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Indium-induced layer-by-layer growth and suppression of twin formation in the homoepitaxial growth of Cu(111)

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We have investigated the effect of In on the homoepitaxial growth of Cu(111) by means of surface x-ray diffraction. At the temperature range investigated (125–300 K), the growth on clean Cu occurs in a three-dimensional mode with the creation of twin crystallites over a small fraction of the total surface area. When the surface is precovered with a submonolayer amount of In, layer-by-layer growth is induced and the formation of twin crystallites is suppressed.

I. INTRODUCTION

The homoepitaxial growth of Cu(111) has been the subject of a number of investigations. Dastoor *et al.* reported,[1] on the basis of helium diffraction, a gradual transition from step flow (400 K) to three-dimensional growth (110 K). Henzler and co-workers[2,3] found, with low-energy electron diffraction (LEED), a reentrant layer-by-layer growth. Above 370 K and below 170 K layer-by-layer growth was observed. In the intermediate temperature range three-dimensional growth was measured.

We will briefly address the growth of clean Cu but the main objective of the present study is to investigate the effect of In on the growth of Cu(111). Such additives ("surfactants") have been found to influence the homoepitaxial growth of a number of metals in a favorable way, by varying mechanisms.[4–8] Henzler, Schmidt, and Luo reported preliminary results on the effect of 1 ML of Pb on the growth of Cu(111). They found layer-by-layer growth over a temperature range from 150 K to 350 K.[2] In the case of the growth of Cu(100), In enhances the interlayer transport through a decrease of the Schwoebel barrier.[8,9] Recently, Breeman *et al.* studied the effect of In on the growth mode of Cu(111) by computer simulations using the embedded atom theory.[9] The calculations indicate that the effect of In is a small decrease of the Schwoebel barrier at step edges and that In causes a larger Cu island density. Breeman *et al.* predicted that both effects will result in an increased interlayer transport for the growth of Cu(111). The present study confirms this.

Another topic we will discuss is the formation of stacking faults and twin crystals. It was shown by Camarero *et al.*[10] that the formation of stacking faults in the growth of Cu/Co superlattices on Cu(111) can be suppressed by using Pb as a surfactant. Here we show that In has the same effect on the homoepitaxial growth of Cu(111).

II. EXPERIMENT

The experiments were performed at the surface diffraction station (BL7) at the European Synchrotron Radiation Facility in Grenoble, France.[11] The incoming beam was generated by an undulator and a wavelength of 0.777 Å was selected by a cryogenically cooled Si(111) double-crystal monochromator. The setup consists of an ultrahigh-vacuum chamber coupled to a six-circle diffractometer that was operated in the z-axis mode.[12] The Cu(111) single crystal (10 mm diameter) was cleaned by standard sputter (775 K, 20 min) and anneal (775 K, 10 min) cycles. After this treatment, the surface was chemically clean as judged by Auger electron spectroscopy. The surface mosaicity was 0.2° full width at half maximum and the miscut was 1°. The deposition rate of Cu was between 2.2 and 20 min/ML. The base pressure was 3×10^{-8} Pa and the pressure during deposition did not exceed 1×10^{-7} Pa. For the labeling of the reflections we use the following primitive real-space lattice with respect to the conventional bulk fcc lattice: $\mathbf{a}_1 = \frac{1}{2}[10\bar{1}]_{\rm cubic}$; $\mathbf{a}_2 = \frac{1}{2}[\bar{1}10]_{\rm cubic}$; $\mathbf{a}_3 = \frac{1}{3}[111]_{\rm cubic}$.

The growth mode was studied by monitoring the intensity of the specular (0 0 1.45) and the ($\bar{2}$ 1 1.45) reflections *during* growth. Both reflections are close to the out-of-phase condition for scattering from consecutive layers, giving high sensitivity to the growth mode and roughness of the surface.[13] The exact out-of-phase conditions are avoided because otherwise the higher-harmonic contributions of the x-ray source would dominate the signal. In the reflection with in-plane momentum transfer, we are also sensitive to the in-plane crystalline quality of the grown layers. In case of layer-by-layer growth the intensity will oscillate during deposition with a period equal to the time needed to deposit a single monolayer of Cu. When the growth is not perfectly layer by layer, the surface will become rougher and damping of the oscillations results. A strong damping of the oscillations indicates a low interlayer diffusion. An exponential decay of the intensity corresponds to three-dimensional growth without interlayer transport.

To investigate the formation of stacking faults during growth we measured the $(\bar{1}\,1)$ crystal truncation rod.[14] When stacking faults occur, a rise in intensity results at l=2, i.e., at the $(\bar{1}\,1\,2)$ reflection. Because of the large penetration depth (compared to, e.g., LEED), x rays are particularly sensitive to the formation of twin crystals.

III. RESULTS

The specular intensity during growth on the clean surface is shown in Fig. 1 at various substrate temperatures and with a deposition rate of 20 min/ML. At all temperatures investigated the intensity decays monotonically. At the higher temperatures this means that the growth proceeds by partial step flow. The growth curve at 125 K closely follows the exponential decay of Poisson growth

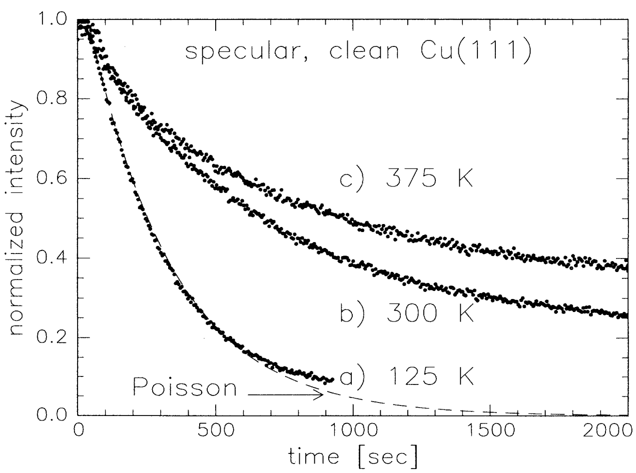

FIG. 1. The intensity of the (0 0 1.45) reflection during Cu deposition on a clean Cu(111) surface with a deposition rate of 20 min/ML at (a) 125 K, (b) 300 K, and (c) 375 K. The curves are normalized to the intensity of the clean starting surface. The dashed line represents the calculated curve for Poisson growth.

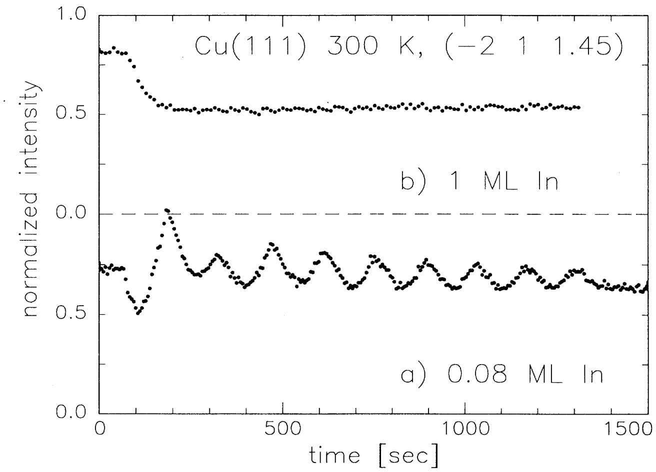

FIG. 2. The intensity of the $(\bar{2}\,1\,1.45)$ reflection during Cu deposition at 300 K with a deposition rate of 130 sec/ML. (a) After predeposition of 0.08 ML In, and (b) after predeposition of 1 ML of In. The curves are normalized to the intensity of the clean starting surface. The In deposition is not shown but resulted in the decreased intensity at the start.

(indicated by the dashed line), which shows that no interlayer transport occurs at this temperature.

In Fig. 2 the effect of In on the growth at 300 K is shown. Here we monitored the $(\bar{2}\,1\,1.45)$ reflection during growth with a deposition rate of 130 sec/ML. After deposition of 0.08 ML of In, intensity oscillations are observed during Cu deposition, indicating that the growth proceeds layer by layer. Initially the height of the maxima alternates between high and low values. When a full monolayer of In is deposited before Cu growth, the intensity decays first, but then remains constant at about 50% of the initial intensity. The deposition of the monolayer

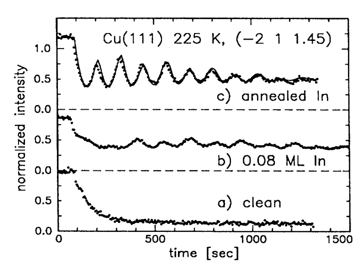

FIG. 3. The intensity of the $(\bar{2}\,1\,1.45)$ reflection during Cu deposition at 225 K, with a deposition rate of 130 sec/ML. (a) On the clean surface, (b) after predeposition of 0.08 ML In, (c) after annealing 0.08 ML In. Dots are the experimental data, the solid line in (c) is a fitted curve using a rate-equation model. The curves are normalized to the intensity of the clean starting surface. The In deposition is not shown but resulted in the decreased intensity in (b) and increase (after anneal) in (c).

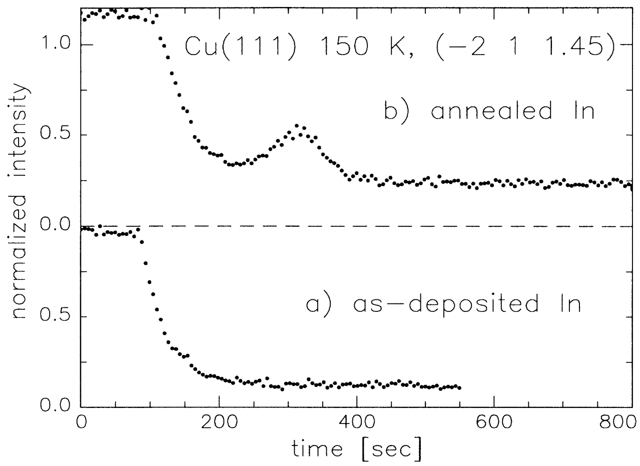

FIG. 4. The intensity of the ($\bar{2}$ 1 1.45) reflection during Cu deposition at 150 K, with a deposition rate of 130 sec/ML. (a) After predeposition of 0.08 ML In, (b) after annealing 0.08 ML In. The curves are normalized to the intensity of the clean starting surface. The In deposition is not shown but resulted in the increased intensity (after anneal) in (b).

of In occurred in a layer-by-layer mode (not shown).

In Fig. 3 the intensity of the ($\bar{2}$ 1 1.45) reflection during growth at 225 K is shown (deposition rate 130 sec/ML). On the clean surface, the intensity decays monotonically but slower than for Poisson growth, showing that still some step flow occurs. After predeposition of 0.08 ML In, oscillations are seen and a smoother film results. When the In is annealed before Cu deposition (5 min at 475 K), the effect is even stronger. The oscillations last longer and have a larger amplitude, which indicates a smoother layer-by-layer growth. The maxima alternate between low and high values for both In precovered surfaces, but with a different sequence.

In Fig. 4 the growth at 150 K (rate 130 sec/ML) is shown. The intensity after deposition of In without annealing decays exponentially, showing that Poisson growth occurs as on the clean surface at 150 K [Fig. 1(a)]. When the In is annealed before Cu deposition, a single intensity oscillation is induced.

To investigate the formation of stacking faults, we have measured the ($\bar{1}$ 1) crystal truncation rod. The rod of the clean surface is shown in Fig. 5(a). After deposition of 20 ML of Cu on the clean surface at 300 K, an extra peak at l=2 appears in the rod [Fig. 5(b)]. This shows that twin

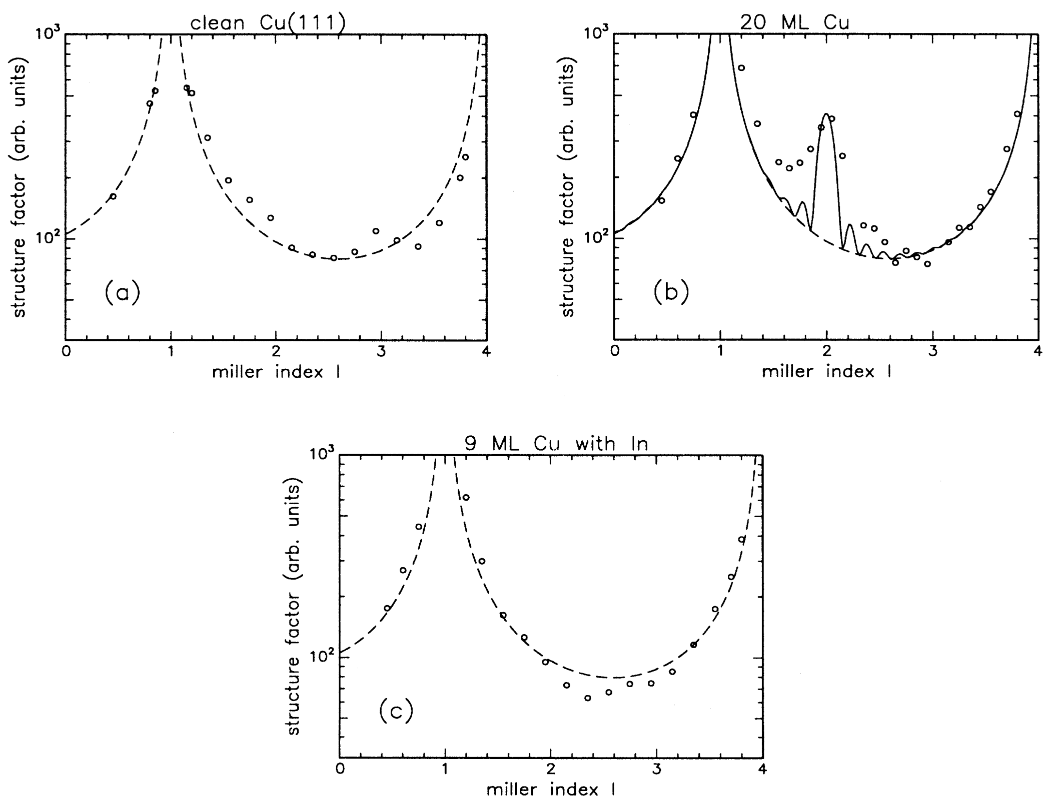

FIG. 5. The ($\bar{1}$ 1) crystal truncation rod of (a) the clean starting surface, (b) the surface after deposition of 20 ML Cu, (c) the surface after 9 ML Cu deposition with 0.08 ML In predeposited. The substrate temperature during deposition was 300 K. The circles represent the experimental data, the dashed line is the fit to the clean starting surface, the solid line in (b) is the fitted model of a twinned crystal of 20 ML thickness covering 1.5% of the surface (see text).

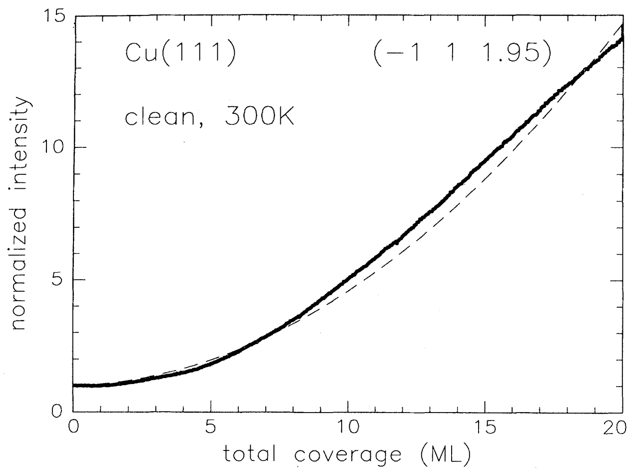

FIG. 6. The $(\bar{1}\,1\,1.95)$ reflection, which is sensitive to stacking faults, during Cu deposition at 300 K on the clean surface. The dashed line is a calculated curve for a surface fraction of 1.1% of twinned stacking.

crystals have been created. The formation of the twin crystals was monitored by measuring the intensity of the $(\bar{1}\,1\,1.95)$ reflection during Cu deposition, see Fig. 6.

When 9 ML Cu is grown on a surface precovered with 0.08 ML In (at 300 K), the formation of twins is suppressed and no extra peak at l=2 is observed [Fig. 5(c)]. The suppression of the twin formation by In is very dependent on the growth conditions. For the growth at 225 K with annealed In, the formation of twins is also suppressed, while for the growth with as-deposited In at low temperatures (165 K and 225 K), with annealed In at 150 K and with a full monolayer of In at 300 K, the twins are again observed (not shown).

Summarizing the experimental results, the effect of In on the growth of Cu(111) is twofold. Under the right conditions, the growth mode changes from three dimensional into layer by layer and the formation of twins is prevented. When the In is annealed before Cu growth the effect on the growth is strongest.

IV. DISCUSSION

A. Interlayer transport

On the clean surface we observe a gradual transition from partial step flow at 375 K to three-dimensional growth at 125 K. The deposition rate (20 min/ML) in our experiment is too low to expect reentrant layer-by-layer growth (*idem* for the clean growth at 225 K with a deposition rate of 130 sec/ML).[2] Our data closely resemble the results of Dastoor *et al.*[1] Because no layer-by-layer growth is observed over a wide temperature range, we conclude that the interlayer transport on the clean surface is hindered by the Schwoebel barrier at step edges.[15,16]

Before discussing the effect of In on the growth, we will determine the position and the segregation efficiency of the In atoms during growth. The segregation efficiency is the fraction of In atoms present in a layer that segregates to the next layer. This efficiency can be deduced from the modulation observed in the heights of the intensity maxima at 225 K. Because the atomic number Z of In (Z=49) is much larger than that of Cu (Z=29), an In-rich layer will scatter more strongly than a layer without (or with less) In. When a significant amount of In is incorporated at the starting surface, the interference of scattering from an odd or even number of layers on top of the In-rich layer will yield the modulation of the intensity in the maxima.

In general, the structure factor of m layers of mixed In and Cu on top of a bulk Cu crystal is given by

$$F_{\text{total}} = F_{\text{bulk}} + \sum_{n=1}^{m} (\theta_n^{\text{In}} f^{\text{In}} + \theta_n^{\text{Cu}} f^{\text{Cu}}) \exp(ni\phi) \quad , \qquad (1)$$

with

$$F_{\text{bulk}} = \frac{f^{\text{Cu}}}{1-\exp(-i\phi)} \quad , \qquad (2)$$

where F_{bulk} is the structure factor of the bulk, f^{Cu} and f^{In} are the atomic scattering factors, θ_n^{In} and θ_n^{Cu} are the fractional In and Cu coverages in the nth layer, and ϕ is the phase difference between successive layers at the given diffraction condition. Here we assume that the position of the In atoms is equivalent to the Cu position.

Using Eq. (1), we have fitted the growth oscillations at 225 K using the segregation efficiency of the (annealed) In as a fitting parameter. A good fit was obtained with a segregation efficiency of 0.4, which means that during growth of each layer 40% of the In amount in the top layer is segregating to the next layer. In this model the In amount at the surface decreases very quickly and in the sixth layer we would have only 0.4^6= 0.5% of the starting amount of In. Because we observe a large number of oscillations this is unlikely. Furthermore, Auger electron spectroscopy showed that after addition of 9 ML Cu on top of 0.08 ML In at 300 K, only 20% of the In was incorporated.

An equally good fit was obtained by a model in which, only in the first layer, (50±10)% of the In is incorporated and subsequent segregation is very efficient, with a constant In concentration at the surface. This resulted in the fit shown in Fig. 3(c). It is impossible to have modulations in the maxima when not a significant amount of In is left at the interface. Therefore both models predict a large In incorporation in the first deposited layer. From the persisting intensity oscillations we conclude that the second model with about 50% incorporation of the In (0.04 ML) but very small subsequent incorporation, is the most likely one. A similar segregation behavior has been observed for Sb during Ag growth on a Ag(111) surface.[17]

From the sequence of the high and low maxima we deduce that the annealed In, before deposition at 225 K, is embedded in the top layer. This is illustrated in the modeled growth curve in Fig. 7, which was calculated using Eq. (1). The embedded In corresponds to situation (b) and yields a high starting intensity (b), a low first (c) and a high second maximum (d), as observed experimentally [Fig. 3(c)].

For the growth with as-deposited In [Fig. 2(a)] at 300 K, we also observe intensity modulations of the maxima indicating significant In incorporation, and long-lasting oscillations showing that In must be present at the surface. This indicates that the segregation happens in a way similar to that at 225 K with annealed In. The difference with the growth at 225 K is the sequence of the high and low maxima. Now we start with a low intensity, and have a high first and low second maximum [Fig. 2(a)]. This means that In is present on top of the surface when we start Cu deposition as in situation (a) in Fig. 7. This situation also occurs for as-deposited In at 225 K [Fig. 3(b)], though here the first high maximum is not as clearly visible.

Indium deposition at 225 K and 300 K on a clean surface leads to a decrease of the intensity because the as-deposited In is present on top of the surface. Only after deposition of In at 150 K [Fig. 4(a)] was no decrease of the intensity observed, which is surprising because at this low temperature the In atoms also should be on top of the surface. This anomaly is not understood. At 150 K with annealed In, only one oscillation is observed, which can be explained when In does promote interlayer diffusion but is quickly incorporated at this temperature [Fig. 4(b)].

On the surface covered with a full monolayer of In at 300 K, no oscillations are observed but instead the intensity decreases to a constant level, a little above 50% of the starting signal [Fig. 2(b)]. Assuming that In floats on top of the surface as a covering layer of about 1 ML thickness, the reflected intensity increases by a factor of 5.5, because In has a larger scattering power than Cu. Therefore, the constant intensity corresponds to a rough surface, and the interlayer transport has not increased. Due to the large lattice mismatch of In and Cu, it is possible that the arriving Cu atoms will move through the In layer and arrive at the Cu surface, but then have a low mobility at the In/Cu interface. However, some mobility remains because the steady-state intensity is larger than zero, indicating that partial step flow occurs. The partial step flow is probably caused by an increased step length of a more irregular step shape. We exclude the possibility that a significant fraction of In is incorporated at the interface, because then modulations in the intensity would arise due to the difference in scattering power of In and Cu.

The effect of In is in most cases an increase of the interlayer transport. This follows directly from the higher intensity in the maxima of the intensity oscillations (after correction for the larger scattering power of In). The calculations of Breeman *et al.* show that In reduces the Schwoebel barrier at step edges and that In induces a larger island density.[9] For the growth on annealed In at 225 K, the intensity decays clearly faster than for the clean growth, showing that enhanced nucleation occurs. When the mobility on top of islands is not affected, an increase in island density can enhance the interlayer transport.[18]

Breeman *et al.* also found that the Schwoebel barrier for steps in the {111} direction is much lower than that for steps in the {100} direction (0.27 and 0.53 eV, respectively). Furthermore, Breeman *et al.* showed that on a clean Cu(111) surface, islands with {100} step edges are energetically favored and, therefore, islands with the larger Schwoebel barrier are dominating. When In would reduce the step energy of {111} steps with respect to the {100} steps, it becomes more probable that the {111} steps with the lower Schwoebel barrier are formed during growth. This would then lead to an enhanced interlayer transport. A similar explanation was proposed earlier for the effect of Pb on the step energies of Co islands on Cu(111).[10]

As we have shown, the increased intensity of the reflected signal after annealing In [Figs. 3(b) and 4(b)], indicates that the In atoms are embedded in the top layer. However, when the In atoms are at step edges this would give rise to the same increase in intensity.[8] Because the annealed In has a stronger effect on the growth, the position at step edges is very unlikely. Instead, annealing should yield a more homogeneous distribution of In over the surface, leaving no parts without In and leading to a smoother growth. This is comparable to the situation for the annealed In on a Cu(100) surface.[8]

B. Stacking faults

On the clean surface we observe a continuous increase in intensity at the $(\bar{1}\,1\,1.95)$ reflection, showing that twin

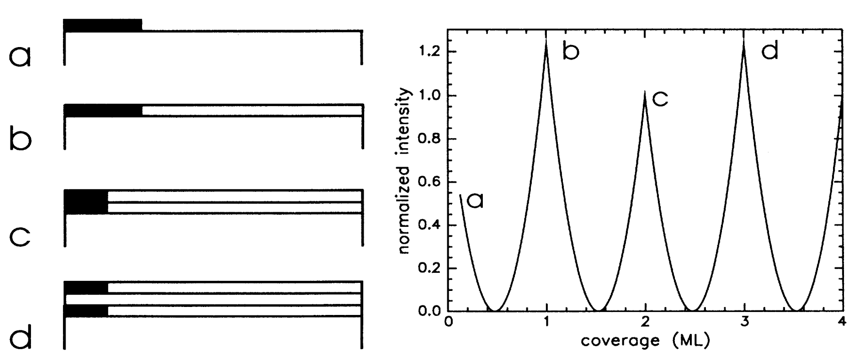

FIG. 7. The origin of alternating high and low maxima for Cu growth with In. Left: schematic picture of the position of the In (black) and Cu (white). Right: calculated intensity during deposition of Cu on surface (a) using Eq. (1), with the intensity normalized to that of a clean Cu surface. From the In coverage used in the calculation (0.08 ML), 50% segregates perfectly and 50% remains at the original interface. Perfect two-dimensional growth is assumed.

crystallites are formed. When the bulk stacking is *ABC*, the twinned crystals have stacking *BAC* with a Bragg peak at $(\bar{1}\ 1\ 2)$. This explains why the intensity rises as the twin crystals are growing (Fig. 6). If the thickness of the twin crystals grows at a constant rate, a parabolic increase in the intensity is expected. The dashed curve in Fig. 6 is calculated assuming that 1.1% of the surface covered with the twinned stacking. We see that the intensity largely follows the calculated parabola. This suggests that the stacking faults only occur at the fresh surface and that the stacking on top of these positions continues with the twinned *BAC* stacking. The small deviation from the parabolic shape indicates that only a few twins are overgrown with the bulk substrate stacking.

The crystal truncation rod measured after Cu deposition [Fig. 5(b)] was fitted with a model with 20 twinned layers with stacking *BAC* on top of the bulk stacking *ABC*. The best fit was obtained when 1.5% of the surface was covered with the twinned stacking, which agrees reasonably with the 1.1% found above. We also tried to fit a model with a constant probability of stacking faults to occur for each layer, resulting in a more random stacking sequence of the grown layers. This model does not yield the extra peak at l=2 that we observed experimentally and is therefore rejected. Therefore, the measured rod confirms that the stacking faults only occur at the fresh surface. The low value of the surface fraction that is covered with twins explains why this was not observed in the LEED experiment by Camarero *et al.*[10]

We have no direct indication how In suppresses the formation of stacking faults. We note that the amount of twin crystallites (1.5%) is of the same order of magnitude as the amount of incorporated In (4% of a ML). Stacking faults can form at existing faulted sites on the starting surface, like contaminations or dislocations. Camarero *et al.* have proposed that Pb decreases the adsorption of Cu at faulted sites on Cu(111).[10] It is possible that In has the same effect and in this way suppresses the creation of stacking faults. The fact that stacking faults occur solely at the starting surface and are only prevented when the In atoms have enough mobility on the starting surface (either by deposition at 300 K or by annealed In at 225 K) supports this. For Cu growth on Cu(100) with In, we also found that In passivates the defects on the starting surface.[8]

V. CONCLUSIONS

In conclusion, we reported both an induced layer-by-layer growth and a suppressed formation of twinned crystallites in the homoepitaxial growth of Cu(111) using In as a surfactant. When the In is annealed before Cu growth the effect on the growth is strongest. The observed increased interlayer transport for growth with In agrees with recent calculations. After a significant incorporation of In in the first layer, the In segregates efficiently during growth of the subsequent layers at 225 and 300 K.

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