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Growth and morphology of Ni(111)/Re(0001) ultrathin films: an in-situ study using scanning tunneling microscopy

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Abstract

A scanning tunneling microscopy (STM) study is presented for the growth of Ni films on Re(0001) at 300 K. A Ni(111) wedge with a slope of 5 ML cm^{-1} was prepared under identical conditions. STM images were recorded in ultrahigh vacuum at 300 K on areas of the wedge with constant coverage. Nearly ideal two-dimensional growth is observed for the first three layers. The second layer grows only after the first layer is 90% complete. For films with thicknesses $2<d\leq 9$ ML, a perfect hexagonal dislocation network which matches the known 9/10 misfit of Ni(111) with respect to Re(0001) is observed across 600×600 nm^2 images. The corrugation of ~0.3 Å, observed at 3 ML, decreases with an increasing number of layers and vanishes completely around 10 ML. The dislocation pattern does not seem to be disturbed by the presence of monoatomic steps. A characteristic change in the pattern of the dislocation network is observed from 1 to 3 ML. © 1997 Elsevier Science B.V.

Keywords: Growth; Magnetic films; Nickel; Rhenium; Scanning tunneling microscopy

1. Introduction

The magnetism of epitaxial transition metal ultrathin films has shown striking and interesting differences to the known bulk behavior [1]. The reduced dimensionality and the strains owing to the lattice mismatch between the substrate and the film allow the magnetic moment to be modified and the easy axis of magnetization to point perpendicular to the surface. By varying the film growth parameters, that is substrate temperature and deposition rate, one can modify the morphology and the magnetic properties of the film [2–7]. A system whose magnetic properties had attracted some interest more than a decade ago is Ni(111)/Re(0001) [8]. One of the first thickness (d) dependencies of the Curie temperature $T_c(d)$ was published for this system, and ferromagnetic long range order above room temperature was found only for films with $d\geq 2.5$ ML. By measuring the ac-susceptibility in situ of this system [1,9] the previously measured $T_c(d)$ curve was confirmed recently down to $d=4$ ML. Surprisingly, for $d<4$ ML no susceptibility peak at the para- to ferromagnetic phase transition could be detected down to 120 K although the T_c of Ni(111) on W(110), for example, is known to be much higher [10]. These magnetic results were interpreted as an indication of structural changes happening in the 1–4 ML range, that is to say for $d<4$ ML island formation could occur, while for $d\geq 4$ ML

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the presence of a susceptibility peak confirms the existence of magnetically homogeneous regions larger than 0.4 μm in lateral diameter [3].

Although motivated by magnetic studies, the present work also has a direct link to studies of epitaxial growth and strain relaxation in hcp metal–metal interfaces. For example, Cu(111) growth on Ru(0001) [11,12] was found to proceed in four different stages, from pseudomorphic (1 ML) to unilaterally contracted (2 ML) to (quasi-) isotropically (triangular) contracted (3 ML) film structures. From the fourth layer on, a fully relaxed, quasi-hexagonal structure (moiré pattern) was observed. Theoretical calculations [13] and recent photo-electron diffraction experiments [14] indicate that a rearrangement of the already deposited layers occurs during growth of the next layer. Similar rearrangements can be expected for the Ni(111)/Re (0001) system, which has the same symmetries and only different lattice constants.

A related issue is how a step edge or Schwoebel barrier [15] is modified by the growth. Studies on several homoepitaxial systems like Fe/Fe(001) [16], Cu/Cu(001) [17], and Ag/Ag(111) [18] have led to the conclusion that on the (001) surface layer-by-layer growth is favored, while on the (111) surface 3D islands are more likely. Quite clearly, there are as yet not enough statistics to warrant such a generalization to all (001) and (111) surfaces, and already the case of Pt/Pt(111) is anomalous. As shown in a series of convincing experiments by the Jülich group [19], homoepitaxy on Pt(111) shows several complexities including the presence of both layer-by-layer growth and 3D island formation under similar conditions [19] which have been attributed to the presence or absence of a reconstructed surface, respectively. We mention this issue here as we find Re (0001) and the reconstruction of underlying Ni layers to be playing an active role in the growth of Ni layers.

In this study we will show that the first few layers grow two-dimensionally, as if there is no step barrier. After deposition of more than 5 ML the growth pattern becomes three-dimensional, as might be expected for homoepitaxy on Ni(111). A regular misfit dislocation pattern with a hexagonal symmetry and a periodicity of 25 Å is observed from the third layer on. For the first and second layer, different topographies were observed whose structure could not be resolved. No clear evidence for a structural modification between 3 and 4 ML, which could be linked to the dramatic change in the magnetic response, is observed [1,8,9]. In the next section we summarize some details of the experiment. This is followed by a presentation of results and their discussion.

2. Experimental

The experiments were performed in an ion-pumped ultrahigh vacuum chamber equipped with an in-situ room temperature STM and 4-grid LEED optics, which was used for LEED and Auger analysis. The rhenium single crystal (disk with 7 mm diameter) was oriented to within 0.2° of the [0001] direction and mechanically polished. After bake out the Re (0001) crystal was sputtered at 3 keV Ar^+ (5 $\mu A\ cm^{-2}$) for 30 min and cleaned by several (~20) heating–cooling cycles between 300 and 2300 K. This resulted in a surface on which terrace sizes with up to 4000 Å distances between monoatomic steps were easily found. Ni was evaporated (0.05 $ML\ min^{-1}$) by sublimation from a 99.995% pure Ni rod onto Re (0001) at room temperature in a vacuum $p \leq 2 \times 10^{-10}$ mbar. During deposition a shutter was moved stepwise in front of the substrate to prepare a Ni-wedge with a slope of about 5 $ML\ cm^{-1}$. Ni stripes with a constant nominal coverage Θ and a width of at least 10 μm were prepared this way. After preparation and LEED/Auger analysis the sample was transferred in situ into the STM mount. The coverage Θ, as indicated in the figures, was measured by counting Θ directly in the images, and is given in pseudomorphic monolayers. All STM images were recorded at room temperature at regions with constant coverage, in the constant current mode at currents of 1 nA and with a sample bias voltage of about 1 V.

3. Results and discussion

In the following we will first discuss the growth of Ni(111) on Re (0001) from 1 to 10 ML. This is followed by a detailed analysis of the topographical changes observed from the first to the fourth layers. In Fig. 1 we show a series of images typical for epitaxial growth of Ni on Re (0001). One finds that almost ideal layer-wise growth occurs (Fig. 1a and 1b), as the first pseudomorphic layer is filled before a second layer is formed. For 0.8 ML total coverage no second layer is observed. The speckles and small, white streaks, observed in the image, indicate that these Ni clusters on the surface move easily and can be pulled around by the STM tip. Note that these features are not observed in Fig. 1b and 1c. The nearly perfect layer-by-layer growth continues up to the third layer. For example, in Fig. 1b we show a total coverage of 3 ML and indeed 80% of the image shows a filled 3 ML film with a few percent of the second and fourth layer. At higher coverages the growth deteriorates somewhat (Fig. 1c), and, for example, at 7 ML coverage as many as seven different layers are found with the thickest being the tenth layer. A pyramidal structure with a triangular base is observed, whose edges run along the [100] in plane Re direction, i.e. the $[1\bar{1}0]$ fcc Ni direction. This feature becomes even more prominent for higher coverage. The growth patterns are evaluated quantitatively in Fig. 2. The actual layer filling is plotted here as a function of total deposition. The data points are obtained by counting the actual area of a layer, numbering from 1 to 10, for several STM images taken at the same total coverage. This analysis shows that layer 1 is almost 90% complete before layer 2 starts to grow. Similarly, layers 2 and 3 are filled before the next layer grows. For higher coverages the layer filling becomes less perfect but is still dominated by layer-by-layer growth up to 7 layers. Such a growth mode indicates that for the first 3 ML the deposited Ni atoms can move freely on the Re (0001) surface and see no Schwoebel barrier [15] at monoatomic steps of the Re substrate and at steps of the first, second and third layer Ni islands. Evidently (arrows in Fig. 1a), the initially deposited Ni atoms diffuse to the bottom of steps in the absence of an energy barrier at the Re steps which would have hindered the downward motion of the Ni atom. The same statement holds for monoatomic steps between the

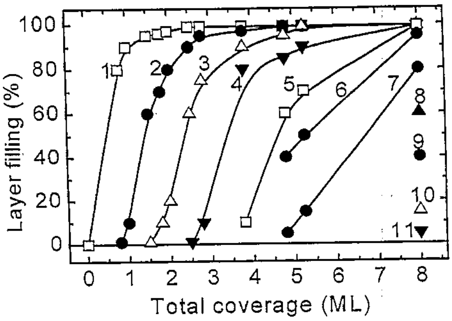

Fig. 2. Layer filling as a function of total coverage. Note that ~80% of the first layer is filled before the second layer starts to grow. Numbers 1 to 11 indicate the first to the eleventh layers.

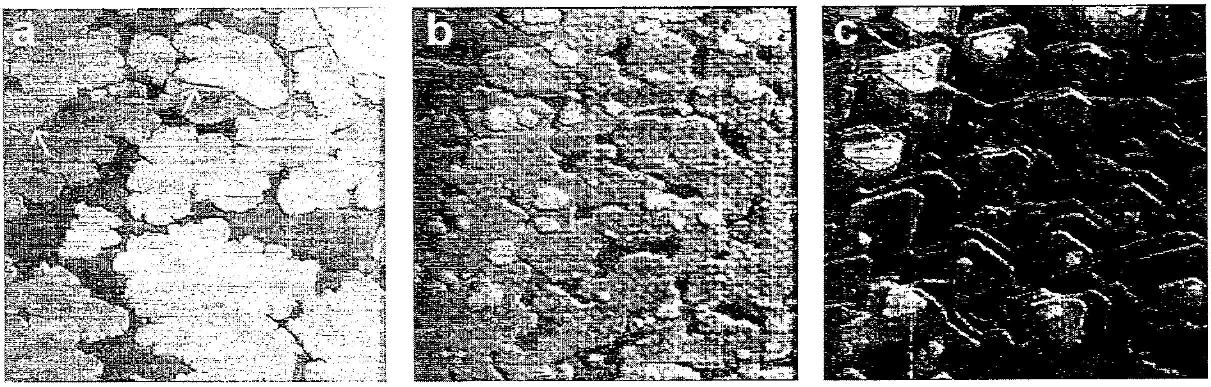

Fig. 1. STM images (80×80 nm^2) of the growth of Ni on Re (0001), prepared in situ at 300 K. Deposition rate 0.05 ML min^{-1}. Coverages: (a) 0.8 ML. The arrows indicate a substrate step. (b) 3 ML. (c) 7 ML. Note the regular dislocation network in (b) which is observed from 3 to 6 ML.

1st and the 2nd, and also between the second and the third Ni layers. Interestingly, the change in the slope of the layer filling curves shown in Fig. 2 indicates that a Schwoebel barrier appears at about the fifth layer, making it energetically unfavorable to jump down from a Ni island. This barrier seems to become higher as a function of coverage and dominates the "pyramidal" growth mode at $d>10$ ML. Now we turn to the details of the topography in the observed growth patterns.

The most striking characteristic is the observed corrugation of the Ni surface at 3 ML and above (see Fig. 1b and 3). The corrugation has an amplitude of 0.3 Å, a hexagonal symmetry and a periodicity of ~25 Å. This modulation length corresponds very well to the known superstructure of Ni/Re (0001) observed by LEED [8,9]. It is the result of the coincidence of two-dimensional symmetries, that is to say the spacing of 10 nearest neighbor Ni atoms $10 \times a_{\mathrm{Ni}}/\sqrt{2} = 24.9$ Å ($a_{\mathrm{Ni}} = 3.524$ Å) coincides very well with the spacing of 9 Re nearest neighbour distances $9 \times a_{\mathrm{Re}} = 24.84$ Å. This reduces the strain in the Ni layer to $(24.9-24.84)/(24.9) = 0.24\%$. In Fig. 3 the linescan (a) across a third layer and a second layer is shown. The corrugation of 0.3 Å and the periodicity of 25 Å is clearly seen in the third layer. The step height of ~1.7 Å corresponds to the expected layer separation of Ni(111). Interestingly, a similar periodic corrugation is also found in the second layer and the periodicity is hardly disturbed by the presence of a monoatomic step. However, the amplitude in the second layer is smaller ~0.25 Å (Fig. 3, line scan b and Fig. 4). The changes from the second to the third overlayer are more evident in the grayscale image (Fig. 3). The quasihexagonal symmetry of the third layer is not seen in the second layer. At the position marked by the arrow in Fig. 3 one sees a change in the periodicity along the direction of the arrow. As indicated by the thin, white line, one crosses a monoatomic Re step without a change in height, that is to say three layers and two layers Ni(111) connect smoothly at the Re step. Similar changes in topography are observed at the Re step at the bottom of the image. One should note that there is some degree of periodicity in the second layer as seen in the linescan (b) of Fig. 3. Unfortunately, due to the

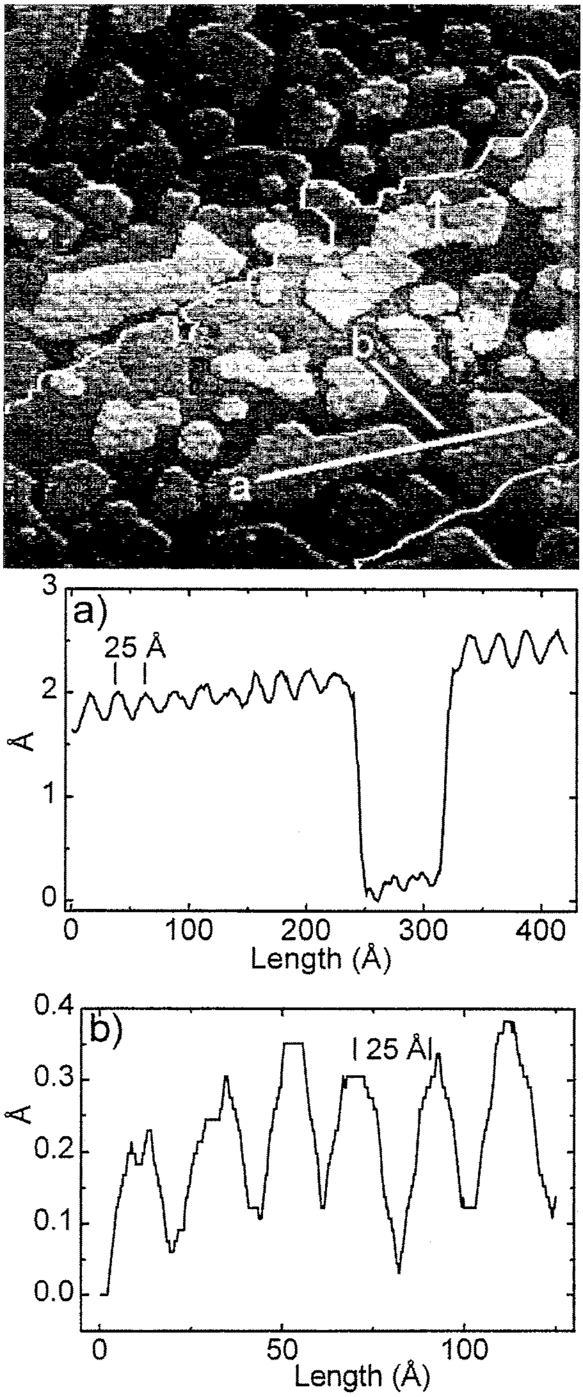

Fig. 3. 80×80 nm^2, periodic distortion network in the second and third layer. Two substrate steps are highlighted by thin solid lines. Note that at the arrow one crosses from 2 ML Ni to 3 ML Ni. Linescans from left to right show the corrugation of the second (b) and the third (a) Ni layer as indicated in the grayscale image.

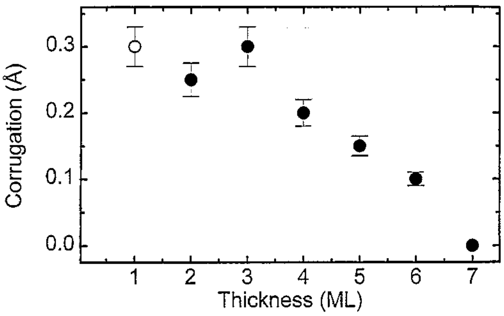

Fig. 4. Corrugation of the top layer as a function of thickness. Note that the corrugation of the first layer is not periodic. Corrugations at higher coverages ($d \geq 3$) have a quasi-hexagonal periodicity of 25 Å, corresponding to 10 Ni nearest neighbor distances.

limited resolution of our experiment the structures of one or two overlayers could not be identified. In Fig. 4 we show the corrugation averaged over many linescans as a function of coverage. The open symbol for the pseudomorphic monolayer indicates that there is no periodicity as for the thicker layers, but rather an irregular corrugation with an average amplitude of ~0.3 Å. For $d \geq 3$ ML a continuous decrease of the periodic corrugation (moiré pattern) is found, which indicates the gradual accommodation of misfit strains originating at the interface. In comparison to the results on Cu/Ru (0001), where only after some moderate annealing the trigonal structure for 3 ML coverage could be resolved [11], we would like to propose that 2 ML Ni(111) might also show a periodic pattern after some moderate annealing. However, this study could not be performed in our present setup. The appearance of the "moiré" pattern at the third layer may show that all three layers have simultaneously relaxed into a structure with almost Ni bulk spacing. This is in analogy to the Cu/Ru system where the same behavior is seen for the fourth layer. There it was also speculated that the corrugation at the surface measured by STM is due to the fact that atoms at the interface are forced into locally unfavorable on top or bridge sites by the minimization of the total energy. This is clearly the result of the changing balance between elastic strain in the Ni layers and misfit strain occurring at the Ni/Re interface. Based on this structural observation one may conclude on the thickness dependence of the magnetism in Ni/Re (0001). In agreement with earlier analyses [8,9] we find no evidence for a percolation of Ni islands in the 2–4 ML range which would explain the reduction of magnetization below 4 ML. However, there is evidence that a dramatic rearrangement of underlying layers occurs when the third monolayer is deposited. This must be associated with a change in nearest neighbor distance and in band structure, which in turn affects the exchange interaction and the spin splitting of the d bands at the Fermi edge, i.e. the total magnetic moment. Consequently, the strongest change in magnetic behavior should be observed when a large percentage of three-layer regions is formed. Unfortunately, the available magnetic measurements do not provide the necessary thickness resolution to confirm this hypothesis.

In conclusion, we find the substrate to be involved in more than a simple mechanical manner in the growth of the first few monolayers of Ni on Re (0001). As the growth pattern indicates, there is initially a very small step edge barrier and as several ML are deposited and Ni(111) starts to have its own characteristics, step edge barriers appear. It would, naturally, be very interesting to calculate and measure this barrier. Studies of these growth patterns as a function of surface temperature will also give insight. Similarly, the choice of another substrate for epitaxy of Ni(111) would also help to answer some questions about the changes induced by the substrate in the electronic and magnetic properties of few ML thick Ni films.

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