"Magic" Heteroepitaxial Growth on Vicinal Surfaces

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The step period (Λ) of vicinal surfaces can be used as a new parameter for the control of metallic heteroepitaxial growth. This is evidenced here in the case of Ag/Cu(211). The deposition of 1 monolayer (ML) exhibits a $c(2 \times 10)$ superstructure leading to the formation of $\{111\}$ steps in the Ag adlayer in contrast with the original $\{100\}$ steps for the Cu substrate. This wetting layer can be viewed as a (133) Ag plane and it will be the starting point for the epitaxial growth. The deposition of 4 ML shows that the thin Ag film results homogeneous and no twins or stacking faults are detected. Moreover, the film grows along the [133] axis which is the orientation that minimizes the misfit between Cu(211) and the Ag film. Thus, the use of a regular stepped substrate allows one to select the crystallographic orientation of the growth and seems to be a way to avoid the creation of stacking faults.

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Metal-on-metal growth is now a long-established and extensively studied phenomenon, at least for substrates with low Miller index orientations [1,2]. Based on the common epitaxial relationships, i.e., the alignment of the most close-packed rows in both metals, and the so-called wetting energy, these pioneering works allow one to predict the growth mode of a thin heteroepitaxial film [2]. Moreover, in the case of two metals with the same crystallographic structure but with very different lattice parameters, the misfit leads to the well-known Moiré effect along the close-packed rows. However, the high symmetry of the dense surfaces often leads to the growth of multidomain films. Therefore, it is of great interest to find a way to control perfectly the crystallographic growth of the deposited film and a key point is the lowering of the substrate symmetry.

In this paper, we show that it is possible to control the heteroepitaxy of a thin film by using a crystal with a regular stepped surface as a substrate in order to force the growth with a long-range correlation. The idea is schematically represented in Fig. 1: the regular stepped surface can be characterized by the step period, Λ, which depends on the step heights and the number of atomic rows within the terraces. In principle, it is possible to choose two metals of different lattice parameters and to search a suitable relationship between the Λs to advantage the epitaxy, as shown in Fig. 1. Therefore, if the misfit between the two Λs is small, an epitaxial relationship is filled, permitting the control of the growth along the direction normal to the steps (of course, for the other direction, the lattice parameter misfit dominates the epitaxy, as described above). However, note that only a few Λ coincidences exist between the two metals. This is what we define as "magic" heteroepitaxy, similarly to Bartolini *et al.* [3] who introduced the notion of magic vicinal surfaces to explain the appearance of favored orientations of pure Au vicinal surfaces with respect to the number of reconstruction cells of the dense Au surfaces.

We consider here the Cu-Ag system, which has been intensively studied both experimentally [4,5] and theoretically [6,7]. It can be viewed as a representative case for systems exhibiting a large difference in the lattice constants ($a_{\mathrm{Ag}}/a_{\mathrm{Cu}} = 1.13$). Moreover, the solubility limits are very weak in the bulk, so that we can consider that no interdiffusion occurs during the whole experimental procedure. This allows one to obtain abrupt interfaces from the chemical point of view and this is reinforced by the strong tendency of Ag to segregate at the surface in Cu-Ag alloys [8]. The choice of Cu(211) as a substrate is motivated by two reasons: first, Λ is very small ($\Lambda = 0.626$ nm), leading to a strong step-step interaction and thus to a roughening transition at a temperature larger than room temperature [9]. This ensures the existence of a well-ordered array of steps over large domains of the sample. Second, the high step density can force a long-range coherence in the growth layer. Moreover, among all (111) vicinal surfaces of Cu and Ag, it appears that Cu(211) and Ag(133) are those that present the magic Λ coincidence (the misfit is only 0.4%). Therefore, one could expect that this epitaxial relationship between the Cu substrate and the deposited Ag film will permit a satisfactory growth process.

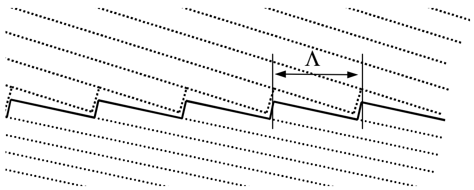

FIG. 1. Scheme of the heteroepitaxial relationship obtained by the matching between the step period Λ of two regular stepped surfaces.

The Cu(211) surface presents a miscut of 19.47° with respect to the (111) planes. It can be considered as a vicinal surface with (111) terraces separated by a periodic array of steps parallel to the $\langle 110\rangle$ direction constituted by $\{100\}$ microfacets. Each terrace exhibits $2+\frac{2}{3}$ close-packed rows of Cu atoms. To define the lattice basis, we use the orthogonal vectors:

$$\mathbf{a}_{211} = [\bar{1}11], \qquad \mathbf{b}_{211} = \frac{1}{2}[0\bar{1}1], \quad \text{and} \quad \mathbf{c}_{211} = [211]. \tag{1}$$

This choice implies that $\mathbf{a}_{211}$ is normal to the steps, corresponding to the period Λ (cf. Fig. 1), $\mathbf{b}_{211}$ is parallel to the steps, corresponding to the system zone axis (its modulus being the interatomic distance of pure copper), and $\mathbf{c}_{211}$ is normal to the surface plane. In the following, all the data (maps, rods) are presented relative to the (211) basis while the indexation of the Bragg peaks refers to the notation of the usual cubic system.

We first study the clean Cu(211) crystal. An electrochemical polished Cu(211) sample was introduced in UHV chambers (2×10^{-10} mbar). The clean surface was prepared by repeated cycles of sputtering with 1 keV Ar^+ ions and flash annealing at 900 K. The sample was then studied by grazing incidence x-ray diffraction (GIXD) at the DW12 beam line of LURE-DCI using 15 keV photons. The surface quality and the miscut angle were checked by mapping the reciprocal space in a large region. In the (211) basis, the actual map corresponds to the $(h\,2\,l)_{211}$ map presented in Fig. 2(a), in which four Bragg peaks can be localized. In Fig. 2(b), we have represented the reciprocal plane normal to the zone axis $[0\,\bar{1}\,1]$ and passing across the $(0\,\bar{2}\,2)$ Bragg reflection of a fcc lattice, the reciprocal space zone investigated in the map is evidenced by the dashed outline. The comparison between the scheme and the experimental Cu map confirms the (211) surface orientation. Moreover, the detailed analysis of the crystal truncation rods, clearly visible in the map, allows us to certify the weak surface roughness.

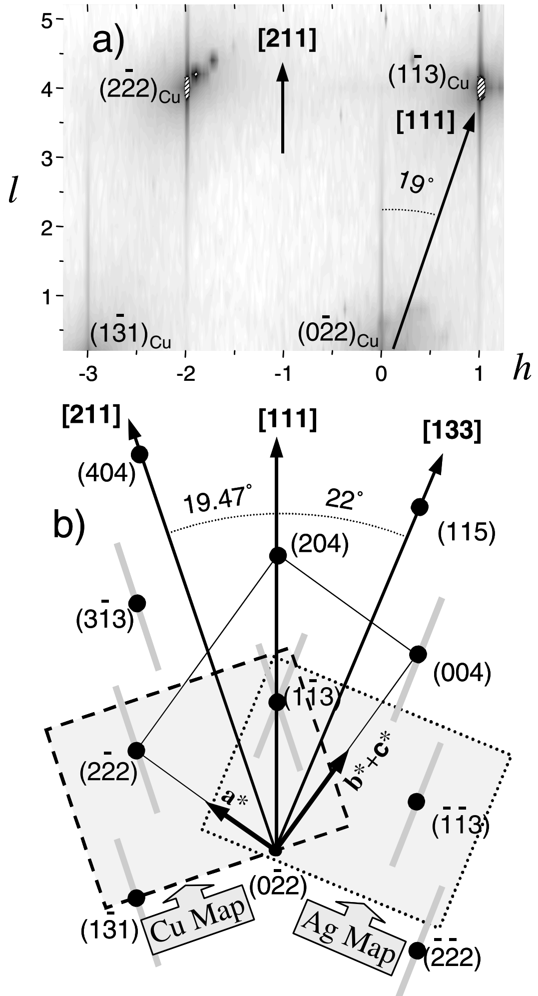

FIG. 2. (a) Reciprocal space map $(h\,2\,l)_{211}$ of the clean Cu surface. Four Bragg peaks are evidenced and crystal truncation rods normal to the surface are visible. (b) Representation of the reciprocal space plane of a fcc crystal, normal to the $[0\,\bar{1}\,1]$ direction and passing through the $(0\,\bar{2}\,2)$ reflection. Two regions are evidenced representing the case of a (211) surface (dashed) and of a (133) one (dotted), respectively. The comparison between this scheme and the collected maps [(a) and Fig. 4] allows one an easy indexation of the Bragg reflections.

The deposition of 1 monolayer (ML) of Ag atoms (i.e., the full coverage of the Cu substrate) is performed in order to understand how the Ag atoms wet the Cu surface. The deposition was done at room temperature with a rate of 0.07 ML/min and was followed by a flash annealing at 550 K. No significant interdiffusion was detected by Auger spectroscopy during this procedure. The LEED diagram showed a $c(2\times10)$ reconstruction with respect to the Cu(211) basis. Moreover, we have collected by GIXD a set of 57 in-plane independent structure factors and eight rods, which are shown in Fig. 3. A simple model can reproduce the observed symmetries: first of all, the "×10" periodicity along the steps is obtained by accommodating the lattice parameter misfit between Ag and Cu and covering ten Cu atoms by nine Ag ones along the close-packed rows on the terraces [6]. Doing that, the resulting Ag interatomic distance is compressed of about 2% with respect to its equilibrium bulk value. Moreover, one Cu (111) terrace is completely covered by adding two close-packed Ag rows to the present one. The centered symmetry and the double periodicity along $\mathbf{a}_{211}$ are obtained if the adjacent Cu terrace is covered by translating the three close-packed Ag chains of a vector $\mathbf{t}=\mathbf{a}_{211}+5\mathbf{b}_{211}$, as shown in Fig. 3(a). Therefore, we obtain a Ag vicinal surface, constituted by (111) terraces covering uniformly the Cu substrate and separated by a regular succession of $\{111\}$ steps. This atomic arrangement corresponds to the expected (133) plane. Note that the modification of the steps orientation predicted by the model (i.e., $\{100\}_{\mathrm{Cu}}\rightarrow\{111\}_{\mathrm{Ag}}$) is energetically favorable [10]. If this rigid lattice model is able to reproduce the in-plane diffracted intensities for k_{211} value multiples of $\frac{9}{10}$

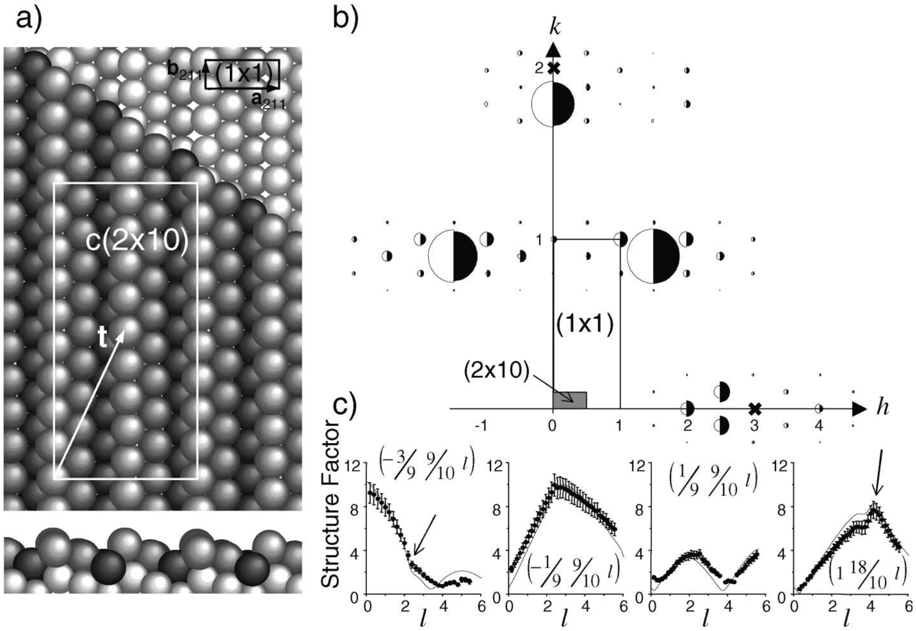

FIG. 3. (a) Structure of the Ag wetting layer obtained after relaxation by quenched molecular dynamics. The Cu(211) lattice basis is shown in the uncovered corner of the substrate. (b) In-plane GIXD data (collected at $l = 0.1$). The circle radii are proportional to the modulus of the structure factors. The empty parts correspond to the data and the filled parts are obtained by simulation with the relaxed model. The crosses denote the positions of Cu bulk allowed reflections. (c) Comparison between four of the eight measured rods and simulated ones. The arrows indicate peculiarities arising from the contribution of the Cu displacements to the rods intensity, due to the Ag adsorbed layer.

[especially the strong reflections in Fig. 3(b)], it cannot account for the existence of the weaker satellite peaks. In fact, their intensity is due to the atomic relaxations between the Cu substrate and the adsorbed Ag atoms.

To account for atomic relaxations, we perform quenched molecular dynamics (QMD) simulations [11], used recently to reproduce successfully GIXD data [12]. The N-body interatomic potentials used in this study are derived from the second moment approximation of the tight-binding scheme [13]. Because of relaxations, the Ag rows adopt an undulatory trend in the terrace plane, which is responsible for the satellite peak intensities observed in GIXD. As shown in Fig. 3(b), the agreement between all the collected data (both in and out of plane) and the relaxed model is very good. Note that only a scale factor is used for the comparison [14]. This completely validates the relaxed model, which allows us to reproduce all the features of the collected diffraction rods [see Fig. 3(c)]. Moreover, we point out that the model reproduces the peculiarities of the fractional rods, indicated by the arrows in Fig. 3(c), which are due to the Cu displacements induced by the Ag adsorbed layer.

At this point, we have shown that the Ag wetting layer is constituted by a regular succession of (111) terraces separated by $\{111\}$ steps. This new atomic arrangement can be viewed as a Ag(133) plane, this orientation minimizing the misfit between Cu and Ag along the direction normal to the steps (i.e., on the parameter Λ). Then, we can ask if the growth direction will be imposed by this thin layer. Therefore a film of 3 ML of Ag was deposited at room temperature to investigate the growth on this new substrate. The film lattice parameter in the direction parallel to the steps was measured by a radial scan performed along $\mathbf{b}_{211}$ and passing through the Cu Bragg peak $(0\,2\,0)_{211}$. A peak corresponding to the film was found at $(0\,1.77\,0)_{211}$. The resulting lattice parameter is 0.406 nm, indicating that the Ag film is less than 1% compressed in this direction. For the determination of the film orientation, a reciprocal space map $(h\,1.77\,l)_{211}$ was measured, in which the intensity diffused by the Ag film was collected. Diffracted intensity rods are clearly visible in the map reported in Fig. 4, the h coordinates of these rods being integer numbers. This proves that the Cu substrate and the Ag film are in a remarkable epitaxial relationship along the direction normal to the steps. Moreover, the intensity is modulated along the rods, presenting well-localized maxima, in correspondence with the positions of the Ag Bragg peaks. A detailed analysis of the rod's profile reveals weak periodic oscillations (not clearly visible in Fig. 4), according to a thickness of 4 ML. Note that the presence of such oscillations is an additional evidence of the 2D character of the film surface and interface. The Bragg peaks of the Ag film are quite useful in understanding the crystallographic orientation of the film with respect to the substrate [see the differences between the peak distribution from Figs. 2(a) and 4]. If the Ag film is supposed cubic, it is possible to identify the Bragg reflections with a set of

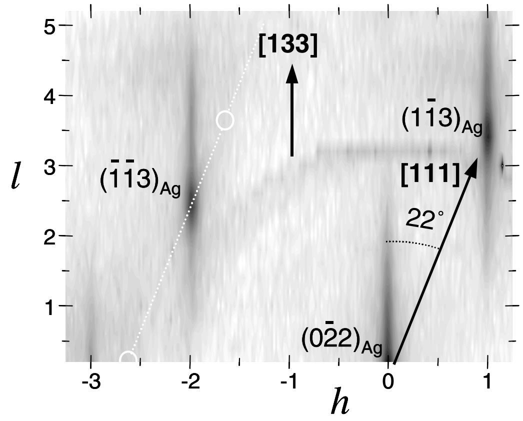

FIG. 4. Reciprocal space map $(h\,1.77\,l)_{211}$ collected after the deposition of 4 ML of Ag. Three Bragg reflections relative to the Ag film are localized. A comparison with the scheme reported in Fig. 2(b) allows one the indexation of the reflections. The presence of rods demonstrates the 2D nature of the film surface and interface. The dotted white line represents the expected direction of diffuse scattering for the stacking faults and the white circles indicate the places of the expected Bragg peaks for the twins. The presence of a parasitic ring of diffuse scattering is due to the hardened area localized at the edge of the copper sample.

Miller indexes which results from a growth of the Ag film along the $[133]_{Ag}$ direction. The dotted region of the scheme reported in Fig. 2(b) corresponds to the Ag map. The relative positions of the peaks can be fitted to those shown in the scheme if an inversion is performed, i.e., a map rotation of 180° about the direction normal to the surface. This indicates that the Ag film is twisted with respect to the substrate (i.e., the bulk stacking *ABCABC* is reversed in *CBACBA* at the surface) and it allows an unambiguous identification of the $[111]_{Ag}$ axis, measured at 22° to the surface normal. This means that the [111] direction of Ag is tilted with respect to the substrate one, which is consistent with the change in the miscut angles between the two vicinal surfaces (2.53°). Thus we can conclude that the film has grown along the expected [133] direction.

Another striking feature is that no diffuse scattering is detected along the $[111]_{Ag}$ direction in the Ag film map (see Fig. 4 for more details), indicating that the film seems to result free from stacking faults and twins. This behavior is completely different from the one observed during the homoepitaxial growth of Ag on dense surfaces. Actually, the growth of the film with a perfect stacking sequence is achieved only in the presence of a surfactant element [15,16]. A similar behavior has been observed very recently in the case of Ag/Cu(111), also [5,17]. This shows that the use of a regular stepped substrate may be another way to avoid the creation of stacking faults during the growth process.

In conclusion, the deposition of 1 ML of Ag on top of a Cu(211) substrate leads to a $c(2 \times 10)$ superstructure. This is characterized by the formation of {111} steps in the Ag film in contrast with the {100} ones for the Cu substrate. Moreover, we have shown that the full understanding of the GIXD data is achieved only if the relaxations both in the deposited metal and in the substrate are taken into account. The efficiency of QMD simulations using realistic *N*-body potentials is proved to be remarkable to obtain reliable models. Then, the new atomic arrangement of the wetting layer leads to the growth of a film with the expected epitaxial relationships, i.e., $(211)_{Cu} \parallel (133)_{Ag}$ and $[0\bar{1}1]_{Cu} \parallel [01\bar{1}]_{Ag}$. This result opens a new way in the field of heteroepitaxial metal-on-metal growth and it is of a general trend as the epitaxial relationship can be predicted by the knowledge of the step period Λ only. Moreover, contrary to the case of dense substrates, the presence of a regular array of steps at the surface allows one to select the crystallographic orientation of the growth and seems to be an efficient way to control the stacking sequence of the atomic layers.

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