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The structure of Cu(110)(2×3)-N; pseudo-square reconstruction of a rectangular mesh substrate

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The structure of the Cu(110)(2×3)-N phase has been investigated by parallel studies using 3-keV Li⁺ and 2-keV He⁺ ion scattering and scanned energy mode normal emission N 1s photoelectron diffraction. The Li⁺ ion scattering results provide clear evidence for an adsorbate-induced reconstruction of the Cu surface and, in particular, indicate a *shortening* of the Cu-Cu atomic spacing along the ⟨100⟩ azimuth to a value of 2.7 ± 0.1 Å, similar to the ⟨110⟩ spacing of 2.55 Å. A model of the surface consistent with this result involves a pseudo-square Cu top atom layer with N atoms occupying alternate hollow sites leading to a local structure which is a 6% distorted Cu(100)*c*(2×2)-N phase. He⁺ ion scattering data provides support for the N hollow adsorption sites. Scanned energy mode photoelectron diffraction is insensitive to the nature of the reconstruction but provides information on the local adsorption sites and, hence, on the lateral registry of the reconstructed overlayer and the underlying substrate.

I. INTRODUCTION

In recent years the phenomenon of adsorbate-induced substrate reconstruction on well-characterized low Miller index crystal surfaces has been recognised as rather widespread. Typically, this effect is characterized by two rather different situations. In the case of small surface mesh structures, typically involving low atomic number adsorbates (C, N, O), the surface structure involves substrate atom row removal or distortion to allow the adsorbed atom to penetrate the surface or form a preferred local bonding geometry (which may be similar to that in a bulk compound). In other cases, involving large surface mesh structures (many associated with S or halogen adsorption), a coincidence lattice structure is formed in which the overlayer may well have the local geometry of one or two layers of a bulk compound. The Cu(110)(2×3)-N (Ref. 1) [and Ni(110)(2×3)-N (Ref. 2)] structure appears to be an intermediate case in which the relatively large surface mesh is strongly suggestive of a reconstruction but it is far from clear whether this is associated with local compound formation or substrate distortion. In this paper we present the results of an investigation of this structure by two very different but highly complementary techniques. Low-energy ion scattering (using 3-keV Li⁺ ions) allows one to investigate the relative location of neighboring atoms on a surface through the process of elastic shadowing, and has proved particularly effective in investigating substrate atom movements.³⁻⁵ 2-keV He⁺ ion scattering provides enhanced sensitivity to low atomic number adsorbates, but quantitative interpretation is difficult due to the complicating influence of trajectory-dependent charge exchange.^{6,7} By contrast scanned energy mode normal emission photoelectron diffraction is rather sensitive to the local adsorption site but far less sensitive to the nature of any substrate reconstruction.^{8,9} One feature which restricts our ability to provide a complete set of precise structural param-

eters for the Cu(110)(2×3)-N structure with these techniques is that this large surface mesh structure almost certainly involves more than one local adsorption site per unit mesh, and that both the techniques we have provided information averaged over these different sites. Nevertheless, our results provide strong evidence for a structure in which the uppermost Cu atom layer adopts a slightly distorted square array, essentially the same as on Cu(100), and in which the N atoms occupy alternate hollow sites within this overlayer, producing a local structure very similar to that in Cu(100)*c*(2×2)-N.

II. EXPERIMENTAL DETAILS

The ion scattering experiments were conducted in a purpose-built ultrahigh vacuum (UHV) spectrometer system at the University of Warwick fitted with a quadrupole mass filtered ion gun and a concentric hemispherical analyzer (VSW HA50) fitted with multichannel detection. The ion gun can provide a beam of Li⁺ ions from a SpectraMat thermal ion source, or He⁺ ions from electron ionization of He gas, at energies up to above 3 keV with currents in the nA range. The scattering angle detected by the spectrometer is fixed at 150°. Further details of this instrument and the mode of data collection can be found elsewhere.^{10,11}

Normal emission N 1s scanned energy mode photoelectron diffraction spectra were recorded in an angle-resolving photoemission spectrometer (VG ADES) of the Fritz Haber Institute at the BESSY synchrotron radiation facility in West Berlin taking light in the 400–800 eV energy range through a high-energy toroidal grating monochromator.¹² Photoelectron diffraction spectra were recorded by measuring short energy distribution curves around the N 1s photoemission peak at each of a succession of photon energies, and the integrated areas of these peaks were plotted as a function

of photoelectron kinetic energy. The details of this approach have been given elsewhere.^{13,14}

Two independent Cu(110) crystals were used for the parallel experiments using similar preparation methods described elsewhere.^{11,13} Surface order was assessed by *in situ* low-energy electron diffraction (LEED), and cleanliness by He⁺ ion scattering or by core-level photoemission and near-edge x-ray absorption spectroscopy. The (2×3)-N overlayer was prepared using a procedure very similar to that described by Heskett *et al.*¹

III. ION SCATTERING RESULTS AND DISCUSSION

In order to investigate the effects of surface atom shadowing, the amplitude of the Li⁺ → Cu ion scattering peak in scattered ion energy spectra was recorded as a function of grazing incidence angle in four principal azimuths from both the clean surface and from the (2×3)-N surface. These results are shown in Fig. 1. Polar angle scans of this kind contain peaks associated with the thresholds of incident beam shadowing (and exit beam blocking) for atoms in the top few atom layers of the surface. The peak or step edge at the lowest grazing angles is of particular interest to us here; this is associated with the mutual shadowing of surface atoms by other atoms within the same layer, and there is a quantitative relationship between the angular value of the threshold and the atom spacing in the direction of the azimuth investigated, large angular thresholds corresponding to the smallest spacings. This quantitative correlation has been established by constructing empirical shadow cones from the clean sur-

face data [and from measurements on Cu(110)(2×1)-O] and from theoretical calculations based on a Thomas-Fermi-Moliere potential.¹⁰

In this grazing-angle surface threshold range the most conspicuous effect of the presence of the N adsorption structure is the appearance of a new threshold at larger grazing angle than from the clean surface in the ⟨100⟩ azimuth. Some vestige of the clean surface threshold remains (probably associated with the absence of structural change in lower Cu atom layers), but the new threshold corresponds to a Cu-Cu spacing of 2.7 ± 0.1 Å compared with 3.61 Å in this azimuth (and 2.55 Å in ⟨110⟩) for the clean surface. In addition, there is a small shift in the threshold to lower angle in ⟨211⟩ corresponding to an increase in spacing from 4.42 Å to 6.4 ± 0.3 Å. Changes at higher grazing angles in the polar angle scans of Fig. 1, associated with the N structure, are related to changes in shadowing and blocking in lower layer scattering due to changes in upper layer-lower layer atom movements, but are generally not distinct, the main changes being in broadening or attenuation of clean surface features.

The reduction in substrate atomic periodicity seen in the ⟨100⟩ azimuth is rather unusual; on fcc(110) surfaces a far more common phenomenon is a doubling of the periodicity associated with missing rows. Possible interpretations of the decrease in spacing are a row pairing, or closer packing due to additional rows of Cu atoms being incorporated within the top Cu atom layer. In fact, we can discount the row pairing model because this would lead not only to pairs of more closely spaced atoms, but also longer nearest-neighbor distances between the pairs, a change which would result in an additional lower grazing angle threshold being seen. Moreover, we note that the ratio of the local nearest-neighbor Cu-Cu spacing in ⟨100⟩ of 2.7 Å deduced from the ion scattering, and the surface mesh periodicity in this azimuth of 10.83 Å deduced from the LEED pattern are almost exactly in the ratio 1:4, consistent with one extra row of Cu atoms for each original three rows on the unreconstructed surface. This

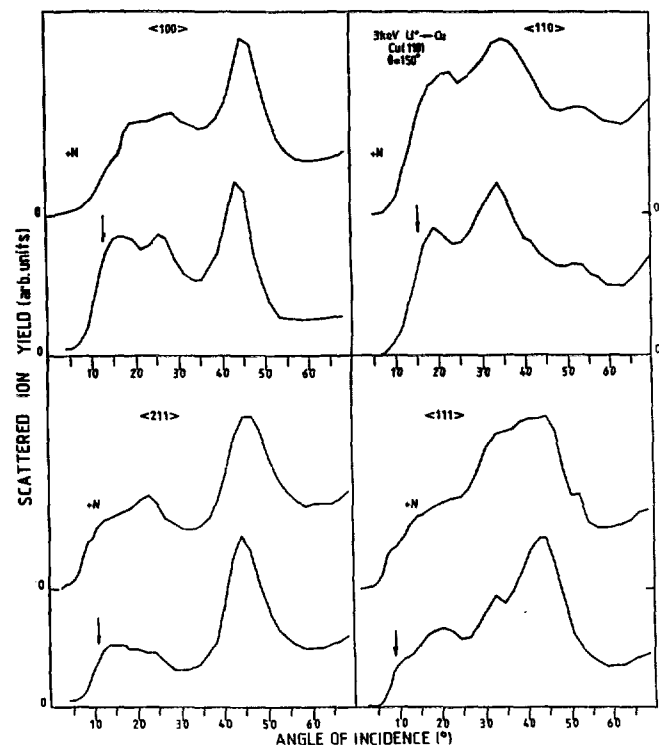


FIG. 1. Plots of the intensity of the 3-keV 150° Li⁺ → Cu ion scattering peak as a function of grazing incidence angle from Cu(110) and Cu(110)(2×3)-N in four principal azimuths of this surface.

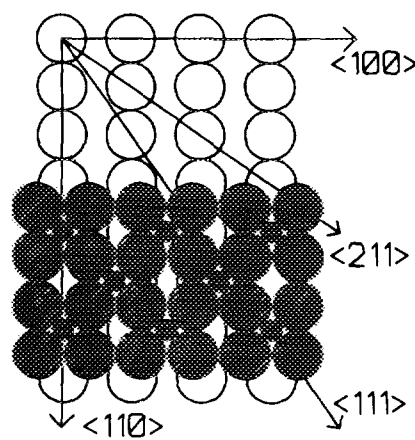


FIG. 2. Schematic diagram of the Cu(110) surface and a model of the Cu(110)(2×3)-N structure, showing the azimuths used in the ion scattering experiments. The top layer Cu atoms of the Cu(110) substrate are shown as large open circles. In the lower half of the figure, the pseudo-square reconstruction model is shown, large and small hatched circles representing Cu and N atoms within this layer.

leads to a model of the surface reconstruction in which the uppermost Cu atom layer is almost a square Cu atom array (the ideal unit mesh of the free overlayer being $2.55 \text{ \AA} \times 2.71 \text{ \AA}$), equivalent to a 6% distortion of a Cu(100) surface layer (unit mesh $2.55 \text{ \AA} \times 2.55 \text{ \AA}$).

Figure 2 shows this model of the surface to which has been added N atoms in alternate hollow sites to produce an overlayer which is a distorted version of the Cu(100) $c(2 \times 2)$ -N structure.¹⁵ The extra row of Cu atoms for every three substrate rows provides a rationalization of the $(n \times 3)$ form of the reconstruction, while the half-filling of equivalent sites within this layer provides an explanation of the specific (2×3) mesh. From the point of view of the LEED pattern and the Li^+ ion scattering data alone, of course, the choice of the hollow site is arbitrary. Prior knowledge of the structure of Cu(100) $c(2 \times 2)$ -N, however, together with similar studies of many such fcc(100) $c(2 \times 2)$ structures, strongly suggests that this is the most likely adsorption site.

So far in this development of the reconstruction model we have only used the measured Cu-Cu spacings in the $\langle 100 \rangle$ and $\langle 110 \rangle$ azimuths, the LEED pattern, and a knowledge of the Cu(100) $c(2 \times 2)$ -N structure. Further consideration of the model indicates, however, that it is consistent with all the qualitative and semiquantitative features of the Li^+ ion scattering data. For example, the changes in the surface threshold region in the $\langle 111 \rangle$ and $\langle 211 \rangle$ azimuths can be shown to be in good quantitative agreement¹¹ although the interpretation is complicated by the fact that these azimuths are not high symmetry directions for the reconstructed overlayer. In addition, the packing of the extra Cu atom row on the surface means that many new surface-subsurface angular thresholds will overlap in a polar angle ion scattering scan, leading to no clear new features but rather to a smearing of the clean surface features, exactly as seen in the data. Finally, we should remark that attempts to interpret the angular threshold changes in terms of N overlayer shadowing without reconstruction proved totally unsuccessful. Indeed, we have found in a parallel study of Cu(110)(2×1)-O surprisingly little evidence for substrate shadowing by adsorbed light atoms.¹⁰

One limitation of the Li^+ ion scattering technique with regard to investigating low atomic number adsorbates is that it is difficult to observe scattering from the adsorbate itself due to the presence of a strong inelastically scattered background from the substrate.¹⁶ He^+ scattering overcomes this problem, but at the expense of a new complication, namely trajectory-dependent neutralization which often makes quantitative structural assignments difficult.^{6,7} We have, however, taken polar angle scans of the $\text{He}^+ \rightarrow \text{N}$ scattering signal and find results which can most easily be reconciled with the structure shown in Fig. 2. In particular, angular scans in the $\langle 100 \rangle$ and $\langle 110 \rangle$ are rather similar to each other and indicate that lines of N atoms in these azimuths are not interrupted by Cu atoms. By contrast, in the $\langle 111 \rangle$ and $\langle 211 \rangle$ azimuths the angular scans indicate that the grazing angle behavior is far more strongly influenced by neutralization from nearby Cu atoms. These results are consistent with hollow site adsorption for the N atoms on the reconstructed Cu atom layer, while the persistence of the $\text{He}^+ \rightarrow \text{N}$ scattering

to grazing angles limited by N-N shadowing indicates that at least some of the adsorbed N atoms lie above (but probably not high above) this Cu layer. Further details of these $\text{He}^+ \rightarrow \text{N}$ scattering data are presented elsewhere.¹¹

IV. PHOTOELECTRON DIFFRACTION RESULTS AND DISCUSSION

The normal emission scanned energy mode N 1s photoelectron diffraction spectrum from the Cu(110)(2×3)-N surface is shown in Fig. 3. In this mode photoelectron diffraction provides a measure of the coherent interference between the directly emitted and elastically backscattered components of the photoelectron wavefield. This provides information on the location of these backscatterers, but under the conditions used here the dominant scatterers are those near neighbors most nearly directly behind the emitter relative to the collection direction, as demonstrated in several recent applications of the method by us.^{8,9,13,14,17} One consequence of this selective sensitivity is that if an emitter (adsorbate) lies close to coplanar with top layer substrate atoms, the normal emission photoelectron diffraction spectrum will have little sensitivity to the relative location of this top substrate layer. This effect is particularly clear in a recent

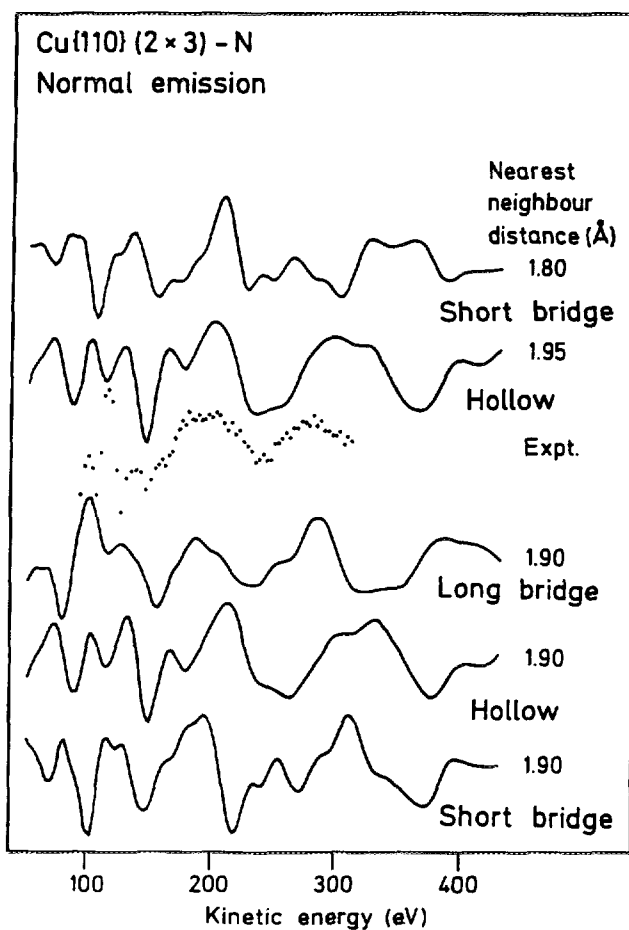


FIG. 3. Comparison of the N 1s normal emission scanned energy mode photoelectron diffraction data from Cu(110)(2×3)-N with the results of calculations based on adsorption sites on an ideally terminated Cu(110) surface.

study we have made of the Cu(110)(2×1)-O (Ref. 17) structure in which there is a general consensus that the O atoms lie within 0.3 Å of the top Cu atom layer. In the present case our initial attempts to understand the data involved calculations (curved wave, double scattering) of the photoelectron diffraction spectrum to be expected from various N chemisorbed sites on an *unreconstructed* Cu(110) substrate. Such an approach is not nullified by our demonstration in the previous section that there is a reconstruction, because the structure proposed in Fig. 2 is highly likely to involve N atoms close to coplanar with the reconstructed layer; in Cu(100)c(2×2)-N the N atoms lie almost exactly coplanar with the top Cu atom layer.¹⁵ These calculations are therefore of primary interest in establishing the overlayer-substrate lateral registry. In this context we should note that the ion scattering data presented above give no significant information regarding the registry of the reconstructed phase relative to the underlying substrate. The registry chosen in Fig. 2 is the one which allows the overlayer to adopt the smallest overlayer-substrate spacing in a simple hard-sphere model, but we have so far presented no experimental evidence to support (or refute) this aspect of the model.

In the lower half of Fig. 3 are shown the results of the model calculations for adsorption in the three main high-symmetry sites for emission from an adsorbed N atom on an ideally terminated Cu(110) surface, in each case assuming that the Cu-N nearest-neighbor distance is 1.90 Å, the value in the bulk compound Cu₃N. Clearly, with these constraints, the long bridge site gives the best fit, although the correspondence of the fine structure between theory and experiment is not particularly good (far worse, for example, than for a similar comparison for the Cu(110)(2×1)-O structure in which O occupies this long bridge site¹⁷). In the upper half of the figure are shown the results of calculations in which the value of the Cu-N bond length has been varied to improve the fit for the other sites. The fit for the short bridge site remains poor, but theory-experiment agreement of comparable quality to that found for the long bridge site can be achieved in the hollow site by a modest lengthening of the bond. Note, incidentally, that in this site the nearest neighbor is actually the Cu atom directly below the hollow in the second layer; for this reason, calculations for the other high symmetry site, atop, are essentially identical to those for the hollow at the same nearest-neighbor distance.

In the absence of the ion scattering data it would be tempting, on the basis of Fig. 3 alone, to suggest that N is simply chemisorbed onto an unreconstructed Cu(110) surface in the long bridge site. The most obvious objection to this view is it provides no rationale for the rather large (2×3) mesh which forms. One possible variant on this model which encompasses the proposals of Kuwahara *et al.* for Ni(110) (Ref. 2) and Heskett *et al.* for Cu(110) (Ref. 1) is that N is, indeed, adsorbed in long bridge sites at a spacing of 1.9 Å, but this site is opened up by lateral distortions of the surface Cu atoms to allow the N to fall 0.6 Å and become coplanar with the top Cu atom layer, thus achieving a local bonding geometry very similar to that in bulk Cu₃N. These distortions could lead to a larger surface mesh and be consistent with the general expectation of reconstruction, although it

remains unclear as to why the surface mesh should be specifically (2×3). Unfortunately, calculations of the photoelectron diffraction for this structure give poor agreement with the experimental data;¹⁸ this model is therefore inconsistent with both the ion scattering and photoelectron diffraction results.

Returning to the distorted square overlayer reconstruction model of Fig. 2, we note that in the overlayer-substrate registry shown in this figure there are three different N sites relative to the underlying substrate. Of the four N atoms per unit mesh one lies atop a second layer atom, one lies in a long bridge site, and two lie at equivalent sites midway between atop and long bridge. In view of the fact that the best agreement in Fig. 3 is for long bridge and hollow (the latter equivalent to atop as explained above) we see that this structure also offers promise in accounting for the photoelectron diffraction data. One complication in pursuing this idea further is that with three different local sites relative to the substrate we should, in principle, investigate different possible layer spacings for each of these sites. As the actual measured spectrum is an incoherent sum of the emission from these three sites it is clear that not only is there a large parameter space to be explored, but also the sensitivity of the fit (particularly to just one experimental spectrum) is unlikely to be sufficient to allow a convincing and unique determination of all the parameters. We have therefore taken a rather more realistic approach with the objective of simply establishing (or otherwise) the essential consistency of our structural model. Firstly, we note that with the reconstructed layer-to-substrate registry of Fig. 2 the variation in the layer spacing of the different Cu atoms in the overlayer to those in the substrate is rather small, at least in a simple hard-sphere model. If we assume that the N atoms in each of the hollow sites lie in the plane defined by their Cu overlayer nearest neighbors (producing a local geometry similar to that in Cu₃N), then the layer spacing variation of the N atoms relative to the substrate is even smaller. We first assume, therefore, that the layer spacings of all N atoms relative to the substrate are identical. The results of calculations based on this model (neglecting the role of scattering from Cu atoms in the reconstructed overlayer) are shown as the lower curve in Fig. 4 for a N-to-top substrate layer spacing of 1.95 Å which aligns the main peaks in the experimental data rather well. Interestingly, the alignment of peaks in the fine structure between this theoretical curve and the experimental data is substantially better than in any of the fits of Fig. 3, although the overall impression of the fit is worse because the fine structure is more clearly resolved, and some of the relative intensities match poorly. Nevertheless, the level of agreement is certainly encouraging. This 1.95-Å layer spacing corresponds to a (entirely reasonable) nearest-neighbor distance relative to the top substrate layer of 1.95 Å for the N atom lying atop a substrate atom, but longer values for the other sites, and particularly for the long bridge site. In the long bridge site the Cu-N nearest-neighbor distance within the overlayer is around 1.86–1.90 Å (depending on the exact layer spacing of the overlayer Cu atoms) but this site lies some 1.3 Å above the site which would bring it into close coordination with the underlying substrate. One variation

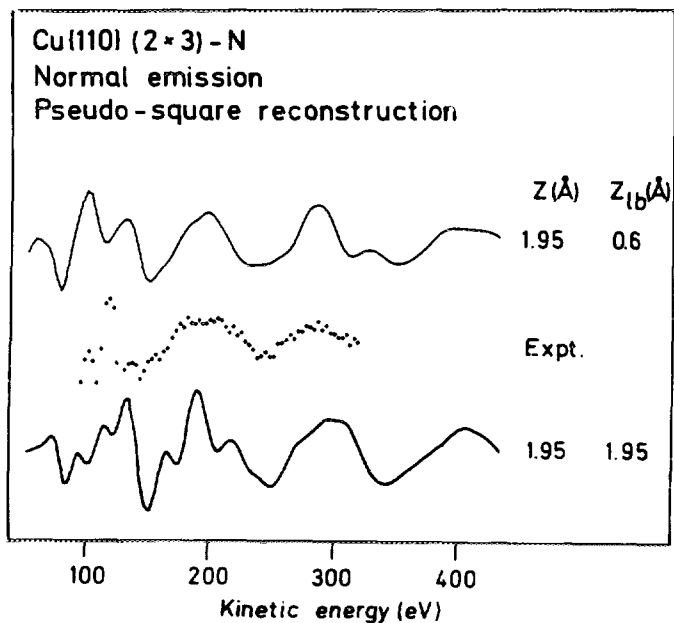


FIG. 4. Comparison of the same photoelectron diffraction data as in Fig. 3 with the results of calculations based on the pseudo-square reconstruction model of Fig. 2. The parameters z_{1b} and z are the layer spacings relative to the top Cu substrate layer of the N atoms in the long bridge site, and of the remaining N atoms.

on the constant N layer spacing model is therefore to allow the N atoms above the long bridge sites to drop down to a much lower spacing to bond to the underlying Cu substrate. The upper curve of Fig. 4 provides an illustration of the fit achieved in this way, the N above the long bridge site being lowered to 0.6 Å above the top substrate layer (nearest-neighbor distance 1.90 Å), while the other N atoms remain 1.95 Å above the substrate. Using this model the sharp fine structure is lost and the overall agreement is at least as good as for adsorption on a simple unreconstructed substrate as seen in Fig. 3.

We have not attempted significant refinement of the parameters of this model because of the likely problems of uniqueness described above. Nevertheless, the photoelectron diffraction results provide clear supporting evidence for the reconstruction model of Fig. 2 derived from the ion scattering results, and in particular, support the specific overlayer-substrate registry depicted in this figure. They also indicate that most of the N atoms in this structure are close to coplanar to the top reconstructed Cu atom layer, although one quarter of these atoms may penetrate through this layer to bond to the underlying substrate.

V. CONCLUSIONS

The combination of low-energy ion scattering and scanned energy mode normal emission photoelectron diffraction has allowed us to define many of the structural parameters of the rather complex Cu(110) (2×3)-N surface. In particular, Li^+ ion scattering provides clear evidence for a reconstruction of the top Cu atom layer to a pseudo-square array which must be achieved by the addition of one Cu atom

row for each 3 Cu atom rows in the original Cu(110) surface. The (2×3) reconstruction can then be understood in terms of alternate N filling of hollow sites within this overlayer to produce a surface phase which, but for a 6% distortion along $\langle 100 \rangle$ is essentially identical to the Cu(100) $c(2 \times 2)$ -N structure. He^+ ion scattering data provides supporting evidence for these hollow adsorption sites. Photoelectron diffraction data have then been used to provide confirmation of this structure and, in particular to define the lateral registry of the overlayer relative to the substrate. Although some fine details of the N-substrate spacings of this structure remain undefined, the photoelectron diffraction results also support N adsorption sites having Cu-N nearest-neighbor distances (and local coordination) very similar to those found in the bulk compound Cu_3N . It is also interesting to note that a very recent study of this adsorption structure by XPS¹⁹ (published since the submission of the original manuscript of this paper), concludes that the N coverage of the (2×3) structure is 0.66 ML, consistent with our model.

Although both this structure and that of the Cu(100) $c(2 \times 2)$ -N phase do involve local coordination similar to the bulk nitride, it is clear from the formation of this near-square overlayer on the lower symmetry rectangular mesh substrate that this geometry must produce a particularly low surface energy structure to compensate for the probable excess interfacial energy involved in this mismatch.

ACKNOWLEDGMENTS

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