Proceedings of the 3rd International Symposium on Scanning Probe Spectroscopy, SPS'03

STM/STS Investigations of Surface Evolution of Si(111)-(7 × 7) Induced with Nickel

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By means of scanning tunneling microscopy and spectroscopy we studied the surface evolution of Si(111)-(7 × 7) induced with nickel followed by annealing at specified temperatures (400, 600, and 800°C). Nickel evaporation resulted with 0.05 ML and 0.2 ML coverage was carried out at room temperature with the use of solid phase epitaxy. The characteristic phase formations occurred after gradual annealing the sample depending on the amount of deposited material. At very low coverages scanning tunneling microscopy observation showed two types of ring clusters (1 × 1-RC and clusters of the $\sqrt{19} \times \sqrt{19}$ reconstruction) accompanied by the Si(111)-(7 × 7) surface reconstruction. All above-mentioned phases appeared in that order as the annealing temperature increased. Deposition of about 0.2 ML of Ni followed by annealing at 600°C formed extended regions of 1 × 1 nickel silicide reconstruction. Very clear, extended regions of $\sqrt{19} \times \sqrt{19}$ reconstruction appeared when annealed to 800°C. The electronic properties of observed structures have been studied by the scanning tunneling spectroscopy. Spectroscopy curves measured above certain surface formations revealed the presence of the Si rest atom, NiSi, and $NiSi_2$ local density of electronic states.

PACS numbers: 68.37.Ef, 68.47.Fg, 73.20.At

1. Introduction

Transition metals' (TMs) silicides are likely the most widely studied silicide systems due to the possibility of practical applications in today's electronics. The ability to control the atomic structure of ultra-thin transition metals' silicides

as well as the opportunity to create clusters and other nanostructures become a very important and attractive matter for many researchers. Scanning tunneling microscopy (STM) technique enables investigations of these systems with a great spatial resolution including determination of the local density of electronic states (LDOS). A lot of structural phases have been observed during the formation process of the TMs on silicon substrate. There are some reports on the atomic structure and the morphology of Si(111)-(7 × 7) induced with TMs [1–8]. Parikh et al. [4] reported that coverage of about 0.08 ML of Ni followed by annealing at 860°C resulted in triangular domains of ring clusters, so-called 1 × 1-RC phase [10, 11], accompanied by clean Si(111)-(7 × 7) surface. The deposition of 0.2 ML at 550°C produced a well-ordered $\sqrt{19} \times \sqrt{19}$ structure. They also noticed the formation of $NiSi_2$ islands at higher coverages of Ni. On the other hand Porter et al. [6] reported that islands of B-type $NiSi_2$ were formed even at 0.12 ML coverage. Others authors [2, 3, 5] also reported that room temperature (RT) deposition of nickel produced $NiSi_2$, NiSi-like islands, 1 × 1-RC phase, $\sqrt{19} \times \sqrt{19}$, $\sqrt{3} \times \sqrt{3}$, and local $\sqrt{7} \times \sqrt{7}$ arrangement at various annealing temperatures and depositions of Ni.

Different experimental conditions seem to be a reason for discrepancy of the reported phase's formation. Nickel deposited on the silicon substrate is known for its extraordinary high reactivity at elevated temperatures. Ni atoms diffuse very easily into silicon bulk crystal during annealing and surface segregation of the dissolved Ni atoms occur during the quenching process [2–5, 8]. Therefore, the phase type strongly depends on amount of deposited material as well as annealing temperature and cooling rate.

In this paper, we report our investigations of surface changes of silicon Si(111)-(7 × 7) surface reconstruction induced with various amounts of Ni followed by annealing at defined temperatures. We employed scanning tunneling microscopy and spectroscopy (STM/STS) measurements in order to obtain pictures with atomic resolution of above-mentioned phases and theirs LDOS. We could not find other reports of the STS characterization of these structures.

2. Experimental

The substrate employed in experiment was cut from Si(111) wafer. The sample was n-type silicon with resistivity between 0.015–0.020 Ω cm. Nickel deposition (0.05 ML and 0.2 ML) was carried out at room temperature by means of solid state epitaxy (SPE) using an OMICRON EFM4 source. Atomic force microscopy (AFM) technique was used to determine a surface coverage of Ni. The coverage was defined by evaluation of the volume of deposited material visible on Si(111)-(7 × 7) substrate (1 ML of Ni amount to 7.83×10^{14} atoms/cm^2). Post-deposition annealing was performed at 400°C, 600°C, and 800°C for 10 minutes by resistive heating. A cooling rate was about 20°C/s. All STM measurements

were performed at room temperatures in an UHV system in the base pressure of about 6.0×10^{-10} Torr using an OMICRON STM/AFM system. We used tungsten electrochemically etched tips.

3. Results and discussion

The deposition of 0.05 ML nickel at RT deteriorated Si(111)-(7 × 7) surface although remains of 7 × 7 pattern are visible (Fig. 1a). Brightly observed Ni atoms form clusters which adsorb preferentially at rest atom sites on the faulted halves of the 7 × 7 DAS structure. It is known that faulted part of 7 × 7 DAS unit cell has a larger charge density than unfaulted one. Moreover, the rest atoms placed in the

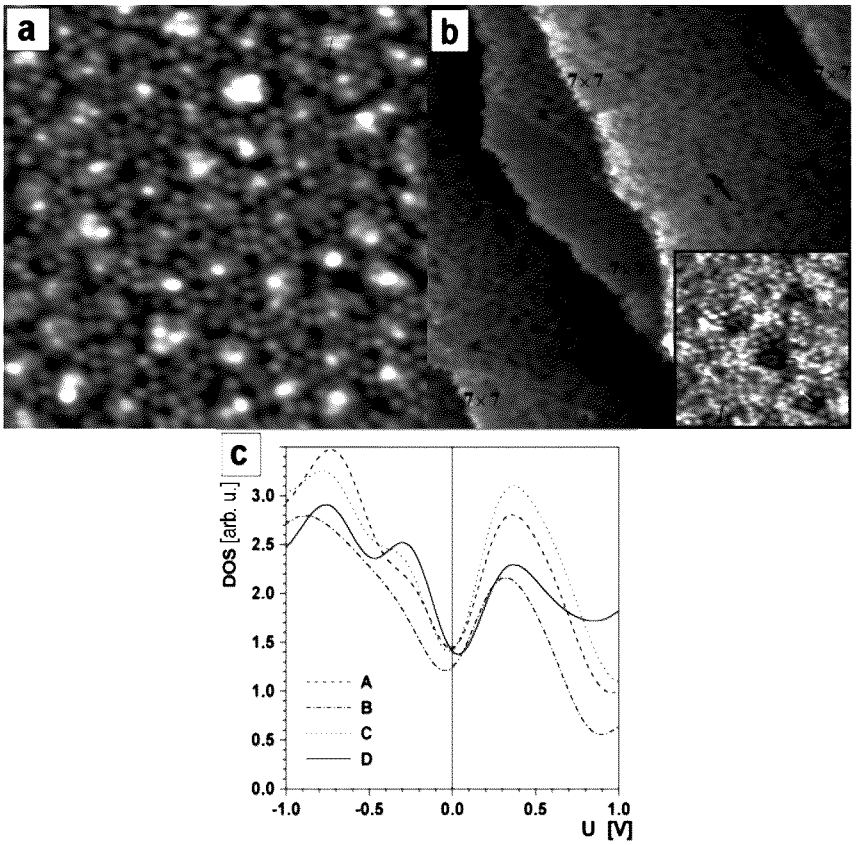

Fig. 1. STM images observed for 0.05 ML of Ni deposited at RT onto Si(111)-(7 × 7) substrate; (a) as-deposited, 20 nm × 20 nm, $V_T = +0.8$ V, $I_T = 0.5$ nA, $T = 25°$C; (b) after annealing at 600°C, 75 nm × 75 nm, $V_T = +2.0$ V, $I_T = 0.2$ nA. The inset: 12 nm × 12 nm, $V_T = +1.0$ V, $I_T = 0.4$ nA; (c) $\mathrm{d}(\ln I)/\mathrm{d}(\ln U)$ curves on: 1 × 1-RC reconstruction (A); bare Si(111)-(7 × 7) (B); atom-like dots (C); dark areas with the highest current flowing for negative bias (D).

faulted half has the largest charge density due to charge transfer from neighboring adatoms [3, 9].

When the sample was annealed at 400°C, the clusters gradually coalesced with a further destruction of the 7 × 7 structure. Annealing of the substrate at 600°C (Fig. 1b with the inset) resulted in a very early stage formation of $\sqrt{19}\times\sqrt{19}$ reconstruction (dark ring clusters) within the dominant phase of 1 × 1-RC placed on the lower terrace (bright ring clusters). Atom-like dots as well as spots of Si(111)-(7 × 7) at the upper terrace were also visibled close to the step edges. After annealing at 800°C Si(111)-(7 × 7) reconstruction disappeared. The $\sqrt{19} \times \sqrt{19}$ reconstruction was developed locally on the cost of 1 × 1-RC one. In our experiment silicide islands were not visible at very low coverages, probably because the cooling rate of about 20°C/s was too fast [4, 8].

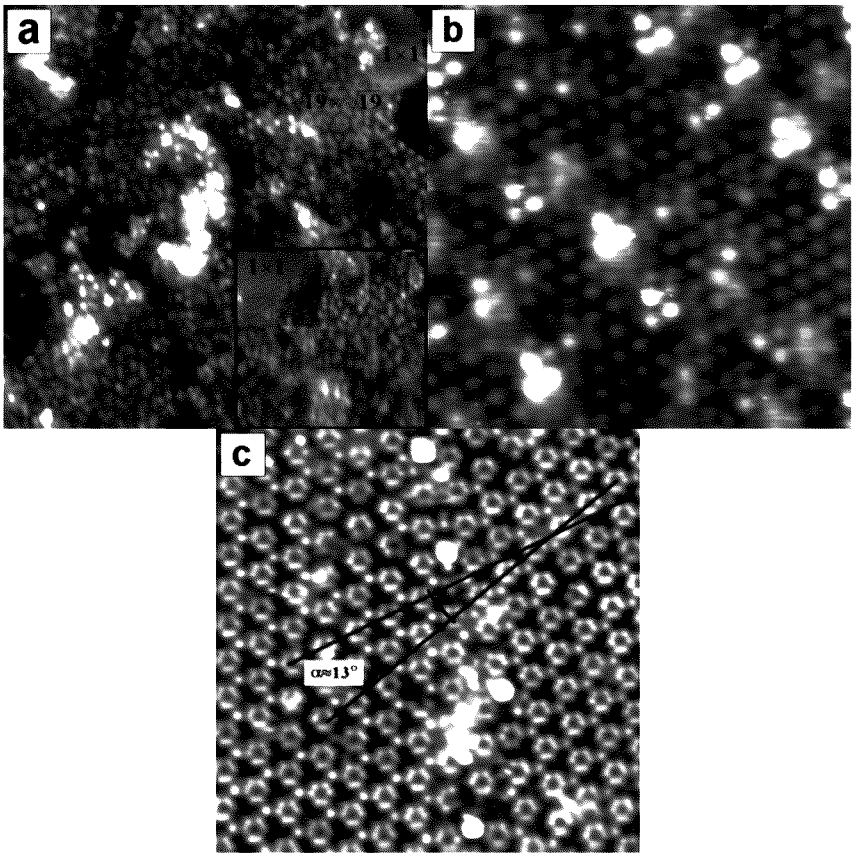

Fig. 2. STM images observed for 0.2 ML of Ni deposited at RT onto Si(111)-(7 × 7) substrate; (a) after annealing at 400°C, 32 nm × 32 nm, $V_T = +1.5$ V, $I_T = 0.4$ nA. The inset: 14 nm × 14 nm, $V_T = +1.0$ V, $I_T = 1.1$ nA. (b) after annealining at 600°C, 8 nm × 8 nm, $V_T = +0.5$ V, $I_T = 1.6$ nA. (c) after annealing at 800°C, 20 nm × 20 nm, $V_T = +2.3$ V, $I_T = 0.5$ nA.

STS was employed to deliver information about density of electronic states of the observed formations. LDOS curves (Fig. 1c) show two characteristic peaks at about –0.9 eV and +0.3 eV on bare Si(111) surface, which corresponded to conduction and valence bands, respectively (B curve). The surface states induced by 1×1-RC (A curve) and atom-like dots (C curve) were found at about –0.7 eV and +0.4 eV. We found also regions (D curve) between above-mentioned formations with peaks at +0.4 eV and two peaks at about –0.3 eV and –0.75 eV.

The deposition of about 0.15–0.2 ML of Ni at RT led to a complete decomposition of the 7×7 reconstruction. The post-deposition annealing at 400°C resulted in the creation of three different coexisting phases: 1×1-RC, early stage of $\sqrt{19} \times \sqrt{19}$ reconstruction, and islands of nickel silicide with 1×1 arrangement (Fig. 2a with the inset). The annealing at 600°C promoted expansion of 1×1 reconstruction of nickel silicide (Fig. 2b). Extended regions of very clean $\sqrt{19} \times \sqrt{19}$ reconstruction appeared at 800°C (Fig. 2c). We observed domains that are twin-related to each other with the angle of about 13° between them as it was proposed by Kinoda et al. [1].

Current imaging tunneling spectroscopy (CITS) was performed for above-mentioned structures (Fig. 3a — CITS taken at –2.0 V). LDOS curves are showed in Fig. 3b. The maxima found on the curve A (measured above single Si atoms) at –1.80 eV and +0.75 eV may be assigned to Si rest atom and the peak at about –0.65 eV to Si back-bond filled state, respectively [5, 9]. The LDOS curves measured above the Y-shaped minima (curve B) show peaks at –1.85 eV and at +0.7 eV. The peaks correspond also to Si atoms states most probably [5]. The maximum on the curve C (measured above ring clusters in $\sqrt{19} \times \sqrt{19}$ reconstruction) at –2.0 eV in the valence band spectrum come from NiSi phase. The peak at

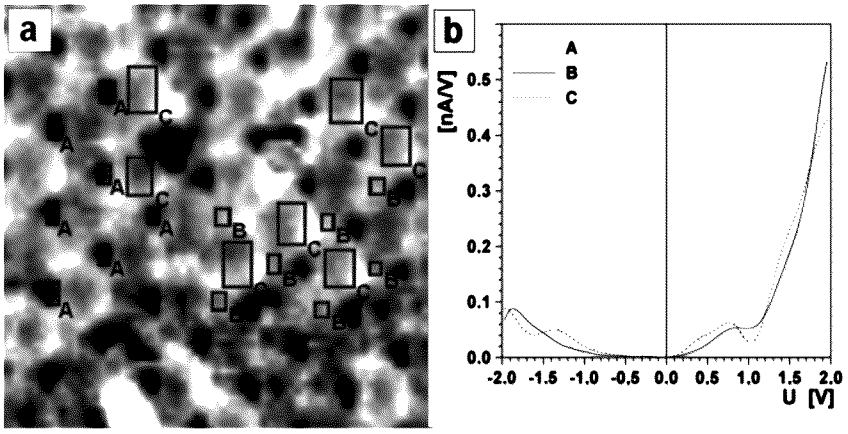

Fig. 3. STS measured for 0.2 ML of Ni deposited onto Si(111)-(7×7) substrate followed by annealing at 800°C. (a) CITS of the 10 nm × 10 nm area acquired at $V_T = -2.0$ V; (b) $\mathrm{d}I/\mathrm{d}U$ curves on: Si atom (A), Y-shape minima (B), ring cluster (C).

–1.3 eV was assigned in [6] to the binding energy of Ni_2Si. However this interpretation seems to be inconsistent with the model of $\sqrt{19} \times \sqrt{19}$ unit cell structure [4]. The peak at +0.8 eV corresponds to the binding energy of the $NiSi_2$.

4. Summary

The structure change of Ni(0.05 ML)/Si(111) and Ni(0.2 ML)/Si(111) by post-annealing was observed by STM/STS technique. Nickel silicide islands were not observed at very low coverages of Ni. The coexistence of four different phases: 1×1-RC, atom-like dot, early stage of $\sqrt{19} \times \sqrt{19}$ formation, and nickel silicide 1×1 reconstruction was observed for samples with 0.2 ML coverages annealed at and above 400°C. The 1×1 reconstruction of nickel silicide was promoted after annealing at 600°C. Clear extended regions of $\sqrt{19} \times \sqrt{19}$ reconstruction were produced after annealing at 800°C.

Spectroscopy curve measured above single Si atoms placed among ring clusters of $\sqrt{19} \times \sqrt{19}$ reconstruction revealed the presence of Si rest atom and back-bond filled states. LDOS maxima found on the curves obtained above Y-shaped minima are also connected with Si atom states. The peaks appeared on the curve obtained above the ring clusters of the $\sqrt{19} \times \sqrt{19}$ reconstruction seem to origin from NiSi and $NiSi_2$ LDOS states.

Acknowledgments

This work was done under PB 62-198/03-BW Project.

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