Structure of ultrathin Fe films on Cu(100) prepared by pulsed laser deposition

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The structures of ultrathin Fe films on Cu(100) prepared by pulsed laser deposition (PLD) and conventional thermal deposition (TD) are compared by means of low-energy electron diffraction (LEED). Below 5 ML coverage, PLD films exhibit up to four times higher integer-order LEED spot intensities, i.e., improved film quality, and show small but significant structural changes as compared to TD films. A quantitative tensor LEED analysis of the 4-ML PLD film reveals a similar 5×1 superstructure to that found previously for TD films, but with an enhanced surface buckling and a flat Cu bulklike iron interface layer. The latter is attributed to the incorporation of Cu atoms in the Fe interface caused by sputter effects in PLD. Above 6-ML coverage, both deposition methods yield comparable LEED I(E) spectra, revealing similar surface structures. The proposed structural models allow a consistent interpretation of the strongly altered magnetic properties observed for PLD-grown iron films.

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I. INTRODUCTION

Deposition by laser ablation is usually used for the preparation of films of at least a few nm thickness, and performed at vacuum pressures of 10⁻⁷–10⁻⁹ mbar. It is only recently that ultrathin films, i.e., a few monolayers, were prepared by pulsed laser deposition (PLD), and investigated at a pressure below 10⁻¹⁰ mbar. Jenniches and co-workers studied the growth and magnetic properties of thin iron films on Cu(111) (Ref. 2) and Cu(100) (Refs. 3 and 4) substrates. Their investigations revealed an improved layer-by-layer growth. Moreover, for Cu(100), PLD-grown iron films exhibit different magnetic properties as compared to conventional thermal deposited (TD) films. The authors related these differences to the altered growth and structure of the PLD films. Based on a kinematic interpretation of low-energy electron diffraction (LEED) data, they concluded that, up to a film thickness of 10 ML Fe has an isotropic fcc structure resulting in a 1×1 LEED pattern. These findings are in striking contrast to iron films prepared by thermal deposition, which show several complex reconstructions in the coverage range of 1–10 ML. Furthermore, recent first-principles local-spin-density investigations predicted complex reconstructions for thin iron films on Cu(100), depending on the film thickness and magnetic structure even for ideally flat, i.e., layer-by-layer-grown films. Thus there is disagreement between the by now established structure-magnetism correlation and the work in Ref. 4, as also pointed out in Ref. 6. Therefore, in the present paper we hope to shed more light onto this issue.

In PLD a pulsed laser beam is applied as an external energy source to evaporate, usually, a solid target, and the expanding material plume is collected on the opposing substrate. Some characteristics of PLD using ns laser pulses were summarized in Ref. 7. Probably among the most important of these is the increase of the instantaneous deposition rate by 4–6 orders of magnitude as compared to TD. Depending on the details of the ablation parameters, the evaporated plume contains not only atoms but ions and to some extent microsized particles. The latter are certainly unwanted in thin-film growth, but can be suppressed using appropriate experimental conditions. While the kinetic energy of the atoms ranges between 5 and 10 eV, the portion of ions and their kinetic energy usually depend on the laser fluence. Both the increased instantaneous deposition rate and the high kinetic energy of the ions alter the film growth and, thus, potentially improve epitaxy.

In the present study PLD and TD are used alternatively to grow Fe films on a Cu(100) single-crystal surface, and we focus on a comparison of the respective film structures for coverages between 1 and 10 ML. Structure models were determined by quantitative LEED. The analysis of PLD films is based, in particular, on the already established results for TD films. Vitaly, both TD and PLD films have been prepared in the same UHV system under comparable conditions, and TD films agree quantitatively with the earlier experiments. For the case of a 4-ML-thick PLD-grown iron film, the outcome of a tensor LEED analysis is given. The quantitative structure analysis presented here significantly extends and improves the qualitative approach of Ref. 4. Since structural and magnetic properties of thin films are closely connected, the revised structure models demand a further explanation of the magnetic features. We address this issue in the discussion, having verified that films prepared here match those of Refs. 3 and 4. To reduce the influence of energetic particles in PLD, all films have been prepared with laser fluences of 3–4 J/cm², i.e., slightly above the ablation threshold. The influence of the laser fluence on the film morphology and quality was addressed elsewhere.

II. EXPERIMENT

All experiments were performed in ultrahigh vacuum, with a base pressure below 8×10⁻¹¹ mbar. The system is equipped with a LEED optics for LEED and Auger-electron spectroscopy (AES), and a quartz microbalance to characterize the evaporation sources. The Cu(100) sample was routinely cleaned by cycles of 1-keV Ar⁺ sputtering and annealing at 820 K. To reduce step bunching, the sample was cooled down to 300 K with a rate of 50 K/min after the final
annealing step.\textsuperscript{13} Surface cleanliness and order were controlled by AES and LEED. For TD an iron wire of 99.99% purity was heated by electron bombardment in an evaporator developed by the Fritz Haber Institute, ensuring a pressure below $3 \times 10^{-10}$ mbar during evaporation. The deposition rate was set to 0.5 ML/min. For PLD a XeCl excimer laser is used (308-nm wavelength, 20-ns pulse duration, 150-mJ maximum pulse energy, and 100-Hz maximum repetition rate). To achieve laser fluences of 2 to 8 J/cm\textsuperscript{2}, the output laser beam was focussed to a spot size of 1.5 mm\textsuperscript{2}, as estimated by the area of the ablation crater on a thin metal foil. The angle of incidence was set to 20° with respect to the target normal.\textsuperscript{14} For laser fluences just above the ablation threshold ($\approx 2$–3 J/cm\textsuperscript{2}),\textsuperscript{15} the pressure during evaporation was below $3 \times 10^{-10}$ mbar, and increased to about $8 \times 10^{-10}$ mbar at a pulse energy of 150 mJ. Two different Fe targets of 99.99% purity were used for PLD. The first target was fixed and the laser beam scanned over the target surface, while the second comprised an additional motion of the target. Scanning of the target and/or laser beam was essential to maintain a nearly constant deposition rate. Holding the laser spot instead on a fixed position results in a rapid macroscopic crater formation, i.e., a roughening of the target surface, and a decrease of the evaporation rate to $1/e$ after a deposition of about 2 ML. Using pulse energies of 40–140 mJ and a repetition rate of 10 Hz, an average deposition rate below $3 \times 10^{-10}$ mbar was obtained.\textsuperscript{12} For these parameters the instantaneous deposition rate corresponds to about $(2$–$6) \times 10^4$ ML/min, assuming a deposition time of 1 µs.\textsuperscript{2} The coverage was carefully calibrated using the microbalance, and controlled by AES in connection with the characteristic LEED patterns observed for the TD-grown iron films.\textsuperscript{5} The overall error is estimated to be below ±0.2 ML. During deposition the sample was held at 300 K, and subsequently cooled down within 3 min to 85 K for LEED and AES measurements. The intensity versus energy spectra $I(E)$ for the different diffraction spots were recorded by an automated video method.\textsuperscript{16} The primary beam incidence was adjusted within 0.5° to the surface normal by a comparison of symmetrically equivalent beams, whose intensities were averaged in order to improve the data quality. All spectra are normalized to the primary beam current.

### III. RESULTS

#### A. Comparison of TD- and PLD-grown Fe films

##### 1. TD iron films

Before we compare films grown by either technique, we review the structure and magnetic properties of TD iron films. While thick iron films exhibit a bcc bulk structure, by epitaxial growth on the Cu(100) substrate, phases of γ-Fe (fcc Fe) are stabilized below 10 ML. Initially the growth can be described as three dimensional. The first two layers are proved to grow as double layers. Above 2 ML, increased surface roughness was observed by various techniques\textsuperscript{17}–\textsuperscript{20} in spite of reflection-high-energy electron-diffraction (RHEED) oscillations starting at 2 ML.\textsuperscript{17} Between 4 and 10 ML, all studies consistently revealed layer-by-layer growth. For fcc iron two coverage regimes can be distinguished: At thicknesses below 4 ML iron grows pseudomorphically, i.e., assuming a Cu(100) lateral lattice parameter, and the entire film is significantly reconstructed.\textsuperscript{21} The reconstruction manifests itself in a 4×1 superstructure at 2 ML, which gradually transforms into a 5×1 pattern at 4 ML. The superstructures result from periodic lateral and vertical displacements of all iron atoms in the film off the ideal fcc positions (for details see Refs. 5 and 21, and Sec. III B). For the entire film the Fe interlayer distances are expanded on average by 5% as compared to the ideal bulk value of fcc iron ($d_{Fe} = 1.78$ Å).\textsuperscript{21} The tetragonal distortion of the unit cell (so-called fct Fe) corresponds to an increase of the atomic volume from 11.4 Å\textsuperscript{3} (fcc Fe) to 12.05 Å\textsuperscript{3} (fct Fe). According to first-principles calculations for γ Fe, it is the rise of the atomic volume above 12 Å\textsuperscript{3} that entails ferromagnetism (FM).\textsuperscript{5,22–26} FM was also predicted for thin fct films including the Fe/Cu and Fe/vacuum interface.\textsuperscript{27} These findings were further corroborated by recent ab initio local-spin-density investigations that considered and indeed predicted a complex reconstruction of the film.\textsuperscript{5} Experimentally a close to linear increase of the saturation magnetization up to 3.5-ML (Refs. 32 and 21) or 4-ML (Ref. 4) coverages was observed by the surface magneto-optic Kerr effect, and the films are believed to be in a high-spin FM phase.

Between 3.5 and 5 ML a transition from a strained pseudomorphic film to unstrained nonpseudomorphic growth occurs.\textsuperscript{5,28,29} This structural transition is accompanied by a significant drop of the saturation magnetization. At 6-ML coverage an ordered (2×1)$_{p2mg}$ LEED pattern is observed. The glide symmetry is caused by a zigzag displacement of atomic rows in the top iron layer.\textsuperscript{30,31} Different from the low-coverage regime, only the first-layer spacing is increased, while the underlying Fe layers adapt the fcc bulk structure without lateral or vertical modulations. Although the 2×1 LEED pattern diminishes at higher coverage because of fading long-range order, the local structure at 6 ML is characteristic of the whole coverage range up to 10 ML.\textsuperscript{21} In agreement the magnetization of the film stays constant up to 10 ML, and it was concluded that FM is restricted to the very surface while the underlying fcc bulk is paramagnetic\textsuperscript{32,33} or antiferromagnetic (AFM).\textsuperscript{34} These results were again corroborated by recent first-principles calculations, which for 6 ML predicted iron bilayer AFM coupling and a 2×1 reconstruction of the film without vertical buckling.\textsuperscript{5} In the whole coverage regime up to 10 ML, the easy axis of magnetization is oriented perpendicular to the film plane.\textsuperscript{17}

##### 2. LEED patterns

Based on this detailed previous knowledge, we can start to analyze the structure of PLD-grown iron films. Figure 1 compares the LEED patterns observed for TD- and PLD-grown films at coverages of 2, 4, and 6 ML, respectively. For both deposition techniques we observe superstructures. The brightness and contrast of the pictures have been adjusted in order to enhance the superstructure spot intensities. The TD film at 4 ML was tempered at 400 K, whereby the superstructure spot intensity improves.\textsuperscript{5} Overall, the patterns are...
very similar for both deposition methods. For 2 and 4 ML, an additional intensity is found as satellites of the integer order spots along the (110) directions. For 6 ML both 2×1 patterns exhibit a glide symmetry, i.e., the spots at \([0, \pm (n + \frac{1}{2})]\) and \([\pm (n + \frac{1}{2}), 0]\), \(n = 0, 1, 2, \ldots\), are missing for the normal incidence of the electron beam.

To facilitate the comparison, line profiles of the (10) spot taken along the [011] direction (indicated in Fig. 1 as a rectangle) are depicted in Fig. 2. The profiles for PLD (solid line) and TD films (dashed line) are extracted from the raw data at energies of 135 eV (2 and 4 ML) and 115 eV (6 ML), respectively. The (10)-spot intensity is set to unity. For 2 and 4 ML the additional feature at \(k = 20% k_{BZ}\) indicates that the mean separation between ordered domains—or, equivalently, the average size of the unit cell—is roughly constant at \(\approx 5\) atomic diameters [\(k_{BZ}\) corresponds to the (01) reciprocal-lattice vector of the (1×1) structure].

Without anticipating the analysis of the LEED \(I(E)\) data, we can already draw several conclusions. In the low-coverage regime the PLD iron films grown in this work do not have an ‘‘isotropic’’ 1×1 fcc structure, but are reconstructed. The systematic extinction of other than satellite-superstructure spots was already observed for TD films, and holds for PLD films too. Therefore, we expect similar structures for both deposition methods. Again a periodicity close to 5×1 is observed at 2- and 4-ML coverage, respectively. The altered spot profiles and intensities suggest that details of the reconstruction may be different. For obvious reasons we again denote the pattern at 4 ML as 5×1. At 6 ML we observe a \((2 \times 1)_{p2mg}\) superstructure. The line scans reveal that, if at all, the superstructure spots appear only slightly weaker for PLD as compared to TD, and the close similarity between the LEED patterns suggests identical structures of either film.

3. LEED intensity levels

As mentioned before, RHEED and scanning tunneling microscopy (STM) results demonstrate that Fe films prepared by PLD grow layer by layer, starting from the very first layer. Since STM does not reveal significant differences between TD and PLD films above 2 ML, it was concluded that the film morphology is comparable between 2 and 5 ML. LEED intensities reflect the degree of order of the film, and a comparison of absolute spot intensities allows one to pin down the structural quality of the film as a whole. Note that LEED probes a macroscopic area of the sample, since the typical electron-beam diameter is \(\approx 1\) mm.

In Fig. 3 (top panel), averaged background-corrected intensities obtained by integrating the (10)-spot intensity over an energy range of 450 eV are depicted. At 6-ML coverage both deposition methods yield comparable intensities. Below 6 ML, PLD films (solid line) exhibit higher intensities than TD films (dashed line), while the opposite is true above 6 ML. The averaged LEED intensity for the TD film at 8 ML amounts to 80% of that for the clean Cu substrate (open square at 0 ML, top panel) confirming the high film quality in this coverage regime. To cross check that the observed changes indeed correlate with the structural quality of the film, the intensity of the background was sampled. Back-
ground and total intensities are compiled in the bottom panel of Fig. 3. Since the diffuse scattered intensity reflects the degree of disorder, the observed opposite trend proves that the envisaged quality differences are genuine. Reaffirming, the total intensity is comparable over the whole coverage range studied.

Overall, for both deposition methods the intensity and thus the film quality deteriorate as the coverage increases to 4 ML, but recovers at 6 ML. The 2–4 times higher intensities for PLD films below 5 ML suggest that the improved initial layer-by-layer growth persists up to this intermediate coverage, and finds its reflectance in an improved film quality.

The comparison of film quality for the two different preparation methods naturally involves some uncertainties. Fe films are very sensitive to the presence of surface contaminants during growth. For example, typical superstructure spots at low coverages disappear when small amounts of sulfur or oxygen are present. In other words, different film qualities may be related to growth parameters still not controlled or even unknown. Nevertheless, the results demonstrate that under given, comparable experimental conditions, the quality of the Fe films at low coverages is improved by PLD.

For TD the entire film orders when the iron coverage is increased above 5 ML. A driving force for this rearrangement is the cutback of the distortion energy of the film, which increases with increasing thickness. Consequently, for higher coverages the structure of the iron film should be less influenced by the details of the growth. In agreement, we find a 2 × 1 LEED pattern at 6 ML for both deposition methods and, moreover, comparable intensities.

Above 6 ML, thermal deposition leads to a better film quality. As mentioned above, besides high deposition rates laser ablation results in kinetic energies of the ablated ions exceeding 10 eV, already slightly above the ablation threshold. Therefore, the quality of the films and, as a result, the LEED intensities may decrease by sputter effects, which will cause surface roughening and increased defect densities. We will come back to this point in Sec. IV A.

4. LEED intensity spectra I(E)

LEED I(E) spectra can be used as a fingerprint to compare the microscopic structure of films obtained with either deposition method. Since the superstructure spots are weak and not well separated, we base our analysis on integer-order spots. Multiple scattering ensures that the latter contain information on the film reconstruction, albeit with a reduced sensitivity as compared to fractional-order beams.

In Fig. 4 spectra of the (10), (11), and (20) spots for TD and PLD Fe films on Cu(100) at 4- and 6-ML film thicknesses. For comparison, spectra of the clean Cu(100) surface are included in the figures on the left.

In Fig. 4 spectra of the (10), (11), and (20) spots for TD and PLD Fe films on Cu(100) at 4- and 6-ML film thicknesses. For comparison, spectra of the clean Cu(100) surface are included in the figures on the left.

FIG. 3. Comparison of LEED intensities integrated over a measurement range of 450 eV as a function of Fe coverage. Solid lines (PLD) and dashed lines (TD) serve as guides for the eye. Top: (10) spot (background corrected). Bottom: Diffuse scattered intensity evaluated on a frame around the (10) spot, and the sum of both, labeled as the total intensity. The square at zero coverage marks the value for the clean Cu(100) surface.

FIG. 4. Experimental LEED spectra of the (10), (11), and (20) spots for TD and PLD Fe films on Cu(100) at 4- and 6-ML film thicknesses. For comparison, spectra of the clean Cu(100) surface are included in the figures on the left.
The structures of the films are identical in the high-
coverage regime, but TD leads to a higher film quality. The
R factors around 0.2 in the low-coverage regime demonstrate
that the films are still quite similar. In particular, a shift of all
interference maxima to lower energies is observed (see Fig.
4, left column), indicating an expansion of the average layer
spacing as compared to the Cu(100) substrate, i.e., a tetragonal
distortion of the iron film.

B. 5×1 reconstruction at 4 ML

In order to extract the structural differences in the low-
coverage regime, we have performed a tensor LEED analysis
of the 4-ML PLD film. Two different models were exam-
ined. (i) A 1×1 fcc structure, as proposed in Refs. 3 and 4.
Adjusted structural parameters were the lateral lattice param-
eter and the vertical layer spacings. (ii) A 5×1 reconstruc-
tion similar to the best fit for the 4-ML film prepared by
TD.21 This model seems, of course, to be a natural starting
point, since experimental PLD and TD spectra deviate only
by an R factor of 0.24, and one expects similar reconstruc-
tions. As mentioned, the 5×1 superstructure pattern is spe-
cial in the sense that, apart from the satellites of substrate
spots, superstructure spots are missing. This considerably
restricts the number of models, and is accounted for in the
assumed 5×1 reconstruction model.5,21 The model allows
for lateral and vertical displacements of all iron atoms in the
film, with only lateral displacements in the [110] direction
considered. In total this leads to a number of 40 structural
parameters. Of course, a large parameter space can result in a
better fit by itself, and one has to take care that the data base
is rich enough to provide sufficient information. Assuming
that each interference maximum contains independent infor-
mation, the compared energy range of ΔE=950 eV and the
width of a single maximum estimated by $4 \times V_{0i}$ (Ref. 36)
(where $V_{0i}=5.5$ eV is the average imaginary part of the inner
potential) leads to a number of $ΔE/(4 \times V_{0i})=43$ indepen-
dent data points which is close to the minimum, i.e., there
is no additional information available in order to make the
structure determination safe. However, the number of structural
parameters could be reduced during the fit procedure to
30, as the interface layer turned out to be practically flat, so
that its parameters did not have to be varied. In Fig. 6 the
calculated (10)-spot intensities for the fcc 1×1 structure and

the (5×1)-reconstructed film are depicted together with the
experimental spectrum. The shaded areas highlight the en-
ergy regions for which clear deviations between the experi-
mental spectrum and the 1×1 structure occur. In contrast,
the 5×1 model describes the experimental spectrum in the
whole energy range very well. Similar signatures are ob-
served for the (11) and (20) spots (not shown). Consistently,
these differences manifest themselves in R factors of 0.29 for
the 1×1 structure and 0.13 for the 5×1 reconstruction.
With the $R$-factor variance being $\text{var}(R)=0.028$, the 1×1
structure can be safely excluded. Moreover, for the recon-
struction model a surface Debye temperature $\Theta_S=280$ K was
found, in good agreement with the fitted value of 300 K for
the TD film,21 whereas the simpler 1×1 fcc model leads to an
unreasonably low value of 200 K. Such a low Debye
temperature probably mimics the large static displacements
of the atoms by the corresponding large vibrational ampli-
tudes (0.14 Å for $\Theta_S=200$ K at 90 K). Consequently, for a
higher Debye temperature the 1×1 fit would be even worse.
Thus, not surprisingly, in view of the superstructure appear-
ing in the LEED pattern the experiment-theory comparison
of the integer-order spots clearly favors a 5×1 reconstruc-
tion of the 4-ML iron film, with the fit quality indeed being
satisfactory. We emphasize that, while the model is based on
a perfectly reconstructed film, the periodicity of five atoms
should be viewed as an average value of the size of the unit
cell, as already indicated by the broad profile of the super-
structure spots. We also stress that the analysis, being based
on integer-order spots only, cannot safely retrieve the dis-
placement of each iron atom. Nevertheless, several conclu-
sions can be drawn. (i) The top two iron layers are consid-
erably buckled, with atomic rows sinusoidally shifted. (ii)
The interface iron layer is flat. (iii) The top two interlayer
spacings are expanded by 5% on average compared to the
fcc-iron equilibrium value. In Table I the vertical layer spac-
ings $d_{ij}$ and the maximum buckling amplitudes $b_{i \text{max}}$ for the
4 ML TD and PLD films are compared.

In contrast to the TD film only the first two vertical layer
distances are expanded, on average, by 5% in the PLD film.
Furthermore, the vertical layer spacing and buckling ampli-

FIG. 5. $R_{\text{Pendry}}$ is evaluated between experimental TD and PLD
LEED spectra as a function of the Fe coverage. The dashed line
marks the reproducibility level between different measurements.

FIG. 6. Intensities for the best-fit 1×1 and 5×1 models, and
the experimental spectrum for the (10) beam recorded at 4-ML
Fe/Cu(100).
TABLE I. Best-fit structural parameters for a 4-ML Fe film prepared by TD and PLD. The vertical layer spacing is \( d_{ij} \) (\( d_{\text{bulk}} = 1.78 \text{ Å} \)), the maximum of the vertical buckling amplitude is \( b_{1, \text{max}} \), and the surface Debye temperature is \( \Theta_s \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TD</th>
<th>PLD</th>
</tr>
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<tbody>
<tr>
<td>( b_{1, \text{max}} ) (Å)</td>
<td>0.24±0.02</td>
<td>0.41±0.03</td>
</tr>
<tr>
<td>( b_{2, \text{max}} ) (Å)</td>
<td>0.11±0.02</td>
<td>0.19±0.04</td>
</tr>
<tr>
<td>( b_{3, \text{max}} ) (Å)</td>
<td>0.12±0.03</td>
<td>0.07±0.05</td>
</tr>
<tr>
<td>( b_{4, \text{max}} ) (Å)</td>
<td>0.21±0.05</td>
<td>( \approx 0 )</td>
</tr>
<tr>
<td>( d_{12} ) (Å)</td>
<td>1.86±0.02</td>
<td>1.91±0.03</td>
</tr>
<tr>
<td>( d_{23} ) (Å)</td>
<td>1.90±0.02</td>
<td>1.82±0.04</td>
</tr>
<tr>
<td>( d_{34} ) (Å)</td>
<td>1.85±0.03</td>
<td>1.76±0.05</td>
</tr>
<tr>
<td>( d_{45} ) (Å)</td>
<td>1.78±0.06</td>
<td>( \approx 1.78 )</td>
</tr>
<tr>
<td>( \Theta_s ) (K)</td>
<td>300</td>
<td>280</td>
</tr>
</tbody>
</table>

attitudes are larger by a factor of 2 at the surface, but reduced toward the Fe-Cu interface. *De facto*, neither buckling nor lateral displacements of the atoms occur at the substrate-film interface, i.e., in the first Fe layer. For the TD film, it was argued that the atoms do not “like” the tensile stress imposed by the Cu(100), substrate and therefore respond by in-plane shifts and vertical buckling.\(^5\)\(^\text{,}21\) The reconstruction indeed includes the whole TD film. As the 4-ML PLD film again grows pseudomorphic, the same tensile stress should result. It is therefore likely that the reduced buckling of the interface layers leads to larger vertical and lateral amplitudes of the surface layer. In conclusion, it is not possible to stabilize an undistorted fcc structure in the low-coverage regime. In conclusion, it is not possible to stabilize an undistorted fcc structure in the low-coverage regime.

IV. DISCUSSION

To begin, we briefly summarize the results of Sec. III. (i) Consistent with the observed layer-by-layer growth mode (Ref. 2), PLD leads to improved film quality up to 5-ML coverage. (ii) Between 6 and 10 ML, LEED spectra are independent of the preparation technique. Therefore, we simply transfer the results of the quantitative LEED analysis for TD films. A (2\(\times\)1)-reconstructed surface layer with increased vertical layer spacing \( d_{12} = 1.87 \text{ Å} \) resides on an undistorted fcc iron bulk (\( d = 1.78 \text{ Å} \)) for details, see Ref. 31. (iii) Below 4 ML a tetragonal distortion of the iron layers occurs. The main structural difference between PLD and TD grown films as revealed by the LEED analysis of the 4-ML iron film is a change of the interface layer, which exhibits a Cu bulklike structure for PLD.

The structure models just summarized do not agree with those proposed in Ref. 4. Based on their LEED results, Jenriches et al. concluded that (i) the films do not show any superstructure spot intensities, and (ii) they are therefore not reconstructed; however (iii) they exhibit a fcc (1\(\times\)1) structure in the whole coverage range of 1–10 ML. The authors based these conclusions on the observed LEED patterns and a kinematic analysis of LEED \( I(E) \) spectra of the (00) spot.\(^3\)

Thus, before we can attempt to discuss the structure of PLD films and connect it to the magnetic properties reported in Refs. 3 and 4, we have to verify that PLD indeed leads to unique film structures. Unfortunately, the LEED spectra in Ref. 4 were taken at an oblique incidence of the primary electron beam, inhibiting direct comparison to the spectra presented above. We therefore followed the experimental approach in Ref. 4, and additionally recorded spectra of the (00) spot with the sample tilted toward the [001] direction by 6° relative to the electron beam. Spectra for the coverage range investigated are depicted in Fig. 7 (dashed line), together with spectra of Fig. 7 (solid line) from Ref. 4. Taking into account that the coverages compared are slightly different, the agreement of the spectra (with the exception of the 4-ML film) is excellent, and we therefore conclude that the film structures are in general indistinguishable. In other words PLD leads to unique structures of Fe/Cu(100) films. We attribute the indeed significant disagreement between the spectra at 3.5 and 4.0 ML to the difference in coverage. The spectrum at 4.5 ML in Fig. 7 is again very similar to the 3.5 ML spectrum of Ref. 4, and illustrates the sensitivity of the LEED \( I(E) \) curves to the iron coverage around 4 ML, i.e., in the transition regime.

Furthermore, we have obtained nearly identical structures [the difference in the \( I(E) \) spectra \( K_{\text{Pendry}} \leq 0.1 \)] at 2- and 4-ML coverages for a variety of laser fluences, and we can exclude different preparation schemes as the cause of the observed disagreement.\(^12\) Obviously, for complex structures the kinematic interpretation runs the risk of oversimplification.
A. Morphology and structure

As stated in Sec. I, there are two main differences between TD and PLD. (i) For PLD the instantaneous deposition rate is significantly increased \([\approx 3 \times 10^4 \text{ ML/min (Ref. 12)}]\) as compared to TD (0.5 ML/min). (ii) Pulsed laser ablation generates ions with nonthermal kinetic energies of 50 eV (Ref. 15) or even 120 eV (Ref. 37) for the engaged laser fluences of \(3-4 \text{ J/cm}^2\).

Following scaling relations, one can argue that for a fixed diffusion constant an increased deposition rate leads to a higher island density during nucleation.\(^{38}\) This was demonstrated in a number of studies where the increased number of critical nuclei achieved by PLD was shown to lead to layer-by-layer growth.\(^{7,10}\) The STM data in Ref. 4 proved, however, that there is no remarkable difference in the initial stage of growth between TD and PLD films. For a submonolayer coverage of Fe on Cu(100), both deposition methods yield high island densities. This suggests that the second characteristics of PLD, the nonthermal kinetic energy of the ablated ions, must account for surface wetting. Usually, and likewise in Ref. 4, it is argued that laser fluences close to the ablation threshold result in a very low ion yield. A recent study on resputtering effects during growth demonstrated, however, that for an Fe target the ion yield is close to 100%, and is moreover independent of the laser fluence.\(^{39}\) Such measurements normally depend on the chosen setup, and may involve large variations if transferred to another experiment.\(^{37}\) Nevertheless, in the present case they demonstrate the importance of high-kinetic-energy particles. These nonthermal kinetic energies, if converted into lateral mobility upon adsorption, will help to overcome surface barriers, e.g., Ehrlich-Schwoebel barriers at island edges, and may in general improve layer-by-layer growth. Furthermore, defects generated by mild sputtering can act as nucleation centers. For even higher kinetic energies ions will cause permanent sputter effects, i.e., a mixing of deposited and substrate material or resputtering of the deposited film.\(^{7,39}\)\(^{40}\) The penetration threshold for Cu atoms into the Cu(100) surface was estimated in a molecular-dynamics study to 150-eV kinetic energy,\(^{41}\) but recent calculations yielded a much lower value of 20 eV.\(^{42,43}\) Experimentally, for a laser fluence of 4.5 J/cm\(^2\), i.e., for a kinetic energy around 60 eV,\(^{15}\) an iron-iron sputter yield of 0.17 was already observed during Fe film growth.\(^{39}\) We conclude that sputter effects cannot be entirely avoided in PLD of Fe on Cu(100). Their occurrence is further corroborated by the fluence dependence of the LEED intensities. For 2- and 4-ML films we find a close to linear decrease of the LEED intensity by almost a factor of 2 when the laser fluence is varied between 2 and 8 J/cm\(^2.\)\(^{12}\) Likewise this degradation of film quality is a clear indication of sputter effects that will cause surface roughness, defects, and intermixing.

Having established that sputtering of the film during growth is important, it seems likely that the improved layer-by-layer growth is also caused by particles deposited with high kinetic energy. A tensor LEED analysis of the 4-ML PLD film reveals that the iron layer at the interface is not buckled, but exhibits the structure of a Cu(100) bulk layer. Without the buckling observed for TD films even at the interface, there has to be a different mechanism to reduce stress at the Fe-Cu interface. Rationalizing the above results, this is achieved by exchange sputter-processes during growth, i.e., incorporating Cu atoms into the first grown iron layers. If stress is reduced, surface wetting is favored, and layer-by-layer growth can be achieved from the very beginning.

Unfortunately, the atomic scattering factors of Fe and Cu are very similar, and reasonable changes of the composition cannot be distinguished at the present state of LEED experiment and theory. Even with high-resolution low-energy electron diffraction, it is only possible to determine atoms with very different masses by energy-dependent angular profile analysis of diffraction beams.\(^{44}\) Furthermore, the STM data of Ref. 4 do not allow one to distinguish between Cu and Fe atoms, since the images are not recorded with atomic resolution or chemical sensitivity. The latter capability of STM was demonstrated in Ref. 45, but is highly demanding. The analysis of surface chemical composition based on, e.g., AES has to fail, since it does not allow one to distinguish reliably between some \emph{a priori} unknown fraction of Fe atoms incorporated in the Cu surface layer or adsorbed on top of it. Substantial alloying of the whole film should, however, lead to larger structural differences between PLD and TD-grown films. The latter are believed to consist of Fe atoms only. In particular, significant mixing should be also noticeable at 6 ML, but both deposition methods yield defectfree identical LEED \(I(E)\) spectra \(\left(R_{\text{Pendry}} = 0.1\right)\). Since LEED probes the near surface region the sensitivity toward the interface drops with increasing film thickness. The change of the interface layer at 4 ML, which should persist over the whole coverage range, is hardly detectable at higher coverages. Below 4 ML, however, structural differences \(\left(R_{\text{Pendry}} \gg 0.2, \text{ Fig. 5}\right)\) may be at least partially ascribed to structural changes induced by interface alloying. We therefore conclude that mixing is restricted to the near interface-layers.

Since the influence of the interface on film structure decreases with increasing coverage we observe identical structures at and above 6 ML. Here sputtering of the near-surface layers can be made responsible for the reduced LEED intensities of PLD films. In addition, different film qualities may be caused by different amounts of bcc precipitates in the fcc film. Those precipitates were observed in the STM investigation by Jenniches \emph{et al.}\(^4\) for both deposition methods, and were made responsible for surface roughness. Finally, we note that the droplet problem, i.e., deposition of microsize particles is not significant for our experimental setup, since the structure (as probed by LEED) of PLD and TD films are identical at 6-ML coverage.

B. Connection to the magnetic properties

We briefly recapitulate the results of the magneto-optical Kerr measurements from Refs. 3 and 4. As for TD films between 2 and 4 ML the magnetization of PLD films increases linearly with coverage, indicating that PLD films have also a high-spin ferromagnetic phase in this coverage regime. At 3.5 ML (TD) and 4 ML (PLD) the magnitude of
magnetization is comparable for both deposition methods.\textsuperscript{3} Surprisingly, however, for PLD films the easy axis of magnetization is not perpendicular to the film plane as in the case of TD films, but in plane. Between 4 and 5 ML the magnetization drops, to stay constant up to a coverage of 7 ML, but at twice the value for the TD films.\textsuperscript{3} Between 5 and 7 ML the film undergoes a spin reorientation from in plane to out of plane. Above 7 ML, the anisotropy is perpendicular to the film plane, and the magnetization drops linearly with coverage to yield the value of TD films at 10 ML.

Following Sec. IV A, in a coarse view the structure of TD and PLD films are rather similar, and one might expect identical magnetic properties. However, the magnetism of fcc iron is shown to be very sensitive toward structural changes. Different kinds of FM or AFM phases can be distinguished from theoretical studies, where the respective ground state depends sensitively on the atomic volume (see, e.g., Refs. 6, 25, and 46).

The first two interlayer distances of the PLD film at 4 ML are expanded on average by 5\%, and considerably buckled (Table I, Fe fcc bulk value: 1.78 Å). As pointed out in the case of TD films,\textsuperscript{5} and outlined in a number of theoretical publications,\textsuperscript{6,22,24,25,27,46} the FM configuration comes along with an increase of the atomic volume. The similarity between TD and PLD films thus suggests that the observed linear rise of the Kerr signal\textsuperscript{4} can be attributed in both cases to an increase of tetragonally expanded iron layers with coverage. At 4 ML the TD film exhibits an expansion of all interlayer distances by \( \sim 5\% \). In contrast, for the interface layers of the PLD film we find a vertical spacing close to the Cu fcc bulk value, and negligible buckling. On average, fcc bulklike layer spacing calculations predict AFM coupling.\textsuperscript{27,46,47} Nevertheless, a similar magnetization of both films is observed at \( \sim 3.5 \)–4 ML. Note that, if present, AFM coupling of the bulklike interface layers may be compensated for by the improved quality of PLD films. Spišák and Hafner suggested that the driving mechanism for the reconstruction is the tendency to expand interatomic distances in the top layer.\textsuperscript{6} Their calculations predicted AFM coupling at 4 ML. Interestingly the true (AFM) ground state is \( 5 \times 1 \) reconstructed. Moreover, the strongest buckling of the surface layer is found for AFM coupling, where the difference between surface and subsurface magnetic moments is strongest.\textsuperscript{6} We emphasize that the calculated \( 5 \times 1 \) structure does not agree quantitatively with the outcome of the LEED analysis for the TD (Ref. 21) or PLD films. However, theory predicts that if reconstruction is suppressed at the interface the surface is expected to exhibit stronger buckling.\textsuperscript{6} This indeed agrees with the model structure presented here.

The main difference in the low-coverage regime is the in-plane easy axis of magnetization reported only for PLD iron films. For the FM phase, theory predicts either in-plane\textsuperscript{26} or out-of-plane\textsuperscript{47} magnetization. Both calculations treat an unstrained fcc iron film with the lattice constant of Cu bulk, i.e., the prominent relaxation effects are not included. In Refs. 26 and 46 the magnetic anisotropy of Fe overlayers is studied both in the high-moment FM phase and for AFM coupling. Based on a full-relativistic spin-polarized band theory, the magnetic-anisotropy energy is modeled by two contributions, namely, the band energy \( \Delta E_b \) and the dipole-dipole interaction energy \( \Delta E_d \). The latter favors an in-plane easy axis and, in the case of FM coupling, outweighs \( \Delta E_b \), which favors perpendicular magnetization. In contrast, Ref. 47 predicts \( \Delta E_b > \Delta E_d \) equivalent to out-of-plane magnetization of the iron film as observed for the FM TD films.

In Refs. 26 and 46 the contribution of the band energy to the magnetic anisotropy was determined, as resolved by layers. It turns out that the main contribution to \( \Delta E_b \) stems from the interface and surface layers. Enhanced magnetic moments at the surface and interface were also predicted in Ref. 48, revealing the importance of the interface structure and composition. Experimentally such an enhancement of exchange coupling at the surface was proven by spin-resolved inverse photoemission\textsuperscript{49} and two-photon photoemission.\textsuperscript{50} Interestingly, for thin films, contributions from the interface and bulk layers are strongly reduced when Cu atoms are incorporated into the interface layer. The calculations in Ref. 26 reveal that there is a negligible band contribution \( \Delta E_b \) to the magnetic anisotropy when 30\% Cu atoms are incorporated in the Fe interface layer. We therefore attribute the switchover of the easy axis of magnetization from out of plane (TD film) to in plane (PLD film) to a mixing of Fe and Cu atoms at the interface proposed for PLD films only.

According to LEED the film structure at 6 ML is independent of the preparation technique. This suggests that structural differences between TD and PLD films at 6 ML will concern only the interface. Above 4 ML the film undergoes a structural transition, resulting in a nonpseudomorphic unstrained fcc iron bulklike structure carrying a reconstructed surface layer.\textsuperscript{5} Extended x-ray-absorption fine-structure measurements revealed that in the case of TD films this transition indeed affects the whole film including the interface.\textsuperscript{29} It was thus concluded that FM coupling is restricted to the reconstructed surface layer, while the bulk is paramagnetic\textsuperscript{31} or in the AFM configuration.\textsuperscript{34} All calculations modeling unstrained fcc Fe films,\textsuperscript{24,46,47,51} as well as recent calculations which include a \( 2 \times 1 \) reconstruction\textsuperscript{6} of the 6 ML film, favor AFM coupling.

The effect of alloying at the interface on the stability of the magnetic structure was studied theoretically by a model structure of 4-ML Fe on top of a \( c(2 \times 2) \) mixed FeCu interface on the Cu(100) bulk.\textsuperscript{51} It turned out that for the \( c(2 \times 2) \) checkerboard arrangement the coupling of iron atoms in the interface layer is weak, and the magnetic interaction is dominated by the coupling with Fe atoms in the adjacent layer, thus resembling an impurity problem, for which the magnetic interaction is known to be FM.\textsuperscript{51} The saturation magnetization of PLD films, which is twice as large, may thus stem from a different coupling scheme introduced by a changed interface layer.

For AFM coupling the calculations in Refs. 46 and 47 predicted that the magnetostatic dipole-dipole interaction energy is reduced, and that the band contribution, which is much higher in the AFM ground state, outweighs the dipole-dipole term, leading to a perpendicular magnetization. Again layer-resolved band-energy contributions to the magnetic anisotropy energy\textsuperscript{46} exhibit a large contribution of the interface
layer. As in the case of FM coupling, one is led to the conclusion that, if intermixing occurs at the interface, these contributions are significantly reduced. This may explain why the coverage range where the reversed spin reorientation is observed extends over three iron layers, and clear out-of-plane magnetization is first observed at 7 ML. Since the structure of the film remains unchanged up to 10 ML, the drop of the magnetization at higher coverages is attributed to sputter effects in PLD, and a consequent reduction of stress. LEED spectra above 6 ML are independent of the deposition method. In combination with theoretical studies, the proposed structural models allow a consistent interpretation of recent results on the magnetic properties of ultrathin iron films prepared by PLD. In particular, we conclude that the observed reverse spin reorientation is dictated by the changed interface properties. Due to the complexity of surface-magnetic phenomena the given models are certainly still oversimplified and comprehensive measurements of both structure and magnetism are highly desirable.

V. CONCLUSIONS

We have studied the structural properties of iron films on Cu(100) prepared by PLD in the coverage range of 1–10 ML. The investigation is based on a comparison with the well-known structural properties of TD iron films and a tensor LEED analysis at 4 ML. For coverages below 5 ML, significant structural differences between the films are observed, namely, an increased reconstruction of the surface layer and a flat Cu bulklike interface. The latter is explained by an intermixing of Fe and Cu atoms at the interface caused by sputter effects in PLD, and a consequent reduction of stress. LEED spectra above 6 ML are independent of the deposition method. In combination with theoretical studies, the proposed structural models allow a consistent interpretation of recent results on the magnetic properties of ultrathin iron films prepared by PLD.

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