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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 ($\alpha \leftrightarrow \gamma$) 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 ≈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].

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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(1 0 0), 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 p(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(1 0 0) [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(1 1 1), 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(1 1 0) 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 (1 0 0) or (1 1 1) orientation were cleaned by sputtering using 3 keV Ar^+ ions ($I_{ion} = 3$ μA, typically for 30 min) and annealing afterwards at temperatures $\geqslant 650$ °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(1 0 0), 532 nm and 355 nm for Fe on Cu(1 1 1)]. 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 H_2 and CO; for both Fe/Cu(1 0 0) and (1 1 1)], 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,