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Nitrogen adsorption and thin surface nitrides on Cu(111) from first-principles

Aloysius Soon ^{a,*}, Lindee Wong ^a, Michael Lee ^a, Mira Todorova ^{a,1}, Bernard Delley ^b, Catherine Stampfl ^a

> ^a School of Physics, The University of Sydney, Sydney, New South Wales 2006, Australia ^b Paul-Scherrer-Institut, CH-5232, Villigen PSI, Switzerland

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Abstract

Experimental studies of nitrogen adsorbed on a Cu(111) surface show that the surface layer undergoes a reconstruction to form a pseudo-(100) structure. We use *ab initio* techniques to demonstrate the theoretical stability of this reconstructed surface phase over a range of conditions. We systematically investigate the chemisorption of N on the Cu(111) surface, from 0.06 to 1 ML coverage. A peculiar atomic relaxation of N atoms for 0.75 ML is identified, which results in the formation of a (metastable) "N-trimer cluster" on the surface. We have also investigated surface nitride formation, as suggested from experiments. A surface nitride-like structure similar to the reported pseudo-(100) reconstruction is found to be highly energetically favored. Using concepts from "*ab initio* atomistic thermodynamics", we predict that this surface nitride exists for a narrow range of nitrogen chemical potential before the formation of bulk Cu₃N. © 2007 Elsevier B.V. All rights reserved.

Keywords: Density functional calculations; Nitridation; Surface structure; Morphology; Copper; Nitrogen; Surface thermodynamics; Surface nitrides

1. Introduction

An understanding of the interactions between metal surfaces and gases is important for the development of new and improved catalysts, since the adsorption of atoms on the surface may modify the chemical properties and thus the reactivity and selectivity. Copper-based catalysts are used in methanol synthesis [1], the reduction and decomposition of nitrogen oxides [2–4], and the oxy-dehydrogenation (i.e. oxidation) of ammonia [5,6]. With regard to the latter, it is reported [6] that partial and total oxidation of NH₃ are catalyzed by Cu₂O and CuO, respectively, at a total pressure of 1.2 mbar. For a lower total pressure of

* Corresponding author.

0.4 mbar, deactivation of the catalyst occurs which is attributed to nitride formation. However, Ref. [5] reports that Cu_2O itself does not promote the reaction of oxy-dehydrogenation of NH₃, but rather Cu_3N or a mixed Cu_3N/Cu_2O surface with adsorbed oxygen ontop, which are the active species, acts as the catalyst. Thus, the intricate role and interaction of nitrogen species on Cu surfaces is still unclear and this has motivated recent experimental studies of N adsorption on Cu surfaces, e.g., Refs. [7–11].

With regard to nitrogen adsorption on Cu(111), with which the present paper is concerned, experimental evidence shows that a pseudo-(100) surface phase forms, with nitrogen adsorbed in a $c(2 \times 2)$ configuration in the fourfold-hollow sites of the pseudo-(100) reconstruction [7–10,12–15]. Relative to an ideal (100) surface, this pseudo-(100) structure is believed to be distorted by (1.04 $d \times$ 1.01d), where d is the nearest neighbor distance in the Cu bulk [12]. Pseudo-(100) surface reconstructions have also been reported for other systems, e.g., S on Ni(111) and C on Ni(111) [15].

E-mail addresses: aloysius@physics.usyd.edu.au (A. Soon), stampfl@ physics.usyd.edu.au (C. Stampfl).

¹ Current address: Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany.

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Despite these experimental studies, the chemical and physical properties of the N/Cu(111) system are not well understood. A scanning tunneling microscopy (STM) study has proposed that the above-mentioned pseudo-(100) phase forms a $(25 \times 7\sqrt{3})$ rectangular coincidence mesh on the (111) substrate [14], while another STM study showed little long range order and argued that this $(25 \times 7\sqrt{3})$ rectangular unit cell is unlikely [10]. Furthermore, there has been debate as to the number of Cu layers involved in the reconstruction. A recent study using medium energy ion scattering suggests that only the outermost copper layer undergoes reconstruction [7], while earlier studies had proposed two Cu-layers are involved [8].

Under ambient temperatures and pressures, molecular nitrogen does not interact with Cu surfaces, due to the strong nitrogen–nitrogen bond. Experimentally, the adsorption of N on Cu surfaces has been achieved typically by nitrogen ion bombardment [11,14].

Density-functional theory (DFT) calculations for $\frac{1}{6}$ monolayer (ML) coverage of nitrogen on a Cu(111) surface shows that the most favorable adsorption site is the fcc site [16]. The fcc site has also been shown to be most favorable for oxygen adsorption on Cu(111) [17]. Furthermore, Ref. [16] reported that the "binding energy of N on the reconstructed pseudo-(100) surface at the fourfold-hollow site is 0.59 eV larger than that on Cu(111), and 0.45 eV lower than adsorption on Cu (100)". We note, however, that in this work no further details were given regarding the atomic structure of the reconstructed pseudo-(100) surface assumed nor the N coverage used.

This paper presents a first-principles DFT investigation of nitrogen adsorption on Cu(111) for coverages 0.06– 1.0 ML, including structures similar to the experimentally reported reconstructed pseudo-(100) surface, as well as subsurface adsorption of nitrogen. For all the structures considered, we investigate the atomic and electronic properties, and determine their relative stability.

2. Calculation methodology and structures considered

The DFT calculations are performed with the DMol³ code, using the generalized gradient approximation (GGA) for the exchange-correlation functional due to Perdew, Burke and Ernzerhof (PBE) [18]. DMol³ is a numerical DFT implementation which uses a highly efficient local orbital basis set to perform the calculations. Further details about the code can be found elsewhere [19,20].

The Cu(111) substrate is modeled using a supercell, with nitrogen coverage on both sides of a seven atomiclayer slab. The vacuum region between repeated slabs is 25 Å. The double numerical basis set with polarization functions (DND) and a real-space cut-off of 9 Bohr are used for all calculations. Brillouin-zone integrations are performed using a $(12 \times 12 \times 1)$ Monkhorst-Pack grid for the (1×1) surface unit cell and a $(6 \times 6 \times 1)$ grid for that of a (2×2) surface cell. These parameters were chosen to ensure that calculated energies are well converged, with an estimated numerical uncertainty less than 1 mHa (0.027 eV).

We firstly consider nitrogen adsorbed on the unreconstructed Cu(111) surface in a (2×2) surface unit cell. For all calculations we relax all atoms until the forces are less than 0.3 mHa/Bohr (0.015 eV/Å). This surface has two high symmetry threefold hollow sites: the fcc and the hcp site. These two hollow sites differ as follows - a nitrogen atom in the fcc site is located above a copper atom of the third atomic layer, while in an hcp site, it is above a copper atom of the second atomic layer. We calculate the binding energy per nitrogen atom for these two sites at coverages of 0.25, 0.5, 0.75 and 1 ML. In addition, the binding energy at low coverages of $\frac{1}{9}$ ML and $\frac{1}{16}$ ML are calculated for the fcc site with (3 × 3) and (4 × 4) supercells, respectively, using $(4 \times 4 \times 1)$ and $(3 \times 3 \times 1)$ k-point grids. The binding energy of N is also determined for the bridge site at coverage of 0.25 ML in order to estimate the diffusion energy barrier of nitrogen on this surface.

We also consider N adsorption at three high-symmetry subsurface sites between the first and second Cu layers, namely, the octahedral (octa) and the two tetrahedral (tetra I and tetra II) sites. In the octa site the N atom is located below the on-surface fcc site and is sixfold coordinated to Cu atoms in the first and second layer. In the tetra I site, the N is found below the on-surface hcp site and is bonded to three Cu atoms in the first and one Cu atom in the second layer. The second tetrahedral (tetra II) site is directly below a first layer Cu atom and is bonded to this Cu atom and to the three Cu atoms below in the second layer. For subsurface adsorption, we consider coverages of 0.25, 0.5 and 1 ML.

To mimic the proposed $(25 \times 7\sqrt{3})$ reconstructed pseudo-(100) structure, we use two surface unit cells. The first and smaller is a rectangular surface unit cell $\begin{pmatrix} 2 & 0 \\ -1 & 2 \end{pmatrix}$ given relative to vectors of the Cu(111) primitive surface unit cell (see Fig. 1b and e). It contains four Cu atoms and two N atoms, thus the N coverage is 0.5 ML. We will refer to this configuration as the '4' structure, since the area of this cell is 4 times the area of the Cu(111) primitive surface unit cell. While the '4' structure has the same surface density of Cu atoms as a (111) layer, the experimentally proposed $(25 \times 7\sqrt{3})$ structure has a surface Cu density 82% of that of a Cu(111) layer [7]. To model this massive surface reconstruction, the unit cell has to consist of 288 Cu atoms and 144 N atoms in the reconstructed layer, with 350 Cu atoms in each Cu(111) layer. Considering this, the '4' structure is significantly strained with respect to both the bulk Cu₃N(100) surface and an ideal Cu(100) surface. The average strain² of this model '4' pseudo-cubic surface structure is -11.7%, relative to the surface unit cell vector of the ideal $Cu_3N(100)$ surface. When compared to that of

 $^{^2}$ The average strain is calculated by determining the area of the surface unit cell, dividing by the number of primitive unit cells of Cu(111) that it contains (i.e. four for the '4' structure, and 16 for the '16' structure), and taking the square root.



Fig. 1. Diagrams of pseudo-(100) reconstruction models: Top view of (a) the '16' structure, (b) the '4' structure for one Cu-layer reconstruction, and (c) the '4' structure for the two Cu-layer reconstruction [with the second layer highlighted as large dark (red) spheres]. (d), (e) and (f) show the corresponding side views of these structures. Large grey circles represent Cu atoms of the unreconstructed Cu substrate, N atoms are shown as small dark (blue) circles, and nitride-layer Cu atoms are represented by small grey (green) circles. The dashed lines indicate the surface unit cells. (For interpretation of the references in colours in Figs. 1–4,7–10 captions, the reader is referred to the web version of this article.)

the ideal Cu(100) surface, the average strain is -6.1%. Thus the stability of the '4' structure can be seen as a lower bound for the stability of the actual reconstructed surface. Using the same surface unit cell, we also considered the possibility of two Cu layers being reconstructed, as has been discussed in the literature [8]. This structure is shown in Fig. 1c and f.

The second surface unit cell that we use is larger, namely, a $\begin{pmatrix} 2 & 0 \\ -3 & 8 \end{pmatrix}$ cell and has a N coverage of $\frac{7}{16}$ ML. It will be referred to as the '16' structure, since the area of this cell is 16 times larger than the primitive Cu(111) unit cell. This structure has an average² strain of -5.2%, relative to the surface unit cell vector of the Cu₃N(100) surface, and +0.82% relative to that of the Cu(100) surface. This structure, which is depicted in Fig. 1a and d, is less strained and more closely resembles the $(25 \times 7\sqrt{3})$ geometry stronger. It can be noticed that there are 14 Cu atoms per surface unit cell in the reconstructed layer, but 16 Cu atoms in each Cu(111) layer of substrate. This gives a surface Cu density of 87.5%, with respect to a Cu(111) layer.

3. Results and discussion

3.1. The Cu(111) surface, bulk Cu and Cu_3N , and the N_2 molecule

We first consider bulk Cu, the clean Cu(111), bulk Cu_3N and the free nitrogen molecule. The calculated lattice

constant of bulk Cu (neglecting zero point vibrations) is 3.64 Å, which is in good agreement with the established experimental value of 3.61 Å [21]. The Brillouin-zone integration for bulk Cu is performed using a $(12 \times 12 \times 12)$ Monkhorst-Pack grid for the $(1 \times 1 \times 1)$ conventional cell with a real-space radius cutoff of 9 Bohr. The computed bulk modulus and cohesive energy (taking into account the spin-polarization energy for the free Cu atom) are 136 GPa and 3.45 eV, which are in excellent agreement with the experimental values of 137 GPa and 3.49 eV [21], respectively. The minor over-estimation of the lattice constant and the under-estimation of the bulk modulus are also observed in analogous studies of other transition metals determined from both the pseudopotential planewave method [22,23] and the FP-LAPW method [28,24,25]. The GGA-PBE functional is chosen for this study as it is known to generally yield a closer agreement to experiment than the local density-functional for Cu [28].

For the clean surface, the obtained inter-layer relaxations $\Delta_{ij} = (d_{ij} - d)/d \times 100\%$, between layers *i* and *j* with respect to the bulk spacing d = 2.10 Å, are $\Delta_{12} = -0.6\%$ and $\Delta_{23} = -0.1\%$ for the topmost layers. These results compare well with experimental values ($\Delta_{12} = -0.7\%$ and $\Delta_{23} = -0.3\%$) [26,27], and other DFT calculations [28,29]. The calculated work function for the clean surface is 4.79 eV, which is similar to the reported experimental value of 4.94 eV [30] and theoretical value of 4.78 eV (as obtained by the full-potential linearized plane-wave (FP-LAPW) method) [28]. The surface energy is calculated to be 0.52 eV per surface unit cell, which is in good agreement with other DFT-GGA (FP-LAPW) [28] and experimental [31] values of 0.50 eV and 0.63 eV, respectively.

Spin-unrestricted calculations using non-spherical densities are performed to study the nitrogen atom and molecule. To achieve high numerical accuracy, the real-space cutoff for the calculation is increased to 20 Bohr, with the largest basis set available in the DMol³ code. The binding energy of N₂ per N atom is calculated to be 5.19 eV, which is in good agreement with the experimental value of 4.90 eV [37]. The bond length and vibrational frequency are 1.11 Å and 2349.6 cm⁻¹ respectively, which compare very well with the reported experimental values of 1.10 Å and 2358.6 cm⁻¹, respectively [37].

The semiconductor, Cu₃N, crystallizes in the (anti-) ReO₃-type structure [32,33], which is an open cubic structure of Cu₆N octahedra that share their apex Cu atoms, with each Cu atom linearly coordinated to 2 N atoms. It is calculated to have a lattice constant (neglecting zero point vibrations) of 3.84 Å, which compares well with reported experimental and theoretical values of 3.81 Å and 3.82 Å, respectively [32]. The Brillouin-zone integration for bulk Cu₃N is also performed using a $(12 \times 12 \times 12)$ Monkhorst-Pack grid for the $(1 \times 1 \times 1)$ conventional cell with a real-space radius cutoff of 9 Bohr. The band structure is plotted in Fig. 2 with the crystal structure shown in the insert. The calculated indirect bandgap is 0.40 eV, which is slightly higher than other reported DFT-GGA and DFT-LDA values of 0.25 eV [32] and 0.23 eV [33], respectively, determined from the FP-LAPW method. However, the bandgap of Cu₃N is reported to be highly sensitive to slight changes in the lattice constant [32]. Thus our calculated bandgap falls inline with other theoretical results. The reported experimental bandgap ranges between 1.2 and 1.9 eV [34–36]. The bulk modulus is calculated to be 113 GPa, which is also in good agreement with the re-



Fig. 2. The band structure of Cu_3N . The calculated indirect bandgap is 0.40 eV. The atomic structure of Cu_3N is shown in the insert. The copper and nitrogen atoms are represented by large grey (green) and small dark (blue) circles, respectively.

ported theoretical value of 104 GPa [32]. The heat of formation of bulk Cu₃N is calculated as,

$$\Delta H_{\rm Cu_3N}^{\rm f} = E_{\rm Cu_3N} - 3E_{\rm Cu} - \frac{1}{2}E_{\rm N_2} \tag{1}$$

where total energies of bulk Cu₃N, bulk Cu and the isolated N₂ molecule are represented by E_{Cu_3N} , E_{Cu} and E_{N_2} , respectively. $\Delta H_{Cu_3N}^{f}$ is found to be +1.16 eV per formula unit, which is endothermic. Thus, with respect to the free nitrogen molecule bulk copper nitride is only metastable. Considering $\Delta H_{Cu_3N}^{f}$ relative to the *free N atom* however, yields a value of -4.03 eV per N atom.

3.2. On-surface and subsurface N adsorption

The calculated average binding energies with respect to the free nitrogen atom (per N atom), are presented in Fig. 3. The binding energy is calculated according the formula,

$$E_{\rm b}^{\rm N} = -\frac{1}{N_{\rm N}} \left(E_{\rm N/Cu} - E_{\rm Cu}^{\rm slab} - \Delta N_{\rm Cu} E_{\rm Cu} - N_{\rm N} E_{\rm N} \right) \tag{2}$$

where $N_{\rm N}$ and $\Delta N_{\rm Cu}$ are the number of nitrogen atoms in the surface unit cell and the difference in the number of Cu atoms between the N/Cu system and the clean surface slab. $E_{\rm N/Cu}$ is the total energy of the N/Cu system, $E_{\rm Cu}^{\rm slab}$ the energy of the clean slab, $E_{\rm Cu}$ the energy of a Cu atom in bulk Cu and $E_{\rm N}$ the energy of a free nitrogen atom. The term $\Delta N_{\rm Cu}E_{\rm Cu}$ will only be required when the total number of Cu atoms on the surface is different to that of the clean substrate, as is the case for the '16' structure. A



Fig. 3. Calculated binding energies of nitrogen on Cu(111) in the onsurface and subsurface sites, for various coverages. Also shown is the binding energy of the '4' structure for one Cu layer (marked as a darker grey cross) and two Cu layers (marked as a lighter grey cross) reconstructions, and the '16' reconstruction (marked as a black cross). The solid and dashed lines connecting the calculated binding energies are used to guide the eye.

positive binding energy indicates that the adsorption is exothermic.

At a coverage of 0.25 ML, the fcc-hollow site is slightly more favorable than the hcp-hollow site, with a binding energy difference of 0.12 eV. As the coverage increases, the binding energy at the fcc- and hcp-hollow sites decreases, indicating an increasingly repulsive interaction between the adsorbates. To correlate this trend and the surface geometry, we examine the structural properties of N adsorbed on Cu. Table 1 lists average bond lengths between adsorbed N and the neighboring Cu atoms, as well as inter-layer spacings between the outer Cu layers. It can be seen that bond length increases with coverage. Exception is the 0.75 ML structure, which forms a kind of a "N₃ cluster". This structural trend indicates that the bond strength peaks at a low coverage, implying that the most stable structure for fcc-hollow site adsorption is reached at a coverage of 0.25 ML, mirroring the conclusions from binding energy calculations. d_{23} is the same, or very close to, the calculated bulk inter-layer spacing, for all coverages. This shows that nitrogen adsorption affects, at most, the second layer of Cu atoms.

It is interesting to note that at 0.75 ML, both the hcpand fcc-hollow sites show an unexpected increase in E_{μ}^{1} \sim 0.3 eV larger than adsorption in the fcc site at 0.5 ML coverage. This peculiarly high $E_{\rm b}^{\rm N}$ is due to the clustering of three N atoms. Upon relaxation, N atoms adsorbed initially at the hcp site move to the neighboring bridge sites (direction shown by arrows in Fig. 4), forming the triangular "N₃ cluster" above the adjacent fcc site, and vice-versa for N adsorption initially at the fcc site. When comparing the binding energies of the optimized structures at 0.75 ML, adsorbing N initially at the hcp site is only found to be slightly more energetically favorable than that at the fcc site, by only 0.06 eV. Examining the Mulliken charges (with respect to atomic nitrogen) at this coverage reveals that there is almost negligible excess charge for the "N₃ cluster", which is somewhat unexpected, as the commonly known azide molecular anion, N_3^- has a linear geometry and is typically charged [39]. The N-N bond length in this "N₃ cluster" is calculated to be 1.43 Å, which is longer than the calculated value for a N_2 molecule (1.10 Å) and the azide ion (1.17 Å) [39]. This prompts us to investigate whether the energy gained in N binding energy is mainly due to N-N interactions or the "N₃"-substrate interaction.

To see how strongly bound this " N_3 cluster" is to the surface, we investigate the interaction energy calculated by,

$$E_{\rm b}^{\rm N_3} = -\frac{1}{N_{\rm N_3}} (E_{\rm N_3/Cu} - E_{\rm Cu} - N_{\rm N_3} E_{\rm N_3})$$
(3)

where N_{N_3} is the number of "N₃ clusters" (which is one since we use the (2 × 2) surface unit cell), and total energies of the adsorbate–substrate system, clean surface and energy of the N₃ cluster are represented by $E_{N_3/Cu}$, E_{Cu} and E_{N_3} , respectively. The atomic positions of the N₃ cluster are kept fixed (using the same supercell) at the positions obtained for the adsorbate–substrate system to largely cancel

urface structures (Θ)	fcc (0.06 ML)	fcc (0.11 ML)	fcc (0.25 ML)	fcc (0.50 ML)	fcc (0.75 ML)	fcc (1.00 ML)	octa (0.50 ML)	'4' (0.50 ML)	'16' (0.44 ML)
N-n2	1.85	1.85	1.84	1.86	2.30	1.92	1.98	1.86	1.85
5	1.04	1.06	1.01	1.03	1.90	1.21	1.15	I	I
42	I	I	I	I	I	I	1.38	I	I
	I	I	I	I	I	I	I	2.48	2.36
2	2.10	2.11	2.12	2.14	2.08	2.18	2.55	2.10	2.10
5	2.10	2.10	2.09	2.09	2.10	2.10	2.12	2.10	2.10
N/Cu	3.78	3.75	3.82	3.12	3.37	2.13	3.16	3.50	4.35

Cu₃N is 1.92



Fig. 4. (a) N atoms at the hcp-hollow site before relaxation and (b) the "N₃ cluster" at the fcc site after relaxation. Large grey circles represent the Cu atoms of the Cu(111) substrate, and the small (blue) circles the N atoms. The surface unit cell is indicated, and the white arrows indicate the direction of the N atom's movement upon relaxation.

out lateral interactions. The resulting binding energy then reflects the "N₃ adsorbate"-Cu(111) binding energy. We obtain a value of 1.06 eV (or 0.353 eV per N atom) which indicates that the "N3 molecule" is weakly chemisorbed on the surface and the significant gain in binding energy at this coverage is due to formation of inter-nitrogen atomic bonds. These inter-nitrogen bonds amount to 3.105 eV/ N, i.e. for the free "N₃ cluster" (with fixed N positions as obtained for the adsorbate-substrate system). We also optimized the structure of this cluster, performing spinpolarized and non-spin-polarized calculations and found the N-N bond lengths reduce slightly to 1.36 Å. The binding energy per N atom is 3.164 eV, which is lowered to 3.236 eV for the case of the spin-unrestricted calculation, where the cluster has a magnetic moment of $1 \mu_{\rm B}$ $(0.333 \,\mu_{\rm B}$ on each N atom). However, upon adsorption on the surface, this magnetic moment is quenched. Hence compared to the binding energy of the free N₂ molecule (5.19 eV/N), the N–N binding in the " N_3 cluster" is weaker, as reflected by the bond lengths. We would like to highlight the possiblity that DFT-GGA overestimates the binding energies of molecules on surfaces compared to atomic adsorption. By taking into account that the N₂ molecule is overbound by 5.92% (i.e. the difference between the experimental and theoretical DFT-GGA binding energy), we verified that even with a reduction of the binding energy of the "N₃ cluster" on the surface by 5.92%, the calculations still predict the relative stability of this structure

and a more favorable binding energy at the 0.75 ML than at 0.5 ML.

To estimate the mobility of N atoms on the surface, the diffusion barrier is approximated as the difference in binding energy of N at the bridge site and that at the fcc-hollow site. This energy barrier at 0.25 ML is found to be 0.29 eV, which is lower than that of O on Cu (111) at the same coverage (0.40 eV) [17]. This could be due to the lower binding energy of N on Cu (by 0.87 eV at coverage 0.25 ML), as compared to O on Cu [17].

It is evident that the binding energies of subsurface N are less favorable than the on-surface hollow site structures at coverages 0.25 and 0.75 ML. For 0.5 ML, however, the octa site is marginally more favorable by 0.04 eV. At 1 ML coverage, the energetically preferred site is below the surface. Subsurface adsorption sites are also preferred for 1 ML O adsorption on Cu(111) [17].

3.3. Reconstructed pseudo-(100)-like structures

From Fig. 3 it can be seen that both the one and two layer '4' structure are more favorable than on-surface or subsurface adsorption at the same coverage of 0.5 ML, where the latter is less favorable than the former. However, clearly, the '16' structure has a considerably stronger binding energy than all of the structures considered. The binding energy difference between the '16' structure and the octa site is 1.19 eV. If a calculation is to be performed for the actual proposed $(25 \times 7\sqrt{3})$ pseudo-(100) reconstructed surface, we expect the binding energy for this structure would be greater than that for the '16' structure, since any unfavorable strain contained in the '16' structure could be better relieved in the actual phase. The binding energy of this model can be seen as a lower bound for the binding energy of the actual pseudo-(100) reconstruction.

The structural properties of the surface nitride-like structures are also shown in Table 1. $d_{N'1}$ is defined as the distance between the middle of the reconstructed surface layer and the underlying Cu(111) substrate. It can be seen that the '16' structure is bonded closer to the substrate when compared to the '4' structure. In addition, it is also clear that the coupling strength of this thin surface nitride-like layer is enhanced by an "anchoring" to the substrate via N_L atoms in the '16' structure (see Fig. 1d). The one and two Cu-layer '4' structures are anchored rather differently: The one Cu-layer '4' structure has its reconstructed layer bonded to the underlying Cu(111) substrate via a Cu atom (see Fig. 1e), producing an alternating 'valley-and-hill' structure. The reconstructed layer of the two Cu-layer '4' structure is also further distorted by half the surface nitrogen atoms forming bonds with the second pseudo-(100) Cu layer, resulting in a buckled 'sawtooth'like configuration (see Fig. 1f). This large distortion to the surface structure could well explain why the one Culayer '4' structure is slightly more energetically favored than the two Cu-layer '4' structure. This gives support to

the experiments reporting that only one Cu-layer is reconstructed [7].

3.4. Electronic properties

The electronic structure of N adsorbates on Cu is now presented. The calculated change in work function, with respect to a clean Cu(111) surface, and surface dipole moment as a function of N coverage in the fcc-hollow site is displayed in Fig. 5. $\Delta \Phi$ increases with coverage, due to the build-up of electronegative N atoms on the surface as the coverage increases. The surface dipole moment, μ (in Debye) is evaluated by the Helmholtz equation,

$$\mu = \frac{A\Delta\Phi}{12\pi\Theta},\tag{4}$$

where A is the area in Å² per (1×1) surface unit cell, and $\Delta \Phi$ is the work function change in eV. The work function is defined as being the difference between the electrostatic potential in the vacuum and the Fermi energy of the slab.

The surface dipole moment is found to decrease with increasing coverage. This can be understood by considering the electron transfer process between adsorbate and substrate atoms: There is a substantial electronegativity difference between N and Cu (3.04 - 1.90 = 1.14) [37], so electrons are transferred (or part thereof) from the Cu to N atoms. However, with increasing coverage, there will be a repulsive interaction among the partially negatively charged N atoms. To counter this repulsion, there will be



Fig. 5. Calculated work function change (relative to the clean Cu(111) surface) $\Delta \Phi$ (top) and surface dipole moment μ (bottom) as a function of coverage for N in the fcc-hollow site. The dashed lines indicate continuation of the trend for similarly bonded structures. For comparison, the work function change and surface dipole moment of the '16' structure (at $\frac{7}{16}$ ML coverage) are marked as a cross on the respective plots.

a partial charge transfer of electron density back to the substrate, thus decreasing the surface dipole moment.

The work function change and surface dipole moment values at 0.75 ML do not follow this overall trend due to the clustering of N atoms. In order to lower the repulsive effect when the N atoms come together to form clusters, there is a reduction of electron density around the N atoms. This depolarization of electron density is reflected in the almost negligible excess Mulliken charge on the N atoms, and thus a significant drop in μ is expected. Correspondingly, $\Delta \Phi$ also decreases at 0.75 ML.

The work function change and surface dipole moment for the '16' structure at $\frac{7}{16}$ ML coverage is calculated to be 0.32 eV and 0.11 D, respectively. For comparison, the change in work function for the fcc site on-surface nitrogen adsorption at a coverage of 0.5 ML is 2 eV which is almost six times as large as that for the '16' surface nitride-like structure. This drastic lowering of the work function change is due to the location of N atoms which are "quasi-embedded" in the reconstructed Cu layer. This affords a much better screening for the partially negatively charged nitrogen atoms, but moreover, it results in a notably smaller component of the surface dipole moment perpendicular to the surface, resulting in a much lower work function change. This effect is also inline with other reports of surface oxide-like formation on metals [23].

Fig. 6 presents difference electron density distributions for both the chemisorbed and surface reconstruction phases, in a plane perpendicular to the surface. This quantity is calculated as

$$n^{\Delta}(\mathbf{r}) = n^{N/Cu}(\mathbf{r}) - n^{Cu}(\mathbf{r}) - n^{N}(\mathbf{r}).$$
(5)



Fig. 6. Side view (perpendicular to the Cu(111) surface) of the difference electron density of (a) the 0.5 ML fcc structure, (b) the '4' reconstruction (Fig. 1b and e) and (c) the '16' reconstruction structures (Fig. 1a and d). The dashed lines represent charge depletion and the solid lines represent charge accumulation. The lowest positive contour line is at 0.001 electron Bohr⁻³, while the highest negative contour line corresponds to a value of -0.001 electron Bohr⁻³. In between, the electron density changes successively by a factor of $10^{\frac{1}{3}}$ electron Bohr⁻³.

Here $n^{N/Cu}$ is the total electron density of the substrate/ adsorbate system, from which the electron density of both the clean surface, n^{Cu} , and that of the corresponding isolated nitrogen adlayer, n^{N} , are subtracted. The positions of the pure Cu surface and nitrogen atoms are taken to be the ones of the relaxed adsorbate system. For both the on-surface 0.5 ML phase and one Cu-laver '4' structure, the impact of the N atom is localized to the N atom itself, and the nearest Cu atoms. For the '16' structure, there are two N atoms, corresponding to N_L, located at the interface between the reconstructed layer and the substrate and thus affect Cu atoms in both the reconstructed layer and the first layer of the unreconstructed Cu(111) slab. The electron densities of nearest neighbor Cu atoms are depleted, while the electron densities of N atoms are enhanced, reflecting the large electronegativity of N. The accumulation of electron density on the vacuum side of the surface for N in the fcc site results in an inward pointing surface dipole moment, and a large positive $\Delta \Phi$, as shown in Fig. 5. From the difference electron density plot, and Fig. 1, we can observe that the '16' surface reconstruction is anchored to the Cu slab through the interaction of $N_{\rm L}$ with the underlying Cu atom, while for the '4' structure, the surface reconstruction is linked to the slab through Cu atoms.

Projected density of states (pDOS) are presented in Figs. 7–9. In all cases, we observe a renormalization of N energy levels to lower energies and a hybridization between N-2p and Cu-3d orbitals. The decreasing stability of N in the fcc-hollow site as coverage increases is reflected in the lower occupancy of the bonding states at higher coverage (see Fig. 7). We define the (estimated) center of the Cu-3d band as the weighted center of the occupied Cu-3d states (i.e half the integrated pDOS from the bottom of the band up to the Fermi level). With increasing N coverage at the fcc site, the center of the Cu-3d states moves to lower energy (with the exception of 0.75 ML). This is a reflection of an increased Cu-N coordination and interaction with increasing N coverage. From Fig. 7c, which shows the pDOS for the "N₃"-like cluster, it can be seen that the Cu-3d bands are significantly narrowed when compared to that at other coverages. This is attributed to a lowering of coordination of the surface Cu atoms (as opposed to those at other coverages), with the vertical distance between the N atoms and the first Cu layer increased to 1.9 Å (see Table 1). In addition, more molecular-like N-related features are also seen at -5 eV and -6 eV and the relatively weak interaction (hybridization) of the "N3 cluster" with the surface can be noticed.

Fig. 8a shows the pDOS for N in the hcp site for 0.75 ML coverage. The results are very similar to those of fcc adsorption at the same coverage (compare to Fig. 7c). The close resemblance of the pDOS is a consequence of the very similar atomic structures and binding energies. This also reflects the diminished role the Cu substrate plays, as the strong N–N bond formed in the cluster is seen to be more important than the coupling of these clusters to the Cu substrate. We can also compare the



Fig. 7. Electronic density of states for (a) 0.25 ML, (b) 0.5 ML, (c) 0.75 ML and (d) 1.0 ML fcc-hollow N adsorption. The dark (blue) continuous line represents the Cu-3d states and the dashed (red) lines represent N-2p states. In (c), the dark (blue) continuous line represents Cu states from non-bonded Cu atoms (i.e. $Cu_{(1)}$ 3d) and the lighter (green) continuous line represents Cu states from Cu atoms bonded to N atoms (i.e. $Cu_{(2)}$ 3d) (see Fig. 4b). The vertical dot-dash (orange) line is the estimated Cu-3d band center.

pDOS for 0.5 ML adsorption at the subsurface octa site, Fig. 8b, with the 0.5 ML fcc adsorption in Fig. 7b. The slightly greater stability of nitrogen at the octa site, than the fcc-hollow site, is reflected in the shifting of the N-2p states to lower energies, a higher occupancy of N-2p bonding states at the octa site, as well as a slightly lower DOS at the Fermi level in Fig. 8b. The pDOS for the octa site also shows narrowing of the Cu-3d band for the surface Cu atoms, due to reduced coordination.

Fig. 9 shows the pDOS for the '16' structure and bulk Cu_3N . The result for the '16' structure shows broadening and splitting of the N-2p bonding states and greater occupancy of the N-2p bonding states than the anti-bonding



Fig. 8. Density of states for (a) the 0.75 ML hcp-hollow N adsorption and (b) 0.5 ML octahedral subsurface adsorption. The dark (blue) continuous line represents the Cu-3d states, the dashed (red) lines represent N-2p states. In (a), the dark (blue) continuous line represents the Cu-3d states from Cu atom 1 (i.e. $Cu_{(1)}$ 3d) and the continuous lighter (green) line represents Cu-3d states from Cu atom 2 (i.e. $Cu_{(2)}$ 3d) (see Fig. 4b). In (b), the dark (blue) continuous line represents the Cu-3d states of second atomic layer Cu (i.e. Cu_{2L} 3d) and the lighter (green) continuous line represents a top layer Cu atom (i.e. Cu_{1L} 3d).

states. There is also a greater hybridization of the N-2p bonding states with Cu-3d states (between the energy range of -7.5 to -4.5 eV), compared to other structures discussed above. The pDOS for bulk Cu₃N in Fig. 9a shows the Cu-3d states are more distinctly split than those of the pseudo-(100) '16' structure. The N-2p states are also shifted from the Fermi level to a greater extent than the '16' structure. There is a characteristic peak which appears in Fig. 9a at -1.4 eV which also appears in the surface reconstruction pDOS. Having a close resemblance of the pDOS between the bulk nitride and the '16' structure is an indication that these ultrathin surface nitrides could well be a precursor phase before onset of the formation of the bulk material. This similar behavior is observed for the O/Cu(111) system [17] where the bulk oxide formation is suggested to be assisted by the formation of a series of surface oxide structures. However, one striking difference is that this pseudo-(100) reconstructed surface nitride is formed in the [100]-direction on the Cu(111) surface, whereas the surface oxides form in the [111]-direction which takes after the crystal surface direction of the substrate.

3.5. Ab initio atomistic thermodynamics

Using concepts from "*ab initio* atomistic thermodynamics" [38] we determine the relative stability of the considered structures over a range of chemical potentials for the



Fig. 9. Density of states for (a) bulk Cu₃N, (b) the '16' structure at Section 1 (see Fig. 1d) and (c) the '16' structure at Section 2 (see Fig. 1d). The dark (blue) continuous line represents the Cu-3d states, the dashed (green) lighter and darker (red) lines represent N-2p states. In (b), the lighter (green) dashed line represents N_U and the darker (red) dashed line represents N_L and the lighter (green) dashed line represents N_L and the lighter (green) dashed line represents N_U (see Fig. 1d). Small black arrows are used to indicate the characteristic peak for both the bulk nitride and the reconstructured surface structure.

nitrogen atom. In particular, we calculate the Gibbs free energy of adsorption,

$$\Delta G(T,p) = \frac{1}{A} \left(G_{\mathrm{N/Cu}} - G_{\mathrm{Cu}}^{\mathrm{slab}} - \Delta N_{\mathrm{Cu}} \mu_{\mathrm{Cu}} - N_{\mathrm{N}} \mu_{\mathrm{N}} \right) \tag{6}$$

where $G_{\rm N/Cu}$ and $G_{\rm Cu}^{\rm slab}$ are the Gibbs free energies of the N/ Cu system and the clean surface, respectively. A is the surface area and $\mu_{\rm N}$ and $\mu_{\rm Cu}$ are the chemical potentials of the nitrogen and copper atoms. The number of nitrogen atoms and the difference in the number of Cu atoms between the N/Cu system and clean surface are represented by $N_{\rm N}$ and $\Delta N_{\rm Cu}$, respectively. The term $\Delta N_{\rm Cu}\mu_{\rm Cu}$ represents the cost of interchanging the Cu species with a reservoir of Cu atoms with chemical potential $\mu_{\rm Cu}$. This reservoir is taken to be bulk Cu, with which the surface is assumed to be in equilibrium. For more details, we refer to Refs. [17,38]. By incorporating Eq. (2) into Eq. (6), we simplify Eq. (6) to give,

$$\Delta G(\Delta \mu_{\rm N}) \approx -\frac{1}{A} (N_{\rm N} E_{\rm b}^{\rm N} - N_{\rm N} \Delta \mu_{\rm N}) \tag{7}$$

where the nitrogen chemical potential is now measured with respect to the free nitrogen atom: $\Delta \mu_N = \mu_N - E_N$ and we neglect contributions due to vibrations and the pV term [38]. The resulting surface free energy of adsorption for the various structures considered are presented in Fig. 10. The nitrogen chemical potential at which bulk Cu₃N is favorable corresponds to the heat of formation of bulk Cu₃N (relative to the free N atom), which we calculate to be -4.03 eV. Hence the nitrogen chemical potential at which the formation of bulk Cu₃N is favorable is simply assigned to be -4.03 eV (per N atom) and this is plotted in Fig. 10 as the rightmost dashed vertical (red) line.

It is difficult to determine which region of the chemical potential range the experimental studies fall into. Experimentally achieved surface pseudo-(100)-reconstructions employ N ion bombardment of Cu(111) in an ultra-high vacuum (UHV) chamber [7-10,12-15], so there is no simple correlation between the chemical potential of nitrogen and other thermodynamic variables such as the temperature and pressure. This means that it is not straight forward to construct a two-dimensional phase diagram showing the equilibrium phase over regions in temperature-pressure space. However, by simply considering the relationship between the change in surface Gibbs free energy and the nitrogen chemical potential it will still yield useful information regarding the relative stability of the various surface structures and how they might play a role in understanding thin film growth mechanisms of Cu₃N [40,41] and initial nitridation of copper.



Fig. 10. Calculated Gibbs free energy of adsorption ΔG (cf. Eq. (7)). All unfavorable adsorption phases are indicated in pale grey. The '16' structure is indicated as a thick black line, the fcc $\frac{1}{16}$ ML phase as a thin black line, the fcc and hcp 0.75 ML structures are also labeled. The dashed rightmost (red) vertical line is the heat of formation of bulk Cu₃N (relative to the free N atom), and the dashed leftmost black vertical line indicates the potential energy where the '16' reconstruction becomes the most favorable structure.

From Fig. 10, showing the Gibbs free energy of adsorption for all considered surface structures versus the nitrogen chemical potential, it can be seen that at low chemical potential energies, the clean Cu(111) surface is the preferred structure. At $\mu_N = -4.34 \text{ eV}$, the '16' structure becomes the most favorable for a narrow energy window, until the chemical potential reaches -4.03 eV, where the preferred structure is then the bulk copper nitride. From the plot, we also find that simple homogeneous chemisorption structures are not energetically favorable, even at very low coverage (i.e. $\frac{1}{16}$ ML). We would also like to note that "N₃ clustering" at both the fcc- and hcp-sites for 0.75 ML coverage is not stable with respect to bulk Cu₃N formation.

To gain an initial insight into the kinetics of the formation of bulk Cu₃N, we estimate the diffusion barrier of Cu on Cu(111) in a (2×2) surface cell by taking the difference of the total energy of having a Cu atom adsorbed at the fcc-site and that at the bridge site. This energy barrier is found to be 0.012 eV which is significantly smaller than that of N (0.29 eV). This indicates that the migration of Cu atoms is much more rapid than that of N, thus favoring the formation of bulk Cu₃N rather than the formation of "N₃" clusters on the surface. However, if we assume the Cu atoms migrate from step edges to terraces, this will require a notable energy barrier. We estimate this barrier as the energy difference between a Cu atom on Cu(111) (using a (2×2) cell) and that where the Cu atom is bound at a kink site at a step (where it has the cohesive energy of bulk Cu). This value is 0.838 eV. Using a simple Arrhenius equation with a standard prefactor of 10^{13} s⁻¹, it indicates that diffusion of N atoms readily occurs at temperatures of around 150-200 K, while Cu diffusion from steps only becomes similarly possible at around 350-500 K. Hence, from this result we can understand why such unexpected clustering has not been reported in literature, where the experiments are conducted at temperatures above 200 K [7,8,14,13], as the formation of the bulk nitride is more favored well before these "N3 clusters" can have the chance to exist on the surface. If however, adsorption of N is performed at temperatures below that at which reconstruction of the Cu(111) occurs, such structures may be observed – provided there are no lower energy pathways (i.e. competition with the N diffusion barrier), for N-induced Cu reconstructions. For conditions typical of catalysis, and for reactions that generate atomic nitrogen, it is likely that surface nitrides or the bulk nitride forms.

4. Conclusions

We have investigated the chemisorption of N on the Cu(111) surface, for coverages 0.06-1 ML through firstprinciples density-functional theory calculations. We considered on-surface and subsurface adsorption, as well as surface-nitride formation. For chemisorption on the surface, N prefers the threefold fcc hollow site for all coverages, except 0.75 ML, and for subsurface adsorption the octahedral site is favored. For the low coverages of 0.06, 0.11, and 0.25 ML on-surface adsorption is preferred over subsurface adsorption, but at 0.5 ML, the subsurface octahedral (octa) site becomes marginally more favorable. For on-surface adsorption at a coverage of 0.75 ML we identified an interesting behavior: The nitrogen atoms strongly relax from their ideal hollow sites and form "N₃ clusters". This occurs for N in both the hcp and fcc sites where the hcp site is slightly more favorable than the fcc. This "N₃" configuration is notably more favorable than adsorption in the fcc site at 0.5 ML coverage, which is attributed to the formation of inter N-N bonds. The binding of the "N₃"-like molecule to the surface is relatively weak (0.353 eV per N atom). We also investigated pseudo-(100) reconstructed surface nitride-like structures, similar to those reported in recent experimental studies. In particular, we considered three different structures: The first involving one reconstructed Cu(100) layer with a nitrogen coverage of 0.5 ML using a surface unit cell containing four Cu atoms, and the second like this, but containing two reconstructed Cu(100) layers. We found the former to be energetically favored over the latter, giving support to the experimental study reporting that there is only one reconstructed Cu(100)-layer involved. The third structure employed a larger surface unit cell corresponding to 16 Cu(111) atoms. This latter structure involved one reconstructed Cu(100) layer, and allowed a greater relaxation of the surface-nitride-like over-layer and greater relief of strain. Consequently, this configuration was found to be the most favorable of all the structures we considered.

By plotting the Gibbs surface free energy of adsorption versus nitrogen chemical potential, μ_N , we clearly find that for low values of μ_N the clean Cu(111) surface is the most energetically favorable, and with increasing values of μ_N the pseudo-(100) surface nitride becomes most favorable for a small range of μ_N . Upon further increase of μ_N (corresponding to increased N content) in the N/Cu(111) system, the bulk Cu₃N nitride is energetically most stable. These results suggest that growing Cu₃N films on the Cu(111) substrate has a very high chance to form through the surface nitride precursor phase. The O/Cu(111) system behaves in a similar fashion [17], forming precursor thin surface oxides before the onset of the bulk oxide.

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