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Density functional theory study of stable configurations of substitutional and interstitial C and Sn atoms in Si and Ge crystals

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ABSTRACT

Group IV semiconductor compounds, e.g., Si and Ge containing substitutional C (C_s) and/or Sn (Sn_s) atoms (mono-doping and co-doping) with contents of several % are attracting attention for application to solar cells because they are good for the environment and have an affinity with Si materials. In this study, we evaluate the stable configurations of C and/or Sn atoms in Si (Ge) crystals with a focus on the formation of interstitial C (C_i) atoms by means of density functional theory calculations. The Hakoniwa method proposed by Kamiyama et al. (2016) is applied to a 64-atom supercell to obtain the thermal equilibrium ratio of C_i to the total C atoms. The results of the analysis are fourfold. First, the isolated C_s atom is stabler than the isolated C_i atom in both Si and Ge crystals, and it is stabler in Si than in Ge. The isolated Sn_s atom is much stabler that Sn_i as well, but it is stabler in Ge than Si. Second, a C_i atom is formed in a [001] oriented C_i-C_s pair in Ge crystals with the ratio of 7.7% to total C atoms at 450 °C when the concentration of uniformly distributed C atoms is about 3%. Third, the difference of the formation energy of C_i and C_s in Si decreases to about 0.3 eV with an increase in the concentration of uniformly distributed C atoms up to 6%. Fourth, the co-doping of C and Sn suppresses the formation of C_i atoms in Si and Ge crystals. The results obtained here are useful for the prediction of possible atomic configurations of C and/or Sn in Si and Ge for solar cell application.

1. Introduction

Multi-crystalline Si crystals are relatively inexpensive, so currently they are the main crystals used in solar cells. However, to achieve higher engineering efficiency in solar cells, the sensitivity zones of wavelengths in sunlight need to be expanded. One alternative candidate is group III–V semiconductors with multi-junction solar cells composed of films with different band gaps [1]. However, some III–V elements negatively affect the environment and lack affinity with Si materials. Group IV semiconductor compounds, e.g., Si and Ge containing C and/or Sn atoms (mono-doping and co-doping) with contents of several %, are attracting attention for their potential to control band structures and band gaps [2,3]. One of the technological problems with this is how to control the atomic configuration, i.e., the substitutional and interstitial sites of doped C and/or Sn atoms in the host Si and Ge crystals [4–13]. The substitutional C and Sn atoms help control the band gaps, but interstitial C and Sn atoms form complexes with other impurities and/or intrinsic point defects, which results in the formation of carrier traps in the band gap. First principles analysis based on density functional theory (DFT) have been performed to obtain the basic data on atomic configurations, such as bond strain and stable sites of substitutional C and Sn atoms in bulk Si or Ge crystals [5–8,10,13].

In this study, we examined the stable configurations of C and/or Sn atoms in Si (Ge) crystals with a focus on the formation of interstitial C_i atoms by means of DFT calculations. The Hakoniwa method proposed by Kamiyama et al. [14] was applied to a 64-atom supercell to obtain the ratio of C_i to total C atoms. A clear difference between Si and Ge was found. We considered not only the mono-doping but also the co-doping of C and Sn.

The phase diagrams of Si-C or Si-Sn allow very little solubility (fractions of percent maximum) of the dopant and rather phase separate into Si and SiC or Si and Sn. One possibility of enhancing the solubilities of C and Sn is to take advantage of non-equilibrium and surface effects in thin films [6,15]. Therefore, most of the structures considered in the present work are probably metastable. However, the results we obtained are useful for the prediction of possible atomic configurations of C and/or Sn in Si and Ge for solar cell application.

Previous experimental and theoretical works [16–18] have considered the effects of co-doping Sn and C in Si crystals in terms of the interactions of the dopants with vacancies, and suppression of

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A-center defect complexes. Such defect complexes should be the scope in a more comprehensive study in the future.

2. Calculation details

2.1. DFT calculation for E_f of C and Sn atoms in Si (Ge) crystals

DFT calculations were performed within the generalized gradient approximation (GGA) for electron exchange and correlation using the CASTEP code [19]. The wave functions were expanded with plane waves, and the ultra-soft pseudo-potential method [20] was used to reduce the number of these waves. The cut-off energy was 340 eV. The expression proposed by Perdew et al. [21] was used for the exchange-correlation energy in the GGA. A density mixing method [22] and the Broyden-Fletcher-Goldfarb-Shanno (BFGS) geometry optimization method [23] were used to optimize the electronic structure and atomic configurations, respectively. A three-dimensional periodic boundary condition was used with cubic 64-atom supercells for Si and Ge crystals. We carried out k-point sampling at 2 × 2 × 2 and 4 × 4 × 4 special points of the Monkhorst–Pack grid [24] for the Si and Ge 64-atom cells, respectively.

For mono-doping of C or Sn atoms in Si, formation energies (E_f) of substitutional m $\mathrm{C_s}$ atoms or n $\mathrm{Sn_s}$ atoms in the Si 64-atom cell are calculated with Eqs. (1a) and (1b) as

$$E_f(\mathrm{C}_{\mathrm{s},m}) = E_{tot}(\mathrm{Si}_{64\text{-}m}\mathrm{C}_{\mathrm{s},m}) - [E_{tot}(\mathrm{Si}_{64})\text{-}m/64E_{tot}(\mathrm{Si}_{64}) + m/64E_{tot}(\mathrm{C}_{64})], \tag{1a}$$

$$E_f(\mathrm{Sn}_{\mathrm{s},n}) = E_{tot}(\mathrm{Si}_{64\text{-}n}\mathrm{Sn}_{\mathrm{s},n}) - [E_{tot}(\mathrm{Si}_{64}) - n/64E_{tot}(\mathrm{Si}_{64}) + n/64E_{tot}(\mathrm{Sn}_{64})], \tag{1b}$$

where $E_{tot}(\mathrm{Si}_{64\text{-}m}\mathrm{C}_{\mathrm{s},m})$ and $E_{tot}(\mathrm{Si}_{64\text{-}n}\mathrm{Sn}_{\mathrm{s},n})$ are the total energies of a Si 64-atom supercell including m $\mathrm{C_s}$ atoms and n $\mathrm{Sn_s}$ atoms, respectively. $E_{tot}(\mathrm{Si}_{64})$, $E_{tot}(\mathrm{C}_{64})$, and $E_{tot}(\mathrm{Sn}_{64})$ are the total energies of a Si 64-atom supercell, a C 64-atom supercell, and a Sn 64-atom supercell, respectively. We also considered the case of one interstitial $\mathrm{C_i}$ included in the total m C atoms. Formation energies (E_f) of one $\mathrm{C_i}$ and substitutional (m−1) $\mathrm{C_s}$ atoms in the Si 64-atom cell are calculated with Eq. (2) as

$$E_f(\mathrm{C}_{\mathrm{i},1}\mathrm{C}_{\mathrm{s},m-1}) = E_{tot}(\mathrm{Si}_{64\text{-}m+1}\mathrm{C}_{\mathrm{i},1}\mathrm{C}_{\mathrm{s},m-1}) - [\{E_{tot}(\mathrm{Si}_{64}) - (m-1)/64E_{tot}(\mathrm{Si}_{64})\} + m/64E_{tot}(\mathrm{C}_{64})], \tag{2}$$

where $E_{tot}(\mathrm{Si}_{64\text{-}m+1}\mathrm{C}_{\mathrm{i},1}\mathrm{C}_{\mathrm{s,m}-1})$ is the total energy of a Si 64-atom supercell including one $\mathrm{C_i}$ atom and (m−1) $\mathrm{C_s}$ atoms.

For co-doping of C and Sn atoms in Si, we considered $\mathrm{C_s}$ and $\mathrm{Sn_s}$ atoms and/or one $\mathrm{C_i}$ atom. The E_f of substitutional m $\mathrm{C_s}$ atoms and n $\mathrm{Sn_s}$ atoms in a Si 64-atom cell are calculated with Eq. (3) as

$$E_f(\mathrm{C}_{\mathrm{s},m}\mathrm{Sn}_{\mathrm{s},n}) = E_{tot}(\mathrm{Si}_{64-m-n}\mathrm{C}_{\mathrm{s},m}\mathrm{Sn}_{\mathrm{s},n}) - [E_{tot}(\mathrm{Si}_{64}) - (m+n)/64E_{tot}(\mathrm{Si}_{64}) + m/64E_{tot}(\mathrm{C}_{64}) + n/64E_{tot}(\mathrm{Sn}_{64})], \tag{3}$$

where $E_{tot}(\mathrm{Si}_{64-m-n}\mathrm{C}_{\mathrm{s},m}\mathrm{Sn}_{\mathrm{s},n})$ is the total energy of a Si 64-atom supercell including m $\mathrm{C_s}$ atoms and n $\mathrm{Sn_s}$ atoms. The E_f of one interstitial $\mathrm{C_i}$ atom and (m−1) $\mathrm{C_s}$ atoms and n $\mathrm{Sn_s}$ atoms in Si is calculated with Eq. (4) as

$$E_f(\mathrm{C}_{\mathrm{i},1}\mathrm{C}_{\mathrm{s},m-1}\mathrm{Sn}_{\mathrm{s},n}) = E_{tot}(\mathrm{Si}_{64\text{-}m+1-n}\mathrm{C}_{\mathrm{i},1}\mathrm{C}_{\mathrm{s},m-1}\mathrm{Sn}_{\mathrm{s,n}}) - [E_{tot}(\mathrm{Si}_{64}) - (m+n-1)/64E_{tot}(\mathrm{Si}_{64}) + m/64E_{tot}(\mathrm{C}_{64}) + n/64E_{tot}(\mathrm{Sn}_{64})], \tag{4}$$

where $E_{tot}(\mathrm{Si}_{64\text{-}m+1-n}\mathrm{C}_{\mathrm{i},1}\mathrm{C}_{\mathrm{s},m-1}\mathrm{Sn}_{\mathrm{s},n})$ is the total energy of a Si 64-atom supercell including one $\mathrm{C_i}$ and (m−1) $\mathrm{C_s}$ atoms and n $\mathrm{Sn_s}$ atoms. Similar calculations were performed for a Ge 64-atom supercell. By using the calculated E_f, we obtained the formation energy of one $\mathrm{C_s}$ and one $\mathrm{C_i}$ in the 64-atom cell including several C and Sn atoms.

A "gap problem" in DFT calculations [25,26] occurs when an incomplete description of the electron self-interaction by the exchange-correlation potential causes the calculated band gap based on GGA to be less than half that of the experimental value [27,28]. A number of methods have been proposed to overcome this problem. GW approximation [29], which is based on many-body perturbation theory, can calculate accurate defect levels [30], but the computational resources required for even a 64-atom supercell are too high. More practical methods, such as the scissors operator scheme, the marker method [31], the LDA + U method [32], the use of adapted pseudopotentials [33], and the application of *ad hoc* extrapolation schemes [34], have been proposed. More recently, hybrid DFT has become popular as an accurate method of calculation [35,36]. Compared with general DFT calculations, these methods and functionals improve the band gap with higher levels of accuracy [37,38]. However, this does not guarantee high levels of accuracy for the calculated defect levels, such as the formation energy of impurities. Chroneos et al. [39,40] found that conventional DFT calculations (e.g., GGA-PBE with ultrasoft pseudopotentials), used in conjunction with aggressive trials designed to improve the theoretical approach, yielded reliable results for some neutral impurities and complexes in Ge crystal. In this work, we use GGA-PBE with ultrasoft pseudopotentials so as to generate useful systematic data on the stable sites of C and Sn atoms in Si and Ge crystals.

2.2. Ratio of each configuration of two C atoms

As discussed later in Section 3.1, the E_f of the isolated $\mathrm{C_i}$ is rather high compared to that of the isolated $\mathrm{C_s}$. Thus, for two C atoms in the 64-atom supercell, we neglected the formation of two $\mathrm{C_i}$ atoms and calculated the ratio of each atomic configuration of two C atoms (($\mathrm{C_s}$ and $\mathrm{C_s}$) and ($\mathrm{C_s}$ and $\mathrm{C_i}$)) in Si and Ge 64-atom supercells by using the Hakoniwa method [14]. This is the case for the uniform distribution of C atoms at 3.12% in Si and Ge crystals. There are 35 configurations of two C atoms (9 of ($\mathrm{C_s}$ and $\mathrm{C_s}$) and 26 of ($\mathrm{C_s}$ and $\mathrm{C_i}$)) in the 64-atom cell. Unfortunately, no reliable data are available for the formation entropy of each atomic configuration of ($\mathrm{C_s}$ and $\mathrm{C_s}$), ($\mathrm{C_s}$ and $\mathrm{C_i}$). Therefore, it is assumed as first order approximation that the formation entropy is constant in the analysis that follows. The ratio P^i of i-th atomic configuration (i = 1–9 for $\mathrm{C_s^{i\text{-}th}}$ at 1st–9th from the other $\mathrm{C_s}$, and i = 10–35 for $\mathrm{C_i^{i\text{-}th}}$ at 1st–26th from $\mathrm{C_s}$) can be calculated with Eq. (5):

$$P^i = \frac{1}{Z} w^i \exp\left[-\frac{E_f^i}{k_B T}\right] \tag{5}$$

$$Z = \sum_i \exp\left[-\frac{E_f^i}{k_B T}\right] \tag{6}$$

where w^i and E_f^i are the coordination number and formation energy of the i-th configuration, respectively, Z is the partition function, k_B is the Boltzmann's constant, and T is the absolute temperature. In the present work, we used T = 723 K (450 °C), which is the typical temperature of Si film growth, and T = 300 K (27 °C).

3. Results and discussion

3.1. E_f of isolated atom in Si and Ge crystals

For interstitial $\mathrm{C_i}$ and $\mathrm{Sn_i}$ atoms, we considered [0 0 1] dumbbell (D)-site, [1 1 0] D-site, tetrahedral (T)-site, and hexagonal (H)-site. The calculated results showed that $\mathrm{C_i}$ ($\mathrm{Sn_i}$) is the most stable at