Formation and structure of Fe/Cu(001) interfaces, sandwiches, and superlattices

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We have used medium- and high-energy Auger-electron diffraction and low-energy electron diffraction to probe the structure of the Fe/Cu(001) interface, the Cu/Fe/Cu(001) sandwich, and the Fe/Cu/Fe/Cu(001) superlattice. Metastable epitaxial fcc overlayers of Fe with good structural quality grow on room-temperature Cu(001) for coverages up to five monolayers (ML). Above 5 ML, the structural quality of the overlayer diminishes. The first monolayer of Fe does not adsorb uniformly, but rather forms two-layer deep clusters. Above 1 ML, the film coalesces into a well-ordered fcc overlayer. When the substrate temperature is held at 125 °C or higher during evaporation, Fe atoms in-diffuse and displace Cu atoms at lattice sites. The fcc Fe overlayer formed at room temperature also acts as an excellent template for subsequent Cu overlayer growth. We show that Cu depositions on 8-ML Fe/Cu(001) adsorb uniformly (no clustering) and form a fcc film with the same level of structural quality as the substrate. Further Fe depositions on the Cu overlayer maintain an fcc structure, illustrating the feasibility of generating Fe/Cu superlattices in which ultrathin layers of metastable fcc Fe can be sandwiched between Cu layers of any thickness.

The formation of metastable, epitaxial overlayers on single-crystal surfaces is currently attracting considerable attention.¹ It has recently been demonstrated that the substrate plays a dominant role in inducing the growth of nonequilibrium phases which do not ordinarily develop at low temperatures and pressures. Indeed, we and others have shown that Co overlayers grown at room temperature assume a bcc structure on GaAs(001) (Refs. 2 and 3) and an fcc structure on Ni(001),⁴ whereas Co is normally hcp at room temperature. Thus, thinfilm growth on suitable substrates generates a significant number of possibilities for forming interesting and unusual phases of matter which may possess unique and useful properties.

One particularly interesting system is the Fe/Cu(001) interface. The room-temperature structure of Fe is bcc (a=2.86 Å) and that of Cu is fcc (a=3.61 Å), but at temperatures above 500 °C, Fe undergoes a bcc-to-fcc phase transition with a=3.64 Å for fcc Fe.⁵ Furthermore, dT/dP < 0 along the phase boundary line so that the phase-transition temperature increases with decreasing pressure.⁶ Transmission electron microscopy (TEM) studies⁷ and recent low-energy electron diffraction (LEED) investigations⁸⁻¹⁰ indicate that fcc films of Fe can be stabilized at much lower temperatures by growth on Cu(001) because of the 0.83% lattice mismatch between fcc Fe and Cu. Furthermore, through the combined use of angle-resolved photoemission and firstprinciples electronic structure calculations, it has been shown that ultrathin fcc Fe overlayers on Cu(001) are ferromagnetic.¹¹ On the other hand, recent neutron scattering measurements and a different set of angleresolved photoemission experiments indicate that supported monolayers of fcc Fe on Cu(001) do not exhibit in-plane ferromagnetic behavior.¹² Furthermore, surface magneto-optic Kerr effect measurements also suggest that Fe overlayers grown at room temperature are not

ferromagnetic, whereas films grown at temperatures in excess of $150 \,^{\circ}$ C exhibit a metastable ferromagnetic state.⁹ Thus, the Fe/Cu(001) interface constitutes an intriguing choice for fundmental correlations of structural, electronic, and magnetic properties in a two-dimensional system.

In the present work, we have used medium- and highenergy Auger-electron diffraction (AED), together with low-energy electron diffraction (LEED), to investigate the details of interface formation as a function of coverage and temperature for the Fe/Ce(001) interface. Furthermore, we have examined the structure of the Cu/Fe/Cu(001) sandwich and Fe/Cu/Fe/Cu(001) superlattice. Of particular interest have been the temperature dependence of the first-layer morphology, the onset temperature for interdiffusion, the maximum Fe overlayer thickness for which the metastable fcc structure can be maintained, and the structural characteristics of the sandwich and superlattice systems.

The experimental system used for the present investigations is described in detail elsewhere.^{3,13,14} A Cu single crystal to cut within 0.5° of the (001) orientation was mechanically polished with 0.05- μ m Al₂O₃ grit and briefly etched in 2N HNO₃ prior to insertion into the vacuum system. Once under ultrahigh-vacuum (UHV) conditions (~4×10⁻¹¹ Torr), the sample was repetitively sputtered with 500-eV Ar ions and annealed at 400°C until the surface was atomically clean and ordered. The resulting surface showed no trace of impurities as judged by Auger spectroscopy and exhibited a sharp 1×1 LEED structure.

Evaporations of Fe and Cu were done from a dual resistive evaporator at pressures never exceeding 2×10^{-10} Torr. The evaporation rate was held constant at 1 monolayer (ML) per minute, and precise control of the amount deposited was realized through a shutter placed between the source and the sample. Coverage

was monitored by a quartz-crystal oscillator, which was calibrated by measuring the rate of attenuation of substrate Auger intensity for Ag/Pd(001), a nonintermixing epitaxial system.¹⁵ In this calibration method, we measure the Pd MNN Auger intensity at various polar angles in the (101) azimuth for each of several Ag coverages. For each data point, we calculate the overlayer thickness from a simple continuum model of Auger emission which takes into account inelastic attentuation only and ignores single-crystal effects. The only input parameter which is not directly measured is the inelastic mean free path, which we calculate from an empirically derived equation for electrons propagating through a wide variety of elemental media.¹⁶ The polar angles at which the measurements are made are chosen to be both coincident and noncoincident with low-index directions, along which forward elastic scattering may affect the accuracy of the model. Then the results are averaged over all polar angles to effectively minimize single-crystal effects. The results of this analysis are shown in Table I. Inspection of the table shows that, in general, the calculated overlayer thickness is within experimental error of the thickness determined by the quartz-crystal oscillator. The major discrepancy is the data for the 2-ML coverage, in which less than 2 ML appears to have been deposited. This method of calibration shows that the overlayer thickness calculated from geometric considerations associated with the positions of the source, monitor, and sample are accurate on an absolute scale. Moreover, our method of overlayer deposition is quite reproducible. Replicate measurements of the Fe LMM polar angular distribution in the (010) azimuth for 1.0 ML of Fe on Cu(001) yielded very nearly the same results, both in terms of the absolute intensities and the overall shape of the angular distributions. These data are shown in Fig. 3 and will be discussed in more detail later. However, for the purpose of demonstrating the reproducibility of the evaporation and thickness measurement scheme we have employed, we mention these results at this point. For evaporations at elevated substrate temperatures, the sample was heated radiatively by a tungsten filament, and temperature was measured with a chromel-alumel thermocouple.

Structure within the Fe overlayers was primarily determined by employing the angular dependence of Fe $L_{2,3}M_{2,3}M_{4,5}$ Auger emission at a kinetic energy of 645 eV, and Cu overlayers were probed using the Cu $L_{2,3}M_{4,5}M_{4,5}$ Auger transition at 916 eV. Both lines

were excited with 5-keV primary electrons. A second method of structure determination involved measuring the intensities of the (10), ($\overline{10}$), (11), and ($\overline{11}$) LEED beams at a fixed collection angle as a function of coverage (hereafter referred to as fixed-angle LEED *I-V* curves). For these measurements the angle-resolving energy analyzer was used to measure the LEED spectrum in high-symmetry azimuths by monitoring the elastic peak intensity as a function of kinetic energy in the pulse-counting mode for normal beam incidence.³

In order to establish what is expected from Auger angular distributions for epitaxial growth of Fe on Cu(001) or Cu/Fe/Cu(001), we have performed kinematical scattering calculations¹⁷ for various model structures. The results are shown in Fig. 1 for 1-5 monolayers (ML) of Fe on Cu(001) and 1-5 ML of Cu on Fe(001) where the predicted polar-angle intensity profiles in the (010) aximuthal plane are given as a function of coverage. For each set of scattering calculations, we have used 100 atoms per layer and 2-4 layers of substrate. The structure of bulk fcc Cu was used in the Fe layers, and the interplanar spacing between the terminal underlayer and the first overlayer was taken to be that of bulk Cu. In practice, these calculations are not particularly sensitive to the details of the substrate because of the forward focusing behavior of electron-atom scattering at the kinetic energies used here. Shown in Fig. 1 are calculated polar-angle intensity profiles in the (010) azimuthal plane as a function of coverage for the two systems. At 1 ML, the intensity weakly modulates with polar angle but does not show any major features for either system. At 2 ML, a peak appears at $\theta = 45^{\circ}$ associated with electrons emitted from atoms in the first overlayer which subsequently forward scatter from second-layer atoms whose angular coordinate is $\theta = 45^{\circ}$ in the (010) azimuth. At 3 ML, a peak appears at $\theta = 90^{\circ}$ as a result of scattering of electrons emitted from first-layer atoms by atoms in the third epitaxial layer. Thus, we are able to follow the development of the [101] and [001] low-index directions at 45° and 90°, respectively, as the epitaxial overlayer is built up. At 4 and 5 ML the features induced by forward scattering at 45° and 90° continue to build, as do weaker structures at $\sim 20^{\circ}$ and 70° which result from more complex interference phenomena.¹⁸ The salient feature of these calculations is that the formation of a second fcc epitaxial overlayer is characterized by a forward-scattering-induced peak at $\theta = 45^{\circ}$ while the third layer is revealed by a similar peak at 90°. This re-

TABLE I. Calibration of quartz-crystal oscillator (QCO) using the nonintermixing, epitaxial Ag/Pd(001) system.

QCO Ag coverage		Calculated Ag thickness ^a (Å)					
ML	Å	$\theta = 90^{\circ}$	$\theta = 78^{\circ}$	$\theta = 74^{\circ}$	$\theta = 45^{\circ}$	$\theta = 30^{\circ}$	Average ^b
1	2.25	2.60	2.50	2.30	2.30	2.40	2.4(1)
2	4.50	4.00	4.20	3.70	3.70	3.70	3.8(2)
3	6.75	6.90	6.70	6.30	6.50		6.6(3)
4	9.00	8.50	10.80		10.60	8.10	9.0(1)
5	11.25	11.31	11.50	11.25	12.10	11.40	11.5(3)

^aThickness $d = -\lambda \sin\theta \ln[I_{pd}(d)/I_{Pd}(0)]; \lambda = 0.54\sqrt{k} = 9.7$ Å for Pd MNN Auger emission with k = 321 eV (Ref. 16). ^bNumber in parentheses is the uncertainty in the last digit of each average thickness.



FIG. 1. Theoretical polar-angle intensity profiles in the (010) azimuth for the Fe/Cu(001) and Cu/Fe(001) systems as a function of coverage. Calculations were performed within the kinematical scattering approximation. The forward focusing nature of electron-atom scattering at these kinetic energies results in major peaks along the close-packed, low-index [101] (θ =45°) and [001] (θ =90°) directions.

sult has been demonstrated previously for both the Cu/Ni (Refs. 18–20) and Ag/Pd(001) (Ref. 15) systems. Although multiple scattering corrections tend to reduce the intensity of forward-scattering-induced features (particularly at high coverage),²¹ such features are not eliminated by dynamical scattering effects. Therefore, peaks at $\theta = 45^{\circ}$ and 90° are reliable qualitative fingerprints for the formation of second and third layers, respectively.

In Fig. 2 we show polar scans in the (010) azimuth (left) and azimuthal scans at $\theta = 35.3^{\circ}$ which span from the (010) azimuthal plane ($\phi = 0^{\circ}$) to the (100) azimuthal plane ($\phi = 90^{\circ}$) for the Fe/Cu(001) interface. The substrate was held at room temperature during each evaporation. The azimuthal scan at 35.3° was chosen to detect the formation of a bcc phase of Fe which, if formed, would exhibit strong forward scattering along the close-packed [111] direction at $\theta = 35.3^{\circ}$. (The azimuthal angle at which [111] would occur depends on the relative orientation of the bcc phase to the underlying fcc phase.)

The polar scans at the left of Fig. 2 show that the

overlayer exhibits strong forward scattering along [101] $(\theta = 45^{\circ})$ but no enhancement along [001] $(\theta = 90^{\circ})$ by an Fe coverage of 1 ML. This result indicates the formation of two-layer-deep epitaxial Fe clusters by a coverage equivalent to 1 ML, analogous to what has been seen for both Co on Ni(001) and Cu on Ni(001) at equivalent coverages of 0.5 and 1.0 ML, respectively.⁴ This important results was highly reproducible. In Fig. 3 we plot the absolute Fe LMM intensity versus polar angle [in the (010) azimuth] for three separate evaporations of 1.0-ML Fe on Cu(001). In all three cases, the absolute intensities are in very good agreement at all polar angles and the diffraction feature at $\theta = 45^{\circ}$ is unmistakably present. As the calculations in Fig. 1 clearly show, this peak is brought about by forward scattering of electrons originating from first-layer atoms by atoms in the second layer along [101]. At 2-ML equivalents, the feature along [101] sharpens and grows and a small peak develops at $\theta = 90^{\circ}$, indicating further growth of the second layer and the formation of limited amounts of a third layer within the clusters. The steep rise in intensity for $\theta \leq 20^{\circ}$



FIG. 2. Experimental polar-angle distributions in the (010) azimuth (left) and azimuthal profiles at $\theta = 35.3^{\circ}$ (right) for the

Fe/Cu(001) interface as a function of coverage. All evaporations were done with the substrate at room temperature.

seen in the experimental data for low coverages is a result of enhanced emission at low θ from layers with thicknesses considerably less than the inelastic mean free path, and is not a diffraction-related effect.

If single-crystal effects are ignored, the polar angle distribution of Auger intensity is given by a Laplace transform of the density function of the emitted material. In a previous publication, we developed a method for extracting the density function from the polar intensity profile and applied the technique to the quantitative description of intermixing at reactive interfaces.¹⁴ It was shown that for overlayers with a thickness less than the inelastic mean free path, an increase in intensity occurred as the polar angle decreased, an effect which is quantitatively accounted for by our model. Qualitatively, this result is easily explained by the fact that the emission path length exceeds the overlayer thickness by a factor of $1/\sin\theta$ for $\theta < 90^\circ$. Thus, the analyzer effectively sees an increasing overlayer thickness along the emission direction as θ decreases. If the mean free path exceeds the overlayer thickness, the Auger intensity from the overlayer will steadily increase as the polar angle drops. For example, the intensity of Fe $L_{2,3}M_{2,3}M_{4,5}$ Auger emission (kinetic energy of 645 eV



FIG. 3. Replicate measurements of the Fe LMM polar-angle distribution for 1.0 ML of Fe on Cu(001) in the (010) azimuth. Experiments a, b, and c represent three separate evaporations onto the clean, ordered substrate. Unlike Figs. 1 and 2 and 6-8, these data are plotted on an absolute intensity scale in order to demonstrate the reproducibility of the results.

and mean free path of about 14 Å) from a 3-ML overlayer (thickness equal to one lattice constant or 3.61 Å) is expected to monotonically rise between $\theta = 90^{\circ}$ and about $\theta = 5^{\circ}$. This estimate is based on the fact that 95% of the signal originates within a distance of three mean free paths from the surface along the emission direction. Examination of Figs. 2 and 3 shows that this phenomenon in fact occurs. If the diffraction-induced features at $\theta = 45^{\circ}$, $60^{\circ} - 80^{\circ}$, and 90° are removed from the data for 1-5 ML, the monotonic increase described above is clearly observed. However, this effect is not reflected in the present calculations because our kinematical scattering model treats inelastic scattering only inasmuch as it affects the attentuation of the primary and elastically scattered Auger waves; we have not included the Laplace transform factor which gives rise to the aforementioned effect.

By 3 ML, the film has become a well-ordered fcc overlayer, as judged by the large anisotropies and characteristic peaks at $\theta = 45^{\circ}$ and 90°. Although the [101] peak is broad due to the relatively low kinetic energy of the Fe $L_{2,3}M_{2,3}M_{4,5}$ line, there is no apparent shift in its position from the expected value of $\sim 45^\circ$, indicating that, within the limits of detectability ($\cong 0.2$ Å), the Fe overlayers are not strained in the direction normal to the interface.²⁰ This result is consistent with LEED I-V curves for the energy dependence of the (00) beam from Fe overlayers on Cu(001) which also showed no measurable strain in the direction normal to the interface.¹² Above 5 ML, the feature along [101] begins to weaken, broaden, and disperse to a higher polar angle, indicating a partial loss of structural order. This process continues up to 30 ML. It is not possible with the data at hand to determine the structural nature of the overlayer once the disordering process begins.

Additional structural insight can be gained by measuring the (10) LEED beam spectrum as a function of Fe coverage. In Fig. 4, we present fixed-angle LEED I-Vcurves averaged over the four equivalent sections of reciprocal space defined by the azimuthal angular coordinates 45°, 135°, 225°, and 315°. Thus, the large feature is the average of the (10), $(\overline{10})$, (11), and $(\overline{11})$ beams, but hereafter we refer to it simply as the (10) beam. The peak height have been normalized to constant intensity for each coverage. The top spectrum is that for the Cu(001) substrate. In Fig. 5 we plot the peak intensities and widths of the spectra shown in Fig. 4 as a function of coverage. Inspection of Figs. 4 and 5 show that upon addition of 1 ML of Fe, there is a slight broadening and shift to lower kinetic energy in the (10) beam, as well as a small drop in peak intensity. Although we make no attempt to interpret the energy shift, the broadening and intensity drop are consistent with the formation of twolayer-deep clusters, as suggested by the Auger diffraction data. If the steps associated with the clusters define a long-range periodicity of their own (as in the case of regular stepped surfaces), we would expect the (10) beam to be split. However, Monte Carlo simulations of heteroepitaxy show that statistical fluctuations in overlayer thickness are expected in the limit of low surface mobility of the adatom, which would be expected to lead to beam broadening, as we observe here.²²

From 1 to 5 ML, the beam intensity fluctuates slightly but the peak width remains constant, suggesting that the level of disorder does not increase over this coverage range. From 5 to 12 ML, the peak width steadily increases and a change in line shape occurs. Moreover, the beam intensity drops over this coverage range. This is the same range over which the Fe *LMM* Auger angular distributions lose a considerable amount of modula-



FIG. 4. Fixed-angle LEED *I-V* spectra averaged over the (10), $(\overline{10})$, (11), and $(\overline{1} \overline{1})$ beams for the Fe/Cu(001) interface as a function of Fe coverage.



FIG. 5. Beam widths and intensities from the LEED spectra shown in Fig. 3.

tion and is consistent with a loss of structural order.

Having demonstrated that well-ordered fcc Fe can be grown up to a coverage of at least 5 ML on Cu (001), it is of interest to see whether this metastable phase can be used as a template for epitaxial growth of Cu, thereby permitting the formation of an fcc Cu/Fe/Cu sandwich. In Fig. 6 we show polar-angle scans of Cu $L_{2,3}M_{4,5}M_{4,5}$ intensity in the (010) azimuth for Cu overlayers grown on an 8-ML Fe film on Cu(001) at room temperature. The top curve is the polar scan for the 8-ML Fe overlayer and is based on the Fe $L_{2,3}M_{2,3}M_{4,5}$ line at 645 eV. This Fe coverage was chosen so that substrate Cu LMM emission would be attenuated as much as possible, thereby minimizing interference with Cu overlayer emission. (When 1 ML of Cu is deposited, only about 20% of the Cu LMM intensity at $\theta = 45^{\circ}$ is attributable to the substrate, and this percentage drops at higher coverages.) The Fe film possesses a high degree of structural order and shows the characteristic peaks at [101] and [001] expected for an fcc overlayer. Upon adding 1 ML of Cu, the Cu LMM polar profile is rather featureless and there is no intensity enhancement along [101]. Therefore, Cu does not cluster on Fe(001) but rather grows as a uniform monolayer. Upon adding a second monolayer, we see a feature along [101], indicating second-layer formation, and a weak peak along [001], indicating limited amount of a third layer. At higher coverages all features grow, and by 20 ML the polar profile is essentially identical to that of the Cu(001) substrate (bottom curve). Furthermore, the [101] peak falls precisely at $\theta = 45^{\circ}$, indicating that no measurable tetragonal distortion has occurred. Moreover, the fixed-angle LEED I-V curves for 20-ML Cu/8-ML Fe/Cu(001) in all high-symmetry azimuthal planes (not shown) are virtually identical to those of the Cu substrate, further demonstrating the high degree of structural quality of the Cu overlayer. Thus, epitaxial Fe on Cu(001) is an excellent template for Cu overlayer growth, and ultrathin fcc Fe films sandwiched between Cu(001) are attainable. In principle, Fe-Cu superlattices involving Fe layers not thicker than 5-8 ML can be grown readily with the substrate at room temperature. Indeed, we found that Fe deposition upon the 20-ML Cu overlayer [Fe/20 ML Cu/8 ML Fe/Cu(001)] leads to high-quality fcc films for coverages up to 8 ML, as judged by Fe *LMM* polar angle distributions and LEED spectra.

It is significant that according to this analysis Fe does



FIG. 6. Experimental polar-angle distributions in the (010) azimuth for the Cu/8-ML Fe/Cu(001) system as a function of Cu coverage, and for the Cu(001) substrate (bottom curve).

not adsorb uniformly on Cu(001) at the 1-ML level, but that Cu does grow uniformly on metastable Fe(001). This is consistent with surface thermodynamic considerations. The free energy of formation of an overlayer which uniformly covers the surface is defined as $\Delta \gamma = \gamma_0 - \gamma_i - \gamma_s$, where γ_0 , γ_i , γ_s are the specific surface free energies of the overlayer, the interfacial layer, and the substrate, respectively.¹ For the formation of an overlayer which is 1 ML deep, $\Delta \gamma$ can be written as $\gamma_0 - \gamma_s$ because the overlayer and the interfacial layer are the same. According to the second law of thermodynamics, uniform wetting is possible only if $\Delta \gamma \leq 0$. Using published values of the specific surface free energies of Fe and Cu, $\Delta \gamma \cong +1$ J/m² \cong 0.4 eV/atom for the formation of a uniform monolayer of Fe on Cu(001) at 25°C, indicating that the process is not thermodynamically favorable.²³ However, the inverse process corresponding to the formation of a uniform monolayer of Cu on Fe(001) has a free energy of formation of -1 J/m^2 , indicating that the process is favored. This correlation with experiment increases our confidence in the semiempirical methods to calculate the surface free energies used in determining $\Delta \gamma$, and suggests that the strong thermodynamic motivation for the formation of uniform 1-ML Cu on Fe(001) overcomes kinetic limitations associated with deposition at room temperature.

The work described above was performed with the sample at room temperature during deposition. In order to see how the structure of the first Fe monolayer depends on substrate temperature, we have measured the angular dependence of Fe $L_{2,3}M_{2,3}M_{4,5}$ Auger emission from the 1-ML Fe/Cu(001) interface grown at 20, 60, 125, and 220 °C, as shown in Fig. 7. The estimated uncertainty for each temperature is $\pm 7^{\circ}$. On the basis of integrated Fe *LMM* intensities measured at $\theta = 78^{\circ}$ and $\phi = 0^{\circ}$, we found that Fe indiffuses into Cu in limited amounts at temperatures as low as 125 °C. (These angular coordinates were used because we did not observe a



FIG. 7. Polar scans in the (010) azimuth and azimuthal scans at $\theta = 45^{\circ}$ for the 1-ML Fe/Cu(001) system as a function of substrate temperature during evaporation. The bottom curves are the analogous scans for the Cu(001) substrate. Maximum anisotropies, defined as $(\Delta I/I_{\text{max}})100$, where $\Delta I = I_{\text{max}} - I_{\text{min}}$, are shown to the right of the azimuthal scans. Inset: Fe $L_{2,3}M_{2,3}M_{4,5}$ intensity at $\theta = 78^{\circ}$ and $\phi = 0^{\circ}$ vs substrate temperature during evaporation. These angular coordinates were chosen to minimize interference of inelastic attenuation associated with in-diffusion with elastic forward scattering related to structural changes.

diffraction peak here at any time; such a peak would confuse the issue of atomic mobility by adding intensity due to forward scattering.) From the inset in Fig. 7 we see that there is no decrease in Fe LMM intensity when the substrate is held at 60° during evaporation, but the intensity drops to 89% of its room temperature value at 125°C and 70% at 220°C. From the polar profiles (left side of Fig. 7), we see that the morphology of the Fe monolayer is the same at room temperature and at 60°C-two-layer-deep clusters, as judged by the presence of a diffraction feature at $\theta = 45^{\circ}$ but no peak at $\theta = 90^{\circ}$. Upon depositing 1 ML of Fe with the substrate at 125°C, the Fe LMM polar profile bears a striking resemblance to the Cu LMM angular distribution for the substrate (bottom curve on left-hand side) despite the difference in kinetic energy between Fe and Cu LMM Auger emission. This result demonstrates that Fe atoms displace Cu atoms and form substantial defects. In so doing, Auger electrons from embedded Fe atoms encounter scatterers at the same relative coordinates as do Cu atoms in the substrate, leading to nearly identical angular distributions. The same result is obtained when the substrate temperature was 220 °C. Similar conclusions about thermally-motivated indiffusion and substitutional displacement have been drawn from polarangle distributions of x-ray photoelectron intensity for Ni/Cu(001) (Ref. 24) and Au/GaSb(110) (Ref. 25). The high degree of similarity between the substrate and the Fe *LMM* polar-angle distributions after in-diffusion also suggests that the lattice is not deformed by the presence of Fe atoms at lattice sites. This conclusion is reasonable in light of the very small difference between atomic radii for Cu and Fe (~ 0.05 Å).

To further verify that substitutional displacement has occurred, we show on the right-hand side of Fig. 7 and in Fig. 8 azimuthal angle distributions at $\theta = 45^{\circ}$, 35.3°, and 18.4°. At each polar angle, there is a strong resemblance to the substrate scan (bottom curve in each panel), indicating the formation of an fcc structure. However, the scans at substrate temperatures of 125° and 225° show stronger anisotropies than those at room temperature and 60 °C. The maximum anisotropy, defined as $(\Delta I_{\text{max}})100$ where $\Delta I = I_{\text{max}} - I_{\text{min}}$, is seen to increase by $\sim 4\%$ at $\theta = 45^\circ$, by $\sim 13\%$ at $\theta = 35.3^\circ$, and by ~18% at $\theta = 18.4^{\circ}$ as in-diffusion occurs. This result is expected if Fe atoms penetrate the substrate and occupy lattice sites in the near-surface region. Auger electrons from substitutional Fe will encounter more forward scatterers (other Fe and Cu atoms) en route to the detector than will Fe atoms in two-layer-deep clusters on the surface. An increased number of scatterers will produce deeper anisotropies, particularly in angular scans that do not pass through close-packed, low-index directions such as [101] and [011]. Along these directions, very strong forward scattering is expected for only a single scatterer, as in a 2-ML cluster. (See, for example,



FIG. 8. Azimuthal scans at $\theta = 35.3^{\circ}$ and 18.4° as a function of substrate temperature for the 1-ML Fe/Cu(001) interface.

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the strength of the [101] diffraction peak at 2 ML on both sides of Fig. 1 compared to those at higher coverages.) Thus, the increase in anisotropy in going from the 2-ML cluster to an array of embedded Fe atoms in the substrate will not be so great, as observed for the scans taken at $\theta = 45^{\circ}$. However, the azimuthal scans taken at $\theta = 35.3^{\circ}$ and 18.4° (which do not encompass any closepacked, low-index directions) are expected to yield much stronger Fe LMM anisotropies when the Fe atoms are substitutionally dispersed throughout the near-surface region of the substrate, as opposed to when they are in 2-ML clusters on the surface. This is a consequence of the increased number of forward scatterers that Fe LMM electrons will encounter in the dilute alloy. Taken together, the data in Figs. 7 and 8 constitute a strong case for substitutional in-diffusion for temperatures at or above 125 °C.

The conclusions we draw about the structure of the first monolayer of Fe on Cu(001) are seemingly at odds with previous work which suggests that the first layer is continuous rather than in the form of two-layer-deep clusters. Lee et al. measured the attenuation of Cu LMM Auger intensity with coverage and obtained LEED patterns for coverages up to 10 ML.8 Moog et al. also monitored the dependence of Fe and Cu Auger intensities on Fe coverage and obtained LEED patterns for coverages up to 4 ML.⁹ Onellion *et al.* measured the Fe and Cu MVV Auger intensities versus Fe coverage and obtained LEED I-V curves for 1 to 4 ML of Fe.¹⁰ Finally, Hezaveh et al. have measured LEED I-V curves for thin epitaxial overlayers of Fe.¹² In many of the above cases, the Auger data were consistent with a layer-by-layer growth model. Moreover, the LEED patterns reported were nominally $p(1 \times 1)$ for most coverages and the I-V curves from Onellion et al. were very similar to those for the Cu(001) substrate, and those calculated by dynamical scattering theory assuming a $p(1 \times 1)$ overlayer structure.¹⁰ LEED *I-V* curves for Fe overlayers obtained by Hezaveh et al. were less similar to those for the Cu(001) substrate, but bore a significant resemblance nonetheless.¹² In what follows, we discuss these results in light of the present work and show that the apparent discrepancies may be resolved by a careful comparison.

In the work of Lee et al., all depositions were apparently done with the substrate at room temperature. Assuming a continuum model for the attenuation of Auger electrons originating in the substrate and a layerby-layer growth mode, these workers obtained an excellent fit to the experimental attenuation of Cu LMM intensity.⁸ However, it is not clear that the layer-by-layer model used provides a uniquely good fit to the data, particularly in the coverage regime around 1 ML where our work suggests that clustering is occurring. Indeed, Onellion et al. modeled both layer-by-layer growth and limited cluster formation and found the two approaches yielded essentially the same level of agreement with experiment (also done at room temperature) for coverages up to 1 ML.¹⁰ Furthermore, Moog et al. actually got a better fit to their experimental data (obtained with a substrate temperature of 150 °C) by assuming a model in

which a given layer grows in competition with the layer beneath it.9 However, these workers concede that the same level of agreement with experiment can be achieved assuming a perfect layer-by-layer model by making slight adjustments in the inelastic mean free path. Furthermore, they found very little difference between the two growth models for coverages up to 2 ML, consistent with what Onellion et al. found.¹⁰ Therefore, continuum models based on attenuation and growth of Auger features may not be sufficiently sensitive to structural details to detect clustering. In contrast, the method described here is extremely sensitive to the onset of second-layer formation, as shown by the presence of a forward-scattering-induced peak at $\theta = 45^{\circ}$ in the (010) azimuth when the second layer begins to form. Furthermore, there is no critical dependence on input parameters (such as the inelastic mean free path) so that the effect of clustering would be obscured by changes in such parameters. The expectation that a peak along [101] will occur in the polar-angular distribution of Fe LMM emission when the second layer begins to form rests on very firm experimental and theoretical grounds.^{15, 18-20} Moreover, theoretical crystal-overlayergrowth calculations²⁶ and related Monte Carlo simulations²² for both homoepitaxy and heteroepitaxy for which the free energy of formation of a continuous monolayer is positive [as in the case of Fe on Cu(001)] indicate that statistical fluctuations in overlayer thickness will occur in the case of limited surface mobility. Surface mobility is certainly limited when the substrate is at room temperature, as was the case in all the growth sequences we are comparing here with the exception of those of Moog et al.9

As we show in Figs. 4 and 5, the LEED pattern (i.e., fixed-angle LEED I-V curves in high-symmetry azimuths) is not terribly sensitive to clustering, particularly when the cluster morphology does not define a periodic structure. We observe a slight broadening and weakening in the (10) beam, but no splitting as occurs in the case of a regular stepped surface. This result is consistent with what was observed by Lee et al., who saw a $p(1 \times 1)$ LEED pattern for all room-temperature evaporations except those accompanied by incorporation of impurities.⁸ The high degree of similarity between the LEED I-V curves for Fe/Cu(001) and those for both Cu(001) and theoretical $p(1 \times 1)$ overlayers of Fe on Cu (001) reported by Onellion et al., may be due to thermally-driven intermixing at the interface.¹⁰ These authors evidently did their evaporations for LEED studies at a substrate temperature of 150-200 °C. Although they state that interdiffusion occurred at temperatures in excess of 240 °C, our work indicates that intermixing begins at temperatures as low as 125 °C, and that Fe atoms displace Cu atoms to produce an fcc alloy in the nearsurface region with a structure essentially the same as that of bulk Cu. In light of the high degree of similarity between Fe and Cu atomic scattering factors, such a surface would be virtually impossible to distinguish from Cu(001) by LEED. Furthermore, recent Mössbauer and x-ray photoelectron spectroscopy results by Chien et al. demonstrate that $Fe_x Cu_{100-x}$ alloys grown by coevaporation assume an fcc structure and are ferromagnetic for $20 \le x \le 70$.²⁷ If applicable to the evaporation of Fe onto hot Cu(001), these results would reconcile the observation of ferromagnetism in epitaxial Fe/Cu(001) grown at elevated substrate temperatures with the surface alloying that our results suggest.

Comparing of the (00) LEED beam spectra of supported Fe overlayers with those of Cu(001) published by Hezaveh et al. shows that they are clearly not identical.¹² Unlike those obtained by Onellion et al., these LEED I-V curves were obtained with films grown at room temperature. There are differences in both the energies and relative intensities of different diffracted beams in the two spectra. One would expect that if the Fe overlayer was a perfect extension of the Cu lattice (i.e., continuous with no clustering), that the spectra would be much closer in appearance, as Onellion et al. observed. Thus, the relative differences between Fe overlayer and Cu substrate LEED spectra reported by Hezaveh et al. may in fact be due to clustering, which we believe occurs during growth at room temperature due to limited adatom mobility and the thermodynamic barrier to uniform coverage of Fe on Cu. These authors do not comment on the differences between spectra but rather use the energy dependence of the (00) beam to extract the perpendicular overlayer spacing, which they find to be the same within experimental error for the two surfaces. This result is consistent with the lack of shift in the position of the [101] diffraction peak at $\theta = 45^{\circ}$ in the polar scans of Fig. 2, which indicates the absence of

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tetragonal distortion in the Fe overlayer.

In summary, we have employed Auger-electron diffraction and low-energy electron diffraction to probe the structure of the Fe/Cu(001), Cu/Fe/Cu(001), and Fe/Cu/Fe/Cu(001) systems as a function of coverage and substrate temperature during evaporation. We have found that Fe forms a well-ordered, metastable, minimally strained fcc overlayer at room temperature for coverages up to 5 ML and that above 5 ML the structural quality diminishes. We have also shown that it is possible to use the fcc Fe overlayer as a template for the growth of fcc Cu, and that additional fcc Fe can be grown on the Cu overlayer. Interestingly, the first monolayer equivalent of Fe on Cu does not wet the surface at room temperature, but rather forms two-laverdeep clusters, whereas the first Cu layer on metastable Fe(001) does wet at room temperature. Finally, we have found that evaporation of 1 ML of Fe onto the Cu(001) substrate leads to in-diffusion and the formation of substitutional defects, provided the substrate temperature is greater than or equal to 125 °C.

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detection limit of this technique, which we estimate to be $\cong 0.2$ Å.

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