Cowern NEB, Simdyankin S, Goss JP, Napolitani E, DeSalvador D, Bruno E, Mirabella S, Ahn C, Bennett NS.

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*Applied Physics Reviews* 2015, 2: 036101.

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The following article appeared in Applied Physics Reviews 2015, 2: 036101, and may be found at:

http://dx.doi.org/10.1063/1.4929762

Date deposited:

06/10/2015
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Citation: Applied Physics Reviews 2, 036101 (2015); doi: 10.1063/1.4929762
View online: http://dx.doi.org/10.1063/1.4929762
View Table of Contents: http://scitation.aip.org/content/aip/journal/apr2/2/3?ver=pdfcov
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Comment on “Diffusion of n-type dopants in germanium”  

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(Received 11 June 2014; accepted 26 June 2015; published online 2 September 2015)

The authors of the above paper call into question recent evidence on the properties of self-interstitials, I, in Ge [Cowern et al., Phys. Rev. Lett. 110, 155501 (2013)]. We show that this judgment stems from invalid model assumptions during analysis of data on B marker-layer diffusion during proton irradiation, and that a corrected analysis fully supports the reported evidence. As previously stated, I-mediated self-diffusion in Ge exhibits two distinct regimes of temperature, $T$: high-$T$, dominated by amorphous-like mono-interstitial clusters—i-morphs—with self-diffusion entropy $\approx 30 \text{ k}$, and low-$T$, where transport is dominated by simple self-interstitials. In a transitional range centered on $475 \text{ C}$ both mechanisms contribute. The experimental I migration energy of $1.84 \pm 0.26 \text{ eV}$ reported by the Münster group based on measurements of self-diffusion during irradiation at $550 \text{ C} < T < 680 \text{ C}$ further establishes our proposed i-morph mechanism.

Our evidence has been disputed by Bracht and co-workers.1,5 Their objection appears to be based on (a) a misunderstanding of our analysis of long-range BI migration in Ref. 2, (b) an erroneous analysis of BI mediated B diffusion in Ref. 1 and a precursor paper.6 To clarify the issues, we first briefly review the disputed analysis of Ref. 2. B diffuses in Ge, as in Si,7 via a fast migrating BI pair formed by the reaction $\text{B} + \text{I} \leftrightarrow \text{BI}$. A parallel reaction, $\text{B} \leftrightarrow \text{BI} + \text{V}$, also occurs but has no significant influence under the conditions of Refs. 1 and 2. BI in Ge, as in Si, has a large migration length, $\lambda$, a quantity closely connected to the difference in Gibbs free energy between BI and I.2 $\text{B}$ this leads to exponential diffusion tails after anneal times short enough that only a fraction of $\text{C}_{\text{B}}$ experiences a reaction with I to form BI. This behavior occurs under both equilibrium and irradiation conditions, with $\lambda$ independent of I supersaturation.7,8

To analyse this behavior, the diffusion of I, BI, and V can be modeled by numerical solution of the coupled equation system as in Refs. 1 and 6 and elsewhere. Under certain conditions, the full system can be reduced to one equation which has an analytical solution involving just $g$, $\lambda$, position, and time—the $g$-$\lambda$ solution.7,9 This is a mathematical approximation to the full equation system that describes the detailed properties of dopant diffusion and is applicable under equilibrium and non-equilibrium conditions. The necessary and sufficient conditions for accuracy of this approximation are

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A recent Applied Physics Review has discussed self-diffusion and B diffusion during irradiation at high temperature.1 Unfortunately, erroneous assumptions in B diffusion data analysis led the authors mistakenly to critique recent work by us that identified two forms of self-interstitial in Ge.2 Here, we show that their work when correctly interpreted confirms our conclusions. In the following discussion, $C_X$ and $D_X$ represent the concentration and diffusivity of species $X$, $E_X$ and $E_m$ ($S_X$ and $S_m$) its formation and migration energies (entropies), respectively, and $D_{SD}$ $= D_X C_X^m / C_0$, where $C_0$ is the lattice density, is the contribution of $X$ to equilibrium self-diffusion with activation energy $E_{SD}$ and activation entropy $S_{SD}$. The species described are the vacancy, V, self-interstitial, I, and B-interstitial pair, BI, and we consider two distinct forms of I; I and I. The first is the compact I, well known from the literature, the second is the i-morph—an extended self-interstitial with properties of a small amorphous pocket.2 This entity, in some ways reminiscent of the high-temperature “liquid drop” proposed by Seeger,3 however, needs to be understood from a fundamentally different perspective; the key feature is an amorphous-like property with corresponding energetic and entropic behavior.2

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that \( C_{BI} \ll C_{Bs} \), the Fermi level at the diffusion temperature, \( T \), is slowly varying in the local region of interest, and there are no significant gradients in \( C_I \) or \( C_F \). The latter condition prevails if \( D_{B} C_{B} \ll D_{F} C_{F}^{eq} \), and no significant gradients are generated by external processes. It is not necessary to assume point-defect equilibrium. When the preceding inequality is relaxed towards \( D_{B} C_{B} \sim D_{F} C_{F}^{eq} \), the rate of the reaction \( I + B \rightarrow BI \) is slightly modified by “chemical pump” effects but the \( g\lambda \) solution still accurately describes \( \lambda \). \(^{10}\)

In the experiments of Ref. 2, all these conditions were satisfied, so the \( g\lambda \) approach could be used to extract accurate \( \lambda \) values from our experimental secondary-ion mass spectrometry (SIMS) profiles, thus avoiding the costly use of a general diffusion solver as kernel in least-squares minimization. Following this analysis, we deduced a \( T \)-dependent free-energy difference between \( BI \) and \( I \), indicating that the latter has two distinct forms. The first, dominating \( I \)-mediated transport at low \( T \), is the simple \( I \). The second, dominating \( D_{SD} \) at high \( T \), is an extended \( I \); the \( i \)-morph. \(^{2}\)

A transitional region, where both defect forms contribute, exists over a \( \sim 10^2 \) \( K \) range centered on \( 475 \) \( K \). Reference 1 cites this analysis, claiming in error that the \( g\lambda \) approach is inapplicable under non-equilibrium conditions.

We now consider the analysis of B diffusion in Refs. 1 and 6. Fig. 17 of Ref. 1 presents B profiles in Ge measured by SIMS after proton irradiation of a B-doped Ge superlattice at 550 and 630 \( K \). To show clearly the detailed B profile shape evolution during diffusion, we have selected and plotted the data for a single marker layer in Fig. 1. The profile shows characteristic exponential-like tails (showing up as almost straight lines on the logarithmic plot of Fig. 1) on each side of the B-doped marker layers. The curves turn up at the edges of the plot owing to overlap of diffusion from neighboring markers. The data at 550 \( K \) show significantly more diffusion than at 630 \( K \), because at lower \( T \) both \( \lambda = (D_{BI}/(k_1 C_I))^{1/2} \) in Bracht’s notation) and the forward reaction rate \( g = k_1 C_I \) are larger. The larger \( \lambda \) reflects the increased number of BI diffusion jumps per migration event as the thermal energy available for dissociation, \( BI \rightarrow B + I \), is reduced. The larger \( g \) reflects the increased number of lattice sites each beam-generated I visits before recombining with \( V \). The static peak represents those \( B \) atoms which have not yet undergone reaction (1)—a statistical effect due to the finite arrival rate of \( I \) at \( B \).

The approach taken in Ref. 1, following Ref. 6, fails to recognize and model these key effects. This seems to be caused by unrealistic assumptions (a) on B clustering during annealing of initially substitutional B, (b) that \( C_{BI} \gg C_{Bs} \). In relation to point (a), Ref. 6 assumed a priori that, at all considered anneal times, \( \tau \), each B marker had a large clustered component, adjusted for each \( T/\tau \) combination to keep \( C_{Bs} \leq 5 \times 10^{18} \) \( cm^{-2} \). This ignores the transient dynamics of B clustering in the MBE-grown doping structure as BI migrates and traps on other B atoms. In the simulations of Ref. 6 (Fig. 17), clustering, unrealistically, actually decreases with time. Point (b) is a result of assuming \( S_{BI}^{eff} \approx 30k \)—a problematic choice as the entropy of \( D_{B} \), \( S_{BI}^{eff} + S_{m}^{eff} \approx 20k \) \(^{11}\) and negative \( S_{m}^{eff} \) is highly unlikely. It is unclear why such a large \( S_{BI}^{eff} \) has been used, unless it is to prevent \( D_{B} \) from varying as \((p/n)^2 \) as the model assumes BI is in a singly positive charge state. \(^{6}\) The result of these several choices is that all the simulated profiles have Gaussian shapes at low B concentration (blue curves in Fig. 1). This is a poor fit to the data, which show a clear exponential-like trend, thus directly demonstrating that \( C_{BI} \ll C_{Bs} \), refuting assumption (b) above and rendering equation (20) and Fig. 6 of Ref. 6 invalid. This key point is further underscored by the fact that proton irradiation experiments with almost identical Frenkel-pair production rates \(^{12}\) to those used in Ref. 1 explicitly show \( g \propto \phi \), where \( \phi \) is the beam flux \(^{8}\) (a test not reported in Refs. 1 and 6). The failure of the assumption \( C_{BI} \gg C_{Bs} \) is most graphically evident in the lower panel in Fig. 1, where we present data from an earlier study \(^{8}\) using very similar processing conditions. The data show essentially the same exponential tails as in Ref. 1, although in this case clustering is entirely absent, all B is available to diffuse, and the static peak represents those B atoms which have escaped interaction with I during the short annealing time. The imposition of \( C_{BI} \gg C_{Bs} \), however, identifies essentially all unclustered B as continuously diffusing BI, leading to a Gaussian diffusion profile.
Fully coupled models as in Refs. 1 and 6 easily reproduce observed exponential tails if model parameters are correct. A first step towards this goal is to eliminate the unrealistic saturation of $C_{BI}$. This can be done by reducing $S_I^I$ from 30 $k$ to below 20 $k$. This then allows extraction of other key parameters, inaccessible with the assumption $C_{BI} \gg C_{BS}$, such as the charge states of BI and I (from data on the Fermi-level dependence of B diffusion), and $E_I^I$, $S_I^I$ (from exponential tails, since $E_I^I$, $S_I^I$ determine the parameter $k_1^+$ in $\lambda = \{D_{BI}/(k_1^+ C_B)\}^{1/2}$ (Refs. 2 and 6)).

In Refs. 1 and 6, the peak $C_B$ is $\sim 10^x$ higher than in earlier experiments.2 In this situation, clustering, chemical-pump, and Fermi-level effects may all influence diffusion, so the data in Ref. 1 are a more complex resource for parameter determination than those in Ref. 2. Nevertheless, to illustrate the robustness of $\lambda$ extraction with the $g$-$\lambda$ approximation, we apply it, outside its strictly applicable range, to the data in Ref. 1, where conditions were optimal for extraction, is $\sim 1$ s$^{-1}$ at RT for $I$ directly observed in aberration-corrected TEM.19 Thus in retrospect one can see that the 1.84 eV value rules out the simple $I$ assumed in Ref. 1 and strongly favors the i-morph mechanism we proposed in Ref. 2. This has vast implications for defect physics which remain to be explored. Finally, taken together with our observed $E_{SD}^I$ = 6.1 eV at high $T$, $E_{SD}^I$ = 1.84 eV implies $E_{SD}^I \approx 4.3$ eV, in the range of recent atomistic calculations in course of publication.20 In conclusion, discussion prompted by conflicting analyses of experiments in Refs. 1, 2, and 6 has significantly progressed understanding of the complex behavior of self-interstitials in Ge.

Having dealt with B diffusion analysis in some detail in this comment, we would like to emphasize that Section V of Ref. 1 also references an elegant analysis of experiments by the Munster group and coworkers on the diffusivity of I in irradiation experiments on Ge isotope superlattices. That analysis revealed $E_{SD}^I$ = (1.84 ± 0.26) eV. This value far exceeds estimates of 0.5–0.6 eV obtained from perturbed angular correlation measurements at low $T$.16,17 0.6 eV obtained for simple I configurations from density functional theory using accurate LDA + U functionals,18 and <1 eV indicated by jump rates exceeding $\sim 1$ s$^{-1}$ at RT for I directly observed in aberration-corrected TEM.19 Thus in retrospect one can see that the 1.84 eV value rules out the simple $I$ assumed in Ref. 1 and strongly favors the i-morph mechanism we proposed in Ref. 2. This has vast implications for defect physics which remain to be explored. Finally, taken together with our observed $E_{SD}^I$ = 6.1 eV at high $T$, $E_{SD}^I$ = 1.84 eV implies $E_{SD}^I \approx 4.3$ eV, in the range of recent atomistic calculations in course of publication.20 In conclusion, discussion prompted by conflicting analyses of experiments in Refs. 1, 2, and 6 has significantly progressed understanding of the complex behavior of self-interstitials in Ge.

12. The beam flux in Ref. 8 is 0.377 that in Ref. 1, but the number of FPs produced per proton is about 3× higher.
13. The doping-independence of $I$ at 550 °C confirms that, at least at this temperature, the reaction $B_i = I \rightarrow BI$ is charge balanced without the involvement of charge carriers.
15. The data point at $\lambda = 1.5$ nm in Fig. 2 of Ref. 2 is suppressed by one with threefold improved accuracy,19 shown here.