Surfactant-Induced Suppression of Twin Formation During Growth of fcc Co/Cu Superlattices on Cu(111)

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Cu/Co bilayers grown by molecular beam epitaxy on Cu(111) present a peculiar defect: the Cu layers display a large fraction of fcc twins, giving rise to a lack of lateral continuity in the film and causing direct ferromagnetic coupling in Co/Cu superlattices. We show how the formation of twins in the epitaxial Cu layers can be suppressed by precovering the clean Cu(111) surface with a monolayer of Pb that floats at the surface of the growing film. The use of this surfactant results in a highly improved structural quality of Co/Cu superlattices.

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Using surface-active agents to produce desired characteristics in crystals grown from liquid solutions is a long-standing practice. Already in 1958, Cabrera described that these "surfactants" may affect growth kinetics, morphology, and accordingly, properties of the crystals [1]. The concept was adopted by Egelhoff and Steigerwald [2], who explored the role of adsorbed gases in metal on metal epitaxy under ultrahigh vacuum (UHV) conditions. It was not, however, until the dramatic example of islanding suppression in the growth of Ge/Si(100) by use of an As surfactant layer [3] that the field achieved momentum. Since then, other examples of the influence of surfactants in the epitaxial growth of semiconductors have been reported [4]. Recently, the first reports of surfactant effects in *homoepitaxial* growth of metals have appeared: Sb and O change the growth mode from 3D to layer by layer for Ag(111) and Pt(111), respectively [5,6]. In this Letter we present the first example of surfactant action on *heteroepitaxial* growth of metallic superlattices. In particular, we demonstrate that a monolayer (ML) of Pb can suppress twinning in the Cu layers during the growth of Co/Cu superlattices on Cu(111) by molecular beam epitaxy (MBE), an effect with important implications for oscillatory magnetic coupling [7] and the related giant magnetoresistance [8].

The experiments have been carried out in a MBE chamber equipped with Pb, Co, and Cu evaporators, rear-view low energy electron diffraction (LEED) optics, a cylindrical mirror analyzer for auger spectroscopy (AES), and thermal energy atom scattering (TEAS). The beam of He has an energy of 67 meV and a monochromaticity of 2%, the corresponding transfer width being ~400 Å. The LEED intensity vs electron energy (*I-V*) curves were recorded with a computer-controlled video system. The Cu(111) sample was cleaned by repeated sputtering and annealing cycles.

Figure 1 summarizes the main message of this Letter. Panel (a) shows the *I-V* curves for clean Cu(111) displaying the threefold symmetry expected for an fcc (111) surface with inequivalent (01) and (10) diffracted beams, i.e., each one has a different evolution of its intensity with electron energy. Deposition of Cu at room temperature (RT) produces *I-V* curves indistinguishable from those of the clean surface. Growth of Cu/Co sandwiches on clean Cu(111) leads to an evident sixfold symmetry in the LEED pattern, as shown by the *I-V* curves for the (10) and (01) beams of a 3 ML Cu/3 ML Co/Cu(111) bilayer depicted in Fig. 1(b): the two types of spots now have identical evolution with the electron beam energy. The sixfold symmetry is not changed by depositing Pb on top of the Co/Cu bilayer. On the contrary, *precovering the initial Cu surface with Pb results in Cu/Co sandwiches*

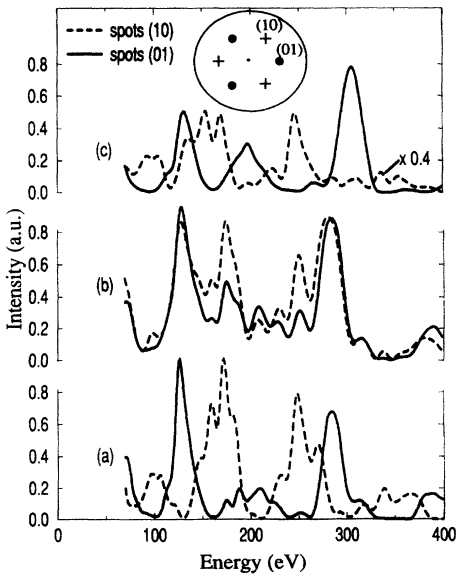

FIG. 1. LEED intensity vs energy (*I-V*) curves for the (10) and (01) beams of (a) clean Cu(111), (b) a 3 ML Cu/3 ML Co bilayer grown on clean Cu(111), and (c) a 3 ML Cu/3 ML Co bilayer grown on a Pb-covered Cu(111) surface. The similarity of curves (a) and (c) indicates that twin formation in the Cu layer is suppressed by the presence of Pb.

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with threefold symmetry resembling that of the substrate, as proven by Fig. 1(c).

Figure 2(a) compares the experimental data of Fig. 1(b) with a fit obtained by taking a linear combination of the intensities of the (10) and (01) beams of the bare Cu substrate. This simple approach is expected to reproduce the experimental data only if the Cu overlayer is composed of twinned islands of the fcc structure with stacking sequences *ABC* and *ACB*, respectively, and a lateral size larger than the transfer width of our LEED instrument. The quality of the fits is quantified by calculating the corresponding Pendry R factors. For a relative weight of 60% and 40%, we obtain excellent Pendry R factors of 0.176 and 0.185 for the bilayer (10) and (01) beams, respectively.

The twinning of the Cu layer is related to by the mode of growth of the previously deposited Co layer. Co deposited at RT on Cu(111) forms double-atomic-height (DAH) islands of triangular shape with two orientations rotated by 60° as revealed by scanning tunneling microscopy (STM) [9]. The islands nucleate at each of the two threefold sites of the fcc (111) face: one of them follows the correct stacking sequence of the fcc substrate (*ABCab*) while the other requires the formation of a stacking fault (SF) at the Co/Cu interface (*ABCbc*), as illustrated by Fig. 2(b) [10]. Analysis of STM images [11] indicates that the relative population of triangular islands of the two orientations at low Co coverages is 60% and 40%, respectively. Triangular islands formed on an fcc (111) face can form either (111)- or (100)-type steps. It has been proposed [9] that Co islands nucleated at the two different adsorption sites change orientation in order to present always the same type of steps. This is supported by recent molecular dynamics calculations [12], suggesting that for Co on Cu(111), the formation of islands with a stacking fault at the interface and low-energy steps may be favored over those with the correct stacking sequence but high-energy steps. Growth of fcc Cu on top of these two kinds of Co islands (with or without stacking fault at the Cu/Co interface) results in twinned Cu crystallites. Figure 2(b) schematically illustrates the case where Cu nucleates on both threefold sites (i.e., with a stacking fault) of the Co surface.

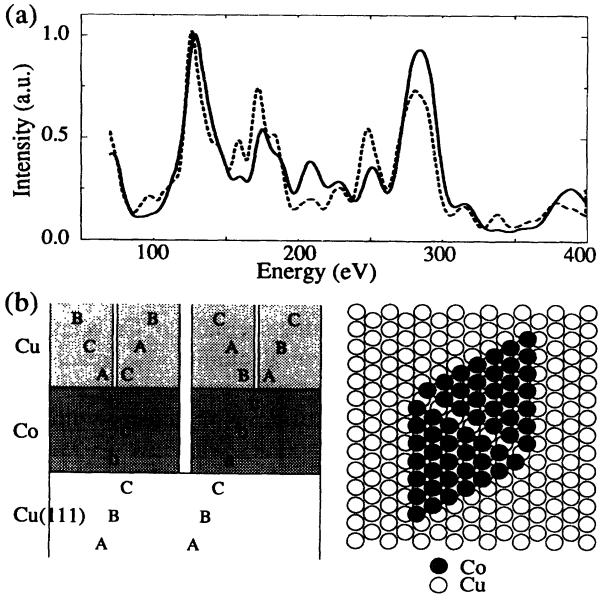

FIG. 2. (a) Solid line: experimental I-V curve for the (01) beams (the three equivalent beams are averaged together) of a 3 ML Cu/3 ML Co/Cu(111) bilayer grown by MBE; dotted line: fit using the (10) and (01) intensities of the bare Cu(111) substrate, $I^* = I_{(01)} + 0.65 \times I_{(10)}$. The Pendry R factor of this fit is 0.185, indicating that the Cu layer is composed of fcc twins. (b) Schematic top view of the islands and illustration of the proposed stacking sequence in the Cu/Co bilayers. The Co islands including a stacking fault at the interface display a local hcp stacking. The Cu layer grown on top is composed of fcc twins (*ACB* and *ABC*).

The twinning of the Cu layers and the associated lack of lateral continuity is most likely the cause of the difficulty in observing antiferromagnetic (AF) coupling in (111)-oriented, MBE-grown Co/Cu superlattices [13]: the Cu twins leave empty trenches in between that can hardly be filled due to the existence of energy barriers at descending steps hindering interlayer mass transport. The unfilled trenches provide direct contacts between consecutive Co layers, resulting in ferromagnetic coupling independently of the Cu-spacer thickness. On the other hand, (111)-textured samples grown by sputtering consistently display antiferromagnetic coupling [8], which indicates that sputtered Cu layers are continuous, probably due to the reduced mobility of deposited species under sputtering conditions.

Let us now discuss the effect of precovering the Cu substrate with a ML of Pb. Pb grows on Cu(111) by forming first a compact ML with an incommensurate $p(4 \times 4)$ superstructure followed by the growth of 3D clusters [14]. After deposition of a Pb coverage slightly above 1 ML on the clean Cu(111) surface at 445 K, a $p(4 \times 4)$ LEED pattern with sharp spots and low background is observed. On this surface we deposited alternated Co and Cu layers at temperatures between 295 and 320 K. In all cases the $p(4 \times 4)$ LEED pattern and the AES peaks of the Pb ML could be observed after stopping deposition, indicating that Pb floats on top of the growing Cu/Co film without detectable losses. The detailed structure of these Pb/Cu/Co films will be described in detail elsewhere [10]; here we would rather concentrate on the influence of the Pb layer on the twinning process. As Fig. 1(c) clearly shows, when a 3 ML Cu/3 ML Co sandwich equivalent to the former one is grown on a *Pb-covered* substrate, no signs of twin formation are observed. This information is obtained from the intensities of the integral-order spots. In spite of the fact that Pb is a heavy scatterer for

low energy electrons, the *I-V* curves of the integral-order beams are weakly sensitive to the presence of the Pb overlayer because the $p(4 \times 4)$ superstructure is not exactly commensurate with the substrate [15]. Thus, the intensities of these spots, shown in Fig. 1(c), reflect mainly the stacking sequence of the substrate. The *I-V* curves for the (10) and (01) spots display the characteristic threefold symmetry and are in fact very similar to those of the clean Cu(111) substrate, although the peaks are somewhat distorted and slightly shifted in energy, indicating a small contraction of the interlayer spacing with respect to the bulk value. Obviously, the predeposition of the Pb ML modifies the growth of the Cu/Co bilayer, eliminating the twinning and producing a pure fcc stacking sequence.

The limited transfer width and sensitivity to defects of our LEED system makes it difficult to determine the perfection of the grown film. In order to do that and, in particular, to find out whether such films constitute adequate substrates for the growth of further bilayers of higher quality than those grown without Pb, we resort to the TEAS data. Because of its lack of penetration and extremely high sensitivity for surface defects, TEAS has been successfully applied to studying *in situ* the growth mode and morphology during epitaxial growth of metals [16,17]. The peak intensity of the specular beam is a direct measure of the concentration of defects on the surface. During epitaxial growth, these defects consist basically of atomic steps. The lower curves of Fig. 3 show the evolution of the specular He intensity during deposition of 3 ML of Co on the clean Cu(111) substrate at 320 K and then 3 ML of Cu on the previously grown Co film. Without Pb, the TEAS intensity rapidly falls down to zero with Co deposition. The nonoscillatory, monotonic

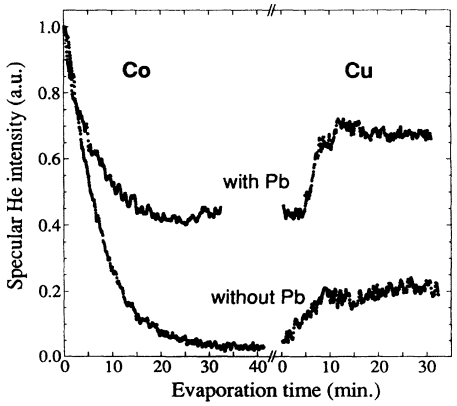

FIG. 3. Evolution of the He specular beam intensity during growth of Co and Cu on Cu(111), both with and without a 1.5 ML Pb layer predeposited on the substrate. The angle of incidence is 71° (out-of-phase condition); the intensity is normalized in each case to the value before starting the deposition of Co. The higher level of intensity reflected by the sample grown with Pb indicates a higher structural perfection.

decrease in the reflected intensity signals the reduced interlayer mass transport, which results in simultaneous multilayer (3D) growth and severe accumulation of defects on the film. Further deposition of Cu on top of the Co layer at 295 K produces a slight recovery of intensity up to saturation at 20% of the initial intensity. This stage corresponds to the formation of the twin-fcc Cu islands described in the LEED experiments above (Fig. 2). The upper curves display the corresponding data obtained during the growth of an equivalent Co/Cu bilayer on a Cu surface precovered with 1.5 ML of Pb. In this case the drop in intensity caused by the deposition of Co is much smaller, and a stable level of reflected intensity above 40% of the initial value is reached. After interrupting the Co deposition, the LEED pattern still shows the $p(4 \times 4)$ superstructure of the Pb ML. The high value of the reflected intensity corresponds to a concentration of defects at the surface of ~4% of a ML [16] and indicates that the Pb/Co film has good structural quality. Also, a Co_{53}/Cu_{60} AES peak ratio larger than without Pb is measured, indicating that the Co islands now are single atomic height (SAH) and cover a larger fraction of the substrate. Evaporating Cu on this layer increases the reflected intensity to a larger extent than in the absence of the surfactant. The LEED pattern is always $p(4 \times 4)$, indicating that Pb has again diffused to the surface.

A key point in the behavior of a surfactant is whether it segregates efficiently to the surface, thus maintaining its influence on the growth mode for several layers. Pb, in fact, leaves the film surface ready for growing additional Co/Cu bilayers, and can therefore be used to grow superlattices of high structural quality. This is illustrated in Fig. 4. There we proceeded to grow a three-(Cu/Co)-period superlattice, on a surface precovered with ~2 ML of Pb. The TEAS intensity is normalized to the initial value before starting the deposition of the first Co layer. The thicknesses of the different layers were varied between 2 and 6 ML. From the second Co/Cu bilayer on, a steady state of high structural quality was reached, as demonstrated by the constant reflected intensity at ≃45%. This means that the concentration of defects within the transfer width of TEAS (400 Å) was low (~3% of a ML) and stationary, i.e., probably the growth of Cu and Co at this stage was taking place by step flow. After finishing growth, the Pb-induced $p(4 \times 4)$ LEED pattern could still be observed, indicating that the Pb layer had floated to the surface. The *I-V* curves of the (10) and (01) reflections again showed the threefold symmetry of fcc stacking without twins. Evidently, this process could be continued to produce superlattices with a large number of periods.

The microscopic role of surfactants has not been clarified yet. Growth processes can be determined both by thermodynamic and kinetic factors. Surfactants have been suggested to influence both. It has been proposed that As and Sb lower the surface tension of Ge/Si(100),

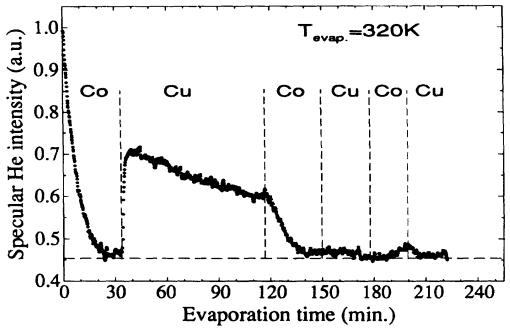

FIG. 4. Specularly reflected He intensity during the growth of three (Cu/Co) bilayers on a Pb-covered Cu(111) surface. The steady value of intensity at a level of 45% of the initial intensity indicates that the growth front is stationary.

thereby increasing spreading and wetting [3] or influence the surface energy anisotropy [4]. Several mechanisms have been suggested by which surfactants could suppress the energy barrier for interlayer mass transport [18]; Sb and O seem to produce such an effect for Ag/Ag(111) [5] and Pt/Pt(111) [6], respectively. Although we still cannot unequivocally identify the mechanism by which the Pb layer produces its surfactant effect, we believe that it prevents the formation of stacking faults at the interfaces by either suppressing adsorption on faulted sites or by acting on the islands steps. As mentioned above, it is most likely the difference in energies between the (100)- and (111)-type steps that determines the formation of DAH Co islands and the rotated orientation of those containing a SF at the interface. On the contrary, Cu does not appear to have a clear preference for any type of steps, and consequently Cu grows on Cu(111) as single atomic height islands without SF's. It is conceivable that the adsorption of Pb atoms at the borders of the Co islands renders the energies of the two types of steps similar. Then, for Co on Cu the situation would resemble that of the growth of Cu on Cu, with the step energies being unable to compensate for the cost of having a SF. In that case, only one type of Co islands will appear. Pb probably acts on the Cu layer by a similar mechanism: either suppressing adsorption on faulted site or promoting one kind of step, thereby forcing the existence of only one type of island. Additional experiments are in progress in order to clarify these points.

In summary, we have illustrated for the first time the possibilities offered by the use of surfactants on the growth of metallic superlattices. The specific effect of Pb in this case is to suppress the twinning in Co/Cu bilayers, which may have a substantial impact on our capability to observe magnetic coupling and giant magnetoresistance in MBE-grown superlattices. This should produce more consistent and reproducible results concerning the origin and applications of these phenomena.

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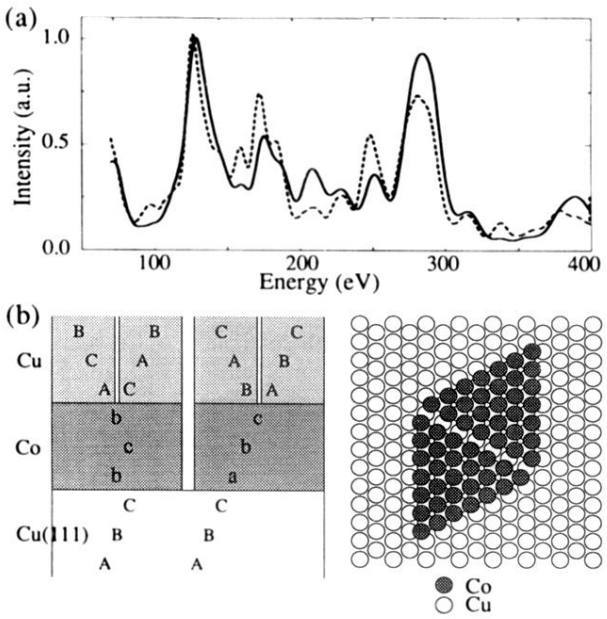

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