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# Initial surface silicidation on Ni(110)

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A B S T R A C T

Initial silicide formation on a Ni(110) surface was studied by scanning tunneling microscopy (STM) in an ultrahigh vacuum. Less than 0.5 ML of Si deposition initiated a Si-Ni mixed layer by displacing substrate Ni, and dark sites were formed in the STM images. A 0.5 ML-Si deposited surface showed that Si and Ni were alternately aligned in a close-packed [1$\bar{1}$0] row whereas Si pairs aligned along the [001] direction forming p(1×2), obliquely aligned forming c(2×2), or even straightly-and-obliquely aligned forming c(4×2) superstructures. A first-principles total energy calculation showed that the p(1×2) and c(4×2) structures had almost the same energy while the c(2×2) structure gave 13 meV/1×1 higher energy. Because a Si-Si bond in the close-packed [1$\bar{1}$0] row is energetically unfavorable, Si deposition of more than 0.5 ML did not further replace the substrate Ni, but silicide islands were nucleated along with a trench structure.

## 1. Introduction

Atomic structures and electronic properties of metal-semiconductor compounds have been the subject of a large number of studies, which were inspired by the application of material knowledge to semiconductor electronic devices. In particular, compounds between silicon and metals, often termed as metal silicides, are of practical importance because they are indispensable to low-resistivity electrical contacts of semiconductor channels connected to metal electrodes. Therefore, extensive research has been conducted on understanding their reaction and interface formation processes, the details of atomic structures, and the electronic properties of reacted films [1]. In particular, 3*d* transition metal (3*d*-TM) silicides, such as Ni and Co silicides, are anticipated to be even lower resistivity contacts for state-of-the-art metal-oxide-semiconductor (MOS) transistors and to be superior gate materials, such as the FUSI (fully silicide), than conventional poly-Si [2].

On the academic side, to understand non-linear carrier transport across metal-semiconductor interfaces due to a potential barrier (Schottky barrier), a wide variety of surface-sensitive techniques has been applied for studying 3*d*-TM silicide formation processes over several decades [3,4]. However, most previous studies were conducted on silicides formed on silicon substrates, which lead to silicon-rich silicides. Although these metal-on-silicon silicides are primarily important for practical applications, converse silicides, i.e., silicon-on-metal silicides, should be studied as well to comprehensively understand the reaction processes of Si with metals, especially TM-rich phases.

Nevertheless, there have been only a few reports so far on the formation and reaction processes of such silicon-on-metal silicides [5–8]. In this Letter, we address initial silicide formation on the Ni(110) surface by scanning tunneling microscopy (STM) in an ultrahigh vacuum. STM is an ideal tool for investigating the initial reaction of these materials on an atomic resolution and studying detailed surface atomic structures and local electronic states. The first-principles total energy calculation was aided by exploring stable surface atomic configurations and interpreting the STM images.

With these techniques, we revealed that Ni in the top layer was displaced by Si impinging on the Ni(110) surface and impinged Si was embedded in the top layer. Embedded Si forms an alternating Si-Ni structure in the [1$\bar{1}$0] row and it is configured as p(1×2), c(2×2), and c(4×2) superstructures locally across the row. These superstructures resemble to the (110) plane of the bulk $Ni_3Si$.

## 2. Experiments

Experiments were performed with an ultrahigh vacuum chamber equipped with an Omicron scanning tunneling microscope (UHV-STM), a sputter ion gun, an electron-beam evaporator for Si deposition, and low energy electron diffraction (LEED) with a base pressure of $4\times10^{-9}$ Pa. An (110)-oriented Ni single crystal was mounted on a molybdenum sample holder. The sample was cleaned by $Ar^+$ sputtering and annealing repeatedly, and its cleanliness was confirmed by STM

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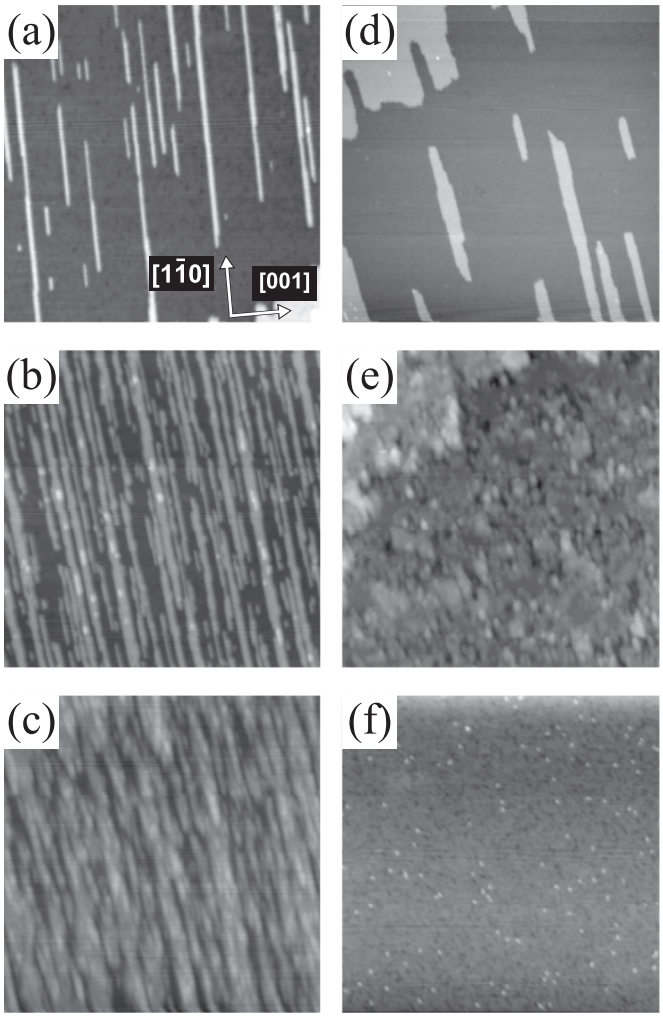


**Fig. 1.** Evolution of surface morphologies by Si deposition on Ni(110). (a)–(c) room-temperature deposition, (d) 373 K, (e) 473 K, and (f) 573 K deposition, respectively. Si coverages are (a) 0.12 ML, (b) 0.35 ML, (c) 0.85 ML, (d) 0.42 ML, (e) 0.85 ML, and (f) 0.85 ML. Scanning areas are 80 nm×80 nm for (a), (b), (e), and (f), 40 nm×40 nm for (c), and 100 nm×100 nm for (d).

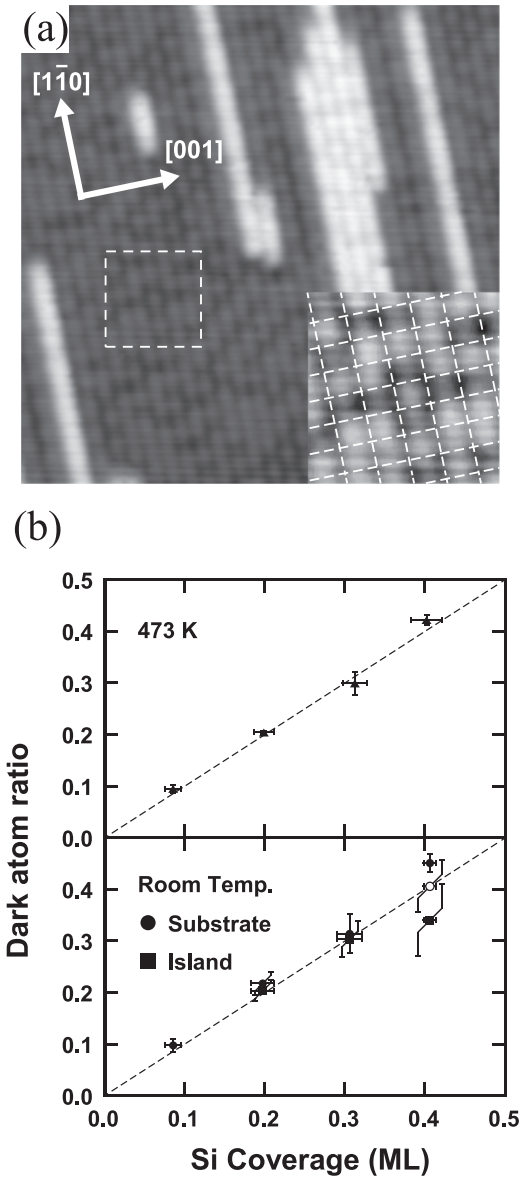


**Fig. 2.** (a) Typical atom-resolved STM image for 0.42 ML Si-deposited surface at room temperature. Scanning area is 10 nm×10 nm. The inset shows magnified image corresponding to the square broken lines. Surface unit cell is overlaid as broken lines. Scanning area is 2 nm×2 nm. (b) Fractions of dark sites to total number of atom sites. Si deposition at room temperature and 473 K are displayed in lower and upper panels, respectively. Filled circles and squares represent substrate and islands, respectively, and their average at 0.4 ML is represented by open circle. Filled triangles are for 473 K-depositions.

and LEED. For Si evaporation, a bundle of floating-zone (FZ) grown single crystal silicon stripes was heated by an electron beam. The Si deposition rate was calibrated with Si deposition onto a Si(111) 7×7 surface at room temperature followed by moderate temperature annealing, which led to the formation of two-dimensional 7×7-reconstructed islands (so called solid phase epitaxy). By measuring island areas using STM images, the impinging rate was deduced to be 0.041 ± 0.002 ML/min, where 1 ML refers to the number of surface Ni atoms for the Ni(110) surface. The sample was heated by a radiative heater behind the sample holder and the temperature was measured by a thermocouple attached close to the sample holder. Si was deposited during heating the sample, followed by 10 min. annealing at the same temperature unless otherwise noted. All STM images shown here were acquired at room temperature with constant current topography with typical sample biases of $V_s$=1.0–20 mV and tunneling currents of $I_t$=2-6 nA.

## 3. Results and discussion

We first give an overview of the evolution of surface morphologies by Si deposition. Figs. 1(a)–(c) show STM images for Si deposition at room-temperature. As shown in Fig. 1(a), initially anisotropic islands elongated along the close-packed [1$\bar{1}$0] direction were formed similar to those of Pd/Ni(110) [9], Ni/Ni(110) [10], and Cu/Ni(110) [11]. Further Si deposition results in increasing the island density with virtually constant island widths, as shown in Fig. 1(b). At less than 0.4 ML, the second layer nucleation was recognized as bright blobs on some of these islands. Increasing Si deposition gives an irregular hill-and-valley structure, as shown in Fig. 1(c), and the surface became rough.

The thermal effects are shown in Fig. 1(d)–(f). A slightly higher substrate temperature such as 373 K dramatically reduces the island density, and the islands became more elliptic as shown in Fig. 1(d). Although a further flat surface would be anticipated for higher-temperature deposition, a 0.85 ML Si deposited surface at 473 K became rough compared to that of Fig. 1(c), as shown in Fig. 1(e). However, as shown in Fig. 1(f), the surface became relatively smooth at the slightly higher temperature of 573 K, where deposited Si can thermally migrate on the silicide surface.