Unusual Strain Relaxation in Cu Thin Films on Ni(001)

Frank Berg Rasmussen, Jeff Baker, Mourits Nielsen, and Robert Feidenhans'1

Risø National Laboratory, DK-4000 Roskilde, Denmark

Robert L. Johnson

II. Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany

(Received 20 May 1997)

Surface x-ray diffraction has been used to study the growth of thin Cu films on Ni(001). We give direct evidence for the formation of embedded wedges with internal {111} facets in the film, as recently suggested by Müller *et al.* [Phys. Rev. Lett. **76**, 2358 (1996)]. The unusual strain distribution within the wedges is determined and provides an explanation to the observed sudden change in growth and film morphology around 20 monolayers. [S0031-9007(97)04663-2]

PACS numbers: 68.35.Bs, 61.10.Eq, 68.55.Jk, 68.65.+g

In epitaxial layer by layer growth it is energetically favorable for thin films to be coherent (pseudomorphic) with the substrate up to a critical film thickness depending on the misfit and elastic properties of the system. Above the critical thickness the strain is relieved by means of misfit dislocations and associated lattice relaxation [1,2].

Nickel and copper both crystallize in the fcc structure with the Cu lattice parameter being 2.6% larger than that of Ni. According to conventional theory Cu on Ni(001) would be expected to grow as a pseudomorphic film up to a thickness of 8 monolayers (ML) [3]. However, recent scanning tunneling microscopy measurements revealed a very different behavior of this system [4]. After deposition of one monolayer of Cu on Ni(001), Müller *et al.* observed one-atom wide stripes of Cu atoms along $\langle 110 \rangle$ directions protruding about 0.6 Å above the surface Cu layer. With each added Cu layer the stripes grew in width by one atom, whereas the height of the protrusion remained constant. The stripes showed an average length of 27 atoms independent of the coverage. This behavior was observed up to coverages of 20 ML when the growth mode changed abruptly due to the formation of bulk dislocations [4]. Based on these results the so-called *internal faceting mechanism* of strain relief was proposed. In this model monatomic chains of Cu atoms of the first monolayer are displaced from fourfold hollow sites to twofold bridge sites and thereby protrude from the surface layer. During subsequent growth the protruding stripes grow in width by one atom per layer forming embedded wedge-shaped defects with {111} facets as shown in Fig. 1 [4]. In doing so, the atoms in the wedges gain lateral freedom of expansion allowing the film to partly relieve its strain. It was speculated that the Cu atoms in the wedges are fully relaxed across the wedges but have the bulk Ni spacing along the long direction of the wedges. The Cu atoms surrounding the wedges were proposed to be coherent with the substrate [4].

Here we present the results of surface x-ray diffraction (SXRD) studies of Cu growth on Ni(001). We have

obtained direct evidence for the existence of the internal {111} facets and have determined an unusual strain distribution in the film as detailed below.

The SXRD experiments were performed at the wiggler beam line BW2 in HASYLAB. The typical sample was prepared according to the prescriptions of [4] in a separate chamber. Then it was transferred to a portable UHV chamber with a hemispherical Be window which was mounted on the diffractometer. The photon energy

FIG. 1. Proposed model of strain relief at the Cu-Ni interface (top) [4]. The dark gray Cu atoms are placed at (pseudomorphic) fourfold hollow sites, and the light gray Cu atoms form a wedge-shaped nanocluster extending along $\langle 110 \rangle$. The entire wedge is displaced half a nearest neighbor distance along $\langle 110 \rangle$ with respect to the pseudomorphic lattice positions. Ni atoms are shown as black. Also shown (bottom) is a section of the reciprocal space. The solid (dashed) arrows indicate longitudinal (transverse) scans in reciprocal space.

was chosen to be 8.1 keV, the surface of the crystal was aligned by total external reflection of the x-ray beam, and the angle of incidence was kept constant and equal to the critical angle $\alpha_c = 0.41^\circ$ [5].

In the following we will use the LEED convention defining the unit cell by a set of orthogonal real space vectors **a**, **b**, and **c** such that **a** and **b** are in the plane of the (001) surface along the [110] and $[1\bar{1}0]$ directions and **c** is along the [001] direction. Values of $a = b = 2.491 \text{ \AA}$ and $c = 3.524 \text{ \AA}$ corresponding to bulk Ni values were used. Note that the wedges in this coordinate system have $\{101\}_L$ facets, the subscript indicating the LEED convention. Scans were performed parallel to the surface by varying either h or k , keeping the momentum transfer perpendicular to the surface l constant. Figure 1 shows typical scan directions in reciprocal space and defines the notions of transverse and longitudinal scans frequently used in diffraction experiments. An extensive data set including several symmetry equivalent reflections were measured on a number of samples with coverages varying from 3 to above 20 ML. Here we focus on a 9 ML film but the conclusions presented are consistent with all of our data.

A perfectly pseudomorphic Cu film on Ni(001) would only give rise to scattering along the vertical crystal truncation rods (CTRs) through the Ni reciprocal lattice points [6]. If embedded wedges exist then streaks of scattering, due to CTRs from $\{101\}_L$ facets, should be observed. Figure 2 shows representative transverse scans through the (10) CTR. In addition to the central CTR extra facet peaks are observed. The facet peaks are solely caused by the wedge-shaped clusters and we shall focus on the analysis of such peaks well separated from the central CTR.

The observed facet peaks occur close to the expected positions for scattering from $\{101\}_L$ facets and, hence, represent the first evidence for the existence of embedded wedges in the Cu film [7]. Facet peaks are also observed in transverse scans through the (30) CTR but are absent when scanning through the (20) CTR (Fig. 2 inset). This observation constitutes a selection rule in that facet peaks are absent (present) in transverse scans when the corresponding fixed in-plane scattering coordinate is even (uneven). Consider one wedge formed in an otherwise ideal Cu film with all atoms in the wedge displaced by $\Delta\mathbf{r} = (0.5, 0, h_{\text{Cu}})$ with respect to the pseudomorphic lattice positions, i.e., with the long side along $[100]_L$. In a simple hard sphere model $h_{\text{Cu}} = 0.11$ (lattice units) [4] and for this orientation of the wedge the important transverse scans are k scans through $(h0)$ CTRs [9]. Assuming no relaxation within the wedge then the scattering amplitude of the film is given by

$$F(\mathbf{q}) = f_{\text{film}}(\mathbf{q}) + f_w(\mathbf{q})(e^{2\pi i(\Delta\mathbf{r} \cdot \mathbf{q})} - 1), \quad (1)$$

where $\mathbf{q} = (h, k, l)$ is the momentum transfer, f_{film} is the structure factor of an ideal pseudomorphic Cu film, and

FIG. 2. Calculated and measured transverse x-ray diffraction profiles through the (10) CTR. The circles represent the experimental data points and the solid lines are the calculated profiles as described in the text. The inset shows a transverse scan through the (20) CTR, where the facet scattering is absent. The individual profiles have been displaced vertically for clarity.

f_w is the structure factor of a single unrelaxed wedge. The term in parentheses arises from the displacement of the entire wedge and is almost equal to -2 for a k scan through the $(h0)$ CTR when h is uneven but approaches zero for h even. The selection rule is therefore a distinct feature of the wedges being displaced half a lattice distance with respect to the surrounding Cu. The observed facet peaks are direct signatures of the wedge facets and, as we shall see, their line shapes are a measure of the strain fields inside and outside the wedges.

Further insight is obtained by noticing that the facet peaks of Fig. 2 have their maximum at $h = 1.00$ when scanning through the facet peaks along the (10) direction. This shows directly that the atoms in the wedge have the lattice spacing of bulk Ni along the long direction of the wedges as suggested by Müller *et al.*

So far we have considered only transverse scans which are symmetrical around the central peak and are only weakly sensitive to the lateral strain distribution of the film perpendicular to the long directions of the wedges. Longitudinal scans can be used to reveal the lateral strain and the intensity distributions depend strongly on the strain field [8,10]. Figure 3 shows representative

FIG. 3. Calculated and measured longitudinal x-ray diffraction profiles through the (10) CTR. The circles represent the experimental data points and the solid lines are the calculated profiles as described in the text. The individual profiles have been displaced vertically for clarity.

longitudinal scans through the (10) CTR. In this case the asymmetry is so large that only one facet peak is observed in each scan. This immediately reveals that substantial lateral lattice relaxation takes place within the film and that the strain distribution is inhomogeneous [8]. If the majority of the Cu atoms in the film had lattice parameters close to those of bulk Cu a peak reminiscent of CTR scattering from bulk Cu should be observed in the longitudinal scans [e.g., for $(h, k) \approx (0.97, 0)$ reciprocal lattice units]. As this is not the case (Fig. 3) we may conclude that the Cu atoms surrounding the wedges are essentially pseudomorphic with the substrate.

In order to obtain quantitative information on the strain distribution we have performed model calculations using kinematical theory and compared these with the experimentally obtained scattering profiles. The calculations are greatly facilitated by the fact that all wedges, apart from fluctuations in the length, are identical at a given coverage [4,11]. As a simple model we may therefore consider a slab of Cu containing one wedge placed on top of a perfect Ni crystal of infinite extent along $[00\bar{1}]$. The calculated diffracted intensity is then found as a simple sum over the contributions from all of the atoms.

In agreement with the discussion above we assume that all atoms outside the wedge are laterally pseudomorphic with the substrate and displace the entire wedge by $\Delta \mathbf{r} =$

$(0.5, 0, h_{Cu})$. For the atoms inside the wedge we set the lattice parameter along the long side of the wedge to the Ni lattice constant. Along the short side we allow the in-plane lattice parameter $b(n)$ to expand laterally as a function of height n above the interface, where n is counted in atomic layers. As a starting point we considered the tentative strain model suggested by Müller *et al.* [4] setting $b(n)$ equal to the Cu lattice constant [$b(n) = 1.026$]. Although this model accounts for the occurrence of facet peaks in the transverse scans, it fails to reproduce the shape of the longitudinal intensity profiles and the relative intensities of the facet peaks observed in the transverse and longitudinal scans (Fig. 4). We have tried several different functional forms for $b(n)$ and found that a large lateral expansion at the bottom of the wedge following a Gaussian dependence with distance away from the interface gives the best fit to the experimental data. The height variation of the lateral lattice parameter within the wedges is given by

$$b(n) = b_{\infty} + \epsilon_{rel} e^{-\left(\frac{n}{n_c}\right)^2}, \quad (2)$$

where b_{∞} is the lateral lattice parameter at the top of thick wedges (large n), ϵ_{rel} is the extra lattice relaxation at the bottom of the wedge ($n = 0$) and n_c determines the decay of the exponential. Furthermore, we assume that all atoms, both inside and outside the wedge, have a common vertical lattice constant, c_0 , which ensures that the protrusion of the wedges is coverage independent. A satisfactory fit to all the measured data is obtained with the parameters listed in Table I and a common scale factor [12]. The simulated intensity profiles obtained with these parameters are shown as solid lines in Figs. 2 and 3 and

FIG. 4. Simulated longitudinal x-ray diffraction profiles through the (20) CTR at $l = 0.30$ compared to the experimental profile (circles). The solid line corresponds to a simulation with the parameters of Table I. The dashed line represents a similar model but with $b_{\infty} = 1.026$, whereas the starred line corresponds to the model of Müller *et al.* [4] (see text). The longitudinal profiles are very sensitive to the strain distribution inside the wedges. As substantial relaxation takes place within the wedges Eq. (1) does not apply and facet peaks are observed in longitudinal scans through the (20) CTR.

TABLE I. Strain parameters obtained for a 9 ML Cu film on Ni(001); see text.

	Lattice units	Å
c_0	1.04	3.67
h_{Cu}	0.14	0.5
b_∞	1.00	2.49
ϵ_{rel}	0.07	0.17
n_c	7 layers	

generally the agreement with the experimental profiles is good. The common vertical lattice constant, c_0 , is determined primarily by the positions of the transverse side peaks. For the 9 ML film we obtain a value of 1.04, i.e., a vertical lattice expansion of 4% with respect to the Ni lattice. This is consistent with the out of plane relaxation reported by Chambers *et al.* [13] and is in agreement with simple arguments based on elasticity theory assuming c_0 to be determined by the Cu film outside the wedges (Poissons ratio: $\sigma_{\text{Cu}} = 0.34$). The protrusion, h_{Cu} , is mostly sensitive to the intensity ratio between the transverse and longitudinal facet peaks. The obtained value of 0.5 Å compares favorably with the 0.4 Å obtained from the hard sphere model and high-resolution LEED (SPA-LEED) measurements [14] and the 0.6 Å originally observed by Müller *et al.* [4]. The remaining parameters (b_∞ , ϵ_{rel} , n_c) determine the intensity profiles of the longitudinal scans. Figure 4 clearly illustrates the sensitivity of the longitudinal scans to the strain distributions inside the wedge. An acceptable fit is obtained only with b_∞ close to 1.00. Setting $b_\infty = 1.026$ (Cu lattice parameter) causes an extra “Cu” CTR-like peak to appear in the simulation, shown by the dashed line in Fig. 4, which is not observed experimentally.

Considering the simplicity of the model presented here the fit to the facet peaks shown in Figs. 2 and 3 is very good and lends strong support to the proposed strain model. Minor improvements may be obtained by including small relaxations of the atoms outside the wedges and other small effects which will be discussed elsewhere [8].

The strain distribution inside the wedge obtained here has several surprising features. At the bottom of a wedge the atoms relax significantly (7%) using almost all the extra space made available by the out of plane displacement of the entire wedge. Away from the interface the relaxation decreases and for a coverage approaching 20 ML ($\sim 3 \times n_c$) the lateral lattice parameter of the topmost layer is close to that of bulk Ni. This suggests that at low coverages it is energetically favorable for the growing film to form wedges and thereby reduce the compressive strain induced by the substrate. However, as the film grows thicker the strain relief initially gained is lost and a sudden and violent change in growth mode and film morphology takes place. Such a change is expected around a coverage of ~ 20 ML in agreement with the observation of Müller *et al.*

In conclusion we have presented SXRD experiments on thin Cu films on Ni(001). We have given direct evidence for the formation of embedded wedges with {111} facets in the Cu film as originally proposed by Müller *et al.* [4]. The Cu surrounding the wedges essentially remains pseudomorphic with the Ni substrate. Whereas the wedges are found to be inhomogeneously strained with a large lateral relaxation near the Cu/Ni interface which decays rapidly with distance away from the interface. This explains the breakdown of layer by layer growth at coverages approaching 20 monolayers.

We thank the staff of HASYLAB for help and assistance. This work was supported by the Danish National Science Foundation through DanSync and the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) under Project No. 05 622GUA1.

- [1] J. H. Van der Merwe, J. Appl. Phys. **34**, 117 (1963).
- [2] J. W. Matthews and J. L. Crawford, Thin Solid Films **5**, 179 (1970).
- [3] A. Chambers and D. C. Jackson, Philos. Mag. **31**, 1357 (1975).
- [4] B. Müller, B. Fischer, L. Nedelmann, A. Fricke, and K. Kern, Phys. Rev. Lett. **76**, 2358 (1996).
- [5] For more details, see, e.g., R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).
- [6] I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).
- [7] As can be seen from Fig. 2 the facet peaks do not follow straight lines converging at a single point as expected for a CTR of an extended facet. This is an effect of the finite size of the wedges and follows directly from the simulations. Further details will be published elsewhere [8].
- [8] F. B. Rasmussen, J. Baker, M. Nielsen, R. Feidenhans'l, and R. L. Johnson (to be published).
- [9] There are two symmetrically equivalent types of wedges formed on the (001) surface; these have their long dimension along the $[100]_L$ and $[010]_L$ directions, respectively. However, for k scans (h scans) through ($h0$) CTRs ($[k0]$ CTRs) only wedges with the long side along $[100]_L$ ($[010]_L$) contribute to the facet peaks.
- [10] A. J. Steinfert, P. M. L. O. Scholte, A. Ettema, F. Tuinstra, M. Nielsen, E. Landemark, D.-M. Smilgies, R. Feidenhans'l, G. Falkenberg, L. Seehofer, and R. L. Johnson, Phys. Rev. Lett. **77**, 2009 (1996).
- [11] The wedges are much longer than they are wide; hence, the distribution in lengths observed by Müller *et al.* has only a negligible influence on the shape of the calculated intensity profiles and may safely be disregarded.
- [12] The film coverage was determined from l (rod) scans; see [8]. The calculated profiles of Figs. 2–4 correspond to a coverage of 9.2 ML (i.e., 80% 9 ML + 20% 10 ML).
- [13] S. A. Chambers, H. W. Chen, I. M. Vitomirov, S. B. Anderson, and J. H. Weaver, Phys. Rev. B **33**, 8810 (1986).
- [14] L. Nedelmann, B. Müller, B. Fischer, K. Kern, D. Erdös, J. Wollschläger, and M. Henzler, Surf. Sci. **376**, 113 (1997).