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Non-coherent growth patches in pseudomorphic films: Unusual strain relief in electrodeposited Co on Cu(001)

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Abstract

The critical thickness for pseudomorphic Co growth on Cu(001) is found to be independent of the onset of lattice constant relaxation. The pseudomorphic film relieves strain by local formation of orthomorphic growth patches within the pseudomorphic matrix. This unusual relaxation mechanism of electrodeposited films is in contrast to current belief of film relaxation. Moreover, a tetragonal distortion of the fcc Co unit cell in the orthomorphic growth regime indicates residual strain in films of up to at least 100 monolayers thickness.

Keywords: Cobalt; Copper; Electrochemical methods; Growth; Solid–liquid interfaces; Surface relaxation and reconstruction; X-ray scattering, diffraction, and reflection

Simple energetic considerations predict pseudomorphic film growth during the initial stages of metal heteroepitaxy up to a critical thickness, which is mainly determined by the lattice constant misfit and the shear moduli of the two metals. Orthomorphic growth is assumed above the critical thickness due to the formation of misfit dislocations in the film [1–4]. It is generally believed that film growth switches completely to orthomorphic beyond this critical thickness, as reported for Co on Cu(001), for example [5,6], and some findings suggest that even the pseudomorphic buffer layer relaxes to orthomorphic, as has been observed in special film/substrate systems as in Cu on Pd(001), for example [7], or Cu on Au(001) and Ag(001) [8]. A delicate balance between temperature, film thickness, and lattice constant misfit seems to determine the total strain energy of the film and hence its actual stable phase.

Whereas pseudomorphic epilayers, lattice constant relaxation, film stress, and misfit dislocation formation have been studied recently in systems with a large lattice misfit of more than 5% [9–12]

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or in semiconductor heteroepitaxy [13], less is known about the transition from pseudomorphic to orthomorphic growth in heteroepitaxial metal/metal systems with a small lattice misfit [14,15]. So far, it is believed that the above considerations are valid for these systems. Findings in the system fcc Cu on fcc Ni(001), however, indicate deviations from this assumption: the strain in the pseudomorphic Cu layer is relaxed by formation of embedded Cu wedges grown with a relaxed Cu lattice constant within the pseudomorphic Cu matrix at film thicknesses well below the critical thickness for pseudomorphic Cu growth on Ni(001) [16,17].

Thus, the application of simple concepts of pseudomorphic growth to ultrathin metal film growth, even for systems with a small lattice constant mismatch, is rather questionable.

In order to study the lattice relaxation of films grown near the thermodynamical equilibrium, the films have been deposited by electrodeposition rather than by an ultra-high-vacuum (UHV) deposition technique. We will show for electrodeposited Co that (1) there is coexisting pseudomorphic and orthomorphic growth even below the critical thickness for pseudomorphic growth, and hence (2) the onset of lattice constant relaxation is not coincident with the critical thickness for pseudomorphic growth.

We chose the system Co on Cu(001) because of the small lattice constant mismatch between fcc Cu and fcc Co of -1.9%. Hence, a critical thickness for pseudomorphic Co growth of between 10 and 20 ML is expected [6,18,19], which is large enough to monitor precisely the transition regime from pseudomorphic to orthomorphic growth as a function of Co coverage. Possible alloying phenomena in this system have been reported to be restricted to 1–2 ML at the interface between Cu(001) and Co [20], and further growth up to 15 ML is found to be layer-by-layer like [6,20]. Thus, Co on Cu(001) seems to be appropriate for studying in detail the transition from pseudomorphic to orthomorphic growth in heteroepitaxial systems.

The in-plane lattice constants were measured by in-situ surface X-ray diffraction (SXRD), which simultaneously provides in-plane sensitivity, an information depth which can be restricted to the interesting interface region of the film and the film/substrate, as well as a high resolution of 0.0017 rlu ($1\ \mathrm{rlu} = q/q_{110}^{\mathrm{Cu}}$ with the momentum transfer q) [21]. The possibility of completely stripping off a previously deposited Co film without altering the surface structure of the Cu(001) substrate, a unique feature of electrochemistry, allows us to study the structure of various Co films in situ on the same Cu(001) sample. The unchanged structure of the lineshape, characteristic of clean Cu(001), has been confirmed before Co deposition and after Co dissolution. As calculated by fits to [1,1,ℓ] crystal surface truncation rod measurements, according to Refs. [22–24], the surface roughness of the Cu(001) crystal was comparable to the roughness of Cu(001) crystals which have been sputtered/annealed in an ultra-high vacuum [25]. All measurements have been performed in situ in a thin electrolyte layer cell [21] under cleanliness conditions equivalent to an ultra-high vacuum (UHV) of 5×10^{-10} mbar [26].

The SXRD measurements were performed at the BW2 beamline at HASYLAB, using focused radiation from the 56 pole hybrid Wiggler, and a photon energy of 8.5 keV, which is roughly 0.5 keV below the K-edge of Cu. The angle of incidence with respect to the crystal surface was set to 0.3° in order to achieve a high surface sensitivity. The X-ray penetration depth under these conditions is of the order of 100 atomic layers. All films were deposited and dissolved with the Mylar window of the cell in front of the crystal inflated to avoid diffusion limitation of the ionic currents. The film thickness was determined from the anodic charge during several deposition/dissolution cycles and was additionally checked by stripping the films after the SXRD measurements. Film preparation as well as measurements were performed at room temperature. The Cu(001) crystal preparation as well as the Co film deposition were performed according to the descriptions given in Refs. [21,26]. As deduced from fits to crystal surface truncation rod measurements, according to Refs. [22–24], a 15 ML Co film was found to be additionally roughened by approximately 2 ML with respect to the clean surface of the Cu(001) crystal [25]. In-plane [2,-2], [4,0] and out-of-plane [1,1,1]

diffraction peaks of fcc Cu were measured for different Co coverages. All obtained data are consistent with our conclusions, although only data obtained from the [2,−2] diffraction peaks are presented in this letter.

From the resolution of our data, it is possible to distinguish two major changes in the lineshapes with increasing Co coverage, as shown, for example, for 12.5 ML Co on Cu(001) in Fig. 1: (1) a symmetric broadening of the Cu diffraction peak at an in-plane momentum transfer of $q=2.000$ rlu (referred to as 'pseudomorphic Co peak') and (2) a shoulder to the right of the Cu peak (referred to as 'orthomorphic Co peak'), both growing in intensity with increasing Co coverage, and the latter additionally shifting to larger reciprocal lattice vectors with increasing coverage. The maximum intensity of the main peak centered at $q=$ 2.000 rlu remains constant with increasing Co coverage up to approximately 15 ML. Due to the constant penetration depth of the X-rays, the Cu intensity at $q=2.000$ rlu was expected to decrease with increasing Co coverage. Neither the orthomorphic intensity, which is too small around $q=$ 2.000 rlu (Fig. 1), nor strain fields into the Cu(001) crystal induced by the increasing Co coverage, which may be expected to result in a broadening of the Cu peak, but not an intensity increase with Co coverage, could explain the constant intensity of the main peak up to Co coverages as high as 15 ML. This has rather to be attributed to the increase of the pseudomorphic Co peak with increasing Co coverage. The larger width (FWHM) of the pseudomorphic Co peak compared to the FWHM of the Cu substrate peak may be attributed to the smaller island size of the pseudomorphic Co film. Each line shape was least-squares-fitted by simultaneous superposition of background and three Gauss curves accounting for the Cu substrate (Fig. 1, thin solid line), the pseudomorphic peak (Fig. 1, dotted line), and the orthomorphic peak (Fig. 1, dashed line), respectively. Thus, with our measurements, it is possible to monitor independently the evolution of the pseudomorphic and orthomorphic Co peak positions and peak integrals with Co coverage.

The evolution of the in-plane lattice constant with Co coverage, as determined from the peak positions, is shown in Fig. 2. The abrupt onset of the in-plane lattice constant relaxation around

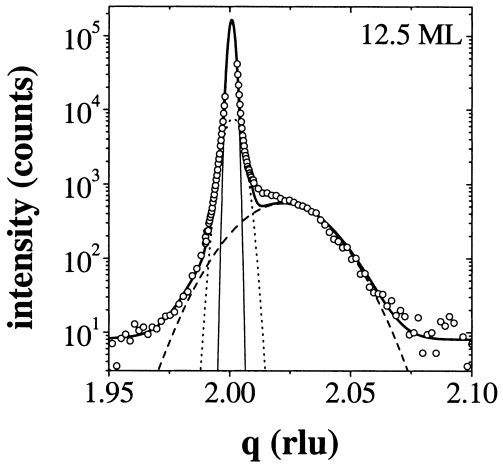

Fig. 1. [2,−2] in-plane diffraction peak of 12.5 ML Co on Cu(001). (○) data; (thin solid line) partial Gauss fit of Cu; (dotted line) partial Gauss fit of the pseudomorphic Co peak; (dashed line) partial Gauss fit of the orthomorphic Co peak; (thick solid line) sum of all Gauss fits, including linear background. The x-axis scale is given in reciprocal lattice units (rlu), which are normalized to $q/q_{110}^{Cu}=2\pi/a_{\text{in-plane}}$, i.e. $q(\text{rlu})=q/q_{110}^{Cu}$.

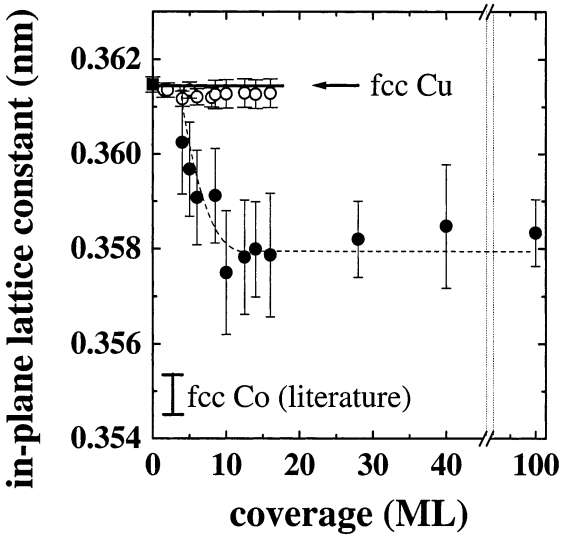

Fig. 2. Dependence of the Co in-plane lattice constant on coverage. Lines are guides to the eye. (○) as derived from the center of the pseudomorphic peak fit; (●, dashed line) as derived from the center of the orthomorphic peak fit. The error bars indicate ±1/4 FWHM of the corresponding peaks.

5 ML is usually interpreted within the framework of conventional continuum theory [1–4] as the critical thickness for pseudomorphic growth, caused by the abrupt onset of the formation of misfit dislocations in the film.

However, this interpretation is unsatisfactory for the following reasons. If it is assumed that film growth switches abruptly to orthomorphic at the onset of lattice constant relaxation, the pseudomorphic peaks as observed in our data above the onset of lattice constant relaxation around 5 ML (Fig. 2, circles) cannot be explained. It remains unclear whether this pseudomorphic intensity originates from a 5 ML thick pseudomorphic buffer layer between the substrate and the orthomorphic film or from a further pseudomorphic growth above 5 ML film thickness. Furthermore, this interpretation cannot explain whether the pseudomorphic buffer relaxes also to orthomorphic upon a further increase in coverage.

In order to show that a simple interpretation of Fig. 2 is not correct, we plot in Fig. 3 the integrals of the pseudomorphic and orthomorphic peaks versus Co coverage. Below 5 ML, there is only a pseudomorphic peak observed. Its integral increases linearly with coverage. This is in good agreement with Fig. 2, which likewise shows no lattice constant relaxation below 5 ML. Above the coverage of the onset of the orthomorphic peak at around 5 ML, however, the pseudomorphic peak integral neither vanishes nor levels off but increases with further increasing Co coverage up to approximately 15 ML and remains constant above. This indicates that pseudomorphic growth does not cease before the 15th ML. The levelling off of the pseudomorphic peak integral around this coverage coincides with a strong increase in gradient of the orthomorphic peak integral vs. coverage (Fig. 3, dashed line). This also proves that pseudomorphic growth ceases around the 15th ML, and film growth switches finally to completely orthomorphic. Thus, the formation of bulk dislocations, resulting in completely orthomorphic growth according to conventional theory [1], occurs around the 15th ML. From this, we conclude that the critical thickness for pseudomorphic growth is approximately 15 ML, and not equal to the coverage of 5 ML, which corresponds to the onset of

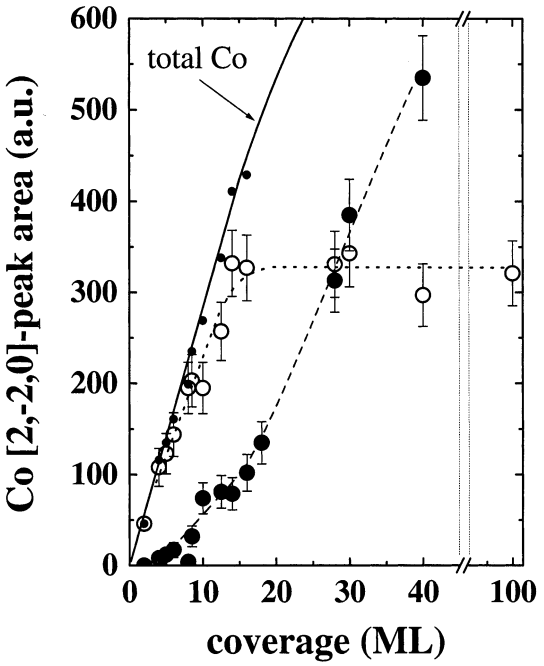

Fig. 3. Peak integral of the pseudomorphic (○, dotted line) and orthomorphic (●, dashed line) peak fits. Both peak integrals add up to the total integrated Co peak (•, solid line), which increases linearly at small coverages, as expected for small film thickness.

the in-plane lattice constant relaxation, as deduced from Fig. 2. Between 5 and 15 ML, there is coexistence of both growth phases.

So far, only the peak integrals of the whole film, as plotted in Fig. 3, have been considered. From Fig. 3, we can deduce that the orthomorphic portion in films with a thickness of 10 ML for example, is approximately 20%. However, the exact portions of pseudo- and orthomorphic phases in each ML, as well as their evolution with coverage, is still unclear. In order to extract the pseudo- and orthomorphic portions of each ML, these have been calculated from the peak integrals, as shown in Fig. 3, and plotted in Fig. 4 as solid and dotted lines, respectively. Fig. 4 shows, that in the fifth ML, approximately 15% of a ML start abruptly to relax. During further growth, the orthomorphic growth patches (Fig. 4, dotted) in each ML increase slightly ML by ML at the expense of the pseudomorphic growth patches

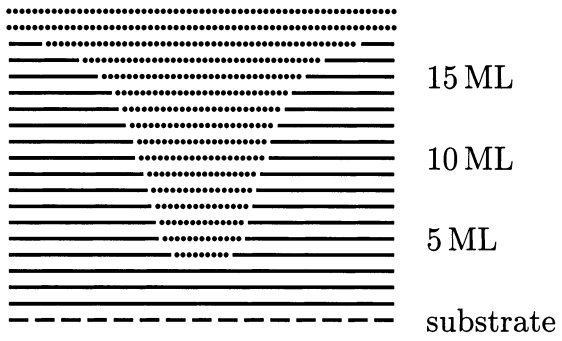

Fig. 4. Schematic representation of film growth. Lines indicate the pseudomorphic portions of each Co layer, dots the orthomorphic portions, as calculated from the data of Fig. 3. It is assumed that the peak integral of the n ML thick film is a linear superposition of the peak integral of the $(n-1)$ ML thick film and the contribution of the nth ML.

(Fig. 4, solid). The critical thickness for pseudomorphic growth is reached in the pseudomorphic growth areas around 15 ML, as indicated by the rapid increase of the orthomorphic portion on cost of the pseudomorphic portion around the 15th ML (Fig. 4). Since it is practically certain that film growth remains orthomorphic in a growth area that has already started to relax, orthomorphic and pseudomorphic growth occur in separated substrate areas. This formation of localized orthomorphic growth patches results in a decrease in the total pseudomorphic strain energy of the film.

There remains the question for the origin of the onset of the in-plane lattice constant relaxation around 5 ML. So far, Co on Cu(001) has been believed to be a Frank-van-der-Merwe growth system at room temperature, or even a Volmer–Weber growth system at a slightly elevated temperature [5]. Neither growth mode is compatible with our data since there is obviously no sharp transition from pseudomorphic to non-coherent growth, and Volmer–Weber islands were expected to grow orthomorphically from the first ML. However, assuming Co on Cu(001) to be a Stranski–Krastanov growth system at room-temperature electrochemical deposition, the onset of the in-plane lattice constant relaxation around 5 ML (Fig. 2) can be interpreted as being caused by the onset of the formation of Stranski–Krastanov islands. There could be either formation of misfit dislocations underneath the Stranski–Krastanov islands or growth of coherent Stranski–Krastanov islands [13] within the pseudomorphic Co film. The increase of the orthomorphic peak integral between 5 and 15 ML is then caused by the growth of Stranski–Krastanov islands and their strain fields, whereas the increase of the pseudomorphic peak integral between 5 and 15 ML results from the growth of the pseudomorphic Co matrix between the Stranski–Krastanov islands. This interpretation would also be consistent with the large orthomorphic peak width (FWHM) compared to the pseudomorphic peak width (Fig. 1), which suggests an orthomorphic island size of the order of 100 Å. The formation of hcp Co islands as a possible relaxation mechanism can be excluded since the total intensity of the fcc Co reflection increases linearly with coverage up to at least 15 ML (Fig. 3).

There seems to be no indication that the pseudomorphic buffer layer relaxes to orthomorphic, if a critical thickness is exceeded, as has been observed recently for Cu on Au(001) or Ag(001) [8]. Whereas these systems initially show growth of bcc Cu and, upon increasing coverage, an energetically driven structural phase transition from bcc Cu to fcc Cu around 8 ML, Co on Cu(001) even initially grows in the energetically favourable fcc phase, likewise in the pseudomorphic or orthomorphic growth regime.

The in-plane lattice constant between 15 and 100 ML is approximately 3.58 Å, (Fig. 2). We find only half of the relaxation that would be expected from the literature values of the fcc Co in-plane lattice constant, as indicated in Fig. 2. Simultaneously, a contraction of the out-of-plane lattice constant to 3.5167 Å, with respect to the literature values, is found in the orthomorphic growth regime up to 100 ML. Neither the enhancement of the in-plane lattice constant nor the simultaneous tetragonal distortion of the unit cell up to at least 100 ML, even in the orthomorphic growth regime, has not been observed before, to our knowledge. This indicates that there is residual strain in films of up to at least 100 ML thickness. This finding is in good agreement with recent observations of residual strain in ultrathin films [6,27] and indicates that even 100 ML thick films

have not yet adopted their unstrained bulk properties, as has been generally assumed so far.

In summary, we have shown by a detailed analysis of X-ray diffraction peaks of Co electrodeposited on Cu(001) close to thermodynamical equilibrium that there is a coexistence of pseudomorphic and orthomorphic growth in ultrathin films even below the critical thickness for pseudomorphic growth, in contrast to current belief of pseudomorphic film relaxation. The total strain energy in the pseudomorphic film can be decreased by local formation of orthomorphic growth patches, which allows the rest of the film to grow pseudomorphically. Since the lattice constant misfit between Co and Cu has been measured to be only approximately 1%, it could be suggested that the start of relaxation well below the critical thickness for pseudomorphic growth is a general feature in the growth of ultrathin films. The onset of lattice constant relaxation then has to be considered generally as a lower limit of the critical thickness for pseudomorphic growth. In contrast to the assumption so far that Co on Cu(001) is a Frank-van-der-Merwe or even Volmer–Weber growth system, the onset of lattice constant relaxation could be interpreted as the onset of the formation of Stranski–Krastanov islands within a pseudomorphic matrix in full agreement with our data. The tetragonal distortion of the unit cell, and the enhancement of the in-plane lattice constant, with respect to the literature values, indicate residual strain in films of up to at least 100 ML thickness.

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