Diffusion and defect reactions between donors, C, and vacancies in Ge. II. Atomistic calculations of related complexes

A. Chroneos[*]

Institute of Material Physics, University of Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany

R. W. Grimes

Department of Materials, Imperial College London, London SW7 2BP, United Kingdom

B. P. Uberuaga

Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

H. Bracht

Institute of Material Physics, University of Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany

Electronic structure calculations are used to study the stability, concentration, and migration of vacancy-donor (phosphorus, arsenic, and antimony) complexes in germanium, in the presence of carbon. The association of carbon with mobile vacancy-donor pairs can lead to energetically favorable and relatively immobile complexes. It is predicted that the complexes formed between lattice vacancies, carbon, and antimony substitutional atoms are more stable and less mobile compared to complexes composed of vacancies, carbon, and phosphorus or arsenic atoms. Then, with the use of mass action analysis, the relative concentrations of the most important complexes are calculated, which depend also on their relative stability not just their absolute stability. Overall, the theoretical predictions are consistent with experimental results, which determined that the diffusion of vacancy-donor defects is retarded in the presence of carbon, especially in samples with a high concentration of carbon. In addition, the calculations provide information on the structure and the equilibrium concentration of the most important complexes and details of their association energies.

I. INTRODUCTION

The advent of high-k dielectrics in conjunction with the need to replace silicon (Si) with higher mobility substrates has regenerated interest in the use of germanium (Ge) in advanced nanoelectronic devices.[1,2] The advantages of Ge include its relative compatibility with Si manufacturing processes, its smaller band gap, and increased dopant solubility compared to those of Si.[3]

The continuous decrease in the size of electronic devices requires the formation of ultrashallow junctions with high electrically active dopant concentrations. In Ge, boron (B) has been integrated as a successful p-type dopant;[4,5] but for n-type dopants such as phosphorus (P), there are problems with diffusion and activation control.[6–8] In recent experimental studies,[9–12] it has been determined that donor diffusion in Ge occurs via a vacancy (V)–mediated process. This is in contrast to Si, where the diffusion of n-type dopants, such as P and arsenic (As), is mediated both by self-interstitials and V.[13,14]

For the development of Ge-based devices, it is important to be able to design specific selective area doping that results in the appropriate distribution of dopants in the region of interest. It is therefore important to determine the migration processes associated with donor (A) atoms in Ge. Density-functional-theory (DFT) techniques can provide information to aid experimental and Monte Carlo investigations regarding the interaction of donor (with $A \in \{P, As, Sb\}$) atoms with V and carbon (C) in Ge. Previous DFT studies have demon-

strated that donor atoms in Ge associate with V forming complexes.[15–19] Equivalent methods have also been used in conjunction with experimental and Monte Carlo techniques to study phosphorus-vacancy (PV) pairs in Si and silicon germanium alloys (SiGe),[20,21] and AsV pairs in Si.[22] In a recent DFT study, the stability of complexes formed between C atoms and donor-vacancy (AV) pairs was discussed.[23] The aim of this study is to predict the stability, concentration, and migration of complexes formed between A, C, and V in Ge.

II. THEORETICAL METHODOLOGY

Equilibrium structures and energies for defects in Ge were calculated using a plane-wave basis with an energy cutoff of 350 eV. The generalized gradient approximation (GGA) was applied using the Perdew-Burke-Ernzerhof (PBE) (Ref. 24) exchange-correlation functional combined with ultrasoft pseudopotentials.[25] All the calculations were performed using the CASTEP code.[26,27] Ge was modeled using a 64 site tetragonal diamond structure (under zero pressure conditions) with Brillouin-zone sampling using a Monkhorst-Pack[28] grid of 2^3 k points. Unit-cell parameters and atomic coordinates were allowed to relax using energy minimization. The efficacy and adequate convergence of the present computational approach was demonstrated in previous studies,[29–32] by comparing the predictions with experimental studies.

To inspect the migration and association energy barriers, the linear synchronous transit (LST) method,[33] as developed

by Halgren and Lipscomb,[34] was implemented. In the LST method, geometric interpolation between a reactant and a product is used to generate a reaction pathway within a constant volume configuration. An idealized set of structures that connect the reactant to the product configuration is generated by interpolating distances between pairs of atoms in the reactant and product. In conjunction with single point energy calculations, this approach can be applied to study transition states. The LST method was recently applied by Zhang *et al.*[35] to study AsV diffusion in Si, Ge, and SiGe alloys.

DFT calculations based on the local-density approximation (LDA) and GGA underestimate the formation energies of defects in Si and Ge, due to the approximate representation of exchange in these functionals.[36,37] For this reason the present work focuses on binding energies and association energy barriers (differences in energy) as these are expected to be less sensitive to systematic errors in the exchange-correlation energy.

III. RESULTS AND DISCUSSION

A. Stability and concentration of complexes

The stability of the predicted AV pairs with respect to the CVA complexes has been compared to the experimental results and discussed extensively in Part I. Here we consider the stability of those complexes that are likely to have significant concentrations in C-doped Ge. As discussed in Part I, negative binding energies imply that the defect complex is more stable than the isolated defect species.

We will first consider complexes formed between substitutional C atoms and V. The binding energy needed to form a CV pair is only −0.07 eV.[23] This suggests that C is unlikely to associate with a V and migrate via a V-mediated mechanism. Therefore, the presence of C will not affect the free V concentration significantly and thus Ge self-diffusion should not be influenced by the presence of C. We cannot exclude, however, the possibility of limited C diffusion via random encounters with V. The limited diffusion of C is consistent with the experimental results in Part I.

The CC pair is not bound (0.90 eV) but can be stabilized by the introduction of a V. In particular, the CVC complex has a binding energy of −0.24 eV.[38] This low binding energy, in conjunction with the low diffusivity of C in Ge, will retard the formation of larger complexes containing only C and V. The formation of these larger complexes will therefore be hindered on experimental time scales. In accordance with this theoretical prediction, transmission electron microscopy did not reveal the presence of complexes containing C within the epitaxial Ge layers (see Part I).

In a recent study,[15] it was predicted that the formation of complexes containing up to but not exceeding four As atoms around a V is energetically favorable in Ge. Equivalent complexes containing P are also predicted to be bound (see Table I). Conversely, the Sb$_5V$ complex is more strongly bound than Sb$_4V$, though by −0.1 eV only (Table I). In Part I, A_2V complexes were determined to be neutral and as such their migration is insensitive to the doping conditions (intrinsic or extrinsic).[39] The concentration of A_2V is important as these complexes act as precursors to the formation of larger A_nV

TABLE I. Predicted binding energies E_b (eV) of C$_m(A_nV)_x$ complexes ($A \in \{$P, As, Sb$\}$), with respect to isolated species, in Ge.

Defect complex	P	As	Sb
AV	−0.52	−0.60	−0.70
AV_2	−1.19	−1.24	−1.39
A_2V	−1.06	−1.22	−1.40
A_3V	−1.54	−1.82	−2.10
A_4V	−2.27	−2.62	−2.75
A_5V	−2.13	−2.51	−2.85
CA	0.24	0.24	0.02
CVA	−0.60	−0.66	−0.72
CAV	−0.47	−0.55	−0.85
C$(AV)_2$	−2.08	−2.21	−2.26

complexes, which in turn contribute to the inactivity of donors in heavily doped Ge.[15,39] In Part I, the A_2V complexes were determined to be relatively immobile compared to the AV pairs. This is consistent with previous DFT studies in Si, which predicted that the migration energy barriers of As$_2V$ complexes are higher, by about 0.8 eV, compared to those of AsV.[40] The high migration energy barriers of A_2V complexes will mean that the formation of the larger complexes via A_2V complexes might be slow.[40] What has not been excluded, however, is that the larger A_nV complex may form via other routes, involving, for example, only the migration of AV pairs with the extra V diffusing away.

In a previous study,[23] it was predicted that both P and As atoms prefer the full-vacancy configuration, where the host atom is situated on a normal lattice site. A constant volume DFT/LDA study by Höhler *et al.*[41] predicted that Sb is more bound in the split-vacancy, or bond-centered configuration, in which the substitutional atom is surrounded by two semivacancies.[42] Conversely, the present zero pressure GGA study predicts that the full-vacancy configuration for SbV is more favorable by −0.10 eV compared to the split-vacancy configuration. The present result is also supported by the constant volume calculations of Coutinho *et al.*[16] that predicted a full-vacancy configuration for all charge states of SbV.

Differences between the binding energies of different donor atoms A_nV originate partly from the greater size of Sb compared to P and As and therefore from the greater lattice strain induced by the introduction of Sb atoms. The predicted nearest-neighbor separation of an Sb substitutional atom to Ge is 2.67 Å, compared to the Ge-Ge bond of 2.48 Å, the P-Ge separation of 2.45 Å, and the As-Ge separation of 2.54 Å.[23] Thus, Sb is more bound to V as it provides more space for lattice relaxation, reducing the strain in the Ge lattice. This is reflected in the binding energies in Table I, where the largest atom (Sb) forms the most stable complexes in each case.

The CA complexes are not stable; however, they do become stable when they are associated with lattice V. In Part I, the formation of C$(AV)_n$ was suggested to explain the different values for the effective concentration C$_C^{\mathrm{eff}}$ of C traps that are required to accurately model the diffusion of the *n*-type
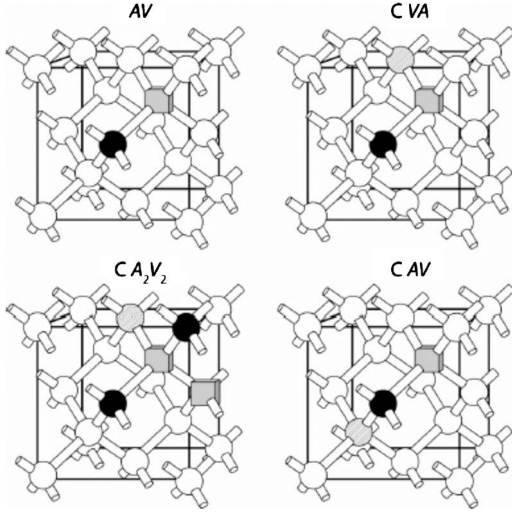
FIG. 1. A schematic representation of the AV, CVA, CAV, and $C(AV)_2$ complexes in Ge. White circles represent the Ge atoms, gray circles the C atoms, black circles the donor atoms, and squares the V.

FIG. 2. The temperature dependence of the $C_m(P_nV)_x$ complexes in Ge. The initial $[C]=[P]=[V]=10^{20}$ cm^{-3}.

dopants in the C-doped Ge-isotope heterostructures. The $C(AV)_n$ complexes can form via trapping of more than one AV pair by a substitutional C atom (see Fig. 1). The calculations predict that the trapping of an extra AV pair by a CVA complex results in an increase in the binding energy of -1.61 eV for $C(PV)_2$, of -1.66 eV for $C(AsV)_2$, and of -1.41 eV for $C(SbV)_2$ (see Table I). For the three donor atoms considered here, the most energetically favorable structure of the $C(AV)_2$ complex is with V in the middle surrounded by a V, a C, and two donor atoms, all at first-nearest-neighbor sites (see Fig. 1).

By using the binding energies of Table I, the relative concentration of $C_mA_nV_x$ complexes can be predicted through mass action analysis.[43] The total concentration of V, A, and substitutional C is required as part of the model. The mass action framework predicts the equilibrium behavior of defects (assuming the total C, V, and A content remains fixed), toward which the system tries to evolve, providing information on the equilibrium state of the system. It should be noted, however, that kinetics can hinder the ability of the system to reach the equilibrium state in experiments. The concentration of a $C_mA_nV_x$ complex, $[C_mA_nV_x]$, relative to the concentrations of its isolated components $[C]$, $[A]$, and $[V]$ is

$$\frac{[C_mA_nV_x]}{[C]^m[A]^n[V]^x} = \exp\left[\frac{-E_b(C_mA_nV_x)}{k_BT}\right], \quad (1)$$

where k_B is the Boltzmann constant; T is the temperature; and $[V]$, $[C]$, and $[A]$ are the concentration of unbound V, C, and A atoms, respectively. A similar methodology has been recently used to study As_nV_m complexes in Ge.[15]

Figure 2 represents the relative concentrations of P_nV ($n \le 4$), PV_2, and $C(PV)_2$, which are calculated to be the $C_mP_nV_x$ complexes with the highest concentrations. In this figure the initial C, P, and V concentrations were assumed to be 10^{20} cm^{-3}. These P and C concentrations correspond to
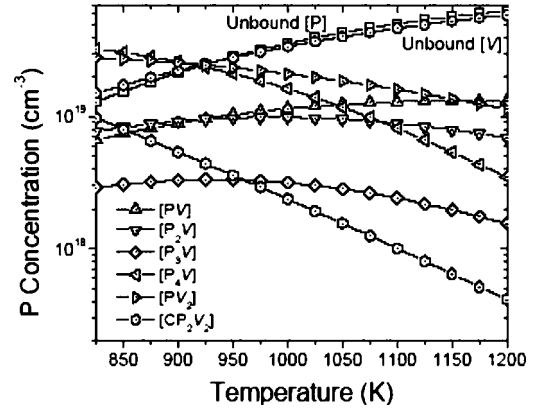
the experimental conditions of Part I. The high V concentrations considered [note that the V concentration exceeds the equilibrium concentration in Ge (i.e., $\sim 10^{15}$ cm^{-3} at 1200 K)[44] by several orders of magnitude] approximate the V concentrations trapped in the C-rich regions described in Part I.

From Fig. 2 it is evident that the predicted unbound $[P]$ is in excellent agreement with the experimentally determined values, where, for example, at 973 K the unbound $[P]$ is on the order of 10^{19} cm^{-3} (see Table I of Part I). The unbound $[P]$, $[V]$, and the $[PV]$ pair concentrations increase with temperature. It is also predicted that over the temperature range considered, the less mobile P_2V complexes are found in large concentrations, containing more than 7×10^{18} cm^{-3} P atoms. Interestingly, at 825 K the CP_2V_2 complexes trap about 10% of the P; this reduces as the temperature increases (for example, 1% at 1100 K). The CVP complex is not included in Fig. 2 as its concentration is significantly below 10^{17} cm^{-3} in the temperature range considered.

A behavior similar to that in Fig. 2 has been predicted for the complexes containing As and Sb atoms. To compare the trapping of the donor atoms by C, the temperature dependence of the A atoms trapped by CA_2V_2 complexes is presented in Fig. 3, for two initial C concentrations: 10^{19} and 10^{20} cm^{-3}. This figure suggests that the CP_2V_2 and CAs_2V_2

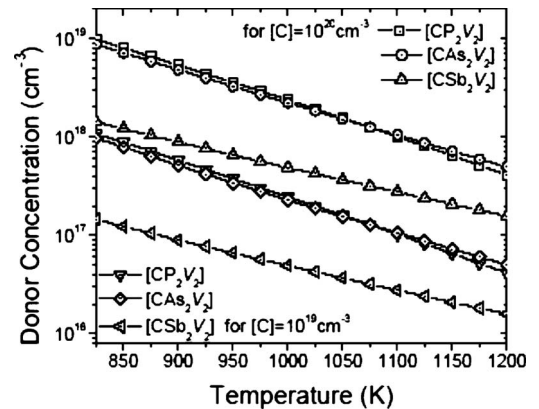FIG. 3. The temperature dependence of the CA_2V_2 complexes ($A \in \{P, As, Sb\}$) in Ge. The initial $[A]=[V]=10^{20}$ cm^{-3}, whereas two initial C concentrations of 10^{19} and 10^{20} cm^{-3} were used.

complexes trap C atoms to the same order of magnitude, for both the low and the high C concentration cases, although up to about 1000 K more P atoms are trapped by these complexes than As atoms. This predicted trend is in good agreement with the results of Table I in Part I, where, for example, at 973 K more P atoms are trapped by $C(PV)_n$ than As are trapped by $C(AsV)_n$ complexes. Quantitatively, however, the predictions are about an order of magnitude lower.

It is predicted that a lower concentration of Sb atoms are trapped by CSb_2V_2 complexes than P (or As) atoms trapped by CP_2V_2 (or CAs_2V_2) complexes (see Fig. 3). Considering only the binding energies of the CA_2V_2 complexes, this is not intuitively obvious as CSb_2V_2 is more strongly bound than CP_2V_2 or CAs_2V_2. However, Table I shows that the immobile Sb_3V and Sb_4V complexes are more bound than their equivalent P_3V and P_4V or As_3V and As_4V complexes. This means that Sb_3V and Sb_4V complexes trap more Sb atoms, effectively reducing the concentration of Sb atoms that are available to be trapped by CSb_2V_2 complexes. Therefore, although the unbound [Sb] is less than [P] or [As], a higher percentage of Sb is trapped by Sb_3V and Sb_4V than by CSb_2V_2, compared to the situation for P or As complexes. At this point it should be stressed that this analysis assumes equilibrium conditions. In experiments, the formation of A_3V and A_4V complexes might be kinetically hindered, since it was determined in previous studies[39,40] that the A_2V complexes, which might act as precursors to their formation, diffuse at a slow rate. Conversely, the formation of $C(AV)_n$ complexes is unaffected as AV complexes are very mobile in Ge.[12] In that respect, if the $C(AV)_n$ complexes are kinetically favored, the $C(SbV)_n$ complexes will trap more Sb atoms than P atoms by $C(PV)_n$ or As atoms by $C(AsV)_n$, since $C(SbV)_n$ complexes have a higher binding energy. This is consistent with the experimental results (Part I), where the diffusion of SbV pairs is retarded more than that of AsV or PV in the presence of C. Finally, from Fig. 3 it can be deduced that more donor atoms are trapped by $C(AV)_n$ complexes, at lower temperatures and higher initial C concentrations. In Sec. III B, in order to gain some insight into the kinetics of complex formation discussed above, the migration energy barriers of AV pairs are examined in the presence of C.

B. Association barriers of AV near C

A previous experimental study by Werner *et al.*[45] concluded that Ge self-diffusion is mediated by V. Previous studies predict V formation energies in the range of 1.7–2.2 eV (Refs. 46 and 47) and the self-interstitial (most stable neutral structure is the $\langle 110 \rangle$ dumbbell)[48] formation energies from 2.3 to 4.1 eV.[49–51] Consequently, in Ge, self-interstitials are not as important as in Si and most diffusion processes are dominated by V.[9–12] A significant exception to the V domination of diffusion processes in Ge occurs for B. Experimental studies determined that B has a very high migration activation energy.[4] Recently, *ab initio* studies by Janke *et al.*[51] were consistent with the experimental results and predicted that B diffusion in Ge is interstitially mediated. It is also interesting to note that the BV pair was predicted to be unstable.[23,51]
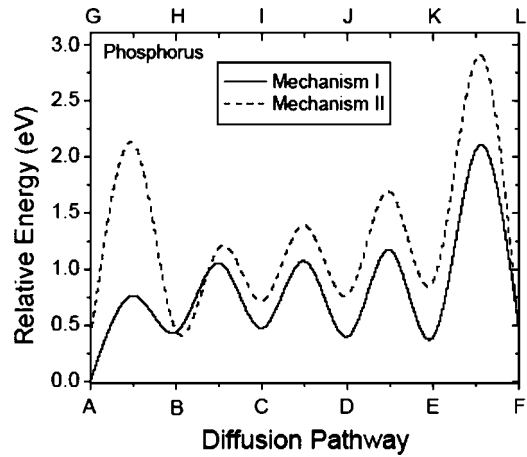

FIG. 4. The migration energy profile of the PV pair in Ge in the presence of C. Position 1 represents the initial configuration of the PV pair and position 6 the final configuration.

It should be appreciated that V-mediated diffusion in the Ge lattice is not a simple exchange of the dopant and the V, as subsequent exchanges of the dopant with the same V will not result in net migration of the dopant. In fact, in the diamond crystal structure, the V must move to the third-nearest-neighbor site in order to return along a different path. This is the so-called ring mechanism for diffusion.[52,53] To study the influence of C on AV diffusion in Ge, a C atom is introduced into a substitutional site within the supercell. The evidence presented in Part I that a substantial amount of C is incorporated on substitutional sites justifies the choice of the substitutional site.

We first consider the diffusion of P and As, which have qualitatively similar migration energy profiles (Figs. 4 and 5), but differ significantly compared to that of Sb (Fig. 6). Two representative cases of AV association with C will be considered (Figs. 7 and 8). In the first case (mechanism I), the initial configuration has the C atom at a second-nearest-neighbor site with respect to the donor atom (A in Fig. 7). The V then moves around in the ring (Fig. 7) until it is positioned in between the C and the donor atom (E in Fig. 7).
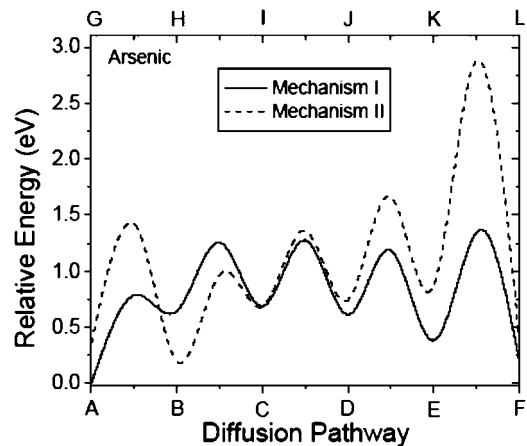

FIG. 5. The migration energy profile of the AsV pair in Ge in the presence of C. Position 1 represents the initial configuration of the AsV pair and position 6 the final configuration.
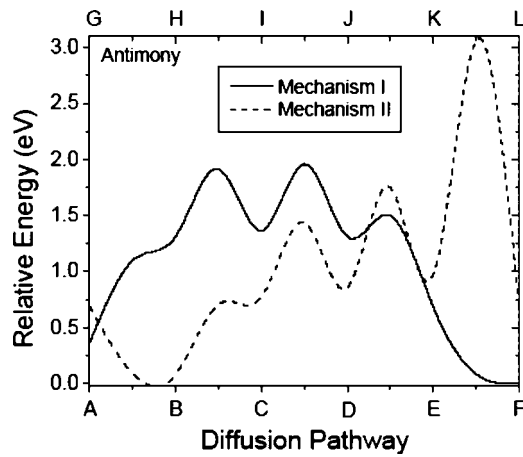
FIG. 6. The migration energy profile of the SbV pair in Ge in the presence of C. Position 1 represents the initial configuration of the SbV pair and position 6 the final configuration.

For mechanism I, Figs. 4 and 5 show that the most significant contribution to the association energy is the exchange between V and P or As (i.e., in Fig. 7 the step from E to F). This corresponds to the progression from CVA to the CAV complex configuration. The energy barriers associated with this exchange are 2.09 and 1.67 eV for P and As, respectively (see Figs. 4 and 5). These are the highest energy (i.e., rate determining) steps for P and As transport via mechanism I.

In mechanism II, the V not only exchanges position with the donor substitutional atom (step G to H in Fig. 8) but also with the C atom (step K to L in Fig. 8). In fact, step K to L evolves the complex VCA to CVA and gives rise to the highest energy barrier associated with mechanism II (2.91 eV for P and 2.88 eV for As). Most of the binding in these complexes results from the association of the donor atom to the V, whereas the CV pair is only weakly bound (by −0.07 eV).[23]
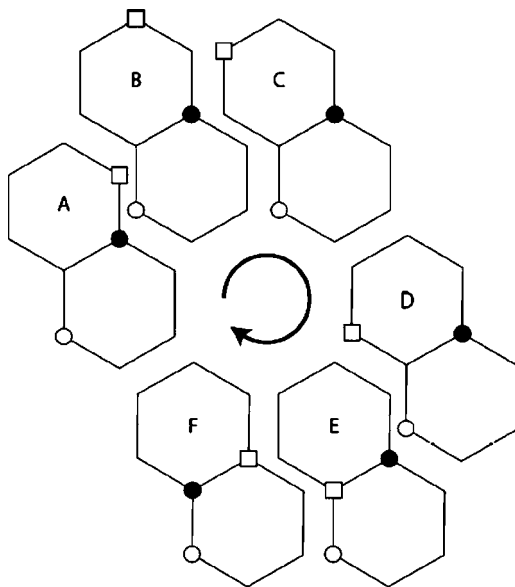

FIG. 7. A schematic view of the diffusion of the AV pair in Ge in the presence of C via mechanism I (A=black circles, C=white circles, and V=squares).
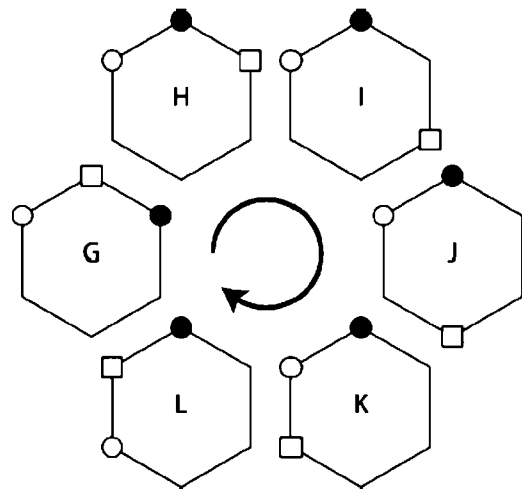

FIG. 8. A schematic view of the diffusion of the AV pair in Ge in the presence of C via mechanism II (A=black circles, C=white circles, and V=squares).

For the SbV complex, in the presence of C, the association energy profiles are qualitatively different from those of PV and AsV (see Figs. 4–6). As can be observed from Fig. 6, the lowest energy position of Sb is the CSbV configuration (see Fig. 1). The CSbV configuration is a particularly stable configuration for Sb because of the space provided to the central oversized Sb by both the V but also by the C substitutional atom (the C-Ge separation is only 2.11 Å compared to 2.48 Å predicted for Ge-Ge). This strain reduction is not as crucial for the smaller P and As. Based on Figs. 4–6 (mechanism I), there is a net attraction between SbV and C, but not between PV or AsV and C, where there is repulsion. For SbV the highest energy barrier via mechanism I is 1.96 eV (Fig. 6).

Mechanism I describes the association of an AV pair to a C atom. Mechanism II is the migration process and is higher in energy (3.08 eV) for Sb (Figs. 4–6). This might, in turn, lead to the enhanced retardation of SbV compared to that of PV or AsV. Nevertheless, the concentration of the donor atoms is also of importance. In Part I the maximum Sb concentration was determined to be about a factor of 10 lower than the maximum concentration of P and As. Therefore, although trapping of SbV pairs by C will be more energetically favorable (efficient) compared to that of PV or AsV, the total concentration of CSbV complexes will be significantly smaller.

IV. CONCLUSION

The stability, concentration, and migration of complexes formed between lattice V, C, and A atoms in Ge were investigated using atomic scale computer simulation. The high formation energy of self-interstitials in Ge, in conjunction with the stability of AV pairs, implies that V-mediated diffusion of P, As, and Sb will be dominant. A significant proportion of the donor atoms will be trapped in $C(AV)_n$ complexes, especially for high C concentrations and at low

temperatures. In cases where the formation of $A_n V$ is kinetically hindered, the higher stability of complexes involving Sb implies that a higher proportion of Sb will be bound to $C(AV)_n$ complexes compared to P or As (assuming equal dopant concentrations). For all the donor atoms considered, comparing mechanisms I and II, it is kinetically more favorable for the AV pair to break free of the C atom than for C and V to exchange positions. Therefore, C will act as a trap of AV pairs, which will not be able to diffuse unless they break free of the C atom. This effect will be more significant at larger C concentrations as it will be more likely for the C to associate with a migrating AV pair. These predictions, derived from simulation studies, are consistent with the experimental results presented in Part I and provide a mechanistic framework which helps to interpret the experimental data.

ACKNOWLEDGMENTS

*alexander.chroneos@imperial.ac.uk

[1] C. O. Chui, K. Gopalakrishnan, P. B. Griffin, J. D. Plummer, and K. C. Saraswat, Appl. Phys. Lett. **83**, 3275 (2003).

[2] M. L. Lee, E. A. Fitzgerald, M. T. Bulsara, M. T. Currie, and A. Lochtefeld, J. Appl. Phys. **97**, 011101 (2005).

[3] P. Ramanarayanan, K. Cho, and B. M. Clemens, J. Appl. Phys. **94**, 174 (2003).

[4] 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).

[5] A. Satta, E. Simoen, T. Clarysse, T. Janssens, A. Benedetti, B. De Jaeger, M. Meuris, and W. Vandervorst, Appl. Phys. Lett. **87**, 172109 (2005).

[6] A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, Appl. Phys. Lett. **92**, 172103 (2008).

[7] A. Chroneos, D. Skarlatos, C. Tsamis, A. Christofi, D. S. McPhail, and R. Hung, Mater. Sci. Semicond. Process. **9**, 640 (2006).

[8] A. Satta, E. Simoen, R. Duffy, T. Janssens, T. Clarysse, A. Benedetti, M. Meuris, and W. Vandervorst, Appl. Phys. Lett. **88**, 162118 (2006).

[9] E. Vainonen-Ahlgren, T. Ahlgren, J. Likonen, S. Lehto, J. Keinonen, W. Li, and J. Haapamaa, Appl. Phys. Lett. **77**, 690 (2000).

[10] H. Bracht and S. Brotzmann, Mater. Sci. Semicond. Process. **9**, 471 (2006).

[11] M. S. Carroll and R. Koudelka, Semicond. Sci. Technol. **22**, S164 (2007).

[12] S. Brotzmann and H. Bracht, J. Appl. Phys. **103**, 033508 (2008).

[13] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).

[14] H. Bracht, H. H. Silvestri, I. D. Sharp, and E. E. Haller, Phys. Rev. B **75**, 035211 (2007).

[15] A. Chroneos, R. W. Grimes, B. P. Uberuaga, S. Brotzmann, and H. Bracht, Appl. Phys. Lett. **91**, 192106 (2007).

[16] J. Coutinho, S. Öberg, V. J. B. Torres, M. Barroso, R. Jones, and P. R. Briddon, Phys. Rev. B **73**, 235213 (2006).

[17] A. Chroneos, R. W. Grimes, and C. Tsamis, Mater. Sci. Semicond. Process. **9**, 536 (2006).

[18] J. Coutinho, V. J. B. Torres, S. Öberg, A. Carvalho, C. Janke, R. Jones, and P. R. Briddon, J. Mater. Sci.: Mater. Electron. **18**, 769 (2007).

[19] A. Chroneos, R. W. Grimes, and C. Tsamis, J. Mater. Sci.: Mater. Electron. **18**, 763 (2007).

[20] S. L. Sihto, J. Slotte, J. Lento, K. Saarinen, E. V. Monakhov, A. Yu. Kuznetsov, and B. G. Svensson, Phys. Rev. B **68**, 115307 (2003).

[21] M. G. Ganchenkova, V. A. Borodin, and R. M. Nieminen, Nucl. Instrum. Methods Phys. Res. B **228**, 218 (2005).

[22] B. P. Haley and N. Grønbech-Jensen, Phys. Rev. B **71**, 195203 (2005).

[23] A. Chroneos, B. P. Uberuaga, and R. W. Grimes, J. Appl. Phys. **102**, 083707 (2007).

[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[25] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[26] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[27] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).

[28] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[29] M. Haran, J. A. Catherwood, and P. Clancy, Appl. Phys. Lett. **88**, 173502 (2006).

[30] D. Caliste, P. Pochet, T. Deutsch, and F. Lançon, Phys. Rev. B **75**, 125203 (2007).

[31] J. J. Xie and S. P. Chen, J. Appl. Phys. **87**, 4160 (2000).

[32] J. Lento, J. L. Mozos, and R. M. Nieminen, Appl. Phys. Lett. **77**, 232 (2000).

[33] N. Govind, M. Petersen, G. Fitzgerald, D. King-Smith, and J. Andzelm, Comput. Mater. Sci. **28**, 250 (2003).

[34] T. A. Halgren and W. N. Lipscomb, Chem. Phys. Lett. **49**, 225 (1977).

[35] J. Zhang, Y. Ashizawa, and H. Oka, J. Phys.: Condens. Matter **18**, 4879 (2006).

[36] R. J. Needs, J. Phys.: Condens. Matter **11**, 10437 (1999).

[37] E. R. Batista, J. Heyd, R. G. Hennig, B. P. Uberuaga, R. L. Martin, G. E. Scuseria, C. J. Umrigar, and J. W. Wilkins, Phys. Rev. B **74**, 121102(R) (2006).

[38] A. Chroneos, Phys. Status Solidi B **244**, 3206 (2007).

[39] A. Chroneos, Ph.D. thesis, Imperial College London, 2008.

[40] J. Xie and S. P. Chen, J. Phys.: Condens. Matter **11**, 7219 (1999).

[41] H. Höhler, N. Atodiresei, K. Schroeder, R. Zeller, and P. H. Dederichs, Phys. Rev. B **71**, 035212 (2005).

[42] V. A. Telezhkin and K. B. Tolpygo, Sov. Phys. Solid State **15**, 740 (1973).

[43] F. A. Kröger and V. J. Vink, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 3, p. 307.

[44] *Germanium-Based Technologies: From Materials to Devices*, edited by C. Clayes and E. Simoen (Elsevier, Amsterdam, 2007).

[45] M. Werner, H. Mehrer, and H. D. Hochheimer, Phys. Rev. B **32**, 3930 (1985).

[46] A. Fazzio, A. Janotti, A. J. R. da Silva, and R. Mota, Phys. Rev. B **61**, R2401 (2000).

[47] B. P. Uberuaga, G. Henkelman, H. Jónsson, S. T. Dunham, W. Windl, and R. Stumpf, Phys. Status Solidi B **233**, 24 (2002).

[48] A. Carvalho, R. Jones, J. P. Goss, C. Janke, S. Öberg, and P. R. Briddon, J. Phys.: Condens. Matter **20**, 135220 (2008).

[49] A. J. R. da Silva, A. Janotti, A. Fazzio, R. J. Baierle, and R. Mota, Phys. Rev. B **62**, 9903 (2000).

[50] P. Delugas and V. Fiorentini, Phys. Rev. B **69**, 085203 (2004).

[51] C. Janke, R. Jones, S. Öberg, and P. R. Briddon, J. Mater. Sci.: Mater. Electron. **18**, 775 (2007).

[52] L. C. Kimerling, H. M. DeAngelis, and J. W. Diebald, Solid State Commun. **16**, 171 (1975).

[53] S. T. Dunham and C. D. Wu, J. Appl. Phys. **78**, 2362 (1995).