First-principles Study of Si-embedded Ni(100) Surfaces

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First-principles total-energy calculations were applied to 0 to 1 ML of silicon-embedded Ni(100) surfaces in the outmost layer within a 2 × 4 unit cell. Up to a half monolayer of embedded silicon, the surface energy decreased monotonically with increasing the number of embedded silicon, and the lowest energy structure was a $\sqrt{2} \times \sqrt{2}$-R45° [or c(2 × 2)] structure with diagonally aligned embedded silicon of 0.5 ML. Beyond the half monolayer, the surface energy increased with increasing the number of embedded silicon. The energy of the silicon-embedded structure in the outmost layer of the Ni(100) surface was compared with silicon embedded in the second layer and silicon adsorbed on the Ni(100) surface. Both configurations gave higher energies, which shows the robustness of the $\sqrt{2} \times \sqrt{2}$-R45° structure on the Ni(100) surface. The present results are in perfect agreement with our recent report [T. Fukuda et al., Jpn. J. Appl. Phys. 59, 065501 (2020)].

Keywords First-principles calculation; Silicon; Ni(100); Two-dimensional silicide

I. INTRODUCTION

Atomic structures and electronic properties of metal-semiconductor interfaces have been the subject of a large number of studies inspired by a variety of applications in semiconductor electronic devices. Alloys and/or compounds are often formed at the interface between metals and semiconductors, and their detailed atomic structure decisively governs electronic transport through the interface. Among them, compounds between silicon and metals, often referred to as metal silicides, are of great practical importance for semiconductor electronic devices because they are essential for low-resistance electrical contacts of silicon channels with metal electrodes. Therefore, extensive research efforts have been devoted to understanding detailed atomic structures and their reaction processes, and electronic properties of reacted films [1–3]. Of these silicides, 3d transition metal (3d-TM) silicides, such as Ni and Co silicides formed on silicon substrates are the most versatile and, therefore, received much attention over several decades.

Inverse silicides, i.e., silicides formed on metal substrates, have been recently reported as counterpart of silicides on silicon [4–11]. It has been reported that $2 \times 2$ and $\sqrt{3} \times \sqrt{3}$-R30° structures were formed by exposing the Ni(111) surface to silane at high temperatures [4]. In a later study [5], one-third monolayer of Si was found to form the $\sqrt{3} \times \sqrt{3}$-R30° structure, which indicated the formation of a two-dimensional (2D) Ni$_2$Si layer. The detailed atomic structures of the $2 \times 2$ and $\sqrt{3} \times \sqrt{3}$-R30° structures were determined by low energy electron diffraction (LEED) [6, 7]. In addition, the Ni(100) surface implanted with Si ions and subsequently annealed was studied by transmission electron microscopy (TEM) and Rutherford backscattering spectroscopy (RBS), and epitaxial NiSi was shown [8]. In addition to those reports, we reported that 2D silicides on the Ni(110) surface with p(1 × 2), c(2 × 2), and c(4 × 2) structures coexisted in a half-monolayer Si, revealed by scanning tunneling microscopy (STM) [9]. A striking feature of these 2D silicides is that Si and Ni alternate in the close-packed [110] row. The stability of these half-monolayer structures was confirmed by first-principles calculations [10]. Furthermore, we recently reported detailed atomic structures of 2D silicides on the Ni(100) surface. Here, a half-monolayer of Si formed a $\sqrt{2} \times \sqrt{2}$-R45° [or c(2 × 2)] structure [11]. In our previous report, the stability of the atomic order of the outmost layer was confirmed by preliminary first-principles...
total-energy calculations within a limited number of atoms and \( k \) points. The present report extends the calculation to a larger unit cell and an increase in the number of \( k \) points, and details the calculation of the Si-embedded Ni(100) surfaces. The stability of the Si-embedded Ni(100) surfaces was investigated in detail, and the detailed atomic arrangement and electronic states of the stable structure were clarified. Furthermore, the stability of the Si-embedded structures was compared with Si embedded in the second layer and Si adsorbed on the Ni(100) surface.

II. COMPUTATIONAL METHOD

A first-principles calculation code based on density functional theory was used to calculate the Si-embedded Ni(100) surfaces [12]. The projector-augmented-wave (PAW) method was used for the Ni and Si potentials [13]. The spin-resolved local density functional was amended by the generalized gradient approximation (GGA) [14]. As shown in Figure 1(a), a slab model in the (100) direction with a \( 2 \times 4 \) surface unit cell was constructed. The slab had a total of 11 layers with a 1.06-nm vacuum gap on each side, containing a total of 88 atoms. Before calculating the Si-embedded structures, the atomic structure of the pristine Ni(100) surface was evaluated. All Ni layers in the slab except the middle layer were completely relaxed until the force drops below 0.1 eV nm\(^{-1}\), and the wavefunction and charge density were iterated until the total electron energy in the slab converged to 10 \( \mu \)eV. In the calculation, 2D \( k \) points were sampled to \((k_a, k_b) = 8 \times 16\) in the reciprocal unit cell, where \( a \) and \( b \) refer to the surface unit vectors in the bulk [011] and [0\( \overline{1} \)1] directions, respectively (see Figure 1). The cut-off energy was set to 350.4 eV for all calculations. The Methfessel-Paxton method was used to evaluate the partially filled electronic bands [15], and the smearing energy width was optimized to \( \sigma = 0.12\) eV.

Si was, then, embedded by replacing 0–8 Ni atoms in the top layer with Si. Possible atomic configurations of Si-embedded structures are schematically outlined in Figure 1(b–i). In order to calculate these structures, the outmost five layers were completely relaxed again under the same condition as the pristine Ni(100) surface.

Figure 1: (a) Ni(100) surface model, and (b)–(i) 1–7 Si-embedded models. A surface unit cell is represented by a red-dashed square in (a), and the \( 2 \times 4 \) unit cell is represented by a blue rectangle in each model.
III. RESULTS AND DISCUSSION

A. Energies for Si-embedded structures

Since the number of constituent atoms varies from model to model, the total energies were compared using the bulk cohesive energies of Ni and Si, represented by $E_{\text{Ni}}^b$ and $E_{\text{Si}}^b$, respectively. Accordingly, the total energy for different numbers of embedded Si atoms can be written as

$$E_{\text{total}} = E_{\text{slab}} - N_{\text{Ni}} E_{\text{Ni}}^b - N_{\text{Si}} E_{\text{Si}}^b,$$  \hspace{1cm} (1)

where $N_{\text{Ni}}$ and $N_{\text{Si}}$ are numbers of the Ni and Si atoms in the slab, respectively. Bulk cohesive energies were calculated, respectively, as 4.760 and 4.611 eV atom$^{-1}$ for Ni and Si with optimal lattice constants, using the same cut-off energy used in the slab calculation. These values are in good agreement with the experimental values of 4.44 and 4.63 eV atom$^{-1}$ for Ni and Si, respectively [16]. The surface energy of the Ni(100) face, which is given by the energy difference between the Ni bulk and the Ni(100) slab, was 0.854 eV/1 × 1 or 2.20 J m$^{-2}$ [17, 19, 20, 21].

Based on the energy of the Ni(100) surface, the relative formation energies, $E_{\text{rel}}$, of the Si-embedded structures shown in Figure 1(b–i) can be compared by using Eq. (1), and they are shown in Table 1 and Figure 2 as a function of the Si coverage. Note that $E_{\text{rel}}$ is taken for the 1 × 1 surface unit cell in both Table 1 and Figure 2. All structures shown in Figure 1(b–i) exhibited negative formation energies. This means that these structures are exothermic with respect to the pristine Ni(100) surface and that these structures are stable. The lowest energy structures with the Si coverage up to 0.5 ML such as b, be, and bef indicate that embedded Si tends to align diagonally along the <100> directions. However, the energy gain by the diagonal alignment of embedded Si is only 0.007 eV by comparing the formation energy between b and e. Diagonally aligned structures of embedded Si were also found in our STM study [11]. There, zigzag and cross structures were observed when the coverage of Si was less than 0.5 ML. On the other hand, the structures in which Si is embedded in the nearest neighbor such as a and c have an energy of about 0.07–0.08 eV/bond higher than the structures arranged diagonally. Therefore, the nearest neighbor Si pair was never observed in our STM study [11].

As shown in Figure 2, a nearly linear decrease in the formation energy of the lowest energy structures as a function of the Si coverage up to 0.5 ML indicates that there is seemingly no interaction between embedded Si. However, a close evaluation of their formation energies revealed a slight discontinuity of 0.005 eV between the 1/8 and 1/4−1/2 ML (b, be, and bef) Si embedded structures. This seems to result from the repulsive interaction between the embedded Si atoms in the 1/8 ML model. Indeed, the formation energy of e is 0.007 eV higher than that of d, indicating that the energy of Si-embedded at a distant is lower. Therefore, the 2 × 4

| Si coverage (ML) | model | $E_{\text{rel}}$ (eV/1 × 1) |
|-----------------|-------|--------------------------|
| 0               |       | 0                        |
| 1/8             | a     | −0.287                   |
|                 | b     | −0.441                   |
|                 | c     | −0.373                   |
|                 | d     | −0.434                   |
|                 | e     | −0.427                   |
| 3/8             | ab    | −0.452                   |
|                 | ad    | −0.507                   |
|                 | bd    | −0.609                   |
|                 | be    | −0.659                   |
|                 | ce    | −0.530                   |
| 1/2             | abc   | −0.478                   |
|                 | abd   | −0.615                   |
|                 | abe   | −0.682                   |
|                 | abf   | −0.606                   |
|                 | abg   | −0.615                   |
|                 | ade   | −0.581                   |
|                 | bef   | −0.878                   |
|                 | beg   | −0.765                   |
|                 | bdg   | −0.780                   |
| 5/8             | DFG   | −0.629                   |
|                 | CDG   | −0.819                   |
|                 | BFG   | −0.681                   |
|                 | BEG   | −0.764                   |
|                 | ABF   | −0.662                   |
| 3/4             | FG    | −0.645                   |
|                 | EG    | −0.676                   |
|                 | DG    | −0.768                   |
|                 | CG    | −0.714                   |
|                 | BG    | −0.738                   |
| 7/8             |       | −0.687                   |
| 1               |       | −0.653                   |

Figure 2: $E_{\text{rel}}$ as a function of Si coverage for each structure model shown in Figure 1. A linear decrease and increase in the relative energy up to and above 0.5 ML are shown by dashed red and blue lines, respectively.
slab is not enough to separate interaction between the embedded Si atoms, and the calculated energy of 1/8 ML is slightly underestimated as the surface energy to replace a singleNi atom with Si in the Ni(100) surface.

The lowest energy configuration of the Si embedded structure is \textit{bef} with the Si coverage of 0.5 ML, which corresponds to the $\sqrt{2} \times \sqrt{2}$-R45°[or c(2 × 2)] structure. The structure is consistent with our previous calculation with a smaller 2 × 2 slab and its formation energy also agrees with the previous calculation [11].

As shown in Figure 2, when the coverage of Si exceeds 0.5 ML, the formation energy increases as a function of the Si coverage. The lowest energy configurations for Si exceeding 0.5 ML are the models where Si is diagonally aligned in the structure such as \textit{CDG} and \textit{DG}. However, these structures were not found experimentally because the formation of the overlayer is energetically less favored than filling the first layer with impinged Si [11].

B. Atomic configuration and band structure for the low energy configuration

We now discuss the atomic configuration for stable structures. For the clean Ni(100) surface, the lattice spacing between the surface layers shows oscillatory relaxation. The results of previous experimental and theoretical studies are listed in Table 2 along with the present calculation. Aside from the early low energy electron diffraction studies [18, 22, 25], there is an about 3–4% contraction between the first and second layers ($d_{12}$) and a 1% expansion between the second and third layers ($d_{23}$), and these have reached a general consensus. The distances in the present calculation are in fairly good agreement with the past numerical values.

The atomic geometry of the stable $\sqrt{2} \times \sqrt{2}$-R45°structure is schematically shown in Figure 3. Embedded Si is pulled down from the bulk lattice spacing by 20 pm ($-11.4\%$ referred to the bulk lattice spacing), and the adjacent Ni on the top layer protrudes from the bulk lattice spacing by 4 pm ($+2.4\%$), resulting in 24 pm rumpling as we noted earlier [11]. Embedded Si is pulled by the surrounding Ni atoms, but adjacent Ni has a longer Si–Ni bond length than the Ni–Ni bond, so Ni is pushed out by the steric effect.

![Figure 3: Atomic geometry for the $\sqrt{2} \times \sqrt{2}$-R45° structure. Bulk lattice spacings are represented by broken lines.](image)

| $d_{12}$ (%) | $d_{23}$ (%) | $d_{34}$ (%) | Refs. |
|-------------|-------------|-------------|-------|
| +2.7        | -3.04       | -3.2        | 18    |
| +2.5        | -0.35       | -0.02       | 22    |
| -3.7        | +1.7        | +1.3        | 19    |
| -3.3        | +1.4        | +1.4        | 26    |
| -3.6        | +0.3        | +0.3        | 20    |
| -3.70       | +0.720      | +0.24       | 21    |

![Figure 4: Band structure of the Si-embedded c(2 × 2) structure.](image)

(a) Bulk and surface Brilliouins. The surface Brillouin zones for the 1 × 1 and 2 × 2 unit cells are represented by pale green and pale blue, respectively. Symmetry points in parentheses correspond to the projections of the bulk symmetry points onto the surface. Surface bands of (b) majority and (c) minority spin components. Bulk projection is overlaid on the band diagrams with pale red.
This effect is also seen in the 1/4- and 3/8-ML Si-embedded models such as b and be. In these models, top Ni is lifted when surrounded by Si. From an energy point of view, protruding Ni reduces the binding energy between the first and second layers but is compensated by the strong Si–Ni bond. As shown in Figure 3, embedded Si is pulled largely inward, so the third layer is also pulled down slightly.

The band structure of the most stable $\sqrt{2} \times \sqrt{2} \cdot R45^\circ$ structure is shown in Figure 4. Since the c(2 × 2) unit cell was used to calculate the band structure, the surface Brillouin zone is reduced to half of the original $1 \times 1$ Brillouin zone, as shown in Figure 4(a). The calculated bands resonate with bulk-projection bands marked by red in Figure 4(b, c). We should note that this calculation includes empty bands up to only about 8 eV from $E_F$, so the projected bulk bands were not reproduced above 8 eV. The original Ni(100) surface band on the backside of the slab is superimposed on the band structure. Unoccupied bands between 2 and 8 eV seen in $\Gamma$–X and M are Ni-induced surface bands. A striking feature is an isolated parabolic band from −8 to −10.5 eV. This band is derived from the embedded Si 3s states and was previously found on the Si/Ni(110) surface [10]. Since the Ni(100) surface has a four-fold symmetry, the Si 3p states are separated from the 3s states and they are hybridized to surrounding Ni with p$^3$ configuration. As a result, the energy of the isolated 3s states was reduced and isolated from the bulk resonance.

Figure 5 shows the spin-resolved projected density of states (PDOS) of bulk and surface atoms. Bulk Ni PDOS was obtained from the middle layer of the slab. As shown in Figure 5(a), bulk Ni has an exchange-splitted 3d PDOS and their widths are around 5 eV. The exchange energy was estimated to be 0.79 eV from the difference of band edge energies between the majority spins (−0.49 eV) and the minority spins (+0.30 eV). The exchange energy is in good agreement with our previous calculations for the Ni(110) surface [10]. Top Ni on the Ni(100) surface in Figure 5(b) shows similar PDOS, but the 3d band is slightly narrower than the bulk band, which is also similar to our previous calculation for the Ni(110) surface [10]. On the other hand, the exchange splitting of surface Ni was 0.83 eV (−0.46 eV for majority spins and +0.37 eV for minority spins), which is larger than that of bulk, and gives a larger magnetic moment of 0.73 $\mu_B$ compared to the bulk value of 0.64 $\mu_B$. In contrast to the pristine Ni(100) surface, the Ni PDOS of the Si-embedded c(2 × 2) structure does not show exchange splitting and both majority and minority spin PDOS are below $E_F$ as shown in Figure 5(c), indicating that the magnetic moment is quenched. Indeed, the calculated magnetic moment was only 0.02 $\mu_B$. This is caused by the fact that Si 3p donates electrons to fill the Ni 3d bands, which pushes the Ni 3d minority bands below $E_F$. To restore the charge balance between Ni and Si, the Si 3p bands are back-donated with the Ni 3s–3p electrons. The isolated Si 3s PDOS can be seen in Figure 5(d) around −8 to −10.5 eV from $E_F$ in accordance with the band structure shown in Figure 4.

**C. Subsurface Si and Si adatom**

To study the stability and robustness of the Si-induced 2D structure, the energy of Si embedded in the second layer of the Ni(100) surface was calculated. A single Si atom substituted in the second layer of the Ni(100) 2 × 4 slab showed +0.18 eV higher energy than the first layer. This indeed demonstrates the robustness of the 2D silicide formed on the outmost surface, consistent with the fact that the structure was intact up to 400°C annealing. The atomic geometry of the Si embedded in the second layer is substantially the same as the Ni(100) surface within ±2 pm, indicating that the substituted Si occupies a twelve-fold symmetric site. This is a clear disadvantage for Si, as it surpassed the surrounding electrons and provides higher energy.

We also studied a single Si adatom on the Ni(100) surface. The optimized structure showed that Si was adsorbed on a
four-fold hollow site with an adsorption energy of 1.20 eV. The optimized atomic geometry is shown in Figure 6. Due to the asymmetric surface unit cell, atomic displacements are not symmetrical along the [010] and [001] directions. Therefore, the atomic displacements shown in Figure 6 along the [010] direction is an averaged vector sum of two directions, i.e., 5 pm along the [010] direction and 3 pm along the [001] direction. This asymmetry indicates the interaction between the adsorbates in the 2 × 4 unit cell and the current cell size is not sufficient to assess the single adsorbate energy. The displacement of substrate Ni due to Si adsorption was slight, but apparently Si is pulled inward, resulting in a corresponding slight expansion of the nearby top Ni. The bond length between adsorbed Si and Ni was 223 pm, which is shorter than a typical Ni-rich bulk silicide such as $\beta_1$-$\text{Ni}_2\text{Si}$, indicating strong Ni–Si bonding [28, 29].

IV. CONCLUSION

In conclusion, we applied first-principles calculations to the Si-embedded Ni(100) surface using a 2 × 4 unit cell. We found that the formation energy decreased monotonically as the number of embedded Si increased up to the Si coverage of 0.5 ML. The most stable structure was a $\sqrt{2} \times \sqrt{2}$R45° [19(2 × 2)] structure with the Si coverage of 0.5 ML with Si embedded diagonally. This structure exhibits an attractive interaction between the embedded Si atoms, but the attractive energy is only a few meV, which is less than the thermal energy during the formation of the 2D silicide layer. Therefore, the Si-induced $\sqrt{2} \times \sqrt{2}$R45° structure does not aggregate or separate as a characteristic surface phase, but embedded Si is paired diagonally and clustered locally, and it is fairly uniformly distributed on the surface [11].

When the Si coverage exceeded 0.5 ML, the formation energy increased as the Si coverage increased. Experimentally, no theoretically predicted surface structure was found at the Si coverages above 0.5 ML. Instead, there was a Si overlayer on top of the $\sqrt{2} \times \sqrt{2}$R45° structure [11]. In contrast to the case of Si deposition on the Ni(110) surface, the Si-embedded Ni(100) surface does not show surface instability due to the formation of an overlayer [9], which demonstrates the robustness of the 2D silicide on the Ni(100) surface.

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