



Surface characterization of nitride structures on Cu(001) formed by implantation of N ions: An AES, XPS and LEIS study

L.J. Cristina^{a,*}, R.A. Vidal^a, J. Ferrón^{a,b}

^aInstituto de Desarrollo Tecnológico para la Industria Química (INTEC), and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

^bDepartamento de Materiales, Facultad de Ingeniería Química, Universidad Nacional del Litoral. Güemes 3450 CC 91, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:

Received 14 May 2008

Accepted for publication 20 August 2008

Available online 11 September 2008

Keywords:

Nanostructure

Self-assembling

Electron spectroscopy

LEIS

Copper nitride

ABSTRACT

By means of Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and low energy ion spectrometry (LEIS) techniques we studied the process of low energy N_2^+ implantation and annealing of a Cu(001) surface, a proposed model system for self-assembled nanostructures. We characterized the N diffusion features as a function of the substrate temperature and we followed the chemical state of N and Cu along the annealing process. We also took advantage of the LEIS surface sensitivity that, together with its elemental detection capability, can give us insight about the surface structure formation process. We found that the N binding energy shifts non-monotonously along the whole process pointing out that the N–Cu bonding environment is changing and it depends on the atomic rearrangement and on the N amount. We also found that N locates on the fourfold hollow site of the Cu(001) surface. Our LEIS results are compatible with a $c(2 \times 2)$ ordering, but at the same time we cannot disregard that some N atoms are either located on other fourfold hollow sites or substituting Cu atoms.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Copper nitrides have been considered in the past mostly for its possible applications in the developing of write-once optical recording media (WORM) [1,2]. Cu_3N is a non-toxic, RT stable transparent insulator that changes into metal under thermal decomposition or electron bombardment, enabling for instance electron induced lithography. It may be obtained over different substrates and by means of different methods, like assisted MBE [3], laser ablation [4] and RF reactive magnetron sputtering [5,6]. The copper nitride features are strongly dependent on the growing characteristics. Thus, for instance Pierson found that the lattice constant and electrical resistivity can be tailored varying the Ar–N relative pressure in the chamber [6]. On the other hand, Maruyama and Morishita [5], under certain experimental conditions obtained conductive Cu_3N compounds that they attribute to the presence of interstitial Cu atoms.

XPS has been extensively used for characterizing copper nitrides. For instance, Prabhawalkar et al. [7] studied the formation of metastable nitrides by nitrogen implantation in polycrystalline copper at high doses and at various temperatures. They found a small positive (negative) shift for copper 2p (nitrogen 1s) binding energy (BE) at room temperature, concluding that several phases of N–Cu compounds may be present simultaneously. The decomposition of these phases starts around 250 °C, but nitrogen may

be seen on the surface at temperatures as high as 500 °C. Gallardo-Vega and de la Cruz [4] found, for pulsed laser deposited copper nitride films, a gradual shift of the Cu 2p_{3/2} peak to higher binding energies for increasing molecular nitrogen pressures in the deposition chamber. Soto et al. [8], through XPS measurements on different nitrogen containing metal films, concluded that it is not possible to make a clear distinction of the bonding character using the N 1s binding energy as unique evidence. They came to the conclusion that the shift of the N XPS line is an evidence of charge transfer from the metal to the N atoms, but it is not specific to any metal–N bond, and thus the N 1s BE senses the global N chemical state in the metal lattice.

The work of Leibsle et al. [9] triggered a renewed interest on the Cu–N system. They found that the mild annealing of a Cu(001) sample implanted with low energy N_2^+ ions gave place to a self-organized square-shaped nanostructure characterized by a $c(2 \times 2)$ N–Cu structure with a lattice parameter of 4 Å. They proposed a model based on the mismatch between Cu(001) and Cu_3N to account for the regularity of the found structures. Since then, the system has been characterized by photoelectron diffraction [10], grazing incidence X-ray diffraction [11], STM [12], and HT-STM [13] just to mention some representative examples. Some features, like the $c(2 \times 2)$ structure and the fourfold hollow site for the N location are now currently accepted, but some controversies about the N height still persists, going from 0.145 nm [14] to almost the same Cu surface plane [15]. Since STM cannot distinguish between N and Cu atoms, it is not able of giving a reliable answer about the relative heights of the atoms above the surface [12]. Recently

* Corresponding author.

E-mail address: lucila.cristina@gmail.com (L.J. Cristina).

Komori et al. published a review with the latest work on the formation of nanopatterns on the nitrogen modified Cu(001) surface [16]. In this work they show that the Cu(001)-N surface is inhomogeneously deformed by two competing interactions: the short range Cu-N interaction is the responsible of the $c(2 \times 2)$ N structure whereas the long range square-shaped nanostructure is associated to the total adsorbate-substrate elastic energy minimization.

The natural following step, from the technological point of view, is the creation of magnetic nanostructures using the N-Cu(001) system as a template. Thus, Co [17] and Fe [18] films have been grown over N-Cu(001) with the idea of obtaining magnetic nanowires separated by insulating self-organized nanostructures. In these cases, STM is the almost exclusively used technique. The creation of magnetic nanostructures based on nitrides grown in a different way that energetic N^+ implantation has been also explored. Thus, magnetic dots ($10 \times 10 \text{ nm}^2$) created by evaporation of Fe in a flux of atomic N over Cu(001) have been fully characterized by means of STM, Mössbauer spectroscopy, Rutherford Backscattering, Magneto Optic Kerr Effect and LEIS-TOF [19].

With this work we begin a study of the basic mechanisms that leads to the formation of the nitride self-organized structures. The study involves the ion implantation, the temperature dependence of N diffusion to the surface, and surface charge rearrangement. In this work, we present results involving AES and XPS to characterize the bulk-surface diffusion and the chemical reaction, and angle resolved LEIS measurements (polar and azimuthal distributions) to determine the N and Cu relative positions.

2. Experimental

The experiments were carried out in two commercial surface analysis systems, with a base pressure in the range of low 10^{-10} mbar. Auger measurements were performed in a PHI SAM 590A equipped with a single pass cylindrical mirror analyser with a coaxial electron gun and a differentially-pumped ion gun was used for N_2^+ ion implantation. Auger data was acquired in differentiated mode (with $4 V_{p-p}$ modulation amplitude), a primary electron energy of 3 keV, and an analyzer resolution of 0.6%. XPS and LEIS experiments were done in a SPECS system equipped with a hemispherical energy analyzer, a differentially-pumped mass analyzed ion gun, and a double anode X-ray source. In order to prevent N and Cu Auger and photoelectron peaks superposition, the XPS data were collected after exciting the sample by an unmonochromatized Al K α line at 1486.6 eV. The energy scale was calibrated using the silver $3d_{5/2}$ XPS peak. The LEIS measurements were performed using a 2 keV He^+ beam with a scattering angle of 125° . In this chamber the sample was mounted on a manipulator with five degrees of freedom, so polar and azimuthal scans are feasible. In both systems the sample can be heated by electron rear bombardment and the temperature controlled by a chromel-alumel thermocouple.

The sample was a mechanically polished Cu(001) single crystal which was cleaned by repeating cycles of Ar^+ sputtering (1 keV) and annealing at 500°C for 5 min. until no sign of contamination was visible in the AES spectra. The cleanliness and order of the crystal were additionally checked by LEIS. The ion implantation was done at room temperature using 500 eV N_2^+ ions produced in the ion source from 99.999% purity N_2 . The incidence angle of the ion gun in the PHI SAM 590A was 54° with respect to the surface normal and 0° in the SPECS system. During N_2^+ implantation the pressure in the first chamber raised at most up to 10^{-9} mbar and to 10^{-8} mbar in the second one. The nitrogen dose was in all cases 1.5×10^{18} ions/cm 2 .

3. Results and discussion

In Fig. 1 we show AES results for the N surface concentration during 500 eV N_2^+ ion implantation as a function of the dose, and during annealing after ion implantation, as a function of the annealing time, for several annealing temperatures. N_2^+ implantation is followed until saturation of the signal (after a total dose of 1.5×10^{18} ions/cm 2). A TRIM simulation [20] gives an implanted zone extending around 3 nm in depth for our experimental conditions. The heating of the sample induces the N diffusion, leading at first, to an increase of the nitrogen KLL Auger yield within the surface layer, i.e. within the Auger electron escape depth. After that, and depending on the substrate temperature, the N Auger yield decreases. However, the N remains in the surface layer up to the highest annealing temperature (400°C).

In Fig. 2 we show XPS results for a 500 eV N_2^+ implanted Cu(001) sample maintained at 400°C . The time evolution of the N 1s peak (position and area) was followed during the annealing and the results are shown in the left panel of Fig. 2. The absolute value for the N 1s binding energy agrees with previously measured ones for a copper nitride compound (398 eV [8] and 397 eV [21]), but the interesting results are on the BE evolution. The first abrupt drop, with almost no change in the N amount at the surface (proportional to the area under the N 1s XPS peak), is followed by a continuous but non-monotonous increase. It appears as the BE changes with time while the N amount stays constant and vice versa, i.e. while the N amount at the surface decreases, the BE stays constant. This behavior is clearly shown on the right panel of Fig. 2 where the N 1s BE is plotted against the N amount. A simple interpretation based on the simultaneous presence of different stoichiometric compounds, suggested by Prabhawalkar et al. [7], with different temperature dependent decomposition rates, does not explain our results. In this model the N 1s BE versus N amount plot would show a sequence of straight lines with different slopes. Constant BEs with decreasing surface nitrogen amounts alternated with varying BEs with constant N amounts are more likely interpreted as the dissociation of stoichiometric compounds followed by N-Cu rearrangements, without N loss.

The implanted N is randomly distributed along the implanted range. As soon as the substrate is heated, the increased mobility

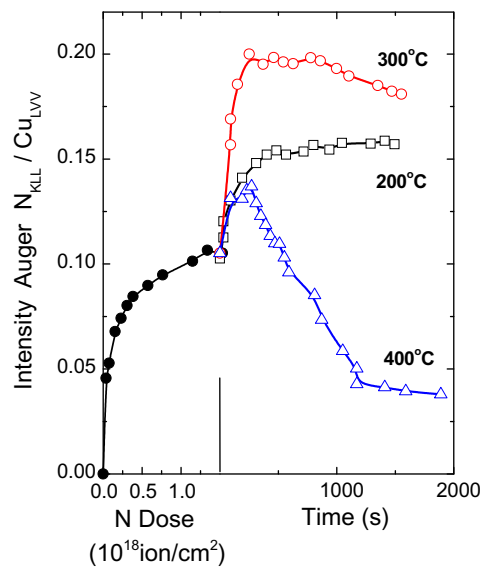


Fig. 1. N KLL/Cu LVV Auger signal ratio evolution during 500 eV N_2^+ implantation. After saturation of the N/Cu AES signal the sample was annealed at different temperatures as shown.

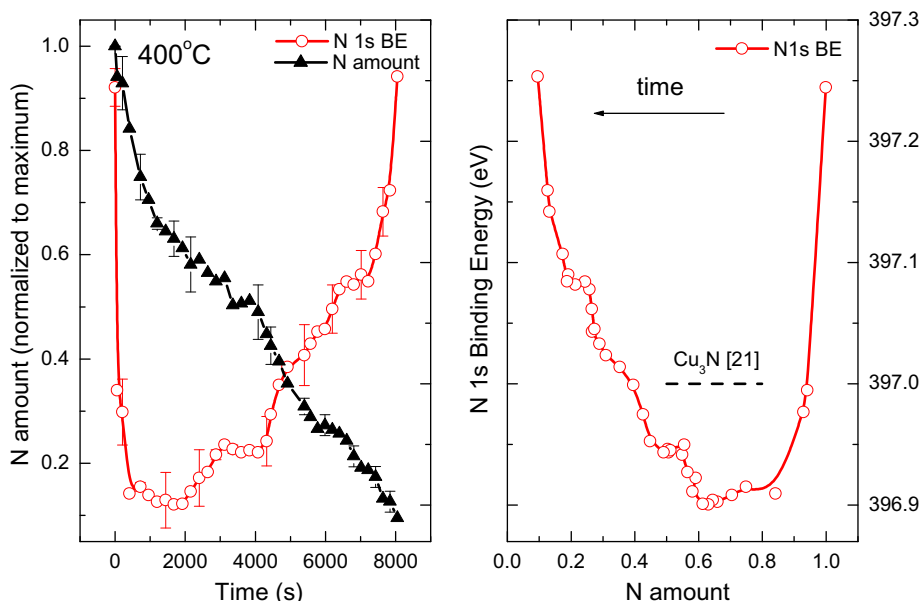


Fig. 2. N 1s BE evolution as a function of time (left panel) and as a function of N amount (right panel) for 500 eV N_2^+ sample, heated at 400 °C. The evolution of N at the surface is also included in the left panel.

of the N atoms favors fast atomic rearrangements and the formation of a Cu_xN compound, characterized by a sharp drop of the N 1s BE. After that the Cu_xN compound dissociates bringing in a reduction of the surface N amount while the BE stays constant. As the nitrogen is reduced, the spacing of clean surface between the islands of Cu_xN is increased. At certain point, the surface N amount keeps constant while the atomic rearrangements generate a new Cu_yN compound with a bigger BE. This can be explained if N atoms are in a weaker electron-acceptor configuration [8], i.e. in a compound where $y < x$. This sequence seems to repeat along the nitrogen desorption process and appears as BE steps on the right panel of Fig. 2. At the end, as the N amount tends to zero, the N 1s BE tends to the initial value, suggesting the presence of isolated N atoms with low chemical reactivity. On the other hand, we also found a small positive shift for Cu 2p binding energy during the annealing process.

When comparing AES and XPS experiments one should take into account that N KLL Auger electrons (380 eV kinetic energy) and Al $K\alpha$ generated N 1s photoelectrons (1090 eV kinetic energy) have different escape depths. This fact is responsible, for instance, for the absence of the maximum in the XPS N 1s evolution as it is observed in the case of AES experiments (Fig. 1).

In order to get structural information on the copper nitride formation on the Cu(001) surface we collected LEIS spectra as a function of both the incident angle (θ) for several fixed azimuthal directions (polar distributions), and as a function of the azimuthal angle (φ) for a fixed incident angle (azimuthal distributions). In Fig. 3 we show azimuthal scans for He^+ scattered from Cu atoms (He^+-Cu , Fig. 3a) and from N atoms (He^+-N , Fig. 3b) for a fixed incident angle (5°). The incident angle is measured relative to the surface plane. The scattered He^+ yields present strong variations due to focusing and shadowing of the ion trajectories on the target atoms along the main azimuthal directions, and they are symmetric with respect to the [110] direction ($\varphi = 0^\circ$). For clean Cu(001) these features constitute a clear evidence of good crystallographic order. After N_2^+ implantation the He^+-Cu yields along the [100] and [110] directions are higher than the clean He^+-Cu yields what is an indication of disorder of the surface induced by the N ion bombardment. The surface recovers some order after a first annealing of 2 min at 200 °C, and the azimuthal distribution of the clean ini-

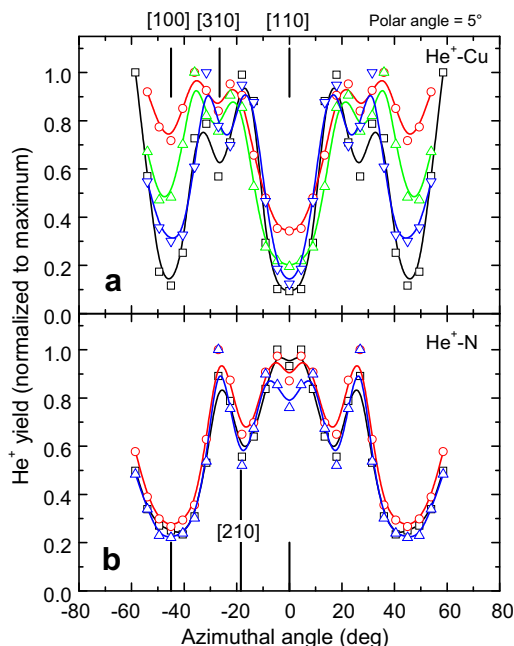


Fig. 3. (a) LEIS azimuthal scans for 2 keV He^+ scattered from Cu atoms. Clean Cu(001) (squares), N-Cu RT (circles), N-Cu 200 °C (triangles up) and N-Cu 300 °C (triangles down). (b) LEIS azimuthal scans for 2 keV He^+ scattered from N atoms. N-Cu RT (squares), N-Cu 200 °C (circles) and N-Cu 300 °C (triangles).

tially ordered Cu crystal is practically recovered after a second annealing at 300 °C.

On the other hand, the He^+-N yields of Fig. 3b shows the following features: 1) a high yield along the [110] azimuth, which means that N atoms are not blocked neither by Cu nor N atoms in this direction; 2) a decreased yield in the [100] and [210] azimuths which shows that Cu atoms do block N atoms in these directions; and 3) small changes in the azimuthal distributions after annealing. These results are compatible with a Cu(001)- $c(2 \times 2)$ -N structure where the N atoms locate at the fourfold hollow site as shown in Fig. 4a. In fact, with a Cu(001)- (1×1) -N structure we would ex-

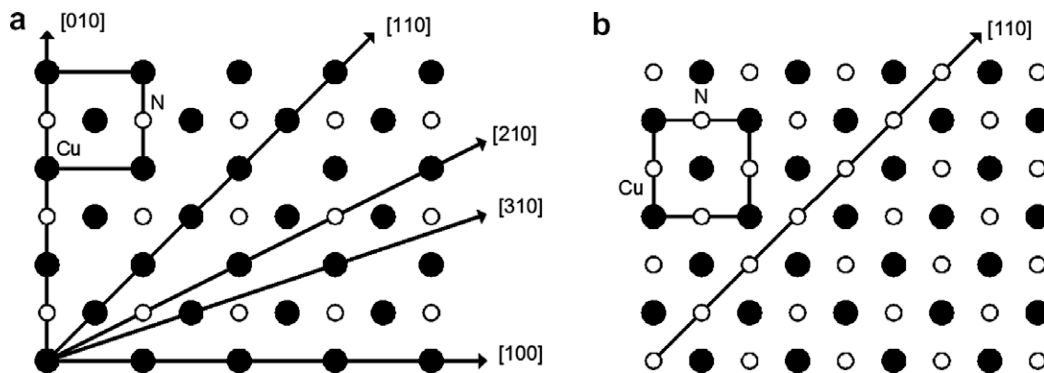


Fig. 4. (a) Top view of the Cu(001)-c(2 × 2)-N surface. (b) Top view of the Cu(001)-(1 × 1)-N surface. The arrows indicate the azimuthal direction.

pect a blocking effect of N atoms by themselves along the (110) direction, as it can be observed in Fig. 4b, where this structure and the (110) shadowing direction is depicted.

In this sense, the slight decrease in the He⁺-N yield observed along the (110) direction for the 300 °C annealed sample may be a fingerprint of either a small amount of N occupying substitutional Cu sites or a small amount of Cu(001)-(1 × 1)-N occupation.

Although the azimuthal scans give useful information about the N atoms surface distribution, i.e. adsorption site, it is difficult from them to evaluate the relative height of the N atoms above the Cu(001) surface, one of the unclear features for this system. The results shown in Fig. 3b suggest that the N atoms locate almost in the same plane as the Cu atoms do, otherwise the minima observed along the [100] and [210] crystallographic directions would be missing, since Cu atoms will not be able to shadow them.

LEIS polar scans are another tool to explore adatom location. In Fig. 5 we show such distributions for the three principal azimuths. In Fig. 5a we show results for the clean Cu(001) surface and in Fig. 5b for a Cu(001) surface implanted with N. The distribution of scattered He⁺ ions shown in Fig. 5a is typical of a flat surface,

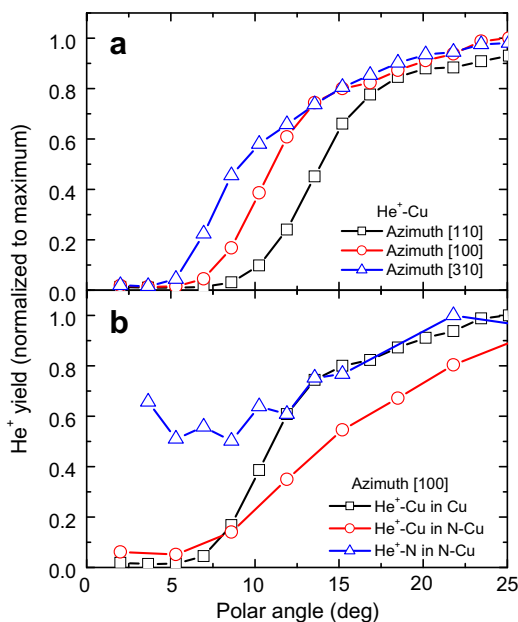


Fig. 5. LEIS polar scans for 2 keV He⁺ scattered from Cu atoms along different azimuths (a), and from Cu and N atoms along the [100] azimuth (b).

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 in the crystal. The critical angle is directly related to the lattice constant of the row of atoms in the azimuthal direction considered [22]. The lower the lattice constant (for Cu(001), $d_{[100]}=0.255$ nm, $d_{[110]}=0.36$ nm, $d_{[310]}=0.57$ nm) the higher the critical angle as it is shown in Fig. 5 (a). There is however a difference between our polar scans and the ones that should be expected from a simple two atoms row scattering model. It is the lack of a “surface flux peak” [23]. This peak arises when the intensified ion flux, at the edge of a shadow cone behind a surface layer atom, interacts with another neighbor surface layer atom, and produces a signal enhancement at the appropriate scattering angle. This particular focusing effect repeats, in a periodic pattern, for every pair of surface atoms along the incident ion azimuthal direction. The lack of the surface flux peak could be due to a disordered structure in the surface plane [23], but this is unlikely in our case as the azimuthal distributions in Fig. 3 show a clear crystallographic structure. Another plausible reason for the absence of the surface peak is the trajectory dependent neutralization. It is known that He⁺ has a high neutralization probability mainly due to Auger neutralization induced by the valence electrons of the solid, and that this neutralization could depend on the incidence and/or azimuthal angle [24]. In a simplistic view the neutralization probability would be higher for grazing angles and this effect will smooth out the sharp “surface peak” [25,26]. Thus He⁺ LEIS provides high surface sensitivity, as only He⁺ interacting with the first layers of the surface will survive and could be detected by the analyzer, but at the cost that only qualitative structural information can be recovered as this is usually obscured by neutralization effects. In spite of this, some useful information can still be obtained from the polar scans. In Fig. 5b we compare He⁺ yields along the [100] azimuth for scattering from Cu and N atoms for an undisturbed clean Cu and a N⁺ bombarded Cu surface. The interesting point to see here is that the He⁺-N yield does not go to zero for low incident angles. This is consistent with a position of the N atoms above the Cu atoms surface plane in such a way that the blocking of the signal by the Cu atoms is not complete in this direction. The very low He⁺-Cu LEIS yield at grazing angles (<6°) for the N₂⁺ bombarded Cu surface shows that this effect is not originated by bombardment induced disorder. Another fact that supports the idea that N atoms lie above the surface Cu atoms layer is the He⁺-N yield at the minima observed in the [100] and [210] directions as shown in Fig. 3b. We used a simple code that calculates shadow cones produced by surface atoms to calculate shadowing regions (in the φ - θ plane) [27] for a particular layer of atoms. It turned out that the He⁺-N yield at the minima does not decrease as should have been expected from the critical angles calculations. These calculations show that when N lies at the same level of the first Cu atoms layer

the yield in the [100] and [210] should be negligible because the signal is blocked by the Cu atoms. This is not seen in our experiments and supports the idea that N atoms lie above the Cu atoms surface. N–N shadowing in the [100] azimuth becomes as important as Cu–N shadowing when the N atoms lies 0.3 Å above the Cu atoms surface. It is also likely that large amplitude vibrations of the N atoms perpendicular to the surface could contribute to the high He⁺–N yield observed at grazing polar angles along the [100] azimuth. However this effect is difficult to estimate as the knowledge of vibrational amplitudes for an absorbed atom is rather poor [10].

4. Conclusions

Through AES, XPS and LEIS we studied the basic processes following low energy N₂⁺ implantation and annealing of the Cu(001) surface. We determined, by means of AES, that the surface N amount is highly dependent on the substrate temperature and by XPS that N chemical state strongly changes as soon as the sample is heated, even with no modification of the N amount at the surface. This result is compatible with N–Cu electron exchange associated with N atoms rearrangement induced by sample heating. For prolonged heating the N at the surface decreases, while the BE increases showing a direct correlation. Through LEIS we found that N locates on the fourfold hollow site slightly above the first layer of Cu atoms, being our results compatible with a c(2 × 2) ordering, but allowing a small amount of N either in other fourfold hollow sites or substituting Cu atoms.

Acknowledgments

ANPCyT through PICT14730, CONICET through PIP 5277, and U.N.L. through grants CAID2005 programs supported this work. Thanks are given to ANPCyT for Grant PME 8–2003 to finance the purchase of the UHV Multi Analysis System. We acknowledge J. Gayone for kindly providing us a copy of the shadowing regions calculation code.

References

- [1] T. Nosaka, M. Yoshitake, A. Okamoto, S. Ogawa, Y. Nakayama, *Appl. Surf. Sci.* 169–170 (2001) 358.
- [2] T. Maruyama, T. Morishita, *Appl. Phys. Lett.* 69 (7) (1996) 890.
- [3] D.M. Borsa, D.O. Boerma, *Surf. Sci.* 548 (2004) 95.
- [4] C. Gallardo-Vega, W. de la Cruz, *Appl. Surf. Sci.* 252 (2006) 8001.
- [5] T. Maruyama, T. Morishita, *J. Appl. Phys.* 78 (6) (1995) 4104.
- [6] J.F. Pierson, *Vacuum* 66 (2002) 59.
- [7] P.D. Prabhawalkar, D.C. Kothari, M.R. Nair, P.M. Raole, *Nucl. Instr. Meth. B* 7/8 (1985) 147.
- [8] G. Soto, W. de la Cruz, M.H. Farías, *J. Electron. Spectrosc. Relat. Phenom.* 135 (2004) 27.
- [9] (a) F.M. Leibsle, C.F.J. Flipse, A.W. Robinson, *Phys. Rev. B* 47 (1993) 15865; (b) F.M. Leibsle, *Surf. Sci.* 514 (2002) 33.
- [10] J.T. Hoeft, M. Polcik, M. Kittel, R. Terborg, R.L. Toomes, J.H. Kang, D.P. Woodruff, *Surf. Sci.* 492 (2001) 1.
- [11] G. Prévot, B. Croset, A. Coati, Y. Garreau, Y. Girard, *Phys. Rev. B* 73 (2006) 205418.
- [12] S.M. Driver, D.P. Woodruff, *Surf. Sci.* 492 (2001) 11.
- [13] H. Ellmer, V. Repain, S. Rousset, B. Croset, M. Sotto, P. Zeppenfeld, *Surf. Sci.* 476 (2001) 95.
- [14] J.M. Burkstrand, G.G. Kleiman, G.G. Tibbetts, J.C. Tracy, *J. Vac. Sci. Technol.* 13 (1976) 291.
- [15] H.C. Zeng, K.A.R. Mitchell, *Langmuir* 5 (1989) 829.
- [16] F. Komori, S. Ohno, K. Nakatsuji, *Prog. Surf. Sci.* 77 (2004) 1.
- [17] F. Komori, K.D. Lee, K. Nakatsuji, T. Iimori, Y.Q. Cai, *Phys. Rev. B* 63 (2001) 214420.
- [18] S. Ohno, K. Nakatsuji, F. Komori, *Surf. Sci.* 523 (2003) 189.
- [19] (a) J.M. Gallego, S.Y. Grachev, M.C.G. Passeggi Jr., F. Sacharowitz, D. Ecija, R. Miranda, D.O. Boerma, *Phys. Rev. B* 69 (2004) 121404. R; (b) J.M. Gallego, S.Y. Grachev, D.M. Borsa, D.O. Boerma, D. Ecija, R. Miranda, *Phys. Rev. B* 70 (2004) 115417; (c) S.Y. Grachev, J.M. Gallego, D. Ecija, D.O. Boerma, R. Gonzales-Arrabal, R. Miranda, *Nucl. Instr. Meth. B* 219–220 (2004) 593; (d) J.M. Gallego, D.O. Boerma, R. Miranda, F. Ynduráin, *Phys. Rev. Lett.* 95 (2005) 136102.
- [20] J.F. Ziegler, J.P. Biersack, *SRIM-2003*. 26.
- [21] Z.Q. Liu, W.J. Wang, T.M. Wang, S. Chao, S.K. Zheng, *Thin Solid Films* 325 (1998) 55.
- [22] H. Niehus, W. Heiland, E. Taglauer, *Surf. Sci. Rep.* 17 (1993) 213.
- [23] J.A. Yarmoff, R.S. Williams, *Surf. Sci.* 165 (1986) L73.
- [24] D. Valdés, J.M. Blanco, V.A. Esaulov, R.C. Monreal, *Phys. Rev. Lett.* 97 (2006) 47601.
- [25] J.A. Yarmoff, R.S. Williams, *Surf. Sci.* 166 (1986) 101.
- [26] M.J. Ashwin, D.P. Woodruff, *Surf. Sci.* 237 (1990) 108.
- [27] J.E. Gayone, R.G. Pregliasco, G.R. Gómez, E.A. Sánchez, O. Grizzi, *Phys. Rev. B* 56 (1997) 4186.