Surface Science 602 (2008) 3454–3458

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

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]

[a] Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
[b] Departamento 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 × 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.

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 × 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 × 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).

0039-6028/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2008.08.019

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 × 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 ($10 \times 10\ nm^2$) 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 unmonocromatized Al Kα 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

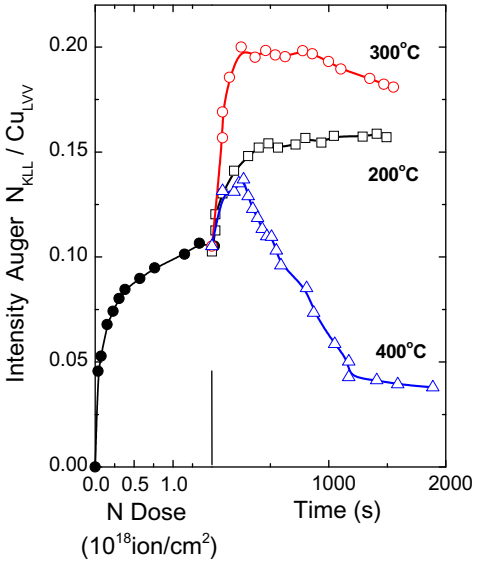

Fig. 1. N KLL/Cu LVV Auger signal ratio evolution during 500 eV N_2^+ implantation. After saturation of the N/Cu AES signal the sample was annealed at different temperatures as shown.