Oscillatory Surface In-Plane Lattice Spacing during Growth of Co and of Cu on a Cu(001) Single Crystal

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The in-plane lattice spacing *during* epitaxial growth of Co and of Cu on a Cu(001) single crystal substrate has been investigated in the pseudomorphic growth regime by an advanced reflection high energy electron diffraction system with improved lateral resolution. The in-plane lattice spacing of the surface is found to oscillate as a function of coverage. For Co/Cu(001) the growing Co monolayers are periodically contracted for half-integer coverages, whereas for the case of Cu/Cu(001) homoepitaxy we find periodic expansions for half-integer coverages.

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For heteroepitaxial thin film growth it is well known that as a function of coverage the initial pseudomorphic growth is followed by strain relaxation due to dislocation formation [1,2]. Owing to the structure-property relationship, it is of crucial interest whether there are additional relaxation mechanisms, which may affect the physical properties. The *in situ* identification of such mechanisms *during* growth represents one of the challenging problems in surface science. In principle, medium energy electron diffraction (MEED) or reflection high energy electron diffraction (RHEED) yield surface-sensitive information on in-plane relaxations [3], but so far continuous measurements as a function of coverage were not feasible. In this Letter, we reexamine in detail the pseudomorphic growth process in real time by using an advanced RHEED system with improved lateral resolution. To this aim the model system Co/Cu(001) has been chosen in comparison to Cu/Cu(001) for the following reasons. On the one hand there is a large community investigating magnetic properties of ultrathin Co films on Cu(001), studying, e.g., the Curie temperature [4], magnetic anisotropies [5,6], and the oscillatory interlayer exchange coupling [7,8]. For these magnetic parameters it is of essential importance how they are related to the structural properties of the ultrathin films [9–11]. Many of these magnetic properties often depend on minute details of the growth process demanding a higher degree of sophistication in the growth characterization. On the other hand, it is of fundamental interest how homoepitaxial growth takes place. In particular, in the case of Cu on Cu(001) diffusion mechanisms of adatoms [12,13], binding energies and stability of adatom clusters [14], as well as nucleation and growth of islands [15–17], have recently attracted considerable attention both experimentally and theoretically.

In this Letter we show that for film thickness of $n + \frac{1}{2}$ monolayers (ML), $n = 0, 1, 2, \ldots$ the resulting islands, comprising the top 0.5 ML, exhibit an in-plane atomic spacing different from the layers underneath. This results in an oscillatory variation of the average surface in-plane lattice spacing with increasing film thickness.

The samples were prepared by molecular beam epitaxy with a pressure never exceeding 3×10^{-10} mbar. The deposition rates were typically around 1 ML per 0.5–5 min. During growth the Cu(001) substrate was held at 300 K to avoid interdiffusion [18]. A series of Co (or Cu) films in the thickness range from 2 to 100 ML (or 2 to 10 ML) were prepared. The incident angle of the RHEED beam was varied in a range of $\pm 0.5°$ to include both Bragg and off-Bragg scattering conditions. A detailed study of Co films thicker than 10 ML will be the subject of a forthcoming publication [19]. The crystallographic quality of the substrate and of the films was monitored by LEED and RHEED and the surface cleanliness was checked by Auger spectroscopy. The film thickness was monitored by a quartz microbalance and RHEED intensity oscillations of the specular beam. For these preparation conditions it is well known that Co films grow layer by layer except the first two ML [9,11] and Cu films grow via nucleation of islands (damped RHEED intensity oscillations) followed by a steady-state growth mode [12].

The in-plane lattice spacing is determined from the measured separation of the $(-1,0)$ and $(1,0)$ RHEED reflections. The RHEED measurements were performed using a 35 keV electron gun and a small-grain phosphorous screen monitored by a charge-coupled device camera connected to a computer. We achieved an instrumental resolution (spot separation over FWHM of the reflections) of 30–40. The RHEED images were recorded during growth every 1 to 3 s and stored on a PC for later analysis. This allowed the real-time observation of the growth process. A careful numerical analysis of the digitized RHEED images by fitting the positions of the RHEED reflections with Lorentzian line shapes enhanced the instrumental resolution of the RHEED system by more than a factor of 20. The possible appearance of Henzler rings accompanying the main reflections [16,17] in the off-Bragg condition is not visible in the raw data of the line scan. Nevertheless the influence of possibly asymmetric side peaks on the fitted peak position was proven to be too small to cause any measurable changes by performing fits with just one Lorentzian covering the

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main and asymmetric side peaks. We achieved a resolution of about 100 pixel/Å with an accuracy of ±0.2 pixel, corresponding to an accuracy of the in-plane lattice spacing (≈400 pixel) of better than 0.05% ≅ 0.002 Å. The lattice spacing is sensed and thus averaged within the RHEED probing depth, which is about 1 to 2 ML.

Figure 1 displays four typical RHEED patterns recorded at an electron energy of 35 keV and an incident angle of about 2°. The RHEED pattern of the Cu single crystal substrate is shown in (a) with $\vec{k}_0 \parallel \langle 100 \rangle$ and in (b) with $\vec{k}_0 \parallel \langle 110 \rangle$. The appearance of sharp reflections and narrow streaks accompanied by Kikuchi lines indicates the quality of the Cu single crystal prior to deposition. Figure 1(c) shows the magnified central section of Fig. 1(b). In the middle the specular beam and on the left [right] side the $(-1,0)$ $[(1,0)]$ reflections are shown. Figures 1(c) and 1(d) show the same section prior to and after evaporation of 40 ML Co, respectively.

In the inset of Fig. 2 a typical RHEED intensity line scan is shown (thin line) as a function of the lateral position on the screen. The fitted intensity (thick line) is in very good agreement with the experimental data allowing for the precise and independent determination of the position, the intensity, and the FWHM of the RHEED reflections. The line scans are chosen such that no Kikuchi lines appear and the data analysis is found to be independent of the chosen position of the line scan. Figure 2(a) shows the fitted RHEED intensity oscillations of the specular spot normalized to its initial ($t = 0$) value as a function of the Co deposition time [20]. After starting the deposition the RHEED intensity decreases rapidly due to formation of Co islands. After about 200 s a coverage of 1 ML is deposited. Our observation that the RHEED intensity does not reach its initial value is in good agreement with scanning tunneling microscopy studies [11] indicating an island growth of 1–2 ML height in this growth regime. After 450 s the second ML is completed and then the film grows layer by layer. After 9 ML the deposition was stopped. Figure 2(b) shows the FWHM of the specular spot normalized to its initial value. The FWHM shows an oscillatory behavior as a function of coverage, as well, in antiphase with the RHEED intensity. From its initial value it increases rapidly due to the formation of islands, which gives rise to diffuse scattering [12]. Since for integer coverages the RHEED intensity and the FWHM reach about their initial values no loss of film quality occurs.

In Fig. 2(c) we show the most interesting result. The separation between the $(-1,0)$ and the $(1,0)$ reflections in k space, which is inversely proportional to the in-plane lattice spacing, displays also an oscillatory behavior. At the start of the deposition the in-plane lattice spacing has been adjusted to the Cu bulk value of 3.61 Å [9]. He scattering [10] and recent LEED measurements [21] indicate that the

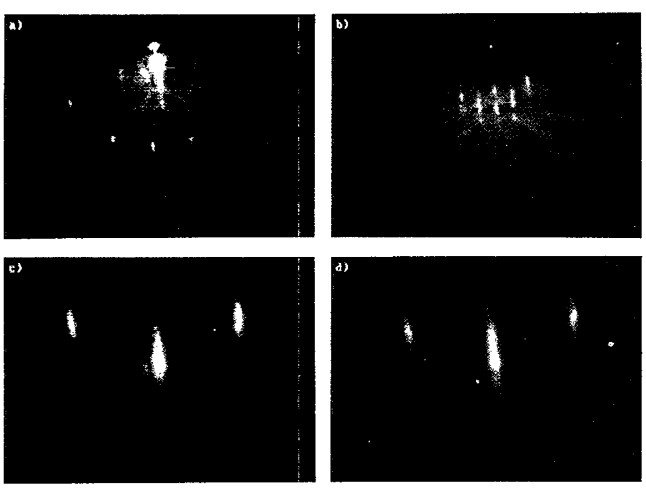

FIG. 1. Four typical RHEED patterns recorded at an electron energy of 35 keV. For the Cu single crystal we chose (a) $\vec{k}_0 \parallel \langle 100 \rangle$ and (b) $\vec{k}_0 \parallel \langle 110 \rangle$. In (c) and (d) the magnified central section of (b) is shown, prior to and after evaporation of 40 ML Co, respectively.

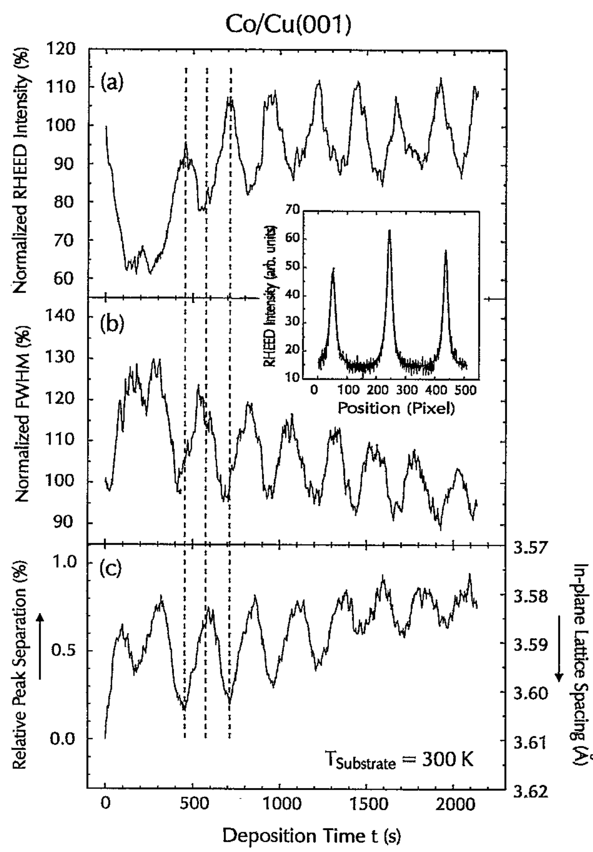

FIG. 2. As a function of deposition time of Co on Cu(001) we show in (a) the normalized RHEED intensity, in (b) the normalized FWHM of the specular beam, and in (c) the relative change of peak separation between the $(-1,0)$ and the $(1,0)$ reflections compared to the initial peak separation and the hence derived in-plane lattice spacing. The inset shows a typical RHEED intensity line scan (thin line) and the fitted intensity (thick line) vs lateral position on the screen.

lattice spacing can be modified due to the reduced number of nearest neighbors. After starting the deposition the peak separation increases, i.e., the surface in-plane lattice spacing is reduced. The maximum peak separation (minimum in-plane lattice spacing) is obtained for coverages equal to $n + \frac{1}{2}$ ML and the minimum separation (maximum in-plane lattice spacing) for integer coverages. The data clearly exhibit that true pseudomorphic growth is at most obtained for integer numbers of ML coverage.

These findings can be interpreted using the following simplified arguments (Fig. 3). We assume a flat Cu substrate prior to deposition [Fig. 3(a)]. After starting the deposition, Co islands nucleate on the Cu surface [Fig. 3(b)]. The RHEED intensity decreases due to increasing diffuse scattering and destructive interference between Co islands and the substrate. Since the lattice spacing of Co is by 2% smaller than that of Cu, the Co islands relax partially to the Co lattice spacing. The reduced number of nearest neighbors of atoms near the island edges causes lower binding energies for edge atoms [14]. These atoms are relaxing in the direction of the center of the island. The in-plane relaxation is then decreasing from the edge toward the center of the island. This gives rise to a reduced average surface in-plane lattice spacing. For coverages lower than about 0.5 ML the relaxation of edge atoms is the dominating process resulting in an increasing peak separation. With the coverage approaching an integer number of ML's [Fig. 3(c)], island coalescence will increasingly dominate and the amount of Co atoms strained to the Cu lattice spacing will increase. At complete coverage the entire Co film is strained to the substrate lattice spacing, and with further increasing deposition the process is repeated until relaxation due to formation of dislocations becomes important. Theoretical calculations [22] pointed out that because of the structure factor the position of diffracted intensity can oscillate as a function of step density and crystal miscut. These structure-factor induced oscillations of the peak positions are at least by a factor of 35 times smaller than the measured shifts.

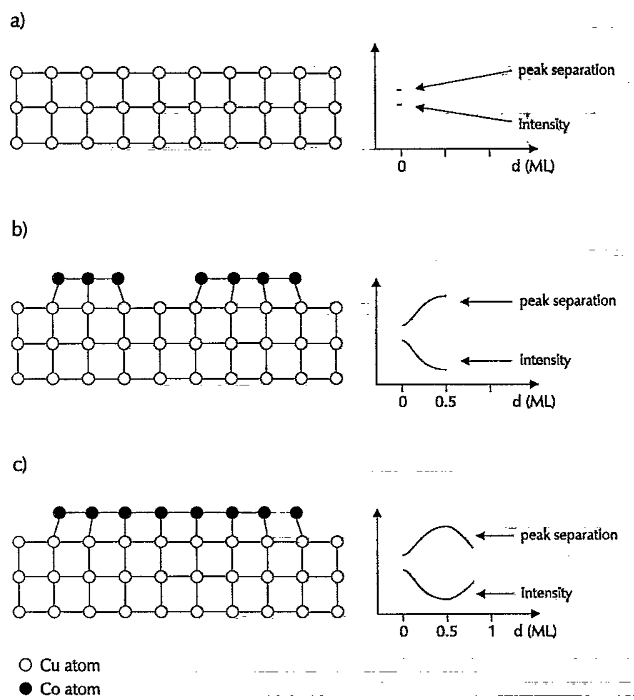

FIG. 3. Schematic sketch of the growth mode of Co on Cu as a function of coverage. On the right-hand side the intensity of the specular RHEED reflection and the separation between symmetric RHEED reflections are shown schematically as a function of ML thickness d.

From our model we would expect that the maximum values of the in-plane lattice spacing are constant and equal to the Cu bulk value. However, experimentally [Fig. 2(c)] we observe that the maxima of the in-plane lattice spacing are reduced for higher coverages although we are still in the so-called pseudomorphic growth regime [4,9]. The latter is supported by following the measurements in Fig. 2(c) to much higher coverages, where the relaxation due to dislocation formation is evidenced by the distinct onset of an additional reduction of the in-plane lattice spacing [19]. The reduction of the maxima of the in-plane lattice spacing with increasing ML coverage in Fig. 2(c), compared to the rather constant maxima of the intensity in Fig. 2(a), is due to an increasing number of islands only in the $n + 1$ layer and holes in the nth layer and thus due to an increasing number of edge atoms. The latter are responsible that for integer coverages the top layer is no more fully strained to the substrate lattice spacing. The enhanced sensitivity of the in-plane lattice spacing to the growth mode in comparison to the RHEED intensity is evidenced by the more pronounced oscillation for one ML coverage.

We now compare the above results to the case of homoepitaxial Cu/Cu(001) growth. Figure 4 shows the normalized RHEED intensity, the relative peak separation, and its inverse, i.e., the in-plane lattice spacing as a function of the Cu deposition time. As expected [12], damped RHEED intensity oscillations are clearly observed. The amplitude of the oscillation in the peak separation is smaller compared to Co on Cu(001) and, in contrast to Co on Cu(001), it is in phase with the RHEED intensity oscillation. This means that for coverages equal to $n + \frac{1}{2}$ ML the average surface in-plane lattice spacing is larger than for integer numbers of ML.

These experimental findings are consistent with recent calculations by Lee *et al.* [13] for Cu coverages on Cu(001) far below 1 ML. In this regime an in-plane lattice expansion at each adatom site was predicted by *ab initio* calculations using the Car-Parrinello molecular-dynamics method [13]. Our experimental results are qualitatively in agreement with this prediction, but quantitatively the experimentally observed changes of the in-plane lattice spacings are about a factor of 10 smaller. We attribute this discrepancy to the fact that (i) in our experiment we

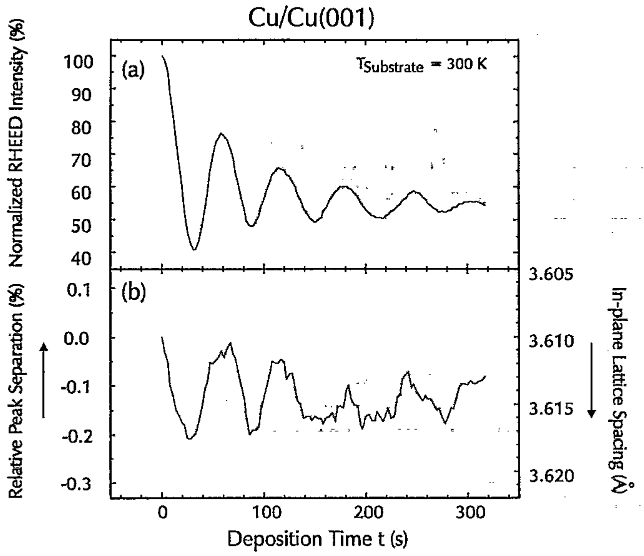

FIG. 4. As a function of deposition time of Cu on Cu(001) we show in (a) the normalized RHEED intensity of the specular beam and in (b) the relative change of the peak separation between the $(-1,0)$ and the $(1,0)$ reflections compared to the initial peak separation and the hence derived in-plane lattice spacing.

measure the in-plane lattice spacing averaged across the entire surface within the electron beam diameter, whereas Lee *et al.* [13] calculate the atomic in-plane spacing at each adatom site and (ii) the local density approximation method used in the calculations overestimates the binding energies of the adatoms [13], and thus the lattice spacing deviation from the bulk value. In the case of Co on Cu(001) the same arguments do not apply because of the lattice mismatch dominating over the binding energy effects of adatoms in the case of Cu/Cu(001) homoepitaxy.

In summary, we have found that for the growth of Co and of Cu on Cu(001) the in-plane lattice spacing oscillates as a function of coverage. In the case of Cu/Cu(001) homoepitaxy we find that the lattice spacing for the top 0.5 ML coverage is distinctively different from the bulk lattice spacing. Our findings emphasize that the existing concepts of pseudomorphic growth need to be revisited. For example, the oscillatory in-plane lattice spacing will modify the energy balance of the surface as a function of coverage, since the binding energies of edge and step atoms might show an oscillating dependence on the coverage and thus the island diameter as well. The expanded surface lattice spacing in the case of $n + \frac{1}{2}$ deposited ML's of Cu/Cu(001) as compared to the contracted spacing in the analogous case of Co/Cu(001) might possibly account for the finding of minor growth quality of Cu/Cu(001) compared to Co/Cu(001). We expect that the same arguments apply to the alternating heteroepitaxial growth of two different metals to form a coherent superlattice structure, as well as to the case of reentrant [23] and surfactant-induced [24] layer-by-layer growth found in some cases of homoepitaxy. Discrepancies between experiments and theoretical modeling might be accounted for by our new findings.

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Note added.—After submission of this paper it came to our attention that similar work on semiconductors has been carried out by J. Massies and N. Grandjean, Phys. Rev. Lett. **71**, 1411 (1993).

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[1] W. A. Jesser and D. Kuhlmann-Wilsdorf, Phys. Status Solidi **19**, 95 (1967).
[2] A. Chambers and D. C. Jackson, Philos. Mag. **31**, 1357 (1975).
[3] Y. Henry *et al.*, J. Appl. Phys. **76**, 2817 (1994).
[4] C. M. Schneider *et al.*, Phys. Rev. Lett. **64**, 1059 (1990).
[5] B. Heinrich *et al.*, Phys. Rev. B **44**, 9348 (1991).
[6] P. Krams *et al.*, Phys. Rev. Lett. **69**, 3674 (1992).
[7] A. Cebollada *et al.*, Phys. Rev. B **39**, 9726 (1989).
[8] M. T. Johnson *et al.*, Phys. Rev. Lett. **68**, 2688 (1992).
[9] H. Li and B. P. Tonner, Surf. Sci. **237**, 141 (1990).
[10] J. J. de Miguel *et al.*, J. Magn. Magn. Mater. **93**, 1 (1991).
[11] A. K. Schmid and J. Kirschner, Ultramicroscopy **42–44**, 483 (1992).
[12] J. J. de Miguel *et al.*, Surf. Sci. **190**, 1062 (1987).
[13] C. Lee *et al.*, Surf. Sci. Lett. **306**, L575 (1994).
[14] M. Breeman *et al.*, Surf. Sci. **323**, 71 (1995).
[15] H.-J. Ernst *et al.*, Surf. Sci. Lett. **275**, L682 (1992).
[16] G. L. Nyberg *et al.*, Phys. Rev. B **48**, 14 509 (1993).
[17] J.-K. Zou *et al.*, Phys. Rev. Lett. **72**, 3064 (1994).
[18] L. Gonzalez *et al.*, Phys. Rev. B **24**, 3245 (1981).
[19] J. Fassbender *et al.* (unpublished).
[20] The noise in Fig. 2(a) is caused by the fact that the intensity is evaluated from a line scan through the center of the specular reflection. An integration of the intensity over a reflection region would result in less noise.
[21] S. Müller *et al.*, Phys. Rev. Lett. **75**, 2862 (1995).
[22] M. Presicci and T.-M. Lu, Surf. Sci. **141**, 233 (1984).
[23] R. Kunkel *et al.*, Phys. Rev. Lett. **65**, 733 (1990).
[24] J. Vrijmoethet *et al.*, Phys. Rev. Lett. **72**, 3843 (1994).