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# Diffusion of tin in germanium: A GGA+$U$ approach

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Density functional theory calculations are used to investigate the formation and diffusion of tin-vacancy pairs (Sn$V$) in germanium (Ge). Depending upon the Fermi energy, Sn$V$ pairs can form in neutral, singly negative, or doubly negative charged states. The activation energies of diffusion, also as function of the Fermi energy, are calculated to lie between 2.48-3.65 eV, in agreement with and providing an interpretation of available experimental work. © 2011 American Institute of Physics. [doi:10.1063/1.3653472]

Replacing native oxides with high-$k$ dielectrics, combined with the requirement for higher mobility of holes and electrons, have renewed the interest of the microelectronics community in germanium (Ge).[1,2] Previous investigations demonstrated that the mobilities of holes and electrons can be increased by the introduction of strain.[3] Recent studies propose the fabrication of strained-Ge (sGe) complementary metal-oxide-semiconductor (CMOS) with germanium-tin (Ge$_{1-x}$Sn$_x$) alloys as stressors.[4]

Studies on Ge$_{1-x}$Sn$_x$ alloys are also motivated by their advantageous optical properties; however, there are still issues that need to be addressed.[5] Furthermore, vacancies generated in Ge$_{1-x}$Sn$_x$ alloys grown at low temperatures can result in Sn$V$ pairs that reduce the local strain around the Sn atom. Sn-$V$ interactions and their diffusion properties have been previously investigated using density functional theory (DFT) but only for neutral defects and defect clusters.[5,6] As it is possible for Sn atoms to diffuse from the Ge$_{1-x}$Sn$_x$ alloy into doped-Ge layers, an understanding of Sn-diffusion in both $n$-type and $p$-type Ge is important.

Here, we use a generalized gradient approximation and Hubbard $U$ (GGA+$U$) approach to efficiently correct the band gap of Ge. The aim is to study the formation energies and activation energies for diffusion of Sn$V$ pairs in Ge over a range of Fermi energies.

Defect energy calculations were performed using DFT as implemented in the Vienna *ab-initio* simulation package (VASP).[7] Electron exchange and correlation were described using the Perdew-Burke-Ernzherof (PBE) functional.[8] For Ge and Sn, the electrons occupying the [Ar]3d$^{10}$ and [Kr]4d$^{10}$ states, respectively, were treated as core electrons and were approximated by a pseudopotential generated according to the projector augmented wave (PAW) method, whereas the 4s$^2$4p$^2$ and 5s$^2$5p$^2$ states were treated as valence electrons.[9] $4 \times 4 \times 4$ k-points grids were generated according to the Monkhorst-Pack scheme in a 64 atom supercell.[10] The kinetic energy cut-off was set to 400 eV. Self-consistency in the energy was achieved by restricting the change in total energy to no more than $1 \times 10^{-5}$ eV and the forces on the atoms were relaxed to below 0.001 eV/Å. The underestima-

tion of the band gap was corrected by employing a GGA+$U$ approach.[11] For an on-site Coulomb parameter, $U = 0$ eV and an on-site exchange parameter, $J = 3.33$ eV, we obtained a band gap of 0.74 eV (i.e., equal to the experimental band gap at 0 K).

Diffusion barriers were calculated using the climbing image nudged elastic band method.[12] The migration energy corresponds to the barrier with the highest energy along the minimum energy path. Calculating migration energies involves the subtraction of the images' energies from each other and for charged systems, this leads to the cancellation of spurious charge-interactions.

The formation energies of the neutral and charged Sn$V$ pairs in Ge were calculated using[13]

$$\Delta H_{D,q}(\mu_e, \mu_\alpha) = E_{D,q} - E_H + \sum_\alpha n_\alpha \mu_\alpha + q\mu_e, \quad (1)$$

where $E_{D,q}$ is the total energy of the defective cell with a charge $q$ and $E_H$ is the total energy of the perfect Ge cell. $n_\alpha$ represents the number of atoms added or removed to the defective cell and $\mu_\alpha$ corresponds to their chemical potentials. $\mu_e$ is the Fermi energy and is measured from the top of the valence band maximum ($E_{VBM}$) and usually has values lying in the band gap: $E_{VBM} \leq \mu_e \leq E_{VBM} + E_g$.

The defect-defect and defect-background interactions were corrected using the Makov and Payne[14] scheme

$$\Delta E = \frac{q^2 a_m}{2\varepsilon L} + \frac{2\pi qQ}{3\varepsilon L^3}, \quad (2)$$

where $a_m$ is the diamond structure Madelung constant, $\varepsilon$ is the dielectric constant of Ge, and $L$ is the defect-defect separation. The second term in Eq. (2) leads to a small contribution ($\sim 10^{-5}$–$10^{-6}$ eV). The shift in the electrostatic potentials between the perfect cell and the defective Ge cell is corrected by the potential alignment correction method[13] by adding $\Delta E_{pa} = q \Delta V_{pa}$, where $\Delta V_{p\alpha}$ is the average electrostatic potential difference between the defective and perfect Ge supercells.

$V$ are the dominant intrinsic defect species in Ge, with previous work establishing their interaction with impurity atoms ($D$) to form $DV$ pairs and larger clusters.[15,16] The diffusion of Sn in Ge is mainly mediated by $V$. The structure of

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near neighbor Sn$V$ pairs can be reasonably described by two geometries: (a) the formal vacancy-substitutional Sn atom configuration and (b) the split-$V$ configuration.[17] In the latter, the Sn atom is positioned in between two semi-vacancies.[17] For all Sn$V$ pairs, it was calculated that the split-$V$ configuration is energetically favourable. Configurations beyond near neighbor are higher in energy.

It is important to identify the charge states of the Sn$V$ pairs for different doping conditions. Fig. 1 presents the formation energies of the Sn$V$ pairs, with respect to the Fermi energy, for various charge states. From Fig. 1, it is deduced that the Sn$V$ pairs are charge neutral up to a Fermi energy of 0.223 eV, above which the singly negatively charged state becomes dominant. Finally, at a Fermi energy of 0.587 eV, the doubly negatively charged pairs are most stable. Positive charge states of this cluster are always significantly less stable.

Having established the dominant charge states of the Sn$V$ pairs, their diffusion behavior merits investigation. Sn$V$ pairs will diffuse *via* the ring mechanism. Beginning with the formal $V$-substitutional configuration, the first step is for the Sn atom to move across to occupy the initially vacant lattice site, thereby progressing in the lattice by one site. The $V$ then moves around the Sn atom in a ring and thus approaches the Sn atom from the other side, ready to exchange positions again and progresses the Sn atom by another site. This process is illustrated at the top of Fig. 2 for the Sn$V$ pair projected onto the (111) surface of Ge. Fig. 2 presents the relative energies along the ring for neutral and singly and doubly negatively charged Sn$V$ pairs. From this figure, the migration energy barrier, $H_{SnV}^m$, is defined as the largest relative energy barrier during the ring cycle. The activation enthalpy for diffusion, $Q_a$, is calculated by using the following definition:[6]

$$Q_a = H_V^f + \Delta E_{SnV}^1 + H_{SnV}^m, \qquad (3)$$

where $H_V^f$ is the formation enthalpy of an isolated $V$ and $\Delta E_{SnV}^1$ is the binding enthalpy of the Sn$V$ cluster.

$n$-type doping will increase the concentration of electrons in the system, causing the Fermi level to shift to higher
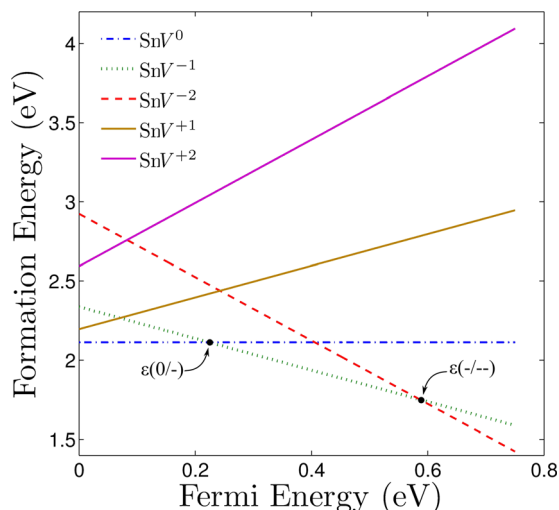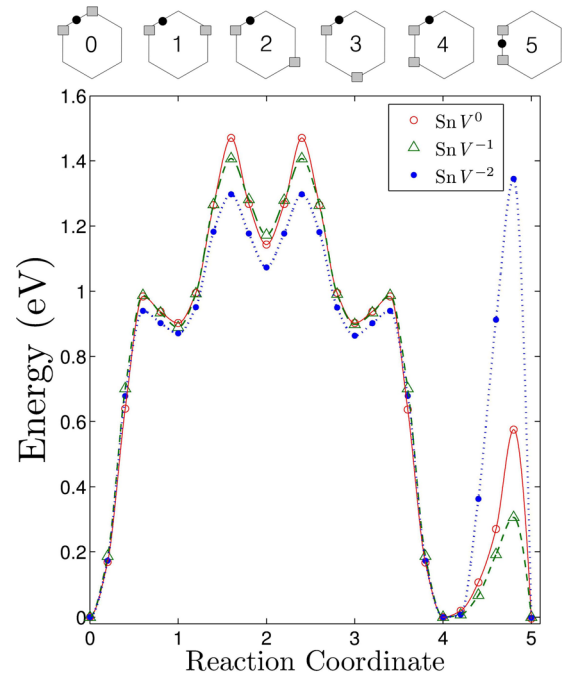


FIG. 2. (Color online) Diffusion path of the Sn$V$ using the NEB technique and the GGA+$U$ approach. On the top of the figure is the ring mechanism of diffusion for the Sn$V$ pair projected onto the (111) surface of Ge.

energies and $p$-type doping, to shift to lower energies. The formation energies of charged $V$ depends upon the position of the Fermi level (i.e., different charged states dominate at different values of the Fermi level). This influences $Q_a$ that depends upon the formation energies of the $V$. It is, therefore, necessary to study $Q_a$ as a function of the Fermi energy.

Recent studies on simultaneous self- and dopant diffusion reveal the doubly negative charge state of $V$ in Ge.[1,15] To investigate the dependence of $Q_a$ on the doping levels, we studied three regions within the band gap. Region I lies between 0 and 0.223 eV, here the binding and migration energies of a neutral Sn$V$ pairs are used in Eq. (4), the $V$ formation energy as a function of the Fermi energy is taken from our previous study (Fig. 3).[11] Region II which extends from 0.223 to 0.587 eV, where the singly negatively charged Sn$V$ pair prevails, the binding and migration energies of a singly negatively Sn$V$ pair were used along with the vacancies formation energies in that region of the Fermi energy (Fig. 3). Finally, region III extends from 0.587 eV to the edge of the conduction band minimum, where we used the values of the binding and migration energies of a doubly negatively charged Sn$V$ pair (Fig. 3).

This significant variation in $Q_a$ with respect to the Fermi energy can explain the many differing experimental results



FIG. 1. (Color online) The formation energies of the Sn$V$ pairs, with respect to the Fermi Energy, using the GGA+$U$ approach.
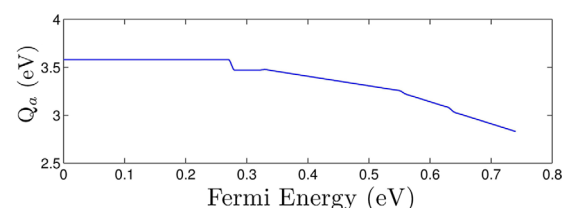


FIG. 3. (Color online) The activation energy's dependence on the Fermi energy.

previously obtained. Overall the range of the calculated $Q_a$ is consistent with the experimentally determined values.[18–20] The SIMS studies of Kringøj and Elliman[18] and Friesel *et al.*[19] provide diffusion activation enthalpies of 3.05 eV and 3.26 eV, respectively, for Sn diffusion in Ge. The radio-tracer study of Riihimäki *et al.*[20] yields 2.90 eV. From Fig. 3, we can see that for the intrinsic case, when the Fermi energy is close to the middle of the band gap (i.e., $E_F \sim 0.37$ eV), we obtain a value of about 3.21 eV for the activation energy, which is in a good agreement with the SIMS results. Shifting the Fermi level below the middle of the band gap (i.e., *p*-type doping the material) results in an increase in $Q_a$. This trend is consistent with the results of Riihimäki *et al.*[20] who measured the activation energy of Sn diffusion in intrinsic Ge to be 2.90 eV and in *p*-type doped Ge to be 3.33 eV.

In summary, Sn*V* pairs are most stable as neutral for Fermi energy up to 0.223 eV, singly negatively charged defects for Fermi energy in-between 0.223 eV and 0.587 eV and doubly negatively charged defects for Fermi energy exceeding 0.587 eV. Positive charged states are not as stable. Depending upon the Fermi energy, we calculated that the activation energies for diffusion are in the range 2.48-3.65 eV, in agreement with available experimental data.

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