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STM STUDY OF NANOSTRUCTURES GROWN ON AG/SI(111)-√3×√3 SURFACE EVAPORATED BY 8.7 ML NI

Abstract. The thermo-evolution of the interface obtained by room temperature (RT) deposition of 8.7 ML Ni onto an Ag/Si(111)-√3×√3 surface has been studied with the use of scanning tunneling microscopy. Annealing the surface within RT- 573 K temperature range leads to the increase in surface roughness which is followed by its drop upon annealing at 673 K. The comparison of the images presented here with those published for both submonolayer Ni and 4.2 ML Ni indicates coverage-dependent features.
Keywords: Scanning tunneling microscopy, Si(111), Ag, Ni, nanostructures.

BADANIA STM NANOSTRUKTUR UTWORZONYCH NA POWIERZCHNI AG/SI(111)-√3×√3 PO NAPAROWANIU 8.7 ML NI

Streszczenie. Ewolucja termiczna interfejsu otrzymanego w wyniku osadzenia 8.7 ML Ni na powierzchni Ag/Si(111)-√3×√3 w temperaturze pokojowej (RT) badana była przy użyciu skaningowej mikroskopii tunelowej. Wygrzewanie powierzchni w zakresie temperatur RT- 573 K prowadzi do wzrostu szorstkości powierzchni, po czym w temperaturze 673 K następuje jej spadek. Porównanie obrazów prezentowanych w niniejszej pracy z obrazami opublikowanymi dla pokryć Ni niższych niż 1 monowarstwa oraz dla pokrycia 4.2 ML wskazuje na występowanie cechy zależnych od pokryć.
Słowa kluczowe: skaningowa mikroskopia tunelowa, Si(111), Ag, Ni, nanostruktury.

Introduction

The early stages of thin metal film formation on semiconductor surfaces attract a great deal of interest because a profound knowledge of the mechanisms behind this phenomenon may help to avoid some serious pitfalls during real industrial processes. For this reason, the reaction of small amounts of metals, in particular transition metals (TMs), deposited onto the surfaces of Si has been extensively studied for decades by using a palette of surface-sensitive methods [9]. Among TMs, Ni has drawn a lot of attention because of the potential of nickel silicides to be integrated as electric contacts [6]. It seems that the conditions for the formation of nickel silicides are currently well established. However, the stoichiometry and the orientation of the final phase depend not only on the amount of deposited Ni atoms, but also on the deposition rate, annealing temperature or annealing time [1].

As-deposited Ni atoms are known to cause dramatic changes to the atomic structure of Si, even if the coverage is small. For example, on a Si(111) surface, the formation of so-called ring-cluster structures (RCs) has been reported by different groups [4, 5]. It is claimed that the RCs serve as precursors for either highly ordered reconstructed patterns (e.g. a $\sqrt{19}\times\sqrt{19}$ or a $\sqrt{7}\times\sqrt{7}$ surface reconstruction) or nickel silicides. However, the completion of the latter requires post-deposition annealing during which Ni species diffuse into the bulk, but segregate back on the surface during cooling [10].

It is of interest to find out whether the modification of the Si(111) surface by the presence of foreign metal atoms may decrease the potential barrier for Ni dissolution and its subsequent sublimation. Yuhara et al. [11] have shown that the co-existence of Ag and Ni atoms on the Si(111) surface increases the stability of Ni atoms as compared to the Ni/Si(111) case. Also, they proved that Ni atoms deposited onto on the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface diffuse inward at temperature lower than that typical of the Ni/Si(111)-7×7 surface system. This finding opens the possibility to produce industrially important phases of nickel silicides at lower temperature. Kovač et al. [3] have found that not only is the formation temperature of nickel silicide lower on the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface but the silicide phase enhances the desorption of Ag atoms from the surface.

In our previous paper, we have presented STM images of the evolution of the Ni/Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface for submonolayer Ni coverage and for 4.2 ML Ni [7]. We have found that the surface evolution reveals coverage-dependent features. In particular, the coverage depended features were observed after annealing at 670K. In the following, we use Ni coverage more than twice higher than previously used in order to re-examine the issue. We find that not only are the differences pronounced at 670 K but they are also apparent at 973 K, at

which the recorded image bears a close resemblance to that typical of submonolayer Ni deposited onto the Ag/Si(111)-√3×√3 upon heating at 870 K.

Experimental

The sample was cut from commercially available n-type wafer (0.001-0.005 Ω×cm resistivity) Si(111) wafer. Prior to introducing into an UHV chamber of a commercial STM (Omicron VT), operating at the base pressure of ~6.0×10^{-9} Pa the sample was ultrasonically cleaned in acetone. The native 7×7 surface was obtained by heating the sample up to 1420 K, followed by slow cooling. The 7×7 substrate was exposed to 1 ML Ag, deposited from a K-cell dispenser, and then annealed at 670 K. This procedure resulted in the formation of the Ag/Si(111)-√3×√3 surface. The final Ni/Ag/Si(111)-√3×√3 surface was prepared by room temperature (RT) deposition of 8.7 ML Ni from an e-bombardment type evaporator onto the Ag/Si(111)-√3×√3 surface (the Ni coverage estimation rests on the premise that 1 ML corresponds to the coverage at which all atoms of the Si(111) topmost layer was covered by Ni atoms. For submonolayer coverage, we have determined the coverage vs. deposition time dependence, which we applied for the determination of the coverage higher than 1 ML). For growth promotion, the surface with the deposit was annealed at the following temperatures: 573 K, 723 K, 873 K, and 973 K for 30 minutes. The temperature of the substrate below 873 K was measured by K-type thermocouple (±2 K accuracy) while that above 873 K was read from an optical pyrometer (accuracy ±10 K). All STM images presented here were acquired at RT and analyzed with the help of WSxM 8.1 software [2].

Results and discussion

Following the preparation recipe, described in the preceding section, we have obtained the Ag/Si(111)-√3×√3 surface whose STM images are presented in Fig.1. Fig.1a shows the features of the surface under interest that covers a large (200×200 nm^2) area of the Si(111). A terraced character of the surface is clearly distinguished. The structure of one terrace is shown in Fig. 1b. One may notice that the Ag/Si(111)-√3×√3 surface consists of Ag-√3×√3 islands grown on the terrace with the same periodicity. The images reported here are in excellent accordance with those published in previous works [e.g. 11]. The measured root mean square (RMS) of the roughness of the surface, obtained from the area of 200×200 nm^2 amounts to 0.12 nm.

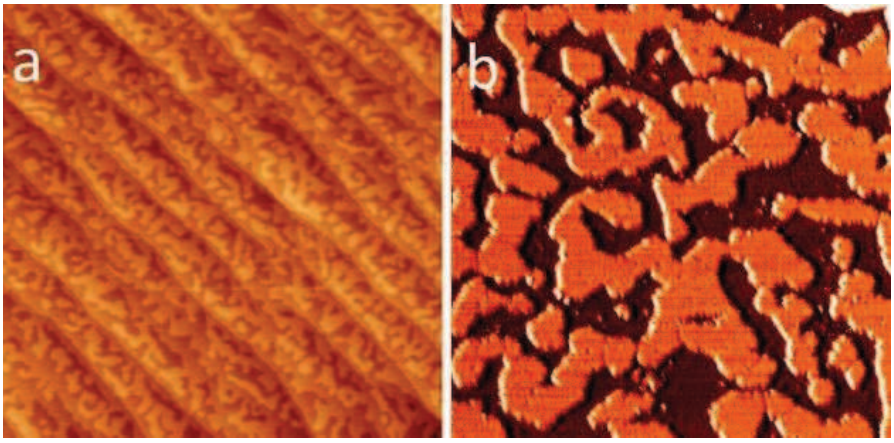

Fig. 1. STM images of an Ag/Si(111)-√3×√3 surface: (a) 200×200 nm^2 image showing the structure of the Ag/Si(111)-√3×√3 surface grown on a terraced surface (bias voltage: 1.7 V), (b) 80×80 nm^2 image showing the structure of one terrace of the Ag/Si(111)-√3×√3 surface on which a number of Ag-√3×√3 islands have grown (bias voltage: -1.1 V)

Deposition of 8.7 ML Ni on the Ag/Si(111)-√3×√3 surface dramatically changes the morphology of the surface on which the unique network of Ag-√3×√3 islands is no longer visible. In Fig.2, the Ni-containing features are represented by bright protrusions that form a rough film on the surface. Some clusters are apparently larger than others, and with the average length of 15.20 (±0.05) nm they clearly outsize the so-called super-clusters, observed for 4.2 ML on the Ag/Si(111)-√3×√3 surface, as described in [7]. The corresponding RMS value amounts to 0.30 nm which indicates a significant increase in roughness at such high coverage, as compared to the roughness of the non-deposited substrate.

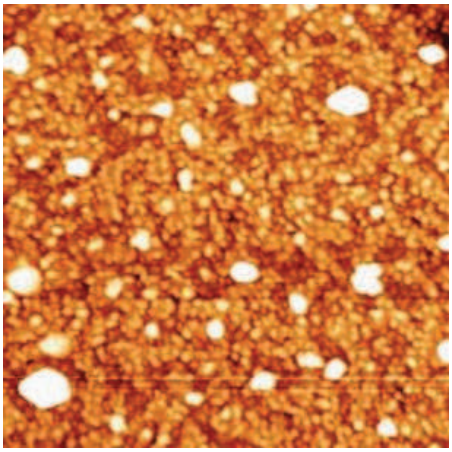

Fig. 2. STM image showing 8.7 ML Ni deposited onto the Ag/Si(111)-√3×√3 surface at room temperature (RT). (size: 200×200 nm^2, bias voltage: 0.8 V)

The STM image obtained after annealing at 573 K (Fig.3 a) bears a close resemblance to that of as-deposited surface (see Fig.2). Apart from the obvious increase in cluster size, which is due to cluster coalescence, other changes are barely seen. The measured RMS value amounts to 0.5 nm and suggests that annealing at RT- 573 K results in roughening of the surface. Further annealing promotes noticeable changes in surface morphology. To start with, after heating the surface at 673 K (Fig.3 b), the occurrence of irregular-shaped islands is observed as a main feature. Also, a depression in the substrate (indicated by arrow) is readily observed. Such a depression might indicate a large consumption of Si from the terraces necessary for nickel-silicides formation. However, the identification of chemical composition of the observed phase is not possible on the basis of STM images only. The RMS amounts to 0.3 nm, indicating that annealing above 573 K leads to surface smoothing. It should be underline that apart from the depression in the substrate, other similarities between the morphology of the surface presented in Fig.3 b and the pictures showing the morphology of the Ni/Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ for submonolayer Ni coverage and 4.2 ML Ni, presented in [7] are hardly seen. This suggests a strong coverage-dependent effect for the interface under study at 673 K.

According to the phase diagram of the Ag/Si(111) surface system, Ag atoms desorb from the surface at 823 K [8]. Indeed, after annealing submonolayer Ni on the Ni/Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface at 870 K [7] we observed the desorption of Ag atoms and Ni-containing islands and the re-occurrence of the native 7×7. However, here, after annealing 8.7 ML Ni deposited onto the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface at 873 K (Fig. 3c) what we observe neither resembles the structure of 7×7 surface nor the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface. Instead, what it can be clearly seen is the presence of relatively large islands which might belong to nickel silicides. Despite the fact that we are able to confirm that the thermo-evolution of the Ni/Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface exhibits coverge-dependent effect, also at such high temperatures, we cannot confirm the enhanced stability of Ag on the Ni/Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface due to the coadsorption of Ag and Ni, as suggested by Yuhara et al. [11].

Finally, the surface was annealed at 973 K and the resulting image is presented in Fig.3 d. Even at first sight, a close resemblance between the morphology of the surface presented here with that obtained after annealing submonolayer Ni deposited onto the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface at 870 K [7] is seen. The 7×7 surface is recovered on the whole area. In addition, some spots (pointed by arrow) are observed here and there. As it was proposed in [7], these can represent small clusters of Ni, Si or Ni, Si, Ag alloy. Also, round-shaped clusters randomly distributed on the surface are seen. In [7], we found that Ni atoms are stable on the surface within the range between RT and 370 K.

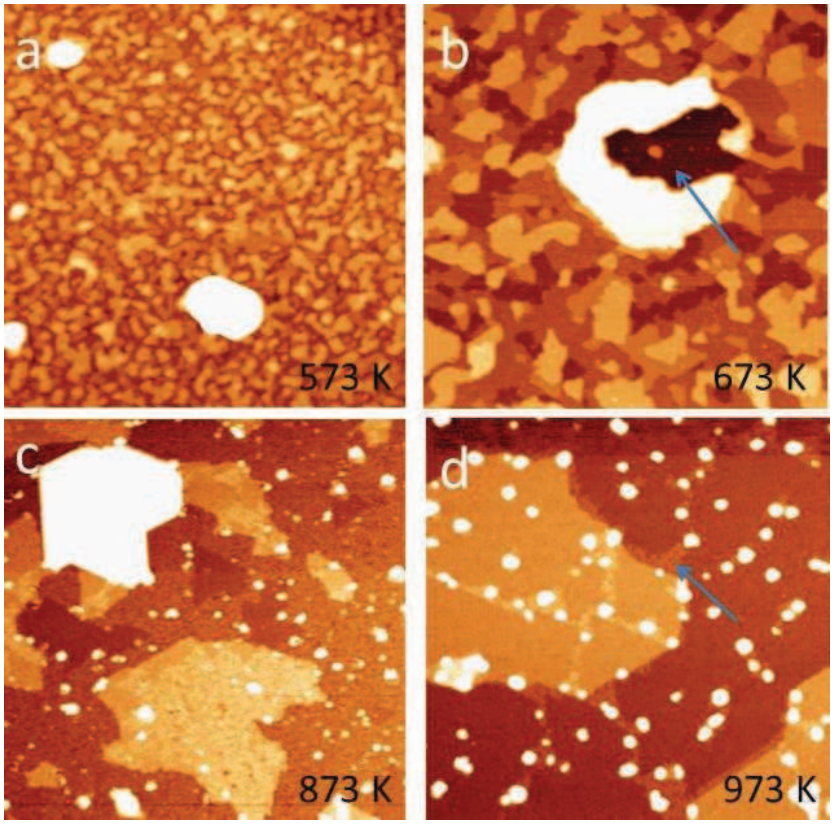

Fig. 3. 200×200 nm^2 STM images showing the thermo-evolution of the Ni/Ag/Si(111)-√3×√3 surface: (a) after annealing at 573 K (bias voltage: 0.8 V), (b) after annealing at 673 K; a depression on the terrace (indicated by arrow) suggests a large material consumption from this place (bias voltage: 1.2), (c) after annealing at 873 K (bias voltage: 0.8 V), (d) after annealing at 973 K, bright spots which are likely to belong to alloys are represented by arrow (bias voltage: -1.5 V)

At temperature higher than 370 K Ni coverage decreases, and at 570 K, reaches 30 % of the initial 4.2 ML value. Yuhara et al. [11] proposed that the dissolved Ni species diffuse inward and segregate back on the surface after Ag desorption. In the light of that it is reasonable to speculate that the observed clusters may represent Ni species.

Conclusions

We have presented STM images illustrating the thermo-evolution of nanonstructures grown on the Ag/Si(111)-√3×√3 surface evaporated by 8.7 ML Ni. We have found that at RT, the deposit forms clusters homogenously distrib-

uted over the surface. Annealing at 573- 873 K results in the appearance of nickel silicide islands, whose formation involves Si consumption from the terraces. At 973 K, Ag desorbs from the surface leaving small amounts of Ni-containing alloys as well as clusters of Ni species distributed on the regained 7×7 matrix. The comparison with our results for Ni coverage up to 4.2 ML leads to the conclusion that the thermal evolution of the Ni/Ag/Si(111)-√3×√3 surface strongly depends on the initial Ni coverage.

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