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Diffusion of E centers in germanium predicted using GGA+ U approach

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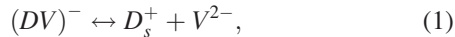
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Density functional theory calculations (based on GGA+ U approach) are used to investigate the formation and diffusion of donor-vacancy pairs (E centers) in germanium. We conclude that depending upon the Fermi energy, E centers that incorporate for phosphorous and arsenic can form in their neutral, singly negatively or doubly negatively charged states whereas with antimony only the neutral or doubly negatively charged states are predicted. The activation energies of diffusion are compared with recent experimental work and support the idea that smaller donor atoms exhibit higher diffusion activation energies. © 2011 American Institute of Physics. [doi:10.1063/1.3625939]

The advent of high- k dielectrics and the requirement for higher mobility of holes and electrons have regenerated the interest in germanium (Ge).¹ Ge is particularly advantageous due to its relative compatibility with Si, however, the fabrication of Ge-based devices requires a precise control of dopants.¹

Previous experimental² and theoretical^{3,4} studies provided evidence that donor atoms (D) such as phosphorous (P), arsenic (As), and antimony (Sb) diffuse in Ge *via* their interaction with vacancies (V). The V in Ge is the dominant defect as its formation energy is lower compared to the self-interstitial. Recent experiments² determined that D diffusion in Ge increases with the square of the free electron concentration. This strong doping dependence of diffusion is described by negatively charged E centers, $(DV)^-$, formed *via* the reaction



Where D_s^+ denotes the singly positively charged substitutional D atom and V^{2-} the doubly negatively charged V . The relevance of V^{2-} has been established by D diffusion in Ge isotope multilayer structures, which directly reveal the impact of doping on V -mediated self-diffusion in Ge.

Previous density functional theory (DFT) studies were limited due to the incomplete description of the exchange-correlation by the generalized gradient approximation (GGA) or the local density approximation (LDA) leading to severe underestimations of the band gap of Ge. Here, we employ a GGA+ U approach, which efficiently corrects the band gap of Ge allowing the investigation of the energetics of both neutral and charged defects in Ge. The aim is to calculate the formation energies, binding energies, and activation energies for diffusion of the technologically important E centers in Ge.

The VASP code was used in all the calculations.⁵ The pseudopotentials are generated by the projector augmented wave method.⁶ The exchange and correlation are described using the PBE/GGA functional.⁷ The Ge core states that were approximated by a pseudopotential are $[\text{Ar}]3d^{10}$ whereas the $4s^24p^2$ states were explicitly treated as valence

electronic states. A $4 \times 4 \times 4$ k -point set was generated according to the Monkhorst-Pack scheme.⁸ A 64 atom supercell was used. Previous studies showed that the use of a 216 atom cell changed the defect energies by only 1.5%.^{9,10} The cut-off energy was 400 eV, changes in total energy no more than 1×10^{-5} eV, and the forces were relaxed to below 0.001 eV/Å.

Ge is predicted to be a metal using LDA or GGA, which are known to severely underestimate the band gap as a result of the lack of the derivative discontinuities by the exchange-correlation potential with respect to occupation number.¹¹ To reproduce the electronic band structure of Ge, we implemented a range of U values while keeping the J parameter set to zero. No opening in the band gap was observed for U up to 12 eV. However, we obtained an excellent band structure by setting the U parameter to 0.4 eV and by varying the J parameter to 4 eV. The GGA+ U was applied to the p electrons, this allowed the self-interaction within the p shell to be corrected. The correction leads to the lowering of the p band energy and hence opening the band gap.

While this approach is able to generate a band gap in predicted structures efficiently, it is only a first order correction. Conversely, the Heyd-Scuseria-Ernzerhof¹² functional (HSE06) which employs a screened short range Hartree-Fock exchange is a more sophisticated and computationally intensive approach. Here, the HSE06 approach is used to compare with the band structure developed using the GGA+ U approach. The minimum energies of diffusion were calculated using the climbing image nudged elastic band (NEB) method.¹³

The formation energies of the defects are a function of the Fermi energy, μ_e , and the chemical potentials, μ_x , of the corresponding atoms and are calculated according to the formula:¹⁴

$$\Delta H_{D,q}(\mu_e, \mu_x) = E_{D,q} - E_H + \sum_x n_x \mu_x + q \mu_e,$$

Where $E_{D,q}$ is the total energy of the supercell containing the defect D in charge state q embedded in the Ge host and E_H is the total energy of the defect free Ge host. μ_x represents the chemical potentials of the different atoms added or removed

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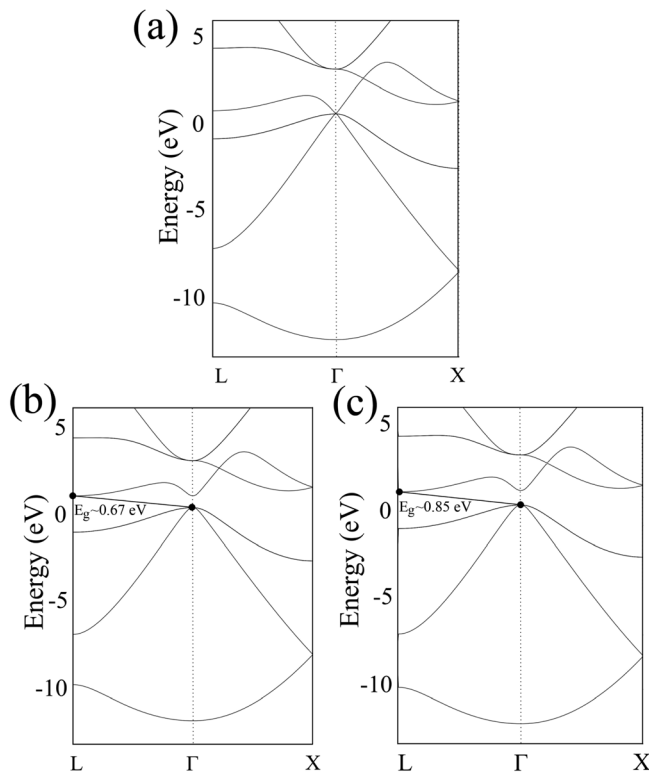


FIG. 1. The band structure of Ge calculated using (a) the GGA, (b) the GGA + U , and (c) the HSE06 approaches.

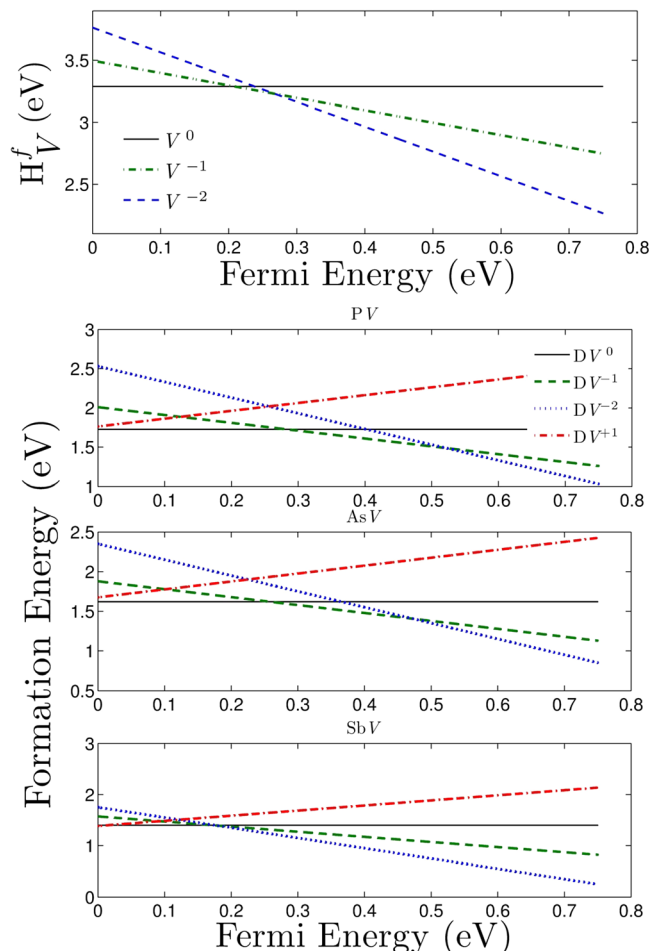


FIG. 2. (Color online) The formation energies of the V and the E centers, with respect to the Fermi Energy, using the GGA + U approach.

TABLE I. Calculated ionization energies for the E centers (eV).

	PV	AsV	SbV	V
$\varepsilon(0/-)$	0.28	0.26	0.17	0.21
$\varepsilon(0/--)$	0.40	0.37	0.17	0.24
$\varepsilon(+/-)$	0.12	0.10	0.09	—
$\varepsilon(+/--)$	0.26	0.23	0.12	—
$\varepsilon(-/--)$	0.52	0.47	0.18	0.27

when the defect is formed. The Fermi energy μ_e is expressed by $\mu_e = E_{VBM} + E_F$ with $0 \leq E_F \leq E_g$. Here, E_g is the band gap and E_{VBM} is the valence band maximum. The introduction of a defect affects the band structure and gives rise to a shift in the electrostatic potentials between the perfect Ge host and the supercell containing the defect. This shift is corrected by using a potential alignment correction method¹⁵ $\Delta E_{pa} = q \cdot \Delta V_{pa}$, where ΔV_{pa} is the average electrostatic potential difference between the defect supercell and the Ge host.

Figure 1 represents the band structures using the GGA, GGA + U (for $U = 0.4$ eV and $J = 4$ eV), and the HSE06 approaches. As it can be observed with the GGA approach, there is no indirect band gap (Fig. 1(a)), whereas for GGA + U , the indirect band gap is 0.67 eV (Fig. 1(b)), which is close to the experimental one of 0.74 eV at 0 K.¹⁶ Furthermore, the electronic structure predicted by the GGA + U approach is consistent with the hybrid functional approach HSE06 (indirect band gap of 0.85 eV). The lattice parameter of an optimized unit cell was found to be 5.59 Å in good agreement with the experimental value of 5.66 Å, extrapolated to 0 K.¹⁷

Figure 2 represents the formation energies of the V , PV, AsV, and SbV for various charge states. The doubly negatively charged vacancy, V^{-2} , is dominant for intrinsic and n -type doping conditions in agreement with experiment.² According to the present calculations, neutral vacancies are expected to mediate self-diffusion in Ge under p -type doping. Table I summarizes the ionization energies determined for the V and the E center. According to the calculations, the E centers are more likely doubly negative than singly negative charged under n -type doping. This should hold for SbV pairs even under intrinsic conditions, but is at variance to previous experiments that reveal the dominance of singly negatively charged E centers.² Of course, the calculations are representative for 0 K and the experiments for high temperatures. Thus, a direct comparison is always difficult

TABLE II. Calculated (GGA + U) binding (for the formal ΔE_{DV}^1 and split- V $\Delta E_{D-splitV}^1$ configurations), migration enthalpies (H_{DV}^m), and activation enthalpies (Q_a) for the E centers (in eV) in their neutral and negative charge states. For comparison, experimental Q_a from SIMS analyzes are given in parenthesis.

Defect complex	ΔE_{DV}^1		$\Delta E_{D-splitV}^1$		H_{DV}^m		Q_a	
	(-)	(0)	(-)	(0)	(-)	(0)	(-)	(0)
PV	-0.54	-1.57	0.38	-0.47	0.91	1.08	2.79	(2.85) ^a
AsV	-0.74	-1.68	-0.30	-1.08	0.99	0.95	2.67	(2.71) ^a
SbV	-0.81	-1.89	-0.93	-2.01	1.17	1.14	2.66	(2.55) ^a

^aReference 2.

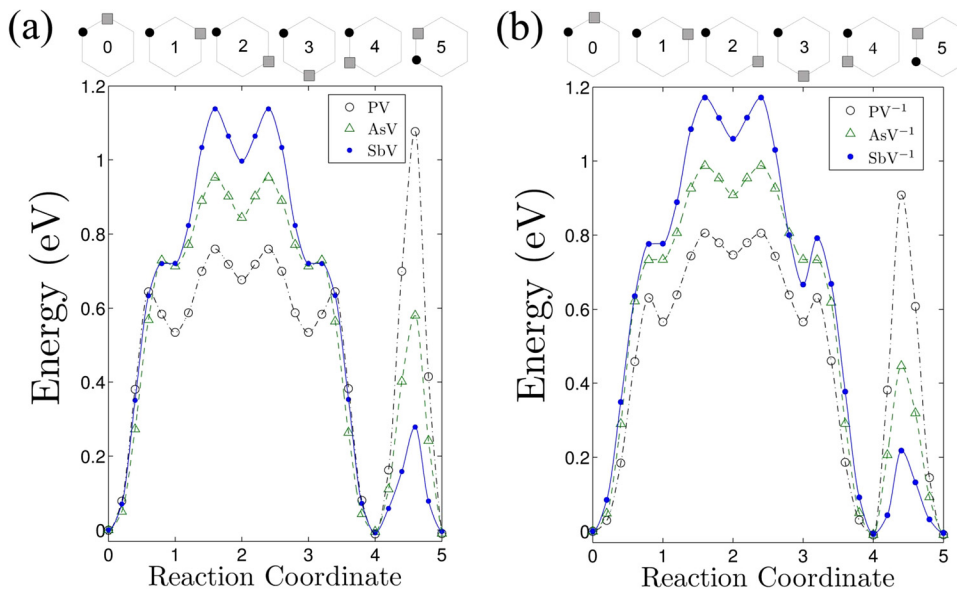


FIG. 3. (Color online) Diffusion path of the E centers using the NEB technique and the GGA+ U approach for (a) the neutral and (b) the singly negatively charged E centers. On the top of the figures is the ring mechanism of diffusion for the DV pair (D =black circles and V =squares) projected onto the (111) surface of Ge.

without any information about the impact of temperature on the level position (e.g., entropy effects).

Having established the formation of the neutral and negatively charged E centers, we calculate their binding energies, migration energies, and activation energies of diffusion. The binding energy is a measure of the attraction of the defect cluster and is defined by the total energy of the cluster minus the energy of the isolated defect components. With this definition, a negative binding energy corresponds to a stable defect cluster. The two geometries considered are the formal V -substitutional D atom configuration and the split- V configuration (here the D atom is positioned in-between two semi- V). In Table II, the calculated (GGA+ U) binding energies are reported for the formal, ΔE_{DV}^1 , and split- V , $\Delta E_{D-splitV}^1$ configurations of E centers in neutral and charged states. Only for the largest D atom (i.e., Sb), the split- V configuration is energetically favorable over the formal V configuration (Table II), consistently with previous DFT work.¹⁸ When the D atom is separated at the next nearest neighbor site to the V , or beyond, the binding energies were calculated to be smaller in magnitude.

E centers migrate in the Ge lattice *via* the ring mechanism of diffusion.¹⁹ In this, the V moves around the D atom and approaches it from a different direction. For the displacement of a D , the V must move away to at least the third-nearest neighbor site and return along a different path. As it exchanges position, the D atom progresses in the lattice by one site. Figs. 3(a) and 3(b) represents the relative energies along the ring for the neutral and negatively charged E centers, respectively. The migration energy barriers H_{DV}^m are defined as the largest relative energy barriers along the ring (Table II). Here, the activation enthalpy of diffusion, Q_a , is defined by

$$Q_a = H_V^f + \Delta E_{DV}^1 + H_{DV}^m, \quad (2)$$

where H_V^f is the formation enthalpy of an isolated V .

Table II compares the calculated Q_a with previous experimental results from SIMS analyses of impurity diffusion profiles.² The calculated results for the singly negative charged E centers are in excellent agreement with the experimental values (i.e., within 0.11 eV).² Both theoretical results

and experiment are consistent with the trend that Q_a decreases with increasing D atom size,^{2,4} although for the (AsV)⁻ and (SbV)⁻, the differences are very small. The calculated Q_a of AsV and SbV are lower than the (AsV)⁻ and (SbV)⁻ indicating that they could diffuse faster. Nevertheless, under n -type conditions, the V^{-2} defect should be dominant and the formation of (DV)⁻, *via* Eq. (1), will prevail.

In summary, we used a GGA+ U approach to simulate the electronic structure of Ge and activation enthalpies of diffusion for the important n -type D atoms in Ge. In excellent agreement with the most accurate experiments,² we predict the underlying trend observed in the activation enthalpy of P, As, and Sb diffusion, that is, with increasing D size Q_a decreases.

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