



Heriot-Watt University  
Research Gateway

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

### Citation for published version:

Cowern, NEB, Simdyankin, S, Goss, JP, Napolitani, E, De Salvador, D, Bruno, E, Mirabella, S, Ahn, C & Bennett, NS 2015, 'Comment on “Diffusion of n-type dopants in germanium” [Appl. Phys. Rev. 1, 011301 (2014)]', *Applied Physics Reviews*, vol. 2, no. 3, 036101. <https://doi.org/10.1063/1.4929762>

### Digital Object Identifier (DOI):

[10.1063/1.4929762](https://doi.org/10.1063/1.4929762)

### Link:

[Link to publication record in Heriot-Watt Research Portal](#)

### Document Version:

Publisher's PDF, also known as Version of record

### Published In:

Applied Physics Reviews

### General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [open.access@hw.ac.uk](mailto:open.access@hw.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.

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

N. E. B. Cowern, S. Simdyankin, J. P. Goss, E. Napolitani, D. De Salvador, E. Bruno, S. Mirabella, C. Ahn, and N. S. Bennett

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>

Published by the [AIP Publishing](#)

---

**Articles you may be interested in**

[Response to “Comment on ‘Diffusion of n-type dopants in germanium’” \[Appl. Phys. Rev. 2, 036101 \(2015\)\]](#)  
Appl. Phys. Rev. **2**, 036102 (2015); 10.1063/1.4929763

[Diffusion of n-type dopants in germanium](#)  
Appl. Phys. Rev. **1**, 011301 (2014); 10.1063/1.4838215

[Interaction of n-type dopants with oxygen in silicon and germanium](#)  
J. Appl. Phys. **112**, 073706 (2012); 10.1063/1.4757406

[Multiple implantation and multiple annealing of phosphorus doped germanium to achieve n-type activation near the theoretical limit](#)  
Appl. Phys. Lett. **101**, 112107 (2012); 10.1063/1.4751845

[On the diffusion and activation of ion-implanted n-type dopants in germanium](#)  
J. Appl. Phys. **106**, 103516 (2009); 10.1063/1.3261838

---



**AIP** | Journal of  
Applied Physics

*Journal of Applied Physics* is pleased to  
announce **André Anders** as its new Editor-in-Chief

## APPLIED PHYSICS REVIEWS

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

N. E. B. Cowern,<sup>1,a)</sup> S. Simdyankin,<sup>1</sup> J. P. Goss,<sup>1</sup> E. Napolitani,<sup>2</sup> D. De Salvador,<sup>2</sup> E. Bruno,<sup>3</sup> S. Mirabella,<sup>3</sup> C. Ahn,<sup>4</sup> and N. S. Bennett<sup>5</sup>

<sup>1</sup>School of Electrical and Electronic Engineering, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom

<sup>2</sup>CNR-IMM-MATIS and Dipartimento di Fisica, Università di Padova, Via Marzolo 8, 35131 Padova, Italy

<sup>3</sup>CNR-IMM-MATIS and Dipartimento di Fisica e Astronomia, Università di Catania, Via S. Sofia 64, 95123 Catania, Italy

<sup>4</sup>Samsung Semiconductor, Inc., 3655 North First Street, San Jose, California 95134, USA

<sup>5</sup>Institute of Mechanical, Process and Energy Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

(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  $\approx 30k$ , 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  $1.84 \pm 0.26$  eV reported by the Münster group based on measurements of self-diffusion during irradiation at  $550^\circ\text{C} < T < 680^\circ\text{C}$  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.<sup>1</sup> 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.<sup>2</sup> 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  $\mathcal{I}$ . 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.<sup>2</sup> This entity, in some ways reminiscent of the high-temperature “liquid drop” proposed by Seeger,<sup>3,4</sup> however, needs to be understood from a fundamentally different perspective; the key feature is an *amorphous*-like property with corresponding energetic and entropic behavior.<sup>2</sup>

Our evidence has been disputed by Bracht and co-workers.<sup>1,5</sup> 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.<sup>6</sup> To clarify the issues, we first briefly review the disputed analysis of Ref. 2. B diffuses in Ge, as in Si,<sup>7</sup> via a fast migrating BI pair formed by the reaction  $B_s + I \leftrightarrow BI$ .<sup>8</sup> 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,  $\lambda$ —a quantity closely connected to the difference in Gibbs free energy between BI and I.<sup>2</sup> This leads to exponential diffusion tails after anneal times short enough that only a fraction of  $C_{B_s}$  experiences a reaction with I to form BI. This behavior occurs under both equilibrium and irradiation conditions, with  $\lambda$  independent of I supersaturation.<sup>7,8</sup>

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.<sup>7,9</sup> 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

<sup>a)</sup>Electronic mail: nick.cowern@ncl.ac.uk

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  $g$ - $\lambda$  solution still accurately describes  $\lambda$ .<sup>10</sup>

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  $D_{SD}^I$  at high  $T$ , is an extended I; the *i*-morph.<sup>2</sup> A transitional region, where both defect forms contribute, exists over a  $\sim 100^\circ\text{C}$  range centered on  $475^\circ\text{C}$ . 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  $630^\circ\text{C}$ . 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  $550^\circ\text{C}$  show significantly more diffusion than at  $630^\circ\text{C}$ , because at lower  $T$  both  $\lambda$  ( $= \{D_{BI}/(k_1^+ C_0)\}^{1/2}$  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  $B_s$  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  $C_{Bs} \leq 5 \times 10^{18} \text{cm}^{-2}$ . 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  $S_f^{BI} \approx 30k$ —a problematic choice as the entropy of  $D_B$ ,  $S_f^{BI} + S_m^{BI} \approx 20k$ <sup>11</sup> 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

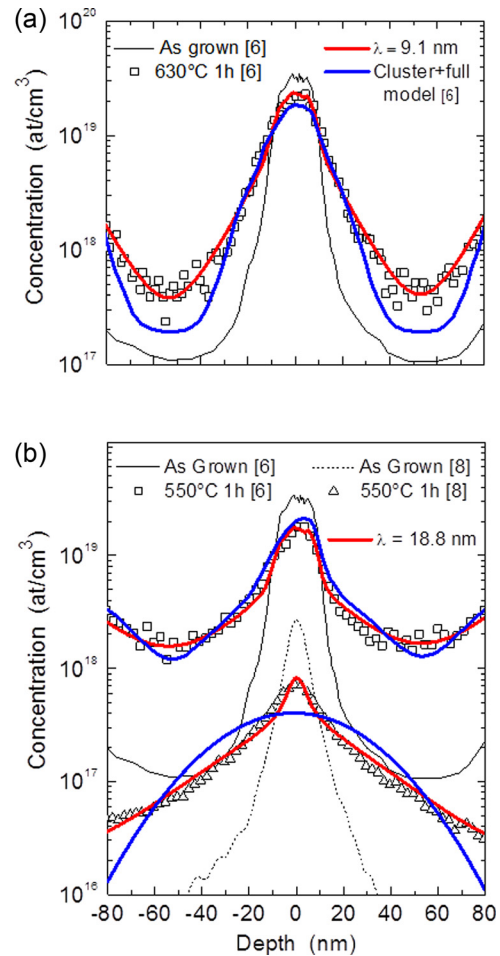


FIG. 1. Fits to data discussed in Refs. 1 and 2 using the method of Ref. 2 (red curves). The high quality of fit assures that extracted values of  $\lambda$  (18.8 nm at  $T = 550^\circ\text{C}$  and 9.1 nm at  $T = 630^\circ\text{C}$ ) are close to the true migration length of BI at each  $T$ . Exponential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

varying as  $(p/n_i)^2$  as the model assumes BI is in a singly positive charge state.<sup>6</sup> 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<sup>12</sup> to those used in Ref. 1 explicitly show  $g \propto \phi$ , where  $\phi$  is the beam flux<sup>8</sup> (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<sup>8</sup> 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.



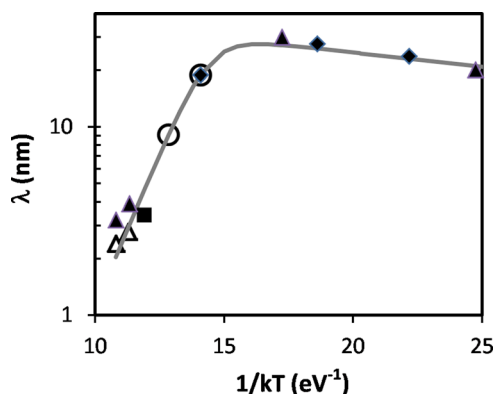


FIG. 2. Migration length of BI in Ge versus  $1/kT$ . Solid symbols: data from proton irradiation experiments using low peak B concentration to ensure ideal conditions for extracting  $\lambda$ .<sup>2</sup> Open circles: values from Fig. 1 (both low and high peak B concentrations). Open triangle: value obtained after furnace annealing in inert ambient.<sup>14,15</sup> 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  $C_{\text{BI}}$ . This can be done by reducing  $S_{\text{f}}^{\text{BI}}$  from  $30k$  to below  $20k$ . This then allows extraction of other key parameters, inaccessible with the assumption  $C_{\text{BI}} \gg C_{\text{BS}}$ , such as the charge states of BI and I (from data on the Fermi-level dependence of B diffusion), and  $E_{\text{f}}^{\text{I}}$ ,  $S_{\text{f}}^{\text{I}}$  (from exponential tails, since  $E_{\text{f}}^{\text{I}}$ ,  $S_{\text{f}}^{\text{I}}$  determine the parameter  $k_1^+$  in  $\lambda = \{D_{\text{BI}}/(k_1^+ C_0)\}^{1/2}$  (Refs. 2 and 6)).

In Refs. 1 and 6, the peak  $C_{\text{B}}$  is  $\sim 10\times$  higher than in earlier experiments.<sup>2</sup> 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).<sup>13</sup> 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  $C_{\text{BI}} \ll C_{\text{BS}}$ . 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.<sup>1</sup> The B model parameters used in Ref. 1, however, are far from correct. We now restate the established position:<sup>2</sup> 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  $475^\circ\text{C}$ ), an i-morph,  $\mathcal{I}$ , with  $S_{\text{SD}}^{\mathcal{I}} \approx 30k$ ,  $E_{\text{SD}}^{\mathcal{I}} \approx 6.1\text{ eV}$  at high  $T$  (significantly above  $475^\circ\text{C}$ ), and a transitional region around  $475^\circ\text{C}$  where both are significant. Finally, it should be noted that the open triangle<sup>14,15</sup> in Fig. 2 shows that B also diffuses via BI under equilibrium conditions. An alternative model based on vacancy exchange<sup>1</sup> would imply jump lengths of only  $0.25\text{ nm}$ .

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.<sup>6</sup> That analysis revealed  $E_{\text{m}}^{\text{I}} = (1.84 \pm 0.26)\text{ eV}$ . This value far exceeds estimates of  $0.5$ – $0.6\text{ eV}$  obtained from perturbed angular correlation measurements at low  $T$ ,<sup>16,17</sup>  $0.6\text{ eV}$  obtained for simple I configurations from density functional theory using accurate LDA + U functionals,<sup>18</sup> and  $<1\text{ eV}$  indicated by jump rates exceeding  $\sim 1\text{ s}^{-1}$  at RT for I directly observed in aberration-corrected TEM.<sup>19</sup> Thus in retrospect one can see that the  $1.84\text{ eV}$  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  $E_{\text{SD}}^{\mathcal{I}} = 6.1\text{ eV}$  at high  $T$ ,<sup>2</sup>  $E_{\text{m}}^{\mathcal{I}} = 1.84\text{ eV}$  implies  $E_{\text{f}}^{\mathcal{I}} \approx 4.3\text{ eV}$ , in the range of recent atomistic calculations in course of publication.<sup>20</sup> 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.

<sup>1</sup>A. Chroneos and H. Bracht, *Appl. Phys. Rev.* **1**, 011301 (2014).

<sup>2</sup>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).

<sup>3</sup>A. Seeger and K. P. Chik, *Phys. Status Solidi* **29**, 455 (1968).

<sup>4</sup>A. Seeger, *Phys. Status Solidi B* **248**, 2772 (2011).

<sup>5</sup>H. Bracht, R. Kube, E. Hüger, and H. Schmidt, *Solid State Phenom.* **205–206**, 151 (2014).

<sup>6</sup>S. Schneider, H. Bracht, J. N. Klug, J. Lundgaard-Hansen, A. Nylandsted-Larsen, D. Bougeard, and E. E. Haller, *Phys. Rev. B* **87**, 115202 (2013).

<sup>7</sup>N. E. B. Cowern, G. F. A van de Walle, D. J. Gravesteijn, and C. J. Vriezema, *Phys. Rev. Lett.* **67**, 212 (1991).

<sup>8</sup>E. Bruno, S. Mirabella, G. Scapellato, G. Impellizzeri, A. Terrasi, F. Priolo, E. Napolitani, D. De Salvador, M. Mastromatteo, and A. Camera, *Phys. Rev. B* **80**, 033204 (2009).

<sup>9</sup>N. E. B. Cowern, K. T. F. Janssen, G. F. A. van de Walle, and D. J. Gravesteijn, *Phys. Rev. Lett.* **65**, 2434 (1990).

<sup>10</sup>N. E. B. Cowern, B. Colombeau, F. Roozeboom, M. Hopstaken, H. Snijders, P. Meunier-Beillard, and W. Lerch, in *Si Front-End Formation Technologies*, edited by D. F. Downey, M. E. Law, A. P. Claverie, and M. J. Rendon (Mater. Res. Soc. Symp. Proc., 2002), Vol. 717, p. 255.

<sup>11</sup>S. Uppal, A. F. W. Willoughby, J. M. Bonar, N. E. B. Cowern, T. Grasby, R. J. H. Morris, and M. G. Dowsett, *J. Appl. Phys.* **96**, 1376 (2004).

<sup>12</sup>The 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.

<sup>13</sup>The doping-independence of  $\lambda$  at  $550^\circ\text{C}$  confirms that, at least at this temperature, the reaction  $\text{B}_s + \text{I} \leftrightarrow \text{BI}$  is charge balanced without the involvement of charge carriers.

<sup>14</sup>G. G. Scapellato, E. Bruno, A. J. Smith, W. Napolitani, D. De Salvador, S. Mirabella, M. Mastromatteo, A. Camera, R. Gwilliam, and F. Priolo, *Nucl. Instrum. Methods Phys. Res. B* **282**, 8 (2012).

<sup>15</sup>The data point at  $\lambda = 1.5\text{ nm}$  in Fig. 2 of Ref. 2 is superseded by one with threefold improved accuracy,<sup>14</sup> shown here.

<sup>16</sup>H. Haesslein, R. Sielemann, and C. Zistl, *Phys. Rev. Lett.* **80**, 2626 (1998).

<sup>17</sup>R. Sielemann, *Nucl. Instrum. Methods Phys. Res. B* **146**, 329 (1998).

<sup>18</sup>P. Śpiewak, J. Vanhellefont, K. Sueoka, K. J. Kurzydowski, and I. Romandic, *Mater. Sci. Semicond. Proc.* **11**, 328 (2008).

<sup>19</sup>D. Alloyeau, B. Freitag, S. Dag, L. W. Wang, and C. Kisielowski, *Phys. Rev. B* **80**, 014114 (2009).

<sup>20</sup>S. Simdyankin and J. P. Goss, private communication (2013).