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Surface characterization of self-assembled N–Cu nanostructures

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ARTICLE INFO

Article history:

Available online 30 April 2011

PACS:

71.15.Mb
68.49.–h
68.37.Ef
62.23.St
61.05.–a

Keywords:

Copper nitride
Nanostructures
Self-assembling
LEIS
STM
Surface spectroscopy

ABSTRACT

We report on the process of low energy N_2^+ implantation and annealing of a Cu(001) surface. Through AES we study the N diffusion process as a function of the substrate temperature. With STM and LEIS we characterize the surface morphology and the electronic structure is analyzed with ARUPS. Under annealing ($500 < T < 700$ K) N migrates to the surface and reacts forming a Cu_xN compound that decomposes at temperatures above 700 K. LEIS measurements show that N locates on the four-fold hollow sites of the Cu(001) surface in a $c(2 \times 2)$ arrangement. Finally, a gap along the [001] azimuthal direction is determined by ARUPS. DFT calculations provide support to our conclusions.

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1. Introduction

Crystalline Cu_3N is a non-toxic semiconductor. It is stable at room temperature and decomposes into Cu and N_2 at 700 K. Thin films of copper nitride can be grown over different substrates and by means of different methods, like assisted molecular beam epitaxy [1], laser ablation [2] and RF reactive magnetron sputtering [3–5]. Since copper nitride easily decomposes under mild annealing and electron bombardment, it is an ideal candidate for write-once optical recording media (WORM) [3,5]. Recently, the interest on Cu–N compounds surfaces has experienced an explosive attraction, related with the possibility of producing self-assembled patterns of square islands [6,7], that can be used as templates for growing different nanoscopic systems [8–11].

The Cu–N nanostructures have been characterized by numerous surface techniques. Some representative examples are: photoelectron diffraction (PhD) [12], grazing incidence X-ray diffraction (GIXD) [13], scanning tunnelling microscopy (STM) [14] and high

temperature STM [15]. Thus, some features characterizing these self-assembled nanostructures are currently accepted. In this category we can include the $c(2 \times 2)$ structure and the four-fold hollow site as the N adsorption place. However, the situation is quite different for other characterizing parameters. For instance, the height of N atoms above the first copper plane is a current matter of discussion. Based on PhD combined with STM experiments a large corrugation of surface layers has been proposed [12], but some years later this has been disregarded based on grazing incidence x-ray diffraction results [13]. In this work, we combine experiments of STM, Auger electron spectroscopy (AES), low energy ion scattering (LEIS) and angle resolved ultraviolet photoelectron spectroscopy (ARUPS) with a full potential density functional theory (DFT) calculation to gain insight about some of the issues that are still under discussion.

2. Experimental setup and DFT calculations

The experiments were carried out in three different surface analysis systems, with a base pressure in the low 10^{-10} mbar range. The systems are equipped with hemispherical and cylindrical energy analyzers, STM, low energy electron diffraction (LEED), UV He gas discharge lamp, electron and multipurpose ion guns, i.e. for sput-

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ter cleaning the samples, N_2^+ implantation and LEIS experiments (2 keV He^+). The sample was mounted on different manipulators depending on the experiment. From fixed ones (STM) to five degrees of freedom for polar and azimuthal LEIS scan experiments. The sample can be heated by rear electron bombardment while the temperature is controlled by a chromel–alumel thermocouple. The sample was a mechanically polished Cu(001) single crystal cleaned by repeated cycles of Ar^+ sputtering (1 keV) and annealing at 800 K for 5 min until contamination is below AES detection limit. The ion implantation was done at room temperature using 500 eV N_2^+ . In all cases the nitrogen dose was 1.5×10^{16} ions/cm², enough to reach N saturation. STM images were obtained at room temperature in the constant current mode, using electrochemical etched tungsten tips with a sample bias voltage of +2.50 V and a tunnelling current of 0.15 nA. Acquisition and image processing were performed using the WSxM free software [16]. ARUPS experiments were done using the HeI resonance line (21.2 eV) and a hemispherical analyzer (SPECS unit). The same system was used to perform LEIS experiments with a mass analyzed ion gun. AES experiments were performed with a PHI 590A CMA based spectrometer, using differential acquisition (4 V modulation).

The DFT calculations were performed using the full potential L/APW+lo method, solving the Kohn-Sham equations within the GGA approximation [17], such as it is embodied in the WIEN2k package [18]. The Cu(001) surface was simulated using a symmetric slab of 11 atomic planes plus 10 vacuum layers, with the capability to form the $c(2 \times 2)$ Cu(001) structure when N is adsorbed at the four-fold hollow sites. In order to obtain the actual height of N over a Cu surface, slab total energy calculations for several relaxed configuration were performed: (i) unrelaxed slab, (ii) only N atoms relax, (iii) both N and Cu surface atoms relax, and (iv) N and all Cu atoms (except those in the center of the slab simulating the bulk) are allowed to relax. The final reported configuration corresponds to that with negligible forces on all the atoms and minimal total energy of the slab.

3. Results and discussion

In Fig. 1, we depict a STM image of the CuN nanostructures, which represent the base of current interest on this material. This figure shows the surface covered by dark square patches, slightly deformed along [010] direction due to a small thermal drift running along the [100] directions and separated by lines of clean Cu(001). These square patches are about 5 nm \times 5 nm in size, and are ascribed to the misfit between the Cu(001) and the CuN structures [6]. Within this model, the black ordered squares patches are assumed to be $c(2 \times 2)$ Cu–N structures, although STM is unable of detecting chemical composition. On the other hand, in the STM image some dark stripes aligned along the [110] directions surrounded by square-shaped islands can be observed as well. These dark stripes have been called trench-like structures, and they relieve the surface strain just like the lines of clean copper between the $c(2 \times 2)$ -N structures [15,19].

Taking into account that the rearrangement of N atoms to form the nanostructures is thermally induced, a question should be how this rearrangement takes place. In Fig. 2, we show a detailed evolution based on AES measurements of the bombardment (500 eV N_2^+) and annealing (700 K) processes. In the left panel, the increasing amount of N at the surface is observed. We have already shown that for larger impinging energies, a lower N amount is accumulated at the surface due to the increasing ion implantation range with energy [20].

After N_2^+ implantation we proceed with the substrate annealing at 700 K (center panel). The increase of the substrate temperature produces N diffusion, quickly increasing the N concentration at

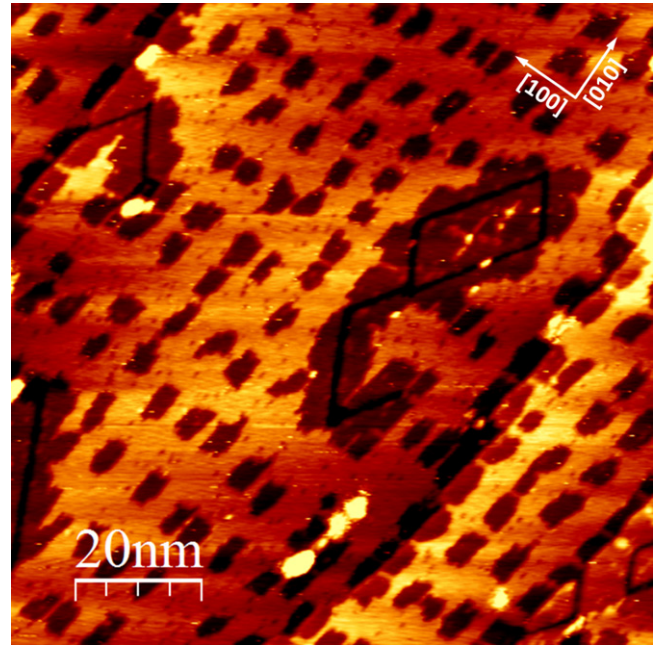


Fig. 1. STM image (100 nm \times 100 nm) of CuN nanostructures obtained after 500 eV N_2^+ bombardment of a Cu(001) single crystal, followed by an annealing at 600 K. The image was acquired at $V_s = +2.50$ V and $I_t = 0.15$ nA.

the surface. This increase is then followed by a slower fall down, due to N desorption. If the annealing time is long enough, the N would disappear completely from the surface. The key experiment is depicted in the right panel, where two depth profiles are performed. Although both profiles start at different points along the thermal annealing process, they have almost the same initial Auger yield. The starting points are circled in the middle panel graph. These points are chosen in this way to make simpler any comparison. It is clear that an isotropic thermal induced N diffusion would give a broader N profile (N distributed deeper in the substrate) for the annealed sample than for the non-annealed one. On the contrary, the depth profiles show an increased concentration of N at the surface suggesting a preferential diffusion towards the surface, followed by a decomposition of the Cu_xN compound. Our experimental results show that impinging energies below 1 keV

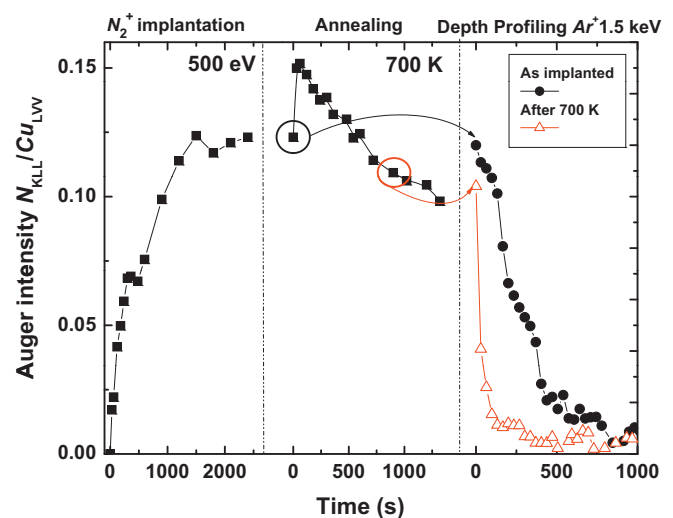


Fig. 2. Evolution of the amount of N at the surface during the implantation, annealing and depth profiling processes.

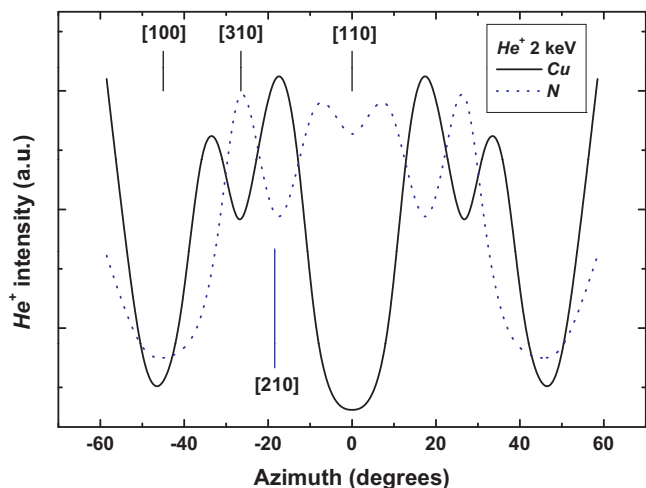


Fig. 3. Intensity of 2 keV He⁺ scattered from Cu and N on an implanted and annealed (600 K) sample, as a function of the azimuthal angle for grazing incidence (polar angle, 5°).

and annealing temperatures around 700 K for 10 min optimize the N location at the surface.

As we previously mentioned, based on LEED experiments [6,21], a consensus has been reached about the surface location of N atoms, i.e. in the four-fold hollow sites in an ordered $c(2 \times 2)$ superstructure. The situation is rather different with respect to the height of the N referred to the Cu surface plane atoms, where PhD [12], GIXD [13], LEED [6,21] and extended X-ray absorption fine structure (EXAFS) [22] appear as giving substantially different heights. Even the surface reconstruction is under discussion, i.e. PhD and GIXD give different results concerning the rumpling of the Cu surface.

LEIS is a highly sensitive surface characterization technique to measure the chemical composition of the first monolayers of a solid sample. Another capability of this technique, not always fully exploited, is the possibility of obtaining structural information of the surface by using the shadow and blocking cones concept. The intensity of the signal in LEIS spectra, and its variation with polar and azimuthal angle convey information about the structure of the surface. This information can be extracted using models that are simpler than those used in electron diffraction spectroscopies, which are basically reciprocal lattice techniques.

In Fig. 3, we show azimuthal scans for He⁺ scattered from Cu and N atoms for a fixed incident angle (5°) measured relative to the surface plane. These results were already shown [23], so we will limit to a brief description of them. The scattered He⁺/Cu yields present strong variations due to focusing and shadowing of the ion trajectories on the target atoms along the main azimuthal directions. These features constitute a good evidence of crystallographic order. The He⁺/N yield is high along the [1 1 0] azimuth, probing that N atoms are not blocked neither by Cu nor N atoms along this direction. On the other hand, a low He⁺ yield is obtained in the [1 0 0] and [2 1 0] azimuths meaning that Cu atoms are blocking the N ones along these directions. These results are compatible with a $c(2 \times 2)$ Cu(001)-N structure, where the N atoms are located at the four-fold hollow sites.

The measurement of LEIS polar angle dependence is another interesting tool to explore adatom locations. In Fig. 4, we show such distributions for the scattering of He⁺ on Cu and N atoms along the [1 0 0] azimuth of the N implanted Cu(001) surface. This polar scan is typical of flat surfaces, i.e. a low signal for small incident angles and a steep increase at a critical angle due to focusing effects of the outermost atoms of the crystal. This critical angle is then related in a direct way to the lattice constant of the row of atoms along

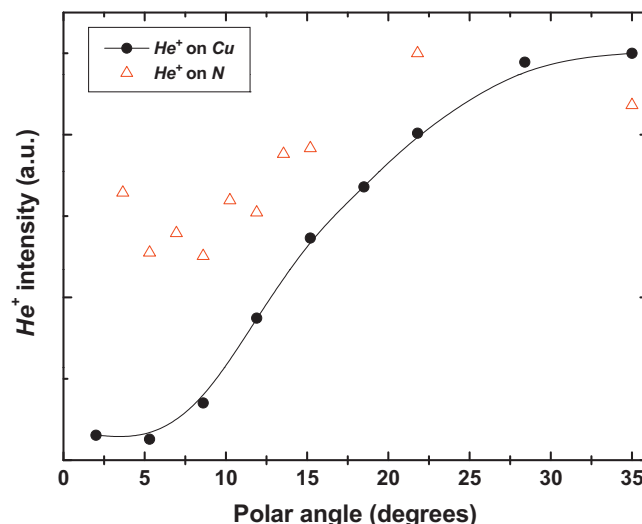


Fig. 4. Intensity of 2 keV He⁺ scattered from Cu and N on an implanted and annealed (600 K) sample, as a function of the polar angle for the (1 0 0) azimuth.

the azimuthal direction considered [24]. On the other hand, the intensity of He⁺ reflected on N shows a different behaviour. The critical angle is clearly lower, i.e. He counts are observed for lower angles, even below 5°. It is quite important to point out here that along this direction the N should be shadowed by Cu atoms if they were at the same plane. Thus, this experiment is clear evidence that N atoms are located in a plane above the copper one.

Although, we can ensure now that N atoms are above the Cu surface, we have still problems to experimentally quantify the actual height. Trying to have a better definition of this height, we performed DFT calculations in order to have a theoretical estimation of this distance.

In Fig. 5, we show the evolution of slab total energy for different N heights in a $c(2 \times 2)$ configuration, considering several possibilities for relaxation.

To obtain the most favourable site for N location we allow the slab relaxation until two different criteria are fulfilled: negligible forces (lower than 2.5 mRy/a.u.) on all the atoms and minimum total energy. This was accomplished along three steps. In the first

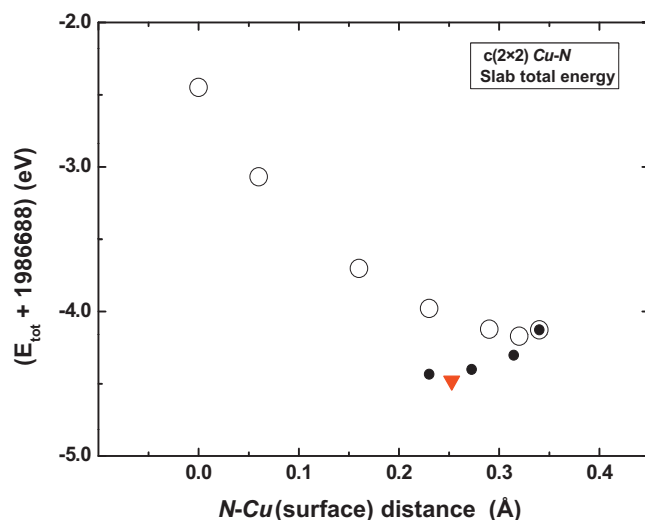


Fig. 5. DFT calculation of total energies for $c(2 \times 2)$ Cu(001)-N slabs as a function of N height: (open circles) only N atoms relax, (full circles) N and Cu surface atoms relax, and (full triangle) last converged geometry for minimal total energy and negligible forces when all the atoms in the slab are allowed to relax.

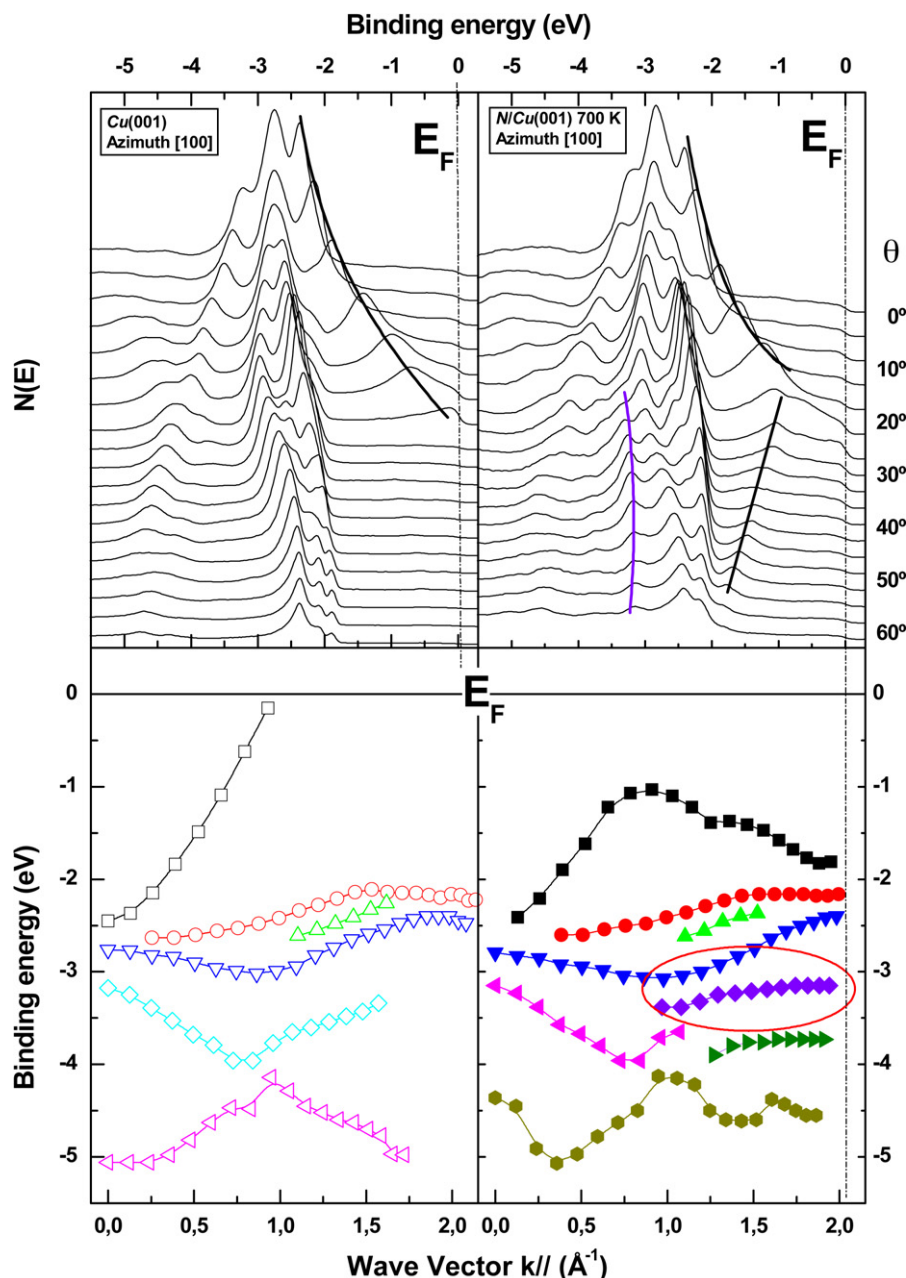


Fig. 6. ARUPS curves obtained from a Cu(001) (left column) clean and N implanted and annealed samples (right column) for the [001] azimuth. Electron distribution (upper panel) and band structure (lower panel).

one, starting from N embedded in the surface plane, only N atoms are allowed to relax (open circles, evolving from left to right). Although a minimum in the total energy is obtained for a N height of 0.32 Å, big forces remain on the Cu surface atoms indicating a still stressed configuration. In the second step, and starting from the last converged geometry, N and Cu surface atoms are allowed to relax, keeping fixed all the other Cu atoms at bulk positions (full circles, evolving from right to left). The minimization procedure continues until the numerical convergence criteria are fulfilled, obtaining a new minimum for the total energy with lower forces on all atoms, compared to the previous step. The N height, with respect to the relaxed Cu surface, is now 0.23 Å, but the forces on the surface Cu atoms, although four times lower than those after the first step, are still significant. Then, in the last step we let all N and Cu atoms (except those at the center of the slab simulating the bulk) to relax. Several proximal geometries, starting from the last converged one,

were tested. In Fig. 5, for clarity we only depict the total energy and N height for the converged geometry of this sequence (full triangle). This is the best configuration it is possible to obtain allowing the real relaxation of N and several Cu layers. The final N–Cu (surface) height obtained for the completely relaxed slab is 0.25 Å for the $c(2 \times 2)$ configuration (red triangle). This result is compatible with our LEIS results and GIXD experiments where a height of 0.16 Å was reported [13].

Using the fully relaxed results, the calculated magnitude of the relaxation for the interlayer distances (d_{12} , between the surface and the first sub-surface layer, and d_{23} , between the first and the second sub-surface layers) turn to be $d_{12} = 8.6\%$ and $d_{23} = 1.3\%$ of the magnitude of the bulk interlayer distance. These results show an outward expansion of the layers, in quite good agreement with the results obtained by GIXD: $d_{12} = 14.0\%$ and $d_{23} = 1.5\%$ [13]. Finally, from the DFT theoretical calculations, we do not obtain any evi-

dence of rumpling at the surface, also in complete agreement with GIXD results [13].

To conclude this study, by means of ARUPS we give an insight of the electronic structure of the nanostructured surface. This last experiment is shown in Fig. 6. In the upper panel, we show the electron distribution as a function of energy for different emitted angles. The band structure (parallel k vector) for both cases is depicted in the lower panel. A couple of lines are introduced in the $N(E)$ curves to guide the eyes about the peak corresponding to the valence band near the Fermi energy (E_F) in the Cu sample, as well as the appearance of a couple of N induced states around -3.5 eV in the nanostructured sample. The appearance of a gap, consistent with the semiconductor character of Cu_3N , is also apparent in the N–Cu sample.

4. Conclusions

Through Auger Electron Spectroscopy, Scanning Tunnelling Microscopy, Low Energy Ion Scattering Spectroscopy and Angle Resolved UV Photoelectron Spectroscopy, supported by density functional theory calculation, we characterize the formation of nanostructures by N ion bombardment followed by mild annealing of a Cu(001) sample. We determine that N locates on the four-fold hollow sites of the Cu(001) surface in a $c(2 \times 2)$ arrangement at a height of 0.25 Å. For temperatures in the range of 500–700 K, N migrates to the surface reacting to form a Cu_xN compound. This compound decomposes at temperatures above 700 K. The appearance of a gap along the [100] azimuth suggests the formation of a semiconductor phase.

Acknowledgments

This work has been financed by the ANPCyT through grants PICT-2006-01138 and PICT 2007-01150, CONICET through PIP 5280, and

Universidad Nacional del Litoral through grants CAID2005 programs. The authors give special thanks to ANPCyT for Grants PME2003-8 and PME-2006-01580 to finance the purchase of the UHV Multi Analysis System.

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