Comment on “Diffusion of n-type dopants in germanium” [Appl. Phys. Rev. 1, 011301 (2014)]

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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 ≈30 k, and low-T, where transport is dominated by simple self-interstitials. In a transitional range centered on 475°C both mechanisms contribute. The experimental I migration energy of 1.84 ± 0.26 eV reported by the Münster group based on measurements of self-diffusion during irradiation at 550°C < T < 680°C further establishes our proposed i-morph mechanism. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4929762]

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^F_X and E^m_X (S^F_X and S^m_X) its formation and migration energies (entropies), respectively, and D_{SD}^X = D_X C_X S_{SD}^X/C_0, where C_0 is the lattice density, is the contribution of X to equilibrium self-diffusion with activation energy E_{SD}^X and activation entropy S_{SD}^X. 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,3a 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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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 B_s + I ↔ BI.8 A parallel reaction, B_s ↔ BI + 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, γ—a quantity closely connected to the difference in Gibbs free energy between BI and I.2 This leads to exponential diffusion tails after anneal times short enough that only a fraction of C Bs experiences a reaction with I to form BI. This behavior occurs under both equilibrium and irradiation conditions, with γ 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 γ, γ, position, and time—the g-γ 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
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 \( C_V \). The latter condition prevails if \( D_{BI}C_{BS} \ll D_I C_{BI}^{q} \), 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 \( D_{BI}C_{BS} \sim D_I C_{BI}^{q} \), the rate of the reaction \( I + B_I \rightarrow BI \) 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 \( D_{BI}^{D} \) at high \( T \), is an extended I: the i-morph. \(^{2}\) A transitional region, where both defect forms contribute, exists over a \( \sim 100^\circ \) range centered on \( 475^\circ \). 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 \( ^\circ \). 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 530 \( ^\circ \) show significantly more diffusion than at 630 \( ^\circ \), because at lower \( T \) both \( g = (D_{BI}/k_{B}T) \) (in Bracht’s notation) and the forward reaction rate \( g = (k_{B}T) \) 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 recombing with \( V \). The static peak represents those B which have not yet undergone reaction (1)—a statistical effect due to the finite arrival rate of I at \( B_s \).

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 \( C_{BI} \ll C_{BS} \). In relation to point (a), Ref. 6 assumed a priori that, at all considered anneal times, \( t \), each B marker had a large clustered component, adjusted for each \( T/t \) combination to keep \( C_{BS} \leq 5 \times 10^{18} \text{cm}^{-2} \). 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 \( S_{BI}^{H} \approx 30k \) —a problematic choice as the entropy of \( D_B, S_{BI}^{H} + S_{m}^{H} \approx 20k \)\(^ {11} \) and negative \( S_{m}^{H} \) is highly unlikely. It is unclear why such a large \( S_{H}^{BI} \) 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.

Fig. 1. Fits to data discussed in Refs. 1 and 2 using the method of Ref. 2 (red curves). The high quality of fit assures that extracted values of \( \lambda \) (18.8 nm at \( T = 550^\circ \) and 9.1 nm at \( T = 630^\circ \)) are close to the true migration length of BI at each T. Exponential tails indicate intermittent diffusion via fast-migrating BI with \( C_{BI} \ll C_{BS} \). Simulations assuming \( C_{BI} \gg C_{BS} \) (blue curves) give poor fits as this choice implies that all non-clustered B atoms diffuse continuously, leading to Gaussian curves at low B concentration (see especially the bottom blue curve).
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 $E_{SD} = (1.84 \pm 0.26)$ eV. This value far exceeds estimates of 0.5–0.6 eV obtained from perturbed angular correlation measurements at low $T$.\cite{16,17} 0.6 eV obtained for simple I configurations from density functional theory using accurate LDA + U functionals,\cite{18} and $<1$ eV indicated by jump rates exceeding $\sim 1 \text{s}^{-1}$ at RT for I directly observed in aberration-corrected TEM.\cite{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 $E_{SD} = 6.1$ eV at high $T$,\cite{2} $E_{SD} = 1.84$ eV implies $E_I \approx 4.3$ eV, in the range of recent atomistic calculations in course of publication.\cite{29} 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.

In Refs. 1 and 6, the peak $C_B$ is $\sim 10\times$ higher than in earlier experiments.\cite{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 “short-time” (1 h) B data of Refs. 1 and 6. The results, using the same $\lambda$ values as in Ref. 2, are shown in Fig. 1 (red curves).\cite{18} The fits are essentially perfect—far better than those obtained in Refs. 1 and 6. Moreover, unlike the fits in Ref. 1 they respect the data from Ref. 8, which explicitly showed $C_{BI} < C_{IB}$. It should now be clear that our analysis in Ref. 2, where conditions were optimal for $\lambda$ extraction, is extremely robust. Moreover, the B data discussed in Ref. 1 support the analysis in Ref. 2, not refuting it as claimed.\cite{1}

The B model parameters used in Ref. 1, however, are far from correct. We now restate the established position:\cite{2} our data (further supported by high-$T$ data in Refs. 1 and 6) show that I-mediated self-diffusion in Ge involves a simple $I$ at low $T$ (significantly below 475 °C), an i-morph, $\chi$, with $S_{SD} = 30 k$, $E_{SD} = 6.1$ eV at high $T$ (significantly above 475 °C), and a transitional region around 475 °C where both are significant. Finally, it should be noted that the open triangle\cite{14,15} in Fig. 2 shows that B also diffuses via BI under equilibrium conditions. An alternative model based on vacancy exchange\cite{1} would imply jump lengths of only 0.25 nm.

FIG. 2. Migration length of BI in Ge versus $1/kT$. Solid symbols: data from proton irradiation experiments using low peak B concentration to ensure ideal conditions for extracting $\lambda$.\cite{2} Open circles: values from Fig. 1 (both low and high peak B concentrations). Open triangle: value obtained after furnace annealing in inert ambient.\cite{14,15} The curve is the fit reported in Ref. 2 based on two forms of self-interstitial in Ge. The data from Ref. 1 are clearly consistent with our modeling and conclusions.

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 $S_{BI}$ from 30 $k$ to below 20 $k$. This then allows extraction of other key parameters, inaccessible with the assumption $C_{BI} > C_{IB}$, such as the charge states of B 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 $k_I^I$ in $\lambda = \langle D_{BI}(k_I^I C_B) \rangle^{1/2})$. (Refs. 2 and 6)).

12The beam flux in Ref. 8 is $0.37\times$ that in Ref. 1, but the number of FPs produced per proton is about $3\times$ higher.
13The doping-independence of $\lambda$ at 550 °C confirms that, at least at this temperature, the reaction $B_0 = I + I$ is charge balanced without the involvement of charge carriers.
15The data point at $\lambda = 1.5$ nm in Fig. 2 of Ref. 2 is superseded by one with threefold improved accuracy,\cite{19} shown here.