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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 $\approx 30\,k$, 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 $D_{SD}^X = D_X C_X^{eq}/C_0$, 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 η. 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,[3,4] 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]

Our evidence has been disputed by Bracht and coworkers.[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 $B_s + I \leftrightarrow BI$.[8] A parallel reaction, $B_s \leftrightarrow BI + V$, 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, λ—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 λ 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, λ, position, and time—the g-λ 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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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 $D_B C_B \ll D_I C_I^{eq}$, 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 $D_B C_B \sim D_I C_I^{eq}$, the rate of the reaction $I + B_s \rightarrow BI$ is slightly modified by "chemical pump" effects but the g-λ solution still accurately describes λ.[10]

In the experiments of Ref. 2, all these conditions were satisfied, so the g-λ approach could be used to extract accurate λ 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 $D_{SD}{}^{I}$ at high T, is an extended I; the i-morph.[2] A transitional region, where both defect forms contribute, exists over a ~100 °C range centered on 475 °C. Reference 1 cites this analysis, claiming in error that the g/λ 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 °C. 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 °C show significantly more diffusion than at 630 °C, because at lower T both λ $(=\{D_{BI}/(k_I^+ C_0)\}^{1/2}$ in Bracht's notation) and the forward reaction rate g $(=k_I^- C_I)$ are larger. The larger λ 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_s 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 $C_{BI} \gg C_{Bs}$. 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 $C_{Bs} \leq 5 \times 10^{18}\,cm^{-2}$. 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 $S_f{}^{BI} \approx 30\,k$—a problematic choice as the entropy of D_B, $S_f{}^{BI} + S_m{}^{BI} \approx 20\,k$[11] and negative $S_m{}^{BI}$ is highly unlikely. It is unclear why such a large $S_f{}^{BI}$ has been used, unless it is to prevent D_B from

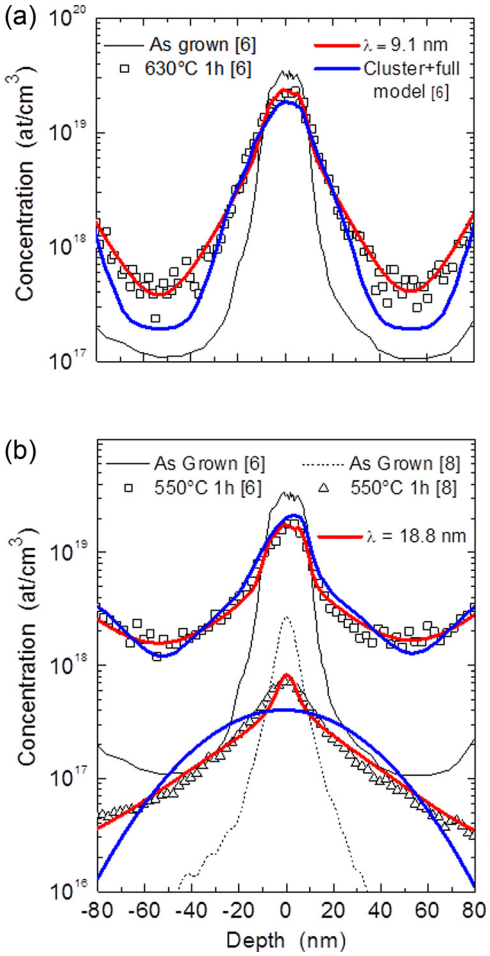

FIG. 1. Fits to data discussed in Refs. 1 and 2 using the method of Ref. 2 (red curves). The high quality of fit assures that extracted values of λ (18.8 nm at $T = 550$ °C and 9.1 nm at $T = 630$ °C) are close to the true migration length of BI at each T. Exponential tails indicate intermittent diffusion via fast-migrating BI with $C_{BI} \ll C_{Bs}$.[7,8] Simulations assuming $C_{BI} \gg C_{Bs}$[1] (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).

varying as $(p/n_i)^2$ 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 ϕ 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.

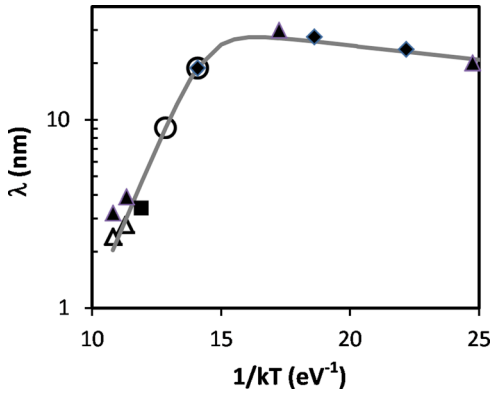

FIG. 2. Migration length of BI in Ge versus $1/kT$. Solid symbols: data from proton irradiation experiments using low peak B concentration to ensure ideal conditions for extracting λ.[2] Open circles: values from Fig. 1 (both low and high peak B concentrations). Open triangle: value obtained after furnace annealing in inert ambient.[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_f^{BI} 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_f^I, S_f^I (from exponential tails, since E_f^I, S_f^I determine the parameter k_1^+ in $\lambda = \{D_{BI}/(k_1^+ C_0)\}^{1/2}$ (Refs. 2 and 6)).

In Refs. 1 and 6, the peak C_B is $\sim 10\times$ 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 λ extraction with the g-λ 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 λ values as in Ref. 2, are shown in Fig. 1 (red curves).[13] 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 $C_{BI} \ll C_{Bs}$. It should now be clear that our analysis in Ref. 2, where conditions were optimal for λ extraction, is extremely robust. Moreover, the B data discussed in Ref. 1 support the analysis in Ref. 2, not refuting it as claimed.[1] The B *model parameters* used in Ref. 1, however, are far from correct. We now restate the established position:[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, $?$, with $S_{SD}^{?} \approx 30\,k$, $E_{SD}^{?} \approx 6.1$ 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[14,15] in Fig. 2 shows that B also diffuses via BI under equilibrium conditions. An alternative model based on vacancy exchange[1] would imply jump lengths of only 0.25 nm.

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.[6] That analysis revealed $E_m^I = (1.84 \pm 0.26)$ eV. This value far exceeds estimates of 0.5–0.6 eV obtained from perturbed angular correlation measurements at low T,[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 $E_{SD}^{?} = 6.1$ eV at high T,[2] $E_m^{?} = 1.84$ eV implies $E_f^{?} \approx 4.3$ 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.

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