

Investigation of effects of inner stress with Sn incorporation on energy band of $\text{Si}_{1-x}\text{Sn}_x$ using density functional theory and photoelectron spectroscopy

Yuki Nagae¹, Masashi Kurosawa^{1,2,3,4}, Masaaki Araidai^{1,2,3},
Osamu Nakatsuka¹, Kenji Shiraishi^{1,3}, Shigeaki Zaima^{1,3}

¹ Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

² Institute for Advanced Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

³ Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

⁴ PRESTO, Japan Science and Technology Agency, 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

E-mail: ynagae@alice.xtal.nagoya-u.ac.jp

Abstract

We investigated the influence of inner stress on the energy band structure of $\text{Si}_{1-x}\text{Sn}_x$ comparing with theoretical and experimental estimations. By alloying Si and Sn atoms, weakening the covalent bonding due to breaking structural symmetry influences on the shape of the valence band density of states of $\text{Si}_{1-x}\text{Sn}_x$. The calculated valence band offset of $\text{Si}_{1-x}\text{Sn}_x$ to Si shifts with upward bowing sensitively with increasing the Sn content compared to conventional linear model, and it well agrees with the experimental result.

1. Introduction

Group-IV semiconductor alloys have been promised for optoelectronic applications of in- and inter-chip optical wiring in the silicon-based high-performance large scale integrated circuits. Si-Sn binary alloy ($\text{Si}_{1-x}\text{Sn}_x$) is an interesting material since its energy bandgap (E_g) is theoretically expected to correspond with a preferable wavelength (1550 nm; $E_g=0.8$ eV) for optical communication applications. However, the formation of high-Sn-content $\text{Si}_{1-x}\text{Sn}_x$ alloy is still a great challenge because of the low thermal equilibrium solubility of Sn in Si (~0.1%). Recently, we experimentally achieved the formation of polycrystalline $\text{Si}_{1-x}\text{Sn}_x$ (poly- $\text{Si}_{1-x}\text{Sn}_x$) layer on insulator with a Sn content as high as 30% [1].

On the other hand, some theoretical calculations were performed for predicting the energy band structure of $\text{Si}_{1-x}\text{Sn}_x$. These studies mainly investigated the threshold Sn content of 31–55% causing the indirect-direct crossover [2–5]. However, in order to design the energy band alignment to realize multi quantum well with various Sn contents, the investigation of not only E_g but also the valence and conduction band offsets are important. D'Costa *et al.* and Sun *et al.* used a regression model for predicting the valence band offset (VBO) of $\text{Si}_{1-x}\text{Sn}_x$ with various Sn contents based on elastic theory using the referenced deformation potential [6, 7]. On the other hand, in the case of $\text{Si}_{1-x}\text{Sn}_x$, its valence state can get more weakly covalent by the atomic displacement from perfect diamond lattice sites due to the large difference of atomic radii between Si and Sn atoms [5]. For more reasonable calculation of VBO, taking into account of inner stress of $\text{Si}_{1-x}\text{Sn}_x$ is necessary.

In this work, we performed density functional theory (DFT) calculation for predicting the VBO of $\text{Si}_{1-x}\text{Sn}_x$ with considering inner stress by Sn incorporation in Si. To examine the consistency of our theoretical prediction, we also experimentally estimated the VBO of poly- $\text{Si}_{1-x}\text{Sn}_x$ layers with various Sn contents of 0–29% using hard X-ray photoelectron spectroscopy (HAXPES).

2. Calculation and experimental details

The first-principles calculation was performed using the Vienna ab initio simulation package (VASP) code [8, 9]. We

used the modified Becke and Johnson (MBJ) exchange potential [10] to avoid the underestimation of E_g in conventional DFT calculation. To consider the electron-ion interaction, we used PAW potential [11]. The unit cell was composed of 8 atoms of diamond lattice ($\text{Si}_{8-n}\text{Sn}_n$, $n=0-8$). We considered all of the unique atomic configuration and the formation probability based on the Boltzmann distribution in a $\text{Si}_{8-n}\text{Sn}_n$ alloy similarly to the previous work [5], which is named “*Hakoninwa-method*” [12]. At first, we calculated the formation energy of $\text{Si}_{1-x}\text{Sn}_x$ cells taking into account the structural relaxation with the isotropic stress for a unit cell under the hydrostatic pressure.

For the experimental estimation of VBO, we prepared poly- $\text{Si}_{1-x}\text{Sn}_x$ (50 nm)/ SiO_2 (1 μm)/Si samples with Sn contents of 0–29% [1]. HAXPES measurement with $h\nu=7938.6$ eV was performed to characterize the valence band structure of $\text{Si}_{1-x}\text{Sn}_x$ layers at BL47XU in SPring-8.

3. Results and discussion

Firstly, we calculated the charge neutrality level (CNL) of $\text{Si}_{1-x}\text{Sn}_x$ based on the interface hybridization that induced dipoles. As shown in Fig. 1, CNL can be estimated as the equilibrium Fermi level after the transportation of electrons between occupied and unoccupied states by interface hybridization as the following equation [13],

$$\phi(\text{CNL}) = \text{VBM} + \frac{E_g D_{\text{VB}}}{D_{\text{VB}} D_{\text{CB}}}$$

where D_{VB} and D_{CB} correspond to the density of states (DOS) of valence and conduction bands, respectively. The CNL of $\text{Si}_{1-x}\text{Sn}_x$ was calculated because it is impossible to simply compare valence band maximum (VBM) values by DFT due to the difference of total electron energy in each $\text{Si}_{1-x}\text{Sn}_x$. So that we estimated the gap between VBM and CNL which is basis of comparison for each Sn-content $\text{Si}_{1-x}\text{Sn}_x$ as shown in Fig. 1.

Figures 2(a)–(e) show the calculated DOS of (a) Si, (b) Si_1Sn_7 , (c) Si_2Sn_6 in which 2 Sn atoms locate at the 1st-nearest-neighbor (1NN) sites, (d) Si_2Sn_6 in which 2 Sn atoms locate at the 2nd-nearest-neighbor (2NN) sites and (e) $\alpha\text{-Sn}$. The integration energy width of conduction and valence bands DOS was 1 eV for the calculation of CNL. Each VBM of $\text{Si}_{1-x}\text{Sn}_x$ indicated by arrow was estimated from the E - k dispersion relationship. By the Sn incorporation into Si, the shape of DOS on VBM shows a small peak. Especially, in results of Si_2Sn_6 , the difference of Sn positions between 1NN and 2NN cases leads to significantly different shapes of DOS of the valence side.

Figure 3 shows the VBO of $\text{Si}_{1-x}\text{Sn}_x$ relative to VBM of Si with setting CNL of each $\text{Si}_{1-x}\text{Sn}_x$ as an equal level. Both experimental and theoretical results are plotted in Fig. 3. The broken line represents a linear approximation of referenced

VBO between Si and α -Sn from the previous report [7]. The linear model doesn't take into account any atomic displacement in $\text{Si}_{1-x}\text{Sn}_x$ by the Sn incorporation. The tendency of upward bowing than linear model can be seen in experimental results of poly- $\text{Si}_{1-x}\text{Sn}_x$.

On the other hand, the calculation result in this study also shows a bowing tendency compared to the linear model. The reason would be attributed to the consideration of inner stress for the calculation model of VBO. It is considered that lowering tetrahedral symmetry by the atomic displacement in $\text{Si}_{1-x}\text{Sn}_x$ weakens the covalent character of atomic bonds in $\text{Si}_{1-x}\text{Sn}_x$. In our previous work [5], it is found that the valence band edge states of sp^3 covalent bonds of $\text{Si}_{1-x}\text{Sn}_x$ are degenerated by breaking the tetrahedral symmetry, so that E_g of $\text{Si}_{1-x}\text{Sn}_x$ shrinks.

It is observed in both calculation and experimental results that the VBO of $\text{Si}_{1-x}\text{Sn}_x$ increases sensitively with the Sn content in the low Sn content region below 12.5%. This phenomenon of VBO increasing depends on shapes of DOS on VBM of $\text{Si}_{1-x}\text{Sn}_x$. The evaluation of CNL values strongly depend on the shapes of valence side DOS with the energy

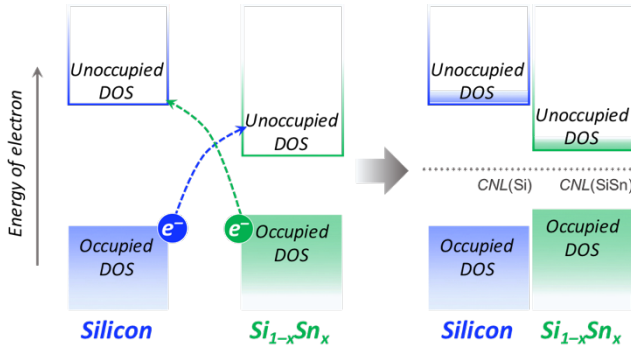


Fig. 1. Schematic view of the calculation of CNL by the correlation between occupied and unoccupied states in $\text{Si}_{1-x}\text{Sn}_x$.

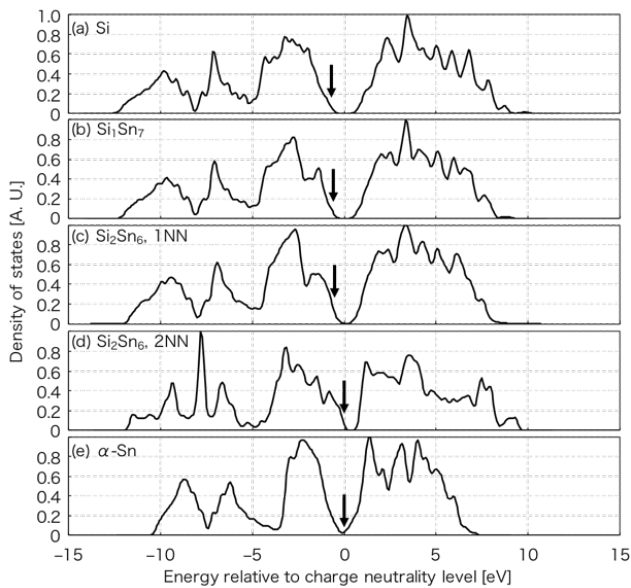


Fig. 2. The calculated DOS of (a) Si, (b) Si_1Sn_7 , (c) Si_2Sn_6 which 2 Sn atoms locate at 1st-nearest-neighbor (1NN), (d) Si_2Sn_6 which 2 Sn atoms locate at 2nd-nearest-neighbor (2NN), and (e) α -Sn. For comparison, DOS of each $\text{Si}_{1-x}\text{Sn}_x$ was normalized. The VBM of each $\text{Si}_{1-x}\text{Sn}_x$ is indicated by arrow.

width of 1 eV. That's why, CNL of $\text{Si}_{1-x}\text{Sn}_x$ is considered to close toward its VBM by changing the covalent characteristics of $\text{Si}_{1-x}\text{Sn}_x$.

4. Conclusions

We investigated the VBO of $\text{Si}_{1-x}\text{Sn}_x$ using both theoretical and experimental approaches. By taking into account of breaking structural symmetry with Sn incorporation, the VBO is deviated from conventional linear model. Since the small peak in valence side DOS which derived from the sp^3 levels in bonding states in $\text{Si}_{1-x}\text{Sn}_x$ contributes for approaching of the VBM toward its CNL, so that the VBO of $\text{Si}_{1-x}\text{Sn}_x$ can be upward. In this work, by considering inner stress in DFT calculation, we found the upward bowing of VBO for $\text{Si}_{1-x}\text{Sn}_x$, so that this theoretical result is in good agreement with the experimental result than conventional calculations.

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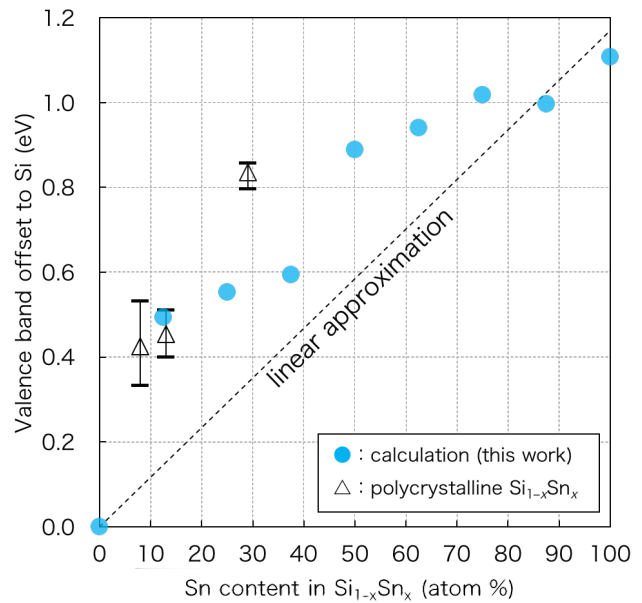


Fig. 3. The VBO of $\text{Si}_{1-x}\text{Sn}_x$ relative to VBM of Si. The calculated results are plotted as blue circle (this work) and experimental results are plotted as blank triangles (polycrystalline). Broken line corresponds to the result of the linear approximation for VBO between values of α -Sn and Si from Ref. 7.