

# Structure of the Cu{100}-c(2×2)N surface: A scanning-tunneling-microscopy study

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Scanning-tunneling-microscopy studies of the Cu{100}-c(2×2)N surface reveal that it is covered with square-shaped structures with sides  $52 \pm 4$  Å long, running parallel to the  $\langle 100 \rangle$  directions. Within these structures it is possible to resolve a square-based lattice, with a lattice parameter of 4 Å consistent with the c(2×2) structure. We use a lattice-parameter-mismatch model based on the bulk-lattice constants of Cu<sub>3</sub>N to account for the regularity in shape and size of the square-shaped structures.

Scanning-tunneling-microscopy (STM) studies of adsorption on metal surfaces, although limited in number, have proved to be an effective tool in the study of adsorbate-induced surface reconstruction. These studies have been used to observe both surface structures and in some cases the mechanisms leading to those structures. An excellent example is the work on the Cu{110}-(2×1)O system, where the observed diffusion of Cu adatoms from step edges demonstrated that the (2×1) reconstruction is best described by an added-row model.<sup>1,2</sup> More recent STM results have shown that when the Cu{110} surface is exposed to subsaturation doses of oxygen at elevated temperatures, an additional long-range periodicity is observed. The surface appears to be covered by stripes running in the  $\langle 100 \rangle$  directions of the (2×1)O reconstruction, separated by areas of clean copper.<sup>3</sup>

In this paper, we report a similar phenomenon occurring on the Cu{100}-c(2×2)N surface. We find that the surface formed using the activated bombardment method results in a highly stepped surface that appears to be covered by dark squares,  $52 \pm 4$  Å across, with the sides oriented parallel to the  $\langle 100 \rangle$  crystallographic directions, rather than stripes. Within the dark squares, atomic resolution has been obtained revealing a structure consistent with the c(2×2) reconstruction. In addition, we propose a simple structural model that accounts for the size and shape of these squares that does not require a long-range interaction. Our STM results also yield insight into the discrepancies that have arisen in the conclusions from previous structural studies of this surface.

The adsorption of nitrogen atoms on the Cu{100} surface has been studied by various techniques. Lee and Farnsworth<sup>4</sup> reported that a c(2×2) low-energy electron-diffraction (LEED) pattern was observed when a clean copper surface was exposed to activated nitrogen produced by an ion gun. Early LEED studies<sup>5-7</sup> suggested that the nitrogen atoms occupy fourfold-hollow (fhh) sites in the copper mesh and are adsorbed 1.45 Å above the first layer of copper atoms. Subsequent LEED intensity analysis by Zeng, Sodhi, and Mitchell<sup>8,9</sup> placed the nitrogen atoms in the fhh sites, 0.06 Å above the top layer of copper atoms, with the spacing between first and second copper layers being 1.85 Å. The most sophisticated refinements of this model also included a downward

relaxation of copper atoms in the second layer which were directly below nitrogen atoms and lateral displacements of copper atoms in the first and third layers. The latter would lead to a *p*4g LEED pattern, which has not been observed for this adsorption system, but is known to exist for atomic nitrogen adsorbed on Ni{100}.<sup>10</sup> A surface-phonon-dispersion study of the c(2×2)N adlayer produced by thermal dissociation of ammonia also places the nitrogen atoms in the fhh site 0.6 Å above the first layer of copper atoms.<sup>11</sup> Extended electron-energy-loss fine-structure (EXELFS) studies on an adlayer produced by the same method also indicates that nitrogen occupies the fhh site.<sup>12</sup>

Our STM results were obtained in an ultrahigh vacuum system containing an Omicron Vacuumphysik STM and the usual facilities for sample bombardment, LEED, and Auger electron spectroscopy. The Cu{100} surface was cleaned by mechanical and electrochemical polishing and *in vacuo* by repeated cycles of argon ion bombardment and annealing to 700 K. The cleanliness and order of the crystal were checked by LEED and STM. The nitride overlayer was prepared by ion bombardment of the crystal at room temperature for 15 min using  $5 \times 10^{-4}$  mbar of N<sub>2</sub> and a beam energy of 500 eV. This produced a diffuse c(2×2) LEED pattern with a high background intensity. Heating the crystal to 600 K produced a sharp c(2×2) LEED pattern with a low background intensity. There was no detectable desorption of nitrogen during the annealing process.

Figure 1 is an  $800 \times 800$  Å<sup>2</sup> STM image of a typical area of the surface following the preparation of the c(2×2)N overlayer. The most striking thing about this is that the surface appears to be covered by dark square-shaped structures, which have a mean side length of  $52 \pm 4$  Å. The dark squares are separated by bright boundary regions that range between 11 and 40 Å across. Careful inspection of these images shows that the surface has a high step density in comparison to the clean surface and that the bright boundaries of the dark squares tend to continue across the step edges, but the dark squares themselves terminate at step edges. This lack of continuity across the step edges is in marked contrast to the behavior of the stripes observed on the Cu{100}-(2×1)O surface,<sup>3</sup> which extend across the step edges. To illustrate the relationship between the dark squares, bright

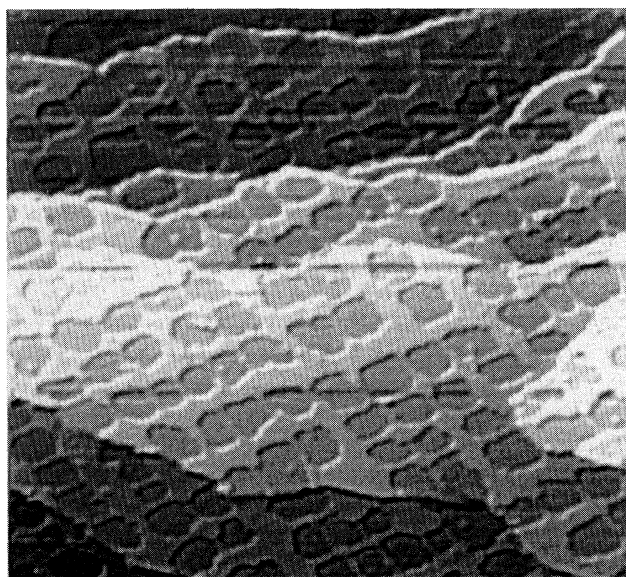


FIG. 1. An image of an  $800 \times 800 \text{ \AA}^2$  area of the  $\text{Cu}\{100\}\text{-}(2 \times 2)\text{N}$  surface, showing a highly stepped surface covered with square structures with a mean size of  $52 \text{ \AA}$ . Image taken with 3-V sample bias and tunneling current of 1 nA.

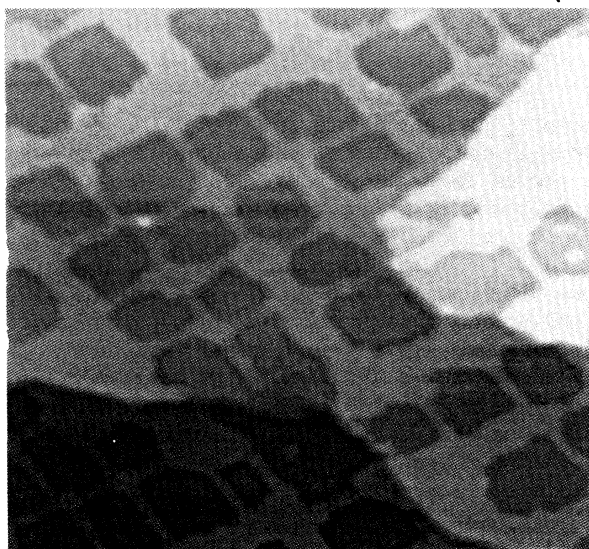
boundary regions, and step edges, we show in Fig. 2(a) a  $400 \times 400 \text{ \AA}^2$  image of the surface. In Fig. 2(b) we have recreated this image with shaded areas added to indicate the square structures and solid lines to denote the step edges.

Figure 3 shows a high-resolution image taken of a small area ( $25 \times 155 \text{ \AA}^2$ ) of the surface. Here we see what appear to be bright features arranged in a square unit cell; the unit cell length ( $4 \text{ \AA}$ ) and orientation are consistent with what we would expect for a  $c(2 \times 2)$  reconstruction on this surface. We interpret our STM images as follows: the bright features visible in Fig. 3 are nitrogen atoms arranged in a  $c(2 \times 2)$  structure in the fourfold-hollow sites of a  $\{100\}$  surface. This is consistent with the LEED studies in Refs. 5–9. We note that the observation of adsorbate atoms, heights, and corrugations depend greatly on the local density of states near the Fermi level. Oxygen on  $\text{Ni}\{100\}$  also adsorbs in the f4h site and forms a  $c(2 \times 2)$  structure. However, it suppresses the density of states near the Fermi level and appears as a depression.<sup>16</sup> We cannot rule out the alternative interpretation that the bright features in the  $c(2 \times 2)$  structure are an increase in the density of states between the nitrogen atoms rather than above them. The boundary between the two square structures has the appearance of two atomically straight rows oriented in the  $\langle 100 \rangle$  direction and separated by  $7.1 \text{ \AA}$ . We were not able to resolve a corrugation within these rows. The closest distance between the row and one of the atomic features within the square is  $6.1 \text{ \AA}$ . Extrapolation of the  $c(2 \times 2)$  unit mesh across the boundary region shows that observed structures are in phase, implying that we are not observing an antiphase boundary between two domains. All of the boundaries that we have observed

appear to be oriented along the  $\langle 100 \rangle$  directions.

We must now attempt to explain the regular size and shape of these crystallites. In determining the structure of atomic nitrogen adsorbed on copper surfaces, comparison is often made with the structure of bulk copper nitride.<sup>8,9,12–14</sup>  $\text{Cu}_3\text{N}$  has a cubic-based lattice, with six copper atoms coordinated around a nitrogen atom.<sup>15</sup> The copper-copper nearest-neighbor distance is  $2.69 \text{ \AA}$ , 5%

(a)



(b)

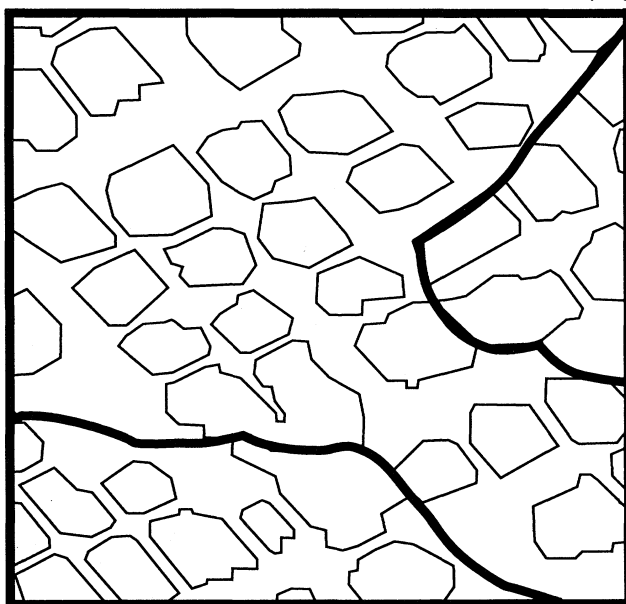


FIG. 2. (a) An image of a  $400 \times 400 \text{ \AA}^2$  area of the  $\text{Cu}\{100\}\text{-}c(2 \times 2)\text{N}$  surface. Image taken with 3-V sample bias and tunneling current of 1 nA. (b) The same image as in (a), recreated with shaded areas representing the square structures and solid lines denoting the step edges. The boundary regions between the squares tend to be continuous across step edges, but the squares themselves terminate at step edges.

larger than the value for bulk copper. Taking a section through a (100) plane of  $\text{Cu}_3\text{N}$  gives a two-dimensional  $c(2\times 2)$  structure. The nitrogen atoms are coplanar with the copper and the nitrogen-nitrogen atomic spacing is 3.8 Å. If we superimpose a layer of the larger  $\text{Cu}_3\text{N}$  lat-



FIG. 3. Image of an area  $25\times 155\text{ Å}^2$  showing portions of two of the square structures, with atomic resolution within the structures. Image taken with  $-0.1\text{-V}$  sample bias and tunneling current of 1 nA.

tice over that of the clean copper surface, with the central atoms of the two layers in register, then the lattice mismatch between the clean surface and copper atoms of this  $\text{Cu}_3\text{N}$  crystallite only allows the copper atoms at the edges of the crystallite to fall into registry with the surface again at 26 Å from the center of the square, leading to a square containing the  $\text{Cu}\{100\}$ - $(2\times 2)\text{N}$  of 52 Å across, remarkably similar in size and shape to the structures observed in Figs. 2 and 3. This structure is shown in Fig. 4. We believe that this simple model accounts for the regular size of the  $c(2\times 2)\text{N}$  crystallites. We note that a similar model based on square domains has been proposed to explain LEED patterns from atomic nitrogen adsorbed on  $\text{W}\{100\}$ .<sup>17</sup> This model involved a contraction of the tungsten lattice spacing, rather than the expansion of the copper lattice spacing proposed in our model. Our simple model assumes that the nitrogen and copper atoms are coplanar, we note that the LEED studies of Refs. 8 and 9 support a near coplanar positioning with the N atoms only 0.06 Å above the Cu atoms.

A square crystallite 52 Å across as pictured in Fig. 4 contains 364 copper atoms in the top layer. The corresponding clean metal surface, which has a smaller copper-copper nearest-neighbor distance, can accommodate 420 copper atoms in the same area. If a nitride crystallite one layer thick is formed from the clean copper surface, then 56 copper atoms must be ejected from the surface layer, i.e., 14 copper atoms per side of the crystal-

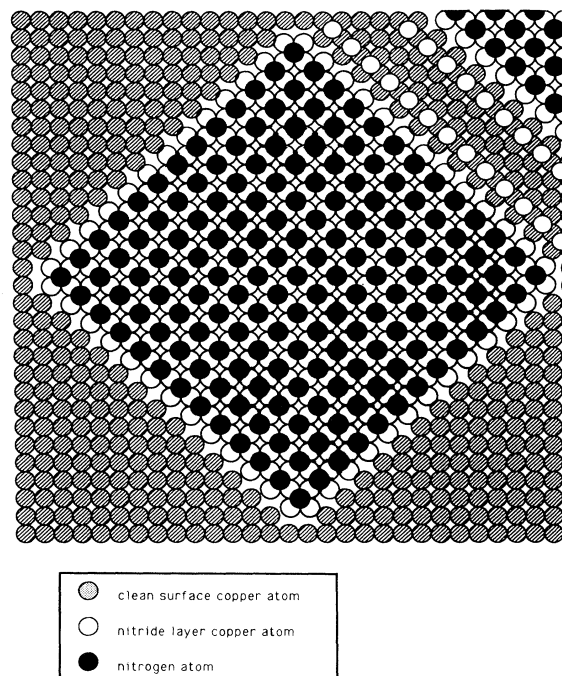


FIG. 4. Structural model of the nitride crystallite, with shaded circles representing substrate copper atoms with the lattice parameter of the  $\text{Cu}\{100\}$  surface (2.55 Å). Open circles represent copper atoms within the nitride crystallite, or those ejected from it, and dark shaded circles represent nitrogen atoms.

lite. If these ejected atoms tend to form a row at the boundary of the crystallite, then this would account for the origin of the rows of atoms visible in Fig. 3 between the two crystallites. Nitride crystallites forming close to step-edge defects will tend to terminate at the step edge, although the step edge itself might be extended by one row by the copper atoms ejected from the top copper layer during the crystallite formation. We have added some of the ejected copper atoms to Fig. 4, in an attempt to model the boundary region shown in Fig. 3. The number of atoms in the rows depends on the thickness of the nitride crystallite. In the figure we have placed the ejected atoms in fourfold-hollow sites close to the boundary. We stress that this is by no means a definitive assignment of the site, but one in which the distance between the two rows is  $7.2 \text{ \AA}$  and the distance between the row and the nearest N atom is  $6.3 \text{ \AA}$ , in fairly good agreement with the distances determined from Fig. 3— $7.1 \text{ \AA}$  and  $6.1 \text{ \AA}$ , respectively.

The manner of the formation of this surface reconstruction, by ion bombardment and annealing to 600 K unfortunately precludes study of the mechanism of formation of the crystallite, as with the present STM, we are unable to heat the sample and take STM images simultaneously.

This study shows the power of the STM in assisting in structural determinations using other experimental

methods; the images produced enable whole classes of structural models to be eliminated, invaluable information when carrying out model-based calculations upon LEED or photoelectron diffraction data. Given the unusual nature of the  $\text{Cu}\{100\}-(2 \times 2)\text{N}$  surface, it is not surprising that there are marked discrepancies in previous structural determinations.<sup>5-9,11,12</sup> Even the most elaborate models based on modeling of LEED data<sup>9</sup> do not produce entirely satisfactory agreement between experiment and calculation for the simple reason that the actual surface topology is so unusual and complicated that it was not considered. Indeed, without the STM images it is unlikely that such a model would have been postulated at all.

In summary, we find that the  $\text{Cu}\{100\}-c(2 \times 2)\text{N}$  surface formed by ion bombardment and annealing, is covered with what appear to be dark squares separated by bright boundaries. The average side length of these squares is  $52 \pm 4 \text{ \AA}$ . The bright boundaries tend to continue across step edges, while the dark squares terminate at the step edge. Within the dark squares, a structure consistent with the  $c(2 \times 2)$  reconstruction is observed. The dark squares are proposed to be crystallites of copper nitride, with the mismatch in the copper-copper spacing of the clean surface and copper nitride accounting for the regularity in their size and shape.

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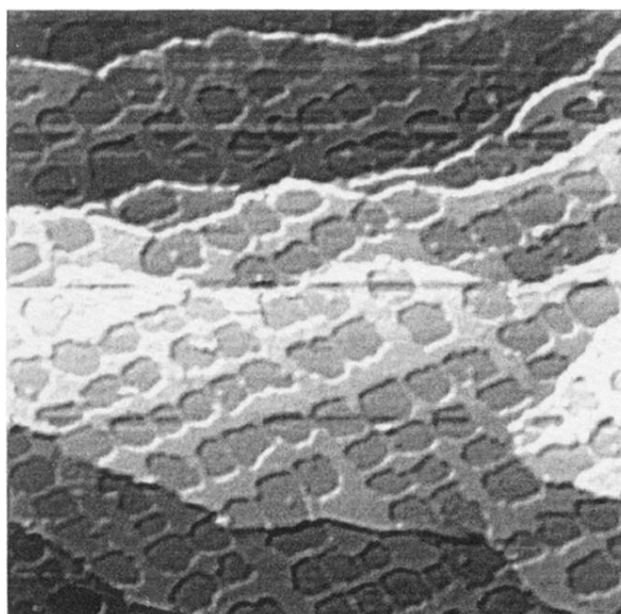


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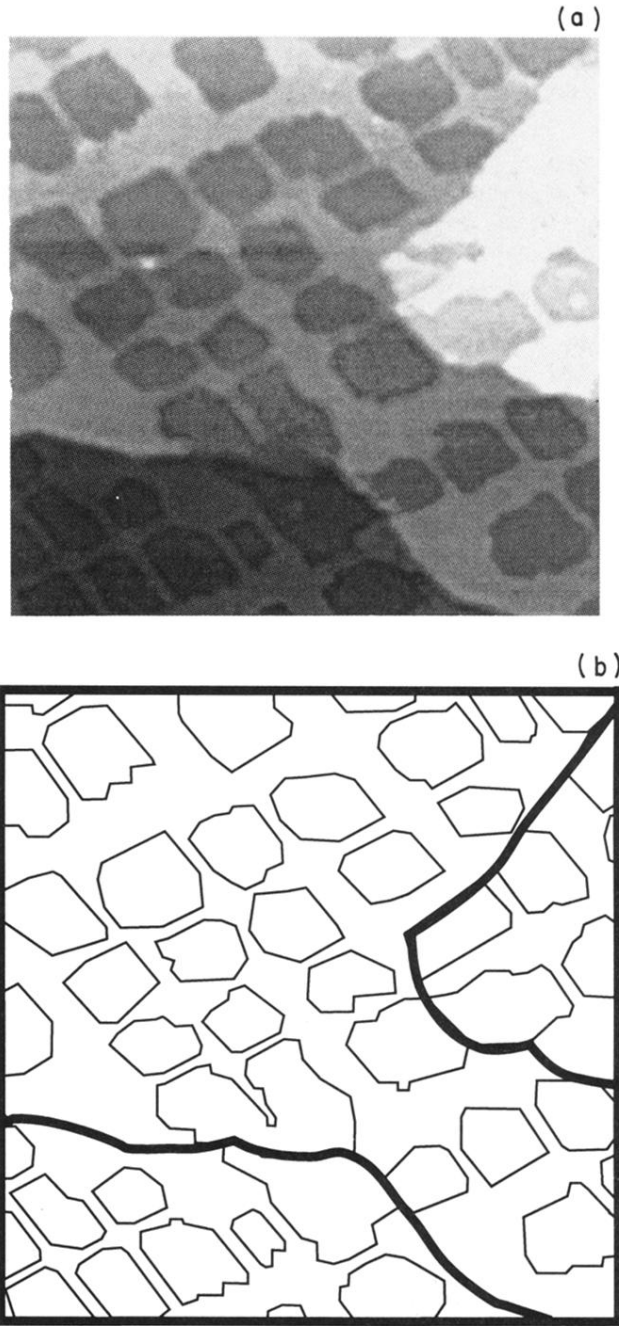


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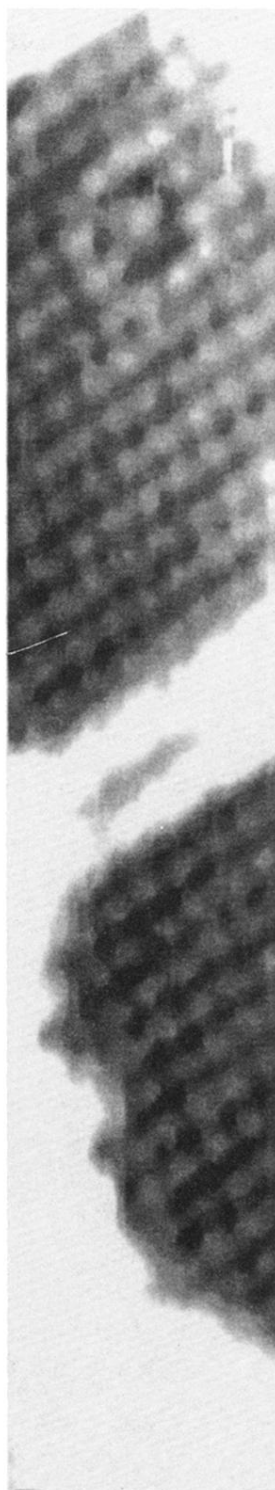


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