and Si using an As-doped Si sample. In Fig. 8 we see the SIMS result of sample that was annealed at  $950^\circ\text{C}$  for 122 hours. The As concentration drops gradually from its maximum in the implanted amorphous layer on top of the Si

isotope sandwich. The as-grown  $^{nat}\text{Si}/^{28}\text{Si}$  structure is shown in deleted lines. Above a depth of 900 nm the sample is extrinsic at the diffusion temperature while deeper in the sample intrinsic conditions exist. Si self-diffusion is faster in the extrinsic region than in the intrinsic part of the sample. Native defects assisting Si self-diffusion must be more abundant in the extrinsic region.

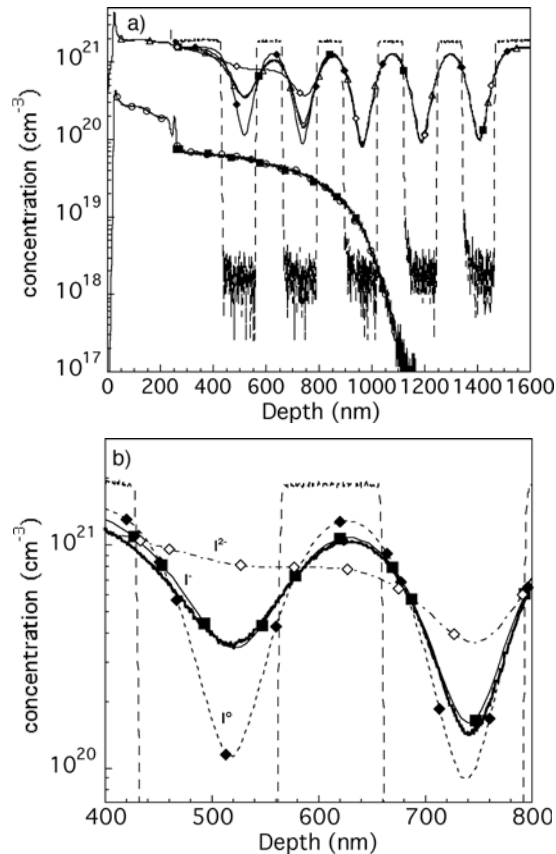


Fig. 8. (a) Concentration versus depth profile for an As implanted Si isotope heterostructure after annealing at 950°C for 122 h. Plot shows pre-anneal  $^{30}\text{Si}$  profile (dashed line) along with the annealed profile. (b) Enlarged view of the region of enhanced Si diffusion. Simulated diffusion profiles of different native defect charge states are included to show the variation of the simulation with the charge state. The singly negatively charged interstitial is shown to lead to the best fit to the data (solid line). [Courtesy H.A. Bracht, et al. Solid State Commun. 133, 727 (2005)]

The essence of our study was to show the simultaneous diffusion of As and Si. Never before had bulk diffusion processes been measured simultaneously. As part of our experiment, we modeled the Si and As diffusion profiles with interstitials in three different charge states: neutral, singly ionized, and doubly ionized. In the As profile, barely any difference can be seen among the lines representing the neutral, singly charged, or doubly charged interstitials. In the Si profile, however, large differences exist among the modeling results using the differently charged interstitials. The doubly charged interstitial clearly overestimates diffusion and the Si profile becomes very flat, much flatter than the underlying experimental data. On the other hand, the neutral

interstitials underestimate the Si self-diffusion. Only singly charged interstitials exactly match the underlying experimental data for both the Si and As profiles. Looking at these two profiles in combination allows us to conclude that the microscopic process of diffusion happens via singly charged interstitials.

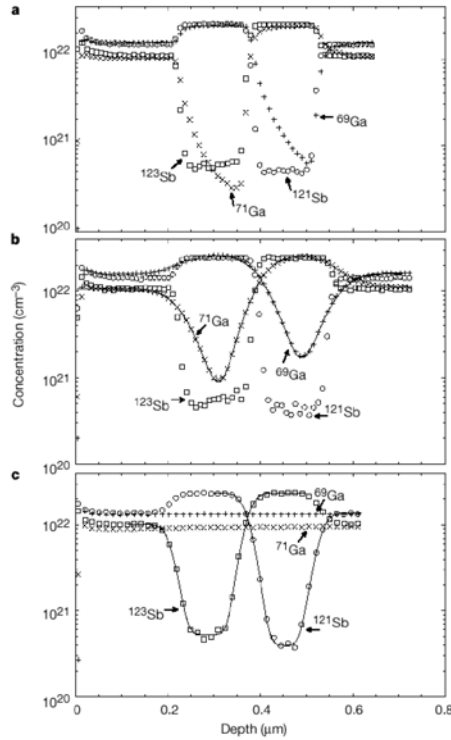


Fig. 9. SIMS depth profiles of  $^{69}\text{Ga}^{121}\text{Sb}/^{71}\text{Ga}^{123}\text{Sb}$  isotope heterostructures. (a) As grown, (b) After annealing under Sb-rich conditions at  $700^\circ\text{C}$  for 105 min and 18 days (c). [Courtesy H.A. Bracht et al. Nature **408**(6808), 69-72 (2000)]

### *GaSb Self-Diffusion*

We had hoped to be able to measure the self-diffusion of the two constituents of the important compound semiconductor GaAs. But, as we saw earlier, As has only one stable isotope and we could only study Ga self-diffusion with an isotope superlattice of  $^{69}\text{GaAs}/^{71}\text{GaAs}$  (Ref. 12). GaSb was the first member of the III-V compound semiconductors in which we could use isotopes to measure self-diffusion in both sublattices. For this experiment, Fernando Briones in Madrid grew a layer of  $^{71}\text{Ga}^{123}\text{Sb}$  on top of a natural composition wafer, then switched to  $^{69}\text{Ga}^{121}\text{Sb}$ , and finally switched back to the natural GaSb for a cap layer. To grow such a structure he required six furnaces in his MBE machine—four for the enriched Ga and Sb isotopes and two for the natural Ga and the natural Sb. All six furnaces had to be in perfect working order. It took two years to complete the task, but the results were indeed worthwhile. In Fig. 9, the as-grown structure shows more or less four square box SIMS profiles of  $^{69}\text{Ga}$ ,  $^{71}\text{Ga}$ ,  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ .

Next, we heated the double layer to 700°C for 105 min. We were then able to observe clearly the pronounced diffusion of the Ga. The square box profiles for both  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  became much flatter, while the Sb profiles remained nearly the same, close to the as-grown state.

After heating the sample for eighteen days, we got an astonishing result. The Ga SIMS profiles had completely flattened out by diffusion, with no hint of the original box profile. The Sb had remained in its place almost untouched.

The data show that the diffusivity of the Ga is at least 1,000 times larger than the diffusivity of the Sb. The reasons why this happens are too involved to be discussed here. I will mention that the reviewers of this paper, which we sent to *Nature*, both agreed that although our explanation seemed quite speculative, they did not have a better one either. The paper was accepted and published (Ref. 13).

### Local Vibrational Mode Spectroscopy

As an example of what can be done with isotopically enriched Ge in relation to local vibrational mode (LVM) spectroscopy, let us consider O in Ge. Just as O in Si does, O in Ge occupies a bond centered interstitial between two neighboring Ge atoms. Because Ge has five stable isotopes, O neighbor combinations can be formed of  $^{70}\text{Ge}$  with  $^{70}\text{Ge}$ ,  $^{70}\text{Ge}$  with  $^{72}\text{Ge}$ , and so forth, with 11 distinct combinations. Combinations with identical average mass (e.g.,  $^{70}\text{Ge}/^{74}\text{Ge}$  and  $^{72}\text{Ge}/^{72}\text{Ge}$ ) lead to the same Oxygen LVM frequency.

Experimentally, at room temperature the various oxygen LVM lines overlap and produce a single peak, while at low temperatures the LVM split into 11 lines. Each line is further split because there are other vibrational modes besides the mode we see here, which is the  $\nu_3$  mode.

If O is placed into isotopically enriched  $^{70}\text{Ge}$ , however, the outcome is only one single LVM line instead of 11 lines. A similar result is obtained with enriched crystals of  $^{76}\text{Ge}$ ,  $^{74}\text{Ge}$ ,  $^{73}\text{Ge}$  or  $^{72}\text{Ge}$ . Figure 10 shows the superposition of four different LVM spectra of oxygen in  $^{70}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$  and  $^{76}\text{Ge}$ .

In addition to illustrating the enormous simplification of Oxygen LVMs in isotopically enriched Ge crystals, we were able to evaluate the coupling between the  $\nu_2$  and  $\nu_3$  vibrational modes of oxygen in  $^{70}\text{Ge}$  (Ref. 14).

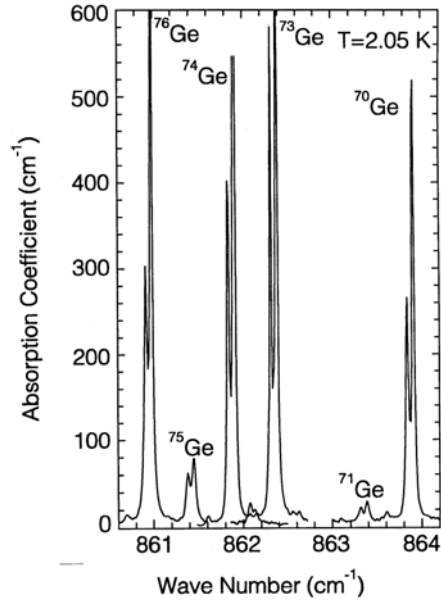


Fig. 10. Superposition of the LVM spectra of oxygen doped, highly enriched samples of  $^{70}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$  and  $^{76}\text{Ge}$ . The line labeled  $^{71}\text{Ge}$  is caused by oxygen sitting between  $^{70}\text{Ge}$  and  $^{72}\text{Ge}$ . The line labeled  $^{75}\text{Ge}$  is due to oxygen centered between  $^{76}\text{Ge}$  and  $^{74}\text{Ge}$ . [Courtesy A. J. Mayur et al., Phys Rev. B **49**, 16293, (1994)]

## Conclusion

I have presented a selection of experimental results obtained with isotopically enriched semiconductors. Many more studies have been conducted and are recorded in the scientific literature. I hope I have stimulated your thinking about the new opportunities offered by the use of stable isotopes in research.

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