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Germanium ^{70}Ge/^{74}Ge isotope heterostructures: An approach to self-diffusion studies

H. D. Fuchs,* W. Walukiewicz, and E. E. Haller
University of California at Berkeley and Lawrence Berkeley Laboratory, Berkeley, California 94720

W. Dondl, R. Schorer, and G. Abstreiter
Walter-Schottky-Institut, Technische Universität München, Am Coulombwall, D-85748 Garching, Germany

A. I. Rudnev, A. V. Tikhomirov, and V. I. Ozhogin
RRC Kurchatov Institute of Atomic Energy, 123182 Moscow, Russia
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We demonstrate a technique to study self-diffusion in germanium, using isotope heterostructures (^{70}Ge/^{74}Ge). After interdiffusing the nominally undoped layers of ^{70}Ge and ^{74}Ge at temperatures between 543 and 690 °C, the diffusion profiles are measured with secondary-ion-mass spectroscopy. The analysis of the experimental data allows an accurate determination of the self-diffusion enthalpy and the self-diffusion entropy. The isotope heterostructures are especially well suited for self-diffusion studies because the diffusion takes place at the interfaces *inside* the crystal. Thus, no surface effects or limited amounts of tracers complicate the measurements. We compare our results with those obtained with the standard techniques where the tracer self-diffusion coefficients are determined based on studying the redistribution of radioactive tracers, initially deposited on the specimen surface. Utilizing the *stable* isotopes in our experiment avoids complications due to decay of the *radioactive* tracers encountered in the traditional measurements.

I. INTRODUCTION

Diffusion processes play an important role in many aspects of modern semiconductor science and technology.[1,2] Diffusion of dopants is utilized to engineer devices in specific ways (e.g., the generation of *p-n* jumctions).[3] In other cases, diffusion can be destructive to delicate structures (e.g., the diffusion of doping impurities of thin epitaxial layers into the adjacent layers or the substrate).[4] In spite of their technological importance, the diffusion mechanisms in germanium, and even more so in silicon as well as in compound semiconductors and their alloys, are not completely understood. Even for the most basic diffusion process, *self-diffusion,* the published value of fundamental quantities such as the diffusion coefficient vary by several orders of magnitude for various authors.[1,2] Such a spread in the experimental data makes it difficult to determine conclusively the underlying physical processes. Reliable diffusion data are therefore crucial to clarify the diffusion *mechanisms* and to accurately determine the corresponding *material parameters.*

The conventional technique to determine the self-diffusion coefficient D_{SD} in semiconductors is to deposit a thin layer of radioactive tracers on the surface of the crystal (e.g., ^{71}Ge, ^{31}Si). In a subsequent annealing step the tracers diffuse into the crystal. The depth profile of the tracer atoms is then determined by serial sectioning and measurements of the corresponding radioactivity. There are several experimental difficulties arising from this method.

(i) Traditionally, lapping and grinding was used for the serial sectioning. This requires that the mean penetration distance $(D_{\mathrm{SD}}t)^{1/2}$ of the tracer atoms during the time t of a diffusion anneal has to be in the μm range. Especially in silicon, the large distance and the short half-life (2.6 h for ^{31}Si) limit this method to be applicable only to higher temperatures (larger D_{SD}). Germanium is more convenient in this respect (the half-life of ^{71}Ge is 11.2 days), but it was not until microsectioning techniques (e.g., sputtering) were invented that the measurements could be extended to lower temperatures in recent years.[5]

(ii) Surface effects such as oxidation, contamination, strain, etc. might influence the tracer diffusion substantially (e.g., through the formation of intrinsic defects).

In this work, we present results of a very accurate method to measure the self-diffusion coefficient of germanium which circumvents many of the experimental problems encountered in the conventional methods. We used *germanium isotopic heterostructures* (stable isotopes), grown by molecular-beam epitaxy (MBE).[6,7] In general, isotope heterostructures consist of layers of pure (e.g., ^{70}Ge, ^{74}Ge) or deliberately mixed isotopes of a chemical element. It was not until very recently that considerable amounts of highly istopically enriched, chemically pure Ge have become available,[8] making the growth of such structures possible.[7] Figure 1 shows the schematic of the particular samples used in this work. At the interface only the atomic mass is changing, while (to first order) all the other physical properties stay the same. In the as-grown samples, this interface is atomically flat with layer thickness fluctuations of about two atomic ML.[7] Upon annealing, the isotopes diffuse into each other (self-diffusion) with a rate which depends strongly on temperature. The concentration profiles were measured with SIMS (secondary-ion-mass spectroscopy), after pieces of the same samples have been separately annealed at

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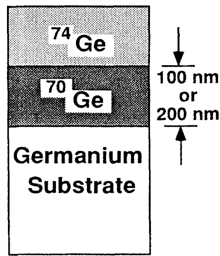

FIG. 1. Schematic of the isotope heterostructure used in this work.

different temperatures. This allows an accurate determination of the self-diffusion enthalpy as well as the corresponding entropy. The isotopic heterostructures are unique for the self-diffusion studies in several respects.

(i) The interdiffusion of germanium isotopes takes place at the isotopic interface *inside* the crystal, unaffected by possible surface effects (e.g., oxidation, stains, and impurities) encountered in the conventional technique.

(ii) One sample annealed at one temperature provides five more or less independent measurements: Germanium consists of five stable isotopes. Their initial respective concentrations vary for the different layers of the as-grown isotope heterostructure. After annealing, the concentration profile of each of the five isotopes can be analyzed separately to obtain five data points for each annealing temperature.

In an experiment somewhat similar to the one presented here, Tan *et al.* attempted to determine the Ga self-diffusion using a ^{69}GaAs/^{71}GaAs isotope superlattice. Unfortunately however, their analysis was only partially successful because native defects and silicon outdiffusion from the doped substrate into the superlattice obscured their results.[9]

In the literature on diffusion, generally two types of diffusion mechanisms are distinguished. The *indirect diffusion* of self-atoms or of foreign substitutional atoms requires intrinsic defects as diffusion vehicle. The vacancy mechanism, depicted in Fig. 2, is by far the most common type of indirect diffusion. It controls not only the self-diffusion of germanium[1,2] but also of practically all metals,[10,11] and yields the main contribution to self-diffusion in silicon at temperatures below about 1000 °C.[1,2] Another example of an indirect mechanism is the so-called kick-out mechanism which is mainly responsible for the self-diffusion in silicon at temperatures above about 1000 °C.[1,2] In contrast, the *direct mechanism* does not involve any intrinsic defects of the crystal. Typical examples for such direct mechanisms are the interstitial diffusion of foreign atoms, the direct exchange of neighboring lattice atoms, or the recently proposed concerted exchange mechanism.[12]

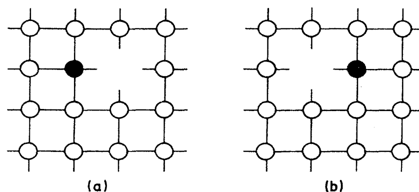

FIG. 2. Vacancy mechanism for self-diffusion: (a) The tagged germanium atom (dark color) moves by jumping into the vacancy to its right. (b) After the jump, it has moved by one nearest-neighbor distance.

II. EXPERIMENTAL DETAILS

The isotopic purification, growth, and characterization of isotopically enriched bulk Ge crystals has been reported in detail elsewhere.[8] The unique samples used in this work (Fig. 1) were grown by molecular-beam epitaxy (MBE) on nominally intrinsic [001] substrates of natural isotopic composition. On top of the substrates a buffer layer of 23 nm was deposited (same material as the first isotopically enriched layer) with a temperature ramp from 180–450 °C in order to prepare an atomically smooth surface. The isotopically enriched layers were then grown at 390 °C—one sample with each layer being 100 nm thick and one sample with each layer being 200 nm thick. The samples were cut into several pieces. One piece was kept for reference (as-grown), the other were separately annealed at five different temperatures (543, 586, 605, 636, and 690 °C).

For the thermal annealing the samples were placed in evacuated ampoules to prevent oxidation or contamination. Even though the samples were sealed in vacuum (10^{-6} Torr), the annealed samples suffered oxidation at the surface to some extent. The oxide evaporated at the elevated temperatures, which means that a certain part of the top layer was lost during the annealing. However, since the self-diffusion process analyzed in this work takes place inside the crystal at the isotopic interface, the oxidation of the *surface* is not expected to significantly alter the diffusion *inside* the sample.

In order to ensure accurate temperature readings, the ampoules and thermocouple were kept in a graphite container inside the heating furnace. The temperature controller permitted a variation of the temperature of 1–2 °C.

The recording of the concentration depth profiles of all five stable Ge isotopes was performed with SIMS. Typical profiles of an as-grown sample as well as those of a diffusion-annealed part of the same sample (636 °C for 19.5 h) are shown in Fig. 3. For clarity, only the profiles of ^{70}Ge and ^{74}Ge are displayed in Fig. 3. The oxygen primary beam had an impact energy of 8 keV per incident ion. The beam was rastered over a square area of about 200 μm in size and the detected secondary ions extracted from the central 30-μm-diameter region of the crater. The precision of the SIMS data was estimated to be within $\pm 5\%$. The depth resolution of the system was determined from profiles taken from the as-grown samples with an atomically flat interface. What theoretically should be a step function in the concentration profile appeared as a slope of about 4 nm per decade of the measured atomic fraction at the leading edge of a layer, and about 16 nm per decade at the falling edge (see Fig. 3). The slight broadening of the real profile is inherent to the

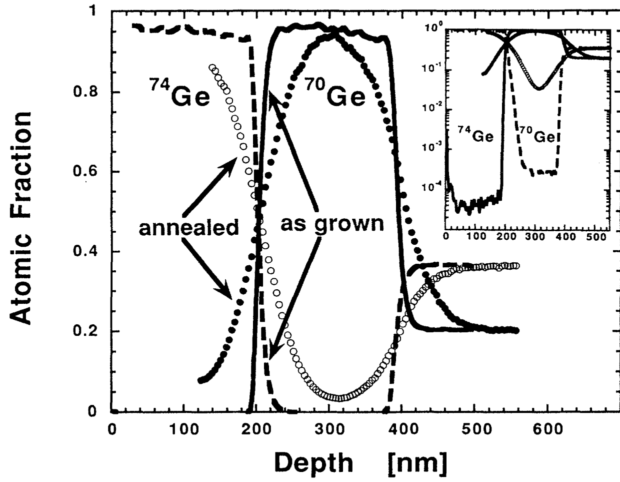

FIG. 3. Experimental depth profile of the atomic fraction of ^{74}Ge and ^{70}Ge. The lines (solid and dashed) represent the *as-grown* (not annealed) sample, whereas the symbols (open and solid) are the data taken from a *diffusion-annealed* part of the same sample (636 °C for 19.5 h). The inset shows the same profile in a logarithmic scale.

SIMS technique and is due to sputtering cascades. This instrumental broadening was corrected for the further analysis of the data.

III. RESULTS AND DISCUSSION

Diffusion in the crystals occurs through atoms jumping thermally activated between different sites in the lattice. In principle, there are many possibilities for such jumps (substitutional or interstitial sites, vacancies, etc.). In germanium crystals, however, it is known that the only process of significance for the migration of germanium atoms is through the vacancy mechanism (see Fig. 2).[1] In this case the self-diffusion coefficient D_{SD} can be written as an Arrhenius expression

$$D_{SD}=gfa^2\nu_0 \exp\left[\frac{-G_{SD}}{kT}\right] =D_0 \exp\left[\frac{-H_{SD}}{kT}\right], \quad (1)$$

where G_{SD} is the Gibbs free energy of self-diffusion,

$$G_{SD}=H_{SD}=TS_{SD}, \quad (2)$$

H_{SD} is the self-diffusion enthalpy, and the preexponential factor

$$D_0=gfa^2\nu_0 \exp\left[\frac{S_{Sd}}{k}\right] \quad (3)$$

contains the self-diffusion entropy S_{SD}, the correlation factor f ($f=\frac{1}{2}$ for the vacancy mechanism in the diamond lattice[13]), the attempt frequency ν_0, the geometric factor g ($g=\frac{1}{8}$ for vacancies in Ge) and the lattice constant a; k is Boltzmann's constant. The enthalpy H_{SD} and the entropy S_{SD} depend on the formation (superscript F) as well as the migration (superscript M) of the vacancy:

$$H_{SD}=H_{SD}^F+H_{SD}^M \text{ and } S_{SD}=S_{SD}^F+S_{SD}^M . \quad (4)$$

The quantity which we can extract from our data is primarily the self-diffusion coefficient D_{SD} as a function of annealing temperature T. This was done by fitting our experimental depth profiles to theory, with D_{SD} being the only fitting parameter. Equation (1) then allows us to determine the self-diffusion enthalpy H_{SD}, and the self-diffusion entropy S_{SD} is deduced using Eq. (3).

Solving Fick's diffusion equation for the specific geometry of our samples (Fig. 1), we obtain the atomic fraction c_i of a given germanium isotope i in terms of error functions (erf):

$$c_i(x)=\left\{\frac{c_i^{0,\mathrm{I}}-c_i^{0,\mathrm{II}}}{2}\operatorname{erf}\left[\frac{h/2+x}{2\sqrt{D_{SD}t}}\right]+c_i^{0,\mathrm{I}}\right\} + \left\{\frac{c_i^{0,\mathrm{II}}-c_i^{0,\mathrm{III}}}{2}\operatorname{erf}\left[\frac{h/2-x}{2\sqrt{D_{SD}t}}\right]+c_i^{0,\mathrm{III}}\right\}, \quad (5)$$

where h is the layer thickness (100 or 200 nm in our samples), and $c_i^{0,\mathrm{I}}$, $c_i^{0,\mathrm{II}}$, and $c_i^{0,\mathrm{III}}$ are the initial concentrations of the isotope i in the enriched ^{74}Ge layer, in the enriched ^{70}Ge layer, and in the substrate, respectively. Figure 4 shows the profiles of all five isotopes of an annealed sample (586 °C for 55.55 h), together with a fit of the data to Eq. (5). For clarity only the fit to the ^{70}Ge profile is shown, but the other profiles can be independently fitted

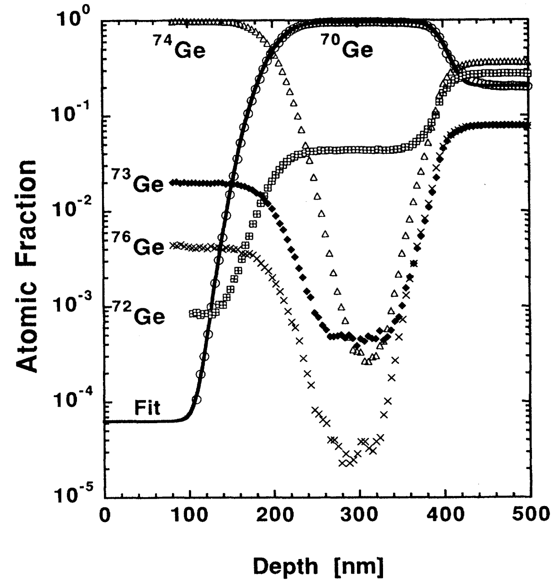

FIG. 4. Experimental depth profile of the atomic fraction of ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge (symbols) of a diffusion annealed sample (annealed at 586 °C for 55.55 h). The solid line is a fit of the ^{70}Ge data to Eq. (5). For clarity, only the fit to the ^{70}Ge data is shown.

as well. The excellent quality of the fit over four orders of magnitude displays the remarkable accuracy of the method used in this work. As a reference, the corresponding concentration profiles for the as-grown sample are displayed in Fig. 5. The annealing time was purposefully chosen such that the plateaus in the annealed samples (around 300 and 100 nm) correspond to the original concentrations in the isotopically enriched layers. Further annealing would lead to a filling in of the low-concentration parts of the sample.

The values for the self-diffusion coefficient D_{SD} obtained at 543, 586, 605, 636, and 690 °C are presented in an Arrhenius plot in Fig. 6. The lines in Fig. 6 represent the results of previous authors.[2] The variations in D_{SD} obtained from different groups is comparable with the scatter of the data within the work of each of the publications. Nevertheless, our data seems to agree better with the latest work by Vogel, Hettich, and Mehrer[14] and Werner, Mehren, and Siethoff,[15] supporting doubts about the accuracy of the older data raised in Ref. 2. At the lowest temperature (543 °C annealed for 192 h) as well as at the highest temperature (690 °C for 1.9 h), our values exceed the ones from Refs. 14 and 15, but are still well within the range of other published values.[16–18] Since for the high-temperature measurements the time for the furnace to reach the desired temperature (about 15–20 min) is relatively long compared to the actual annealing time (1.9 h), it is not surprising that the apparent $D_{SD}t$ is slightly larger than expected. The deviation of the low-temperature measurement, however, is not so clear. Experiments using a rapid-annealing furnace and including the entire temperature ramp into the analysis are underway.

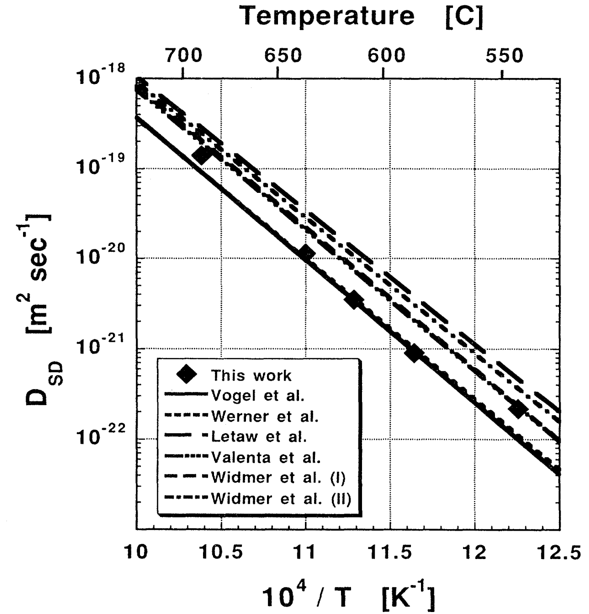

FIG. 6. Arrhenius plot of the self-diffusion coefficient as a function of temperature. The present work agrees favorably well with the most recent data (Refs. 14 and 15). The older data by Letaw, Portnoy, and Slifkin (Ref. 16), Valenta and Ramasatry (Ref. 17), and Widmer and Gunther-Mohr (two different methods were described in Ref. 18) might be less accurate (Ref. 2).

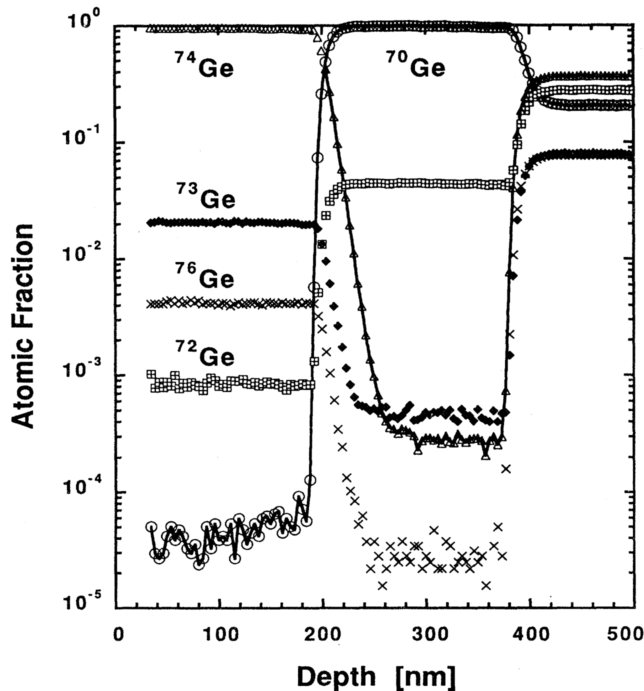

FIG. 5. Experimental depth profiles of the same sample as Fig. 4, but *before* annealing.

Since our results are in excellent agreement with previously published values, and the emphasis of this paper is to present an accurate *method* to study self-diffusion in semiconductors rather than a detailed analysis of the diffusion *mechanisms,* we will only briefly summarize our results and refer the reader to the literature for details.

(i) Fitting our experimental values of D_{SD} to Eq. (1) we obtain the self-diffusion enthalpy H_{SD} to be 3.0(5) eV. This is in excellent agreement with previously published values of 2.95–3.14 eV.[2]

(ii) Our experimental preexponential factor D_0 is 1.2×10^{-3} m^2 s^{-1}. This compares to previously published values of $0.78–4.4\times10^{-3}$ m^2 s^{-1}. Converting D_0 into the self-diffusion entropy S_{SD} through Eq. (3), we obtain $S_{SD}\approx 9k$ (using $\nu_0=8\times10^{12}$ s^{-1} and $a=0.565$ nm). The self-diffusion entropy for Ge is larger than for metals $(2k–4k)$. As an explanation, Seeger and Chik invoked the idea of extended (spread-out) defects,[1] and Bourgoin and Lanoo have proposed that the vacancy in Ge is strongly relaxed.[19]

Finally, we want to mention the effect of the isotopic mass on the self-diffusion coefficient. The many-body treatment of atomic jump processes leads to an expression for the strength of the isotope effect in terms of the correlation factor f of Eq. (3) and the fraction ΔK of the kinetic energy which is associated with the motion in the jump direction:[20,21]

$$\frac{\left[\dfrac{D_{\rm I}}{D_{\rm II}}\right]-1}{\left[\dfrac{m_{\rm II}}{m_{\rm I}}\right]^{1/2}-1}=f\Delta K \ . \tag{6}$$

In previous Ge self-diffusion experiments, Campbell found $f\Delta K$ values between 0.26 and 0.30,[22] which translates into a ratio of $D_{\rm SD}^{70\rm Ge}/D_{\rm SD}^{74\rm Ge}$ between 1.007 and 1.008. This small difference, however, is below the precision of the present work. When fitting the experimental depth profiles to Eq. (5), we could indeed not detect any appreciable difference between the different isotopes. In addition, such small deviations would be insignificant in the Arrhenius plot (logarithmic scale of $D_{\rm SD}$ in Fig. 6) for the determination of the self-diffusion enthalpy $H_{\rm SD}$ and entropy $S_{\rm SD}$.

IV. CONCLUSIONS AND OUTLOOK

We demonstrated how *isotope heterostructures* (^{74}Ge and ^{70}Ge) can be used conveniently to obtain accurate low-temperature germanium self-diffusion data. After interdiffusing isotopically enriched layers of ^{70}Ge and ^{74}Ge at temperatures between 543 and 690 °C, the diffusion profiles were measured with SIMS. The analysis of the experimental data allows an accurate determination of the self-diffusion enthalpy (3.05 eV) and self-diffusion entropy ($9k$). Because the self-diffusion takes place at the isotope interface *inside* the crystal, surface effects which are usually encountered with conventional methods can be bypassed.

In the future, this method could possibly be applied to silicon, where an accurate knowledge of the material properties governing the self-diffusion is still lacking. Our present results also lay the groundwork for studying doping effects on the germanium self-diffusion (Fermi-level-related effects).[2] The *n*-type as well as *p*-type doping can be provided with neutron transmutation doping (NTD) of isotope heterostructures.[6] NTD-doped isotope heterostructures would also lend themselves to the study of impurity diffusion in germanium (As, Ga, and Se). Furthermore, using NTD-doped isotope heterostructures, effects of applied electric fields could be examined. In forward-biased GaAs diodes, e.g., a 10^{15}-fold increase in the diffusion coefficient of impurities has been reported.[23]

Our knowledge of the diffusion properties of isotopically enriched germanium crystals lays the foundation for future work on low-dimensional, layered structures which might open another field of exciting physical studies as well as promising applications.

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*Present address: Bosch GmbH, Research and Development Center, D-70049 Stuttgart, Germany.

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