Rare earth substitutional impurities in germanium: A hybrid density functional theory study

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ABSTRACT

The Heyd, Scuseria, and Ernzerhof (HSE06) hybrid functional by means of density functional theory has been used to model the electronic and structural properties of rare earth (RE) substitutional impurities in germanium (RE_{Ge}). The formation and charge state transition energies for the RE_{Ge} (RE = Ce, Pr, Er and Eu) were calculated. The energy of formation for the neutral charge state of the RE_{Ge} lies between -0.14 and 3.13 eV. The formation energy result shows that the Pr dopant in Ge (Pr_{Ge}) has the lowest formation energy of -0.14 eV, and is most energetically favourable under equilibrium conditions. The RE_{Ge} induced charge state transition levels within the band gap of Ge. Shallow acceptor levels were induced by both the Eu (Eu_{Ge}) and Pr (Pr_{Ge}) dopants in Ge. The Ce_{Ge} and Er_{Ge} exhibited properties of *negative-U* ordering with *effective-U* values of -0.85 and -1.07 eV, respectively.

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1. Introduction

Germanium (Ge) is being considered as a material for new generation of microelectronic devices, as a result of its unique properties (carrier mobilities, low dopant activation temperatures and smaller band-gap of 0.78 eV at 0 Kelvin) [1–3]. Several studies of point defects in Ge using experimental [4–7] or theoretical [8–12] techniques have been reported. It has been reported that defect processes of dopants in Ge semiconductors can be influenced by doping and double-donor doping, which may be an effective way to engineer the active donor concentrations of Ge [9]. Rare earth (RE) impurities in semiconductor material have attracted interest due to their unique predictable optical properties [13]. Another interesting property of the RE is its ability to participate in photoluminescence process. For instance, the Er^{3+} ions have been discovered to participate in an energy transfer process during optical or electrical pumping of Er-doped SiO_2 [14]. In another development, according to report by Kanjilal et al. [15], the Er-doped amorphized Ge nanoclusters can recrystallized in absence of Ge out-diffusion during flash-lamp annealing. Channelling experiments by Jones *et at* [16] have given support for a Er tetrahedral interstitial location in Si. Visible emission as well as an infrared 1.53 μm signal from the Er doped Ge nanowires at room temperature have been observed [17]. Recently, Tm [10] substitutional impurity in Ge was predicted to induce in the band gap of Ge an acceptor level $(-1/-2)$ at $E_C - 0.05$ eV (E_C and E_V are the energies of the conduction band minimum and the valence band maximum respectively), and double donor levels at $E_V + 0.10$ and $E_V + 0.19$ for the $(+2/+1)$ and $(+1/0)$ charge state transitions, respectively. The interaction energy between two electrons in a two-level defect is referred to as Hubbard-U [18,19]. Hubbard-U is regarded as a *negative-U* when the neutral charge state is excited, and it becomes energetically less favourable. A good number of defects in Ge and Si have been observed to exhibit charge state *negative-U* ordering [2,10,20]. The Tm^{3+} and Ce^{3+} interstitials in Ge are found to exhibit charge state *negative-U* ordering [20,10].

It has been reported that materials in the future (due to miniaturization) will have shallow junctions with high conductivity [21,22]. For Ge based device processing damage occurs during ion implantation. As a result, the role of defects that enhance diffusion of the implanted dopant will have to be well understood. Bracht et al. [7] in a review reported the mechanism of self- and dopant diffusion in Ge under thermal equilibrium and non-equilibrium conditions. In this case, the non-equilibrium conditions can be realized by irradiation or implantation. While RE ion defects in Si and other materials have been studied either by theoretical modelling or by experimental techniques [23–25]. Except for the Tm [10], the structural and electronic properties of RE substitutional defects in Ge have not been theoretically studied. In

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order for us to provide a frontier insight for the experimental study of the electronic properties of defects resulting from the implantation of the RE in Ge, we have used the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) [26] by means of density functional theory (DFT) to calculate the structural and electronic properties of rare earth substitutions in Ge (RE_{Ge} for RE: Ce, Pr, Eu and Er). The energies of formation for the Ce_{Ge}, Pr_{Ge}, Eu_{Ge} and Er_{Ge} are calculated for charge states $(-2, -1, 0, +1, +2)$. The charge state transition levels with the accessible thermodynamic region are examined and presented as well.

2. Computational details

Results of this report are based on DFT. We used the projector-augmented wave (PAW) [27,28] to separate the core electrons from the valence electrons. Vienna *Ab initio* Simulation Package (VASP) [27] code was used. All calculations were carried out using Heyd, Scuseria, and Ernzerhof (HSE06) [26] hybrid functional. According to the HSE06 approach, the short-range exchange potential is calculated by mixing 25% fraction of nonlocal Hartree–Fock exchange with the Perdew, Burke, and Ernzerhof (PBE) [29] functional. In the past, defects in Ge were difficult to study theoretically, since the local density approximation (LDA) and the generalized gradient approximation (GGA) functionals incorrectly predict Ge to be a metal [2,30]. However, the HSE06 functional has been used to predict accurately the electronic band gap and improve charge state transition properties for group−IV semiconductors [2,12,30]. According to our previous reports [10,20], the modelling and prediction of the electronic properties of material with the *f* orbital valence shell was difficult, because the *f* orbital is highly localized. Recently, the hybrid functional has been successfully used to predict the electronic and band gap properties of several materials with the *f* orbital in the valence shell [10,31,32]. Following this success of the hybrid functional, the *f* orbital in the valence shell of RE can be handle.

To calculate the properties of the RE substitutional impurities in Ge, a periodic supercell containing 64 atoms of Ge was used. A regularly spaced mesh of $2 \times 2 \times 2$ Monkhorst–Pack [33] scheme k-point was used to integrate the Brillouin zone. We set the plane wave cutoff of the wave function expansion to 400 eV. To obtain an equilibrium geometry of a perfect supercell, we refined the geometry until the final change in the total energy and the forces were less than 10^{-5} eV and 0.001 eV/Å, respectively. The formation energy of a strongly correlated system is strongly dependent on the spin−orbit coupling (SOC) due to the presence of relativistic effects in heavy atomic systems. The scalar relativistic effect was taken into consideration by including in the PAW potential the mass−velocity and Darwin correction terms. In addition, spin orbit coupling was taken into account for all calculations. The formation energy (E^f) of defects is derived directly from total energies, allowing the calculation of equilibrium defect *concentrations* [34]. To determine the defect formation energy and transition energy ($\epsilon(q/q')$) levels, we calculated the total energy $E(RE_{Ge}, q)$ for a supercell containing an optimized defect RE_{Ge} in its charge state q. The RE substitutional impurity in Ge formation energy $E^f(RE_{Ge}, q)$ as a function of electron Fermi energy (ε_F) is given as [35]

$$E^f(RE_{Ge}, q) = E(RE_{Ge}, q) - E(pristine) + \sum_i (\triangle n)_i \mu_i + q[E_V + \varepsilon_F] + E_{cor}^q,$$

(1)

where $E(pristine)$ is the total energy of a supercell containing 64 atoms of Ge, $(\triangle n)_i$ ($\triangle(n) < 0$, when a RE atom is included to a supercell containing 64 atoms of Ge and $\triangle(n) > 0$ when a Ge atom is removed from a supercell containing 64 atoms of Ge) is the difference in the number of constituent atoms of type i between the

supercell containing 64 atoms of Ge and the supercell containing the defect, μ_i represents the chemical potential of different constituent atoms and as mentioned earlier, E_V is energy of the valence band maximum (VBM). The E_{cor}^q is the Freysoldt, Neugebauer, and Van de Walle (FNV) correction term. The E_{cor}^q accounts for the potential alignment between the charged defect and bulk at a point far from the defect. In addition, the E_{cor}^q accounts for the charge corrections in a supercell of finite size [36,35]. The FNV scheme explicitly uses the electrostatic potential obtained from DFT calculations to obtain an electrostatics model. The defect transition energy level $\epsilon(q/q')$ which is the Fermi energy at which two different charge states of the same defect have the same energy of formation, is given as [35]

$$\epsilon(q/q') = \frac{E^f(RE_{Ge}, q; \varepsilon_F = 0) - E^f(RE_{Ge}, q'; \varepsilon_F = 0)}{q' - q}$$

(2)

As reported in ref [2], we took the modelled band gap of the pristine Ge to be 0.78 eV.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the relaxed geometric structures of RE substitutional impurities in Ge. Fig. 1a and b display relaxed geometric structures of the Ce_{Ge} and Pr_{Ge}, respectively, and Fig. 1c and d display the relaxed geometric structures of the Eu_{Ge} and Er_{Ge}, respectively. Table 1 lists the predicted shortest bond distance (β_d) in (Å) between a RE and its nearest neighbour Ge atom, and the difference Δ_d between the β_d and the relaxed Ge−Ge bond length. After structural relaxation, we obtained the bond angle between three Ge atoms to be 109.4° and Ge−Ge bond length to be 2.46 Å. This bond length is in close agreement with both experimental (2.45 Å) [37] and GGA theoretical (2.48 Å) [38] results. The shortest bond length between Ce, Pr, Eu, Er and its nearest neighbour Ge atom is 2.80, 2.78, 2.74 and 3.18 Å, respectively. The difference
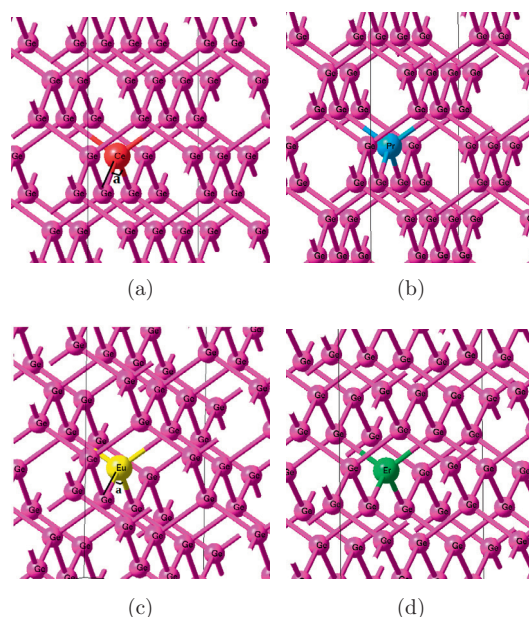

Fig. 1. Relaxed geometric structures of RE substitutions in Ge. (a) Ce_{Ge}, (b) Pr_{Ge}, (c) Eu_{Ge} and (d) Er_{Ge}. According to a and c, the black line and the text "**a**" represent the shortest bond length and the angle formed between a RE and two nearest neighbour Ge atoms. This same pattern applies to all other RE_{Ge} systems.