Diffusion of tin in germanium: a GGA+U approach

How to cite:

For guidance on citations see FAQs

© 2011 American Institute of Physics
Version: Version of Record
Link(s) to article on publisher’s website:
http://dx.doi.org/doi:10.1063/1.3653472
http://apl.aip.org/resource/1/applab/v99/i16/p162103.s1

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online’s data policy on reuse of materials please consult the policies page.
Diffusion of tin in germanium: A GGA+U approach
H. Tahini, A. Chroneos, R. W. Grimes, and U. Schwingenschlögl

Citation: Appl. Phys. Lett. 99, 162103 (2011); doi: 10.1063/1.3653472
View online: http://dx.doi.org/10.1063/1.3653472
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i16
Published by the American Institute of Physics.

Related Articles
Computational methodology for analysis of the Soret effect in crystals: Application to hydrogen in palladium
Spectroscopic analysis of Al and N diffusion in HfO2
Copper centers in copper-diffused n-type silicon measured by photoluminescence and deep-level transient
spectroscopy
Bonding and diffusion of nitrogen in the InSbN alloys fabricated by two-step ion implantation
Shift of Ag diffusion profiles in CdTe by metal/semiconductor interfaces

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT

Universal charged-particle detector for interdisciplinary applications:
- Non-scanning Mass Spectrometry
- Non-scanning Ion Mobility Spectrometry
- Non-scanning Electron Spectroscopy
- Direct microchannel plate readout
- Thermal ion motion and mobility studies
- Bio-molecular ion soft landing profiling
- Real-time beam current/shape tuning
- Diagnostics tool for instrument design
- Compact linear array for beam lines

Contact OI Analytical: +1-205-733-6900
Diffusion of tin in germanium: A GGA+U approach

H. Tahini,1 A. Chronesos,1,a) R. W. Grimes,1 and U. Schwingenschlögl2

1Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom
2PSE Division, KAUST, Thuwal 23955-6900, Saudi Arabia

(Received 17 August 2011; accepted 28 September 2011; published online 18 October 2011)

Density functional theory calculations are used to investigate the formation and diffusion of tin-vacancy pairs (SnV) in germanium (Ge). Depending upon the Fermi energy, SnV 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 (Ge1-xSnx) alloys as stressors.4 Studies on Ge1-xSnx alloys are also motivated by their advantageous optical properties; however, there are still issues that need to be addressed.5 Furthermore, vacancies generated in Ge1-xSnx alloys grown at low temperatures can result in SnV 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 Ge1-xSnx 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 SnV 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-Ernzerhof (PBE) functional.8 For Ge and Sn, the core electrons were treated with an approximate potential generated according to the projector augmented wave (PAW) method, whereas the 4s24p2 and 5s25p2 states were treated as valence electrons.9, 8×8×8 k-points grids were generated according to the Monkhorst-Pack scheme in a 64 atom supercell.9 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 × 10−5 eV. The underestimation 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 SnV pairs in Ge were calculated using

$$\Delta H_{D,q}(\mu_e, \mu_q) = E_{D,q} - E_H + \sum \nabla_n \mu_q + q \mu_e,$$  \hspace{1cm} (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. $\mu_q$ represents the number of atoms added or removed to the defective cell and $\mu_e$ 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 Payne14 scheme

$$\Delta E = \frac{q^2 a_m}{2 d L_e} + \frac{2 \pi q Q}{3 d L_e^3},$$ \hspace{1cm} (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 method13 by adding $\Delta E_{pa} = q \Delta V_{pa}$, where $\Delta V_{pa}$ 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

---

a)Author to whom correspondence should be addressed. Electronic mail: alexander.chronesos@imperial.ac.uk.
near neighbor SnV pairs can be reasonably described by two geometries: (a) the formal vacancy-substitutional Sn atom configuration and (b) the split-V configuration. In the latter, the Sn atom is positioned in between two semi-vacancies. For all SnV 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 SnV pairs for different doping conditions. Fig. 1 presents the formation energies of the SnV pairs, with respect to the Fermi energy, for various charge states. From Fig. 1, it is deduced that the SnV 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 SnV pairs, their diffusion behavior merits investigation. SnV 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 SnV 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 SnV pairs. From this figure, the migration energy barrier, $H_{m}^{\text{SnV}}$, 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:

$$Q_{a} = H_{f}^{V} + \Delta E_{\text{SnV}}^{b} + H_{m}^{\text{SnV}}$$

where $H_{f}^{V}$ is the formation enthalpy of an isolated V and $\Delta E_{\text{SnV}}^{b}$ is the binding enthalpy of the SnV cluster.

$n$-type doping will increase the concentration of electrons in the system, causing the Fermi level to shift to higher 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. 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 SnV 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). Region II which extends from 0.223 to 0.587 eV, where the singly negatively charged SnV pair prevails, the binding and migration energies of a singly negatively charged SnV 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 SnV pair (Fig. 3).

This significant variation in $Q_{a}$ with respect to the Fermi energy can explain the many differing experimental results.
previously obtained. Overall the range of the calculated $Q_a$ is consistent with the experimentally determined values.\textsuperscript{14–20} The SIMS studies of Kringøj and Elliman\textsuperscript{18} and Friesel et al.\textsuperscript{19} provide diffusion enthalpies of 3.05 eV and 3.26 eV, respectively, for Sn diffusion in Ge. The radio-tracer study of Riihimäki et al.\textsuperscript{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.\textsuperscript{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$^+$ 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 experimental data.

This publication was based on research supported by King Abdullah University for Science and Technology (KAUST). Computing resources were provided by the HPC facility at ICL.