PHYSICAL REVIEW B VOLUME 48, NUMBER 23 15 DECEMBER 1993-I

Nonpseudomorphic and surface-reconstructed ultrathin epitaxial fcc Fe films on Cu(100)

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(Received 29 June 1993)

A high-precision low-energy electron-diffraction (LEED) structure analysis for an eight-monolayer ultrathin fcc Fe film epitaxially grown on Cu(100) is presented. The film is free of strain, i.e., its lattice coincides with that of equilibrium fcc iron rather than with that given by the Cu substrate. The top layer is reconstructed and its distance to the second layer is expanded. Similar features hold also for films in the range 5–11 monolayers. The theory-experiment fit is the best ever achieved in a LEED structure determination with a Pendry R factor of 0.09.

It is well established that fcc-like ultrathin iron films can be stabilized by epitaxial growth on a Cu(100) substrate. Much interest in these films comes from their intriguing magnetic properties. The fact that the exchange coupling depends on interatomic distances makes the knowledge of the precise structure of the films important. Therefore, we present a high-precision surface-structure determination of an eight-monolayer (ML) fcc Fe film using low-energy electron diffraction (LEED). Our results show that, different from current assumptions for such films, the in-plane lattice parameter of the first few Fe layers—to which LEED is sensitive—is different from that of Cu(100) releasing the strain imposed by the lattice mismatch between fcc iron and copper. Additionally, we show that the top Fe layer is reconstructed. Last but not least we present what we believe to be the best theory-experiment fit ever achieved in a full dynamical LEED analysis.

In recent years there was much effort to determine the structure of fcc Fe epitaxial films grown on Cu(100).[1–18] It is commonly accepted today that at or below room temperature there is island growth up to a coverage of 2–3 ML followed by layer-by-layer growth. This proceeds until about 11 ML above which the fcc structure of the iron film breaks down. At certain coverages superstructures appear (e.g., Refs. 10, 14, and 17). From 5 to 11 ML there is ferromagnetism with the magnetic moment perpendicular to the surface and localized at or near the surface of the film.[19] This is in agreement with an expanded first interlayer distance of the film which has been found by quantitative LEED structure analysis for films for various thickness between 5 and 12 ML (Refs. 2, 5, 8, and 11) and the fact that for increased interatomic distances ferromagnetism is predicted.[20] However, all analyses performed so far assumed that the surface parallel unit mesh length a_p of all iron layers coincides with that of the Cu substrate according to an ideal pseudomorphic growth with $a_P(\mathrm{Cu})=2.55$ Å at 90 K. This compares to a value of $a_P(\mathrm{Fe})=2.52$ Å for fcc iron extrapolated from the high-temperature equilibrium phase of fcc Fe. So, the validity of pseudomorphism means that all Fe layers must be strained. Also, all analyses—except for the reconstructed 2×1 phase at 6 ML (Ref. 8)—did not take into account any top-layer reconstruction. This is in spite of the observation that 1×1 patterns show substantial background indicating disorder or can even display diffuse 2×1 superstructure spots indicating some reconstruction as reported recently.[21]

Therefore, we performed a detailed LEED investigation of an 8-ML iron film allowing for both lateral and vertical lattice relaxation as well as reconstruction of the top layer. Iron deposition and LEED intensity measurements were carried out within an ultrahigh vacuum (UHV) system with a base pressure of 5×10^{-9} Pa and equipped with such standard sample preparation and characterization facilities as ion bombardment and Auger-electron spectroscopy (AES). The Cu(100) sample was cleaned by repeated cycles of Ar ion bombardment (600 V, 1 μA, 800 K) with subsequent annealing above 1000 K. This resulted in a sharp and low background 1×1 LEED pattern whereby surface impurities including C and O were below the Auger detection limit. Iron deposition was made by indirect heating of a small iron rod of 99.99% purity whereby the substrate temperature was kept at 300 K in order to avoid copper segregation.[13] The deposition rate was adjusted to about 0.5 ML/min as controlled by a quartz crystal microbalance and independently by AES using the Auger transitions at 651 and 920 eV for Fe and Cu, respectively. The results evaluated by both methods agree within an accuracy of 0.3 ML. LEED intensity vs energy spectra, $I(E)$, were taken with the sample cooled down to 90 K using a video-based and computer-controlled technique as described in detail earlier.[22,23] Due to the high automation of the method, spectra for normal incidence of the primary beam and for an energy range of 50–600 eV could be measured for the (10), (11), (20), (21), (22), and (30) beams and their symmetrically equivalent counterparts within 15 min after film preparation, thereby leaving residual gas adsorption negligible. Equivalent beams were averaged in order to improve the quality of the data.

Figure 1 presents data of a selected beam in a restricted energy range for the clean substrate as well as for different coverages of iron. The values of the latter are given on the left and appearing superstructures are indicated on the right. Apparently, the shape of the spectra changes above 5 ML and then remains nearly constant until it changes again at a coverage around 12 ML. This is in agreement with and confirms the layer-by-layer growth in this coverage regime.[10,12,18,19,24,25] However, it

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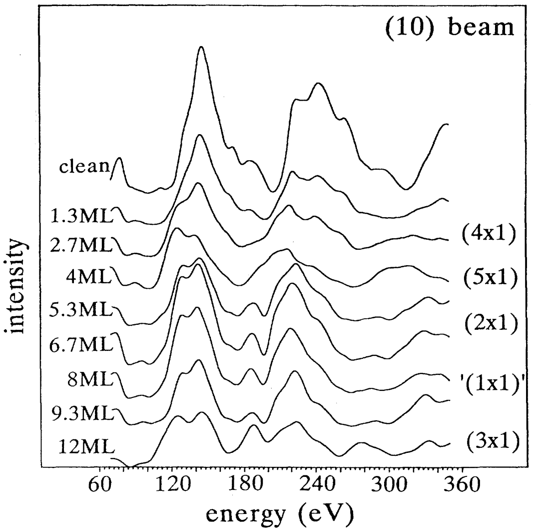

FIG. 1. Spectra of the 10 beam for the clean Cu(100) substrate and various iron coverages (in ML, left) together with the appearance of superstructures (right).

also tells that the film surface must be reconstructed in a way similar to that of the 2×1 phase. In fact, in agreement with Ref. 21, we observe 2×1 superstructure spots in the whole range of 5–11 ML which, however, are considerably lower in intensity than in the well-ordered 2×1 phase at 6 ML. Obviously, the long-range order of the reconstruction is poor, i.e., the reconstruction is only local but locally resembles that of the 2×1 phase for which our group has carried out a LEED intensity analysis recently.[8] Figure 2 displays the reconstruction found: adjacent atomic rows of the top iron layer are shifted with respect to each other by the displacement $2s_D$ with $s_D=0.14$ Å.

This type of reconstruction marks the starting point of our full dynamical analysis of the 8-ML phase. As the missing long-range order prevents the measurement and analysis of superstructure spot intensities, the reconstruction can be retrieved only by the modifications it causes to integer order spots. Also, as intensities are formed locally[26] we can assume long-range order in the calculation and simulate the influence of disorder by a suitable Debye-Waller factor. So, standard computer programs[27] can be used. Moreover, because of the finite penetration depth of the electrons we are neither sensitive to the copper substrate nor to the copper/iron interface which possibly is of complicated structure. The full dynamical calculations were restricted up to an energy of 400 eV in order to save computer time. A maximum of 11 relativistically calculated and spin-averaged phase shifts and a total of 143 symmetrically inequivalent beams were used. Layer diffraction matrices were calculated by matrix inversion whereby the reconstructed top layer was treated as a composite layer. Layer stacking was performed by the layer-doubling method.[28] The electron attenuation was simulated by an energy-dependent optical potential $V_{oi}\sim E^{1/3}$ with $V_{oi}=4.5$ eV at 90 eV. The real part of the inner potential was adjusted in the course of the theory-experiment fit. For the fit procedure the Pendry R factor R_P (Ref. 29) as well as the Zanazzi-Jona R factor R_{ZJ} (Ref. 30) and the relative quadratic deviation R_2 between calculated and measured intensities[31] were used. This resulted in the same best-fit parameters within the limits of error. The latter were estimated from the variance of the Pendry R factor, $\mathrm{var}(R_P)=\sqrt{8V_{oi}/\Delta E}$, whereby ΔE is the total-energy overlap between measured and calculated spectra[29] being $\Delta E=1050$ eV in the present case.

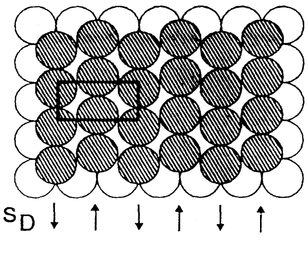

FIG. 2. Model of the top-layer reconstruction.

In a first step we tried—as a test—a fully pseudomorphic ($a_P=2.55$ Å) and unreconstructed array of eight iron layers allowing for the variation of the first three interlayer distances d_{12}, d_{23}, and d_{34} as well as for the layer-independent distance d_b of subsequent "bulk layers." We get essentially the same result as in a recent investigation by Wuttig and Thomassen,[11] i.e., an expansion of the first-layer distance compared to the "bulk" value $d_b=1.77$ Å holding for deeper-layer distances. Also, the best-fit R factor is the same ($R_P=0.23$). However, this level of the R factor leaves room for structural refinement. So we allowed—led by the arguments given above—for a top-layer reconstruction as displayed in Fig. 2. The obvious missing long-range order as well as thermal vibrations were considered by an effective Debye-Waller factor for the surface layer. By still applying the lattice parameter of the substrate ($a_P=2.55$ Å) both the reconstructive displacement s_D and the effective surface Debye temperature Θ_s were varied to find the best fit. The latter results for $s_D=0.16$ Å and $\Theta_s=200$ K compared to $\Theta_b=467$ K applied for deeper layers. The Pendry R factor decreases to $R_P=0.14$. Again the first-layer distance turns out to be expanded by $\Delta d_{12}=0.095$ Å ($\Delta d_{12}/d_b=5\%$). The expansion is in agreement with the surface reconstruction geometry, i.e., the shift of atomic rows by s_D produces exactly Δd_{12} if atomic hard spheres are assumed.

In spite of the excellent R factor the fitted value of the inner potential $V_{0r}=7.5$ eV (defined with respect to the vacuum level) is much too low compared to values of 11–12 eV found for different surfaces of bcc iron or reported for other fcc transition metals.[32,33] We interpreted this as a hint for a too-large in-plane lattice constant a_P. So, we allowed for additional variation of a_p and repeated the systematic and independent variation of all eight parameters d_{12}, d_{23}, d_{34}, d_b, s_D, a_P, Θ_s, and V_{0r}. The odd value of V_{0r} is removed and the overall best fit results for $d_b=1.77\pm0.015$ Å, $d_{12}=1.865\pm0.0006$

Å or $\Delta d_{12}/d_b=+5.4\pm0.3\,\%$, $d_{23}=1.782\pm0.015$ Å or $\Delta d_{23}/d_b=+0.7\pm1\,\%$, $d_{34}=1.755\pm0.030$ Å or $\Delta d_{34}/d_b=-0.3\pm2\,\%$, $s_D=0.16\pm0.04$ Å, $a_P=2.52\pm0.015$ Å, $\Theta_s=200\pm30$ K, and $V_{0r}=11.5\pm1$ eV, with a clearly further reduced R factor $R_P=0.090$. The error limits result from the variance of the R factor $\text{var}(R_P)=0.020$. This is an extremely good theory-experiment fit and to our knowledge it corresponds to the best ever achieved. This is also true when other R factors are applied ($R_{ZJ}=0.026, R_2=0.028$). The sensitivity of R_P with respect to the quantities a_P, d_b, and s_D is displayed in Fig. 3. The excellent fit between experimental and calculated spectra is demonstrated in Fig. 4 for two selected beams.

The accuracy of our structure determination tells that the top layer of the fcc iron film is reconstructed and that at least the first four to six iron layers—to which LEED is sensitive—have relaxed to the equilibrium lattice of fcc iron rather than maintaining the value given by the Cu substrate. The three-dimensional lattice constant derived from the high-temperature fcc phase of iron by extrapolation to 90 K varies between $a_0=3.55$ and 3.58 Å. Extrapolations of room-temperature x-ray-diffraction results[34] from Fe precipitates give values in the same range. This means that $a_P=a_o/\sqrt{2}$ varies between 2.51 and 2.53 Å, i.e., our result $a_P(\text{Fe})=2.52$ Å lies right in the middle of that range. Also, it agrees with recent investigations by surface-extended x-ray-absorption fine-structure (SEXAFS) experiments which find a nearest-neighbor distance of 2.52 Å, too.[15] Our error limits definitely exclude the copper value $a_P(\text{Cu})=2.55$ Å. The bulk interlayer distance corresponding to $a_P=2.52$ Å is $d_b=a_P/\sqrt{2}=1.78$ Å, which within the limits of error agrees with our result. So, we can conclude that the copper film is—at least within about its first four to six layers—totally relaxed and the strain caused by the lattice mismatch with respect to copper is more or less completely released. In this sense the film is nonpseudomorphic in contrast to the common belief to date. Of course, the difference of 0.03 Å between the film and substrate lattice parameters means that dislocations must appear at least every 80 lattice constants or 200 Å. However, this will not affect LEED intensities because of the limited coherence length (≈ 100 Å) but is in agreement with the background intensities observed.

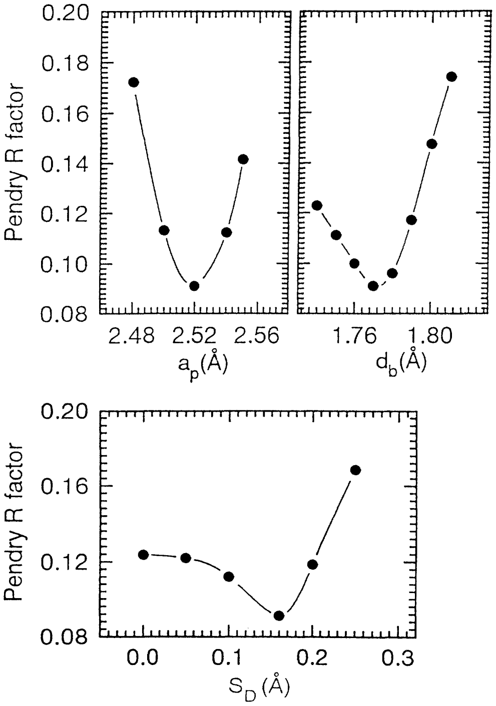

FIG. 3. R factor as function of the in-plane lattice constant a_P and the bulk layer distance d_b (top) as well as of the reconstruction amplitude s_D (bottom).

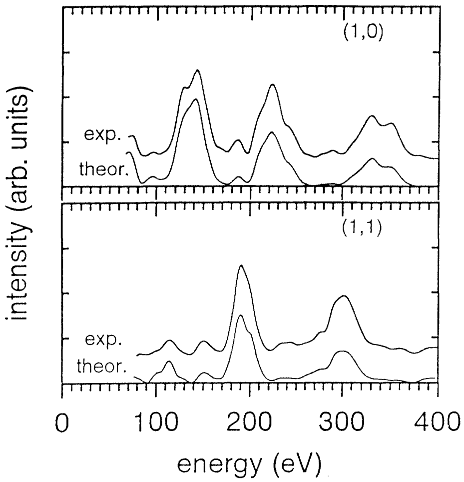

FIG. 4. Experimental and calculated best-fit spectra for two selected beams (all beams average R factors: $R_P=0.090$, $R_{ZJ}=0.026$, $R_2=0.028$).

The first interlayer distance of the film is clearly expanded by about 5% with respect to d_b, a behavior which is different from the contraction usually observed for transition metals. Deeper-layer distances are bulklike within the limits of error. Also, the top layer is reconstructed. We point out that the expansion is in geometrical agreement with this surface reconstruction, i.e., the displacement of atomic rows by $s_D=0.16$ Å produces exactly the expansion $\Delta d_{12}=0.095$ Å when constant hardcore diameters of 2.52 Å are used. This means that the expansion does not change nearest-neighbor distances in the surface, but the coordination of atoms is reduced and the unit-cell volume in the surface is increased. According to total-energy band calculations[20,35,36] this can create the appearance of surface ferromagnetism. In fact this has been found experimentally and the magnetism has been shown to be concentrated to the top surface slab only independent of the film thickness.[19] Again this is in agreement with the results demonstrated in Fig. 1, which shows that the film structure is practically constant in the coverage range 5–11 ML.

In conclusion, we have shown that, different from current assumptions, fcc iron films of 5–11-ML thickness grown on Cu(100) are practically strain-free and the surface is geometrically reconstructed. The top-layer distance is expanded, which is likely to account for surface ferromagnetism. Due to the high precision of our analysis, our results correlate nicely structural and magnetic properties of the films and may be input to ongoing theoretical work on surface magnetism.

The authors are indebted to the German Research Foundation (DFG), the Höchstleistungsrechenzentrum Jülich (HLRZ), and the Leibniz-Rechenzentrum München.

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