

First-principles calculation of atomic configurations of carbon and tin near the surface of a silicon thin film used for solar cells



Kai Tadano, Koji Sueoka*

Department of Communication Engineering, Okayama Prefectural University, 111 Kuboki, Soja, Okayama 719–1197, Japan

ARTICLE INFO

Keywords:

First-principles calculation
Atomic configuration
Si thin film
Formation energy
C and Sn doping

ABSTRACT

To achieve higher engineering efficiency in solar cells, group-IV compound semiconductors, such as silicon (Si) or germanium (Ge), in the form of thin films containing carbon (C) and/or tin (Sn) atoms, are gaining attention as alternatives to poly-silicon crystals. Atomic configurations of C and Sn atoms near the (001) surface of a Si thin film were analyzed by first-principles calculation based on density functional theory (DFT). The results of the analysis are threefold. First, C and Sn atoms are most stable at the first atomic layer of the Si thin film, and the surface does not affect the stability of C or Sn atoms deeper than the fifth layer. Second, C and Sn atoms deeper than the fifth layer do not affect the stability of newly arrived C and Sn atoms at the surface during film growth. The effects of the (001) surface and interacting C and/or Sn atoms on the thermal-equilibrium concentrations of C and Sn in each layer of the Si thin film were evaluated in consideration of the degeneracy of the atomic configurations. Third, in the case of mono-doping, formation energy of C (Sn) at the (001) surface increases with increasing concentration of surface C (Sn). In the case of co-doping at C/Sn concentration ratio of 1:1, the formation energies of C and Sn decrease with increasing surface concentrations of C and Sn. It is concluded from these results that co-doping enhances the incorporation of C and Sn atoms in the Si thin film.

1. Introduction

Recently, as alternative poly-silicon crystals for achieving higher engineering efficiency in solar cells, group-IV compound semiconductors, such as silicon (Si) or germanium (Ge), in the form of thin films containing carbon (C) and/or tin (Sn) atoms are gaining attention [1,2]. The purpose of C and/or Sn doping is to control the band structures and bandgaps of these semiconductors. Several studies have been reported on C doping in Si [3–7]. The electronic structure by C doping showed a decrease of the bandgaps from that of pure Si [3] which was previously predicted by Demkov and Sankey [4] with *ab initio* tight-binding molecular-dynamics method. This result was unexpected since both ordered SiC and pure carbon (diamond) have much larger band gaps than Si. The incorporation of C atoms with % order in growing Si film was explained by calculating the formation energy of C atoms near (001) Si surface [5]. The atomic simulations also have been performed to obtain the atomic configurations, namely bond strain and stable sites of substitutional C atoms in Si thin films [5–7] and substitutional C, Ge, Sn (C, Si, Sn) atoms in bulk Si (Ge) crystals [8,9].

The purpose of this study is to clarify the mechanism to determine the atomic configurations of C and Sn atoms in both cases of mono C (Sn) doping and co (C and Sn) doping in a (001) Si thin film by first-

principles calculation based on density functional theory (DFT). In particular, the stability of C and Sn atoms near the (001) surface of a Si thin film was analyzed by calculating the formation energy (E_f) of these doped atoms in each atomic layer. The effects of the Si (001) surface on the stability and thermal-equilibrium concentration of C or Sn atoms are evaluated in the cases of both mono-doping and co-doping in consideration of the degeneracy of the atomic configurations [10,11]. The authors consider that from the viewpoint of solar-cell applications, the evaluation results will be useful for predicting atomic configurations of C and Sn in Si thin films.

2. Calculation method and conditions

2.1. DFT calculation of formation energy of carbon and tin at each layer in a Si thin film

The DFT calculations in the present study are based on a standard approach, using a local density approximation with ultrasoft pseudo-potentials [12], and plane waves as a basis set for efficiently optimizing the atomic structure. The expression proposed by Hammer et al. [13] is used for the exchange-correlation energy in the generalized gradient approximation (GGA) for atom relaxation. The cutoff energy used for the plane-wave expansion was 340 eV. The CASTEP code [14] is used

* Corresponding author.

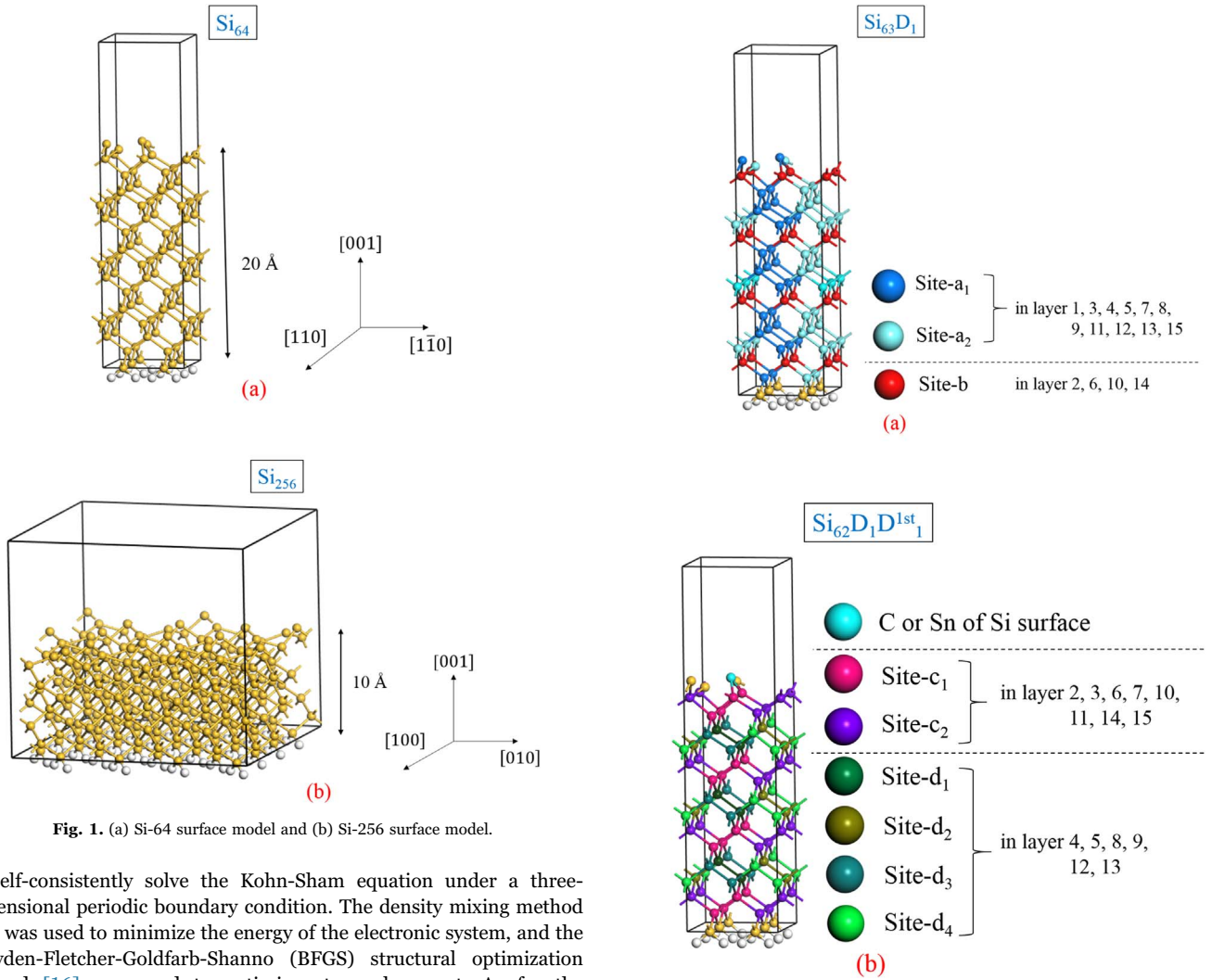


Fig. 1. (a) Si-64 surface model and (b) Si-256 surface model.

to self-consistently solve the Kohn-Sham equation under a three-dimensional periodic boundary condition. The density mixing method [15] was used to minimize the energy of the electronic system, and the Broyden-Fletcher-Goldfarb-Shanno (BFGS) structural optimization method [16] was used to optimize atom placement. As for the convergence condition used in the electronic-state calculation, the total energy change was less than 5.0×10^{-7} eV/atom.

Two types of models (with $p(2 \times 2)$ dimer structures) of a Si (001) surface, as shown in Fig. 1(a) and (b), were fabricated. In these models, a vacuum slab with thickness of 10 Å is attached to a 64-atom cell (Fig. 1(a)) and to a 256-atom cell (Fig. 1(b)). The bottom Si atoms and their terminating hydrogen (H) atoms are constrained during optimization of the atomic structures. Note that the Si 64-atom surface model (Fig. 1(a)) includes four Si atoms in each atomic layer, while the Si 256-atom surface model includes 32 Si atoms in each atomic layer. For k-point sampling, the $2 \times 2 \times 2$ special points of the Monkhorst-Pack [17] grid are used for the Si 64-atom cell, and the $1 \times 1 \times 1$ special points for the Si 256-atom cell.

The Si 64-atom surface model was used to investigate (i) the influence of the (001) surface to the stability of C or Sn atoms in each layer and (ii) the interaction of C or Sn atoms in the Si thin film with other newly arrived C or Sn atoms at the (001) surface during film growth. Substitutional sites in each layer of the thin film are not equivalent due to the existence of a $p(2 \times 2)$ asymmetric dimer at the (001) surface. For investigation (i), the degeneracy number of substitutional sites for one doped atom was four or two depending on the atomic configuration in each layer. The case of a degeneracy number of two, that is, two independent sites (“Site- a_1 ” and “Site- a_2 ”) and the case of a degeneracy number of four, that is, one independent sites (“Site- b ”) for one doped atom, are shown in Fig. 2(a). For investigation (ii), the degeneracy number of substitutional sites for one doped atom was one or two in each layer with the other atom at the (001) surface. The

Fig. 2. (a) Si (001) surface model showing Site- a_1 , Site- a_2 , and Site- b and (b) Si (001) surface model including one C or Sn atom at the surface and showing Site- c_1 , Site- c_2 , Site- d_1 , Site- d_2 , Site- d_3 , and Site- d_4 .

case of degeneracy number of two, that is, two independent sites (“Site- c_1 ” and “Site- c_2 ”) and the case of a degeneracy number of one, that is, four independent sites (“Site- d_1 ”, “Site- d_2 ”, “Site- d_3 ”, and “Site- d_4 ”) for one doped atom with the newly arrived atom at the (001) surface during film growth, are shown in Fig. 2(b). The Si 256-atom surface model was used to investigate (iii) interactions between two doped atoms (C and C, Sn and Sn, and C and Sn) in the (001) surface as their surface concentrations were changed.

Formation energies (E_f) of D (C or Sn) atoms in the Si 64-atom surface model were calculated with Eqs. (1) and (2) using calculated total energy E_{tot} of the cell as follows.

$$E_f = E_{tot}(Si_{63}D_1) - [E_{tot}(Si_{64}) - 1/64E_{tot}(Si_{64})] + 1/64E_{tot}(D_{64}). \quad (1)$$

$$E_f = E_{tot}(Si_{62}D_1D^{1st}_1) - [E_{tot}(Si_{64}) - 2/64E_{tot}(Si_{64})] + 1/64E_{tot}(D_{64}) + 1/64E_{tot}(D^{1st}_{64}). \quad (2)$$

Here, Eq. (1) represents the case of one D atom in the model, while Eq. (2) represents the case of one newly arrived D atom (D^{1st}) at the surface and another D atom (D) in the film. These equations were used to evaluate E_f of a newly arrived C or Sn atom (D^{1st}) at the first layer under the effect of the other C or Sn atom (D) in the Si thin film.

E_f of D (C or Sn) atoms at the surface in the Si 256-atom surface model were calculated with Eqs. (3) and (4) as follows.

Download English Version:

<https://daneshyari.com/en/article/5006123>

Download Persian Version:

<https://daneshyari.com/article/5006123>

[Daneshyari.com](https://daneshyari.com)