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Surface X-ray diffraction analysis of Fe nanostructured films grown on c(2×2)-N/Cu(100)

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ABSTRACT

We report the results of a Surface X-Ray Diffraction (SXRD) study of Fe nanostructured films deposited on c(2×2)-N/Cu(100) at room temperature (RT), with Fe coverage $\Theta_{Fe}=0.5$ ML and $\Theta_{Fe}=1$ ML. The c(2×2)-N/Cu(100) surface is an example of self-organised system, that can be used for growth of arrays of metal nano-islands and organic molecules assemblies. We chose two different values of N coverage, $\Theta_N=0.3$ ML and $\Theta_N=0.5$ ML, the second value corresponding to N saturation. We monitored the presence of surface diffraction peaks in hk scans and we performed Crystal Truncation Rods (CTR) analysis with ROD fitting programme. In the case of $\Theta_N=0.5$ ML, i.e. at saturation coverage, the CTR could be fitted with one surface domain with *p4gm*(2×2) symmetry. In the surface cell adopted, N atoms occupy four-fold hollow sites, with Fe (intermixed with Cu) giving rise to a "clock" reconstruction previously observed on iron nitride films obtained by co-deposition and annealing. This result is an indirect confirmation of N surface segregation on top of the Fe films, occurring during the growth at RT. When subsaturation N coverage ($\Theta_N=0.3$ ML) is used as a substrate for Fe deposition, the best results could be obtained with a model where two surface domains are present: the first one corresponds to a surface cell with Fe sitting in four-fold hollow sites on bare Cu areas, with possible interdiffusion in the second lattice. The second domain is assigned to growth of Fe on the N-covered square islands occurring once the bare Cu areas are fully covered. The SXRD analysis on N-covered surface domains shows that the mechanism of reconstruction and of N segregation on top layer is already active at RT for all N-coverage values.

1. Introduction

The use of self-organised surfaces as templates for the production of nanostructures is of great interest, as it could be used to produce assemblies of particles covering the entire substrate [1–15]. An example of this bottom–up method is the formation of island films of transition metals on c(2×2)-N/Cu(100). N atoms adsorbed on Cu(100) occupy a four-fold hollow site with formation of a c(2×2) superstructure after annealing [15–30]. Moreover, if the amount of adsorbed N atoms is less than the one required for the saturation coverage (here defined as $\Theta_N=0.5$ monolayers, ML), formation of square islands is observed by Scanning Tunnelling Microscopy (STM) with island size of approximately 5×5 nm. The islands are arranged in regular arrays running along the <100> azimuth directions, regularly spaced by one or two rows of bare Cu atoms, whilst the distance between each array is inversely proportional to the N coverage [9–12]. It was found that this periodic arrangement is caused by difference of surface stress in their clean and nitrided domains, and their competition with the domain boundary energy [13,14]. The regular disposition of the islands can be monitored not only with STM, but also with Low Energy Electron Diffraction (LEED) [11,12] and Surface X-ray Diffraction (SXRD), by direct observation of four-fold satellite peaks appearing around the (10) diffraction spots [14]. In particular, the preferential growth of Fe islands on bare Cu(100) areas was assigned to the occurence of an initial, very low Fe coverage stage corresponding to the inclusion of Fe atoms. These inclusions would then act as nucleation centres for the growth of 2D (monolayer high) Fe islands on top of the Cu(100) [24]. Once the bare Cu areas are fully covered, the growth continues on the N covered patches [15,24]. When $\Theta_N=0.5$ ML, i.e. at saturation coverage, the square islands coalesce, and a uniform N layer is produced, interrupted by trenches running in the <011> directions [10]. The depth of the trenches is one mono-atomic layer, whilst their width is of few nanometers. More recent studies on Co films grown on the N-saturated surface revealed that Co form islands on the N-covered surface, and that N atoms segregate on top of the islands [26,27,28]. The segregation starts when the Co islands have a critical size of about 25 atoms, supporting the hypothesis that there is a potential barrier for N segregation

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decreasing with the Co island size. The reason for this decrease is attributed to strain in the substrate, induced by formation of Co islands [28].

X-ray Absorption Fine Structures (XAFS) studies [31–34] showed that for $\Theta_N < 0.5$ ML Fe islands are preferentially formed on the surface areas which are not covered by the N square patches, directly confirming the surface morphology observed by STM. The spectra could be fitted with a model where Fe is arranged in fcc lattice, in agreement with previous XAFS experiment on Fe films grown on Cu(100) [31]. The average lattice parameter values together with the detailed analysis of XAFS amplitudes indicate the presence of some degree of structural disorder in the islands, with inhomogeneous lattice distortion possibly caused by tetragonal expansion and the presence of surface atoms arranged in nano-martensitic phase [34]. The nano-martensitic phase was previously observed with STM on Fe ultrathin films grown on clean Cu(100) [35–37]. This phase, which is a strained bcc-like phase at the surface of Fe films with $\Theta_{Fe} < 5$ ML, has been considered at the origin of of the magnetic properties of the film [38–42]. Ab initio local spin density calculations [43] revealed instability of tetragonal Fe against monoclinic shear deformation of fcc Fe. This instability allows in plane shifts of Fe rows, leading to a 4×1 and 6×1 reconstruction with twinned bcc-like atomic arrangement. Calculations for 3 ML Fe films also predict that shearing is not homogeneous through the different layers, but gives rise to a complex reconstruction involving the whole film.

When Fe is adsorbed on saturated c(2×2)-N surface, XAFS data show a signal due to photoelectron scattering from N atoms. The analysis gave a value of Fe–N bond length close to the one of N adsorbed on Fe(100) surface [34], and amplitude values compatible with a geometry where the Fe atoms substitute the Cu atoms underneath the N layer. Fe–Cu bond length values are instead typical of Fe in an fcc site. Adsorption of Fe on N-saturated surface has also been investigated with low temperature STM and DFT calculations [44], revealing a new position of Fe, sitting on a "bridge site" between two N atoms, and directly on top of a surface Cu atom [45]. This site, which is in principle compatible with XAFS analysis [33,34], induces a strong local distortion of the substrate [44].

At variance with results obtained on the N precovered Cu(100) surface (at N subsaturation coverage), simultaneous deposition of N and Fe at temperature T = 700 K results in the formation of ordered arrays of ferromagnetic square Fe_4N islands with lateral size of 10 nm [29]. Iron nitride ultrathin films could also be grown by Fe evaporation N saturated Cu(100)at room temperature and annealing at T = 720 K [30]. The produced films shown a *p4gm*(2×2) LEED pattern, caused by a reconstruction where N atoms sit on 4-fold hollow site of a Fe layer. The four Fe atoms rotate around the N atom ("clock reconstruction"), to produce the *p4gm* symmetry [30].

The aim of this study is to perform an investigation on Fe films deposited on c(2×2)-N/Cu(100) system at RT and for a variable N-precoverage, i.e. both at N saturation and subsaturation coverage. In particular we want to investigate the possiblity that RT Fe deposition on a N subsaturated Cu(100) may lead to the formation of an iron layer with inhomogeneous composition and/or structure. Most of the previous work carried out on this system consists in STM experiments. The reported works were effective in reporting a two stage mechanism of growth for Fe (on bare Cu first, followed by spillage over the N covered areas [15–24]) but they did not provide detailed quantitative information about the resulting film structure. In order to understand the atom geometry of RT deposited Fe films on the N precovered Cu(100) surface we focus on the following items:

- Possible presence of different types of surface periodicity.
- Modification of the lattice strain with respect to the situation observed on c(2×2)-N/Cu(100);
- Intermixing in deeper layers and N segregation.

The Surface X-Ray Diffraction (SXRD) technique is of great value, as it provides detailed information on the surface atom arrangement and on the vertical displacement of subsurface atom layers, giving in this way a clear picture of ultrathin films structures [46,47]. Moreover, it is complementary to surface XAFS (which describes the local geometry around the photoabsorbing atoms) as it is intrinsically related with lattice periodicity and long-range order. We chose therefore to study with SXRD experiments the structure Fe films deposited at RT on c(2×2)-N/Cu(100), for $\Theta_N \leq 0.5$ ML, i.e. at coverage values corresponding to formation of the regular arrays of square N-islands, and at saturation coverage. The Fe coverage Θ_{Fe} was 0.5 and 1.0 ML. We concentrated our analysis on Crystal Truncation Rods (CTR), that give information about the arrangements of the atoms in surface and sub-surface layers. We also monitored the surface periodicity looking at the surface diffraction peaks, and at the satellite spots around the (10 *l*) peaks, typical of the regular arrays of square N islands.

2. Experimental

All the experiments have been carried out at the beamline ID03 [48], of the European Synchrotron Radiation Facility (ESRF) in Grenoble (Fr). The beamline is equipped with a six-circle ultra-high vacuum (UHV) diffractometer operated in the *z*-axis mode, at a wavelength of 0.7287 Å. The sample was prepared *in situ*, in a UHV chamber (with base pressure $p = 4 \cdot 10^{-10}$ mbar) connected with the diffractometer. Clean Cu(100) surface was obtained by Ar^+ ion sputtering (pressure $p = 2 \cdot 10^{-5}$ mbar, ion beam energy $E_b = 2.0$ keV) and annealing to temperature T = 940 K. The cleanliness of the surface was checked with Auger Electron Spectroscopy (AES). N was adsorbed on the Cu surface by mild ion sputtering ($E_b = 500$ eV $p = 5.5\text{x}10^{-5}$ mbar) followed by annealing at temperature T = 630 K. In order to monitor the amount of N dosing, we measured the intensity of the N KLL structure in AES and we looked at the different SXRD peaks from the N-covered surface. In particular, we used Θ scans and hk scans to observe semi-integer peaks, and the satellite spots around the integer peaks, which are associated with the presence of the regular arrays of square N-islands [12,14]. In this work, we will use as unit cell the tetragonal cell composed of two primitive vectors of the square surface lattice (with length $a_s = 2.56$ Å), and a third vector (in the z direction) belonging to the conventional bulk unit cell for fcc lattice, (with length $a_b = 3.615$ Å). Fe was evaporated onto the surface with a Knudsen cell source at RT. The evaporation rate, previously calibrated with a quartz crystal thickness monitor, was verified by AES, looking at the ratio between the intensity of Fe LMM and Cu LMM signal. The amount of Fe evaporated, or Fe coverage, Θ_{Fe}, will be given here in monolayers, where 1 monolayer corresponds to the number of atoms in a Cu(100) layer on the whole clean surface. We observed the surface diffraction spots also after Fe evaporation, to monitor changes in diffraction pattern. The CTR structure factor amplitudes were obtained using the ANA data reduction programme, whilst the fitting was performed with ROD [49]. In particular, we obtained structure factor amplitudes from the following CTR: (10 *l*), (01 *l*), (11 *l*), (20 *l*), (02 *l*) , (21 *l*) and (12 *l*). The equivalent rods were averaged, with an agreement factor ranging between R = 0.02 and R = 0.13, with average <R> = 0.07. All the SXRD data here reported were taken at temperature T = 170 K, in order to minimise the effect of thermal disorder in the intensity of the diffraction peaks.

3. Results and discussion

Our analysis starts with SXRD taken from Cu(100) and c(2×2)-N/Cu(100) surface, in order to better explain the results from Fe films on this system. As an example, we show in Fig. 1 the (10 *l*) CTR structure factor amplitudes from Cu(100) and c(2×2)-N/Cu(100) ($\theta_N = 0.5$ ML), together with the best fit curves. The CTR of the N-covered surface clearly shows different behaviour with respect to the one taken from the