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Mixed layer formation of copper overlayers on Ni(1 1 0) surface

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Abstract

Copper overlayer formation on the Ni(1 1 0) surface was studied by scanning tunneling microscopy (STM) in an ultrahigh vacuum. Atom-resolved STM images showed that initially deposited Cu is replaced with surface Ni atoms forming atom-size depressions on the Ni(1 1 0) terraces and a Ni-rich quasi-one-dimensional island along the $[1\ \bar{1}\ 0]$ direction. Further Cu deposition yields a mosaic structure on the islands, indicating Cu/Ni mixed layer formation. From the quantitative measurement of the Cu/Ni ratio on the substrate and the islands, impinging Cu will be replaced with surface Ni whereas expelled Ni and directly impinging Cu to the island form the mixed island. The number of Cu atoms in the islands, however, more than the directly impinging Cu, indicate significant Cu/Ni replacement at the periphery of the island.

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1. Introduction

Copper (Cu) and nickel (Ni) are both fcc metals and their atomic radii resemble each other (only 2.6% larger for Cu). Therefore Cu and Ni are miscible with any fraction and they form stable bimetallic alloys without any intermetallic compound. Because the surface energy of Cu is smaller than that of Ni, Cu tends to be segregated on the Cu/Ni alloy [1]. Thus the surface of these alloys has been of great concern to surface science for several decades. Particularly, time-of-flight atom probe field ion microscopy (AP-FIM) revealed Cu accumulation at the topmost layer for annealed Cu/Ni alloys [2]. Other element-selective techniques such as Auger electron spectroscopy (AES) [3] and photoemission spectroscopy (PES) [4] also showed Cu segregation at the surface layers. For epitaxial overlayers between Ni and Cu, most studies so far have been focused on the thin film magnetism for Ni overlayers on the paramagnetic Cu substrates [5]. The inverse case, i.e., Cu overlayer on Ni substrates has not been studied in detail. Only the Cu/Ni(1 0 0) surface was studied by scanning tunneling microscopy (STM) and atomic size defects due to the lattice mismatched Cu overlayer were reported [6,7]. The Ni substrate is considered to be intact in the Cu/Ni(1 0 0) formation and therefore no Cu/Ni mixing was reported at the interface. Because a low surface atom density has a higher surface energy, one would expect the promotion of Cu/Ni mixing for the low density surface. However, Cu heteroepitaxial growth on the low index surfaces with smaller surface atom density has not been studied so far.

In this report, we have explored a possible mixing of Cu into the Ni(1 1 0) surface where the surface atom density is the lowest among the low index faces. Utilizing ultrahigh vacuum scanning tunneling microscopy, we studied the evolution of surface morphologies and details of their atomic structures. We could discriminate Cu and Ni atoms in the topmost surface layer on the terrace-and-island structure. From the quantitative measurement of the Cu/Ni ratio, we conclude that most impinging Cu are replaced with surface Ni. Furthermore, we find the Cu/Ni ratio on the island is significantly larger than that expected from the simple Cu/Ni exchange during deposition, indicating that another Cu/Ni exchange mechanism during island formation plays a significant role for the enhancement.

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2. Experimental

A Ni(1 1 0) single crystal sample 1 cm in diameter and 1 mm thick was introduced into a UHV chamber equipped with a sputter ion gun, low energy electron diffraction (LEED) and STM. After it was alternatively sputtered by 2 keV Ar^+ ion and annealed at 1050 K for several cycles, final annealing was performed at 780 K to expose a defect-free surface. Cu was deposited on the room-temperature surface with a conical tungsten basket with a liquid nitrogen shroud. Cu coverages were determined from wide scan STM images. An areal fraction of islands in the middle of wide terraces more than 300 nm was used to determine the coverages. The base pressure of the chamber was below 1.3×10^{-8} and 3×10^{-9} Pa during Cu deposition and STM observation, respectively. STM observation was carried out at room temperature with a typical sample bias of 5–15 mV and a tunneling current of 5–15 nA. All images shown below were acquired with the constant current mode.

3. Results and discussion

Fig. 1 shows a typical wide scan STM image for the initial island formation. The surface exhibits an anisotropic-quasi-one-dimensional island along the $[1\,\bar{1}\,0]$ direction where the surface atoms are close-packed. The widths of the islands are a few atomic rows and some islands extend over 100 nm along the close-packed direction. Monoatomic-row islands were occasionally found but they diminished in the course of scanning. Even without continuous scanning they did not survive beyond a few hours after deposition. A magnified STM image for one of the islands is shown in Fig. 2. For this particular island, four atomic rows are resolved. The feature of the anisotropic island formation is quite similar to that for the Ni-deposited surface [8], where one-dimensional monatomic-row islands were formed at low temperatures and they became wider above 280 K. For the Ni deposition, the average island width at 300 K was 1.5 ± 0.3, which is smaller than that for the Cu deposition even though the deposition rate is an order of magnitude larger than the previous Ni deposition [8].

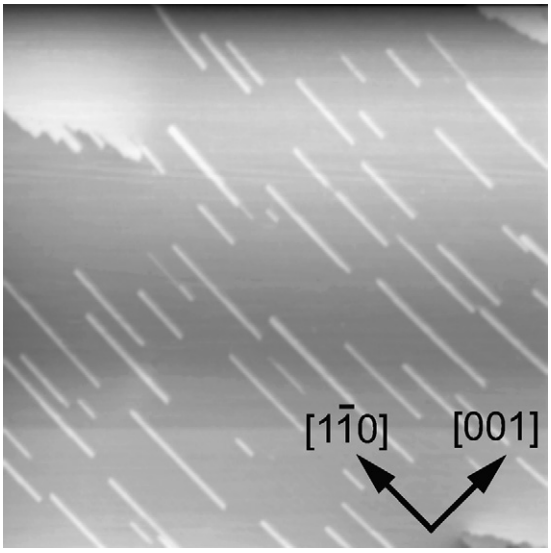

Fig. 1. Wide scan STM image for 0.08 ML Cu deposition on the Ni(1 1 0) surface. Scanning area is 200 nm × 200 nm.

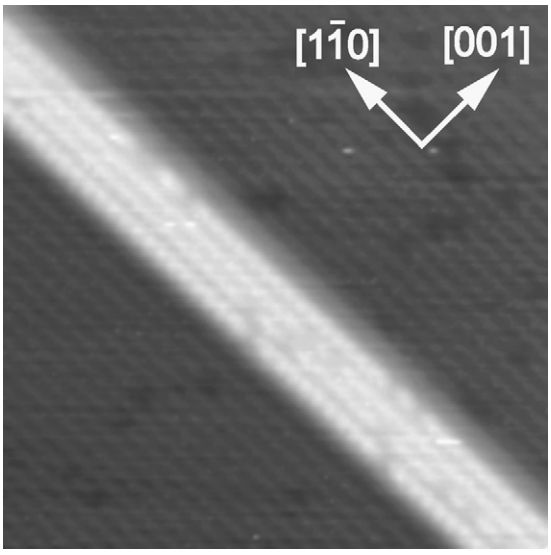

Fig. 2. A magnified image showing an island for the 0.08 ML Cu deposited surface. Scanning area is 10 nm × 10 nm.

By further Cu deposition, the atomic structure of the islands was dramatically changed. Fig. 3 shows a part of an island for the 0.45 ML Cu-deposited surface. The width of the island increased compared to Fig. 1, and the image exhibits a mosaic structure. Looking closely at the mosaic, atomic size protrusions and depressions can be resolved. The registry of the protrusions and depressions exactly coincides with the atomic site for the non-reconstructed (1 1 0) 1×1 surface, which is indicated by the lines in Fig. 3(b). The height of the protrusions was only 30 pm, far smaller than the atomic size, so they are not due to defect, i.e., lack of surface atoms, but it should be caused by the difference in surface local density of states (LDOS). Because Ni has non-filled 3d orbitals, large LDOS originating from an unfilled narrow 3d band will be expected at E_F, whereas the Cu 3d band is located 2.3 eV below E_F [9] and only the 4s band contributes to the LDOS around E_F. So if the surface Ni is replaced with deposited Cu, the large difference in LDOS at E_F leads to the protrusive Ni and depressive Cu in the STM image. This naïve assumption has been founded with a first principles calculation described elsewhere [10].

We assumed that the impinging Cu is initially replaced with the substrate Ni, and the expelled Ni will migrate and form the Ni island. By increasing the Ni island, directly impinging Cu onto the island leads to mixing of Cu in the island as shown in Fig. 3. Because the second layer was not observed before completion of the first layer, expelled Ni on the island will be attached to the periphery of the island. The Cu/Ni replacement can indeed be justified by closely looking at the substrate. In Fig. 2, some defect-like depressed sites have already been seen due to the Cu/Ni replacement. Also in Fig. 3, the magnified image for the substrate nearby island presented in Fig. 3(c)