

Radiation Enhanced Silicon Self-Diffusion and the Silicon Vacancy at High Temperatures

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We report proton radiation enhanced self-diffusion (RESD) studies on Si-isotope heterostructures. Self-diffusion experiments under irradiation were performed at temperatures between 780 °C and 872 °C for various times and proton fluxes. Detailed modeling of RESD provides direct evidence that vacancies at high temperatures diffuse with a migration enthalpy of $H_V^m = (1.8 \pm 0.5)$ eV significantly more slowly than expected from their diffusion at low temperatures, which is described by $H_V^m < 0.5$ eV. We conclude that this diffusion behavior is a consequence of the microscopic configuration of the vacancy whose entropy and enthalpy of migration increase with increasing temperature.

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Although Si is by far the most thoroughly investigated crystalline semiconductor, the thermodynamic properties of its vacancies (V) are still not known [1]. Earlier electron paramagnetic resonance (EPR) and deep level transient spectroscopy (DLTS) studies of electron irradiated Si revealed a migration enthalpy of V lower than 0.5 eV below room temperature [2]. Without any direct experimental evidence, this low value is generally accepted for V migration at temperatures up to the Si melting point ($T_m = 1412$ °C) [3–5].

Methods such as positron annihilation spectroscopy (PAS) and thermal annealing experiments after rapid quenching, which are generally used to determine the properties of native point defects in metals at high temperatures, have not been successful in the case of Si. This is because the concentration of V and self-interstitials (I) in thermal equilibrium are below the detection limit of these methods. Dannefaer *et al.* [6] determined the formation enthalpy of V in Si using PAS, but their result has been challenged as it could not be verified by PAS studies performed by other groups [7]. Numerous experimental [1] and theoretical studies [3,8–10] have been performed over the past decades but no conclusive results about the properties of V at high temperatures were obtained. Here we report the first experimental approach to directly determine the high temperature properties of V in Si.

We performed experiments on radiation enhanced self-diffusion (RESD) utilizing isotopically controlled Si heterostructures. The structures were grown by chemical vapor deposition at 800 °C on (100)-oriented B-doped floating-zone Si wafers with a specific resistivity higher than 10 Ω cm. Structure No. 1 consists of a 280 nm thick highly enriched ^{28}Si ($> 99.92\%$) layer, sandwiched between a 80 nm thick natural Si cap and a ca. 100 nm thick natural Si buffer. Structure No. 2 consists of a five-period superlattice of $^{28}\text{Si}(140 \text{ nm})/\text{natSi}(100 \text{ nm})$ grown on

ca. 200 nm thick natural Si buffer and with a 190 nm thick natural Si cap. The layers are undoped and the C and O concentrations are below 10^{16} cm^{-3} and 10^{17} cm^{-3} , respectively. Samples of $5 \times 5 \text{ mm}^2$ dimensions were thinned to a thickness of $(40 \pm 5) \mu\text{m}$ and mounted in a vacuum chamber on a stainless steel holder with tungsten foil between sample and holder. At a pressure below 10^{-5} mbar, the samples were heated from the back side by means of two halogen lamps. The temperature was monitored with an accuracy of ± 5 K by a thermocouple connected to the back side of the holder. When the desired temperature was reached, the front side of the sample was irradiated with 2 MeV protons which were supplied to the chamber via a beam line from a 5 MeV Van de Graaf accelerator. The beam was swept and defocused in order to obtain a homogeneously irradiated circular area with 1 cm in diameter. The longitudinal range and straggling of 2 MeV protons in Si, as calculated with SRIM [11], is 48.4 and 1.2 μm , respectively; hence, the protons do not stop and generate end-of-range defects in the 40 μm thick samples. Self-diffusion experiments under irradiation were performed at temperatures between 780 °C and 872 °C for various times and proton fluxes. The diffusion time equals, to a very good approximation, the time the sample was exposed to the proton beam since self-diffusion under irradiation is several orders of magnitude larger than the thermal diffusion (see below). In most cases, a flux of $\Phi = 1.0 \mu\text{A}$ was used, which corresponds to a dose rate of $8.0 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$.

Figure 1 shows profiles of the stable isotope ^{30}Si measured by means of secondary ion mass spectrometry (SIMS) after irradiation at various temperatures. The measurements reveal a pronounced intermixing of the isotope structure at the $^{28}\text{Si}/\text{natSi}$ interfaces compared to the as-grown structure. SIMS measurements at positions of the sample which were covered by tungsten, and thus had not been exposed to the high energy protons, did not

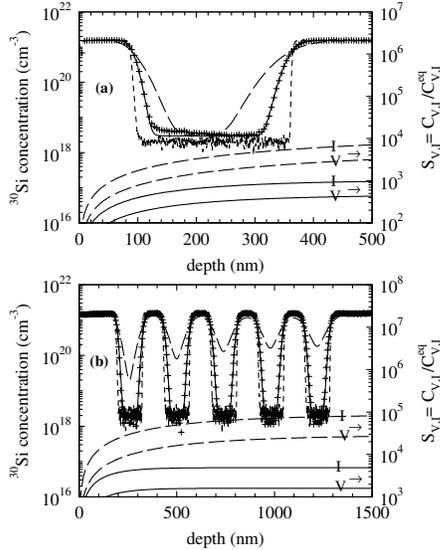


FIG. 1. SIMS concentration-depth profiles of ^{30}Si in $^{28}\text{Si}/\text{natSi}$ isotope structures No. 1 (a) and No. 2 (b) before (short dashed lines) and after (+) annealing at 832°C for 240 min and $\Phi = 1.0 \mu\text{A}$ (a) and at 795°C for 135 min and $\Phi = 1.6 \mu\text{A}$ (b). For clarity, only every fifth (a) and eighth (b) data points are plotted. The upper solid lines in each plot represent best fits to the RESD profiles. The upper long-dashed lines indicate the RESD which is expected when C_V^{eq} equals the low values determined from modeling the defect dynamics during crystal growth [12]. The lower solid and long-dashed lines show the corresponding calculated supersaturations S_I and S_V .

show any significant intermixing. This is consistent with the low self-diffusion under thermal equilibrium [13]. As a direct probe for the $^{28}\text{Si}/\text{natSi}$ intermixing, the $^{28}\text{Si}/\text{natSi}$ interface at a distance of 360 nm (sample No. 1) and 330 nm (sample No. 2) beneath the surface was chosen. The intermixing is accurately described by the solution of Fick's law for self-diffusion across a buried interface [13] with a composition-independent self-diffusion coefficient. RESD data obtained in this way for samples irradiated at constant temperature and flux but various times t reveal a \sqrt{t} dependence of the diffusion length. On the other hand, the flux dependence of self-diffusion was found to vary as $\sqrt{\Phi}$. These results reveal a steady state of native defect concentrations that is established during irradiation [14]. Data for RESD corresponding to $\Phi = 1.0 \mu\text{A}$ and the intermixing of the $^{28}\text{Si}/\text{natSi}$ interface at a distance of 360 and 330 nm beneath the surface of samples No. 1 and No. 2, respectively, are shown in Fig. 2(a) in comparison to self-diffusion under thermal equilibrium. The data are accurate to within 20%. This accuracy is mainly due to the uncertainty in measuring the proton flux and the depth of the SIMS craters. The temperature dependence of RESD is described by the Arrhenius equation $D = D_0 \exp(-Q/k_B T)$ with the Boltzmann constant k_B and $Q = (0.92 \pm 0.26) \text{ eV}$ and $\ln(D_0/\text{cm}^2 \text{ s}^{-1}) = -27.5 \pm 2.7$. As demonstrated in the literature [14,17], the activation enthalpy Q of RESD equals $0.5H_X^{\text{m}}$ of the migration enthalpy H_X^{m} of the native

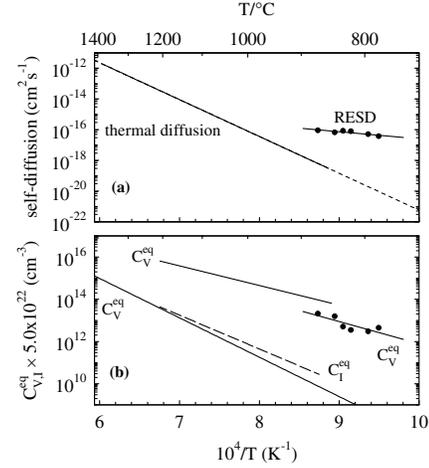


FIG. 2. Temperature dependence of Si self-diffusion (a) and of the thermal equilibrium concentrations (b) of V and I. (a) Comparison of RESD (filled circles) to thermal self-diffusion (solid line, [13]; dashed line, extrapolation). (b) The upper [15] and lower [12] solid lines form the boundary of C_V^{eq} reported in the literature [1]. C_V^{eq} data (filled circles) were determined from accurate modeling of RESD, taking into account the definitive upper bound for C_I^{eq} (dashed line, [16]).

defect $X \in \{V, I\}$ which controls self-diffusion under irradiation. As will be shown in the following, this defect must be the vacancy, thus, $H_V^{\text{m}} = (1.8 \pm 0.5) \text{ eV}$.

In order to identify the native defect which mainly mediates the observed depth dependent RESD, we performed a more detailed numerical analysis of our profiles. This analysis is based on numerical solutions of three coupled nonlinear differential equations. The first two equations, of the form

$$\frac{\partial C_{V,I}(x,t)}{\partial t} - D_{V,I} \frac{\partial^2 C_{V,I}(x,t)}{\partial x^2} = k_0 - k_{IV} C_V(x,t) C_I(x,t), \quad (1)$$

describe the concentration profile in time t and space x of V and I, respectively. The third equation is Fick's second law of Si self-diffusion:

$$\frac{\partial C_{\text{Si}}(x,t)}{\partial t} - \frac{\partial}{\partial x} D_{\text{Si}}(x,t) \frac{\partial C_{\text{Si}}(x,t)}{\partial x} = 0, \quad (2)$$

with a self-diffusion coefficient $D_{\text{Si}}(x,t)$ which depends on the local defect concentrations $C_{V,I}(x,t)$:

$$\begin{aligned} D_{\text{Si}}(x,t) &= f_V C_V(x,t) D_V + f_I C_I(x,t) D_I \\ &= f_V C_V^{\text{eq}} D_V S_V + f_I C_I^{\text{eq}} D_I S_I, \end{aligned} \quad (3)$$

where $S_{V,I} = C_{V,I}(x,t)/C_{V,I}^{\text{eq}}$ represent the local V and I supersaturation established by irradiation. $f_V (= 0.5)$ and $f_I (= 0.73)$ are the temperature independent diffusion correlation factors via the vacancy and interstitialcy mechanisms [13]. D_V and D_I in Eqs. (1) and (3) are the individual diffusion coefficients. k_0 in Eq. (1) represents the production rate of V and I due to the irradiation and is proportional to the flux density. Since I and V are created

simultaneously, k_0 is equal for both defects. Thermal formation of I and V can be neglected compared to the generation of I and V by irradiation. The parameter k_0 is considered to be a constant across the entire isotope structure, in good agreement with binary collision simulations performed with CRYSTAL-TRIM [18]. The second term on the right-hand side of Eq. (1) describes the annihilation of V and I via the Frenkel pair reaction $I + V \rightleftharpoons 0$, where 0 represents a Si atom on a regular lattice site. k_{IV} denotes the rate of annihilation. For a diffusion limited reaction, k_{IV} is given by $4\pi r(D_I + D_V)C_0$ [19], where r is the capture radius and $C_0 (= 5 \times 10^{22} \text{ cm}^{-3})$ the Si atom density. For solving Eqs. (1)–(3) numerically, the initial concentration $C_{V,I}(x, t = 0)$ is considered to equal the concentration $C_{V,I}^{\text{eq}}$ in thermal equilibrium. This is an appropriate assumption because prior to irradiation the isotope samples were heated to the diffusion temperature within about 10 min before the proton beam was switched on. The sample surface is assumed to be an ideal sink for I and V ; hence, the surface concentration is kept at $C_{V,I}^{\text{eq}}$. Internal sinks were not considered in Eq. (1). This assumption was verified by means of transmission electron microscopy (TEM) of some of the irradiated samples. TEM analyses did not reveal any evidence of a significant microdefect density. Calculations, which include the formation of C- I and O- V pairs with a binding energy of 2.5 eV, reveal no significant impact of these pairs on RESD as long as the concentrations of C and O are below 10^{19} cm^{-3} . The Si-isotope samples have C and O concentrations of about 10^{17} cm^{-3} . Accordingly, the formation of C- I and/or O- V pairs does not affect our experiments and, hence, is neglected in Eq. (1).

Altogether six model parameters, k_0 , k_{IV} , D_V , D_I , C_I^{eq} , and C_V^{eq} , enter Eqs. (1)–(3). The products $C_I^{\text{eq}}D_I$ and $C_V^{\text{eq}}D_V$ have been determined separately from Zn in- and out-diffusion experiments, respectively [15,16,20]. The high accuracy of these products is supported by the excellent agreement of the total measured self-diffusion coefficient D_{Si} under equilibrium conditions [13] with the sum of $f_I C_I^{\text{eq}} D_I$ and $f_V C_V^{\text{eq}} D_V$. The temperature dependence of $C_V^{\text{eq}} D_V$ ($C_I^{\text{eq}} D_I$) yields $Q_V = (4.10 \pm 0.14) \text{ eV}$ [15,20] [$Q_I = (4.95 \pm 0.03) \text{ eV}$ [16]] for the activation enthalpy of self-diffusion via V (I), which equals the sum of the enthalpy of formation H_V^f (H_I^f) and migration H_V^m (H_I^m) of V (I): $Q_X = H_X^f + H_X^m$, $X \in \{V, I\}$. Definitive upper bounds for C_I^{eq} and, since the product $C_I^{\text{eq}} D_I$ is known, corresponding lower bounds for D_I were recently determined from Zn diffusion in Si [16]. Similarly accurate results for C_V^{eq} and D_V at high temperatures are not available. For a specific proton flux, the generation rate k_0 is determined by the number of V - I pairs created by 2 MeV protons. Calculations with CRYSTAL-TRIM [18], SRIM [11], and KING99 [21] yield numbers for the pairs which are consistent within a factor of 2.5. Taking into account a proton flux of $1 \mu\text{A}$ and an irradiated area of 0.785 cm^2 , k_0 is about $4 \times 10^{-7} \text{ s}^{-1}$. This number comprises all I - V pairs created by irradiation, even those

correlated pairs produced by low-energy recoil events which are separated by less than one lattice constant. However, such close pairs will very likely annihilate before they contribute to self-diffusion. In order to consider this effect in the calculation of a realistic value for k_0 , a capture radius is introduced in the ballistic calculation of the 3D distribution of V - I pairs. If a recoil ejected from a lattice site stops at a distance from this site less than the capture radius, the recoil itself (I) and the correlated empty site (V) are annihilated. As expected, the number of surviving defects decreases with increasing capture radius. For $r = 0.5 \times 0.543 \text{ nm}$, $1.0 \times 0.543 \text{ nm}$, and $1.5 \times 0.543 \text{ nm}$, we obtained $k_0 = 2.6 \times 10^{-7} \text{ s}^{-1}$, $1.3 \times 10^{-7} \text{ s}^{-1}$, and $6.4 \times 10^{-8} \text{ s}^{-1}$, respectively. These values of r , and the corresponding values of k_0 and k_{IV} , represent the limits within the intermixing of all $^{28}\text{Si}/^{\text{nat}}\text{Si}$ interfaces of a particular sample can be described. The upper solid lines in Figs. 1(a) and 1(b) show a simulation based on $r = 0.543 \text{ nm}$. The lower two solid lines in each plot are the corresponding calculated V and I supersaturations. These $S_{V,I}$ profiles represent a steady state, i.e., the local V and I supersaturations are constant at a specific depth, which according to our simulations has been established within a few seconds. For fitting of all RESD profiles C_V^{eq} was used as fitting parameter, and C_I^{eq} was set to the values given by the black dashed line in Fig. 2(b) [16]. Data obtained for C_V^{eq} are shown in Fig. 2(b) in comparison to literature data. Taking the limits for r and k_0 described above, our data are accurate within a factor of 5. The temperature dependence of $C_V^{\text{eq}} [= \exp(S_V^f/k_B) \exp(-H_V^f/k_B T)]$ yields a V -formation enthalpy of $H_V^f = (2.1 \pm 0.7) \text{ eV}$ and entropy of $S_V^f = (-0.8 \pm 6.8) k_B$. Irrespective of the limited accuracy of H_V^f and S_V^f , our data for C_V^{eq} by far exceed the results obtained from modeling of point defect dynamics during crystal growth [12].

Assuming the low values for C_V^{eq} in our simulations of RESD and keeping all the other parameters unchanged, we obtained the upper dashed lines in Figs. 1(a) and 1(b), which predict too strong an intermixing of the $^{28}\text{Si}/^{\text{nat}}\text{Si}$ interfaces. Even in the case when we assume lower values for k_0 and correspondingly higher capture radii r , which are beyond the above-mentioned limits for these parameters, a simultaneous fit to the intermixing of the $^{28}\text{Si}/^{\text{nat}}\text{Si}$ interfaces located at various depths cannot be obtained. If varying instead the products $C_I^{\text{eq}} D_I$ and $C_V^{\text{eq}} D_V$ within their experimental accuracy, accurate fits with low C_V^{eq} values are still not possible. These attempts to describe the Si profiles with other settings of the model parameters demonstrate the sensitivity of RESD on the thermal equilibrium concentration of the native point defects. This sensitivity can be illustrated by the I and V supersaturations shown in Figs. 1(a) and 1(b). Since the slowest diffusing native defect is the main one that determines the shape of the $S_{V,I}$ profiles, this shape becomes flatter with increasing C_V^{eq} (i.e., decreasing D_V). Experimentally this shape is profiled by the magnitude of intermixing,

i.e., the RESD, at the various $^{28}\text{Si}/^{\text{nat}}\text{Si}$ interfaces. Figure 1(b) shows that RESD is almost independent of depth; hence, $S_{V,I}(x, t)$ is fairly flat. This tells us that either I and V possess the same low mobility or that one of these defects is less mobile than the other. Taking into account the definitive upper bound for C_I^{eq} [16], which reveals a high mobility of I , we must conclude that D_V is significantly smaller than D_I . On the other hand, since $C_I^{\text{eq}}D_I$ and $C_V^{\text{eq}}D_V$ are of the same order of magnitude [13,22], C_V^{eq} must be significantly larger than C_I^{eq} . Hence, our RESD experiments reveal that $C_V^{\text{eq}} \gg C_I^{\text{eq}}$ is fulfilled at high temperatures.

At 800 °C, we obtain $C_V^{\text{eq}} \approx 10^{-8}$ at. % which is about 4 orders of magnitude higher than the data obtained from modeling the dynamics of crystal growth [12]. The sum $H_V^{\text{m}} + H_V^{\text{f}} \approx 1.8 \text{ eV} + 2.1 \text{ eV} \approx 3.9 \text{ eV}$ is consistent with the activation enthalpy $Q_V = (4.10 \pm 0.14) \text{ eV}$ of self-diffusion via V [15,20]. Considering $H_I^{\text{m}} = (1.77 \pm 0.12) \text{ eV}$, which was determined from Zn diffusion experiments [16], the migration enthalpies of I and V are equal. The relationship $D_V \ll D_I$ must be due to different preexponential factors of the diffusivities rather than to different migration enthalpies. Our result for $H_V^{\text{m}} = (1.8 \pm 0.5) \text{ eV}$ at high temperatures is clearly at variance with $H_V^{\text{m}} < 0.5 \text{ eV}$ determined for low temperatures [2]. Since the earlier EPR and DLTS studies on electron irradiated Si and our analysis of RESD yield highly reliable results, we conclude that H_V^{m} increases with temperature. In experiments performed at constant pressure p , the relationship

$$\left(\frac{\partial H_V^{\text{m}}}{\partial T}\right)_p = T \left(\frac{\partial S_V^{\text{m}}}{\partial T}\right)_p \quad (4)$$

is fulfilled [23]. This in turn indicates that an increase of H_V^{m} with temperature is associated with an increase of the entropy of migration S_V^{m} . Accordingly, we conclude that the configuration of V in Si changes with temperature such that more modes of migration become possible at high temperatures compared to low temperatures. Such a configuration corresponds to the concept of spread out defects which was proposed by Seeger and Chik [24] already in 1968. Considering the different prefactors of the individual I and V contributions to self-diffusion, which yield $S_I^{\text{f}} + S_I^{\text{m}} = 13.2k_B$ [16] and $S_V^{\text{f}} + S_V^{\text{m}} = 6.6k_B$ [20], it can be concluded that I spreads out much more than V when the temperature is raised.

In conclusion, our investigations of RESD in Si-isotope structures reveal the first direct evidence that (i) the concentration of V in thermal equilibrium at high temperatures is several orders of magnitude higher than the concentration of I and (ii) the migration enthalpy of V at high temperatures exceeds the corresponding value at low temperatures. (iii) We conclude that the temperature dependent thermodynamic properties of V are a consequence of the microscopic V configuration; i.e., at low temperatures the vacancy is more localized than at high temperatures. Our experimental results confirm the con-

cept of delocalized native defects in Si which was proposed 35 years ago.

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