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# Stress oscillations in a growing metal film

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## Abstract

The stress in Co monolayers has been measured during epitaxial growth on Cu(0 0 1). The Co-induced stress is found to oscillate with a period of one atomic layer. Simultaneous stress and medium energy electron diffraction identify maximum stress for filled Co layers. Strain relaxation in Co islands leads to a reduced stress contribution of 2.9 GPa in the partially filled top layer as compared to 3.4 GPa for the filled layers. The corresponding variation of the elastic energy is 1 meV per Co atom. Atomic scale calculations reveal that the size-dependent mesoscopic mismatch is the driving force for stress relaxation in Co islands. © 2002 Elsevier Science B.V. All rights reserved.

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The variation of the elastic energy is one of the key parameters which determines morphological changes of mesoscopic structures [1], the self-organized formation of ordered nanostructures [2], and the transition from two-dimensional to three-dimensional growth [3]. A comprehensive understanding of the effect of strain on structural or morphological transitions in mesoscopic structures requires a detailed knowledge of both atomic distances and interatomic forces. With shrinking structural size, which may approach atomic distances in one or more directions, the validity of classical stress–strain relations cannot be assumed a priori [4] and only a direct measurement of stress in mesoscopic structures provides the necessary information on the elastic energy.

An oscillatory variation of the in-plane lattice spacing of epitaxial islands has been observed by diffraction techniques for semiconductor [5] and metal growth [6]. Surface stress oscillations during molecular beam growth have been reported for III–V compounds [7], but not for a metal-on-metal system.

Stress measurements based on the curvature technique [8] are a powerful tool to gain *quantitative* information on forces with sub-monolayer sensitivity, and consequently about strain energy.

In this Letter we present stress measurements during the epitaxial growth of Co monolayers on Cu(0 0 1). We show here, that small curvature changes of order $(1000 \text{ m})^{-1}$ can be analyzed to give quantitative information on the stress and strain energy in a growing Co film with a sensitivity of 1 meV/atom. The stress induced by the Co layers is found to oscillate as a function of film thickness with a period of one atomic layer. We have combined the stress measurements with

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medium energy electron diffraction (MEED) analysis of the film morphology and found maximum stress for filled layers. Atomic scale simulations performed by means of the quasi-ab initio molecular dynamics method show that strain relaxation in Co islands causes this novel effect of stress oscillations. The stress measurements indicate a reduction of the strain energy per atom by 1 meV for island coverage at partial layer filling, which is too small to induce a transition from two-dimensional to three-dimensional growth mode.

The experiments were performed in a ultra-high vacuum chamber equipped with Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The Cu(0 0 1) crystal (15 mm long, 3.5 mm wide) with a thickness of $t_S = 0.14$ mm was prepared by cycles of Ar ion bombardment (2 μA, 2 keV) and subsequent annealing at 800 K until no traces of contamination were detected by AES and a sharp LEED pattern was recorded. Co was evaporated from an high purity (99.99+%) rod at a rate of ≈1 monolayer (1 ML fcc-Co: 1.78 Å) per 100 s at a pressure below $3 \times 10^{-10}$ mbar onto the front surface of the crystal, which was clamped at its top end to a sample manipulator. The Co growth rate was checked by a quartz thickness monitor and by MEED oscillations.

As shown in Fig. 1, stress changes and growth-induced roughness of the Co film were measured simultaneously during growth. Film stress is calculated from the stress-induced curvature of the substrate, and film roughness is monitored by measuring the intensity of a 3 keV electron beam after specular reflection from the sample surface.

The stress-induced curvature $\kappa$ of the crystal was detected by reflecting two laser beams from the Co covered crystal onto two position sensitive detectors. The curvature was then calculated from the difference of the two position signals. The Co-induced bending of the substrate is small: the deposition of 1 ML Co induces a radius of curvature $R = 1/\kappa \approx 615$ m, and a displacement of the bottom end of the crystal of 80 nm results.

The substrate curvature $\kappa$ is induced by the bending moment acting on the film-covered side of the substrate. The source of the bending moment is
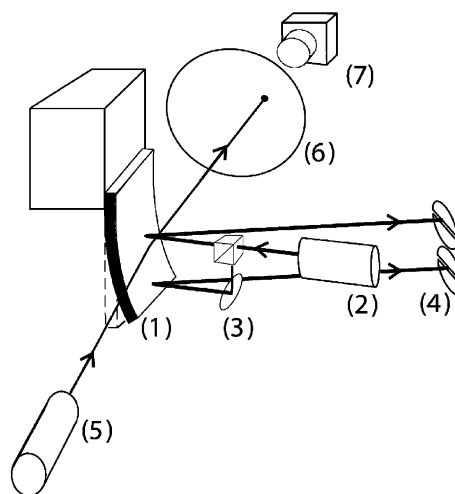


Fig. 1. Schematic of the two-beam optical deflection technique: (1) Cu crystal, (2) laser, (3) beamsplitter, (4) position sensitive detector, (5) e-gun, (6) LEED screen, (7) CCD camera.

the thickness integrated stress in the cross section of the film.

For constant film stress $\tau_F$, the curvature $\kappa$ increases in proportion to the film thickness $t_F$, $\Delta(\tau_F t_F) = Y'_S t_S^2 \Delta\kappa/6$, with the biaxial elastic modulus of the Cu substrate $Y'_S = 113$ GPa. [1] The $\Delta$ indicates that we exploit the change of curvature with respect to the reference state of the uncovered Cu substrate. The large length-to-width ratio of our sample of 4 leads to an almost perfect biaxial bending with negligible influence of the sample clamping on the curvature [9].

A typical measurement of the Co-induced stress $\tau_F \times t_F$ during deposition is shown in Fig. 2(a). We see that the total stress in the film increases monotonically. After deposition of 6 ML Co the stress has increased by 3.6 N/m, which corresponds to an average film stress of 3.37 GPa. The main result of this work is that the stress curve in Fig. 2(a) shows periodic changes of its slope. This is obvious from the plot of the slope in Fig. 2(b), where a monolayer period of the stress oscillations is apparent. Before we discuss a model, which ascribes this finding to stress relaxation in Co islands,
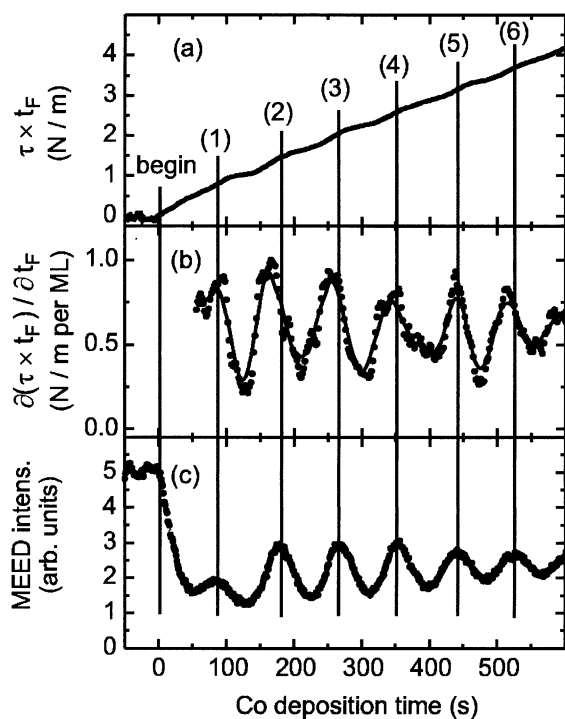
Fig. 2. Stress and simultaneous MEED intensity measurements during the growth of Co on Cu(0 0 1) at 300 K: (a) Stress as deduced from curvature measurements during growth. The numbers indicate complete layer filling as determined from MEED measurements in (c). (b) Calculated slope of the stress curve (a) shows pronounced monolayer oscillations. The continuous curve serves as a guide to the eye. (c) Intensity of the specular reflected electron beam during Co deposition. Extrapolation back to the beginning of growth identifies maximum intensity for filled layers.

we elucidate the important result of an almost bulk-like stress behavior of Co monolayers, which is reflected by the average film stress of 3.37 GPa.

The different lattice constants of fcc-Co (3.55 Å) and Cu (3.61 Å) induce a lattice mismatch $\epsilon = 1.7\%$ for the pseudomorphic growth regime. A film stress of $\tau_F = Y_F' \epsilon = 3.23$ GPa is calculated from continuum elasticity, with the biaxial modulus of fcc-Co $Y_F' = 190$ GPa (see footnote 1).

This close agreement between measured average film stress of 3.37 GPa and the continuum elasticity value of 3.23 GPa, indicates the dominant role of film strain for the measured stress. This result cannot be taken for granted as several previous experimental studies have found complete failures of stress–strain models in monolayers [4]. In contrast to these studies, we suggest that for Co growth on Cu charge transfer between film and substrate, which has been proposed as an important factor for surface stress changes [10], seems to be of minor relevance, making film strain the decisive source of the measured stress.

Pronounced periodic changes of the slope of the stress curve are shown in Fig. 2(b). Minima of the slope are observed for less than half-filled layers, and maxima of the slope are observed for almost filled layers. This phase relation between stress and layer filling is evident from the MEED and curvature data simultaneously taken. The stress oscillation shown in Fig. 2(b) indicate that, starting from a filled layer, the increase of stress due to newly arrived Co atoms is less than average ($\approx 0.6$ N/m) for the first half monolayer and higher than average for the second half of the monolayer. This new result is explained in the following.

For $t_F > 2$ ML Co-growth on Cu(0 0 1) is a prototype of layer-by-layer growth [11], and we concentrate on this thickness regime. The smaller increase of the integrated film stress for less than half-filled layers relative to filled layers is correlated with the existence of many Co islands on top of the completed Co layer. Our in situ MEED analysis indicates maximum film roughness for half-filled layers. Therefore, one might wonder, why does the system proceed with a layer-by-layer growth, although this will lead to a larger elastic energy content of the film? The low magnitude of the elastic energy offers an answer.

The elastic energy density of the biaxially stressed Co film is calculated within continuum elasticity as 4.3 meV per Co atom. The application of continuum elasticity to the filled layer is physically justified by the validity of the stress–strain relation discussed above. The elastic energy content of the fully strained Co layer is roughly two orders of magnitude smaller than the energy scale which governs alloy formation and surface diffusion [12]. This comparison elucidates the small magnitude of the elastic energy and we propose that it is not sufficient in magnitude to induce island growth.

This conclusion neglects the kinetics of surface diffusion, i.e. we assume that flat and rough

surfaces could be realized by surface diffusion under the given experimental conditions. Therefore we cannot exclude that in addition to elastic energy also kinetic arguments might be important for the growth mode.

Note, that due to the quadratic dependence of the elastic energy density on film stress, the elastic energy contribution to the energetics of heteroepitaxial growth is not necessarily small, and will be dominant for larger stress, as measured in other epitaxial systems [13].

How much elastic energy is gained from the reduced stress contribution of the Co islands? The elastic energy contribution of the Co–Cu system could be reduced at most by 4.3 meV for total stress relaxation. However, our stress measurements of Fig. 2(a) indicate incomplete stress relaxation in the growing islands. The amplitude of the oscillatory stress relaxation is given by the plot of the slope of the stress curve presented in Fig. 2(b). The average value of the minima of the slope curve (b) is 0.35 N/m per ML. The slope oscillates around the average value of 0.6 N/m per ML and reaches maxima for slightly less than completely filled layers.

The large value of the average maximal slope of 0.9 N/m per ML is ascribed to the stress signature of the percolation of Co islands. Additional Co atoms lead to the creation of fewer extended Co islands, which contribute a larger stress as compared to smaller islands, due to the diminished stress relaxation in extended islands.

To get a deeper understanding of the local stress relaxation on an atomic scale, forces at each atomic site are calculated and both island and substrate atom positions are relaxed. We use the quasi-ab initio molecular dynamics method [14], which is based on the tight-binding approximation for many body potentials and on the KKR Green's function methods for low dimensional systems [15]. Accurate first principle spin-polarized calculations of cluster–substrate properties are performed to construct the many body potentials for the Co/Cu(0 0 1) system. A database derived from ab initio calculations is used for interatomic potentials at the surface. Surface and bulk properties are well described by this method [14]. The stress distribution in the islands and at the substrate is calculated by the atomic level stress components [16] as

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0}\left[\frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{4}\sum_j\left(r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta\right)\right]$$

where $(\alpha\beta) \equiv (x, y, z)$, $m_i$ and $p_i$ are the mass and momentum of atom $i$, $\vec{r}_{ij}$ is the distance between atom $i$ and $j$, and $\vec{f}_{ij}$ is the force acting on atom $i$ due to atom $j$, $\Omega_0$ is the average atomic volume [17].

Our calculations give quantitative information on structural relaxation in both islands and underlying layers and on the resulting stress [18]. The consideration of strain relaxation is essential for the calculation of stress in partially filled layers. Former calculations on stress relaxation were based on the assumption that atomic relaxation in the island is connected with a concurrent dragging of the substrate atoms [19]. The underlying physical principle of coherency between island and substrate lattice is, however, challenged by our calculations. We calculate considerable bond length variations for both island and substrate atoms, as shown in Fig. 3(a) and (b), respectively. The atomic positions in the Co island correspond to a reduced strain as compared to the pseudomorphic growth value (dashed line). Near the island edge, the bond lengths differ significantly for island atoms and atoms in the filled Co layer underneath: all Co island atoms show some strain relaxation, but atoms of the layer underneath near the island edge have a larger bond length as compared to the pseudomorphic value. The assumption of lattice coherency is clearly not fulfilled near the island edge, but it is approached near the island center, as indicated by the almost identical values of the bond lengths in Fig. 3(a) and (b), respectively.

Based on our atomically resolved stress calculations, we approximate the extent of the relaxation to a fictitious thickness of two atomic layers. For half layer coverage, the average stress distribution in the top two layers is (0.6 N/m + 0.5 × 0.35 N/m) per 1.5 ML. This corresponds to a reduced average stress of 0.52 N/m per ML (2.92 GPa), which amounts to 87% of the value of the filled layer. The elastic energy per Co atom of the top two layers is consequently reduced from 4.3 to 3.3 meV.
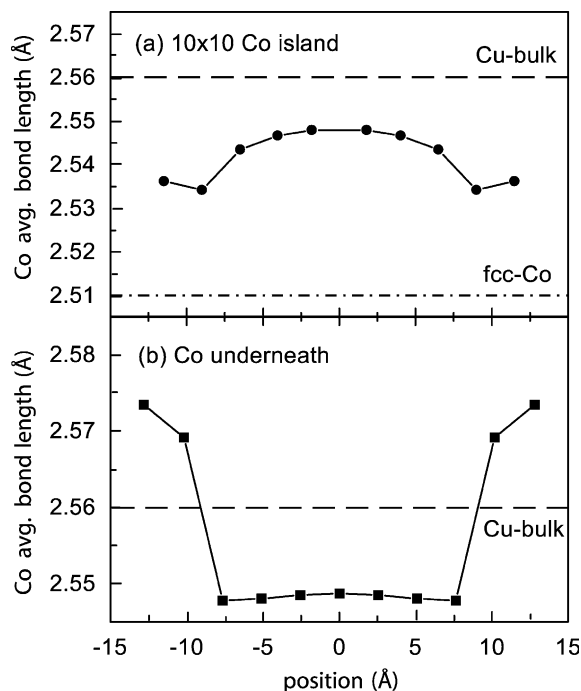
Fig. 3. Calculated atomic distances in an island of $10 \times 10$ Co atoms (a) and in the filled Co layer underneath (b). (a) Co atoms are relaxed to give a Co–Co bond length considerably smaller than the pseudomorphic growth value ((– – –) Cu-bulk). (b) The Co atoms underneath have a larger bond length relative to the pseudomorphic growth value (– – –) at the edge of the island. In the center region, a compressed bond length is calculated.

Our stress calculations reveal that an island size of $20 \times 20$ Co atoms on a Co layer on Cu(0 0 1)
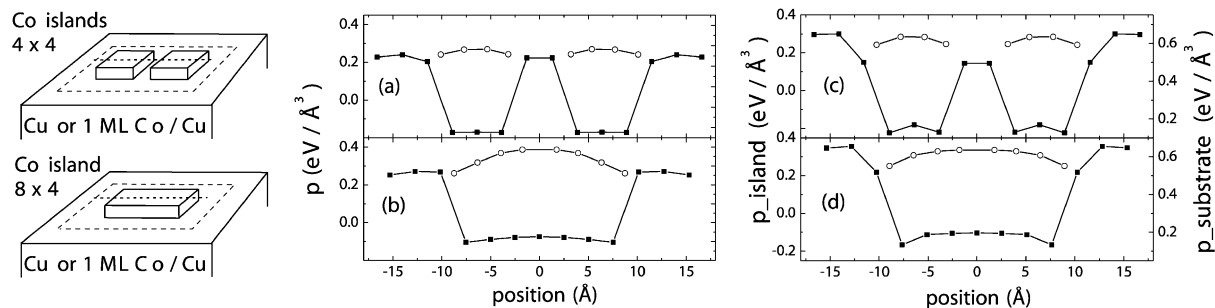
induces a stress of 88% of the respective value for the filled layer, which is close to reduced stress of 87% measured for half layer filling. This close agreement between measured and calculated stress is the physical justification to estimate the average island size from the measured reduced stress. This estimate gives an island edge length of 3.5 nm, in fair agreement with STM studies which show islands of comparable size for a Co coverage of 2.5 ML [11].

Our calculations indicate a pronounced dependence of the island-induced stress on the island size with the stress being larger for larger island sizes. For Co islands of size $4 \times 4$, $4 \times 8$, $10 \times 10$, and $20 \times 20$ atoms, the stress with respect to the filled layer is 59%, 68%, 81% and 88%, respectively.

Larger stress for larger Co coverage is also calculated if we take intermixing into account. For a Co coverage in the first layer of 0.3, 0.5, 0.6 and 0.8 we find a reduced stress of 52%, 55%, 59% and 75% with respect to the filled layer, respectively.

We present in Fig. 4 the calculated stress distribution in Co islands and in the substrate underneath for Co growth on Cu (Fig. 4(a) and (b)) and for Co growth on a filled Co layer (Fig. 4(c) and (d)).

When Co islands are in close proximity in the precoalescence state, a strongly inhomogeneous stress is induced at the island–substrate interface (Fig. 4(a)). The Cu-substrate atoms underneath the Co islands exhibit a strong compressive stress, while the outer atoms are under tensile stress. Our



Fig. 4. Hydrostatic stress $p$, $p = \mathrm{Tr}(\sigma_{\alpha\beta})$, for Co islands on Cu(0 0 1) ((a) and (b)) and on 1 ML Co/Cu(0 0 1) ((c) and (d)). The stress in the island is indicated by circles, the stress in the substrate is shown by squares. The solid lines serve as a guide to the eye. The stress is calculated along [1 1 0], for pre- and post-coalescence, and shown in the upper and lower panels, respectively, as indicated by the sketch. The area over which $p$ is integrated to calculate the stress increase due to coalescence is indicated by the dashed rectangle. In (c) and (d) the stress axes for island and substrate stress have been slightly shifted for clarity.

calculations show that the island coalescence (Fig. 4(b)) increases the tensile stress in the coalesced islands and reduces the compressive stress in the Cu substrate. The stress induced by Co islands on the first Co layer is similar to the case of hetero-epitaxy shown in Fig. 4(a) and (b), island coalescence increases the tensile stress in the islands and decreases the stress in the Co layer underneath. The average stress per atom integrated over an rectangular area surrounding the islands is increased by 4% for the $8 \times 4$ island as compared to the $4 \times 4$ island. The measured smaller stress for the beginning of the layer filling is therefore ascribed to the size-dependent island-induced stress, which is smaller for smaller islands. For this calculation, the size of the integration area has been chosen to accommodate atoms on undistorted sites at the outer limit of the integration area.

In conclusion, we have found stress oscillations during the epitaxial growth of Co on Cu(0 0 1) with a period of 1 ML. Stress for filled layers of 3.37 GPa is followed by a reduced stress for less than half-filled layers. Our experiments and atomic scale calculations ascribe the stress variation to the relaxation of epitaxial mesoscopic misfit strain in the islands. The stress measurements indicate an elastic energy per Co atom of 4.3 meV for filled layers, which is reduced to 3.3 meV for Co atoms in the top two layers of the island structure. The small magnitude of this energy variation indicates the dominant role of other energy contributions which lead to layer-by-layer growth in spite of maximum strain energy in filled layers.

Curvature measurements on thinner substrates will provide access to even smaller energy changes per surface atom in the µeV range. Thus, subtle aspects of the energetics of adsorption, film growth or magnetization, can be studied quantitatively by the curvature technique.

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