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Quantitative structural analysis of fcc Fe(2×1) on Cu(001): A medium-energy ion-scattering study

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The detailed structure of a 6-ML Fe film grown epitaxially at 310 K on a Cu(001) substrate was determined by high-resolution medium-energy ion scattering through comparisons with Monte Carlo simulations of the ion-scattering experiment. The observation of excess ion scattering from the Cu substrate atoms indicates that the lattice parameter of the Fe film deviates from the Cu lattice constant, i.e., the Fe film grows nonpseudomorphically. The Fe film is ordered fcc and has a reconstructed surface layer in the form of atom row glide along [110] directions with an expansion of the surface atom layer. Improved agreement between the ion-scattering simulation and the experimental data is obtained when the Fe lattice is rotated by about 1.2° relative to the Cu substrate.

The epitaxial growth of Fe on a Cu(001) substrate has been extensively studied over the last decade (e.g., Ref. 1). A driving force for this effort is the intriguing magnetic behavior of these films, which is intimately related to their structural properties.[2] It is widely believed that the small lattice mismatch (1.1%) between fcc Fe and Cu(001) leads to formation of strained pseudomorphic fcc films for growth at room temperature. This view was put into question by a recent low-energy electron diffraction (LEED) study.[3] It was reported that instead of following the Cu lattice exactly, 5–11-ML Fe films have the extrapolated lattice parameter of low-temperature fcc Fe. This LEED study is consistent with earlier results for the Fe nearest-neighbor distances in fcc Fe films on Cu(001) as determined by surface-extended x-ray-absorption fine structure (SEXAFS).[4] LEED calculations for an 8-ML Fe film conclude, in addition, that the Fe surface layer is reconstructed with an enhanced spacing between the first and second Fe layers.[3,6]

In this paper we present results of a high-resolution medium-energy ion-scattering (MEIS) analysis of a 6-ML fcc Fe film grown on Cu(001) near room temperature. Our ultrahigh-vacuum system with a base pressure $<1\times10^{-10}$ Torr has been described in detail elsewhere.[8] The Cu(001) crystal was cleaned by cycles of Ne sputtering (1700 eV, 1 μA, 300 K) and annealing to 1000 K. X-ray-photoemission spectroscopy (XPS) measurements showed that the surface concentration of C, the principal contamination, was well below 1%. The Fe films were grown from a high-purity Fe rod heated by electron bombardment with the Cu(001) crystal between 310 K and room temperature, temperatures where interdiffusion between the Cu substrate and the Fe layer is negligible.[9] The contamination level of the films was very low (C, $0<1\%$), as observed by XPS. Typical deposition rates were 1 ML/min. For the structural analysis, a 198-keV Li^+ beam was used in combination with a high-resolution toroidal electrostatic energy analyzer[10] in a backscattering geometry resulting in separable ion-scattering signals from Fe and Cu atoms, as can be seen in Fig. 1(b). Li doses (1×10^{15} ions/cm^2) were kept below the threshold of beam damage. The MEIS data were taken with the crystal at 107 K. This is an appropriate measurement temperature for relating the present results to previous LEED structural analyses[3,11] and to magnetic MOKE (magneto-optic Kerr effect) measurements.[14,15] Our observations indicate that the gross structural features are the same whether the Fe films are held near 100 K or held at room temperature, but it is not yet known whether there are subtle changes in the structural details upon changing the Fe-film temperature. In accordance with previous work,[3,6,11] a $p2mg(2\times1)$ LEED superstructure was observed for the 6-ML film.

The scattering geometry employed is schematically shown in Fig. 1(a). In this double-alignment scattering experiment the normally incident ions would predominantly hit the first two layers of a perfect fcc(001) face and the scattered ions from the second and deeper layers would be well blocked along the nearest-neighbor (NN) direction [101]. Lateral deviations from lattice sites result in increased hitting probabilities, and vertical expansions or contractions change the blocking probability and shift the blocking angle. A MEIS energy spectrum at 122° is shown in Fig. 1(b) along with the corresponding data of the clean surface, where the two Cu isotopes, near 140.5 and 142 keV, are clearly separated. Each Cu isotope surface peak (SP) has contributions from several atom layers. The relative-intensity contribution of layers 1 and 2 is 1.0 from each, layer 3 is 0.21, and the rest of the layers combined is 0.1. It is evident that for the Fe-covered surface there is a low but significant yield from Cu at the Fe/Cu interface, observed as backscattered ions at energies higher than the Fe SP, which is near 135 keV in Fig. 1(b). The energy of the ion yield from Cu is lower than that of ions backscattered from the clean Cu surface because of electronic energy losses of the Li ions in the Fe film. The size of the energy shift of the Cu signal shows that the Cu is entirely covered by the Fe. The contributions from the individual layers and isotopes are smeared out due to energy straggling effects.[13] The increased energy width of the Fe signal relative to the clean Cu signal indicates relatively higher scattering from the third and deeper layers in the Fe film. The low shoulder, near 133 keV, on the low-energy side of the Fe SP is due to the 53.9-amu Fe isotope, which has ~6% abundance compared to ~92% abundance for the principal isotope at 55.93 amu.

To analyze the structure of the thin Fe film, the in-

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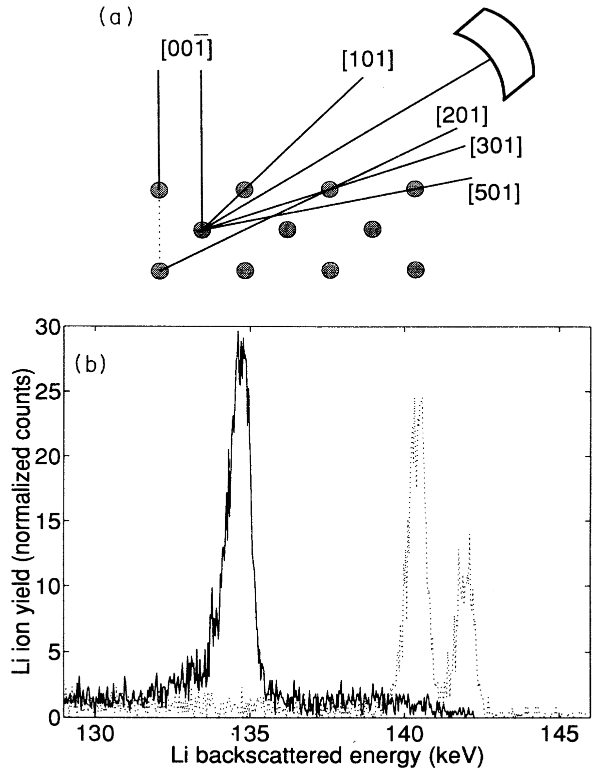

FIG. 1. (a) Schematic of the (010) crystal-plane scattering geometry with the ion-beam incident normal to the surface, the analyzer centered at 122°, and the principal blocking directions identified; (b) energy spectrum at 122° scattering angle; solid line, 6-ML Fe on Cu(001); dotted line, clean Cu(001), $T=107$ K.

dependent blocking curves for both the Fe and the Cu signals were determined from the Li-ion-scattering data. The Fe blocking curve is derived by integrating the area of the Fe SP, including isotopes, as a function of scattering angle. The accuracy of this procedure is estimated to be about ±3%. This yields the experimental blocking curve for Fe as shown in Fig. 2(a). Included with the data are simulations of the ion-scattering experiment for several model lattice structures. The simulations come from Monte Carlo calculations performed using the VEGAS simulation package.[12] The integrated yield of the Cu SP, which comes from Cu residing six or more layers below the surface, amounts to ~0.5 atom/row of Cu in the fcc nonblocking direction at a scattering angle of 128°. For comparison, this is more than 20 times the ion yield from the sixth and deeper Cu layers in the Cu SP from clean Cu(001). For 3- and 4-ML Fe films grown and measured under identical conditions this value is even higher, and amounts to 1.4 and 1.2 atoms/row of Cu, respectively. The Cu yield was simulated for several pseudomorphic Fe lattice structures, including vertical expansions in all six Fe layers and for a surface glide/expansion reconstruction on an fcc bulk, as described below. In all cases, as illustrated in Fig. 3, the actual Cu yield for 128° scattering angle is far larger by more than a factor of 20 for the 6-ML Fe case than the simulated yields for pseudomorphic growth. The only viable explanation for the enhanced Cu scattering is the existence of substantial (of order 0.2 Å on average) lateral deviations of the Fe [001] atom columns relative to the Cu fcc lattice. Since the Fe scattering shows a strong fcc character, these deviations imply that the Fe fcc lattice grows nonpseudomorphically on Cu(001) with lattice constant different from Cu. Note that the deviations between the modeled ion yield from Cu and the experimental data for 3 and 4 ML of Fig. 3 indicate that the Fe film is incommensurate at these coverages as well. Obtaining the Fe lattice parameter directly from MEIS is rather difficult in the present case. MEIS principally probes the geometric configuration of a lattice and thus provides a good value for the ratio of the in-plane atom spacing to the atom layer spacing, but generally requires referencing to the known lattice constant of the substrate, which is unavailable for this Fe thickness, to derive the absolute overlayer lattice constant. Our analysis shows the ratio to be 1.41±0.02, the ideal value for a cubic lattice, and verifies that the detailed results are rather insensitive to the actual in-plane spacing. Another contribution to this insensitivity to the lattice constant of the film's interior is that >95% of the Fe signal comes from the first three Fe layers. In accordance with previous LEED and SEXAFS studies,[3,4] we use a NN spacing of 2.52 Å for the Fe film

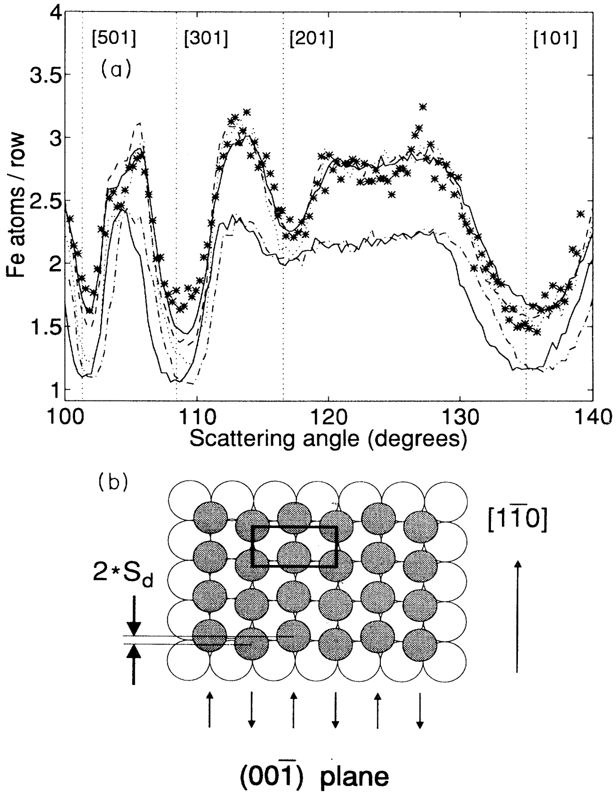

FIG. 2. (a) MEIS blocking curve for the Fe signal of a 6-ML Fe fcc film ($*$), simulation of perfect fcc Fe lattice (lowest solid line), an expanded surface layer (dot-dashed line), (2×1) glide reconstruction with surface expansion (dotted line), 1.2° rotation of Fe reconstructed film relative to Cu substrate (dashed line), and same model with inclusion of atomic disorder perpendicular to Fe film (upper solid line); (b) schematic model of the fcc Fe (2×1) reconstructed surface.

in our final models, satisfying the criterion of the Fe being incommensurate with the Cu (2.56-Å NN distance). Thus, an atom layer spacing of 1.78 Å is used for the Fe film's interior.

For a quantitative determination of the Fe-film structure the blocking curve data are compared to the Monte Carlo simulations of the scattering experiment, which are iteratively refined.[7] For the bulk-Fe thermal-vibrational amplitudes we found 0.045 Å, a value close to the bulk value from bcc Fe (0.042 Å), with a 1.8-fold enhancement at the surface. Variations of the vibrational amplitudes and the surface enhancement demonstrated that these are the best values, although changes of ±15% had little effect on the fits. Figure 2 shows several simulations for a progression of model lattices. The first (lowest solid line) assumes a perfect fcc lattice with no expansions or reconstructions. It clearly demonstrates the fcc character of the data, but has little else in common with the actual film structure. The second simulation is a fcc Fe film with a top-layer expansion of 5%, and is shown in Fig. 2(a) as the dot-dashed line. The shape of the simulated curve and the positive shifts of the blocking dips agree roughly with the data. Models with an expansion in all the Fe layers were also evaluated, but there was little additional improvement in the comparison of the model to the blocking curve. Note that the overall intensity of the simple expansion is too low and that the [201] blocking dip comes out much too shallow. The higher intensity and depth of the [201] blocking dip in the data suggest that the third Fe layer is partially exposed to the ion beam. Hence we allowed for a (2×1) surface reconstruction of the Fe-film analogue to the model derived from LEED.[3,6,11]

A schematic model of this reconstruction is shown in Fig. 2(b). Alternate [110] rows on the surface are shifted by $\pm S_d$ along the [110] direction, corresponding to a (2×1) superstructure. Due to the displacements of the surface atoms, the hitting probability of the third Fe layer when scattering in the (010) plane is increased by about a factor of 3, if S_d is 0.15–0.20 Å. With this model a search for the best-fit parameters (the interlayer distances d_{12} and d_{23}, the shift of the surface atoms S_d, and the surface and bulk vibrational amplitudes v_s and v_b), was performed. The corresponding best-fit simulation [dotted line in Fig. 2(a)] demonstrates that now the intensity and the [201] dip of the blocking curve agree fairly well with the data. Within this model surface geometry, with a least-square difference of 0.018 (we use the least-square difference L as a measure of the quality of the fit: $L = 1/N[\sum(Y_{\text{expt}} - Y_{\text{calc}})^2]^{1/2}$, where Y_{expt} and Y_{calc} are the experimental and calculated yield, respectively, and N is the number of data points), the best match to the data is given by $S_d = 0.18 \pm 0.02$ Å, $d_{12} = 1.895 \pm 0.03$ Å, $d_{23} = 1.79 \pm 0.03$ Å, $v_s = 0.086$ Å, and $v_b = 0.045$ Å.

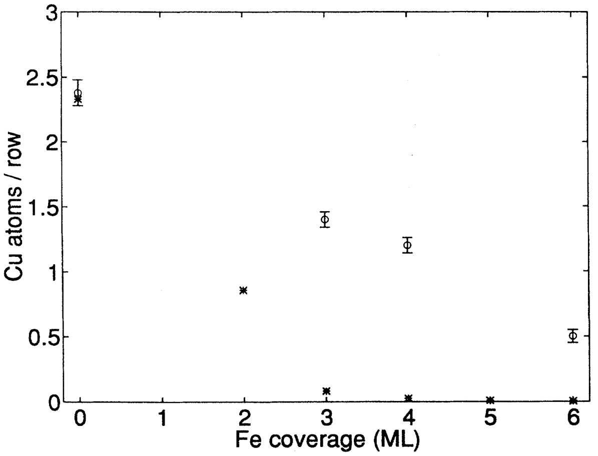

FIG. 3. Integrated Cu surface-peak yield for [00$\bar{1}$] incidence and 128° scattering angle as a function of Fe coverage (○) and the corresponding calculated yields from model simulations of pseudomorphic fcc Fe/Cu(001) films with a glide reconstruction and surface expansion (∗). The disagreement between data and simulations shows that the Fe growth is nonpseudomorphic.

The values for the optimal (2×1) structure are in excellent agreement with the LEED results.[3] Some improvement of the fit is obtained if we allow for small random displacements of Fe atoms perpendicular to the film plane. This provides a better match to the [301] and [501] blocking dips without degrading the rest of the fit. Introduction of disorder is in accordance with the poor quality of the (2×1) LEED pattern[3] and scanning tunneling microscope (STM) data, which resolved dislocations on Fe films grown at 300 K.[5] Since it is quite difficult to model local atomic disorder exactly, we approximate it by assigning displacements randomly with a normal distribution, which is characterized by a mean displacement equal to the standard deviation of the distribution. The best match of the data to a model simulation, having the same disorder in all Fe layers, is obtained for a z disorder (perpendicular to the Fe film) of mean displacement of 0.06±0.02 Å. The size of the unit cell in modeling the disorder was 10×10 Fe atoms per layer. Introducing disorder within the film plane makes the fits significantly worse. A reason for the vertical disorder is the lattice mismatch between the Cu substrate and the Fe film. Fe atoms at the interface must reside on different stacking positions on the underlying Cu lattice, which likely leads predominantly to vertical distortions in the film. In agreement with LEED (Ref. 3) we note that the magnitude of the outward relaxation of the surface layer is in accordance with a ball model of the reconstruction, i.e., the vertical displacement can simply be understood as a necessary result of the shift of the surface atoms along [110] towards the bridge positions of the second layer.

Even though the shape of the [101] blocking dip is well reproduced, the [301] and [501] blocking dips in the simulation are markedly deeper than in the data. This effect is suggestive of an unidentified structural feature. Hence a search was performed including small rotations of the film. Indeed, an improved fit is obtained for a rotation of 1.2°±0.3° of the Fe film [dashed line in Fig. 2(a)]. This leads to a significantly reduced least-square difference of 0.013 when combined with the atomic disorder discussed above [solid line in Fig. 2(a)]. There is indirect evidence for an Fe-film rotation from the STM studies of Giergiel *et al.*,[5] where the nucleation of some bcc Fe regions is observed to be aligned about 3° off the [110] direction.

In the process of optimizing the Fe-film structure, several other possible structures were examined. These included glide reconstructions in other Fe layers in addition to the surface glide. As will be discussed in a future publication[15] and as was recently discussed,[16,17] 3- and 4-ML Fe films show glide reconstructions in all layers of the Fe. It is not currently clear why the Fe films, upon addition of Fe to between 6 and 8 ML, recover the fcc Fe bulk with only a surface reconstruction. Nevertheless, we conclude that second-layer glide along [110] is ≤0.02 Å and third-layer glide is ≤0.04 Å. Glide reconstructions at the Fe/Cu interface, where there is glide for thinner films, is more difficult to assess and could be as large as 0.12 Å on average in the fifth layer and 0.18 Å on average in the sixth (interfacial) layer before the model simulations deviate significantly from the data. Associated expansions would also be possible. Another suggestion is that of a laterally contracted fcc Fe film residing on a pseudomorphic 3–4-ML Fe film.[5] Our observation of excess Cu scattering seems to rule this model out. Additionally, the ion-scattering probability of the fourth layer, in particular, but of all the layers below the second, would be enhanced beyond our observations due to poorer shadowing of the Fe in these layers, if this strain were actually in the film.

With these results in mind it is reasonable to ask the following: Is the ferromagnetism at the surface, at the interface, or at both in room-temperature-grown Fe films between 6- and 8-ML Fe? A unit-cell volume equal to the volume imposed by the observed surface expansion is understood as a reason for a ferromagnetic moment, whereas unit volumes equivalent to the interior layers of the Fe are believed to be coupled antiferromagnetically.[2] In the absence of direct magnetic measurements, these arguments have been used to infer that the ferromagnetism of these Fe films results entirely from the glide-reconstructed layer.[3] Although this is an eminently rational conclusion, there is one report[18] using spin-polarized secondary electrons which finds no surface ferromagnetism in these films. Considering the uncertainty of the atomic structure at the Fe/Cu interface and this disconcerting magnetic measurement, it is possible that the interface Fe layer(s) contribute to the ferromagnetism. Further study will be required to completely clarify this situation.

In has been widely believed that fcc Fe grows coherently on Cu(001) due to the small lattice mismatch. The observation here and previously by LEED (Ref. 3) of nonpseudomorphy clearly rejects this assumption and, thus, raises a question regarding the importance of the small lattice mismatch in the epitaxial growth. The fcc Cu clearly has a strong influence and acts as a template for fcc Fe, but the actual atom spacing taken by the Fe during growth up to and including the fcc structure at 6–8 ML, which involves nonpseudomorphic (see Fig. 3) and highly distorted structures by 3-ML Fe with local atomic disorder in the Cu substrate,[15] are apparently controlled by other factors. These factors will include the cohesive energies, the compressibilities, and defect-formation energies in the Fe and the Cu, and the presence of magnetism in the Fe. With the available information it is really not possible to identify a dominant factor or to get a complete and clear understanding of the resultant interface structure. Nevertheless, it does appear that the energy balance within the interface has been struck in such a way that the Fe is partially, but not entirely, free of the Cu, as evidenced by the incommensurate epitaxy, and that the strain associated with the bonding across the interface resides to a significant extent in the Cu, as evidenced by the local atomic disorder we have observed at Fe coverages near 3 ML. It is interesting to note within this context that the cohesive energy of Fe is about 20% greater than for Cu, and that the interfacial free energy for the formation of incoherent Fe/Cu boundaries is relatively low (< 10% of the cohesive energy).

Summarizing the Fe layer structure, a detailed MEIS analysis of a 6-ML Fe film grown between 310 K and room temperature was performed. The model of the (2×1) surface reconstruction where alternate Fe [110] rows are shifted along [110] is confirmed, as is the incommensuration of the Fe/Cu interface. In good agreement with earlier studies, the glide displacement is determined to be 0.18 Å and the outward relaxation of the top layer to be 6%. There is disorder in the Fe film perpendicular to the film plane. On average the films are rotated by approximately 1.2° with respect to the Cu-substrate lattice. At present, there is not enough certainty in the detailed structure of the Fe/Cu interface to exclude the possibility of ferromagnetic coupling in the interfacial Fe layers.

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