I. INTRODUCTION

Atomic adsorbates such as carbon, nitrogen, oxygen and sulfur, induce various types of reconstruction on metal surfaces [1]. At adsorbate coverages lower than the saturation, reconstructed domains often separate from remaining bare regions. In some cases, the domain separation results in the formation of self-organized nanometer-scale pattern [2-6]. Adsorption-induced compressive stress is considered to play a major role in the self-organization. Surface stress and its effects (on both bare and adsorbed surfaces) are discussed widely in literatures [7-10]. Among self-organized nanopatterns, a grid-like pattern on nitrogen(N)-adsorbed Cu(001) has been attracting a lot of attention [3,11-16]. Nitrogen atoms occupy 4-fold hollow sites on a Cu(001) surface in c(2×2) arrangement. At appropriate N coverages, square N-adsorbed islands of the size, ca. 5 nm × 5 nm, are aligned along both [100] and [010] directions, resulting in the grid pattern. The square N-islands are separated by two types of boundaries, narrow monoatomic lines and wide multiatomic belts. We previously proposed structural models for the two boundaries and discussed the relief mechanisms of compressive stress induced by N adsorption [16].

In this paper, we report a scanning tunneling microscopy (STM) study on a N/Cu(001) specimen annealed fairly long. We find for the first time a ribbon-like (or raft-like) nanopattern in regions vicinal toward [100]. In the region, parallel steps run along [010] and each (001) terrace accommodates only a single N-adsorbed island in width. The N-islands are aligned along [100], across the steps. Bare Cu(001) stripes separating N-islands also run perpendicular to steps, and thus the ribbon-like pattern results. N-adsorbed islands in the ribbon pattern are changed to rectangles. They are in marked contrast with squares in the grid. We discuss the square-to-rectangle deformation by considering the shearing strain between the topmost N-adsorbed layer and the second Cu layer. [DOI: 10.1380/ejssnt.2016.43]

Keywords: Scanning Tunneling Microscopy; Self-assembly; Copper; Nitrogen atom; Vicinal single crystal surfaces; Nano-scale pattern; Shearing strain

II. EXPERIMENTAL

The experiments were performed in an ultra-high vacuum system composed of two chambers, a sample preparation chamber and a main chamber housing an STM unit. A Cu(001) specimen was cleaned by argon ion bombardment (1 kV) and subsequent annealing at 850 K. The temperature was measured with an infrared pyrometer. Since molecular nitrogen is not adsorbed on Cu(001) surfaces, we utilized a modified Bayard-Alpert type miniature gauge to activate nitrogen. By adjusting the gauge electrode potentials, the energy of ions impinging on the Cu specimen was reduced to less than 100 eV. After exposure to the activated nitrogen, the specimen was annealed to obtain ordered structures. The ribbon-like nanopattern reported here was observed after fairly long anneal-
ing (45 min) at 650 K. STM measurements were carried out at room temperature in a constant current mode.

III. RESULTS AND DISCUSSIONS

Figure 1 shows STM images obtained from two different areas on the same surface. This makes sure that the imaged areas were prepared under exactly the same conditions. Nitrogen-adsorbed regions appear as dark islands and bare Cu(001) regions appear as bright boundaries between the N-islands. The image of Fig. 1(a) exhibits a well-known grid-like pattern. Square N-islands are aligned along both [100] and [010] directions. Boundaries of two types, monoatomic lines and multiatomic belts, separate square N-islands. Multiatomic belts are wide and bright, whereas monoatomic lines are narrow and less bright. Three monoatomic steps run across the image, and two screw dislocations are observed. However, these irregularities do not disturb the grid-like pattern seriously.

Figure 1(b) shows a newly-found ribbon-like nanopattern. From the image, we estimate that the area is vicinal toward [100] by ca. 2°. Many steps of monoatomic height run parallel along a [010] direction. Each (001) terrace between steps becomes so narrow that it can accommodate only a single N-island in width. It is noteworthy that N-islands are deformed to rectangles. The rectangular N-islands and bare Cu(001) boundaries are aligned across steps, and thus forming the ribbon-like pattern. Square lattice of a Cu(001) surface is expanded isotropically upon N-adsorption [15]. Therefore, the rectangular shape means that the number of N-atoms perpendicular to steps is smaller than that parallel to the steps in the N-island.

Figure 2 shows a wide-view STM image of the size, 500 nm × 500 nm, exhibiting the coexistence of the grid-like pattern and the ribbon-like pattern. A very large (001) terrace extends in the lower-right of the figure, and the surface descends toward [100] in the upper-left. Note that the slope direction is reverse to that in Fig. 1(b). Expanded views demonstrate that a typical grid-like pattern develops in the flat (001) region whereas a new ribbon-like pattern appears in the vicinal, step-accumulated region. Grid- and ribbon-like patterns coexist very closely to each other, suggesting that the presence or absence of parallel [010] steps is the only factor determining which pattern develops.

Copper is a face-centered cubic (fcc) metal, and its (001) face displays 4-fold symmetry (point group, 4mm). It is quite natural that a grid-like nanopattern of 4-fold symmetry develops on the (001) surface. On the other hand, a ribbon-like nanopattern displays 2-fold symmetry (point group, 2mm). A single-domain ribbon pattern does not fit on the (001) surface. There should be another ribbon domain running perpendicular to the former. These two ribbon domains of small size should be placed side by side to match with the 4-fold symmetry of the (001) surface. As for a region vicinal toward [100], many monoatomic steps run parallel along [010]. The presence of periodic steps lowers the surface symmetry from 4-fold to mirror (point group, m). This seems to be the reason why the ribbon pattern develops in the vicinal Cu(001) region.

Ribbon-like nanopatterns have been reported on other systems, such as O/Cu(110) [2] and O/Pt(110) [6]. Cu and Pt are metals of fcc structure and their (110) faces are of 2-fold symmetry (point group, 2mm). Twofold symmetric patterns such as ribbon are expected to develop on the (110) surfaces. As discussed above, a Cu(001) surface vicinal toward [100] displays mirror symmetry. Although the symmetry is lower than that of fcc (110) surface, it is compatible with a ribbon pattern. Literature data support our idea that surface symmetry determines a nanopattern on the surface.

STM image shown in Fig. 3 demonstrates the transition from grid- to ribbon-like nanopattern. The surface descends locally toward [100]. In the upper-left corner, we see a grid-like arrangement of N-adsorbed islands. The grid extends to the right across descending steps. Steps run parallel along [010], and some terraces are so narrow that only two rows of N-islands can sit between the neighboring steps. However, the characteristics of a grid pattern, such as square N-islands and two types of bound-

![Figure 1](http://www.sssj.org/ejssnt)  
**FIG. 1.** Two STM images (100 nm × 100 nm) obtained on the same surface at sample bias voltage $V_b = \pm 2.0$ V and tunneling current $I_t = 1.0$ nA. (a) Grid-like pattern and (b) ribbon-like pattern. Nitrogen-adsorbed dark islands are square in the grid pattern, whereas they are rectangular in the ribbon pattern.
FIG. 2. Wide-view STM image (500 nm × 500 nm) recorded at sample bias voltage $V_b = -2.0$ V and tunneling current $I_t = 1.0$ nA. Expanded views (100 nm × 100 nm) demonstrate a grid-like pattern on a large (001) terrace in the lower-right and a ribbon-like pattern on the surface vicinal toward $[\bar{1}00]$ in the upper-left.

FIG. 3. STM image exhibiting transition from grid- to ribbon-like pattern. Image size 200 nm × 200 nm, $V_b = +2.0$ V, and $I_t = 1.0$ nA. Boundaries between N-islands in the ribbon region connect continuously to those in the grid region. Rectangular N-islands in the ribbon result from shortening of the sides perpendicular to steps.

In the right half of Fig. 3 where parallel steps become closer, a ribbon-like pattern develops. Characteristics of a ribbon pattern, such as a single row of N-islands on each terrace and rectangular N-islands, are observed again. We note that the majority of boundaries separating N-islands are of wide, multiatomic type. The N-islands and boundaries are aligned across steps, and then the ribbons extend perpendicular to steps. Most boundaries in the ribbon region continuously connect to those in the grid region.

FIG. 4. Mechanism leading to rectangular N-islands. (a) Schematic of a ribbon pattern. (b) Section parallel to steps. Hollow arrows indicate the displacement of Cu atoms in the topmost layer. Note that two second-layer Cu atoms are dragged in the same direction as shown by solid arrows. (c) Section perpendicular to steps. Chain lines indicate that N-island centers are registered with the deep bulk. Note that two Cu atoms collide against each other under a step edge.

In Fig. 4, we consider why N-islands are deformed to rectangles in the ribbon region. Figure 4(a) shows schematically a ribbon pattern composed of two rafts of N-islands and a bare Cu(001) belt. Figure 4(b) illustrates a section of the pattern parallel to steps. N-islands and a bare Cu belt are at the same level. Figure 4(c) illustrates the section perpendicular to steps through N-adsorbed
islands. N-adsorbed (001) terraces are separated periodically by monoatomic steps descending to the right. Adsorbed N atoms expand laterally the topmost Cu lattice by 2-3% [15], while tensile stress is present in bare Cu(001) regions. However, centers of N-islands (indicated by chain lines in Fig. 4) should be in exact registry with the deep Cu substrate. If the distance between N-island centers were slightly longer than the corresponding bulk distance, the discrepancy would grow in proportion to the extension of the ribbon pattern, and finally cause a serious strain deep into the bulk. Therefore, to avoid energy cost due to the deep strain, N-induced surface strains should be compensated within the shallow bulk.

We start with the parallel-to-step case (Fig. 4(b)). Due to the homogeneous 2-3% lattice expansion in the N-island, Cu atoms in the N-island are outward displaced larger as the distance becomes longer from the island center. Hollow arrows in the drawing indicate schematically the displacement in the topmost layer. Cu atoms in the top layer will drag Cu atoms in the second layer. We focus on two second-layer Cu atoms located just inside and just outside a boundary between an N-adsorbed island and a bare Cu(001) belt. The just-inside Cu atom moves to the right. At the same time, the next, just-outside Cu atom will also moves to the right, since the lattice contracts in the bare Cu(001) belt due to inherent tensile stress. Since the two second-layer Cu atoms move in the same direction as indicated by solid arrows, shearing strain between the topmost and second layers is kept small at the N-island edge. The same argument applies to the grid pattern on the flat (001) surface. Therefore, the period of nanopattern is the same in the grid pattern as in the ribbon pattern parallel to steps.

In the perpendicular-to-step case illustrated in Fig. 4(c), the second layer on the left terrace turns out to be the topmost N-adsorbed layer on the right terrace at a descending step. The second-layer Cu atoms on the left terrace are dragged similarly to the right. However, the Cu atom under the step edge is blocked by the next Cu atom. The next Cu atom belongs to the N-island on the lower terrace, and moves to the left due to N-induced lattice expansion. Therefore, shearing strain is larger in this case. To avoid excessive strain, the step edge has to be in a short distance from the N-island center. This seems to be the reason why N-island sides become shorter perpendicular to steps and rectangular N-islands are formed in the ribbon region.

As mentioned with Fig. 1(a), sparse steps do not affect N-islands. A ribbon-like pattern is realized only when many steps run parallel along [010] with short spacing (only a single N-island row sitting between steps). When a (001) terrace between steps accommodates two or more N-island rows, island boundaries run parallel to the [010] steps. These boundaries (monoatomic lines and/or multiatomic belts) can relieve N-induced compressive stress effectively [16]. Therefore, the registry with the deep substrate can be kept without deformation of N-islands.

In the STM image shown in Fig. 2, a large, flat (001) terrace is adjacent to a step-accumulated, vicinal face. It seems improbable that the vicinal region suitable for a ribbon pattern had been prepared at the beginning, i.e., before N-atom adsorption. It is more likely that the vicinal region was formed by small lateral flow of both Cu and N atoms during long anneal after N adsorption. Figure 5 shows the STM image suggesting the above idea. A big contaminant pins the pattern. A ribbon pattern extends on the left side of the contaminant, and the slope becomes steep near it. On the right side, (001) terraces become wider and a grid-like pattern develops. The image reminds us of “viscous lava flow disturbed by a rock”, and suggests that lateral mass flow occurred to the right during the long anneal. The ribbon-like pattern is fairly stable thermodynamically since it coexists with the normal grid-like pattern. Although the offset angle is small (ca. 2°), the vicinal face with a ribbon pattern can be regarded as a kind of facet in the N/Cu(001) system of the present N coverage.

IV. CONCLUSION

We report for the first time a ribbon-like nanopattern on an N-adsorbed Cu(001) surface. The ribbon pattern occurs in the regions vicinal toward [100], and coexists with the well-known grid-like nanopattern in flat (001) regions. We consider that local surface symmetry (mirror in the vicinal region vs. 4-fold in the flat region) determines which pattern develops. Nitrogen-adsorbed islands are rectangular in the ribbon whereas they are square in the grid. We can explain why the N-island sides are shortened perpendicular to steps running along [010]. The key is shearing strain between the topmost N-adsorbed layer and the second Cu layer. We suggest finally that the vicinal face was formed by lateral mass flow during long anneal after N adsorption.

It has often been claimed that surface nano-scale patterns are caused by two coexisting stresses (compressive
and tensile) or stress anisotropies [7–10]. But, these stresses are considered within the two-dimensional framework, as looking down from the above. Shearing strain has not been considered explicitly. Rectangular N-islands in the ribbon pattern are the first example that requires consideration on shearing strain. The presented model is very simple, and does not contain characters specific to Cu and N. It would be applicable to other nanopatterns. For example, it would provide some clues for solving the problems why isolated N-islands on Cu(001) are already of regular size [12,13,15], and what determines the size of MnN islands on Cu(001) [17,18].

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