Geometric contrast mechanisms in helium atom scattering: The growth of the Fe/Cu(100) system

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(Received 18 October 2002; published 6 June 2003)

The extremely short de Broglie wavelengths of thermal helium atomic beams make them ideally suited as sensitive probes of surface structures. Recent developments in the methods used to analyze helium atom scattering data make it possible to measure interlayer spacings on metal surfaces with high precision. We present results of the application of this technique to the growth of a heavily reconstructed system. Helium atom scattering has been used to study the variation of interlayer spacing during the growth of ultrathin iron films on copper(100). Using the parameter-independent analysis technique, the interlayer spacings of iron films up to five-monolayers thick have been directly measured. The results show that it is possible to identify three distinct regions from 0 to 5 ML of Fe coverage. In the regime from 0 to 2 ML of Fe there is a large initial expansion of the out-of-plane lattice parameter of the iron film. In the regime from 2 to 4 ML of Fe, the interlayer spacing contracts to a value that is slightly expanded relative to the bulk spacing expected for fcc Fe. Above 4 ML of Fe the interlayer spacing approaches that expected for bulk fcc Fe. The results are discussed in the context of the latest models for the growth of Fe/Cu(100).

DOI: 10.1103/PhysRevB.67.245403 PACS number(s): 68.55.−a

I. INTRODUCTION

Helium atom scattering is an extremely powerful surface analytical technique with the capability of directly probing the interlayer spacing of thin metal films with extremely high precision.[1] In principle, this sensitivity to the interlayer spacing present on the surface can be used to identify, and differentiate between, different chemical species present on a surface during growth.[2] For the growth of cobalt on copper(111), we have shown that it is possible to directly measure the interlayer spacings of the different geometric structures that occur on a surface. In these experiments, the growth and variation of interlayer spacing as a function of cobalt coverage was studied using helium atom scattering.[3–5] The algorithms developed during the course of these investigations for the analysis of helium atom scattering data make no recourse to fitting parameters and, as such, offer the unique opportunity of directly measuring the interlayer spacing of a growing system *in situ*.[4] The results of the study of cobalt on the copper(111) system, showed that the out-of-plane lattice parameter asymptotically decreases from that of the bulk copper interlayer spacing to a contracted bulk cobalt spacing.[5] However, the formation of cobalt films on copper(111) is structurally a relatively simple growth system, since there is no dramatic reconstruction of the surface during growth.[3] The deposition of iron films on copper(100) is a much more challenging heteroepitaxial system to study with this analysis technique, since it is well known that the surface is dramatically reconstructed during the growth process.[8]

The iron on copper(100) system is one of the most heavily studied metal thin-film growth systems, with numerous studies using a variety of analytical techniques taking place over the last ten years.[6–13] The main driving force behind these investigations has been the unique magnetic properties of these thin-film growth structures, which make them potentially suitable for fabrication into magnetic storage media (Ref. 14, and references therein). Furthermore, since these magnetic properties are also a strong function of the surface morphology, it is essential that the structures of these thin films be well understood.[15] The growth mode of these films is extremely complex, especially during the first few monolayers of iron deposition.[16] However, analysis of the growth using area integrating techniques such as medium-energy electron diffraction,[8] helium atom scattering (HAS),[13] and low-energy ion scattering[9] reveals that the growth of iron on copper(100) occurs in four distinct stages as a function of iron coverage.

Stage I, which occurs between 0 and 2 ML of Fe deposition involves exchange between the deposited Fe atoms and Cu surface atoms.[10] Scanning-tunneling microscopy (STM) studies have revealed that the Fe atoms are incorporated as inclusions, which are predominantly located in the Cu surface layer. The growth is also characterized by the presence of double height steps on the surface during this coverage regime.[13]

In stage II, which occurs between 2 and 4 ML of Fe, a partial ordering of the surface occurs. Both low-energy electron-diffraction[17] (LEED) and STM (Ref. 18) data indicate that the Fe films appear to be tetragonally expanded but the structure is not regular and appears to be laterally and vertically buckled. The transition to a more layerwise growth mode appears to occur gradually, with the transition occuring for iron films that are approximately three-monolayers thick. During stage III, which occurs at higher iron coverages between 4 and 10 ML, the consensus appears to be that iron grows pseudomorphically in an approximately face-centered-cubic structure. Finally, during stage IV and above 10 ML the film undergoes a structural phase transformation from a predominately face-centered- to a body-centered-cubic structure.

In this paper, the algorithms developed by the authors for the analysis of helium atom scattering data have been used to revisit the growth of ultrathin iron films on copper(100) surfaces. In general, the results of the analysis are consistent with earlier studies of the structural transformations that occur during the growth of this system. However, the analysis does provide insights into the growth structures that form during deposition. In particular, the HAS results provide information on the growth of Fe on Cu(100) in the low coverage regime. In addition, the results of the analysis demonstrate the ability of the technique to provide geometric contrast during HAS investigations of thin-film structures.

II. EXPERIMENT

All of the experiments were conducted in a purpose-built ultrahigh vacuum chamber with a base pressure below 1×10^{-10} mbar. The helium diffractometer used for the experiments presented here had an angular resolution of 0.44° and is described in detail elsewhere.[19] The helium beam was produced by a supersonic expansion and the nozzle was kept at room temperature resulting in a beam energy of 71 meV ($k_{\bigcirc}=11$ Å^{-1}).

The iron evaporation was carried out using a purpose-built metal evaporator positioned so as to allow *in situ* measurement of the growth. During evaporation the total background pressure, excluding helium from the beam, was less than 2×10^{-10} mbar. An out-of-phase scattering geometry of 52.7° was used, giving destructive interference for monatomic interlayer spacing on (100) terraces. This geometry maximizes any oscillation in specular helium intensity, which is the signature of layerwise growth. The qualitative form of the resulting plot of specular helium intensity against deposition time (uptake curve) was used to provide an indication of the growth mode.[1] The copper (100) crystal was cut to within 0.5° of a (100) plane and mechanically polished before insertion into the vacuum chamber. Preparation of the surface followed the usual cycles of argon-ion bombardment and annealing until only a narrow intense specular helium peak was observed.

The specular peak of the clean copper(111) surface exhibited a full width at half maximum of approximately 0.7°, significantly larger than the inherent instrument resolution. This broadening was attributed to the existing mosaic structure of the copper surface. Indeed, the oscillations in the specular intensity as a function of perpendicular momentum transfer (lattice rod scan) indicated the presence of a small number of monatomic steps on the surface.[3] The corresponding step density, however, was found to be less than the value implied by the maximum misalignment (0.5°) of the crystal surface.

At each film growth temperature, the deposition was interrupted at several points and the variation of specular helium intensity was measured as a function of scattering angle (trackscan). The specular helium intensity was transformed to a function of perpendicular momentum transfer (lattice rod scan) as described elsewhere.[3]

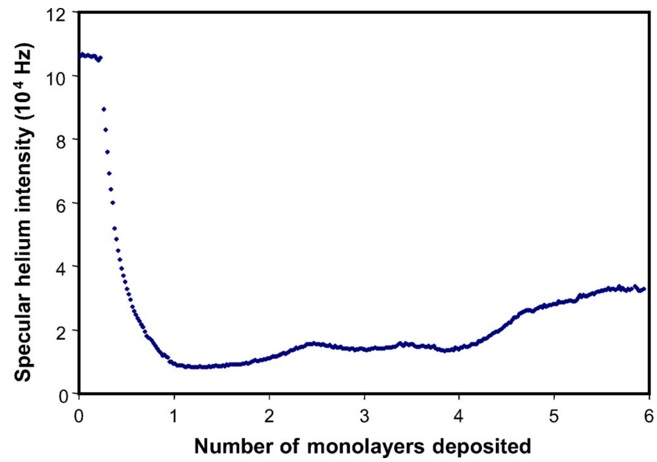

FIG. 1. Variation of in-phase specular helium intensity as a function of coverage for iron films deposited on copper(100) at room temperature. The helium beam is incident at approximately 52° with an energy of 63 meV. Small but regular oscillations in the data are observed above 2-ML iron coverage. The abscissa is calibrated using the characteristic period of one oscillation.

III. RESULTS AND DISCUSSION

Figure 1 shows the variation in specular helium intensity as a function of coverage for iron films deposited at room temperature. The horizontal axis has been calibrated in the usual way, using the oscillation period (in the regions of oscillatory behavior) as a measure of monolayer growth time. It is estimated that the relative error in the calibration is less than $\pm20\%$.[12] The helium intensity profile shown in Fig. 1 is consistent with those obtained using other comparable techniques and demonstrates that layerwise growth does not occur for the first few monolayers of iron on copper(100). In an earlier publication, we showed that it is possible to use the variation of scattered helium intensity as a function of perpendicular momentum transfer (lattice rod scan) to obtain further information about the morphology of the growing film. The results showed that the morphology of the growing film below approximately two monolayers was dominated by the presence of multilayered islands, while above two monolayers a transition towards layer-by-layer growth was observed, entirely consistent with the subsequently defined stages I and II of the growth process.[13]

More recently, we have developed a technique for the analysis of lattice rod scans obtained during thin-film growth. This technique, which is described in more detail elsewhere, essentially extracts the distribution of interlayer spacings on the surface using a Fourier-transform-based algorithm.[4] This analysis technique, which is analogous to that used in extended x-ray-absorption fine structure spectroscopy, therefore provides a direct measure of the interlayer spacing without recourse to fitting algorithms. As an illustration, the results of the analysis for 1 ML of iron deposited on copper(100) at 298 K are shown in Fig. 2. Although the ideal HAS lattice rod scan consists only of sinusoidal terms,[4] experimentally, the data of Fig. 2 is modulated by diffuse scattering effects (including Debye-Waller attenuation). The top left-hand panel illustrates how this back-

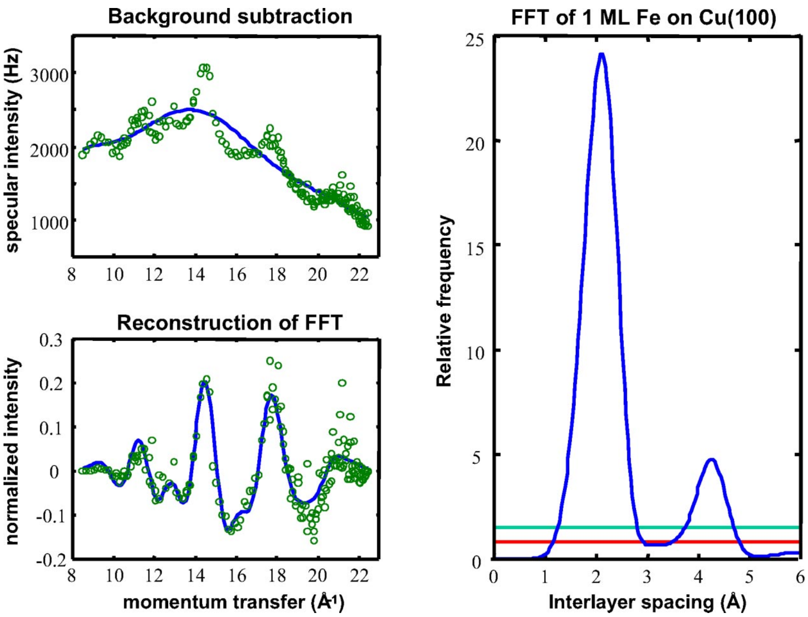

FIG. 2. Lattice rod scan analysis of the 1-ML iron film deposited onto a copper(100) surface. The top left panel shows the original data (open circles) and the background function (solid line) that is subtracted from the data. The Fourier transform (right-hand panel) shows that there are two significant interlayer spacings present on the surface (at approximately 2 Å and 4 Å). The robustness of the analysis technique is indicated in the bottom left-hand panel by the quality of the match between the reverse Fourier transform of the significant peaks in the right-hand panel (solid line) and the experimental data with the background removed (open circles).

ground modulation is removed with a high-order polynomial, since it is not of interest. The form of the fitted background function is selected to ensure that the overall shape of the data envelope is matched without introducing any oscillatory behavior itself. An appropriate background function is indicated by the removal of the fundamental oscillation component in the data (one half wave over the data set): this forms one criterion for the background subtraction algorithm. The other criterion is the requirement that the choice of background function should not affect evaluation of the interlayer spacing. This latter criterion is satisfied by checking the stability of the interlayer spacing to changes in the order of the fit. Typically, the fast Fourier transform (FFT), and hence the measured interlayer spacing, is stable (within the accuracy of the technique) to changes of plus or minus two units in the background polynomial order. The raw data is then normalized by the fitted function.

The main window shows that there are two main interlayer spacings present on the surface and provides a measure of these spacings. The bottom left-hand panel shows the results of the inverse Fourier transform of just the significant peaks (i.e., only those that rise above the 99% significance level). The quality of the fit to the original data is excellent and thus the data is indeed dominated only by the significant peaks in the Fourier transform.

Lattice rod scans were obtained for 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.5, and 5.0 ML of iron together with the clean copper(100) surface. The distribution of interlayer spacings present on the surface was analyzed for each of the lattice rod scans using the analysis methodology. The interlayer spacings of the first two significant peaks were measured and are listed in Table I. Figure 3 shows the variation of the dominant interlayer spacing as a function of iron coverage. There appear to be three distinct stages during the growth of Fe/Cu(100) up to a coverage of 5 ML of iron, which is in agreement with the general consensus for this growth system.

Stage I ($0<\theta_{\mathrm{Fe}}<2$ ML) involves a dramatic expansion of the interlayer spacing compared with that for the bulk copper surface. The dramatic expansion in the out-of-plane lattice parameter that occurs immediately upon iron deposition is unexpected and, to the best of our knowledge, has not previously been reported. It is at 1 ML that the specular helium intensity drops to a deep minimum (Fig. 1), suggesting that the surface is highly disordered. STM of these surfaces reveals that the surfaces in this coverage regime are highly disrupted, with iron atoms becoming incorporated in the substrate and copper islands growing on the surface.[6] The STM data suggests that the first-layer growth is dominated by intermixing of iron and copper.[20] Moreover, these early STM studies of these surfaces indicated that it was possible to distinguish small iron clusters in the substrate and

TABLE I. Values of interlayer spacing obtained from the Fourier transform of the lattice rod scans for ultrathin iron films deposited on copper(100). The values of primary and secondary interlayer spacings are obtained from the first and second most significant peaks in the Fourier transform. Entries marked with an asterisk indicate surfaces for which there was only one significant peak present in the Fourier transform. All of the listed spacings are for films grown at room temperature except for the entry labeled 5*, which was obtained for a film grown at 220 K.

Iron coverage (ML)	Primary interlayer spacing (Å)	Secondary interlayer spacing (Å)
0	1.82	*
1	2.13	4.24
1.5	2.12	4.07
2	1.86	*
2.5	1.93	*
3	1.90	*
4.5	1.82	*
5	1.85	*
5*	1.78	*

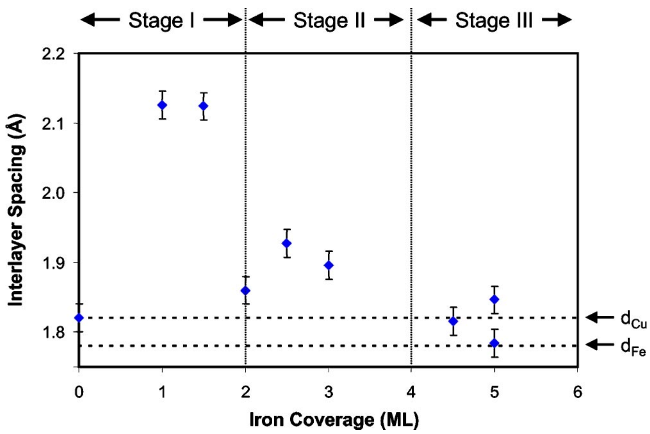

FIG. 3. Variation of measured interlayer spacing as a function of coverage for iron films deposited on copper(100) at room temperature. The filled diamonds show the measured interlayer spacings obtained from helium atom scattering using the different analysis technique. The upper point at 5-ML coverage was obtained for a film grown at room temperature whereas the lower point was obtained for a film grown at 220 K.

at the edges of copper islands at low iron coverages ($\theta_{Fe}<0.2$ ML).[10] These features were observed as patches on the surface whose appearance was highly tip dependent, indicating that these regions were chemically different from the clean Cu(100) surface. The origin of this specific chemical contrast was unclear and was not observed for larger Fe islands. More recent STM studies confirmed the presence of this chemical contrast. These studies revealed the presence of islands with bright features (as observed in STM) located at the island periphery. These bright regions (which occured either as a ridge around an existing island or as self-contained small island) were attributed to Fe-containing moieties. STM line scans across islands with bright peripheries revealed that the apparent height of the periphery was approximately 2.6 Å,[21] while the height of the interior of the island corresponded with the interlayer spacing of Cu(100). In their paper, Dulot *et al.*[21] noted that the measured height of 2.6 Å was too large to be due to any reasonable relaxation effects and too small to be due to double height steps at the island edge. They therefore attributed this measured expansion entirely to electronic structure effects between Fe and Cu atoms, noting that at the typical bias voltages used, the partially integrated density of states is expected to be larger for iron than for copper.[21]

However, the fact that the HAS data of these surfaces also suggests that these intermixed layers have an interlayer spacing that is dramatically expanded with respect to the bulk copper spacing indicates that perhaps electronic structure differences are not the only source of this measured expansion. Indeed, further analysis of the HAS data reveals that there are higher-order peaks in the FFT of the lattice rod scan. These peaks occur at interlayer spacings of 4.24 Å and 4.07 Å for the 1-ML and 1.5-ML films, respectively. Interestingly, these values are approximately twice the fundamental interlayer spacings of 2.13 and 2.12 Å measured for the 1-ML and 1.5-ML iron films, respectively, rather than the sum of the fundamental copper and iron interlayer spacings (2.12 Å + 1.82 Å = 3.94 Å). It is known that interference shifts in the phase of helium atoms scattered from growing islands do occur. These shifts arise from changes in the local potential well which can, under certain circumstances, influence the interlayer spacings measured using HAS. However, these effects are anticipated only to be significant for small islands of approximately 4×4 atoms in size.[22] At a coverage of 1 ML or 1.5 ML, the iron islands are significantly larger than 4×4 atoms and it would therefore be unlikely that the large interlayer expansion that is measured is due to electronic effects alone. Indeed, the tip-dependent chemical contrast effects are only observed in STM measurements of Fe films whose coverage is significantly less than 1 ML.[21,23] Moreover, given that these electronic effects are only going to influence the outermost electronic corrugation, the presence of double height steps whose height is twice the expanded value measured for single height steps is further evidence that the measured expansion is not purely electronic in origin. Further support for the observation of an expansion in the out-of-plane spacing is provided by the reflection high-energy electron-diffraction (RHEED) measurements of Schatz and Keune.[24] Their accurate RHEED measurements show that the average in-plane spacing of Fe films on Cu(100) goes through a minimum at a coverage of 1 ML. Furthermore, this minimum is both less than the equilibrium Cu(100) spacing and the expected spacing for fcc iron. As such, it seems reasonable to expect that there would be a corresponding expansion of the out-of-plane lattice parameter. Although the contraction of the average in-plane lattice parameter measured by Schatz and Keune is too small to completely explain the large interlayer expansion measured by HAS, the RHEED technique does sample over a few atomic layers and thus the actual contraction of the Fe monolayer alone is likely to be greater than that measured.

Stage II (2 ML $<\theta_{Fe}<4$ ML) involves a dramatic decrease in the measured expansion of the deposited iron film. The average interlayer spacing of the film between 2 and 4 Ml is 1.89 ± 0.03 Å, which represents a small but significant expansion over both the original Cu interlayer spacing ($d_{Cu}=1.82$ Å) and the expected interlayer spacing for an fcc Fe film ($d_{Cu}=1.78$ Å). A number of previous studies have also identified that this stage of growth of iron films on a copper(100) surface is characterized by an expansion of the out-of-plane lattice parameter of the growing surface. LEED studies have shown that the iron films go through a number of structural reconstructions with increasing iron coverage.[25] At approximately 2 ML, a 4×1 LEED pattern is observed, which changes to a 5×1 pattern after 4 ML of iron have been deposited on the surface. Full dynamical LEED structural analyzes of the 2-ML and 4-ML films indicate that the iron films are highly distorted and buckled in both the lateral and vertical directions.[26] At a coverage of 2 ML (4×1 phase), the average out-of-plane lattice spacing of the iron film is 1.86 Å, which is in close agreement with the value obtained from the HAS analysis. The dynamical LEED results of Müller *et al.* show that the best fit to the data for a 4-ML Fe film occurs for surfaces with the first four layers reconstructed.[17] There is a vertical buckling of the [110] rows with an average maximum buckling amplitude of 0.2

Å. The average maximum lateral shift is 0.35 Å. There is no evidence of any contraction of the surface layers from the earlier LEED analyzes. At a coverage of 4-ML Fe/Cu(100), the average interlayer distance as measured by LEED is 1.87 Å and it appears that all of the reconstructed layers have a spacing that is expanded by $\sim 5\%$. More recently, accurate measurements using quantitative STM profiling suggest that the interlayer spacing 4-ML Fe films on Cu(100) is 1.93 Å, which is again in close agreement with the value obtained using HAS.[21]

Stage III ($\theta_{Fe} > 4$ ML) involves a further decrease in interlayer spacing of the growing film. This spacing approaches the value of 1.78 Å expected for strained fcc iron films on copper(100).[16] This observation is in agreement with the general consensus for the growth of iron films between 4 and 10 ML, with a number of structural LEED analyzes that suggests the surface consists primarily of fcc iron islands. However, STM data has shown that the fcc surface is unstable and that at a coverage of 10 ML the film has transformed to a bcc structure.[27,28] This transformation is a result of the formation of dislocationlike elongated ridges on the surface that transform into a complex system of bcc precipitates.[29–30] More recent STM data indicate that needlelike bcc precipitates form the nucleation centers for the growth of the subsequent bcc phase.[18] Although there is continued debate about the details of the growth structures that occur in this growth regime, it is generally accepted that iron films above 4-ML coverage grow as primarily fcc structures and the interlayer spacings measured using other techniques are in close agreement with those obtained here. For example, the average interlayer spacing for the iron film between 4.5 and 5 ML is 1.83 ± 0.02 Å which is in very close agreement with LEED measurements of the 4-ML film (5×1 phase), indicating that the average interlayer spacing is 1.84 Å. Finally, it is timely to comment on the general issue of geometrical contrast within the HAS experiment. The analysis of the HAS results for growth of the Fe/Cu(100) system demonstrates that it is now possible to clearly distinguish between the presence of different structural phases on the basis of an accurately measured interlayer spacing. There is extremely close agreement between the HAS data and the generally recognized phases that exist during the growth of this complex system. Such a result indicates that the analysis techniques described here could form the basis of using geometrical contrast to identify surface structures in a helium-based imaging instrument.

IV. CONCLUSIONS

The use of a different methodology for the analysis of helium atom scattering data has been applied to a complex heteroepitaxial growth system, that of iron on copper(100). The HAS data reveal that the growth commences via a dramatic expansion of the out-of-plane lattice parameter. This expansion decreases systematically with increasing iron coverage. Although this measured expansion may have a component associated with differences in the electronic structure of iron and copper, the close agreement between the interlayer distances measured with HAS (at higher Fe coverages) and those obtained using other surface science techniques suggests that the expansion originates from a real change in geometric structure. The interlayer separations observed with HAS correlate extremely well with previous structural analyzes conducted using LEED and STM and confirm the observation that there are three distinct stages in the growth of iron on copper(100) below 5 ML. These stages can be summarized as follows:

(i) $0 < \theta_{Fe} < 2$ ML: Intermixing between iron and copper is accompanied by a dramatic expansion of the interlayer spacing.

(ii) $2 < \theta_{Fe} < 4$ ML: A disordered and strained fcc iron phase grows which is tetragonally expanded with respect to the expected fcc iron lattice.

(iii) $\theta_{Fe} > 4$ ML: A less strained pseudomorphic fcc iron film forms.

The results also demonstrate the effectiveness of the analytical technique in providing quantitative geometric contrast of complex surface structures from helium atom scattering data.

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