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Epitaxial submonolayer cobalt films on Cu(100) studied by X-ray diffraction

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The surface morphology of submonolayer Co deposits on Cu has been investigated by analyzing the profiles of surface X-ray diffracted beams along parallel momentum transfer directions. The profiles may be decomposed in two components of different width. The wide component contains direct information on the sizes of the cobalt islands. A two-level model gives a good description of the data for coverages below 0.5 ML. The kinetics of the island rearrangement involving the growth of large islands at the expense of small ones has also been investigated.

1. Introduction

The suitability of diffraction techniques to study the disorder and defects of crystalline surfaces has been recognized since many years [1,2]. Imperfections on a surface broaden a diffracted beam, which contains information on the statistical distribution of surface defects [3,4]. The control and characterization of the surface perfection is very important in different areas of surface science. In epitaxial growth of thin films or superlattices, imperfections may alter in an undesirable way the electronic properties of the films. The most utilized techniques to characterize growth perfection are electron diffraction either LEED or RHEED. These techniques are relatively simple from the experimental point of view but have the disadvantage that the interpretation is complicated by multiple scattering effects. Recently, the advent of high resolution LEED apparatus with transfer widths as large as 200 nm has given new breath to these studies [5,6]. On the other hand, neutral atom scattering for low defect densities and X-ray diffraction are purely kinematical techniques that allow, in a simple way, the extraction of quantitative information on the distribution of surface defects [7,8].

In this Letter we present an X-ray diffraction study on the early stages of growth of cobalt on Cu(100). From previous work [9,10] it is known that Co grows in a layer by layer mode when it is deposited on the copper substrates at temperatures in the range 270–450 K. The film is pseudomorphic with the fcc substrate, and has sometimes been (incorrectly) termed "fcc" cobalt, although in fact it is not cubic ($a=b\neq c$) because of the lattice strain.

We have performed transverse scans of diffracted beams from a surface consisting of Co islands on the Cu substrate to get information on the island size distribution. Also, the degree of surface perfection has been evaluated by utilizing previously published analytical results for the diffraction from two-level surfaces [11]. Finally, the

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kinetics of the reordering of a 0.5 monolayers deposit of Co has been studied by analyzing the temporal evolution of the intensity profiles.

2. Experimental details

The measurements were made at beamline X16A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. 5 mrad of bending magnet radiation were monochromated with Si(111) crystals. The beam was focused on a sample inside an ultrahigh vacuum system [12]. The Cu substrate was cleaned by sputtering and annealing cycles until no traces of carbon contamination were detected by AES. Cobalt was deposited from a home made evaporator consisting in a 0.1 mm thin Co wire wrapped around a 0.5 mm tungsten wire that was resistively heated. The surface cobalt concentration was determined by measuring the ratio of the intensities of the Co 95 and 716 eV to the Cu 104 eV Auger peaks and by using previously published data [9] on the Auger intensity calibration for this particular system. The estimated accuracy of the coverage is 10%.

3. Results

The scattering wave vector is described in the reciprocal coordinate frame commonly used in LEED: the h and k directions are parallel and the l direction is perpendicular to the sample surface. This is related to the coordinate frame usually employed in bulk X-ray diffraction in the following way: $(100)_{surf} = (110)_{bulk}$; $(010)_{surf} = (1\bar{1}0)_{bulk}$; $(001)_{surf} = (001)_{bulk}$ [13]. In this way the (10) beam in LEED notation is $(100)_{surf}$ which is located midway between $(111)_{bulk}$ and $(11\bar{1})_{bulk}$.

At the (100) point, (the subscript surf will be omitted from now on) the scattered waves from two consecutive crystal planes have opposite phases and therefore the diffracted intensity from the set of crystal planes parallel to the surface is very small. This is an important result for surface studies, since it makes the intensity at this position very sensitive to the surface roughness. The intensities in between bulk Bragg peaks have been called crystal truncation rods [14].

The (100) reciprocal lattice point is not experimentally accesible since it lies in the surface plane. Therefore, the measurements presented here were performed at (1, 0, 0.1). The surface sensitivity if not optimum is still very large.

Fig. 1 shows transverse scans at (1, 0, 0.1) measured along [010]. Data are shown before and after deposition of 0.5 monolayers (ML) of Co at room temperature. The profile for the clean substrate has been fitted with a Gaussian lineshape of FWHM $\Delta h = 0.0035$ reciprocal lattice units (RLU). We will assume this to be an effective resolution function even though it is mainly determined by the sizes of the areas at the surface which scatter coherently.

Deposition of 0.5 ML of Co produces a spectacular change in the intensities as is apparent in the figure. These data have been fitted with a

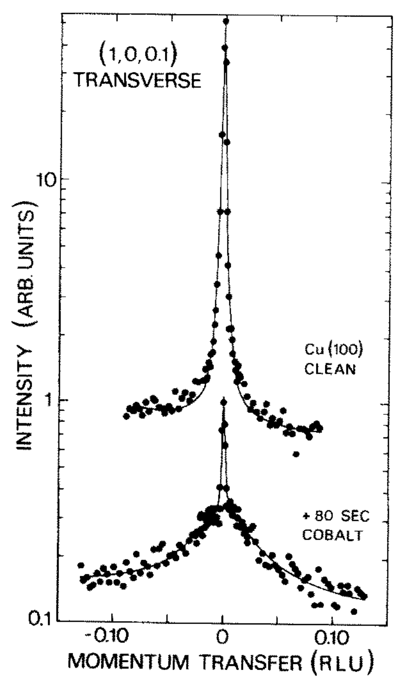

Fig. 1. Transverse momentum transfer scans at (1, 0, 0.1) for the clean and ordered Cu surface (top) and after deposition of 0.5 monolayers of Co at room temperature (bottom). The curves are offset for clarity. The continuous lines are the fitted curves: a Gaussian for the clean surface and a Gaussian and a Lorentzian for the covered surface.

two-component lineshape: a Gaussian with the same width as for the top curve and a Lorentzian of FWHM = 0.034 RLU. The relatively large width of the broad component is due to the small sizes of the Co islands.

We will use previously published analytical results for the diffraction from rough surfaces [11]. The simplest case is for a surface with only two levels where the angular distribution of the diffracted intensity is shown to consist in two components: a sharp central one resulting from the convolution of the ordered surface diffraction profile with the instrument reponse function and a broad one that comes from the shape transform of the islands at the surface. The scattered intensity will depend on the position along the crystal truncation rod where the data are acquired, but for constant I this gives a constant prefactor. Ignoring this, the intensity may be written:

$$I = I_B + I_D,$$

$$I_B\{1 - 2\theta(1-\theta)[1-\cos(q_z d)]\}\,\delta(q_x), \qquad (1)$$

$$I_D = 2\theta(1-\theta)[1-\cos(q_z d)]\,\frac{1/\pi L}{1/L^2 + q_x^2}, \qquad (2)$$

θ is the upper layer coverage i.e. the Co coverage in our case, $q_z d$ is the phase change along the surface normal due to the two surface levels a distance d apart. In our case $q_z d = 0.45 \times 2\pi$ which, by eq. (2), is close to the most sensitive "anti Bragg" condition ($q_z d = 0.5 \times 2\pi$). q_x is the parallel momentum transfer deviation, and L is the correlation length on the surface. In our case this corresponds to the mean size of the Co islands.

The equations above predict for "anti-Bragg" conditions and $\theta = 1/2$, zero intensity for the narrow component corresponding to complete destructive interference between the upper and lower surface levels. For an heteroepitaxial system such as Co on Cu however, this situation is not exactly fulfilled. For that case the intensity of the Bragg component is:

$$I_B = \left(\frac{1}{2} - \theta\frac{f_{Co}}{f_{Cu}}\right)^2, \qquad (3)$$

with f_{Co} and f_{Cu} the atomic scattering factors of Co and Cu respectively and where constant prefactors are again ignored. The ratio of the atomic scattering factors is approximately equal to the ratio of the atomic numbers of the two elements: $f_{Co}/f_{Cu} = \frac{27}{29} = 0.93$. From eq. (3) we see that zero intensity will not occur at $\theta = 0.5$ but at the slightly larger value $\theta = 0.5 \times f_{Cu}/f_{Co} = 0.54$. Eq. (3) also shows that the predicted shape as a function of θ is still parabolic, except that the parabola is truncated for $\theta = 1$ at an intensity $I_B = 0.74$.

The diffracted intensity I should be convoluted with the appropiate instrumental function. This affects the width of the sharp component but it does not appreciably enlarge the width of the broad one. From the data in fig. 1, one may evaluate the correlation lengths at the surface before and after Co deposition. For the clean surface, the full width $\Delta h = 0.0035$ RLU of the diffracted peak is found to be close to the resolution limit. From this we can say that the clean surface correlation length is at least 700 Å (equal to $a/\Delta h$ being a the nearest neighbour distance) which is a reasonably good value for a metal surface.

Within the two level model, the Lorentzian lineshape of the broad component after depositing Co is characteristic of an exponential correlation function at the surface. The correlation length L in this case corresponds to the mean size of the islands and it is given by [11] $L = a/\pi\,\Delta h$ where Δh refers to the FWHM of the Lorentzian in reciprocal lattice units. For the data in fig. 1 we obtain $L = 24$ Å as the mean Co island size after depositing 0.5 ML at room temperature.

From He diffraction experiments on the growth of Cu on Cu(100) an average terrace size of 100 Å was found after depositing 0.5 ML at 318 K [7].

Similar beam profiles to the ones depicted in fig. 1 were recorded for different Co coverages and fitted with a sharp Gaussian peak and a broad Lorentzian one. The results are shown in fig. 2. The height of the Gaussian peak decreases to a value close to zero and then it increases back to 30% of the initial value.

If the two-level model discussed above were applicable in the complete coverage range, then the normalized peak height of the sharp component should follow a parabola as a function of θ,

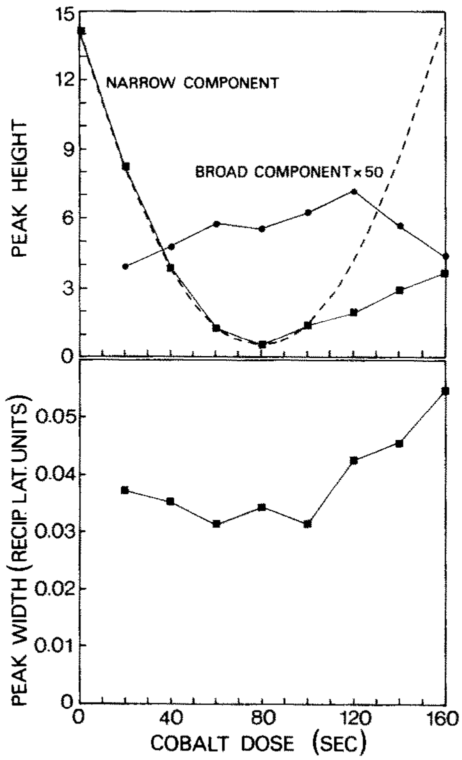

Fig. 2. Top: evolution of the heights of the sharp and broad components of the scattered intensity at (1, 0, 0.1) as a function of Co deposition time. 80 s deposition corresponds to 0.5 monolayers. The dashed line is the theoretical prediction of the two-level model. Bottom: evolution of the parallel momentum transfer width of the diffracted intensity as a function of deposition time.

centered at $\theta = 0.5$ as it is indicated in the figure by the dashed line. As it may be seen, the peak height follows a fairly parabolic behaviour in the coverage range 0–0.5 ML but it clearly deviates in the range 0.5–1 ML. This is the result of the build up of Co concentration on additional surface levels. A recent paper on photoelectron diffraction studies [15] on the same epitaxial system showed a significant concentration of Co islands of bilayer height for coverages above 0.5 ML, in good agreement with our findings. The height of the broad component shows also some variation with coverage. Eq. (2) at $q_x = 0$ gives $I_D \sim L\theta(1-\theta)$. Since we did not detect a large θ dependence of L (lower panel of fig. 2), the curvature of the intensity plot I_D versus θ should be negative in agreement with the data shown in the figure.

The bottom part of fig. 2 shows the evolution with coverage of the width of the broad component. Within a two-level model the L versus θ curve should be symmetrical around $\theta = 0.5$. As it may be seen in the figure the widths are larger above 0.5 ML. This is consistent with the two-level model being no longer applicable. A third surface level results in further destructive interference which in turn causes an extra broadening of the diffraction profile.

The step atoms located at the edges of the 2D Co islands on the substrate contribute to the surface free energy in the same way as the surface tension does in a 3D system. For a fixed coverage, the equilibrium configuration will be achieved by minimizing the island perimeter. This should cause large islands to enlarge at expense of the small ones. As a consequence the sizes of the domains of Co or the empty patches of the substrate should increase causing a narrowing of the diffracted intensity. Fig. 3 shows an illustrative example. An anneal to 100°C of a surface with a fresh deposition of 0.5 Co layers, results in a change in width of the broad component from 0.04 to 0.01 RLU

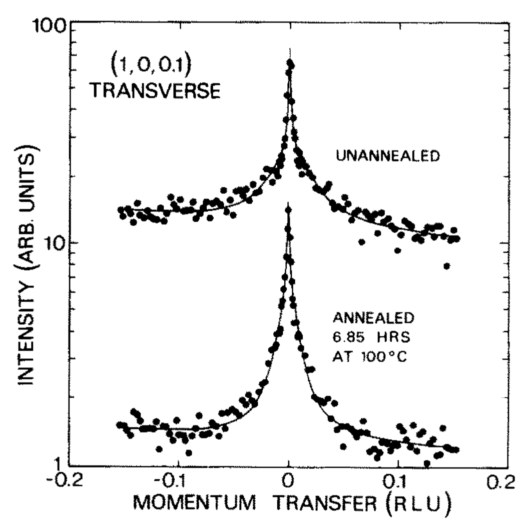

Fig. 3. Changes of peak profiles due to annealing. The top curve is for 0.5 ML of Co deposited at room temperature. The bottom one is for the same surface after 6.85 h of annealing at 100°C.

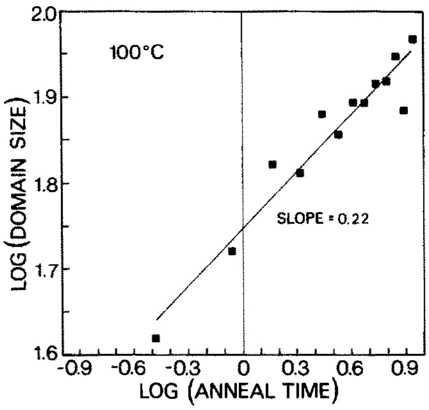

Fig. 4. Dependence of the average island size L with annealing time for 0.5 ML of Co on Cu at 100°C.

indicating that the mean island size increased from 18 to 37 Å upon annealing.

We investigated the kinetics of the island rearrangements in some detail. Fig. 4 shows the results expressed as log L versus log(annealing time). The value of the slope of the line that fits the data is 0.22. This indicates that the rate limiting step for the island reorganization is in fact a very slow one. Ordinary diffusion of adatoms follows a $(\text{time})^{1/2}$ type of law according to the Einstein equation for the diffusion length.

3. Summary

(i) The angular profile of the diffracted X-ray intensity from a surface containing 0.5 ML of Co on Cu(100) consists of a two component lineshape that can be rationalized as diffraction from a stepped surface in a two level model. The width of the broad component indicates that the mean size of the Co islands is 24 Å for room temperature deposition.

(ii) The evolution of the heights of the narrow and broad components may be also understood with a two-level model. Below 0.5 deposited layers the data agree with the model but from 0.5 to 1 ML the model fails since another surface level should be considered.

(iii) The kinetics of the island rearrangements from small to large islands for a coverage of 0.5 ML and a temperature of 100°C has been investigated by evaluating the mean island sizes as a function of annealing time. It has been found that the mean island size increases with annealing time with a dependence $(\text{time})^{0.22}$.

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References

[1] J.E. Houston and R.L. Park, Surf. Sci. 21 (1970) 209.
[2] J.M. Cowley and H. Shuman, Surf. Sci. 38 (1973) 53.
[3] M. Henzler, in: Electron Spectroscopy for Surface Analysis, Ed. H. Ibach (Springer, Berlin, 1979).
[4] T.M. Lu and M.G. Lagally, Surf. Sci. 120 (1982) 47.
[5] G. Meyer, J. Wollschlager and M. Henzler, Surf. Sci. 231 (1990) 64.
[6] H.N. Yang, T.M. Lu and G.C. Wang, Phys. Rev. Lett. 63 (1989) 1621.
[7] J.J. de Miguel, A. Cebollada, J.M. Gallego, J. Ferron and S. Ferrer, J. Cryst. Growth 88 (1988) 442.
[8] E. Vlieg, A.W. Denier van der Gon, J.F. van der Veen, J.E. Macdonald and C. Norris, Phys. Rev. Lett. 61 (1988) 2241.
[9] L. Gonzalez, R. Miranda, M. Salmeron, J.A. Verges and F. Yndurain, Phys. Rev. B 24 (1981) 3245;
A. Clarke, G. Jennings, R.F. Willis, P.J. Rous and J.B. Pendry, Surf. Sci. 187 (1987) 327.
[10] J. Ferron, J.M. Gallego, A. Cebollada, J.J. de Miguel and S. Ferrer, Surf. Sci. 211/212 (1989) 797;
S. Ferrer and J.J. de Miguel, Vacuum 41 (1990) 464.
[11] E. Vlieg, J.F. van der Veen, S.J. Gurman, C. Norris and J.E. Macdonald, Surf. Sci. 210 (1989) 301;
C.S. Lent and P.I. Cohen, Surf. Sci. 139 (1984).
[12] P.H. Fuoss and I.K. Robinson, Nucl. Instrum. Methods 222 (1984) 171.
[13] I.K. Robinson, E. Vlieg and S. Ferrer, Phys. Rev. B 42 (1990) 6954.
[14] I.K. Robinson, Phys. Rev. B 33 (1986) 3830.
[15] L. Li and J. Tonner, Surf. Sci. 237 (1990) 141.