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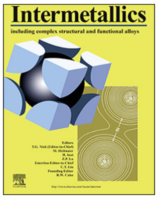

Pair interaction energies and local structures of titanium and nickel atom-pairs in β-Sn type silicon

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ABSTRACT

Pair interaction energies (PIEs) of Ti-Ti, Ti-Ni and Ni-Ni pairs and optimized local structures around these pairs in β-Sn type Si are studied by first principles calculation to elucidate typical local structures of transition-metal (TM) atoms in Si-rich amorphous silicides or alloys. In the calculations, TM pairs are located at substitutional sites along a long axis of cuboid $Si_{432}(TM_2Si_{430})$ supercell (6×3×6 unit cells of β-Sn type Si) to calculate interatomic distance dependences of PIEs up to 6 Å-distance (up to the 12th nearest neighboring (NN) distance). We find that interatomic distances of Ti-Ti and Ti-Ni pairs with largely negative PIEs agree with those in Si-rich ordered silicides such as $TiSi_2$ and $Ti_4Ni_4Si_7$, and that the optimized local structures around Ti-Ti and Ti-Ni pairs commonly have Si-hexagons, which typically appear in early-TM silicides, and thus expected to be observed in the amorphous Si-rich silicides or alloys. On the contrary, Ni-Ni pair in β-Sn type Si indicates no significant feature in PIE profile or in local structures. Properties of Ni-Ni or Ni-Si bonding in Si-rich silicides may be governed by sp^3-like Si lattices.

1. Introduction

Transition-metal (TM) silicide has been widely studied as spintronics and thermoelectric materials. Recently not only ordered but also amorphous TM silicides have been investigated to develop new semiconducting materials, especially for junction or anode of semiconductor device. For example, Ma has reported amorphous Ti silicides with Ti-composition of 35–65 at% formed around interfaces of Ti-Si thin-film multilayers [1]. Okada et al. realized a low barrier and low resistance electrical junction by amorphous W silicidde with the typical local structure of $WSi_n(n = 8\text{-}11)$ [2,3]. They have also investigated amorphous TM silicides composed of the local structure of $TMSi_n$ (TM = Zr, Nb or Mo, n = 7-20), which have an optical gap (>0.4 eV) and large electron and hole mobilities [4]. Moreover, Fukuhara et al. proposed a super capacitor fabricated by dealloying amorphous ternary Ti-Ni-Si alloy followed by anodic oxidization, where nanoporous titanium oxides are formed [5,6]. A Si-Ti-Ni alloy based on $Ti_4Ni_4Si_7$ matrix also has been investigated as an anode for all-solid-state Li-ion battery [7]. To achieve required performance in applications and to explore newly functional materials, it is very important to elucidate local structures of these amorphous silicides, where typical (but not rigidly fixed) structures are expected to be observed.

Zhang et al. reported atomic and electronic structures of 3d-TM single atoms (V-Ni) as a dopant in diamond type Si on the basis of first principles calculation [8]. They found, by comparing the formation energy of different dopant sites, that these 3d-TM atoms are energetically favorably located at the tetrahedral interstitial site in the diamond-Si lattice (actually at the hexagonal site only for Ni atom with the almost same energy as the tetrahedral site). Similar results of the preferred atomic site for single Ti and Ni atom in the diamond type Si have been obtained theoretically by Kamon et al. [9]. Their results give a fundamental knowledge of TM atoms as dopants in diamond type Si.

However, structures of TM-silicides, even for Si-rich one, are not always based on the sp^3-like diamond structure. Then to discuss structures and properties of TM-silicides or alloys, especially local structures in amorphous alloys, we have to elucidate the interactions between TM atoms and those between TM-Si atoms in non-diamond type Si.

There are several slightly complicated structures in Si-rich Si-TM alloys, while we can recognize some common structures among these. For example, structures of late-TM disilicides, $CoSi_2$ and $NiSi_2$ are CaF_2-type(cF12), where a Si atom connects with four Co/Ni atoms as the sp^3-like manner, that is, they constitute a regular tetrahedron. On the other hand, early-TM disilicides, $TiSi_2$(C54:oF24), VSi_2(hP9) and $CrSi_2$(hP9) have Si-hexagons in-plane, where a Ti/V/Cr atom is located at the center of Si-hexagon, which suggest sp^2-like Si bonds. These typical Si

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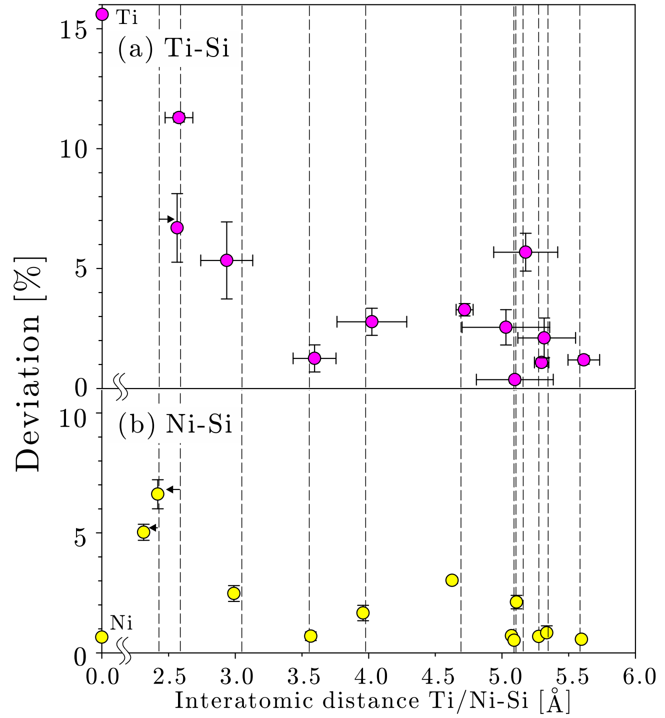

Fig. 1. Deviations of atom positions from the initial(ideal) lattice points around a substitutional Ti and Ni atom in β-Sn type Si as a function of the optimized interatomic distances between Ti/Ni and Si atoms. The deviation is expressed as a ratio to the 1st NN Si bond length (2.43 Å). The vertical (horizontal) error bar shows the distribution of deviation (interatomic distance) around the value (circle) averaged on the equivalent lattice points. The vertical dashed lines indicate the initial(ideal) interatomic distances.

structures of course should appear in such ordered compounds. However, these are also expected to appear as locally stable (metastable) partial structures in amorphous or disordered Si-rich compounds.

In the present paper, we calculate pair interaction energy (PIE) of Ti-Ti, Ti-Ni and Ni-Ni pairs in β-Sn type Si by first principle calculation to discuss energetically favorable site of the impurity-pair and the local atomic structures around the pairs. PIE indicates the energy deference between impurity pairs which are located at relatively different positions in a host material. A largely negative PIE means that the pair is energetically preferred to be at the position, and give a relatively stable structure around the pair under the precondition of dissolution of impurities in the host material. Therefore, PIE with structural relaxation is considered to be one of suitable tool to discuss the local structure of minority elements in both ordered and disordered host materials. We have studied atomic structures of Al-rich Al-TM alloys by using TM-TM PIEs in fcc Al calculated by the full-potential Korringa-Kohn-Rostoker Greens function method, and clarified the origins of the $L1_2$ and DO_{22} structures of Al_3Sc and Al_3V, etc [10,11]. For Ni-rich Ni-Si alloys, effective pair interaction energies of Ni-Si in fcc-Ni have been calculated by using short-range order parameters [12].

Titanium and Nickel are selected here as a representative of early- and late-3d element of TM silicides, respectively. Although not the ground state of Si under atmospheric pressure, we employ the β-Sn type structure as a host lattice because the coordination number or density is more suitable for silicides than that in diamond type Si.

We find that Ti-Ti interatomic distances in the relaxed local structures with low PIEs almost agree with those in ordered Si-rich Si-Ti or Si-Ti-Ni alloys and that some common local structures appear around a Ti atom or the Ti-Ti pair. We also find that a similar situation to Ti-Ti PIEs appears in Ti-Ni PIEs. However, it is found that all the Ni-Ni PIEs in β-Sn type Si are positive and give no information about the energetically favorable structure. Instead, we show that the optimized Ni-Ni interatomic distances with low PIEs in the diamond type Si agree with the Ni-Ni interatomic distances in ordered Si-rich Ni silicides. The optimized Ni-Ni interatomic distances almost correspond with the Si-Si interatomic distances in the diamond type structure.

2. Calculations

We calculate PIE of Ti-Ti, Ti-Ni and Ni-Ni on substitutional sites in β-Sn type Si crystal (A5,tI4) with full structural optimization. TM-TM PIE with structural optimization, $\Delta E_{\mathrm{opt}}^{\mathrm{TM-TM}}$ is defined as a total energy difference between a optimized system with two TM atoms with a distance R, $E_{\mathrm{opt}}^{\mathrm{TM-TM}}(R)$, and that with the infinitely separated (non-interacting) two TM atoms, $E_{\mathrm{opt}}^{\mathrm{TM-TM}}(\infty)$ (here TM-TM = Ti-Ti, Ti-Ni or Ni-Ni):

$$\Delta E_{\mathrm{opt}}^{\mathrm{TM-TM}}(R) = E_{\mathrm{opt}}^{\mathrm{TM-TM}}(R) - E_{\mathrm{opt}}^{\mathrm{TM-TM}}(\infty). \tag{1}$$

We employ 432-atom supercell (2×216-atom cuboid: 28.14×14.07×15.48 $Å^3$) for the two-impurity system (TM_2Si_{430}), and $E_{\mathrm{opt}}^{\mathrm{TM-TM}}(\infty)$ is approximated by the total energy $E_{\mathrm{opt}}^{\mathrm{TM-TM}}(R = 14.07\ Å)$. The TM-TM distance R is taken along the long axis (a-axis) of the supercell. We calculate PIEs from the 1st nearest neighboring(NN) pair (initial distance of 2.43 Å) to the 12th NN pair (initial distance of 5.59 Å) in the supercell.

In the β-Sn type Si, Si atoms align in a zigzag along the a and b axes with the interatomic distance of 2.43 Å and align linearly along the c

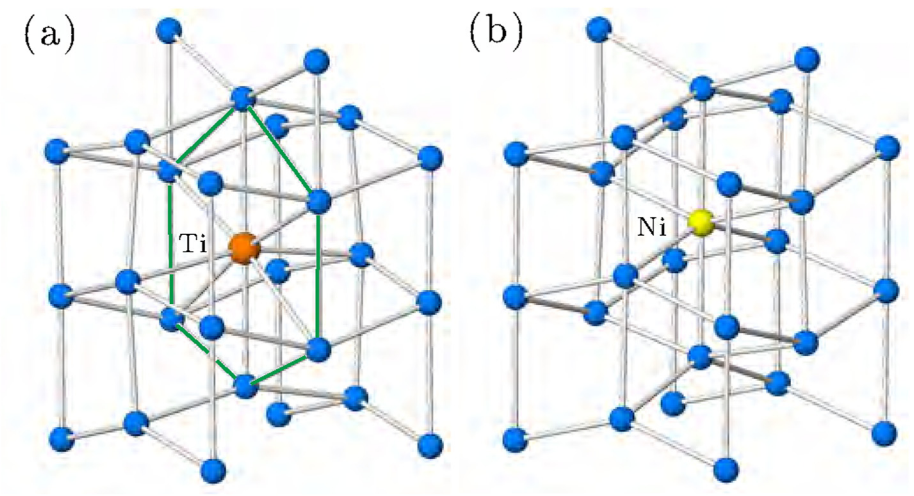

Fig. 2. Local atomic structures of β-Sn type Si around (a) Ti and (b) Ni atoms. The Si lattice is largely distorted around a Ti atom, and constitutes a distorted hexagon (indicated by dark-colored bonds of 2.45–2.79 Å). The numbers (1~5) indicate the initial atomic sites of the n-th (n = 1 ~ 5) NN Si atoms from Ti/Ni atoms.