Appl. Phys. A 69, 553–557 (1999) / Digital Object Identifier (DOI) 10.1007/s003399900155

Applied Physics A
Materials
Science & Processing

Epitaxial growth of metals with high Ehrlich–Schwoebel barriers and the effect of surfactants

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Received: 21 April 1999/Accepted: 17 August 1999/

Abstract. Interlayer diffusion in epitaxial systems with a high energy barrier at the atomic steps – the so-called Ehrlich–Schwoebel (ES) barrier – is strongly reduced. As a consequence of this, a continuous accumulation of roughness takes place during growth. This undesirable effect can be corrected by using surfactant agents. We have studied the influence of the ES barrier on the preparation of epitaxial films on Cu(111), and the surfactant effect of a monolayer of Pb.

PACS: 68.35.Fx; 68.55.-a; 81.10.-h

The field of epitaxial growth has been an active area of research for a long time. Recently, great expectations have been awaken by the possibilities to design and produce new, artificial materials with exotic properties from their basic constituents. The search for efficient methods to prepare these materials has drawn renewed attention to the microscopic magnitudes that ultimately determine the outcome of the growth process.

The Ehrlich–Schwoebel (ES) barrier is one of these important parameters: it is the supplementary energy required by a diffusing adatom to cross an atomic step. Compact metallic faces show a very weakly corrugated electronic density, and therefore surface diffusion on them is very fast. In these cases, atoms deposited during growth find it much easier to move away from the steps than to cross them: as a result, interlayer mass transport can be severely reduced. This in turn strongly affects the film morphology, causing a steady increase of surface roughness. In the following we will describe a thorough characterization of the effects associated with the existence of a high ES barrier on Cu(111), and its modification by means of surfactant layer of Pb. This study has been performed with a variety of experimental techniques such as thermal energy atom scattering (TEAS), X-ray diffraction (XRD), and scanning tunneling microscopy (STM), combined with numerical simulations.

1 Influence of the Ehrlich–Schwoebel barrier on sample preparation

1.1 *Step bunching upon annealing*

The existence of a high ES barrier manifests itself already at the stage of sample preparation. Very soon after the introduction of the concept of the Ehrlich–Schwoebel barrier [1], it was realized that the resulting asymmetry in the rates of adatom incorporation to steps from each side could lead to morphological instabilities. For instance, due to this effect, fluctuations about the mean terrace size force atomic steps to move across the surface with different velocities. During growth, the amplitude of the perturbation decreases exponentially to zero, and the final configuration is a train of equidistant steps; however, during evaporation the perturbation amplitude increases exponentially resulting in grouping together or "bunching" of the steps [2]. This can easily be understood: during sublimation, steps recede by losing adatoms that detach from them and diffuse across the surface before desorbing into the vacuum. When the ES barrier is high, these adatoms cannot cross the steps: they are confined to the terrace right below the step from which they were released. Obviously, wide terraces admit more atoms than narrow ones, until they reach the equilibrium monomer density. Therefore, steps adjacent to these wider terraces move faster backwards and catch up with the slower ones.

Under ultra-high vacuum (UHV) conditions, metallic surfaces are usually cleaned by means of ion sputtering, followed by annealing the sample at high temperature to enhance atom mobility and allow the surface to reorder. During this part of the process, significant evaporation of the substrate material can take place, resulting in the formation of wide terraces separated by groups of very narrow ones, the so-called bunch of steps. This phenomenon can be detected with diffraction experiments such as the one shown in Fig. 1a: there, the specular TEAS intensity is depicted as a function of the incidence angle θ_i – measured with respect to the surface normal – of the He beam onto the Cu(111) sample. This kind of measurement is usually referred to as a "$\theta - 2\theta$" scan. In this case, the sample was prepared by extensive high-temperature an-

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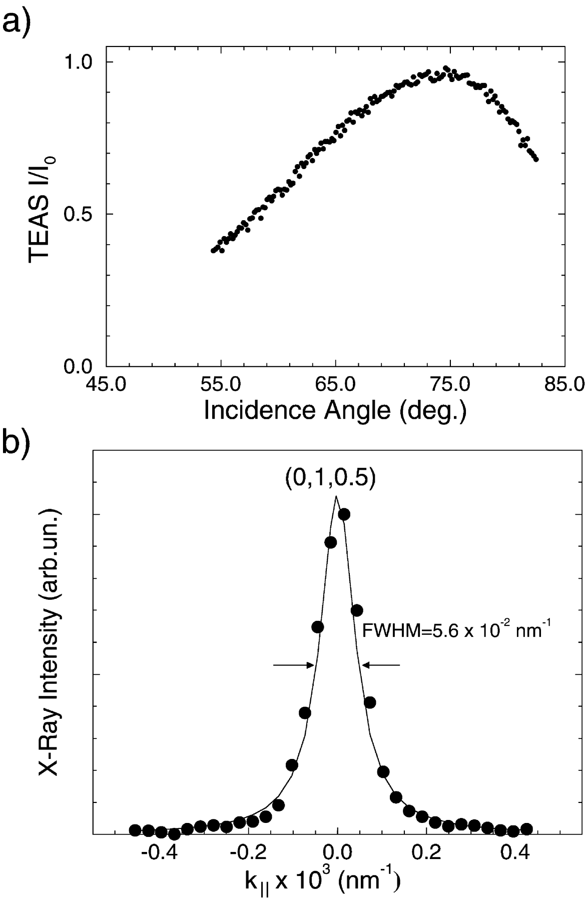

Fig. 1. **a** TEAS $\theta - 2\theta$ scan on a Cu(111) surface presenting considerable step bunching: the size of the flat terraces on the surface is estimated to be $\approx 1\,500$ Å, corresponding to 8–10 times the nominal width due to the sample miscut (1°). **b** S-XRD profile of the same surface: the FWHM of this scan indicates that the flat domains on the surface have an average size of 1100 Å, in reasonable agreement with the TEAS estimate

nealing, so that step bunching can be expected. The intensity decreases at high θ_i (grazing incidence) because the sample surface does not fully intercept the He beam; for more perpendicular incidence, on the other hand, the reduction of the reflectivity is of thermal origin, and can be described by the surface Debye–Waller factor [3]. The scan shows no traces of the intensity modulation that is associated with the variation of the interference conditions between consecutive terraces. This means that the flat areas of the surface must be much larger than the transfer width W_t of our He diffractometer, which is about 150 Å; typically, one can expect the average terrace size to be up to 10 times larger than W_t [5], that is, nearly 1500 Å. These flat areas must be separated by bunches of steps, with narrow terraces not larger than ≈ 25 Å, so that they would be totally covered by the cross section for diffuse scattering from the edges and not contribute to the specular intensity. This rough estimate is supported by additional surface X-ray diffraction (S-XRD) data obtained at the surface diffraction beamline (ID03) of the E.S.R.F. Figure 1b shows an angular scan across the {0,1} CTR (crystal truncation rod [4]) at the out-of-phase condition [3]. From the FWHM of this profile (5.6×10^{-3} Å^{-1}), one can calculate an average domain size of ≈ 1100 Å on the Cu(111) surface, in reasonable agreement with the former value.

1.2 Step debunching during growth

The phenomenon of step bunching is of kinetic nature, and can be reverted by inverting the experimental conditions, i.e., depositing material onto the surface instead of removing it. In this case, each terrace receives a number of atoms proportional to its area. If their mobility is high enough, these atoms will be able to reach the rising step on one side of the terrace and stick to it; crossing the downward step is forbidden by the ES barrier. Therefore, the sample will grow in the step-flow mode, but once again with different step velocities: the ones whose lower terrace is wider will receive more atoms, advance faster, and detach from the bunch. This process continues until all terraces have recovered their equilibrium width.

From these observations we can conclude that, when interlayer diffusion is strongly hindered by the presence of a high ES barrier, the traditional method of surface preparation, based on sputtering and annealing cycles alone, is not enough to obtain a well-ordered surface presenting a regular array of equally spaced steps. To achieve this goal, once the surface has been conveniently cleaned, one should evaporate a few monolayers of the same substrate material at high temperature.

The efficiency of this method is demonstrated by the TEAS data depicted in Fig. 2a. This $\theta - 2\theta$ scan is similar to the one presented in Fig. 1a, but was taken after growing 5 ML of Cu with the Cu(111) substrate at 400 K. Superimposed to the curve shape described above, can now clearly be seen the intensity oscillations corresponding to the different interference conditions between consecutive terraces. The fact that we can now observe this modulation means that the average distance between atomic steps on the surface is of the same order of our instrument's transfer width. Therefore, the step bunches have dissolved and the terraces must be close to

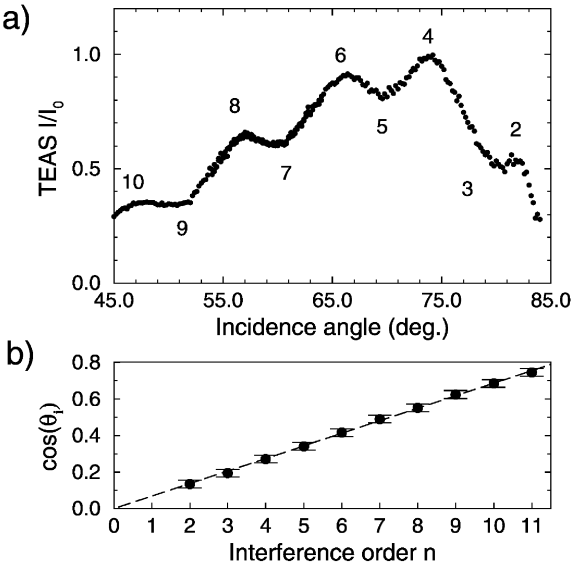

Fig. 2. **a** TEAS $\theta - 2\theta$ scan on the same Cu(111) surface, after growing 5 ML of Cu at 400 K. The intensity oscillations correspond to the different interference conditions between adjacent terraces. **b** From the angular positions of the maxima and minima, and by making use of the Bragg law, the height of the monoatomic steps on the surface can be found

their nominal size. The maxima and minima in the figure have been labelled with the corresponding values of the interference order n; by applying Bragg's law [6]: $2hk \cos\theta_\mathrm{i} = \pi n$, as shown in Fig. 2b, one can obtain the height of the atomic steps: $h = (2.08 \pm 0.02)\,\mathrm{\AA}$, in excellent agreement with the bulk interplanar spacing.

2 Homoepitaxial growth with high ES barrier

The growth mode is strongly influenced by the initial substrate morphology. When interlayer mass transport is inhibited and the clean surface consists of equally-sized terraces, growth proceeds in a multilayer fashion; it is well established that the occupation of each atomic layer follows a Poisson distribution, and the surface reflectivity decays exponentially [3, 7]. However, surfaces with high ES barriers not prepared in the way described in the previous section are likely to exhibit step bunching; in these cases, surface morphology evolves in a more complicated way. Figure 3 shows a set of TEAS data depicting the evolution of the specular He intensity during Cu deposition at several substrate temperatures, on a Cu(111) surface containing step bunches. The solid lines are the fits obtained with a kinetic growth model which is described in detail elsewhere [3]. Basically, this model takes into account the formation of pyramidal islands with no interlayer diffusion, and the gradual transition towards the step-flow mode with increasing adatom mobility.

Figure 3 clearly demonstrates that there exist two different growth regimes: initially, the intensity diffracted at the out-of-phase condition exhibits the expected exponential decay, which can be well described by the mentioned growth model. This indicates that the surface reflectivity is dominated by the nucleation and growth of multilayer islands on the large flat areas. The narrow terraces of the bunches, on the other hand, are much shorter than the adatom mean free path, and so growth there takes place in the step-flow mode. With increasing film thickness, the crossover to a different regime can be observed. This is associated with the disappearance of the original step bunches. Diffusion of Cu adatoms on Cu(111) is very fast, and for the substrate temperatures used in this experiment a large fraction of the deposited material is able to reach the atomic steps and attach to them. The advancing steps absorb the islands nucleated initially and the size of the wider flat areas of the surface diminishes. At some point during deposition, all the arriving adatoms are able to reach an already existing step, and from that moment on growth proceeds in the step-flow mode throughout the whole surface, without nucleation of any new islands.

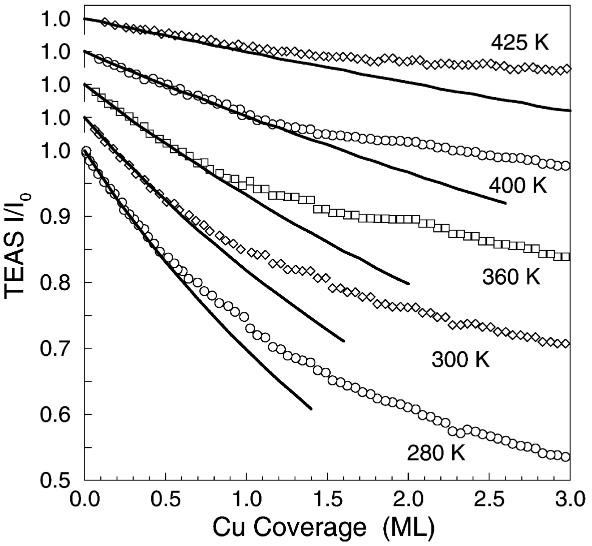

Fig. 3. Deposition of Cu on a surface with step bunches proceeds in two different stages: initially, multilayer islands appear at the wider terraces, causing an exponential decrease of the diffracted intensity. With increasing film thickness, the substrate steps detach from the bunches and advance absorbing the islands. Growth then continues in the step-flow mode, but with steadily increasing roughness of the edges

It is commonly assumed that during growth by step flow the surface morphology continuously replicates itself without any increment of the defect density. This should result in a constant level of diffracted intensity. Contrary to these expectations, the data in Fig. 3 show a steady decrease of the reflectivity during this second stage of growth, although the shape of the curves no longer corresponds to an exponential. This behavior reveals that the surface continues to accumulate roughness, even under step-flow conditions. This is another phenomenon associated with poor interlayer diffusion, and it is usually referred to as the "Bales–Zangwill instability" [8]. When adatom incorporation from the upper side of the advancing steps is suppressed, any kinetically-limited shape fluctuations that may appear during growth tend to be amplified. Atoms arriving from the lower terrace are easily captured by the protruding sections of the step, whereas the concavities remain shadowed and can only be filled by atoms moving along the edge. If this mode of diffusion is slow, as seems to be the case for many compact faces such as the fcc-(111), then the steps develop a dendritic shape whose roughness continuously increases until it eventually covers the whole terrace width. This process can easily be detected with TEAS due to the large cross section for diffuse scattering from steps [9]. A detailed analysis of these results is presented elsewhere [3]. In summary, limited interlayer transport results in an accumulation of roughness of different types, severely limiting the possibilities to produce artificial heterostructures of good structural quality.

3 Surfactant effect of a Pb monolayer

Using surfactant agents to assist growth can be an efficient method to induce layer-by-layer growth in systems with poor interlayer diffusion. A surfactant is an additive introduced during growth whose presence modifies the structure of the epitaxial film without incorporating into it. A good surfactant must segregate continuously to the surface of the growing film in order to maintain its activity indefinitely.

In our experiments, we have used Pb as surfactant, covering the Cu(111) surface with a full monolayer. Pb grows on this face in the Stranski–Krastanov mode, forming a wetting layer with a $p(4 \times 4)$ structure followed by relaxed 3D islands. Pb has a low surface energy and tends to float on top of the growing Cu or Co films [10]. Atoms deposited on the surface quickly exchange their positions with the Pb ones, getting buried below the surfactant layer; in this way, the fast diffusion by hopping on top of the clean Cu(111) surface is suppressed, resulting in a higher density of islands

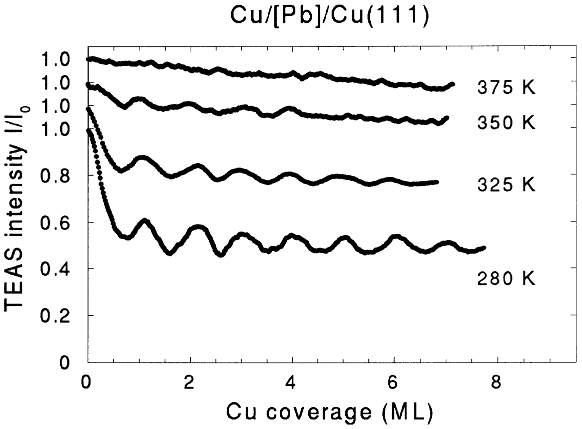

Fig. 4. A monolayer of Pb covering the Cu(111) substrate enhances interlayer diffusion and induces layer-by-layer growth during Cu deposition

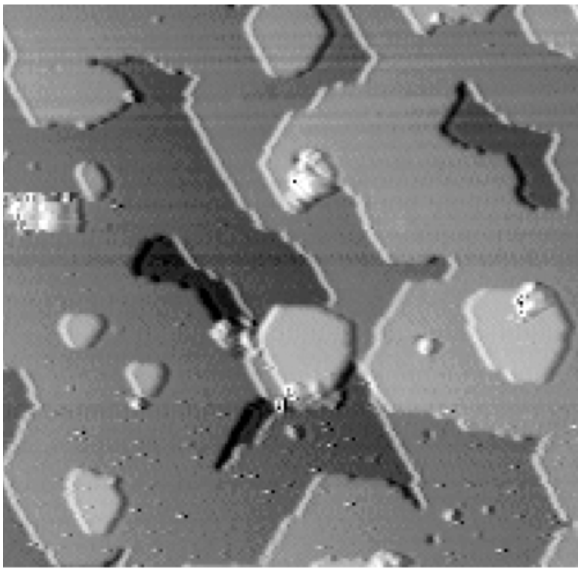

Fig. 5. STM image showing the surface morphology after the growth of 5 ML of Cu at room temperature on a Cu(111) surface covered with 1 ML of Pb. The presence of the surfactant greatly enhances interlayer diffusion and induces layer-by-layer growth

with smaller average size and irregular shape. Atoms landed on top of these islands find it easier to reach their borders and fall to the lower level. The surfactant thus enhances interlayer diffusion and induces layer-by-layer growth. The TEAS data presented in Fig. 4 illustrate the growth of Cu films at different substrate temperatures in the presence of Pb, and demonstrate the good structural quality of these films. The intensity oscillations reveal the periodic filling of single atomic layers; on the other hand, the high average level of diffracted intensity indicates that the film surface is well ordered, with a small amount of defects. These observations are confirmed by the STM data shown in Fig. 5: the image corresponds to a 5-ML-thick Cu film grown at room temperature in the presence of Pb: no more than three atomic levels are exposed, indicating good layer-by-layer growth, with a low density of atomic steps. This positive effect caused by the surfactant is not restricted to the growth of Cu: a similar behavior has been observed during the heteroepitaxy of Co on the same Cu(111) face.

4 Atomistic mechanism of the surfactant effect

To gain some insight into the mechanisms of the surfactant effect at the atomic level we have resorted to numerical simulations. The use of empirical potentials to describe the atomic interactions within a Monte Carlo (MC) scheme has proved to be an efficient method to study complicated problems such as growth, involving many different atomic processes [11]. Our potentials have been optimized to reproduce several bulk and surface properties of transition and noble metals [12–14].

Full details about our simulations are given elsewhere [15]; in brief, we deposit a layer of Pb on the surface of a Cu(111) slab, and allow the system to order: starting with a disordered arrangement of Pb atoms, the simulation correctly reproduces the $p(4\times4)$ superstructure. We then deposit Cu adatoms at random positions of the surface and follow their displacements. Figure 6 shows the main result obtained from these calculations: it shows how the height of the Cu adatom with respect to the surface evolves while the simulation progresses. Shortly after landing on the surface, and without any lateral displacements, the Cu atom exchanges positions with a Pb one and gets buried in the surfactant layer: this process is marked by the first jump in the z coordinate shown in the graph. This process is extremely efficient, as demonstrated by the small number of MC steps required in all simulations for it to be completed. Once there, the Cu atom cannot move sideways because all neighboring sites are blocked by other Pb atoms; the only diffusion process allowed seems to be the site exchange with other Cu atoms from the substrate surface. These events do indeed take place, as can be seen in Fig. 6; however, their frequency is much lower: the number of MC steps that it usually takes for the second jump down in atomic height to appear is higher, indicating that the likelihood of the Cu–Cu exchanges is smaller, almost independently of substrate temperature. In summary, it seems that the main effect of the surfactant is to suppress the extremely fast diffusion by hopping over the surface, and force the Cu adatoms to displace more slowly by the exchange mechanism. In this way, the atoms spend a longer time near the steps and the probability to cross them and fall to the lower terraces is increased.

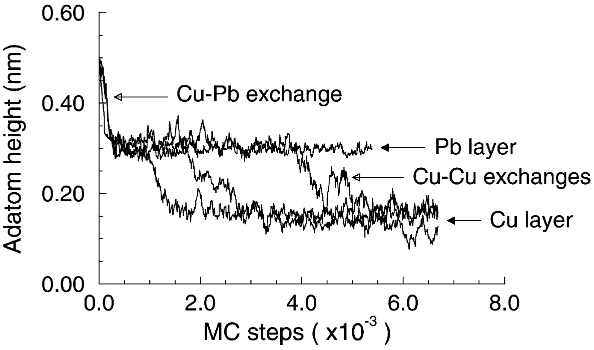

Fig. 6. Monte Carlo simulation showing the evolution of the height of a Cu adatom deposited on a Cu(111) surface covered with a monolayer of Pb. After arrival, the Cu atom gets buried in the surfactant layer without diffusing on top of it; later, it can move below the Pb layer by exchanging its position with other Cu atoms from the substrate surface

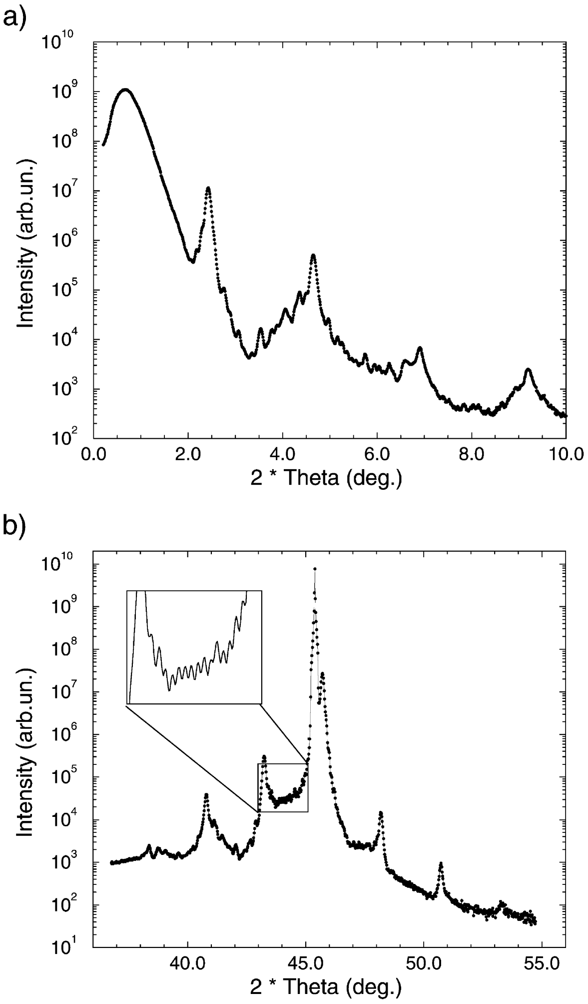

Fig. 7a,b. X-ray reflectivity curves at **a** low and **b** high angle, for a $\{Co_{0.6}Cu_{0.4}/Cu\}_{23}$ superlattice grown with the aid of a surfactant Pb layer. A large number of superlattice peaks and Kiessig fringes can be observed, indicating that the chemical periodicity is well defined and interfacial roughness is very small

5 Surfactant-assisted growth of crystalline superlattices

In the previous sections we have demonstrated the ability of a Pb layer to improve the growth characteristics of ultrathin epitaxial films. However, for practical purposes it is necessary to grow thicker, more complex structures. To test the usefulness of our method for this kind of systems, we have grown several superlattices of alternating Co and Cu layers, on the same Cu(111) surface covered by Pb. The crystallinity of these samples has been studied by means of X-ray diffraction experiments performed at Beamline ID01 at the E.S.R.F. A typical result is presented in Fig. 7, which shows two reflectivity scans measured at (a) low and (b) high angle on one of these superlattices. This particular sample contains 23 periods, each one made up of one layer containing a mixture of 60%Co − 40%Cu with a total thickness of ≈ 26 Å, and another Cu layer of ≈ 14 Å. The large number of superlattice peaks observed demonstrates the high structural quality of this sample; Kiessig fringes are also visible both at low and high angles, implying that the interfacial roughness is very small, since these features are strongly sensitive to disorder [16]. After finishing the growth of these heterostructures, more than 900 Å thick, the LEED pattern of the well-ordered $p(4 \times 4)$ superstructure of Pb could still be observed at the crystal surface. This extremely efficient segregation process of the Pb layer ensures the applicability of the surfactant method to the preparation of artificial structures involving many atomic layers of different materials.

Acknowledgements. Work by the spanish group has been supported by the CICyT under Grant MAT98-0965-C04-02. J. Ferrón thanks Fundación Antorchas for financial support. V. Cros thanks the EU for a scholarship.

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