PHYSICAL REVIEW B VOLUME 49, NUMBER 8 15 FEBRUARY 1994-II

# Substrate diffusion in metastable ultrathin films: Iron on Cu(001)

Th. Detzel and N. Memmel
*Max-Planck-Institut für Plasmaphysik, Euratom Association, D-85748 Garching, Germany*

(Received 31 August 1993)

Temperature stability and diffusion properties of ultrathin iron films grown at room temperature on a Cu(001) single-crystal surface have been investigated using low-energy ion scattering. None of the as-grown films is found to be thermally stable. Instead an enrichment of the surface with substrate atoms is observed. Below two monolayers, where the Cu substrate is not completely covered by Fe, the onset of Cu diffusion occurs at 300 K. Iron films wetting the substrate entirely appear to be more resistant against thermal treatment. It is shown explicitly that initially a single monolayer of copper migrates onto the films, leaving the underlying Fe layers mainly intact. This overlayer adopts the same crystal lattice as the as-grown films; in particular a monolayer of Cu atoms is found in bcc lattice sites on top of iron films exhibiting bcc structures.

## I. INTRODUCTION

The structure and properties of epitaxially grown ultrathin films form an integral part of the scientific and technological landscape. The far-reaching importance of these artificially produced materials in both fundamental research and application has led to tremendous experimental and theoretical efforts in recent years. Particularly interesting are ultrathin films revealing ferromagnetism with the easy axis of magnetization perpendicular to the surface. Such out-of-plane anisotropies are observed uniquely in magnetic systems with reduced dimensionality.

Regarding the chart of the measured elemental surface free energies,[1] it becomes evident that nearly all of the most promising two-dimensional magnetic films should be in metastable states. Examples include Fe on Cu, Co on Cu, Fe on Ag, and Fe on Au. Common to all these adsorbate-substrate combinations is the attempt to grow a high-surface-free-energy metal on a low-surface-free-energy substrate. Since the interfacial free energies are expected to be small and often positive, Bauer's equilibrium criterion[2] predicts the deposit to agglomerate into large three-dimensional crystallites in order to minimize the total free energy. However, none of the as-grown films under consideration is found in this Volmer-Weber morphology. Instead, a two-dimensional structure of the deposit is observed, necessarily leading to metastable nonequilibrium configurations. In addition, the epitaxial arrangement of the grown layers often does not represent their bulk lattice structure enhancing the metastability even further. On the other hand, thermal treatment should enable the grown layers to reach their true thermodynamic equilibrium.

Both the strain energy and the surface-free-energy balance might cause a disruption of the films to form three-dimensional islands with the bulk lattice configuration exposing parts of the substrate area. Another possible mechanism to reach thermodynamic equilibrium may be the intermixing of overlayer and substrate atoms. Finally, the development of sandwich structures is conceivable with substrate atoms covering the adsorbate.

In many of the magnetic overlayer systems fairly high temperatures are employed to investigate their magnetic properties such as the Curie temperature. These annealing procedures are likely to cause a gross rearrangement of the overlayer resulting in conflicting information. Regardless, in many instances the substrate is assumed to be a rigid stationary template, neither being influenced by the deposition process nor by the thermal treatment. Furthermore, in magneto-optical storage devices only materials have to be used which are not affected by moderate temperatures.

In contrast to the enormous amount of work dedicated to characterize and to understand the epitaxial growth process of ultrathin metal films, their aging by virtue of heat treatment has not yet been studied in a satisfactory depth. In this paper we present a comprehensive study of the temperature stability and diffusion behavior of ultrathin iron films grown on a Cu(001) single-crystal surface. The Fe-on-Cu(001) system is often called a benchmark system for metal-on-metal epitaxy as well as for magnetic investigations. Growth, structure, and morphology have been studied most intensively employing essentially all available surface analytical techniques.[3–14] Concerning the initial room-temperature growth mode the various experimental results seem to be contradictory. While in scanning tunneling microscopy (STM) only islands of monolayer height are observed,[9,10] low-energy ion-scattering[12] and x-ray photoelectron diffraction[5] experiments detect Fe atoms with about equal amounts in both the first and second layer, even at very low coverages ($\leq 0.1$ ML). In order to explain these observations, a growth mode has been suggested which involves (partial) incorporation of Fe atoms into the original substrate surface,[9,12] thereby necessarily leading to a diffusion of Cu atoms onto the original surface. At a coverage of 2 ML the surface is almost completely (90%) covered with iron and at even higher coverages layer-by-layer growth occurs, leading to well-ordered fcc iron films. Above ten monolayers the fcc structure breaks down in favor of the formation of bcc iron with a [110] surface normal.[12–14]

0163-1829/94/49(8)/5599(8)/$06.00

The analytical method mainly used in the present investigation was low-energy ion scattering (LEIS), which in recent years has been established as an advantageous approach to study surface, interface, and thin-film phenomena.[12,15–19] This technique is element specific, quantitative (once calibrated), and extremely surface sensitive. Moreover, due to shadowing effects this method provides structural information with atomic resolution in the surface plane as well as normal to the surface. Therefore, LEIS supplies mass-selective real-space information on the local atomic arrangement at the surface including surface defects. As a further advantage the evaluation schemes are straightforward and do not require sophisticated and time-consuming model calculations.

## II. EXPERIMENT

All experiments were carried out in an UHV apparatus (base pressure $<3\times10^{-9}$ Pa) equipped with standard low-energy electron diffraction (LEED), Auger-electron spectroscopy (AES), and sample preparation facilities. The specially designed LEIS setup consists of a differentially pumped ion source allowing primary ion energies up to 5 keV and a hemispherical energy analyzer to detect the scattered ions. A high-precision computer-controlled sample manipulator with three translational as well as three rotational degrees of freedom permits us to record polar and azimuthal LEIS spectra.[20]

The Cu(001) single crystal (miscut $<0.3°$, as verified by Laue diffraction and LEIS) was cleaned by $Ar^+$ ion bombardment and annealing cycles to exhibit a sharp $(1\times1)$ LEED pattern with low background intensity. After the preparation procedure the contamination levels were below the detection limits of LEIS. Iron was deposited onto the Cu substrate from a small iron pin of purity 99.999% heated by electron bombardment. During evaporation the pressure stayed below $1\times10^{-8}$ Pa. An analysis of the residual gas by a quadrupole mass spectrometer revealed that the slight increase in pressure was mainly due to an increase in the partial pressure of hydrogen.

Coverages were controlled independently by means of AES and medium-energy electron diffraction (MEED) (Refs. 6, 7, and 12) and are given in units of a nominal monolayer [ML], i.e., $1.53\times10^{15}$ atoms/cm$^2$. The evaporation rates ranged from 0.5 to 1 ML/min in the different experiments. For details about the calibration techniques see Ref. 12.

In the diffusion experiments the as-grown films were subjected to isochronal annealing procedures. The specimens were heated resistively and the temperature was measured with a calibrated NiCr-CuNi thermocouple being in direct thermal contact with the crystal. A feedback system stabilized the temperature to within ±2 K. Diffusion-induced changes in the surface composition as well as modifications in the crystallographic and morphological order were monitored by LEIS, AES, and LEED.

All ion-scattering experiments presented in this work were carried out using a monoenergetic beam of $Ne^+$ ions with a primary energy of 5 keV, and a scattering angle of 160°. Polar impact-collision ion-scattering spectroscopy (ICISS) scans were recorded along the [100] azimuthal direction since this arrangement allows the sequential detection of first- and second-layer atoms. Details about the experimental setup have been described elsewhere.[16] The incident flux as well as the recording time were kept low in order to avoid possible damage of the surface by the impinging ions. The maximum ion fluence per spectrum never exceeded $5\times10^{13}$ ions/cm$^2$. Conceivable beam damage can be estimated easily, using low-energy ion-scattering itself. However, no measurable radiation damage was observed under the conditions employed in the following experiments.

## III. RESULTS

The thermal behavior of various metastable iron films was studied by isochronal annealing experiments. Iron coverages ranging from 1 to 14 ML were heated for 5 min and cooled down to room temperature. Subsequently, the chemical composition as well as the morphological and crystallographic structure of the surface layers were monitored by LEIS, AES, and LEED.

Figure 1 shows the intensity of $Ne^+$ ions backscattered from Fe or Cu as a function of their kinetic energy recorded for a 2-ML-thick Fe film before [Fig. 1(a)] and after [Fig. 1(b)] annealing to 573 K. The angle of incidence $\Psi$ of the probing ion beam with respect to the surface plane was chosen equal to 40° and the scattering plane was oriented along the [100] direction. In this scattering geometry only the outermost atomic layer is analyzed, since the second-layer atoms are hidden in the

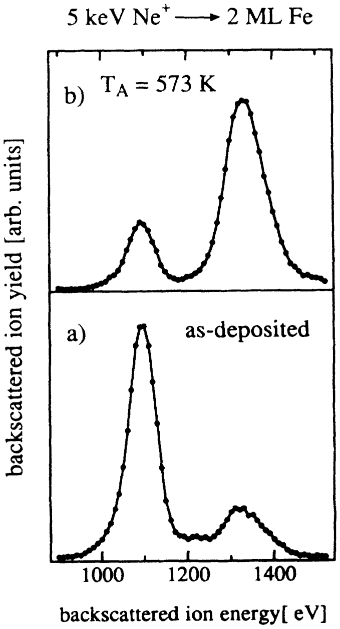

FIG. 1. LEIS spectra of 2-ML Fe/Cu(001) before (a) and after annealing to 573 K. A 5-keV $Ne^+$ beam was incident at an angle of 40° relative to the surface plane along the [100] azimuth and the scattering angle was 160°. The peaks at ≈1100 and ≈1330 eV result from backscattering by iron and copper atoms, respectively. Both spectra are normalized with respect to the incident ion current.

shadow cones produced by the neighbors in the first layer.[12] The as-deposited film exhibits a dominant peak at ≈1100 eV due to backscattering at Fe atoms and a small peak at ≈1330 eV which represents the Cu atoms still to be found at the surface after Fe deposition. After the annealing step the intensity ratio of the Fe and Cu peak is nearly inverted. This indicates that the surface layer now consists mostly of copper atoms. It should be invoked that due to the difference in nuclear charge as well as due to possible deviations in the neutralization probabilities of iron and copper, the "scattering cross sections" differ to a small extent. This difference was determined experimentally using pure elemental standards. We found a 10% lower cross section for iron compared to copper. This deviation is small and has essentially no influence on our qualitative and quantitative interpretations. As a first important result, we state the enrichment of the surface layer with copper atoms as a consequence of the thermal treatment of the film-substrate system.

The Cu/(Cu+Fe) LEIS signal ratio from the topmost surface layer as a function of annealing temperature for various iron coverages is depicted in Figs. 2(a)–2(d). Upon annealing all the iron films show an increase in the backscattered Cu/(Cu+Fe) intensity ratio, pointing to an enrichment of the surface with copper. However, it is apparent from this LEIS data that the onset of the surface compositional changes depends on film thickness. As mentioned in the Introduction, the initial room-temperature growth of Fe on Cu(001) does not proceed in a layer-by-layer mode. Thus, one nominal monolayer of the deposit is not enough to wet the substrate completely. Instead about one-half of the copper surface remains uncovered at this overlayer thickness. Heating such a one-monolayer (ML) film [Fig. 2(a)] leads to an increase of the amount of copper detected in the first surface layer, with the strongest change occurring right at room temperature. At 573 K a value of about 85% Cu is reached, leaving still some iron at the surface. At this point it seems necessary to note that in all our experiments the annealing program was stopped below 700 K in order to avoid the contamination of deeper substrate layers with Fe. Beyond this temperature considerable bulk diffusion has to be expected.[21] Eventually, all Fe atoms will dissolve into the bulk of the substrate crystal by this mechanisms and disappear from the surface, resulting in a surface which consists of pure copper.

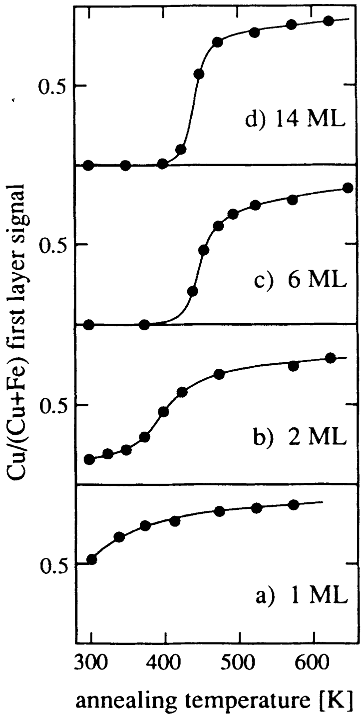

FIG. 2. Cu/(Cu+Fe) intensity ratio of the surface layer signal as a function of the annealing temperature. Upon annealing all the iron films show an enrichment of the surface with copper. The solid lines are guides to the eye.

A 2-ML Fe/Cu(001) system exhibits a thermal behavior which is already quite different as compared to the single monolayer case [Fig. 2(b)]. The onset of copper enrichment at the surface is observed at ≈350 K, pointing to an enhanced resistance to the heat treatment.

Recent structural and morphological investigations of a 6-ML film showed an essentially pseudomorphic fcc structure with a slight reconstruction of the surface layer and comparatively little surface defects.[7,10–12] At this coverage we do not observe any modifications in the surface composition below annealing temperatures of 420 K [Fig. 2(c)]. However, at slightly higher values a drastic augmentation in the Cu/(Cu+Fe) ratio is detected, which levels off above 520 K. Almost the same behavior is found for a 14-ML film [Fig. 2(d)]. While the Cu enrichment begins nearly at the same temperature, the transition is even more pronounced than in the 6-ML-thick layer.

The results presented in the foregoing paragraphs nicely demonstrate the metastablity of the Fe layers grown on a Cu(001) substrate. On the other hand, no conclusions can be drawn so far on the actual microscopic process. Hitherto, this information is consistent with the possibilities adduced earlier, namely, disruption of the iron films and formation of large three-dimensional islands exposing vast parts of the substrate area, intermixing of the two elements, or diffusion of Cu atoms through the films resulting in a sandwich structure. Evaporation of the adsorbate can be ruled out as this mechanism is activated only at much higher temperatures.[22] Several questions arise. Which of the two species is the diffusing element? Are the films homogeneously interspersed by copper or is the Cu enrichment restricted to the surface layer? Is the system undergoing not only compositional but also structural and morphological transitions upon annealing?

In order to answer these questions we performed experiments using ICISS. This technique is based on the shadow cone concept[23] and allows, in our case, the layer-resolved chemical and structural analysis of the two outermost surface layers. To avoid multiple-collision events scattering angles near 180° must be used. In a typical ICISS experiment the electrostatic analyzer is tuned to the energy of the $\mathrm{Ne}^+$ ions singly scattered at the species to be probed (i.e., 1100 eV for Fe, 1330 eV for Cu; see Fig. 1). Then the backscattered intensity is recorded as a function of the incident angle $\Psi$. An angular scan of the clean Cu(001) surface taken along the [100] azimuthal direction is depicted in Fig. 4(a). Near grazing incidence ($\Psi=0°$) on an ideal crystalline surface each target atom is hidden in the shadow cone cast by its nearest neighbor in the surface plane. No head-on collisions as required for $\approx 180°$ backscattering can occur and the backscattering intensity vanishes. If the angle of incidence is increased, the atoms of the topmost layer will leave the shadow cone of the adjacent atoms (see Fig. 3, top), leading to a strong augmentation of the ion yield with a sharply peaked maximum due to the flux concentration near the cone edge.[16] Upon further increase of the angle of incidence $\Psi$ the neighbors in the second layer are also leaving the cone (Fig. 3, bottom) and a second significant enhancement of the ion yield is observed at $\Psi=63°$. As can be seen from Fig. 4(a), the signal of the second layer is approximately reduced by a factor of 4 with respect to the first-layer signal, mainly due to the higher neutralization probability of $Ne^+$ ions backscattered from the subsurface layer.

Figure 4(b) shows an ICISS spectrum recorded at a 6-ML film after annealing to 493 K; as before the electrostatic analyzer was tuned to the energy of ions scattered at Cu atoms. Immediately striking is the fact that the second-layer Cu intensity at $\Psi=63°$ is missing to almost full extent, meaning that essentially no subsurface Cu is detected. Aging models involving clustering of the adsorbate into large three-dimensional islands as well as strong intermixing must, therefore, be excluded. Instead, a single monolayer of Cu appears on top of the iron layers. The angular scan of the film annealed to 493 K recorded by means of $Ne^+$ ions backscattered at iron atoms [Fig. 4(e)] exhibits the complementary behavior as compared to the copper ICISS spectrum. Here, an enormous second-layer yield is measured compared to the as-deposited film [Fig. 4(d)]. This indicates that we find about four times as many Fe atoms in the second than in the topmost layer. ICISS spectra associated with a 6-ML film annealed to 650 K are shown in Figs. 4(c) and 4(f). At this temperature the second-layer copper intensity has significantly increased and amounts to about 65% of the subsurface signal found for the clean substrate. Thus, about $\frac{3}{4}$ of the capping overlayer now has a thickness of at least two monolayers. Comparing the fractional distribution of the residual Fe atoms in the first two layers after the two different annealing steps we do not observe major changes. The appearance of subsurface copper at 650 K might be explained by the onset of bulk diffusion leading to an intermixed film. However, by an analysis of the elemental composition of the surface with Auger-electron spectroscopy monitoring the 705- and 920-eV transitions of Fe and Cu, respectively, a Fe/(Fe+Cu) peak-to-peak intensity equal to 44% was found. Modeling the annealed film-substrate system by a Cu-Fe-Cu sandwich structure an average copper overlayer thickness of slightly less than 2 ML can be estimated. Taking together the AES and LEIS results severe intermixing throughout the whole film must be excluded even at 650 K.

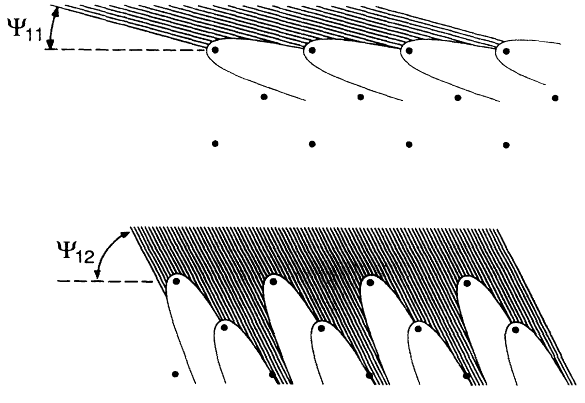

FIG. 3. The shadow-cone concept of ICISS. Only the trajectories of the incoming beam are shown in this figure. Top: situation where atoms in the outermost layer just "leave" the shadow cone of their nearest neighbors in the surface plane. Bottom: atoms in the first subsurface layer "leave" the shadow cone caused by the surface atoms.

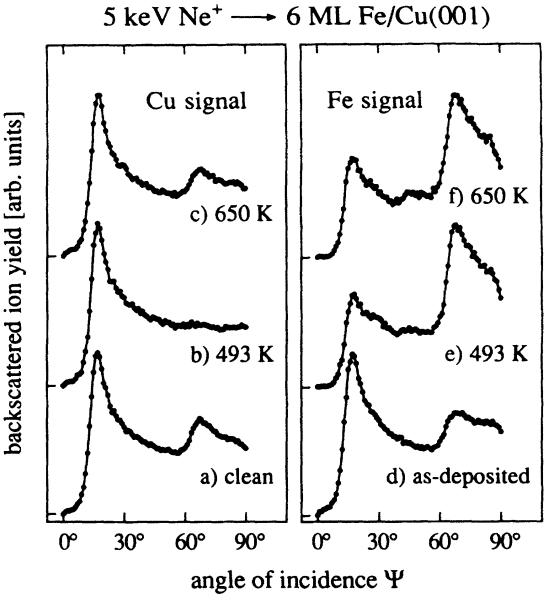

FIG. 4. ICISS spectra taken at a 6-ML Fe/Cu(001) after two different annealing steps. In the panel on the left-hand side (a)–(c) the ions were scattered at copper atoms whereas in the panel on the right-hand side the ions were scattered at iron atoms (d)–(f). 5-keV $Ne^+$ ions were incident along the [100] azimuth and the scattering angle was 160°. All spectra are normalized to the same height at maximum intensity.

As a further important result we notice that in all the spectra presented, the angular positions of the prominent features, i.e., the critical angles associated with the focusing at first- and second-layer atoms, are within our experimental uncertainty of 0.5° the same as on the clean Cu(001) surface. This proves that there are no gross structural rearrangements as a consequence of the thermal exposure. The deposit conserves its fcc structure and the Cu overlayer adopts the lattice structure of the film.

As shown in earlier work,[12,24,25] surface defects like steps and adatoms can be detected effectively in an ICISS experiment. The small intensities near grazing incidence point to a smooth sample surface with a defect density comparable to the clean substrate. LEED investigations corroborate the preceding findings. After the annealing procedure a $(1\times1)$ LEED pattern was observed with the same sharpness of the reflexes as obtained at the well-prepared Cu template before Fe evaporation.

The LEIS, AES, and LEED results provide clear evidence for the system to reach thermal equilibrium via the formation of a Cu-Fe-Cu sandwich structure, in which the diffusion process leaves the buried iron layers more or less undisturbed. Moreover, from our findings we conclude that Cu is the diffusing element. Migration of Fe atoms into the substrate necessarily would lead to an intermixed configuration in the second and deeper layers.

A further open question is the possibility of alloy formation in the topmost layer at 493 K although the bulk phase diagram[26] does not permit any intermixing of the two components at the temperatures used. Figure 2(c) shows that still some 30% of a ML of Fe remains at the surface after this annealing cycle. Unfortunately, LEIS is not able to give a direct answer to this problem. Due to the rather small difference in nuclear charge of Fe and Cu the shadow cones of the two elements do not differ significantly and, therefore, no shifts in the critical angles will be observed in the two conceivable scenarios: A surface consisting of a Fe-Cu alloy or a surface in which not the entire iron film is covered by Cu atoms, leaving some Fe patches open. Nevertheless, if there is significant alloy formation it has to be restricted to the outermost layer, as practically no subsurface copper is found at this temperature.

By LEIS, STM, and LEED investigations it is now well established that Fe films with thicknesses larger than 10 ML grow in a bcc manner with a [110] surface normal.[12–14] The obvious question arising is certainly, what kind of structure adopts the capping Cu overlayer on such a thick film? Angular scans obtained before and during the annealing program applied to a 14-ML-thick film are depicted in Fig. 5. The iron-ICISS spectrum recorded at the as-deposited system [Fig. 5(c)] is indicative of the bcc structure mentioned before. As compared to the spectra of the fcc film both critical angles are shifted, with the first-layer focusing peak broadened considerably and the second-layer feature spilt into a double-peak structure. Splitting and broadening are due to the existence of two pairs of inequivalent (with respect to the scattering plane) domains of bcc (110) iron on the fcc (001) substrate. After annealing to 473 K the second-layer peak is missing completely in the copper signal [Fig. 5(b)], whereas the iron spectrum [Fig. 5(d)] shows a strongly enhanced subsurface intensity with a prominent feature split into two peaks. As before, this leads us to conclude that a single ML of Cu diffused onto the film. Position and shape of the peak at ≈10° due to backscattering at Cu in the overlayer are different from the clean Cu signal [Fig. 5(a)] but compare well to the Fe signal of the as-grown system [Fig. 5(c)]. Intriguingly, this proves that the copper atoms are found in bcc lattice sites on top of the bcc iron film. As expected, the buried Fe maintains its body-centered-cubic symmetry.

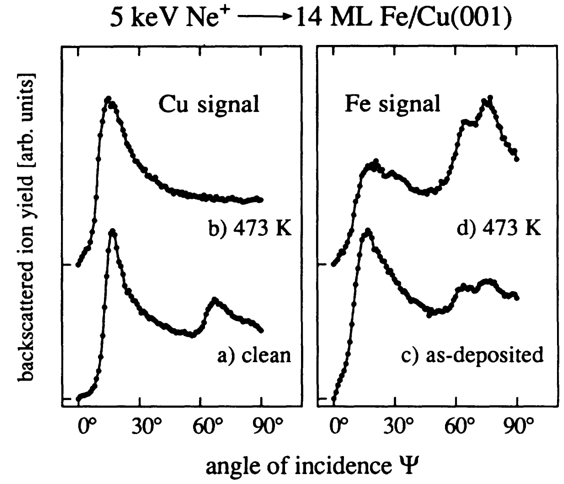

FIG. 5. ICISS spectra taken at 14-ML Fe/Cu(001) before and after annealing to 473 K. The signal of the clean Cu(001) substrate surface is included. 5-keV Ne$^+$ ions were incident along the [100] azimuth and were scattered at copper atoms (a),(b) and iron atoms (c),(d), respectively. The scattering angle was 160°. All spectra are normalized to the same height at maximum intensity.

These interesting findings are further illustrated by azimuthal ion-scattering scans, which provide an additional instructive possibility to get an overview of the short-range crystallographic order in the surface layer. Here, the backscattered ion intensity is recorded as a function of the azimuthal angle $\Phi$. The angle of incidence $\Psi$ is chosen constant near the first critical angle ($\Psi=11°$ in our case), so that along high-symmetry directions of the surface (with their rather small interatomic distances) atoms are hidden in the shadow cones of their nearest neighbors, whereas along low-symmetry directions (with larger interatomic distances along these directions) this is not the case. Therefore backscattering along high-symmetry directions is impossible, marking these directions by pronounced minima in the azimuthal scans. This statement, however, holds only for a one-domain surface. On a multidomain surface the superposition of the backscattering signals from the different domains is measured and no one-to-one assignment can be made between experimentally observed minima and high-symmetry directions in one of the different domains.

Figure 6 shows azimuthal scans taken at the 14-ML film before and after heating to 523 K. As in the polar measurements the electrostatic analyzer was set to the kinetic energy of Ne$^+$ ions scattered at Fe or Cu, respectively. The spectra of the clean surface [Fig. 6(a)] and the as-deposited film [Fig. 6(b)] are discussed in Ref. 13 and serve as fingerprints of the fcc (001) and a four-domain bcc (110) surface, respectively. After the thermal treatment the Cu signal [Fig. 6(c)] exhibits exactly the same characteristic features as the Fe reference spectrum, nicely confirming that the copper overlayer adopts the lattice structure of the underlying bcc iron.

Eventually, we want to draw attention to the thermal behavior of films deposited at elevated temperatures. In a recent publication by Arnott, McCash, and Allison[8] the

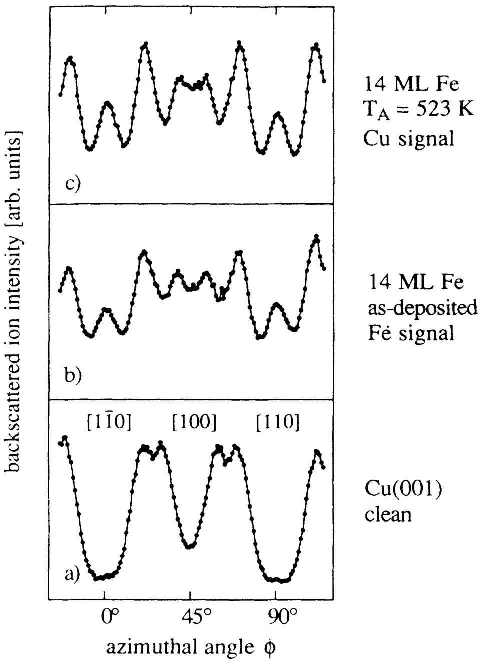

FIG. 6. Azimuthal scans recorded for clean Cu(001) (a) and for 14-ML Fe/Cu(001) before (b) and after (c) annealing to 523 K. 5-keV $Ne^+$ ions were backscattered from Cu (a),(c) and Fe (b) atoms, respectively. The scattering angle was 160° and the angle of incidence was 11°. All spectra are normalized to the same height at maximum intensity.

thermal properties of a film of a coverage between 8 and 9 ML deposited at 420 K were investigated by specular thermal-energy helium atom scattering. Their experimental data as well as Auger spectroscopy measurements suggested a growth mode with pronounced copper diffusion resulting in an iron-copper surface alloy. In order to explain the unusual temperature behavior of the scattered He intensity found during a cooling and heating loop, the authors believe in an unstable surface composition. Cooling the film down to 250 K is supposed to result in the spinodal decomposition of the alloy into a surface film enriched by one component of the binary mixture.

To check these proposals we deposited an iron film in the coverage range reported by Arnott, McCash, and Allison keeping the substrate at 420 K. Our LEIS data distinctly confirm the appearance of a large amount of Cu at the surface during the growth process. We found a surface composition of the as-grown film consisting of 35% Fe and 65% Cu. However, during cooling down to 170 K and subsequent heating to 420 K no significant changes in the surface composition are observed. The maximum deviation of the Fe to Cu ratio from the constant average value amounts merely to 2%, which is about the experimental accuracy in our experiment. Based on our findings we claim that the unusual thermal properties revealed in the specular helium scattering investigations are not due to an enrichment of the surface with one component during the cooling process. If precipitates were to occur at the surface upon cooling, the formation of patches, enriched by one component leaving the overall composition of the surface layer unchanged, would be more consistent with our data.

## IV. DISCUSSION

The diffusion and aging behavior of ultrathin metal films epitaxially grown on metal substrates, including Fe/Cu(001), has been approached previously.[7,8,22,27–32] Common to all these investigations was the idea to study the compositional and structural response of metastable overlayers subjected to annealing procedures, i.e., to study systems in which the adsorbate has a larger surface free energy than the underlying substrate.

In a comprehensive work by Schmitz *et al.*,[27] the thermal properties of ultrathin Rh films on Ag(100) were studied. In terms of thermodynamic parameters this metal combination exhibits a great deal of analogy to the Fe-on-Cu system. The surface free energy of Rh is about twice that of Ag and the mutual solubility of the two elements is negligible at the temperatures employed in these investigations. Upon annealing the authors found a Ag-Rh-Ag sandwich structure representing the thermodynamic equilibrium state of the system. For the capping silver overlayer a thickness of merely one or two atomic layers is reported. scanning electron micrographs indicated that the Ag diffusion begins at randomly dispersed point sources rather than to emerge uniformly as it would be the case for surface segregation in an equilibrium alloy. Furthermore, photoemission data suggest the absence of alloy formation by virtue of the thermal treatment. The onset of the diffusion process was found to be about 360 K for a 1-ML film and 420 K for larger coverages. A similar phenomenon has been seen at ultrathin cobalt and nickel films on Cu(001) (Refs. 30 and 31) using the x-ray photoelectron diffraction technique.

The results found for Rh on Ag(100) and Co and Ni on Cu(001) show a remarkable resemblance to the findings in the present investigation. As was demonstrated in the preceding section we observed a similar sandwich structure. In particular, we could show explicitly that the thickness of the diffused overlayer initially is of monatomic height and that the second layer of the new film-substrate configuration consists of almost pure iron. Therefore, we believe that the buried Fe layers are not homogeneously interspersed by copper, and we exclude alloy formation in the film in analogy to Ref. 27.

Comparing the temperatures for the initiation of the enrichment of the surface with Cu atoms, one becomes aware that the temperatures involved are far below the threshold for bulk diffusion. A significant mass transport due to the usual vacancy mechanism is not expected in the Fe-Cu system below 700 K.[21] In order to explain the low thermal stability, two conceivable channels mediating the mass transport may be invoked, namely, surface diffusion and migration through the films along discontinuities. Surface diffusion is the process with the smallest activation energy and can be of significant magnitude already at room temperature.[33] At low Fe coverages ( $<2$ ML) bare patches of the Cu substrate are exposed providing the possibility for copper atoms to diffuse onto the Fe films by surface migration, explaining the early onset of the enrichment of the topmost layer with Cu. At larger coverages this scenario is not applicable any more as no substrate area is exposed in the as-grown layers. Thomassen, Feldmann, and Wuttig[7] attribute the low diffusion temperatures in Fe films in which the bcc structure has already evolved to a mass transport along dislocations. In the coverage regime in which good layer-by-layer growth is observed they state, however, a constant Fe/Cu Auger signal ratio even after increasing the annealing temperature to 577 K. According to them, this suggests that the films possess a high degree of crystalline perfection, since a diffusion characteristic corresponding to pure bulk diffusion is found. Their AES results are severely conflicting with our LEIS data, which show a prominent diffusion process in a 6-ML film well below 470 K.

Scanning tunneling microscopy (STM) results for 4-ML Fe/Cu(001) (Ref. 10) strongly support our LEIS data: For the as-deposited film they show a rather smooth surface due to the formation of an almost pure Fe surface produced by coalescence of the Fe islands observed in the initial stage of the growth process. The STM pattern is similar to that of a 6-ML film, indicating that the layer-by-layer growth regime has already been reached at a coverage of 4 ML. Annealing such a 4-ML film to 500 K for 10 min gives rise to significant changes of the film morphology. Rectangular holes appeared, with a depth clearly exceeding the thickness of the iron film. These holes were interpreted as sources for Cu atoms spreading out onto the Fe film. Similar result were also obtained for Co/Cu(001).[32]

A recent high-precision LEED study on 8-ML Fe/Cu(001) shows that within the layer-by-layer growth regime, iron grows in a nonpseudomorphic way, i.e., "Its lattice coincides with that of equiliburm fcc iron rather than with that given by the Cu substrate."[34] This finding necessarily implies that dislocations also exist in these films.

Bearing in mind these investigations as well as our LEIS results, it seems to be very unlikely that the Fe films in the layer-by-layer growth region will resist treatment up to temperatures for which bulk diffusion becomes important. Instead, we propose a different diffusion model for all coherent iron films deposited on Cu(001): Annealing the samples causes the formation of migration channels, most likely along discontinuities in the films, widening defects to holes. By simple surface diffusion along the walls of these craters the mass transport necessary to bury the Fe films primarily with a single monolayer is readily achieved even at moderate temperatures. Since initially our LEIS analysis detects essentially no Cu in the subsurface layer, the total area of the migration channels must be small, which is confirmed by STM studies. The absence of substrate atoms in the second layer is also a distinct indication that apart from the diffusion holes the entire Fe layer remains intact. This is in accordance with the Fe-Cu bulk phase diagram, not permitting any intermixing at the temperatures employed.[26] The driving force for the enrichment of the surface with copper is the interplay of the surface and interfacial free energies. For the Cu-Fe-Cu sandwich structure the total free-energy balance is reduced, if the energy gained by covering the surface with copper instead of iron exceeds the energy necessary for the formation of a second Fe-Cu interface. Possibly the energy is lowered most effectively by covering the adsorbate with one or two Cu monolayers. Strain energy built up in the Cu overlayer might prevent the migration of further substrate material onto the film.

## V. CONCLUSION

In summary, we have applied low-energy ion scattering to study the diffusion behavior of ultrathin iron films epitaxially grown on Cu(001). By annealing experiments it was shown that none of the as-grown layers is thermally stable even at temperatures far below values at which bulk diffusion becomes important. The onset of compositional changes at the surface depends on the iron coverage. Films not wetting the substrate to a full extent exhibit significant diffusion already at room temperature. Larger coverages are more stable. Investigations using impact-collision ion-scattering spectroscopy impressively indicate the initial enrichment of the surface with a single monolayer of copper. Consistently, the first subsurface layer was found to consist of almost pure iron confirming that the modifications in surface composition are not due to Fe agglomeration. Instead, copper atoms must penetrate the films leaving the buried iron layers more or less untouched. In the thinnest films ( $<2$ ML) the mass transport occurs most likely via lateral surface diffusion. For larger coverages we propose a mechanism in which substrate atoms are spreading out from local point sources rather than diffusing homogeneously through the film. This supposition is corroborated by STM studies at ultrathin iron and cobalt films on Cu(001).[10,32]

Furthermore, our LEIS results show that for Fe films exhibiting a well-characterized bcc structure, a copper overlayer of monatomic height continuing the film's bcc lattice could be produced by annealing.

Similar to related systems of metastable ultrathin films with mutual immiscibility of the components, the Fe-on-Cu system in thermodynamic equilibrium seems to prefer a sandwich structure, with a few layers of substrate material coating the deposit, instead of a Volmer-Weber morphology in order to satisfy energetic constraints.

It has been demonstrated that the use of ion-scattering methods offers a unique chance for a more comprehensive understanding of the thermodynamic behavior of metastable ultrathin films. Further application to others systems is a promising challenge for future work.

## ACKNOWLEDGMENTS

The authors thank V. Dose for continuous interest and support and Th. Fauster for helpful discussion and a critical reading of the manuscript.

---

[1] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988), p. 11.

[2] E. Bauer, Z. Kristallogr. **110**, 372 (1958); **110**, 395 (1958).

[3] A. Clarke, P. J. Rous, M. Arnott, G. Jennings, and R. F. Willis, Surf. Sci. **192**, L843 (1987).

[4] Y. Darici, J. Marcano, H. Min, and P. A. Montano, Surf. Sci. **217**, 521 (1989).

[5] D. A. Steigerwald, I. Jacob, and W. F. Egelhoff, Jr., Surf. Sci. **202**, 472 (1988).

[6] H. Glatzel, Th. Fauster, B. M. U. Scherzer, and V. Dose, Surf. Sci. **254**, 58 (1991).

[7] J. Thomassen, B. Feldmann, and M. Wuttig, Surf. Sci. **264**, 406 (1992).

[8] M. Arnott, E. M. McCash, and W. Allison, Surf. Sci. **269/270**, 724 (1992).

[9] D. D. Chambliss, R. J. Wilson, and S. Chiang, J. Vac. Sci. Technol. A **10**, 1993 (1992); D. D. Chambliss, K. E. Johnson, R. F. Wilson, and S. Chiang, J. Magn. Magn. Mater. **121**, 1 (1993); K. E. Johnson, D. D. Chambliss, R. J. Wilson, and S. Chiang, J. Vac. Sci. Technol. A **11**, 1654 (1993).

[10] A. Brodde and H., Neddermayer, Surf. Sci. **287/288**, 988 (1993).

[11] H. Landskron, G. Schmitt, K. Heinz, K. Müller, C. Stuhlmann, U. Beckers, M. Wuttig, and H. Ibach, Surf. Sci. **256**, 115 (1991).

[12] Th. Detzel, N. Memmel, and Th. Fauster, Surf. Sci. **293**, 227 (1993).

[13] N. Memmel and Th. Detzel, Surf. Sci. (to be published).

[14] M. Wuttig, B. Feldmann, J. Thomassen, F. May, H. Zillgen, A. Brodde, H. Hannemann, and H. Neddermayer, Surf. Sci. **291**, 14 (1993).

[15] E. Taglauer, in *Ion Spectroscopies for Surface Analysis,* edited by A. W. Czanderna and D. M. Hercules (Plenum, New York, 1991), p. 363.

[16] Th. Fauster, Vacuum **38**, 129 (1988).

[17] H. Dürr, R. Schneider, and Th. Fauster, Phys. Rev. B **43**, 1802 (1991).

[18] H. Niehus and R. Spitzl, Surf. Interface Anal. **17**, 287 (1991).

[19] Yi-sha Ku and S. H. Overbury, Surf. Sci. **273**, 341 (1992).

[20] H. Dürr, Th. Fauster, and R. Schneider, J. Vac. Sci. Technol. A **8**, 145 (1990).

[21] D. B. Butrymowicz, J. R. Manning, and M. E. Read, J. Phys. Chem. Ref. Data **2**, 643 (1973); D. B. Butrymowicz, J. R. Manning, and M. E. Read, *ibid.* **5**, 103 (1976).

[22] K. Meinel, M. Klaua, and H. Bethge, Ultramicrosc. **20**, 261 (1986).

[23] M. Aono, C. Oshima, S. Zaima, S. Otani, and Y. Ishizawa, Jpn. J. Appl. Phys. **20**, L829 (1981).

[24] M. Aono, Nucl. Instrum. Methods B **2**, 374 (1984).

[25] H. Niehus, Surf. Sci. **145**, 407 (1984).

[26] T. B. Massalski, *Binary Alloy Phase Diagrams* (American Society for Metals, Metals Park, OH, 1986), p. 916

[27] P. J. Schmitz, W.-Y. Leung, G. W. Graham, and P. A. Thiel, Phys. Rev. B **40**, 11 477 (1989).

[28] M. G. Goldiner, V. B. Sabozhnikov, M. Klaua, and K. Meinel, J. Phys. Condens. Matter **3**, 5479 (1991).

[29] W. F. Egelhoff, Jr. and D. A. Steigerwald, J. Vac. Sci. Technol. A **7**, 2167 (1989).

[30] Hong Li and B. P. Tonner, Surf. Sci. **237**, 141 (1990).

[31] W. F. Egelhoff, Jr., J. Vac. Sci. Technol. A **7**, 2060 (1989).

[32] A. K. Schmid, D. Atlan, H. Itoh, B. Heinrich, T. Ichinokawa, and J. Kirschner, Phys. Rev. B **48**, 2855 (1993).

[33] M. T. Kief and W. F. Egelhoff, Jr., Phys. Rev. B **47**, 10 785 (1993).

[34] P. Bayer, S. Müller, P. Schmailzl, and K. Heinz, Phys. Rev. B **48**, 17 611 (1993).