

## Morphological change of Si(100) surface from (2×n) to (2×1) reconstruction by hydrogen termination

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Morphological change caused by the adsorption of hydrogen on a nickel-contaminated Si(100) surface was studied by using scanning tunneling microscopy. We found that hydrogen termination led to a significant reduction in the density of missing dimer defects, resulting in a surface phase transition from (2×n) to (2×1). The morphological change was found to be a result of the blocking of the diffusion of impurities into Si substrate by the hydrogen termination and the difference in energies of hydrogen chemisorption between to Ni and Si. On the hydrogen-terminated surface, small islands of nickel silicide were observed, suggesting that nickel atoms incorporated in the surface were expelled to the surface adsorption sites, becoming mobile on the surface.

Key words : STM, hydrogen-terminated Si(100), impurity induced defect, (2×n) surface structure, nickel silicide

### 1. INTRODUCTION

Si(100) substrate is one of the most widely used semiconductor materials. The surface structure of Si(100) has been studied extensively not only for use in industrial applications but also because it has a variety of reconstructions, each with attractive attributes. On a clean Si(100) surface, dangling bonds of neighboring Si atoms form dimers, and a (2×1) surface reconstruction is commonly observed at room temperature by using scanning tunneling microscopy (STM) [1]. The saturation exposure of the Si(100) surface to atomic hydrogen at 350-400°C leads to the formation of a (2×1) monohydride surface [2,3], which is used for fabricating atomic structures [4-7]. Müller *et al.* [8] observed a defect-ordering (2×n) reconstruction by using low-energy electron diffraction (LEED). Other groups studied this (2×n) structure prepared by various surface preparations such as thermal annealing and quenching [9], and intentional Ni contamination [10,11]. Yoshimura *et al.* [12] reported that the reaction of deposited Ni with Si was suppressed by hydrogen adsorbed on a Si(100) surface. They showed that the substrate structure surrounding NiSi<sub>2</sub> islands, which were formed by annealing at 600°C after Ni deposition on a hydrogen-terminated Si(100) surface, was a defect-ordering (2×n) structure, while a disordered defect structure was shown on a Si(100) clean surface. Higai *et al.* [13] found that the penetration of a Ni atom

from a hydrogen terminated Si(100)-(2×1)-H surface into the subsurface is blocked because Ni is less energetically stable at Si interstitial sites of the second and third layers than at the most stable site on the surface by their first-principles calculations. On the other hand, their calculations showed that Ni easily penetrates into the subsurface of a clean Si(100). Another effect of the hydrogen adsorption was shown to take place on a Ge-covered Si(100) surface. Rudkevich *et al.* [14] and Kobayashi *et al.* [15] reported that the irradiation of atomic hydrogen onto a Ge/Si(100) surface causes Ge to migrate into the Si substrate because there is greater bonding energy in Si-H than in Ge-H. A good agreement was shown on the experiments and theoretical treatments for the segregation of Ge in a hydrogen-terminated Ge/Si system by Rudkevich *et al.* [14].

In this paper, we report that hydrogen termination induces a phase transition from a (2×n) to a (2×1) structure on a Ni-contaminated Si(100) surface. The mechanisms of this morphological change are based on the blockage of Ni from the surface phase to the bulk phase and the suppression of the surface segregation of Ni atoms. The formation of small islands of nickel silicide on hydrogen-terminated Si(100) surface is also discussed.

### 2. EXPERIMENTAL

An ultrahigh-vacuum (UHV) STM was used for surface preparation and measurement. The

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scanning tips were electrochemically-etched  $\langle 111 \rangle$ -oriented single-crystal tungsten wires. A Si(100) sample (P-doped, n-type, 7 to 18  $m\Omega\cdot\text{cm}$ ) was cut into a  $2 \times 13\text{mm}$  rectangular piece from a commercial wafer. Stainless-steel tweezers were used for handling the sample when preparing the Ni-contaminated Si(100) surfaces. This treatment increased defect density, resulting in the  $(2 \times n)$  surface structures [11]. A clean Si(100) surface was obtained by a series of resistive heating up to  $1220^\circ\text{C}$  after overnight outgassing at  $700^\circ\text{C}$ . The pressure in the preparation chamber was kept below  $2 \times 10^{-10}$  Torr during the final cleaning step. The hydrogen termination was done by impinging atomic hydrogen to a bare Ni-contaminated Si(100) surface with a flux of  $3 \times 10^{-2}$  ML/s (one ML is the number of Si atoms on the bulk-terminated ideal Si(100) surface;  $6.78 \times 10^{14}$  atoms/ $\text{cm}^2$ ). This was done for 10 min, keeping the sample temperature at  $400^\circ\text{C}$  and the pressure in the UHV preparation chamber at  $2 \times 10^{-8}$  Torr [5]. We use a tungsten filament surrounded by an alumina tube kept at approximately  $1500^\circ\text{C}$  to dissociate hydrogen gas molecules. The base pressure of the STM observation chamber was kept below  $7 \times 10^{-11}$  Torr. The STM images were taken at a sample bias voltage ( $V_s$ ) of  $-2.0\text{V}$  and a constant tunneling current ( $I_t$ ) of 20 pA.

### 3. RESULTS AND DISCUSSION

Figures 1 (a) and (b) show STM images of the bare Ni-contaminated Si(100) surface. We can see many defects aligned in the  $[110]$  direction, perpendicular to the dimer rows, resulting in a  $(2 \times n)$  structure.

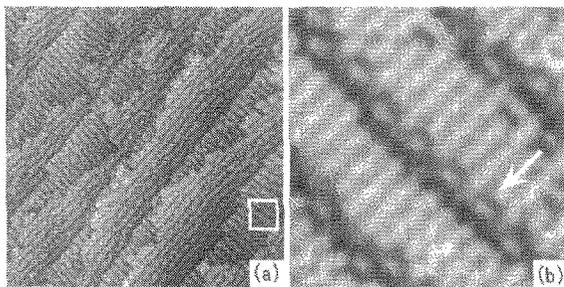


Fig. 1. STM images of Ni-contaminated Si(100) surfaces showing  $(2 \times n)$  structures. The scanned area is (a)  $100\text{ nm} \times 100\text{ nm}$  and (b)  $10\text{ nm} \times 10\text{ nm}$ . Enlarged portion marked by an open square in (a) is shown in (b). An arrow indicates an example of a defect complex.

It is known that the high density of missing-dimer defects leads to ordering or to the formation of a  $(2 \times n)$  structure because of the minimized surface strain energy. Zandvliet *et al.* [16] explained that the two driving forces in the ordering of missing-dimer defects are the short-range interaction between defects in the adjacent dimer rows and the

long-range repulsive interaction between defects in the same dimer rows. Hamers and Köhler [17] classified the defects on a clean Si(100) surface into three types, single-dimer-vacancy defect, double-dimer-vacancy defect, and a pair of adjacent half-missing dimer defects. The predominant ones in the bare Ni-contaminated surface observed in this work were complexes of a single-dimer-vacancy, double-dimer-vacancy, and a split off dimer between them. An example of the defect complex is highlighted as shown in Fig. 1 (b) by an arrow. These images agree with the reported STM observations [10,11] and with the theoretical calculations reported by Wang *et al.* [18].

In this study, Fe, Cr and Ni are the most likely surface impurities from stainless steel tweezers used to handle the samples. Since the diffusion coefficient and solubility of Ni in Si are much higher than those of other metals like Fe or Cr, Ni atoms are most included into the Si bulk after annealing the samples, whereas most of the Fe or Cr atoms evaporate from the surface [11,19]. A number of researchers have concluded that the  $(2 \times n)$  structure is a result of Ni contamination [9–11]. They found that the surface structure changes from  $(2 \times 1)$  to  $(2 \times n)$  as increase in Ni surface concentrations measured by the Auger electron peak ratio, Ni LMM/Si LVV [9], or by X-ray photo-electron intensity [10]. Niehus *et al.* [10] suggested that surface impurities lead to higher local Si evaporation rates at 1500 K creating a higher defect density at the surface. On the other hand, Martin *et al.* [20] found few Ni atoms on the thermally quenched  $(2 \times n)$  surface. Aruga and Murata [21] observed  $(2 \times 1)$  structures and  $(2 \times n)$  structures in different areas of the same Si(100) surface after quenching the sample. They argued that the lattice distortion and macroscopic strain caused by not only Ni contamination but also sample holding resulted in the  $(2 \times n)$  structure. In any case, it is accepted that a high density of missing-dimer defects leads to the formation of a  $(2 \times n)$  structure as a result of the minimized surface strain energy. In our study, Ni atoms were the most likely origin of increased defects.

The hydrogen termination process, in which hydrogen atoms chemisorb to dangling bonds of surface Si atoms, led to a  $(2 \times 1)$  structure resulting from a decrease in the density of missing-dimer defects and in the disordering defects, as shown in Fig. 2 (b). Missing-hydrogen defects, or dangling bonds, are shown as bright spots, and missing-dimer defects are shown as dark spots. Note that the dimer-defect complexes, predominant on the bare Si(100) surface, were rarely seen and only isolated clusters of missing-dimer defects were observed. This suggests that the defect distribution that gives the minimum surface energy on a hydrogen-terminated Si(100) surface is different from that on a bare surface because of the hydrogen passivation.

Furthermore, flashing the sample at  $1220^\circ\text{C}$ , to desorb hydrogen atoms from the surface, resulted

in a Si(100)-(2×n) structure as shown in Fig. 2 (c). The density of missing-dimer defects on the hydrogen-desorbed surface is almost the same as that on the first-formed bare surface shown in Fig. 2 (a). Repeating the hydrogen termination and desorption, we found that the hydrogen termination decreased density of defects by approximately 2/3.

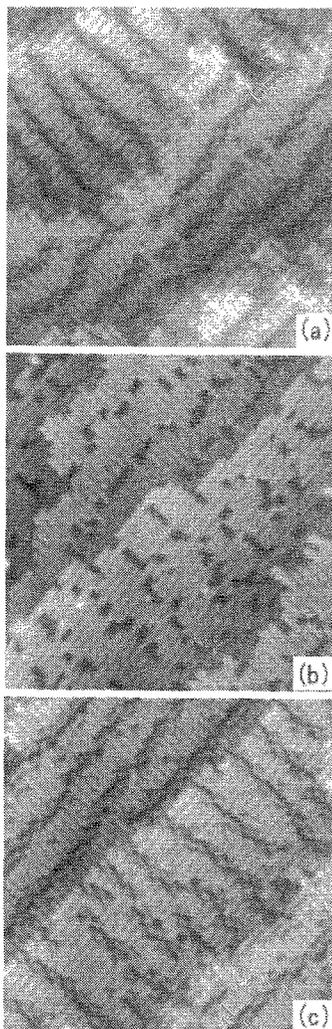


Fig. 2. STM images of the Ni-contaminated Si(100), (60 nm×60 nm) (a) bare surface with (2×n) structure, (b) hydrogen-terminated surface, and (c) bare surface after hydrogen desorption.

One possible explanation for the morphological change from a (2×n) structure is that chemisorption of hydrogen suppressed surface segregation of Ni atoms. We estimated the atom fraction of Ni to that of Si in the surface phase by using the traditional theory of surface segregation driven by chemisorption [22,23]. In a regular solution model, the atom fractions are expressed as

$$\frac{x_{\text{Ni}}^s}{x_{\text{Si}}^s} = \frac{x_{\text{Ni}}^b}{x_{\text{Si}}^b} \exp\left(\frac{-\Delta H_{\text{seg}}}{kT}\right), \quad (1)$$

where  $x_{\text{Ni}(\text{Si})}^{s(b)}$  is the equilibrium atom fraction of Ni (Si) in the surface phase (in the bulk phase),

$\Delta H_{\text{seg}}$  is the enthalpy, or heat, of surface segregation of Ni,  $k$  is Boltzmann constant, and  $T$  is the temperature of the sample treatment. In this case,  $\Delta H_{\text{seg}}$  is the heat of adsorption, the driving force in the segregation process, representing the enthalpy change resulting from the substitution of atoms. Note that when  $\Delta H_{\text{seg}} > 0$ , the atom fraction of Ni to Si is lower in the surface phase than in the bulk phase, i.e., the segregation of Ni atoms is suppressed. We calculated the bonding energy change associated with the substitution of a Ni atom for a Si atom to be 0.20 eV, assuming Si-H and Ni-Si to be formed bonds, and Ni-H and Si-Si to be broken bonds. The ratio of the atom fraction of Ni in the surface phase of a bare surface to that of a hydrogen-terminated surface becomes approximately 1/30 by using Eq. (1). In this estimation, we assumed that fraction deviations of Si and Ni in the bulk phase are negligible, and that one hydrogen atom chemisorbs on a Ni atom when the Ni atom stays on the Si surface, although a structural model for the (2×n) phase is unavailable. Our experimental result deviates somewhat from the estimated value based on the traditional theory of the chemisorption-induced segregation, assuming that one defect complex corresponds to by one impurity atom [10].

Another possible mechanism causing the morphological change induced by hydrogen termination is the blocking of Ni penetration into a Si bulk phase as discussed by Higai *et al.* [13]. In their first-principles calculations, it was showed that a Ni atom is energetically unstable when it is located at the interstitial site underneath the hydrogen terminated Si(100)-(2×1)-H surface and is blocked to penetrate from the surface adsorption site into a subsurface. On the other hand, a Ni atom easily penetrates into the hydrogen-free subsurface. To study this effect, we further annealed the sample at 400°C for two hours applying atomic hydrogen flux to the Ni-contaminated surface. Figures 3 (a) and (b) show island-like precipitates formed on the hydrogen-terminated Si(100) surface after annealing. The islands are distributed over the surface as shown in Fig. 3 (a). Most of them are bar shaped with inclined facets as shown in Fig. 3 (b). In addition, scanning tunneling spectroscopy measurements over the surface showed metallic I-V characteristics on the islands. Khang *et al.* [24] reported that islands of nickel silicide with a (111) facet were grown on a Ni-deposited Si(100) substrate by annealing the sample at 450-550°C. Thus, it is reasonable to conclude that the islands observed in our experiments are nickel silicides.

Assuming that all silicides were NiSi<sub>2</sub> with CaF<sub>2</sub> crystal structures and composed of Si and Ni atoms from the surface phase, we estimated the number of Ni atoms based on the volume of the observed silicide islands and determined the surface density of Ni included in silicides to be  $2 \times 10^{13}$  atoms/cm<sup>2</sup>.

The Ni density was the almost same as the difference in the density of defects between the bare Ni-contaminated surface and the hydrogen-terminated surface after annealing. Thus, we conclude that the Ni atoms in the surface phase were predominately expelled from the subsurface onto the surface, resulting in the formation of silicides.

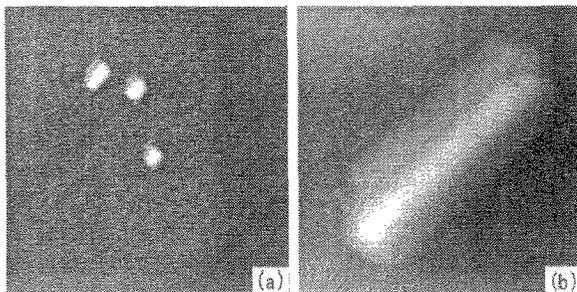


Fig. 3. STM images of islands of nickel silicide on the hydrogen-terminated Ni-contaminated Si(100) surface ( $V_s = -2.0$  V,  $I_t = 20$  pA). Scanned areas are (a)  $400 \times 400$  nm and (b)  $60 \times 60$  nm, respectively.

In conclusion, we observed a surface phase transition from  $(2 \times n)$  to  $(2 \times 1)$  on the Ni-contaminated Si(100) surface by hydrogen termination. The predominant mechanism causing the reduction in the density of defects due to hydrogen termination is the energetic instability of Ni atoms in the subsurface and the blocking of Ni penetration into the Si bulk phase. And the difference in energies of hydrogen chemisorption between to Ni and to Si also contributes to the reduction in the defect density. The former causes nickel silicides to form, which we observed as small silicide particles on the Si surface, while the latter suppresses the surface segregation of Ni atoms.

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