

Stability and Electronic Structures of Group IV Semiconductor Alloy Nanosheets: A First Principles Study

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Abstract

The structural stability and electronic properties of graphene-like alloy nanosheets composed of group IV elements, such as monolayer $\text{Si}_x\text{Ge}_{1-x}$, $\text{Si}_x\text{Sn}_{1-x}$, and $\text{Ge}_x\text{Sn}_{1-x}$, are investigated by means of density functional calculations. Our calculations demonstrate that buckled configuration is stabilized over the entire composition range. The analysis of band structures reveal that a linear band dispersion with Dirac cone at K point similar to graphene appears for $\text{Si}_x\text{Ge}_{1-x}$ over the entire composition range whereas small energy gap within ~ 0.23 eV appears in $\text{Si}_x\text{Sn}_{1-x}$ and $\text{Ge}_x\text{Sn}_{1-x}$. These results suggest that composition control is of importance in tailoring the electronic properties of group IV alloy nanosheets.

1. Introduction

Two-dimensional (2D) nanostructures in the honeycomb lattice have currently been paid much attentions due to their peculiar electronic properties. Furthermore, Si (silicene), [1,2] Ge (germanene), [3] Sn (stancene) [4] monolayers are expected to be potential alternatives to graphene for electronic devices. In contrast to flat 2D nanosheets consisting of sp^2 hybridization such as graphene, silicene, germanene, and stancene form a mixture of sp^2 and sp^3 hybridization, resulting in the buckled hexagonal configuration. Recent theoretical calculations within density functional theory (DFT) have suggested that despite buckled atomic configuration these materials possess a linear band dispersion with Dirac cone at K point. [5] Moreover, it has been suggested that monolayer SiGe with buckled configuration also has a linear band dispersion similar to graphene. [6] However, there are few systematic studies for the atomic structure and electronic properties of monolayer group IV binary compounds from theoretical viewpoints.

In this work, structural stability and electronic properties of group IV semiconductor alloy nanosheets, such as monolayer $\text{Si}_x\text{Ge}_{1-x}$, $\text{Ge}_x\text{Sn}_{1-x}$, and $\text{Si}_x\text{Sn}_{1-x}$ are systematically investigated on the basis of electronic structure calculations within the DFT. Detailed atomic structures such as bond lengths and buckling distances are analyzed, and its miscibility is also examined. Furthermore, for various atomic configuration, the realization of linear band dispersion with Dirac cone at K point is examined.

2. Calculation procedure

The calculations are performed by the plane wave pseu-

dopotential approach using the generalized gradient approximation [7] within the DFT. Norm-conserving pseudopotentials [8] are used to describe electron-ion interaction and partial-core correction [9] is adopted for Ge and Sn atoms. In our calculations, the spin-orbit coupling is not included. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 20.25 Ry. The 2×2 unit cell consisting of eight atoms is used to simulate monolayer alloy sheets composed of group IV elements. We use 16-k point sampling in the Brillouin zone integration. The conjugate gradient technique is utilized for both electronic structure calculation and geometry optimization. These calculations have been performed using Tokyo *Ab initio* Program Package (TAPP). [10] In order to assess thermodynamic stability of alloy nanosheets, we calculate the excess energy ΔE of A_xB_{1-x} alloy nanosheet given by

$$\Delta E = E_{\text{tot}}(\text{A}_x\text{B}_{1-x}) - xE_{\text{tot}}(\text{A}) - (1-x)E_{\text{tot}}(\text{B}), \quad (1)$$

where $E_{\text{tot}}(\text{A}_x\text{B}_{1-x})$, $E_{\text{tot}}(\text{A})$, and $E_{\text{tot}}(\text{B})$ are the total energies of A_xB_{1-x} , A, and B nanosheets, respectively.

3. Results and discussion

Figure 1 shows the averaged bond length, averaged buckling distance, and the excess energy of monolayer $\text{Si}_x\text{Ge}_{1-x}$, $\text{Ge}_x\text{Sn}_{1-x}$, and $\text{Si}_x\text{Sn}_{1-x}$. It is found that the average bond length shown in Fig. 1(a) decreases with increasing composition x , which corresponds to Vegard's law. We also find that the total energy of monolayer nanosheets with buckled configuration is lower than that of flat monolayer nanosheets by ~ 0.12 eV/atom, indicating that buckled hexagonal structure is stabilized for group IV alloy nanosheets, in contrast to graphene. Furthermore, the buckling distance decreases with increasing composition x , as shown in Fig. 1(b). This indicates that sp^3 hybridization mainly contribute to the covalent bonds consisting of heavy elements. As shown in Fig. 1(c), monolayer $\text{Si}_x\text{Sn}_{1-x}$ exhibits large excess energy (~ 130 meV/atom) due to large lattice mismatch between Si and Sn ($\sim 20\%$). However, this value is comparable to that of bulk phase (tetrahedrally-coordinated structure, such as zinc-blende structure). Therefore, it is expected that the miscibility of group IV alloy nanosheets are similar to that of bulk phase.

Figure 2 shows calculated band structure of monolayer $\text{Si}_x\text{Ge}_{1-x}$, $\text{Ge}_x\text{Sn}_{1-x}$, and $\text{Si}_x\text{Sn}_{1-x}$, along with those of silicene, germanene, and stanene. The calculated energy gap of silicene, germanene, and stanene [shown in Figs. 1(a), 1(b),

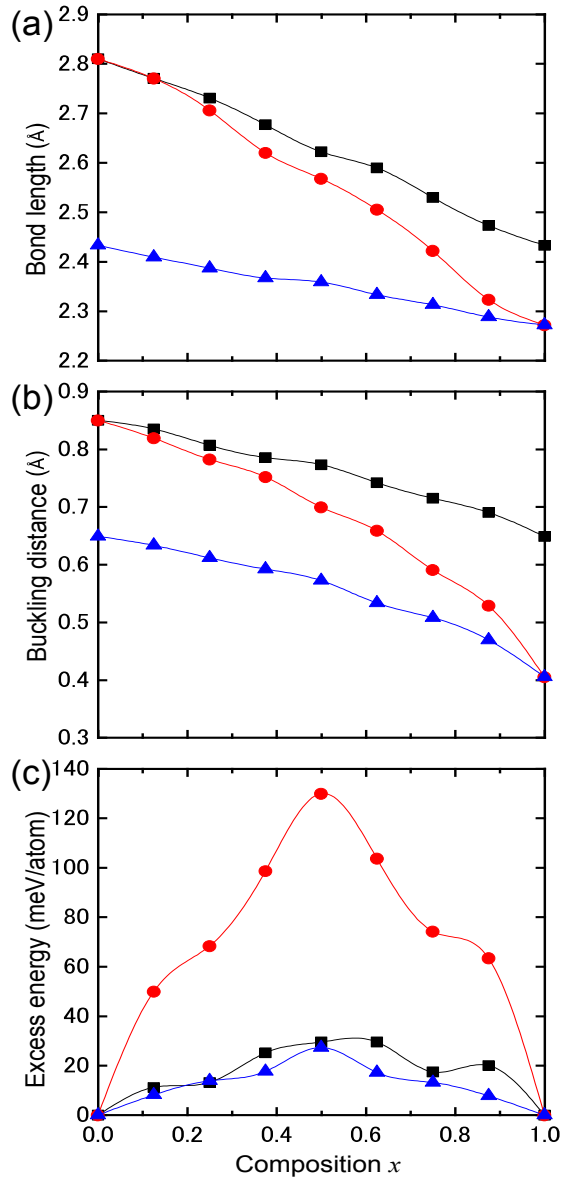


Fig. 1 Calculated (a) bond length, (b) buckling distance, (c) excess energy of monolayer $\text{Si}_x\text{Ge}_{1-x}$, $\text{Ge}_x\text{Sn}_{1-x}$, and $\text{Si}_x\text{Sn}_{1-x}$ sheets as a function of composition x . Squares, triangle, and circles represent data for $\text{Si}_x\text{Ge}_{1-x}$, $\text{Ge}_x\text{Sn}_{1-x}$, and $\text{Si}_x\text{Sn}_{1-x}$, respectively.

and 1(c), respectively] are almost zero-gap and a linear band dispersion like Dirac cone appears at K point. This feature is maintained even in $\text{Si}_x\text{Ge}_{1-x}$ nanosheets over the entire composition range. A typical band structure of monolayer $\text{Si}_x\text{Ge}_{1-x}$ ($\text{Si}_{0.5}\text{Ge}_{0.5}$) is shown in Fig. 2(d). In contrast, a linear band dispersion at K point disappears in monolayer $\text{Ge}_{0.5}\text{Sn}_{0.5}$ and $\text{Si}_{0.5}\text{Sn}_{0.5}$ [Figs. 2(e) and 2(f)] and small energy gap (~ 0.23 eV) is formed at K point. This indicates that semiconducting character with small energy gap can be realized in monolayer $\text{Ge}_x\text{Sn}_{1-x}$ and $\text{Si}_x\text{Sn}_{1-x}$, and the gap energy of these monolayer materials could be changed by composition control.

4. Conclusions

We have investigated structural stability and electronic

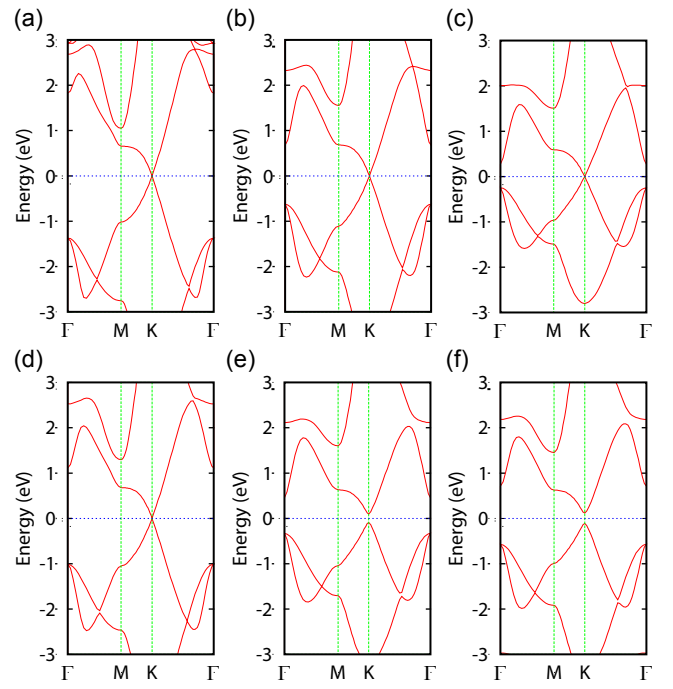


Fig. 2 Calculated Kohn-Shan band structures of (a) silicene, (b) germanene, (c) stanene, (d) monolayer $\text{Si}_{0.5}\text{Ge}_{0.5}$, (e) monolayer $\text{Ge}_{0.5}\text{Sn}_{0.5}$, and (f) monolayer $\text{Si}_{0.5}\text{Sn}_{0.5}$. The Fermi energy is set at zero.

properties of graphene-like alloy nanosheets composed of group IV elements are investigated on the basis of DFT calculations. We have found that buckled configuration is stabilized over the entire composition range. We have also revealed that the excess energy of monolayer nanosheets are found to be comparable to that with tetrahedrally-coordinated structure. A linear band dispersion with Dirac cone at K point is found to for $\text{Si}_x\text{Ge}_{1-x}$ over the entire composition range, whereas small energy gap appears in $\text{Ge}_x\text{Sn}_{1-x}$ and $\text{Si}_x\text{Sn}_{1-x}$.

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