Scanning tunneling microscopy study of surface reconstruction induced by N adsorption on Cu (100) surface*

Dou Wei-Dong(窦卫东)[a)b)], Zhang Han-Jie(张寒洁)[a)†], and Bao Shi-Ning(鲍世宁)[a)]

[a)] *Physics Department, Zhejiang University, Hangzhou* 310027, *China*
[b)] *Physics Department, Shaoxing College of Arts and Science, Shaoxing* 310027, *China*

(Received 16 October 2008; revised manuscript received 10 August 2009)

The reconstructed structure of Cu (100) surface induced by atomic N adsorption is studied by using scanning tunneling microscopy (STM). The 2D structure of copper boundary between neighbouring N covered islands is found to be sensitive to the growth conditions, e.g. N^+ bombardment time and annealing temperature. The copper boundary experiences a transition from nano-scale stripe to nano-particle when the substrate is continuously annealed at 623 K for a longer time. A well-defined copper-stripe network can be achieved by precisely controlling the growth conditions, which highlights the possibility of producing new templates for nanofabrication.

Keywords: nitrogen adsorption, surface reconstruction, surface strain relief, template

PACC: 6820, 6865, 0779

1. Introduction

Ultrathin insulating films serve as proper substrates for the nanoscale controlling over the coupling of the adsorbates to the surface electronic density of metal substrates.[1−4] For example, the adsorbates on insulating films suffer tremendous reduction of electronic mixing with the substrate, thereby enabling one to directly image the molecular orbitals, which is similar to the free molecule and spin-flip spectroscopy of single atoms.[2] One of these kinds of surfaces is the nitrogen covered surface. Investigations have found that despite being only one monolayer thick, the film of adsorbed nitrogen on Cu surface acts as an insulator with a band gap exceeding 4 eV.[5] This property has been exploited to decouple the magnetic moment of atomic-scale structures from the surface electron density.[3] Therefore, the adsorption of nitrogen, carbon or oxygen on metal surface is an interesting and meaningful subject.[6]

With regard to the N adsorption on Cu (100) surface, earlier studies reported on a c(2×2)N local structure with the N atom occupied fourfold coordinate hollow site on the surface almost coplanar with the outermost Cu layer.[7−9] Later, some scanning tunneling microscopy (STM) experiments revealed that this c(2 × 2)N local structure formed islands on Cu(100) surface, and that in a certain condition these c(2×2)N islands covered ∼5 nm^2 in size and were aligned into a regular square lattice separated by square network of clean surface lines.[10,11] These data have even suggested to imply that the c(2×2)N phase is actually incommensurate. In a systematic STM study by Driver and Woodruff,[12] they obtained STM images of commensurate c(2 × 2)N islands on Cu(100) surface by varying imaging and tip conditions, and demonstrated a symmetry-lowering surface reconstruction involving periodic rumpling of the outermost Cu layer perpendicular to the surface, which is understood as the means of relieving adsorbate-induced compressive surface stress.

Due to the unique structural property, the reconstructed Cu (100) surface induced by N adsorption can serve as a good template for nanofabrication, e.g. growing ultrathin films of organic molecule just on the copper lines. We focus in this paper on the structural variation of copper networks with atomic nitrogen coverage and annealing time in hopes of finding the key factors in generating appropriate templates for the self-assembly of organic molecules.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60506019 and 10674118).
†Corresponding author. E-mail: zhj_fox@zju.edu.cn
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2. Experimental method

The Cu (100) surface was cleaned by cycles of Ar^+ sputtering followed by annealing at a high temperature (800 K). The cleanliness was checked by low energy electron diffraction (LEED), STM and x-ray photoelectron spectroscopy (XPS). The template was produced by implanting the atomic nitrogen into the near-surface region of Cu (100) with using low energy (500 eV) ion bombardment on the sample in a nitrogen atmosphere (10^{-6} mbar) at room temperature and then annealing it at 623 K. The annealing removed the sub-surface nitrogen and left only the chemisorbed atomic N which gave a clear c (2×2) LEED pattern with a nominal 0.5 ML (monolayer) thick coverage . The coverage of N overlayer was controlled by the dosing time of N^+ beam. The STM experiments were conducted at room temperature by using an Omicrom "VT-STM" mounted in UHV. Electrochemically etched polycrystalline W tips were used. Constant current mode was used during the imaging.

3. Results and discussion

We first present the general systematics of the behaviours of N adsorption system as revealed by STM which are essentially identical to those of the earlier STM studies.[10−12] Here, we assume that the Cu(100)–c(2×2)–N phase has a local coverage of 0.5 ML of N atoms, and we thus estimate the average coverage from the fraction of surface covered with this phase in the presence of other regions of clean surface. When the N coverage is significantly smaller than the saturation value, i.e. 0.5 ML, the substrate surface is covered with separate square islands [the dark patches in Fig. 1(a)] with lateral dimension of 5–6 nm. Although the N covered islands are randomly aligned on the surface, a tendency to form lines along $\langle 001 \rangle$ azimuthal orientations can be observed. This tendency becomes more obvious when the N coverage was increased [see Fig. 1(b)]. The boundaries between clean surface (bright regions) and N-covered regions strongly favour the $\langle 001 \rangle$ azmuthal directions of the supporting substrate. Note that although the N-covered islands show an apparent depression relative to the surrounding clean surface by about 0.02–0.05 nm, these two kinds of regions are actually lying in the same layer. The depression in STM images is attributed to the electronic effect associated with N adsorption.

The lateral dimension of clean surfaces continuously decreases if the N coverage is successively increased [see Figs. 1(b) and 1(c)]. The N covered islands become closer and begin to aggregate into bigger islands at a sufficiently higher coverage [approximately 0.4 ML, see Figs. 1(d)]. However, this aggregation leads to an inhomogeneous surface, and narrow "trenches" (missing rows of Cu atoms) along $\langle 110 \rangle$ azimuth can be observed. It is notable that the N atoms were introduced by bombardment. Therefore, N atoms may penetrate into the deep layers of the substrate. After annealing at high temperature for a sufficiently long time, multilayer of N covered regions can form [see Fig. 1(d)]. On the large aggregated islands,

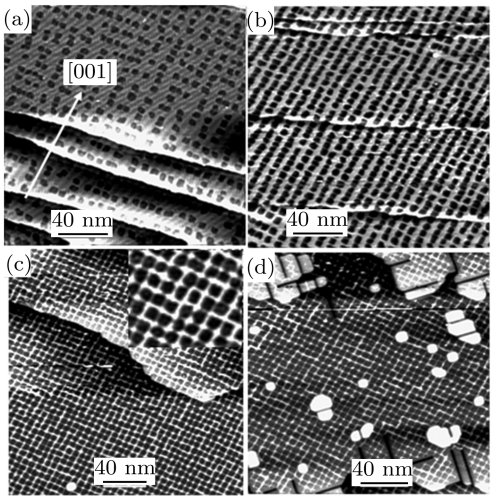


Fig. 1. STM images representing the structural variation as a function of N coverage. The substrate was annealed at 623 K for a fixed time of 2 min after being bombarded by N^+ continuously for longer time, and then cooled down to room temperature for imaging. (a) 0.10 ML; (b) 0.20 ML; (c) 0.35 ML; (d) 0.45 ML. Lateral dimensions: (a), (b), and (d) 200 nm × 200 nm; (c) 213.28 nm × 224.22 nm. Tunneling conditions: (a) $V_t = -0.135$ V, $I_t = 0.504$ nA; (b) $V_t = -0.475$ V, $I_t = 0.927$ nA; (c) $V_t = -0.495$ V, $I_t = 0.712$ nA; (d) $V_t = 0.395$ V, $I_t = 0.762$ nA.

the N covered regions are surrounded by clean copper regions, leading to copper lines (domain boundaries) that are similar to those at lower coverage. However, the copper lines can hardly form if the island is very small. The formations of islands and trenches were interpreted as the relief of elastic strain due to the adsorption of N atom on supporting surface.[12] If the islands are small enough, the trenches themselves are broad enough accounting for the elastic strain release.

At high N coverage, the N covered islands are separated randomly by un-uniform copper strips (or trenches). The ununiformity of the width of copper strips (or trenches) was translated into a random parity of outward and inward rumpling of the outer layer Cu atoms, perpendicular to the surface. Some strips (or trenches) have narrow widths because the adjacent islands have the same parity (in phase), while the others are broader since the adjacent islands have opposite parity (out-of-phase). Due to the symmetry nature of the Cu (100) surface, the parity of the rumpling is arbitrary, indicating the impossibility to produce copper stripes with exactly equal width. However, stripes (network) with approximately uniform width are possible to be made if the growth condition is appropriately controlled.

The boundaries of N covered islands are sensitive not only to N coverage (i.e. dosing time at a constant dosing rate) but also to the heating time and temperature. In Fig. 2, the variation of copper strips that separate the N covered regions is presented as a function of annealing time. Figure 2(a) shows an STM image of surface that suffered N^+ bombardment (500 eV) for 8 min followed by annealing at 623 K for 2 min. On some large islands, copper stripes with almost uniform width were observed. An enlarged image of the rectangular region in Fig. 2(a) is shown in Fig. 2(b). The copper strips were found to have a width of about 1.2–1.3 nm, and surround almost rectangular islands with a lateral dimension of 5–6 nm [see Fig. 2(e)]. The cross regions of the copper strips are protruding relative to the N covered regions by about 0.04 nm [see Fig. 2(f)], much smaller than the atomic step height (0.18 nm), which means that the strips and the N covered regions are still coplanar at this regime.

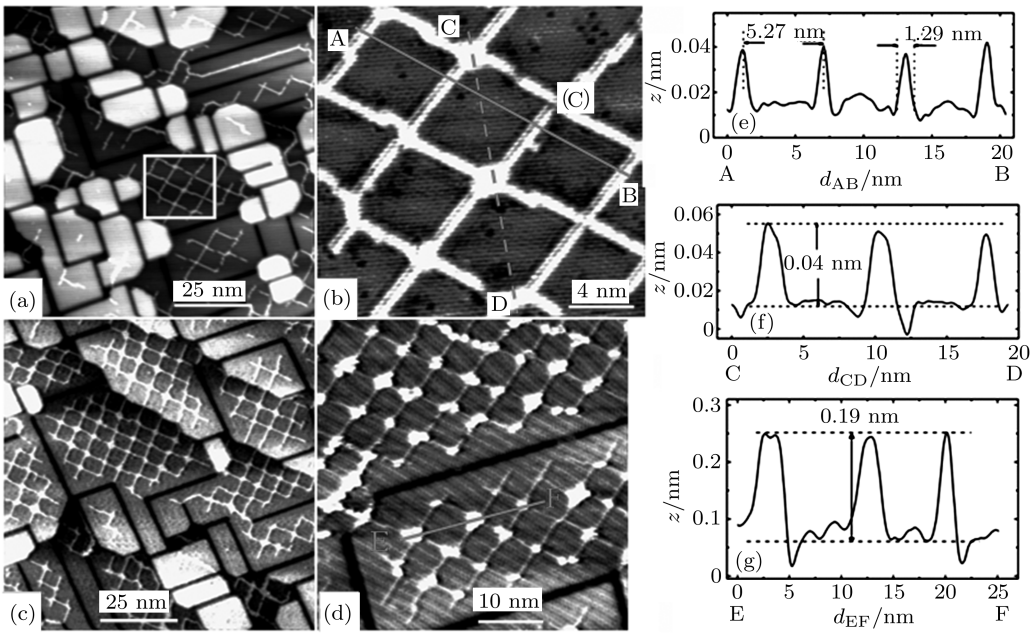


Fig. 2. (a)–(d) STM images representing the structural variation as a function of annealing time, where the annealing temperature is fixed at 623 K and annealing times are 2 min for (a) and (b), 7 min for (c), 17 min for (d), and (e)–(g) the line profiles corresponding to the lines drawn in panels (b) and (d), where lateral dimensions are 100 nm × 100 nm for (a) and (c), 19.82 nm × 18.82 nm for (b), 46.3 nm × 46.3 nm for (d). Tunneling conditions are $V_t = -0.685$ V, $I_t = 0.908$ nA (a), $V_t = -0.671$ V, $I_t = 2.949$ nA (b), $V_t = -0.537$ V, $I_t = 0.985$ nA (c), and $V_t = 0.429$ V, $I_t = 2.005$ nA (d).

After a longer time of annealing at 623 K, more adsorbed N atoms become desorbed and some of the small islands seem to aggregate together and form larger islands which are covered by the N atoms survived. In Fig. 2(c), a surface which was annealed at 623 for 7 min is shown. In addition to the obvious decrease in number of small islands, the cross regions of the copper stripes seemly accommodate more atoms. In Fig. 2(g), line profile from E to F is presented. The difference in height between the cross region and nearby depression islands is about 0.19 nm which is comparable with the step height, indicating that copper atoms form the second

layer in the cross region. The accumulated atoms can partially be attributed to the "melting" of N ex covered regions. These atoms are less likely to be filled into the N covered region to avoid the breaking of elastic balance in local region. Also, the clean crossed region seems to be more favorable for the growth of copper atoms than the N covered region.

4. Summary

In this article, we studied the variations of N covered islands and the copper strips as functions of dosage (N coverage) and time of annealing, aiming to find a way of making proper templates for nanofabrication. It is found that both N coverage and high temperature annealing strongly affect the patterns of the N covered islands and the copper boundaries. By precisely controlling the growth conditions, it is possible to fabricate an ordered network of copper strips with almost uniform width.

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