PHYSICAL REVIEW B **94**, 125208 (2016)

# Self-diffusion in crystalline silicon: A single diffusion activation enthalpy down to 755 °C

Tobias Südkamp and Hartmut Bracht[*]
*Institute of Materials Physics, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany*

(Received 10 June 2016; revised manuscript received 5 August 2016; published 29 September 2016)

Self-diffusion in silicon and the contribution of vacancies and self-interstitials have been controversially discussed for 50 yr. Most recent results show that the intrinsic silicon self-diffusion coefficient deviates from an Arrhenius-type, single exponential function for temperatures below 950 °C [Y. Shimizu, M. Uematsu, and K. M. Itoh, Phys. Rev. Lett. **98**, 095901 (2007); R. Kube, H. Bracht, E. Hüger, H. Schmidt, J. L. Hansen, A. N. Larsen, J. W. Ager, E. E. Haller, T. Geue, and J. Stahn, Phys. Rev. B **88**, 085206 (2013)]. This led us to propose temperature-dependent thermodynamic properties of vacancies in order to achieve full consistency to vacancy-mediated dopant diffusion in silicon. Concepts of temperature-dependent properties of native defects or distinct forms of defects with different formation entropies suggested by Cowern *et al.* [N. E. B. Cowern, S. Simdyankin, C. Ahn, N. S. Bennett, J. P. Goss, J.-M. Hartmann, A. Pakfar, S. Hamm, J. Valentin, E. Napolitani, D. De Salvador, E. Bruno, and S. Mirabella, Phys. Rev. Lett. **110**, 155501 (2013)] question the present understanding on atomic transport in semiconductors. To verify these concepts, additional self-diffusion experiments under particular gettering conditions were performed. As a result, silicon self-diffusion was found to be accurately described by one single diffusion activation enthalpy of $(4.73 \pm 0.02)$ eV down to 755 °C. This provides full consistency to dopant diffusion without claiming native-defect concepts that were originally proposed by Seeger and Chik in 1968 [A. Seeger and K. P. Chik, Phys. Stat. Sol. **29**, 455 (1968)] and confirms most recent density functional theory calculations on the activation energy of self-diffusion via vacancies and self-interstitials. Overall, this unravels the old debate of self-diffusion in silicon with the supposed intrinsic temperature dependence.

DOI: 10.1103/PhysRevB.94.125208

## I. INTRODUCTION

Understanding the self-diffusion of silicon (Si) is important both scientifically and industrially. Early Si self-diffusion studies that utilized the radioactive isotope $^{31}$Si were limited in the time of diffusion due to its short radioactive half-life of 2.6 h (see data collection [1]). More recently, Si structures with alternating layers of different Si isotopes ($^{28}$Si, $^{29}$Si, and $^{30}$Si) were prepared for studying the mechanisms of self-diffusion and dopant diffusion. Combined with state-of-the-art depth profiling and scattering methods such as secondary ion mass spectrometry (SIMS) [2–7], Raman scattering [8,9], and neutron reflectometry (NR) [7,10–12], even small diffusion lengths of a few nanometers were determined. Most recent results on Si self-diffusion reported by Kube *et al.* [7] confirmed the data of Shimizu *et al.* [9], for temperatures between 735 and 875 °C. Combining the experimentally determined self-diffusivity between 735 and 1388 °C an activation enthalpy of 3.6 eV is suggested for self-diffusion via vacancies ($V$). This value is significantly lower than the activation enthalpy of self-diffusion via self-interstitials ($I$) that according to metal-diffusion studies is equal to or above 4.8 eV [13–19]. The low-activation enthalpy for $V$-mediated self-diffusion gives rise to inconsistencies in $V$-mediated dopant diffusion [7]. In order to solve this inconsistency, temperature-dependent thermodynamic properties of $V$ were proposed, which describe a defect that gets more extended or spread out with increasing temperature. This concept of extended point defects, which was first introduced by Seeger and Chik [20], seems to be strengthened by recent experiments and computational modeling of Cowern *et al.* [21]. Moreover, it was discussed that vacancies generated at carbon and/or vacancy clusters could give rise to the bowing in the temperature dependence of self-diffusion [22,23]. Before moving forward with such scientific discussions [22–25], we decided to verify the "intrinsic" annealing ambient condition, which may be difficult to achieve at low temperatures for realistic annealing times. As a result we report Si self-diffusion experiments to modify the low-temperature data reported recently [7,9].

## II. EXPERIMENT

Three different isotope structures (#1, #2, and #3) were used for the self-diffusion experiments. Structure #1 consists of 8 bilayers of (10 nm $^{\mathrm{nat}}$Si/10 nm $^{28}$Si) grown by means of molecular beam epitaxy (MBE) on top of an $n$-type (100)-oriented Cz-Si wafer with a specific resistivity of $>$ 2000 Ω cm. Structure #2 with 28 bilayers of (6 nm $^{\mathrm{nat}}$Si/6 nm $^{28}$Si) was grown by MBE under the same conditions as structure #1 on top of a $p$-type (100)-oriented Si wafer (1–20 Ω cm). Details about the MBE growth that was performed at Keio University are described in Refs. [26–28]. Finally, structure #3 consists of an isotopically enriched $^{28}$Si layer sandwiched between layers of natural Si, i.e., 200 nm $^{\mathrm{nat}}$Si/670 nm $^{28}$Si/200 nm $^{\mathrm{nat}}$Si. This structure was prepared by means of chemical vapor deposition on B-doped ($\rho > 10$ Ω cm) (100)-oriented natural floating-zone Si substrates. The latter structure, #3, was also used for the self-diffusion experiments reported in Refs. [29,30] (labeled as #5) and in Ref. [7] (labeled as SW-structure).

Samples with lateral dimensions of 4 mm × 4 mm were cut from wafers with isotope structures #1, #2, and #3, cleaned in organic solvents, etched in 5% diluted HF, and purged in distilled water. Natural boron-doped float-zone (FZ)

---

[*] bracht@uni-muenster.de

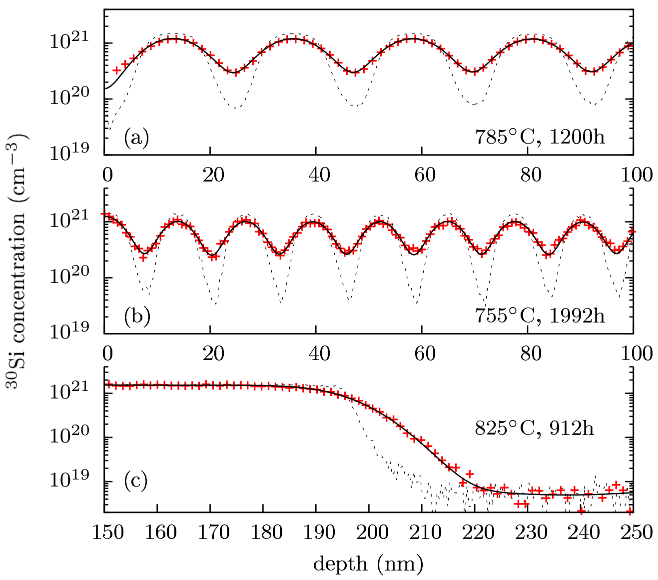

FIG. 1. $^{30}$Si concentration-depth profiles measured with SIMS before (dashed lines) and after (symbols) annealing of the isotope structures #1 (a), #2 (b), and #3 (c) at the temperatures and times indicated in the figure. Solid lines show best fits to the experimental Si profiles based on solving Fick's second law of diffusion. A reduced number of data points are shown for clarity.

TABLE I. Self-diffusion coefficients $D_{\mathrm{Si}}^{\mathrm{SD}}$ determined from $^{30}$Si concentration profiles after annealing Si isotope structures #1–#3 at temperatures $T$ between 755 and 825 °C for times $t$.

| Structure | $T$ (°C) | $t$ (h) | $D_{\mathrm{Si}}^{\mathrm{SD}}$ (cm$^2$ s$^{-1}$) |
|---|---|---|---|
| #1 | 755 | 1992 | $3.21 \times 10^{-21}$ |
| #2 | 755 | 1992 | $3.53 \times 10^{-21}$ |
| #1 | 766 | 1536 | $5.16 \times 10^{-21}$ |
| #2 | 766 | 1536 | $6.29 \times 10^{-21}$ |
| #1 | 775 | 912 | $6.63 \times 10^{-21}$ |
| #2 | 775 | 912 | $7.81 \times 10^{-21}$ |
| #3 | 775 | 912 | $5.72 \times 10^{-21}$ |
| #1 | 785 | 1200 | $1.64 \times 10^{-20}$ |
| #1 | 800 | 1536 | $2.82 \times 10^{-20}$ |
| #2 | 800 | 1536 | $3.37 \times 10^{-20}$ |
| #1 | 825 | 912 | $8.80 \times 10^{-20}$ |
| #2 | 825 | 912 | $7.48 \times 10^{-20}$ |
| #3 | 825 | 912 | $8.70 \times 10^{-20}$ |

Si with a specific resistivity of 800 Ω cm with carbon and oxygen concentrations of $\leqslant 5 \times 10^{15}$ cm$^{-3}$ and $\approx 3 \times 10^{15}$ cm$^{-3}$, respectively, was crushed into pieces of about 1 to 5 mm. The crushed FZ Si (crushed Si) was etched 30 s with CP6 etching solution composed of nitric acid (70 vol%), hydrofluoric acid (50 vol%), and acetic acid (98 vol%) in a volume fraction of 2:1:1. The etching process was terminated by purging with distilled water. Samples of structures #1, #2, and #3 were embedded in crushed Si within quartz glass ampoules, evacuated to a pressure of $10^{-6}$ mbar after flushing several times with argon beforehand (purity of 99.998%), and finally sealed. The sealed ampoule volume filled with crushed Si and the isotope samples is about 3 cm$^3$. The ampoules were placed in a resistance heated furnace and annealed at temperatures between 755 and 825 °C for appropriate times. The temperature was monitored by a type-S thermocouple contacting the ampoule with an uncertainty of 1 K. Time-of-flight (TOF) secondary ion mass spectrometry (SIMS) was applied to measure the concentration profiles of the Si isotopes before and after diffusion annealing. SIMS was performed in a dual beam mode with 1-keV oxygen ions for sputtering and 25-keV bismuth ions for analysis. The depths of the SIMS craters were determined with an optical profilometer and used to convert the sputter time to penetration depth assuming a constant sputter rate during SIMS analysis.

## III. RESULTS

Figures 1(a), 1(b), and 1(c) show $^{30}$Si concentration profiles of structures #1, #2, and #3, respectively, before and after annealing in crushed Si at the temperatures and times indicated. A distinct diffusional broadening is observed for all three isotope structures. Experimental Si profiles are accurately described by numerical solutions of

$$\frac{\partial C_{\mathrm{Si}}}{\partial t} = D_{\mathrm{Si}}^{\mathrm{SD}} \frac{\partial^2 C_{\mathrm{Si}}}{\partial x^2}. \tag{1}$$

Equation (1) represents Fick's second law of self-diffusion in solids. The profile measured before annealing is considered as the initial profile. Data obtained for $D_{\mathrm{Si}}^{\mathrm{SD}}$ from all self-diffusion experiments at temperatures between 755 and 825 °C are summarized in Table I.

In the case of Si, both vacancies ($V$) and self-interstitials ($I$) exist under thermal equilibrium and contribute to self-diffusion (see, e.g., Ref. [31]). Accordingly, the self-diffusion coefficient reads

$$D_{\mathrm{Si}}^{\mathrm{SD}} = D_{\mathrm{Si}}^{V} + D_{\mathrm{Si}}^{I} = f_V C_V^{\mathrm{eq}} D_V + f_I C_I^{\mathrm{eq}} D_I. \tag{2}$$

The first (second) term considers the contribution of $V$ ($I$) to self-diffusion. Self-diffusion via direct exchange of lattice atoms is neglected in Eq. (2), since theory predicts that this does not play a role [32–34] and no experimental evidence has been found for it. $C_{V,I}^{\mathrm{eq}}$ and $D_{V,I}$ are the thermal equilibrium concentrations in atomic fractions (unitless) and diffusion coefficients of $V$ and $I$, respectively. $f_{V,I}$ are the diffusion correlation factors, which were calculated to be $f_V = 0.5$ [35] and $f_I \approx 0.6$ [36] for self-diffusion via vacancies and dumbbell self-interstitials in the diamond lattice.

## IV. DISCUSSION

The self-diffusion coefficients determined in the framework of this work are shown in Fig. 2 in comparison to high- and low-temperature data given in the literature. The new data for $D_{\mathrm{Si}}^{\mathrm{SD}}$ are lower than the results reported by Shimizu *et al.* [9] and Kube *et al.* [7]. Kube *et al.* [7] and Shimizu *et al.* [9] performed diffusion anneals in quartz ampoules without crushed Si and under flowing inert gas, respectively. The authors of both papers took extra care to avoid oxidation during the long annealing time; i.e, no significant thermal oxide growth was detected by ellipsometry and neutron scattering after the diffusion anneals. However, their data may still be affected by residues of oxygen, hydroxyl groups, or other

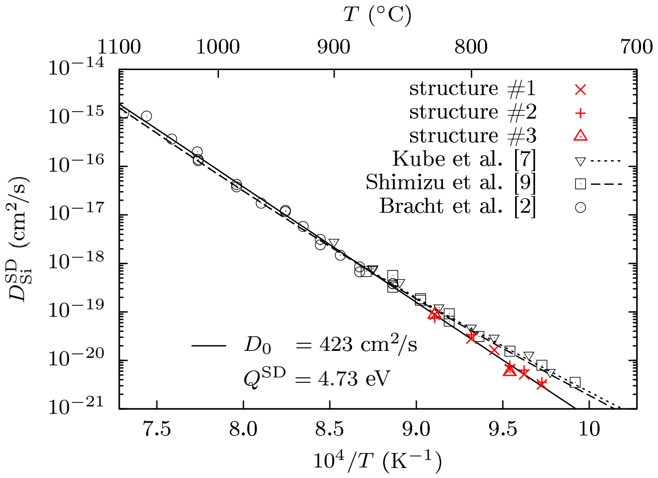

FIG. 2. Silicon self-diffusion coefficients $D_{\mathrm{Si}}^{\mathrm{SD}}$ (red symbols) obtained from diffusion annealing of Si isotope structures #1–#3. Data reported in the literature (black symbols) and the respective temperature dependence (dashed lines) are shown for comparison. $D_{\mathrm{Si}}^{\mathrm{SD}}$ data for low temperatures (red symbols) and high temperatures (circles [2]) are accurately described by a single Arrhenius equation with pre-exponential factor $D_0 = 423^{+113}_{-89}$ cm$^2$/s and activation enthalpy $Q^{\mathrm{SD}} = (4.73 \pm 0.02)$ eV (solid line). Note, only literature data of $D_{\mathrm{Si}}^{\mathrm{SD}}$ for $T < 1100$ °C are shown for clarity.

crucial contaminants such as transition metals. Interaction of such residues with the Si surface can inject native point defects. Accordingly, their concentration will exceed the thermal equilibrium concentration and, as a consequence, will enhance self-diffusion.

Self-diffusion data given in the literature for high temperatures were also deduced from diffusion experiments in closed ampoules without crushed Si. However, the diffusional broadening of the isotope structures strongly exceeds the values established in this and previous works at low temperatures. Moreover, small oxygen or hydroxyl residues released during annealing at high temperatures will affect self-diffusion mainly at the onset of the diffusion annealing due to the increased reaction rates at higher temperatures. The agreement in the Si self-diffusion coefficients for temperatures above 800 °C given in the literature [2,3,5,9] and determined in this work from self-diffusion in crushed Si supports that the high-$T$ data are representative for intrinsic, i.e., thermal, equilibrium conditions. The higher self-diffusion data obtained for temperatures below 800 °C from diffusion experiments performed in closed quartz ampoules [7] or in quartz tubes under a continuous flow of inert gas [9] remain unsolved in detail. However, first experiments are presented in the following that demonstrate a gettering of unintentionally introduced impurities by annealing in crushed Si.

First, it is noteworthy that self-diffusion is the slowest process of transport of matter in Si, i.e., all foreign atoms investigated so far diffuse faster than self atoms [37]. This is not self-evident since results on self- and foreign-atom diffusion in germanium (Ge) demonstrate that the diffusivity of, e.g., boron is several orders of magnitude lower than Ge self-diffusion [37,38]. The peculiar case of Si is a consequence of the contribution of both $V$ and $I$ to the atomic transport.

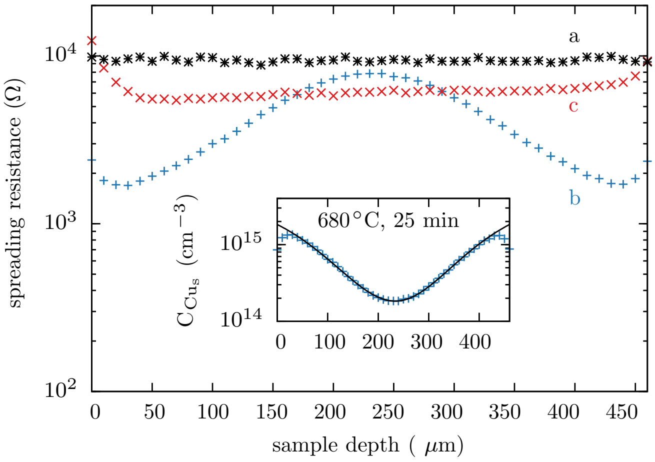

FIG. 3. Spreading-resistance profiles of Ge samples prepared in cross section. Profile a represents the resistance profile of the as-received high-purity intrinsic Ge. Profiles b and c are the resistance profiles of Ge samples annealed in quartz ampoules at 680 °C for 25 min without and with crushed Si, respectively. The inset shows the concentration profile that is deduced from the resistance profile b assuming substitutional copper ($\mathrm{Cu}_s$) as the main impurity atom. The solid line shows the best fit to the $\mathrm{Cu}_s$ concentration profile (see text for details).

Consequently, it is very unlikely if not impossible to retard self-diffusion in Si by an imbalance of one type of native defect because this imbalance would increase the contribution of the other native defect to self-diffusion. Accordingly, any reaction at the Si surface taking place during annealing can enhance self-diffusion. This may be due not only to oxygen or hydroxyl residues in the diffusion ampoule but also to transition metal impurities that react with Si to form metal silicides. A critical element in this respect is copper (Cu). As trace impurity Cu is omnipresent but hardly detected directly by, e.g., SIMS since its solubility in Si is below $10^{17}$ cm$^{-3}$ for temperatures lower than 800 °C [39]. Moreover, Cu is mainly dissolved on interstitial lattice sites, diffuses exceptionally fast in Si (see, e.g., Ref. [40] and references therein), and tends to form small precipitates when the saturated Si sample is cooled to room temperature. This behavior of Cu in Si explains why its direct electrical detection is difficult. On the other hand, Cu in Ge is mainly dissolved on the substitutional lattice site and acts as a triple acceptor (see, e.g., Ref. [40]). Accordingly, Cu in Ge is readily detected electrically even for concentrations well below $10^{17}$ cm$^{-3}$.

In order to demonstrate the gettering effect of annealing in crushed Si, natural high-purity Ge samples with a specific resistivity of ≈30 Ω cm were sealed in quartz glass ampoules filled with and without crushed Si and annealed at 680 °C for 25 min in a resistance heated furnace. Figure 3 demonstrates resistance profiles measured by means of the spreading-resistance technique before and after the different anneals. Compared to the as-received intrinsic Ge sample (see profile a in Fig. 3) a clear decrease in the resistance is observed for the Ge sample annealed in the quartz ampoule without crushed Si (see profile b). On the other hand, the sample annealed in crushed Si shows a much less pronounced decrease in the resistance. The observed resistivity change is attributed to Cu because the diffusion coefficient and surface concentration obtained from fitting the concentration profile [41] shown in the inset of Fig. 3 show a distinct correlation to Ge self-diffusion: The concentration profile is accurately described by Cu indiffusion from the two opposite surfaces [42] as demonstrated by the solid line in the inset of Fig. 3. An effective diffusion coefficient of $3.18 \times 10^{-8}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and surface concentration of $1.7 \times 10^{15}\,\mathrm{cm}^{-3}$ is obtained whose product multiplied by the diffusion correlation factor of 0.5 for Ge self-diffusion via $V$ and divided by the Ge atom density ($4.413 \times 10^{22}\,\mathrm{cm}^{-3}$) yields $6.12 \times 10^{-16}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. Within an experimental accuracy of 20% this value is in accurate agreement to the Ge self-diffusion coefficient $D_{\mathrm{Ge}}^{\mathrm{SD}} = 7.16 \times 10^{-16}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at $680\,^\circ\mathrm{C}$ given by the temperature dependence reported by Hüger *et al.* [10]. The interrelation between the detected impurity in Ge provides strong evidence that Cu is unintentionally introduced by annealing in quartz ampoules without crushed Si but effectively gettered by annealing in crushed Si. This interpretation would also explain the strong impact on self-diffusion at low temperatures. Cu silicide formation with an associated injection of native defects is mainly expected for temperatures below the eutectic temperature $T_{\mathrm{eu}}$ of the Si:Cu binary phase diagram, i.e., below $T_{\mathrm{eu}} = 802\,^\circ\mathrm{C}$ [39].

The impact of unintentional contaminations is, in particular, very critical for diffusion experiments at low temperatures where the diffusional broadening even for long diffusion times is still small so that any enhanced diffusion at the onset of the diffusion anneal will provide a diffusivity that exceeds the true intrinsic diffusion coefficient. In this respect, diffusion in crushed Si with its high-Si surface area is a protective measure to suppress the impact of any possible unintentional contamination on diffusion at low temperatures. More generally, the present study shows that diffusion experiments in Si at low temperatures must be considered very critically to identify those experiments that reflect intrinsic diffusion conditions. Previous experiments on Si self-diffusion at low temperatures [7,9] were all performed without taking extra care to suppress contamination by transition metals. Accordingly, the reported self-diffusion data do not reflect the intrinsic, thermal equilibrium Si self-diffusion coefficient.

Taking into account the $D_{\mathrm{Si}}^{\mathrm{SD}}$ of this work (red symbols in Fig. 2) and of Bracht *et al.* [2] (open circles in Fig. 2) the temperature dependence of self-diffusion can be accurately described over 9 orders of magnitude by an Arrhenius equation with a single diffusion activation enthalpy of $(4.73 \pm 0.02)$ eV and a pre-exponential factor of $D_0 = 423^{+113}_{-89}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ (see black solid line in Fig. 2). This clearly disproves the bowing in the temperature dependence of the $D_{\mathrm{Si}}^{\mathrm{SD}}$ reported by Shimizu *et al.* [9] and Kube *et al.* [7] and indicated in Fig. 2 by the long- and short-dashed lines, respectively. The single Arrhenius dependence not only demonstrates that identical experimental diffusion conditions prevailed at low and high temperatures but also shows that the activation enthalpies for the contributions of $V$ and $I$ to self-diffusion must differ less than 1 eV [43].

The uncorrelated contribution $C_I^{\mathrm{eq}} D_I$ of $I$ to self-diffusion [see Eq. (2)], often called the $I$-transport capacity, is accurately known from diffusion studies of gold (Au) [13–15], zinc (Zn) [16,17], and platinum (Pt) [18,19] in dislocation-free Si. These elements diffuse rapidly in Si via interstices but are mainly dissolved on substitutional lattice sites. The associated interstitial-substitutional exchange is described by the kick-out and dissociative diffusion mechanisms. The indiffusion of these elements in undoped Si is mainly mediated by $I$ via the kick-out mechanism. Data reported for $C_I^{\mathrm{eq}} D_I$ from Au, Pt, and Zn diffusion studies are summarized in Fig. 4. The temperature dependence of all experimental results is described by a single Arrhenius equation with an activation enthalpy of $Q_I^{\mathrm{SD}} = (5.01 \pm 0.05)$ eV and a pre-exponential factor of $D_{0,I} = 4227^{+2397}_{-1530}\,\mathrm{cm}^2/\mathrm{s}$ (see red dashed line in Fig. 4). Considering the various metal-diffusion studies in more detail, the data given by Mantovani *et al.* [18] are likely less reliable since the solubility $C_{\mathrm{Pt}}^{\mathrm{eq}}$ of Pt was not independently measured to determine $C_I^{\mathrm{eq}} D_I$ via the product $C_{\mathrm{Pt}}^{\mathrm{eq}} D_I^*$. In the case of the other metal-diffusion studies the diffusion coefficient $D_I^* = C_I^{\mathrm{eq}} D_I / C_{\mathrm{X_s}}^{\mathrm{eq}}$ extracted from metal profiles is multiplied with the solubility $C_{\mathrm{X}}^{\mathrm{eq}}$ of the metal $X \in \{\mathrm{Au,Pt,Zn}\}$ measured independently [14,16,19]. This solubility equals to a good approximation the concentration $C_{\mathrm{X_s}}^{\mathrm{eq}}$ of the substitutional dissolved metal. Neglecting the $C_I^{\mathrm{eq}} D_I$ data reported by Mantovani *et al.* [18] the temperature dependence of $C_I^{\mathrm{eq}} D_I$ is best described by $D_{0,I} = 819^{+497}_{-309}\,\mathrm{cm}^2/\mathrm{s}$ and $Q_I^{\mathrm{SD}} = 4.82 \pm 0.05$ eV (see red solid line in Fig. 4).

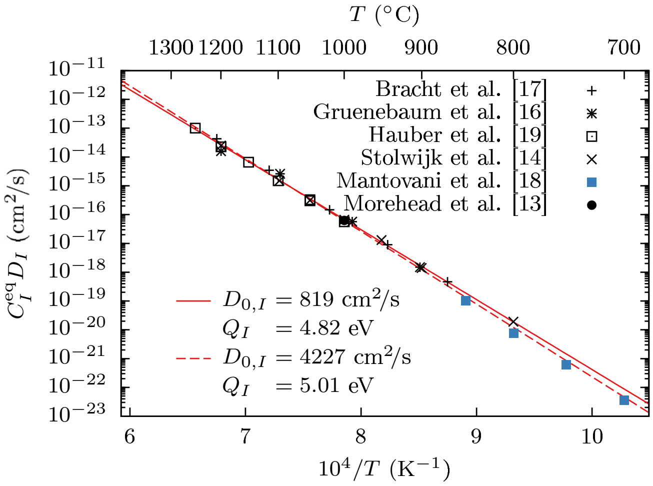

FIG. 4. Temperature dependence of the uncorrelated transport capacity $C_I^{\mathrm{eq}} D_I$ of Si self-interstitials $I$ deduced from Au, Zn, and Pt diffusion experiments. The literature data are best described by an Arrhenius equation with $D_{0,I} = 4227^{+2397}_{-1530}\,\mathrm{cm}^2/\mathrm{s}$ and $Q_I^{\mathrm{SD}} = (5.01 \pm 0.05)$ eV (dashed line). Neglecting the data of Mantovani *et al.* [18] the temperature dependence is best described by $D_{0,I} = 819^{+497}_{-309}\,\mathrm{cm}^2/\mathrm{s}$ and $Q_I^{\mathrm{SD}} = (4.82 \pm 0.05)$ eV (solid line).

Taking into account the temperature dependence of $C_I^{\mathrm{eq}} D_I$ from metal diffusion and the diffusion correlation factors $f_V = 0.5$ [35] and $f_I \approx 0.6$ [36] for self-diffusion via $V$ and $I$ dumbbells, respectively, the uncorrelated $V$ contribution $C_V^{\mathrm{eq}} D_V = (D_{\mathrm{Si}}^{\mathrm{SD}} - f_I C_I^{\mathrm{eq}} D_I)/f_V$ to self-diffusion is obtained. Based on the temperature dependence of $C_I^{\mathrm{eq}} D_I$ obtained with and without the results of Mantovani *et al.* [18] (see Fig. 4), $C_V^{\mathrm{eq}} D_V$ is best described by an Arrhenius equation with $D_{0,V} = 62^{+35}_{-22}\,\mathrm{cm}^2/\mathrm{s}$ and $Q_V^{\mathrm{SD}} = (4.51 \pm 0.05)$ eV and $D_{0,V} = 206^{+112}_{-72}\,\mathrm{cm}^2/\mathrm{s}$ and $Q_V^{\mathrm{SD}} = (4.65 \pm 0.05)$ eV, respectively. The two temperature dependencies of $0.5\,C_V^{\mathrm{eq}} D_V$ are

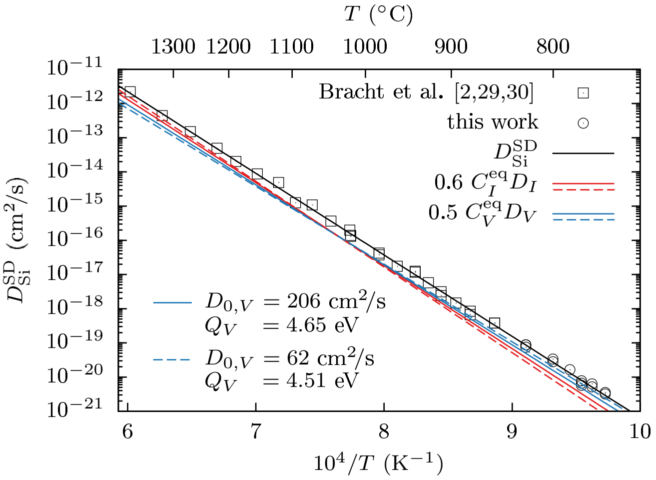

FIG. 5. Temperature dependence of Si self-diffusion determined in this work (open circles) and reported by Bracht *et al.* [2,29,30] (open squares). The $V$ contribution (blue lines) to self-diffusion is calculated by means of Eq. (2) via $f_V C_V^{\mathrm{eq}} D_V = (D_{\mathrm{Si}}^{\mathrm{SD}} - f_I C_I^{\mathrm{eq}} D_I)$ taking into account the total self-diffusion coefficient $D_{\mathrm{Si}}^{\mathrm{SD}}$ (symbols), the correlation factors $f_V = 0.5$ and $f_I \approx 0.6$, and the $I$ contribution $f_I C_I^{\mathrm{eq}} D_I$ (red lines) to self-diffusion from metal diffusion. Considering $f_I C_I^{\mathrm{eq}} D_I$ (red dashed line) from all data shown in Fig. 3, the uncorrelated transport capacity $C_V^{\mathrm{eq}} D_V$ of $V$ is best described by an Arrhenius equation with a pre-exponential factor of $D_{0,V} = 62^{+35}_{-22}$ cm$^2$/s and an activation enthalpy of $Q_V^{\mathrm{SD}} = (4.51 \pm 0.05)$ eV (blue dashed line). Neglecting the data of $C_I^{\mathrm{eq}} D_I$ reported by Mantovani *et al.* [18], $C_V^{\mathrm{eq}} D_V$ is described by $D_{0,V} = 206^{+122}_{-72}$ cm$^2$/s and $Q_V^{\mathrm{SD}} = (4.65 \pm 0.05)$ eV (blue solid line).

shown in Fig. 5 (see blue lines) together with the corresponding dependence of $0.6\, C_I^{\mathrm{eq}} D_I$ (see red lines) by the dashed and solid lines in comparison to the total Si diffusion coefficient $D_{\mathrm{Si}}^{\mathrm{SD}}$ (see symbols and black solid line). It is obvious that the $V$ and $I$ contributions to self-diffusion are of similar magnitude. This confirms the results of Ural *et al.* [3,4]. These authors studied the impact of oxidation and nitridation on dopant diffusion and self-diffusion. The fractional self-interstitial components $f_{\mathrm{Si}I} = 0.57^{+0.08}_{-0.10}$ and $f_{\mathrm{Si}I} = 0.50^{+0.08}_{-0.10}$ reported by Ural *et al.* for 1000 and 1100 °C, respectively, are considered to be most reliable [44,45]. $f_{\mathrm{Si}I}$ equals the ratio $D_{\mathrm{Si}}^{I}/D_{\mathrm{Si}}^{\mathrm{SD}}$ between the $I$ contribution $D_{\mathrm{Si}}^{I}$ to self-diffusion and the Si self-diffusion coefficient $D_{\mathrm{Si}}^{\mathrm{SD}}$ under thermal equilibrium. Taking into account the temperature dependence of $D_{\mathrm{Si}}^{\mathrm{SD}}$ given in this work and of $0.6\, C_I^{\mathrm{eq}} D_I$ obtained without (with) data reported by Mantovani *et al.* [18], a fractional self-interstitial component $f_{\mathrm{Si}I}$ of 0.51 (0.47) and 0.54 (0.56) is obtained for 1000 and 1100°C, respectively. The comparison to the values given by Ural *et al.* [3,4] reveals an accurate agreement for the individual contribution of $I$ to self-diffusion determined from metal- and dopant-diffusion experiments. The $I$ contribution to self-diffusion extracted by neglecting the results of Mantovani *et al.* yields a slightly better agreement on $f_{Si\,I}$ compared to the case where all metal data for $C_I^{\mathrm{eq}} D_I$ are considered. This favors activation enthalpies of 4.82 and 4.65 eV for self-diffusion via $I$ and $V$, respectively, rather than 5.01 and 4.51 eV. Overall, the $V$ and $I$ contributions to self-diffusion derived from self-diffusion, metal-diffusion, and dopant-diffusion studies are in excellent agreement.

The value determined in this work for $Q_V^{\mathrm{SD}} = (4.65 \pm 0.05)$ eV is also consistent with the activation enthalpy of dopant diffusion. For example, antimony (Sb) in Si mainly diffuses via $V$ [46] and is described by an activation enthalpy of 4.08 eV [47]. Assuming the difference between the activation enthalpy of self-diffusion and dopant diffusion in Si to be similar to that of Ge [48], that is, 0.3 to 0.6 eV [49], the activation enthalpy of $V$-mediated self-diffusion in Si is expected to be in the range of 4.4 to 4.7 eV (see Ref. [50]). This shows that the value of 4.65 eV for $V$-mediated self-diffusion is consistent with $V$-mediated dopant diffusion without claiming temperature-dependent thermodynamic $V$ properties as recently proposed by Kube *et al.* [7]. Moreover, the similarity between the activation enthalpy of $V$- and $I$-mediated self-diffusion confirms recent theoretical predictions of Bruneval *et al.* [51].

The data of $D_{\mathrm{Si}}^{\mathrm{SD}}$ summarized in Fig. 5 (see symbols) are accurately described by one single diffusion activation enthalpy ($Q_{\mathrm{Si}}^{\mathrm{SD}} = 4.73$ eV). This not only sets constraints with regard to the activation enthalpy of self-diffusion via $V$ and $I$ (see above) but also provides additional insight on the nature of the native point defects involved. Obviously, self-diffusion in Si under thermal equilibrium is accurately described by $V$ and $I$ contributions with constant, i.e., temperature-independent, diffusion activation enthalpies that are equal within 0.2 eV. This strongly questions the occurrence of distinct forms for both $I$ and $V$ with low and high entropies that were recently proposed by Cowern *et al.* [21]. Instead, the pre-exponential factors $D_{0,V}$ and $D_{0,I}$ provide activation entropies of $S_V^{\mathrm{SD}} = (10.9 \pm 0.4)\, k_B$ and $S_I^{\mathrm{SD}} = (11.6 \pm 0.5)\, k_B$ for self-diffusion via $V$ and $I$ [52]. No evidence of different types of either $V$- or $I$-related native defects at high and low temperatures is found. Accordingly, the concept of extended defects in Si with the temperature-dependent properties first proposed by Seeger and Chik [20] and recently renewed by Kube *et al.* [7] and Cowern *et al.* [21] is not supported by Si self-diffusion at temperatures in the range from 750 to 1400 °C.

## V. CONCLUSIONS

Self-diffusion experiments were performed with Si isotope structures annealed in high-purity crushed FZ-Si. Annealing in crushed Si effectively getters any possible residues of oxygen, hydroxyl groups, and transition elements due to the high-Si surface area. This limits surface reactions to the very beginning of the diffusion anneal and facilitates establishing thermal equilibrium conditions. Combining self-diffusion data determined in this work for low temperatures with equilibrium diffusion data reported in the literature for high temperatures, the Si self-diffusion coefficient $D_{\mathrm{Si}}^{\mathrm{SD}}$ is accurately described by

$$D_{\mathrm{Si}}^{\mathrm{SD}} = 423^{+113}_{-89} \exp\left(-\frac{(4.73 \pm 0.02)\,\mathrm{eV}}{k_B T}\right) \mathrm{cm}^2\,\mathrm{s}^{-1} \qquad (3)$$

for temperatures between 750 and 1400 °C. Taking into account results of the self-interstitial contribution to self-diffusion determined from metal-diffusion studies, the contributions of self-interstitials and vacancies to self-diffusion are given by

$$D_{\mathrm{Si}}^{I} = 0.6 \times 819^{+497}_{-309} \exp\left(-\frac{(4.82 \pm 0.05)\,\mathrm{eV}}{k_B T}\right)\mathrm{cm}^2\,\mathrm{s}^{-1}, \tag{4}$$

$$D_{\mathrm{Si}}^{V} = 0.5 \times 206^{+112}_{-72} \exp\left(-\frac{(4.65 \pm 0.05)\,\mathrm{eV}}{k_B T}\right)\mathrm{cm}^2\,\mathrm{s}^{-1}, \tag{5}$$

where 0.5 and 0.6 represent the diffusion correlation factors $f_V$ and $f_I$ for self-diffusion via the respective point defect. The activation enthalpy for self-diffusion via $V$ is consistent with dopant diffusion in Si without claiming temperature-dependent properties for native point defects. Overall the equilibrium self-diffusion data demonstrate that the properties of $V$ and $I$ do not change with temperature, i.e., the sum of the formation $H^f_{V,I}$ ($S^f_{V,I}$) and migration $H^m_{V,I}$ ($S^m_{V,I}$) enthalpy (entropy) equals $H_V^{\mathrm{SD}} = (4.65 \pm 0.05)$ eV [$S_V^{\mathrm{SD}} = (10.9 \pm 0.4)\,k_B$] and $H_I^{\mathrm{SD}} = (4.82 \pm 0.05)$ eV [$S_I^{\mathrm{SD}} = (11.6 \pm 0.5)\,k_B$] for $V$ and $I$, respectively.

## ACKNOWLEDGMENTS

This work was funded by the Deutsche Forschungsgemeinschaft under Grant No. BR1520/16-1 as well as an individual grant for H.B. within the Heisenberg program (BR1520/10-2). The authors appreciate Kohei M. Itoh, Mashashi Uematsu, Yasuo Shimizu, and Taiga Isoda (Keio University) for the MBE growth of the isotope structures #1 and #2.

---

[1] N. A. Stolwijk and H. Bracht, in *Diffusion in Semiconductors and Non-Metallic Solids*, edited by D. L. Beke, Landolt-Börnstein New Series, Vol. III/33, Subvolume A (Springer, Berlin, 1998), Chap. 2.

[2] H. Bracht, E. E. Haller, and R. Clark-Phelps, Silicon Self-Diffusion in Isotope Heterostructures, Phys. Rev. Lett. **81**, 393 (1998).

[3] A. Ural, P. B. Griffin, and J. D. Plummer, Self-Diffusion in Silicon: Similarity between the Properties of Native Point Defects, Phys. Rev. Lett. **83**, 3454 (1999).

[4] A. Ural, P. B. Griffin, and J. D. Plummer, Fractional contributions of microscopic diffusion mechanisms for common dopants and self-diffusion in silicon, J. Appl. Phys. **85**, 6440 (1999).

[5] S. R. Aid, T. Sakaguchi, K. Toyonaga, Y. Nakabayashi, S. Matumoto, M. Sakuraba, Y. Shimamune, Y. Hashiba, J. Murota, K. Wada, and T. Abe, Si self-diffusivity using isotopically pure $^{30}$Si epitaxial layers, Mater. Sci. Eng., B **114**, 330 (2004).

[6] H. Bracht, H. H. Silvestri, I. D. Sharp, and E. E. Haller, Self- and foreign-atom diffusion in semiconductor isotope heterostructures. II. Experimental results for silicon, Phys. Rev. B **75**, 035211 (2007).

[7] R. Kube, H. Bracht, E. Hüger, H. Schmidt, J. L. Hansen, A. N. Larsen, J. W. Ager, E. E. Haller, T. Geue, and J. Stahn, Contributions of vacancies and self-interstitials to self-diffusion in silicon under thermal equilibrium and nonequilibrium conditions, Phys. Rev. B **88**, 085206 (2013).

[8] E. Silveira, W. Dondl, G. Abstreiter, and E. E. Haller, Ge self-diffusion in isotopic $(^{70}\mathrm{Ge})_n(^{74}\mathrm{Ge})_m$ superlattices: A Raman study, Phys. Rev. B **56**, 2062 (1997).

[9] Y. Shimizu, M. Uematsu, and K. M. Itoh, Experimental Evidence of the Vacancy-Mediated Silicon Self-Diffusion in Single-Crystalline Silicon, Phys. Rev. Lett. **98**, 095901 (2007).

[10] E. Hüger, U. Tietze, D. Lott, H. Bracht, D. Bougeard, E. E. Haller, and H. Schmidt, Self-diffusion in germanium isotope multilayers at low temperatures, Appl. Phys. Lett. **93**, 162104 (2008).

[11] E. Hüger, J. Rahn, J. Stahn, T. Geue, and H. Schmidt, Diffusivity determination in bulk materials on nanometric length scales using neutron reflectometry, Phys. Rev. B **85**, 214102 (2012).

[12] E. Hüger, R. Kube, H. Bracht, J. Stahn, T. Geue, and H. Schmidt, A neutron reflectometry study on silicon self-diffusion at 900°C, Phys. Status Solidi B **249**, 2108 (2012).

[13] F. Morehead, N. A. Stolwijk, W. Meyberg, and U. Gösele, Self-interstitial and vacancy contributions to silicon self-diffusion determined from the diffusion of gold in silicon, Appl. Phys. Lett. **42**, 690 (1983).

[14] N. A. Stolwijk, B. Schuster, and J. Hölzl, Diffusion of gold in silicon studied by means of neutron-activation analysis and spreading-resistance measurements, Appl. Phys. A **33**, 133 (1984).

[15] N. A. Stolwijk, J. Hölzl, W. Frank, E. R. Weber, and H. Mehrer, Diffusion of gold in dislocation-free or highly dislocated silicon measured by the spreading-resistance technique, Appl. Phys. A **39**, 37 (1986).

[16] D. Grünebaum, Th. Czekalla, N. A. Stolwijk, H. Mehrer, I. Yonenaga, and K. Sumino, Diffusion and solubility of zinc in dislocation-free and plastically deformed silicon crystals, Appl. Phys. A **53**, 65 (1991).

[17] H. Bracht, N. A. Stolwijk, and H. Mehrer, Properties of intrinsic point defects in silicon determined by zinc diffusion experiments under nonequilibrium conditions, Phys. Rev. B **52**, 16542 (1995).

[18] S. Mantovani, F. Nava, C. Nobili, and G. Ottaviani, In-diffusion of Pt in Si from the PtSi/Si interface, Phys. Rev. B **33**, 5536 (1986).

[19] J. Hauber, W. Frank, and N. A. Stolwijk, Diffusion and Solubility of Platinum in Silicon, Mater. Sci. Forum **38**, 707 (1989).

[20] A. Seeger and K. P. Chik, Diffusion Mechanisms and Point Defects in Silicon and Germanium, Phys. Status Solidi **29**, 455 (1968).

[21] N. E. B. Cowern, S. Simdyankin, C. Ahn, N. S. Bennett, J. P. Goss, J.-M. Hartmann, A. Pakfar, S. Hamm, J. Valentin, E. Napolitani, D. De Salvador, E. Bruno, and S. Mirabella, Extended Point Defects in Crystalline Materials: Ge and Si, Phys. Rev. Lett. **110**, 155501 (2013).

[22] M. Suezawa, Y. Iijima, and I. Yonenaga, Comment on "Contributions of vacancies and self-interstitials to self-diffusion in silicon under thermal equilibrium and nonequilibrium conditions", Phys. Rev. B **90**, 117201 (2014).

[23] R. Kube, H. Bracht, E. Hüger, H. Schmidt, J. L. Hansen, A. N. Larsen, J. W. Ager, E. E. Haller, T. Geue, J. Stahn, M. Uematsu, and K. M. Itoh, Reply to "Comment on 'Contributions of vacancies and self-interstitials to self-diffusion in silicon under thermal equilibrium and nonequilibrium conditions' ", Phys. Rev. B **90**, 117202 (2014).

[24] H. Bracht, T. Südkamp, M. Radek, and A. Chroneos, Response to "Comment on 'Diffusion of n-type dopants in germanium' " [Appl. Phys. Rev. **2**, 036101 (2015)], Appl. Phys. Rev. **2**, 036102 (2015).

[25] N. E. B. Cowern, S. Simdyankin, J. P. Goss, E. Napolitani, D. De Salvador, E. Bruno, S. Mirabella, C. Ahn, and N. S. Bennett, Comment on "Diffusion of n-type dopants in germanium" [Appl. Phys. Rev. 1, 011301 (2014)], Appl. Phys. Rev. **2**, 036101 (2015).

[26] Y. Shimizu, M. Uematsu, K. M. Itoh, A. Takano, K. Sawano, and Y. Shiraki, Behaviors of neutral and charged silicon self-interstitials during transient enhanced diffusion in silicon investigated by isotope superlattices, J. Appl. Phys. **105**, 013504 (2009).

[27] Y. Shimizu and K. M. Itoh, Growth and characterization of short-period silicon isotope superlattices, Thin Solid Films **508**, 160 (2006).

[28] T. Kojima, R. Nebashi, K. M. Itoh, and Y. Shiraki, Growth and characterization of $^{28}\mathrm{Si}_n/^{30}\mathrm{Si}_n$ isotope superlattices, Appl. Phys. Lett. **83**, 2318 (2003).

[29] H. Bracht, E. E. Haller, K. Eberl, M. Cardona, and R. Clark-Phelps, Self-Diffusion in Isotopically Controlled Heterostructures of Elemental and Compound Semiconductors, Mater. Res. Soc. Symp. Proc. **527**, 335 (1998).

[30] H. Bracht, Diffusion mediated by doping and radiation-induced point defects, Phys. B (Amsterdam, Neth.) **376**, 11 (2006).

[31] H. Bracht, in *Defects and Impurities in Silicon Materials*, edited by Y. Yoshida and G. Langouche, Lecture Notes in Physics Vol. 916 (Springer, Tokyo, 2015), Chap. 1.

[32] K. C. Pandey, Diffusion without Vacancies or Interstitials: A New Concerted Exchange Mechanism, Phys. Rev. Lett. **57**, 2287 (1986).

[33] K. C. Pandey and E. Kaxiras, Entropy Calculation Beyond the Harmonic Approximation: Application to Diffusion by Concerted Exchange in Si, Phys. Rev. Lett. **66**, 915 (1991).

[34] P. E. Blöchl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, First-Principles Calculations of Self-Diffusion Constants in Silicon, Phys. Rev. Lett. **70**, 2435 (1993).

[35] K. Compaan and Y. Haven, Correlation factors for diffusion in solids, Trans. Faraday Soc. **52**, 786 (1956).

[36] M. Posselt, F. Gao, and H. Bracht, Correlation between self-diffusion in Si and the migration mechanisms of vacancies and self-interstitials: An atomistic study, Phys. Rev. B **78**, 035208 (2008).

[37] H. Bracht, in, *Silicon, Germanium, and Their Alloys: Growth, Defects, Impurities, and Nanocrystals*, edited by G. Kissinger and S. Pizzini (Taylor & Francis, London, 2014), Chap. 6.

[38] A. Chroneos and H. Bracht, Diffusion of n-type dopants in germanium, Appl. Phys. Rev. **1**, 011301 (2014).

[39] E. R. Weber, Transition metals in silicon, Appl. Phys. A **30**, 1 (1983).

[40] H. Bracht, Copper related diffusion phenomena in germanium and silicon, Mater. Sci. Semicond. Proc. **7**, 113 (2004).

[41] Details about the conversion of spreading-resistance data into concentrations are given in Ref. [42].

[42] H. Bracht, N. A. Stolwijk, and H. Mehrer, Diffusion and solubility of copper, silver, and gold in germanium, Phys. Rev. B **43**, 14465 (1991).

[43] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Point defects and dopant diffusion in silicon, Rev. Mod. Phys. **61**, 289 (1989).

[44] H. Bracht and E. E. Haller, Comment on "Self-Diffusion in Silicon: Similarity between the Properties of Native Point Defects", Phys. Rev. Lett. **85**, 4835 (2000).

[45] A. Ural, P. B. Griffin, and J. D. Plummer, Reply to "Comment on 'Self-Diffusion in Silicon: Similarity between the Properties of Native Point Defects' ", Phys. Rev. Lett. **85**, 4836 (2000).

[46] P. Fahey, S. S. Iyer, and G. J. Scilla, Experimental evidence of both interstitial- and vacancy-assisted diffusion of Ge in Si, Appl. Phys. Lett. **54**, 843 (1989).

[47] A. N. Larsen and P. Kringhoj, Diffusion of Sb in relaxed $\mathrm{Si}_{1-x}\mathrm{Ge}_x$, Appl. Phys. Lett. **68**, 2684 (1996).

[48] Self- and dopant diffusion in germanium under thermal equilibrium conditions are fully described by $V$ via the vacancy mechanism. A significant contribution of self-interstitials to diffusion in germanium under equilibrium conditions is not observed.

[49] S. Brotzmann and H. Bracht, Intrinsic and extrinsic diffusion of phosphorus, arsenic, and antimony in germanium, J. Appl. Phys. **103**, 033508 (2008).

[50] H. Bracht and A. Chroneos, The vacancy in silicon: A critical evaluation of experimental and theoretical results, J. Appl. Phys. **104**, 076108 (2008).

[51] F. Bruneval, Range-Separated Approach to the RPA Correlation Applied to the van der Waals Bond and to Diffusion of Defects, Phys. Rev. Lett. **108**, 256403 (2012).

[52] The pre-exponential factors are given by $D_{0,V} = g_V a_o^2 \nu_o \exp(S_V^{\mathrm{SD}}/k_B)$ and $D_{0,I} = g_I a_o^2 \nu_o \exp(S_I^{\mathrm{SD}}/k_B)$, where $g_V = 1/8\,(g_I = 1/4)$ is the geometry factor for diffusion via $V$ $(I)$; $a_o = 5.431$ Å, the lattice constant; and $\nu_o$, the attempt frequency that is of the order of the Debye frequency ($\approx 10^{13}\ \mathrm{s}^{-1}$).