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LETTER TO THE EDITOR

Cu(100)c(2 × 2)-N: a new type of adsorbate-induced surface reconstruction**S M Driver¹, J-T Hoefft², M Polcik², M Kittel², R Terborg², R L Toomes¹, J-H.Kang¹ and D P Woodruff^{1,2}**¹ Physics Department, University of Warwick, Coventry CV4 7AL, UK² Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

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Abstract

Using a combination of photoelectron diffraction and scanning tunnelling microscopy the Cu(100)c(2 × 2)-N surface is shown to undergo a symmetry-lowering reconstruction with a strong (0.34 Å) periodic distortion of the outermost Cu layer perpendicular to the surface. The rumpling reconstruction is shown to account for N–N attractions which create c(2 × 2) islands and the systematic behaviour of inter-island boundary widths in the mesoscopic self-organization of this surface.

It is now well established that some clean metal surfaces and many adsorbate-covered metal surfaces reconstruct [1]; i.e. the substrate atoms in the outermost layer(s) adopt a structure significantly different from those in the underlying bulk. One class of such reconstructions involves large changes in the surface layer density; for example, the density may be reduced by ‘missing rows’, or (for a few clean metal surfaces) may be increased through the formation of a close-packed overlayer. A second class of reconstruction involves displacements of atoms parallel to the surface, such as in the ‘clock’ reconstructions seen in Ni(100) in the presence of adsorbed C or N [2]. In many cases these reconstructions are believed to relate to the relief of surface stress, which is typically tensile for a clean surface and compressive in the presence of many adsorbates. Here we present clear evidence from two quite different experimental techniques of a reconstruction of Cu(100) induced by adsorbed N in which the Cu surface layer distortions involve periodic movements *perpendicular* to the surface and which *lowers the point group symmetry* of the surface. Small amplitude (symmetry-preserving) perpendicular distortions often occur in sub-surface layers, typically distinguishing substrate atoms which are ‘covered’ or ‘not covered’ by adsorbed atoms. In the case of alkali atom adsorption on some close-packed surfaces, this can even occur in the outermost layer of the substrate when the adatoms occupy atop sites and this local distortion is an important factor in stabilizing this unusual geometry [3]. In the Cu(100)/N case presented here, the large amplitude rumpling (0.34 Å) is in the outermost layer, is symmetry lowering and is the primary signature of the reconstruction. We propose that this type of distortion provides an alternative route to the relief of surface stress. We also show how this unusual reconstruction helps to explain some key aspects of the novel self-organization of c(2 × 2) islands previously seen in this system using scanning tunnelling microscopy (STM). Our own STM investigation of this surface also

provides a clear demonstration of the dangers of over-simplistic interpretation of such data in terms of adsorbate atomic coordinates.

The small number of previous quantitative structural studies of the Cu(100)c(2 × 2)-N surface phase have concluded that the N atoms adopt 4-fold-coordinated hollow sites on the surfaces which are almost coplanar without the outermost Cu layer [4–6]. There is, however, evidence that the situation is more complicated than this. The most recent quantitative low-energy electron diffraction (LEED) study [5] found a significantly better fit to the LEED intensities for a structure involving a ‘clock’ reconstruction in which Cu atoms around the N atoms rotate alternately clockwise and counter-clockwise, also shifting radially outwards by a small amount. This distortion, however, leads to a (2 × 2) periodicity which is not consistent with the observed LEED pattern, so there is a fundamental contradiction in this finding. Another special aspect of this system is revealed by STM studies which have shown an unusual pattern of behaviour in which approximately 50 Å × 50 Å square islands of the c(2 × 2) phase form ordered arrays on the surface at ‘subsaturating’ N coverages (in the approximate coverage range 0.15–0.35 ML). Because the structure of bulk Cu₃N is rather similar to the local structure proposed for the Cu(100)c(2 × 2)-N phase, but involves a 5.5% larger lateral periodicity, this self-organization behaviour was initially interpreted as evidence that the islands were effectively of this nitride which were incommensurate with the Cu substrate [7, 8]. However, some of the published STM images contained in these papers show that this cannot be the case, and a recent spot-profile-analysis LEED investigation has provided clear quantitative evidence that the c(2 × 2) phase is truly commensurate [9]. A more probable reason for the self-organization is related to the minimization of total elastic strain energy in a system comprising N-covered islands with compressive surface stress and clean surface regions with tensile surface stress, similar to that which is known to occur in the clean Si(100)(2 × 1) and Cu(110)/O surface phases [10, 11]. In the absence of any quantitative information on the induced surface stress or island boundary energy for the Cu(100)/N system, however, it is not possible to provide a quantitative model of the island sizes in this self-organization. Such a general model, however, cannot account for some essential details of the island behaviour. The fact that islanding occurs shows clearly that one must have N–N attraction on this surface at low coverage. By contrast, the behaviour of the islands at higher coverage indicates a local repulsion; only at the highest ‘saturation’ coverages (≥ approximately 0.4 ML) does one no longer see the ⟨100⟩ inter-island boundaries, and in this case narrow monolayer-deep trenches create boundaries along ⟨110⟩ directions between different regions.

In an attempt to gain a better understanding of this system, we have conducted experiments using two quite different techniques, STM to build on previous studies in characterizing atomic-scale aspects of the long-range ordering behaviour and scanned-energy mode photoelectron diffraction (PhD) to provide quantitative local structural information. In each of these experiments the sample was prepared by the usual combination of *ex situ* polishing and *in situ* argon ion bombardment and annealing. Cu surfaces do not dissociate N₂ so the N-covered surfaces were prepared as in all previous Cu/N surface studies [4–8], by low-energy (typically 500 eV) nitrogen ion bombardment (with typical doses of a few hundred μC) followed by annealing to 575–650 K. In all experiments *in situ* sample characterization by LEED and either Auger electron or x-ray photoelectron spectroscopy was used.

Using N 1s scanned-energy mode photoelectron diffraction we have investigated the local geometrical structure around the N adsorbates. The methodology we have developed for this technique has been described in many previous structure determinations [2, 12] and is based on typical data-sets comprising 5–10 PhD modulation curves in different emission directions, each covering a kinetic energy range of around 400 eV; following preliminary evaluation by a method of direct data inversion, the final structure determination was effected by comparison

with the results of multiple scattering calculations for a range of trial structures. As in the earlier LEED studies, these results clearly favour N adsorption in the hollow sites, but the relatively poor quality of the fits for an unreconstructed surface indicates some aspect of the structure is missing. Including a clock reconstruction significantly improved the fits but, as remarked upon above, this model is inconsistent with the observed LEED pattern. A periodic rumpling of the surface Cu layer, however, gave an even better fit to the PhD data, and the optimized form of this model is shown in figure 1 as the best-fit structure; the values of the detailed structural parameters, defined in the figure, are $z_N = 1.98 \pm 0.05 \text{ \AA}$, $z_{1a} = 1.71 \pm 0.06 \text{ \AA}$ and $z_{1b} = 2.05 \pm 0.10 \text{ \AA}$ giving a Cu outermost layer rumpling of $0.34 \pm 0.12 \text{ \AA}$. The structural optimization was conducted using 12 PhD modulation spectra in different emission directions each covering the electron energy range 70–440 eV and gave an overall *R*-factor [12] of 0.20. Figure 2 shows a selection of these spectra and their associated best-fit simulations, together with the results of simulations for an optimized model without rumpling (*R*-factor = 0.30). Notice that the rumpling lowers the rotational symmetry of the hollow sites occupied by the N atoms from 4-fold to 2-fold, although the N atoms retain four Cu nearest neighbours at essentially the same spacing.

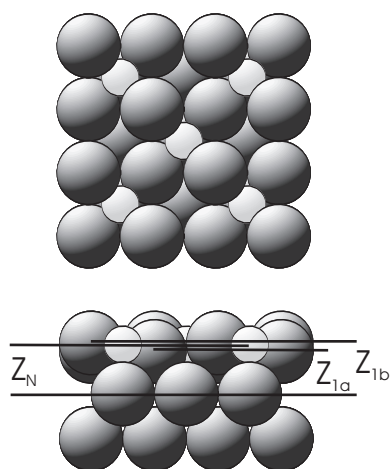


Figure 1. Schematic plan and side views of the local geometry of the Cu(100) $c(2 \times 2)$ -N phase as determined by scanned-energy mode photoelectron diffraction, defining the main structural parameters. Cu atoms are shown as larger darker spheres.

All published STM images of this adsorbate phase [7, 8] show a $c(2 \times 2)$ array of bright atomic-scale asperities (local height maxima in a constant tunneling current mode) which have been interpreted as corresponding to the adsorbed N atoms. In all of these images the $c(2 \times 2)$ islands appear 0.2–0.5 Å lower than the surrounding clean surface (see, for example, Figs. 3(a) and 3(d)) which we attribute to an electronic effect. Theoretical calculations indicate that N on Pt(111) should appear in STM as a dip of depth $\approx 0.2 \text{ \AA}$, with tails extending more than 4 Å from the N atoms [13], consistent with the apparent lowering of an ordered N ad-layer island; however, this theoretical result also suggests that the observed asperities may not, in fact, correspond to the N atom sites. In adsorbate studies on metal surfaces it is well established that different tip conditions (probably involving adsorbed atoms) can strongly modify the imaging, and in particular can allow imaging of either adsorbate or substrate species at the surface under different conditions [14, 15]. We have therefore undertaken a new STM study to try to explore the range of possible atomic-scale images which can be obtained from this surface and, in particular, to try to obtain images of the surface Cu atoms.

The results of this new investigation led to two important conclusions. The first is that it is possible to obtain images in which asperities in the $c(2 \times 2)$ -N islands show the same

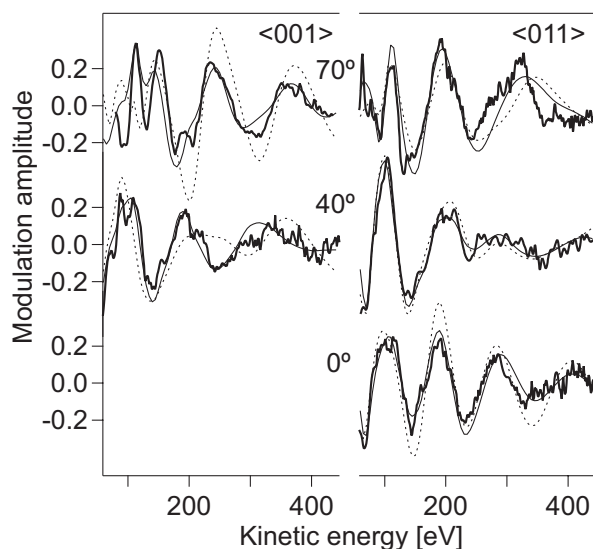


Figure 2. Experimental N 1s scanned-energy mode photoelectron diffraction modulation curves (bold lines) measured from a Cu(100) $c(2 \times 2)$ -N surface in two azimuths at several polar emission angles, compared with the results of multiple scattering simulations for the best-fit (ruffled) structural model (fine lines) and for an optimized hollow site model without rumpling (dashed lines).

(1×1) periodicity as the clean surface, although the detailed appearance depends on the exact tip condition and images are often somewhat noisy. Usually these images comprise alternating bright (high) and dim (low) asperities which might imply a physical rumpling perpendicular to the surface (figure 3(b)). By comparing the registry of these asperities with those on the surrounding clean surface (which can almost certainly be associated with Cu atom sites) we find that the lateral positions of all of the asperities in the $c(2 \times 2)$ islands correspond to unreconstructed Cu atom sites (figure 3(b)). In clear contradiction to earlier conclusions, inspection of the previously-published STM images in which the islands only show asperities with $c(2 \times 2)$ periodicity (cf figure 3(c)) but in which atomic resolution is also obtained in the surrounding clean surface region (notably figure 4(a) of reference [8]) shows the same result: the $c(2 \times 2)$ asperities correspond to Cu atom sites. Bearing in mind that all quantitative structural techniques have found that the N atoms occupy hollow sites in the top layer, this leads us to our second conclusion that even the original STM images are actually indicative of a $c(2 \times 2)$ perpendicular rumpling of the outermost Cu layer; these images show asperities at *only* the uppermost Cu atoms, and fail to image either the lower Cu atoms or the N atoms. Both the PhD and STM techniques thus indicate Cu surface layer rumpling in the Cu(100) $c(2 \times 2)$ -N surface.

Although this type of primary rumpling reconstruction of a metal surface has not previously been observed, it seems clear that this could also be understood in terms of the relief of adsorbate-induced compressive surface stress. Indeed, on a macroscopic scale bending or rumpling is the most common form of such relief. Moreover, this adsorbate-induced rumpling may account for the occurrence of islanding in this system. If we assume that local rumpling distortion is also present in the case of isolated N atoms at this surface, one may understand the observed N–N attraction as due to a minimization of the long-range elastic energy associated with the local distortion. Notice that this type of rumpling distortion is possible at a local level,

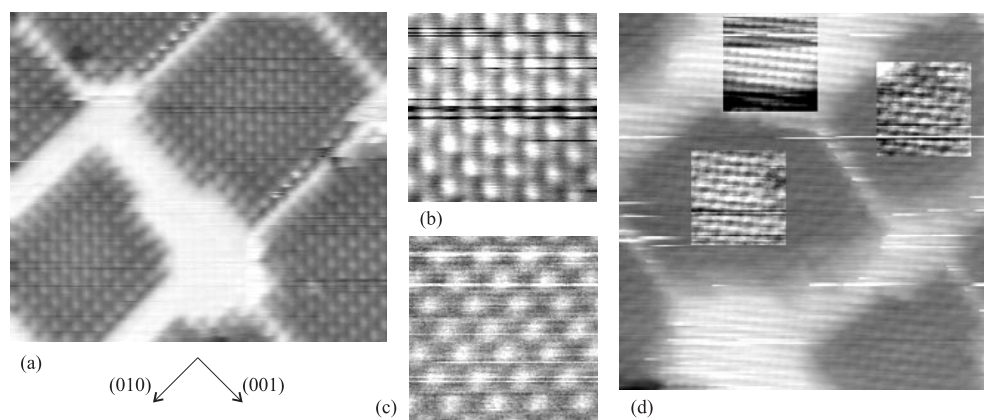


Figure 3. STM images of the $c(2 \times 2)$ -N island structure on Cu(100). Panels (a) and (d) ($100 \times 90 \text{ \AA}^2$ and $100 \times 100 \text{ \AA}^2$) show these islands surrounded by (bright) clean surface strips with the wider strips separating islands with the brightest asperities out of phase. (b) shows an enlarged image ($25 \times 25 \text{ \AA}^2$) taken from the centre of one island with a grey-scale corresponding to a smaller height variation, clearly showing alternating bright and dim asperities (sample bias +77 mV, 5.0 nA); (c) shows a similar $25 \times 25 \text{ \AA}^2$ region from a more typical lower resolution image (-0.17 V , 1.2 nA). In (d) regions of both the $c(2 \times 2)$ -N islands and clean surface strips are shown with similarly expanded grey-scales, allowing the relative registry of the asperities to be established more clearly (+41 mV, 6.7 nA).

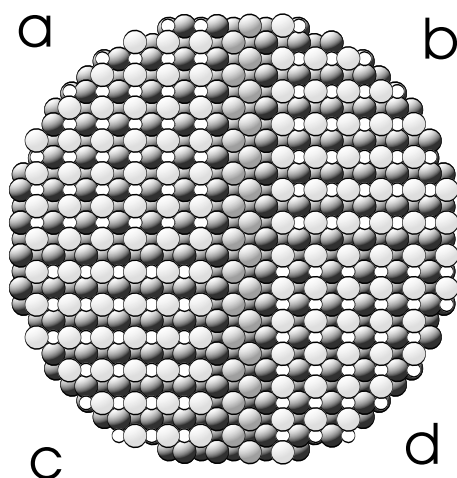


Figure 4. Schematic diagram of the different types of structural domains and antiphase domain boundaries to be expected in the rumpled Cu(100) $c(2 \times 2)$ -N structure. The N atoms are shown as small unshaded spheres; the upper Cu atoms in the outermost layer are shaded light relative to the lower Cu atoms. Domains a and c have opposite parity of Cu top layer rumpling to domains b and d leading to the wide vertical anti-phase boundary. Domains a and b involve different N atom site occupation from domains c and d leading to the narrow horizontal boundary wall.

whereas the lateral distortion associated with the alternative clock reconstruction requires concerted movement of many more atoms and cannot lead to similar long-range attraction.

The rumpling also allows us to understand the unusual nature of the interaction of adjacent $c(2 \times 2)$ islands. In our STM study we noticed that as the N coverage is increased and the

islands become closer, the width of the boundaries between islands is systematically narrower when the observed asperities in two islands are in phase with one another than when they are not. This effect can be seen most clearly in figure 3(a) by comparing the registry of the brightest asperities. We recall that these asperities correspond to the upper Cu atoms of the rumpled layer, so anti-phase boundaries correspond to boundaries across which the parity of the rumpling changes (as in the vertical boundary of figure 4). Evidently, this parity change can only occur over several atomic rows, whereas if the rumpling is in phase this rumpling can propagate across the clean surface between the islands and does not prevent such islands approaching very close to one another. Even for islands having in-phase Cu rumpling, however, there may be antiphase boundaries associated with the two locally-equivalent adsorption sites which may be occupied by the N atoms (see the horizontal boundary in Fig. 4). Because the N atoms are not imaged directly, these domains should appear in-phase in the STM images, yet the change in N adsorption site must lead to a narrow strip of clean surface between the islands. We therefore associate the narrow boundaries with those in which the Cu rumpling is in phase but the N sites are out of phase; the wider boundaries correspond to those between domains in which the Cu rumpling is out of phase. Notice that this distinction arises only because of the reduced point group symmetry of the N-covered rumpled surface.

In conclusion, we have shown that the Cu(100) $c(2 \times 2)$ -N surface phase involves a novel adsorbate-induced surface reconstruction in the form of a strong periodic symmetry-lowering rumpling of the outermost Cu layer perpendicular to the surface. The increase in Cu–Cu nearest-neighbour distances within the surface layer produced by this reconstruction may be seen as relieving the adsorbate-induced compressive surface stress in a fashion comparable to that seen in the Ni(100) (2×2) -C ‘clock’ reconstruction involving atom movements parallel to the surface. This rumpling distortion also provides a rationalization for several aspects of the mesoscopic self-organization which had been observed previously but were not well understood; specifically, it provides a consistent description of the tendency of the adsorbed N atoms to form islands as well as the behaviour of inter-island boundaries noted in the present work.

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