Ultra-thin Fe films grown on Cu by pulsed laser deposition: Intermixing and bcc-like structures

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Abstract

Pulsed laser deposition (PLD) with nanosecond pulses has been used for growing ultrathin Fe films on Cu(100) and Cu(111) single crystal surfaces. We have studied the morphology as well as the crystallographic structure of these films by scanning tunneling microscopy, and we compare the films with thermally deposited (TD) films. For Fe/Cu(100), bcc-like (nanomartensitic) structures are found in roughly the same thickness range for PLD and TD films but occupy a lower fraction of the films when deposited by PLD. The situation is different for thin Fe/Cu(111) films, where PLD films exhibit a higher bcc-like fraction, especially in islands of two monolayers thickness. Similar to TD films, we also observe surface reconstructions with bcc-like bond angles for the otherwise fcc Fe/Cu(100) films in the thickness range above 5 ML. For both Fe/Cu(111) and Fe/Cu(100), we find a stronger intermixing between substrate and film compared to films grown by thermal deposition. Even in the seventh monolayer of Fe/Cu(100), approximately 10% Cu have been measured. We argue that the compositional heterogeneity is the reason for the absence of long-range order in the bcc-like phases, hiding them from diffraction techniques. We also discuss the results in the context of the magnetic properties of these films described in the literature.

Keywords: Scanning tunneling microscopy; Pulsed laser deposition; Physical vapor deposition; Growth; Copper; Iron; Magnetic films; Metal-metal magnetic thin film structures

1. Introduction

Among the investigations of magnetic ultrathin film systems, epitaxially grown fcc Fe on Cu(100) has attracted special attention due to its prototypical character concerning the phase transitions of Fe (α ↔ γ) and, accordingly, the rich magnetic behaviour. The metastability of fcc Fe grown on Cu(100) allows commensurate or pseudomorphic growth up to a thickness of 10 monolayers (ML) at room temperature. The technique used for growing these films was usually thermal deposition (TD). Magneto-optical Kerr effect (MOKE) measurements led to a magnetic phase diagram [1,2] for room-temperature grown films. Films below 5 ML thickness (regime I) were found to be uniformly magnetized in out-of-plane direction. Thicker films (up to 10 ML) only show a ferromagnetic surface with perpendicular magnetization (“magnetic live surface layer”, regime II) while the deeper Fe layers show non-ferromagnetic behaviour [1]. The Curie temperature \( T_c \), has been found to be \( \approx 370 \) K for films of 2–3 ML thickness and about 250 K (surface \( T_c \)) for thicknesses between 5 and 10 ML [1,2]. For thicker films an fcc-to-bcc phase transformation of the film occurs [3]. Till the turn of the century it was believed that the magnetization in regime I could be described by a “ferromagnetic fcc model”. The ferromagnetism was attributed to a substantial increase of the film volume (~5%) caused by a distortion of the fcc lattice [4–6].
More recently, scanning tunneling microscopy (STM) investigations brought new insights concerning the atomic structure of TD-grown films [7–10]. Already in the initial phase of film growth, bcc-like distorted groups of Fe atoms have been observed. With increasing coverage, the bcc-like ordered areas grow and form a new phase with typical bond angles around 75°, quite close to the bond angle of 70.5° of undistorted bcc Fe. This phase consists of alternating sequences of stripes of bcc-like twins, and, hence, was named “nanomartensite” (NM) due to its similarity to Fe bulk martensite [8,9]. In STM images of Fe on Cu(100), the NM appears brighter compared to the fcc neighbourhood because of the 5–6% larger interlayer distance, which had been also found in low-energy electron diffraction (LEED) studies [5,6,11,12]. At a thickness of three monolayers the NM content reaches a maximum of more than 80%. Above 3 ML, the NM content measured at room temperature decreases with increasing coverage and is completely replaced by an fcc structure at 5 ML Fe. In contrast to room temperature, where the surface structure of these fcc films was found to be unreconstructed (1 × 1), the surface reconstructs with a local bcc-like bonding geometry at low temperature [9,10,13]. In the range above 5 ML, a low density of another bcc-like phase in form of needle-shaped nanocrystals is found and was explained as a precursor of the fcc → bcc transformation [7,9]. Considering that bcc and bcc-like Fe phases are ferromagnetic and, on the other hand, fcc Fe is not, the STM measurements are able to explain the MOKE results mentioned above in a very natural way by the bcc-like Fe content varying with increasing coverage. Therefore, the hypothesis of ferromagnetic fcc iron became obsolete.

In recent years, another deposition technique became increasingly popular. Pulsed laser deposition (PLD) shows distinct advantages concerning improved layer-by-layer growth [14,15]. Based on LEED, early structural investigations suggested pseudomorphic fcc growth below a thickness of 10 ML also for PLD films of the system Fe/Cu(100) [16], while a newer LEED study found reconstructions very similar to those of TD films [17]. For thicker films a phase transition to bcc has been found. So far this seems to be quite similar to the TD films mentioned above. Differences have been stated concerning the magnetic phase diagram, however. In astonishing contrast to TD films, in-plane magnetization has been reported for the thickness range from 2 to 5 ML. Between the 5th and the 7th ML the films experience a reverse spin reorientation from in-plane to perpendicular (measured at T = 145 K). Above 10 ML, the magnetic behaviour equals that of TD films (in-plane magnetization of thick films) [15,16].

For the related system Fe/Cu(111), ultrathin films have been investigated especially up to about 5 ML thickness. TD films have been found to grow in a multilayer mode at a deposition temperature of 220 K and early LEED measurements indicated a pseudomorphic fcc structure in the initial stage of film growth [18,19]. Within the coverage range from 2 to 4 ML an increasing content of three-dimensional (3D) bcc(110) precipitates has been found, indicating an fcc → bcc phase transition, which is complete above the 4th ML. More recent STM investigations document coexisting fcc and bcc-like Fe phases also for coverages below 2 ML [20]. In agreement with this observation, magnetic measurements showed a continuous increase of the saturation magnetization with thickness [18,21]. The magnetization curves of PLD films are distinctly different, however [18,21]. For PLD-grown films, there is a steeper increase at low coverages. At a thickness of 2 ML the magnetic moment in the case of PLD films is about four times higher compared to TD films. At the 3rd ML a sudden decay of the magnetization has been observed. Afterwards it slowly increases again with film thickness. Concerning the magnetic anisotropy, an out-of-plane magnetic moment of PLD-grown films has been reported in the initial stage up to the 2nd ML, followed by in-plane magnetization above 2 ML. The TD films undergo a similar spin reorientation between 3 and 4 ML [15,21].

Whereas previous studies [9,20] of TD films have shown that ferromagnetism in Fe films is always related to bcc or bcc-like structures, structural information is still incomplete for PLD-grown films. The aim of the current work is to gain more information on the structure of PLD-grown films on the atomic scale, and thereby to correlate the atomic-scale structure and the previous results, especially concerning the magnetic properties of the films.

2. Experimental

The experiments were carried out using an ultrahigh vacuum (UHV) system consisting of two chambers, one mainly used for film preparation, the other for scanning tunneling microscopy measurements. The Cu single crystals in (100) or (111) orientation were cleaned by sputtering using 3 keV Ar⁺ ions (I_{ion} = 3 μA, typically for 30 min) and annealing afterwards at temperatures ≥ 650 °C for about 20 min. For growing the films we used pulsed laser deposition by a Nd:YAG laser [10 ns pulse length, 10 Hz repetition rate, wavelength 532 nm for Fe on Cu(100), 532 nm and 355 nm for Fe on Cu(111)]. The laser beam is directed into the preparation chamber by a system of mirrors and lenses enabling us to focus and defocus it, thereby changing the spot size on the rotating Fe target (purity 99.99+%). In order to reach a steady state ablation process, conditioning of the target by laser ablation was required. We have determined the velocities and accordingly the energies of the ablated Fe ions by a time-of-flight (TOF) spectrometer [22]. The pressure during film preparation was about 3 × 10⁻¹⁰ mbar [mainly H₂ and CO; for both Fe/Cu(100) and (111)], which is about one order of magnitude higher than the base pressure.

We have used rather low deposition rates (between 0.006 and 0.017 ML/s), near the ablation threshold, in order to avoid droplet formation. The deposition rate has been calibrated by a quartz crystal microbalance. As the high particle energies lead to thermal energy on the quartz crystal,
the crystal was kept at the minimum of the frequency vs. temperature curve to reduce thermal effects. Nevertheless, we found that the accuracy of the rate determined by the quartz crystal was lower than in case of thermal deposition and we had to obtain a series of STM images with increasing thickness to make sure that the number of monolayers was correctly identified for the thicker films. The films of Fe/Cu(100) have been grown at room temperature (RT).

In the case of Fe/Cu(111) we cooled the substrate during deposition and transfer into the STM chamber to 200 K to ensure comparability of the results with previous work using roughly the same deposition temperature [18,20,21,23,24]. At this temperature, thermally driven Cu diffusion to the top of Fe islands is negligible. For the investigation of the films we used a low-temperature scanning tunneling microscope (Omicron LT-STM) cooled by liquid nitrogen. The base pressure in the STM chamber was $1 \times 10^{-11}$ mbar; the pressure at the position of the STM (shielded by LN2 cooled surfaces) is expected to be lower. The electrochemically etched tungsten STM tips were conditioned in vacuo by Ar+ sputtering and by voltage pulses while tunneling.

Previous works have shown that in particular the laser fluence influences film growth [23,24]. The laser fluence can be modified by varying the laser spot size on the target or the laser pulse energy (independently of each other). Varying both enables us to keep the deposition rate constant while choosing different fluence values. Unfortunately, for several reasons we cannot determine the laser fluence with high accuracy [23]: (a) due to the inhomogeneous beam profile the fluence varies over the cross-section of the beam, (b) the spot size cannot be determined exactly due to the soft edge of the spot and (c) decreasing transmission due to Fe deposition at the entrance window. For the investigation of different fluence conditions during deposition on the appearance of nanomartensite, we investigated two series of films of the system Fe on Cu(100), one prepared by high- and the other by low-fluence ablation. The laser power was adjusted to yield similar deposition rates on the Cu surface. The fluence conditions named “high” and “low” indicate not very different fluence values, but significantly different ablation rates per area on the Fe target (by a factor of more than 3, when assuming that the deposition rate at the target is proportional to the ablation rate, i.e., if the angular distribution of the ablated material remains the same). In the experiments presented in this work, “low fluence” means about 0.6 J/cm². The corresponding spot size on the target is in the range of about 20–30 mm². “High fluence” means about 0.8 J/cm² (spot size: 6–8 mm²). Both fluence values do not take the inhomogeneous beam profile into account, thus the maximum fluence in the beam is significantly higher. Using the time-of-flight spectrometer [22], we are able to determine the energies of the ablated ions for the different fluence conditions. Fig. 1 demonstrates that a difference of $\sim 30\%$ in laser fluence can cause an increase of the particle energy by a factor of more than 3.

Also the Fe films on Cu(111) have been investigated with regard to different laser fluence. In that system a fluence dependent growth mode was observed in the first two monolayers [22,23]. The change from bilayer to layer-by-layer growth was observed between 40 and 60 eV (maxima of the distribution).

3. Results

3.1. Fe on Cu(100)

3.1.1. Morphology

For Fe on Cu(100), we observe layer-by-layer growth from the first up to the seventh monolayer, and the onset of 3D growth at a thickness of 8 ML. Especially during the growth of the 1st monolayer the island size remains small ($\sim 3$ nm²) until coalescence. Also for thicker films, the islands are smaller and more irregularly shaped compared to TD films (Fig. 2). From single measurements at coverages somewhat above an integer number of monolayers (closed surface), we found a mean island density slightly

![Fig. 1. TOF ion spectra, converted into the energy domain, for high fluence (0.8 J/cm²) and low fluence (0.6 J/cm²; fluence values are averaged over the whole spot).](image)

![Fig. 2. Representative STM images (100 × 100 nm²; −1 V, 1 nA) of Fe islands on the 3rd monolayer of Fe/Cu(100) deposited at room temperature by (a) TD and (b) PLD (small spot, high fluence, cf. Section 2). Black spots are holes in the 3rd ML.](image)
above 0.01 nm\(^{-2}\) for the PLD films. It does not vary significantly with the film thickness. For thermally deposited films the island density is about one third of this value.

### 3.1.2. Composition

Analysing STM images (Fig. 3) of the Fe films (1–8 ML), we find height variations showing that the surface is not homogeneous. As it is known that Fe appears higher (brighter) compared to Cu [9], this indicates intermixing between substrate and film, which is quite pronounced in the first monolayers (large fraction of dark Cu). With increasing thickness and continuing intermixing, the Cu content of the surface monolayer decreases gradually, as illustrated in Fig. 3. This series of STM images gives a qualitative visual impression of the distribution of the elements within the surface monolayer for various film thicknesses. We see the large Cu content (dark grey areas) in the first monolayer and the rising fraction of Fe (bright grey areas) for thicker films. The white spots are islands of the next monolayer, the black spots holes in the surface layer. It is not possible to determine the exact Cu content from these images because the borders between areas of different elements cannot be located with sufficient precision. We could also distinguish between the two elements by scanning tunneling spectroscopy (STS; cf. Ref. [9]), but also this method also suffers from insufficient lateral resolution in case of small Fe and/or Cu areas.

For the best accuracy, we analyze the height contrast of images with atomic resolution (like those in Section 3.1.3). For instance, we find 53% Cu atoms in the first monolayer in the case of preparation with low laser fluence. The second monolayer contains 22% Cu, the fifth monolayer 9% Cu. In Fig. 4, we show the values for preparation with low laser fluence (large spot) as well as for high laser fluence (small spot). The corresponding curves are quite similar. We realize that at least up from the second monolayer (atomically resolved images of the first monolayer for high fluence are not available) a difference in particle energy of about 100 eV (150 eV at high fluence, 50 eV at low fluence) does not affect the Fe/Cu intermixing seriously. Interpreting Fig. 4, it has to be kept in mind that the measured values show the concentration in the surface of the films and not the Cu distribution in the layers below.

Comparing the Fe/Cu intermixing of PLD films with equivalent TD films [25] we find that especially for the thicker films, the Cu content of the surface monolayer is much higher in case of PLD. Fig. 5 compares the surfaces of 5 ML films. It can be clearly seen that the fraction of

![Fig. 3. Surface layer of 1–8 ML Fe/Cu(100). The height contrast on the terrace is due to intermixing of Fe (bright grey) and Cu (darker). \(V_t = -1.0\) V, \(I_t = 1.0\) nA, 25 nm × 25 nm each.](image)

![Fig. 4. Cu content of the surface monolayer of Fe/Cu(100), obtained by counting the different species of atoms in atomically resolved STM images. There is no significant difference between high and low laser fluence.](image)
dark grey areas (Cu) is negligible in TD films, but much higher for the PLD film.

3.1.3. Structure

A main goal of this work was to characterize the nanomartensitic structures as a function of film thickness. Our different laser fluence conditions during preparation (cf. Section 2) led to similar results. Therefore we will discuss them simultaneously.

The first monolayer consists of a Cu matrix, surrounding Fe areas with typical sizes of 1–4 nm² (Fig. 6). Even if we disregard the border atoms, whose apparent position may be influenced by the apparent height difference between Fe and Cu, we find that not all Fe atoms are arranged in an fcc(100) square lattice like the substrate. We find areas with significant distortions, which can be explained as local bcc(110) structure [9]. The single cross-shaped spots at fourfold hollow sites (small circles in Fig. 6) have been found at the surface for all film thicknesses. They mark the positions of adsorbed contamination atoms.

In two-monolayer films, Fe takes over as the majority species of the surface layer (Fig. 7a). Cu is incorporated in form of mostly elongated patches (dark). Compared to the first monolayer, the bcc-like areas are larger. In the bcc-like areas we observe bond angles between 75° and 80°, other areas are close to fcc (≈90°). Like the first, the second monolayer does not show long-range nanomartensitic order.

Also the third monolayer of a 2.9 ML thick film (Fig. 7b) exhibits a variety of irregular strained and distorted small zones with typical bond angles of 75–80°. The areas of uniform nanomartensitic order are larger compared to the second monolayer but still rather small. The fine distribution of the nanomartensite makes it impossible to get a clear impression of its amount when using not atomically resolved images, where the nanomartensite structure appears brighter than fcc Fe [9]. The high-resolution images, however, reveal that Fe areas unambiguously showing the fcc structure are a minority.

Fig. 7c shows the atomic arrangement within the 4th ML. The surface nearly entirely consists of nanomartensite. As for TD films [8,9], we observe characteristic bond angles of about 75°. Areas with uniform nanomartensitic arrangement are in many cases limited by the Cu inclusions. That differs from TD films, where the undisturbed
Fe areas are larger, due lower Cu content. Bond angles of 90°, indicating fcc Fe zones, are rare. In the STM images (Fig. 7c) it can be also seen that the areas with a well-developed nanomartensitic structure appear ~20–30 pm higher than the fcc patches due to the slightly larger interlayer distance of strained bcc(110) compared to fcc(100) [9]. Thus, it is possible to detect the nanomartensite by high contrast also in images without atomic resolution (Fig. 8), though with a much lower accuracy concerning the nanomartensitic area fraction – a problem similar to that of Fe/Cu discrimination mentioned earlier. In rare cases, we have also observed needle-shaped bcc nanocrystals (not shown) already in the 4th monolayer. These needles also exist in thicker films and are comparable to those found in TD films [7,9].

Surfaces of 5 ML films look quite similar to the 4th monolayer. Again, in low-magnification images (not shown) we find extended, more or less continuous nanomartensitic areas, which constitute roughly 30% of the 5th ML, less than in the 4th ML. The atomically resolved images of Fig. 9 show areas of fcc structure as well as areas of nanomartensite. The fcc areas locally show a (2√2)p4g reconstruction.

For the 6 ML films, our STM images did not show any nanomartensite in the surface, but a very small content cannot be ruled out. Fig. 9c shows an fcc(100) lattice with a few domains of a (1×2) p2mg as well as a (2×2) p4g reconstruction [10]. Occasionally we found needle-shaped bcc nanocrystals (not shown). Fig. 9d illustrates that the structure of the 7th ML looks quite similar to the 6th ML, but the distortions locally forming a (1×2) p2mg and (2×2) p4g surface reconstructions are weaker.

### 3.2. Fe on Cu(111)

In this section, we will focus on films with 2 ML thickness. Besides the results already published [23], the aim of
investigation was to determine whether bcc-like structures can be found in Fe films on Cu(111). Using low resolution, we found regions of different apparent height in the surface of the second monolayer (Fig. 10). We have shown previously that the brighter (higher) areas at the borders of the TD-grown islands (Fig. 10a) are distorted bcc structures [20]. The image of a film grown with lower ion energy (Fig. 10b), where the initial growth mode is bilayer growth as for TD [23], shows structures similar to those of TD films, but at a smaller length scale. In both cases, the height contrast in the 2nd monolayer is around 50 pm, indicating that the bright grey areas are bcc-like also in the PLD-grown films. Comparing Fig. 10a and b directly shows that the bcc-like (bright) fraction in PLD films is significantly larger than in TD films. In the case of the higher particle energies (Fig. 10c), the height variations occur on an even smaller scale and are only around 10 pm. We have shown previously that the Fe films grown under high-fluence conditions (high ion energies) contain finely dispersed Cu due to intermixing between substrate and film (Fig. 11 and Ref. [23]). Comparison with the Fe/Cu(100) system suggests that these Cu inclusions influence the shape and size of the bcc-like areas, so we have to resort to atomically resolved images to discriminate between fcc and bcc-like structures in this case.

In contrast to Fe on Cu(100), the difference between fcc(111) and distorted bcc(110) is far less obvious when analyzing the bond angles in STM images, and the main difference lies in the different stacking of the layers, which cannot be directly observed by STM [20]. Thus it is more difficult to discriminate between fcc and bcc based on bond angles, and a small distortion of the STM image due to thermal drift has a larger impact on the identification of fcc and bcc-like areas. Nevertheless, atomically resolved images of the same surface as in Fig. 10c clearly show bond angles deviating from 60° by more than the experimental uncertainty of ±2° in most areas (Fig. 11a). We also find nearby rows of atoms with clearly different orientation, providing further support for a non-fcc lattice. The largest in-plane bond angles observed are about 68°, much closer to the 70° bond angle of undistorted bcc(110) than to fcc(111). Comparison with TD-grown films tells us that also smaller deviations from 60° must be seen as an indication of bcc-like structures (in Ref. [20], distorted bcc Fe with in-plane bond angles deviating by only 3° from the fcc lattice has been found). In spite of a rather strong distortion of the STM image by thermal drift, by comparing atom rows that should have the same orientation in an fcc lattice we can also demonstrate the existence of domains with non-fcc-like bond angles in Fig. 11b, which shows a closed 2nd monolayer.

4. Discussion

4.1. Fe–Cu intermixing

STM measurements with atomic resolution have resulted in detailed information about the Fe/Cu distribution in PLD films of varying thickness. Fig. 4 shows the composition of the surface monolayer of films from 1 to 7 ML thickness. The high Cu content of the 1st ML (~55%) is the result of strong intermixing between substrate and film. The Cu content of the 1st ML (~55%) is the result of strong intermixing between substrate and film. Cu is displaced out of the substrate’s original surface by the energetic Fe ions during the deposition process and the resulting Cu adatoms attach to the first monolayer of the film. Since Cu(100) is a more open surface than Cu(111), implantation causing an exchange process between incoming Fe and Cu occurs more frequently on Cu(100), leading to a higher Cu concentration than in the Fe films grown on Cu(111) (55% vs. 30% in the 1st ML, cf. Ref. [23]). An easy exchange between Fe and Cu on the (100) surface also explains why the surface...
composition hardly depends on the Fe ion energy ($\approx 50$ vs. $150$ eV): Obviously, an Fe ion energy of $\approx 50$ eV is sufficient for implantation with a very high probability. For the Fe/Cu(100) films deposited at room temperature, thermally driven exchange processes will also contribute to the Cu surface concentration. This is in contrast to Fe/Cu(111), where the exchange barrier is expected to be higher (close-packed surface) and the deposition temperature was low enough (200 K) to exclude thermally activated Fe–Cu intermixing. On both Cu(111) and Cu(100), the lower surface energy of Cu compared to Fe is expected to favour Cu at the surface, thus after implantation of Fe, a reverse process with Fe moving onto the surface and Cu being buried by the collision cascade of a later ion impact will be rather unlikely (similar to ion-induced segregation in sputtering of alloys). Thus the difference of surface energies is partly responsible for the high Cu surface concentration.

For both, Fe/Cu(100) and Fe/Cu(111), the Fe/Cu distribution is not random. Our STM images rather show small Fe patches embedded in Cu (1st monolayer, Fig. 6) or patches of Cu embedded in the Fe surface for thicker films (Figs. 7 and 11). This observation is in line with the immiscibility of the Fe and Cu in the bulk, but it also tells us that the surface mobility after Fe implantation is sufficient to allow for this rearrangement.

4.2. bcc-like structures

On both substrates, Cu(100) and Cu(111), we find nanomartensitic structures similar to those in TD films, but with variations on a shorter length scale. The absence of
a long-range order in PLD films may explain why, in contrast to the \((1 \times n)\) superstructures of TD Fe/Cu(100) \([5,8]\), the nanomartensite was not detected as a superstructure in an early LEED study \([16]\). More recent LEED work reveals superstructure spots that are significantly more diffuse than those of TD films \([17]\). A similar argument holds for Fe/Cu(111), where, in addition to the disordered distortion pattern, the bond angles of distorted bcc and fcc are much closer to each other, impeding a discrimination of these phases by LEED. We consider it likely that the absence of a long-range order is due to Cu inclusions, which interrupt the bcc-like Fe lattice and also lead to inhomogeneous strain due to the size difference between Fe and Cu. For Fe/Cu(100), the bcc-like or nanomartensitic structures occur in almost exactly the same thickness range for TD \([9]\) and PLD films; in both cases the first signs of bcc-like distortions are found already in the first monolayer and a large fraction of the Fe surface exhibits nanomartensitic distortions at 2–4 ML thickness. For 4 ML TD films, nanomartensite is usually present at 80 K, the temperature of the STM used for the current study, while its presence or absence at room temperature depends on the hydrogen coverage, see Ref. \([26]\). We attribute the existence of non-nanomartensitic areas in 4 ML thick PLD-grown films at 80 K to Cu inclusions. Our PLD films show some nanomartensite in the 5th ML, while it is absent in the 5th ML of TD films. We think that this difference is mainly related to Fe–Cu intermixing at the interface, making the pure Fe film locally thinner than the number of deposited monolayers in some places.

Given the higher \(H_2\) and CO background pressure during the PLD experiments we must also consider their possible influence on the fcc/bcc ratio. The Fe–C bulk phase diagram implies that C impurities should favour fcc Fe, and the same observation was made for CO on the surface of thicker Fe/Cu(100) films \([27]\), so CO cannot explain the presence of nanomartensite in 5 ML PLD films. C and O impurities may contribute to the inhomogeneity of the films, however. The hydrogen coverage of the Fe/Cu(100) films grown at room temperature depends on the \(H_2\) dose and the exact temperature due to the onset of desorption around RT \([28]\). Hydrogen may contribute to the extended stability range of nanomartensite in PLD-grown films, but given its limited coverage we do not expect it to play a major role. Fe/Cu(111) was grown at lower temperature; for this system the influence of \(H_2\) has been studied previously \([20]\). Hydrogen was found to nudge the fcc–bcc balance towards the bcc side, but this effect was found only after \(H_2\) doses of more than \(\approx 1\) L \((1\text{ Langmuir} = 1.33 \times 10^{-6}\text{ mbar s})\), well above the \(H_2\) doses adsorbed in the present experiments.

4.3. Structure and ferromagnetism

Ferromagnetism of TD-grown Fe/Cu(100) and Fe/Cu(111) is strictly correlated with bcc or bcc-like structures \([9,20]\). Our structural investigations show that the occurrence of ferromagnetism in PLD-grown films can be also explained by bcc or bcc-like structures. For Fe/Cu(100), the structural similarity between TD and PLD films is largest in the range of the so-called live magnetic surface layer \([1]\), around 6 ML thickness, where the Cu content in the surface is low and the fcc subsurface layers do not contribute to the ferromagnetism. Only the \((1 \times 2)p2mg\) or \((2 \times 2)p4g\) surface reconstruction with bcc-like bond angles is responsible for the ferromagnetism \([9,10]\). These films show out-of-plane magnetization, and thickness-independent saturation magnetization at least in a thickness range around 6 ML, independent of the growth method (TD or PLD) \([1,2,16]\). There are no measurements in the literature that would allow us to compare the absolute value of the magnetization of TD and PLD films, but assuming an equal value of the saturation magnetization for the 6 ML films, a comparison of Refs. \([1,2]\) and \([16]\) indicates a lower saturation magnetization of the PLD films in the 2–4 ML range compared to TD films by a factor of \(\approx 0.5–0.7\). This observation nicely fits the fact that TD films are almost 100% nanomartensitic around 3 ML \([9]\) whereas PLD-grown films always show some fcc Fe fraction, related to the higher content of fcc Cu and possibly to other impurities (C, O).

Concerning the magnetic properties, the main difference between TD and PLD-grown Fe/Cu(100) in the 2–4 ML range is the direction of the easy axis, which is out of plane for TD and in plane for PLD. Our structural investigations do not provide a direct explanation for this difference, but it must be noted that magnetic anisotropy is a very subtle effect. Compared to the energy differences between fcc and bcc Fe or the nonmagnetic and ferromagnetic state, which are usually in the 10–100 meV/atom range, magnetic anisotropy energies are far below the meV/atom range. Furthermore, magnetic anisotropy, determining the easy axis, is influenced by several factors including strain in the film as well as the structure of the surface and interface. Due to the Cu inclusions and intermixing in PLD, it is conceivable that these factors are different for PLD and TD.

For Fe/Cu(111), the bcc-like distortions in 2 ML islands explain the ferromagnetism of both TD \([20]\) and PLD \([18]\) films. PLD films show an almost four times higher magnetization than TD films, and it was estimated that the magnetic moment around 2 ML coverage is close to that of bulk-like bcc Fe \([18]\). Even considering that the magnetic moment is enhanced at the surface, this means that most areas of the PLD films must be in a bcc-like phase. Indeed, our STM images (Figs. 10b, 11) indicate that this is the case, and the fcc areas are a minority. The low magnetization of TD films grown at 220 K reported in Ref. \([18]\) can be directly correlated to the large islands (mostly \(>20\) nm) observed by the same group \([21]\). For TD-grown large islands, it was observed that only a narrow rim \((\approx 2\) nm) is in the bcc-like phase, whereas the interior is fcc and thus nonmagnetic \([20]\). The fraction of islands with bulk-like bcc structure, easily identified by 3D ridge-like structures, was observed to be low at 2 ML \([21]\). It was...
already observed for TD films that small (<5 nm) bilayer islands are entirely bcc-like and explained by the fact that a distorted bcc(110) lattice can still fit onto the fcc(111) substrate for such small islands without atoms being placed in unfavourable on-top sites [20]. This factor limiting the extent of the bcc areas in the TD films is relieved in the smaller structures of PLD-grown films: The high density of steps as well as the strain and inhomogeneity caused by Cu inclusions facilitate the formation of small areas with different distortion directions, as observed by STM. Thus, the Fe atoms at the interface are displaced from the favourable hollow site by rather short distances, and the energy price to pay for the bcc-like distortions at the interface is rather low. Therefore, the PLD films can assume a bcc-like phase more easily.

For thicker PLD-grown films, which are still growing layer by layer and not in a bulk-like bcc phase, a sudden decrease of the magnetization was observed at 3 ML thickness [20]. Although we have not obtained structural data for this phase, we consider it possible that the bcc-like distortions are limited to thin films, similar to the nanomartensitic phase of Fe/Cu(100). This may be due to the lower influence of the surface with its enhanced magnetic moment and, thus, enhanced driving force to become bcc [9], and/or due to the reduced structural and strain heterogeneity as the lower monolayers are closed and the Cu content decreases.

5. Summary

For both, Fe/Cu(100) and (111) we found a higher Cu concentration on the surface for PLD in comparison to the thermally deposited films. This can be explained considering the ion energies of ≈40–200 eV in our PLD experiments, leading to Fe implantation in the surface. Finely dispersed Cu and the smaller island sizes generally lead to a larger inhomogeneity of the PLD films compared to TD.

Our experiments show bcc-like structures in PLD Fe films. For Fe on Cu(100) we found nanomartensite up to the 5th monolayer. Starting with bcc-like distorted groups of atoms already in the 1st ML, the nanomartensitic (bcc-like) content of the films rises until it covers nearly all the surface at the 3rd ML, and then decreases, with still some nanomartensite present at 5 ML thickness. Typical bond angles vary between 72° and 80°. In contrast to thermally deposited films, the long-range nanomartensitic order is impeded by the higher Cu content of the PLD films. The non-nanomartensitic (fcc) areas of the 5 ML films, as well as the 6 and 7 ML thick films, which are almost entirely fcc, show the (2 × 2)p4g and (1 × 2)p2mg surface reconstructions at low temperature (80 K).

For Fe on Cu(111), atomically resolved images of the second monolayer demonstrate the coexistence of mainly bcc-like structures with a few fcc(11 1) areas. Here we find a significantly larger bcc-like fraction than in TD films. For both, Fe/Cu(100) and Fe/Cu(111), the bcc-like structures neatly explain the ferromagnetism observed in previous studies without having to resort to the hypothesis of a ferromagnetic fcc phase of iron.

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References