PHYSICAL REVIEW B VOLUME 52, NUMBER 16 15 OCTOBER 1995-II

Unusual surfactant effect and the stability of pseudomorphic γ-Fe films

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(Received 10 August 1995)

An interesting type of surfactant-mediated growth is observed in epitaxy of Fe on Cu(001). It differs from the usual phenomenon by the fact that *two* species, oxygen and carbon, are required to suppress three-dimensional islanding. Alone they have little or no detrimental effect on the growth mode. One of the species dissolves in Fe, drastically affecting the stability of this pseudomorphic ultrathin film system.

In general the epitaxy of ultrathin films proceeds in a complicated fashion depending on details of surface energetics and kinetics but rarely in a highly desirable layer-by-layer mode. For example, many semiconductor and the majority of metal epitaxial systems exhibit a strong tendency for three-dimensional (3D) islanding. Several recent reports have shown that this tendency can be effectively suppressed by preseeding the substrate with a small (less than a monolayer) amount of the third substance. It is usually a single element that acts as a surfactant, e.g., Sn in Si/Si growth,[1] As in Ge/Si growth,[2] and Sb in homoepitaxy of Ag.[3] Such surfactant mediated growth is a promising method for controlling the morphology of thin epitaxial films.

In this paper an interesting type of surfactant-mediated growth is reported. It differs from the usual phenomenon by the fact that *two* elements are required to suppress the 3D islanding; in this case carbon and oxygen. Alone they have little or detrimental effect on suppression of islanding in Fe/Cu growth.

In heteroepitaxial growth, it is sometimes possible to grow films that assume the structure of the substrate even if this deviates from the equilibrium bulk phase. An example of such a system is a high-temperature fcc phase of Fe that can be grown on Cu. Such pseudomorphic films offer the unique possibility of studying the physical properties of solids in unusual states but their investigation is often hindered by the inherent instability of such systems. Again the Fe/Cu system provides a good example—a martensitic transformation is observed starting as early as 4–5 ML and resulting in a complete transformation into bcc at 10–12 ML.[4,5] There are indications that the onset of this transformation may be connected with unusual changes in properties of this widely studied magnetic system.[6–8,4]

In this paper we will also report on the structural stabilization of the pseudomorphic fcc iron films obtained with a small admixture of interstitial carbon. The stabilization is quite dramatic; "perfect" fcc films of up to 60-ML thickness with excellent surface quality can be obtained. The fact that pseudomorphic films can be stabilized with interstitials opens a completely different way to control the structural properties of ultrathin systems.

The presence of carbon is expected to stabilize the γ phase of Fe.[7,11] Carbon is partially soluble in iron where it occupies interstitial sites. The octahedral interstice in γ-Fe is 0.52 Å while the tetrahedral interstice in α-Fe is 0.36 Å with the corresponding carbon solubilities of 8.9 and 0.095 at. %, respectively.[9] It seems plausible that the martensitic transformation observed at 4–5 ML in "pure" fcc iron films could be sterically hindered in γ C–Fe films as any transformation to bcc would require substantial precipitation of carbon. Furthermore, 6 at. % of interstitial carbon is estimated to cancel another source of instability due to the lattice mismatch between fcc-Fe and Cu[10] since the carbon content increases the lattice constant.

The iron films were deposited in an ultrahigh vacuum (UHV) chamber (base pressure 4×10^{-11} mbar) with Auger electron spectroscopy, low- and medium-energy electron diffraction (LEED and MEED), and magneto-optical Kerr effect (MOKE) characterization facilities. Scanning tunneling microscopy (STM) images were taken in a separate chamber with similar capabilities. Fe was evaporated (0.8–1.2 ML/min) onto the clean and annealed Cu(001) surface kept at 300±5 K. Carbon and oxygen contamination of directly deposited iron was in the range of 1–2 at. %. Carbon-assisted stabilization was attempted by introducing carbon-containing gases through a leak valve during the deposition of iron.

Fig. 1(a) shows MEED data for a "pure" Fe film. The intensity shows well-defined oscillations up to thicknesses of 10–12 ML. They are characteristic of a good layer-by-layer growth. LEED patterns suggest the film is fcc over the entire 0–10-ML range. However, recent real-space STM data indicate the onset of a martensitic fcc→bcc transformation already at 4–5 ML.[4] Only at a much more advanced transformation stage does this bcc phase become evident in the diffraction data. The transformation into bcc is essentially completed at 10–12 ML. The sudden collapse of the MEED intensity at this thickness, seen in Fig. 1(a), is due to the pronounced roughness of the final bcc phase.

Figure 1(b) presents the corresponding MEED data for a film grown in the presence of acetylene (C_2H_2). The acetylene was chosen because it is known to dissociate on most transition-metal surfaces. With acetylene MEED oscillations are observed to continue well above the thickness where the nonassisted "pure" growth shows a fully transformed bcc film. The STM images of this film confirm the fcc character of the entire film. The step heights are those of the fcc phase, but the quality of the film surface is poor. This is reflected in the MEED data—the oscillations persist but their amplitude is decaying rather precipitously. The thickness at which this film converts finally into bcc is not known. No traces of bcc phase have been detected in STM images, neither have there been any changes in the LEED pattern symmetry. Almost

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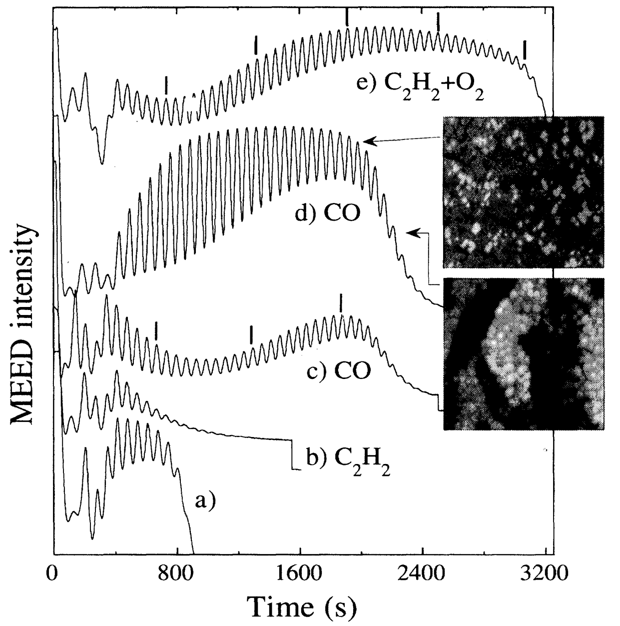

FIG. 1. MEED intensity vs growth time under different growth conditions: (a) "pure" growth, (b) $p_{C_2H_2}=3\times10^{-9}$ mbar, (c) $p_{CO}=3\times10^{-9}$ mbar, (d) $p_{CO}=6\times10^{-9}$ mbar, and (e) mixture of $p_{C_2H_2}=2\times10^{-9}$ and $p_{O_2}=6\times10^{-9}$ mbar. Each periodic maximum of the MEED data corresponds to the completion of one layer. The insets show surface morphology (same 100-nm^2 area) of a CO-deposited film before (top, 30 ML) and after (bottom, 34 ML) the fcc-bcc transformation. The gray scale is adjusted to show the full vertical range and corresponds to 0.54 and 2.6 nm, respectively.

identical MEED behavior is seen for films grown in ethylene (C_2H_4) but films deposited in the presence of methane (CH_4) are indistinguishable from those deposited in a clean vacuum. The lack of any effect of methane on the growth of the film is consistent with Auger data: only acetylene and ethylene cause incorporation of carbon into the growing film; methane-grown films show only residual increase in carbon content. This is consistent with known adsorption properties of all three hydrocarbons: the reactivity of methane is substantially lower than that of the other two hydrocarbons.[12,13]

The data discussed above present clear evidence for carbon-induced stabilization. Almost a twofold increase in stability of the fcc phase is obtained (up to minimum of 20 ML). The martensitic transformation is suppressed, no traces of the bcc phase that are clearly visible in "pure" Fe films[4] could be detected over the entire thickness range. This stability must be due to the incorporated carbon. The evidence for the carbon incorporation comes from Auger data and from the interplanar expansion observed in the IV-LEED data as will be discussed later.

Surprising results were obtained when iron was deposited in the presence of carbon monoxide. Little effect was initially expected because CO does not chemisorb on γ-Fe surfaces.[14] Figures 1(c,d) show MEED data for films grown in the presence of CO and indicate a different behavior. The presence of CO strongly affects the Fe growth; the MEED oscillations continue up to 35 ML. Moreover, the oscillations almost completely recover the original intensity between 15 and 30 ML, as can be seen in Fig. 1(d). This MEED behavior is supported by the excellent surface topography observed in STM images (see inset, Fig. 1). Apparently the deposition in the presence of CO not only stabilizes the fcc phase but also modifies the growth mode, i.e., CO acts also as a surfactant. In the entire thickness range below 35 ML the film is clearly fcc. The evidence is multifold: (a) the LEED patterns do not show any signs of the bcc phase and remain sharp throughout the entire range, (b) the step heights measured by STM are those of the fcc phase, and (c) the IV-LEED data show the features characteristic of the fcc phase. Corresponding data for films thicker than 35 ML show that the collapse of MEED intensity is due to the film starting to convert into bcc form. Significantly, the collapse into bcc appears to be independent of the partial pressure of CO [Figs. 1(c) and 1(d)].

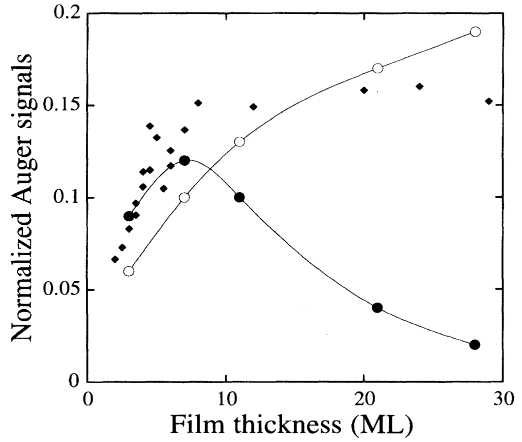

FIG. 2. Carbon and oxygen uptakes for Fe film grown in the presence of 6×10^{-9} mbar CO. Normalized carbon and oxygen peak amplitudes are plotted: $C_{272}/(Fe_{703}+Cu_{920})$ for carbon (full circles), and $O_{503}/(Fe_{703}+Cu_{920})$ for oxygen (open circles). Also shown is the carbon Auger signal for films grown with 3×10^{-9} mbar of acetylene (diamonds).

As was the case with ethylene and acetylene, the films grown in the presence of CO show an increased carbon content. The uptake, however, is much different from what is observed for hydrocarbons where a linear increase of Auger signals followed by an electron-escape-depth-induced saturation is consistent with the constant rate of carbon incorporation.

The Auger data for the CO-assisted growth (Fig. 2) show continuous increase of the oxygen signal with coverage, while carbon slowly drops down to the level typical of the "pure" growth. These observations strongly imply a dissociation of adsorbed CO followed by "floating out" of oxygen to the surface with carbon left behind. This mechanism is indirectly but convincingly confirmed by the appearance of a $c(2\times2)$ LEED superstructure on top of the γ-Fe pattern. This superstructure appears only if a sufficient amount of CO is dissociated and is identical to the structure induced by a small amount (1–8 Langmuir) of O_2 adsorbed onto a clean fcc Fe(001) surface. Furthermore, the energy dependencies of these structures (IV-LEED) are identical in both cases, which would be an unlikely coincidence unless the oxygen does actually float out to the surface.

As no stable chemisorption is observed on clean fcc Fe(001) at 300 K (Ref. 14) this unexpectedly strong interac-

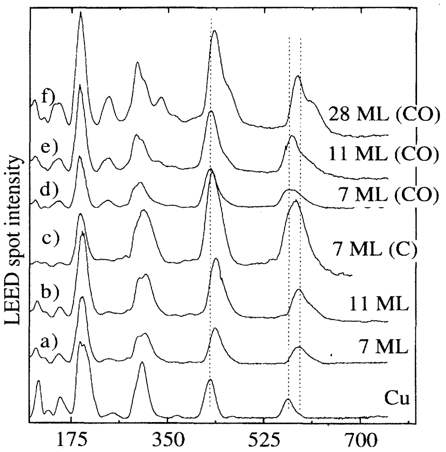

FIG. 3. Energy dependence of the intensity of the (11) LEED reflex for Cu substrate and Fe films of various thicknesses and under different preparation conditions. For the CO and C_2H_2 assisted deposition a partial pressure $p_{CO} = 6\times10^{-9}$ mbar was used. Positions of the two highest energy peaks at approximately 420 and 600 eV are used to deduce the interplanar spacing of Fe relative to Cu. The contraction seen in 7-ML-thick Fe film is almost eliminated when film is deposited in the presence of CO.

tion of CO with fcc Fe must have its origin in the dynamical conditions existing on the surface during growth. The presence of a large number of energetic, mobile adatoms may facilitate the creation of "transient" active sites that are responsible for the dissociation of CO. It is difficult to speculate about the nature of such sites—steps are unlikely because they are also present on inert fcc Fe surfaces. Small clusters are more likely because they could have much different adsorption properties. Furthermore, energy accommodation processes may be involved in bond breaking.

With increasing thickness the amount of carbon in the topmost three to four layers drops down to background level. We suggest that this drop is connected with the higher coverage of oxygen on the surface of thicker films. Oxygen may block whatever special sites were originally responsible for dissociation of CO, which would result in the observed CO uptake behavior. This conclusion appears more plausible if we note that a similar blocking effect is, indeed, observed in the interaction of CO and O_2 on bcc-Fe surfaces.[15]

Figure 3 shows the IV-LEED data for the clean Cu substrate and for Fe films deposited in the presence of C_2H_2 (c), CO (d–f), and without any gases present (a,b). In a simple kinematic approximation, the position of the main features of the IV-LEED spectra can be related to the interplanar distances of the topmost two to three surface layers. In clean Fe films these are clearly contracted relative to Cu—note the shift of 400 and 600 eV peaks toward higher energies.[16] In films that were stabilized with carbon, the shift is compensated, partially for C_2H_2-assisted growth and almost completely in the case of CO. These observations strongly suggest an expanded lattice constant that must be due to the incorporation of carbon into the iron lattice. For thicker films [28 ML—Fig. 3(e)] the peaks move back to higher energies, confirming the blocking effect discussed above. The final collapse into bcc is observed at around 35 ML and may be associated with carbon depletion observed in the later stages of the CO-assisted growth.

As discussed above, the main difference between films deposited in the presence of CO and films grown in the presence of acetylene is the quality of the film surface. The CO-grown films show very good, almost ideal layer-by-layer growth over most of the thickness range. Since the hydrocarbons alone produce much worse surfaces, we have to conclude that oxygen acts as a strong surfactant. To test this hypothesis a film was deposited in the presence of one of the hydrocarbons (C_2H_2) and oxygen. The relevant MEED data are shown in Fig. 1(e), revealing a striking result, especially in comparison with the film deposited in C_2H_2 alone, see Fig. 1(b). 50-ML-thick γ-Fe films of exceptional surface quality can easily be obtained, note the full recovery of the original MEED intensity around 30 ML. The exact behavior of MEED oscillations depends on the relative ratios of the iron flux and the partial pressures of both acetylene and oxygen in a way that strongly suggests oxygen to be playing an identical self-poisoning role (i.e. blocking the incorporation of C_2H_2) that had been observed for the CO-assisted growth. There is also some evidence that even thicker films (up to 80 ML) can be stabilized by optimizing the growth conditions.

On the other hand, the films grown in the presence of oxygen alone ($p = 0.5-10\times10^{-9}$ mbar) show the MEED behavior to be practically indistinguishable from that of "pure" iron, i.e., there is no stabilization and the growth mode does not appear affected in any perceptible way.[17] This happens despite the fact that oxygen is present on the surface as indicated by the appearance of a c(2×2) LEED superstructure and by Auger data. Clearly, oxygen alone is insufficient to modify the growth mode of iron films, the presence of carbon is required.

Neither of the techniques employed in this study can provide a detailed understanding of this remarkable surfactant effect. The usual model is that of a single surfactant dramatically enhancing the rate of interlayer transport either by reducing the step-crossing barriers or by increasing the nucleation density or by some other mechanism. At present it is not clear in which way the interlayer transport is modified by the presence of the two adsorbates.

Preliminary MOKE data for thicker (10–60 ML) CO and C_2H_2/O_2 stabilized films do not show any ferromagnetic ordering down to 100 K. This is in good agreement with properties of small fcc-Fe particles precipitated in Cu; they are antiferromagnetic with a Neél temperature of about 60 K.[18]

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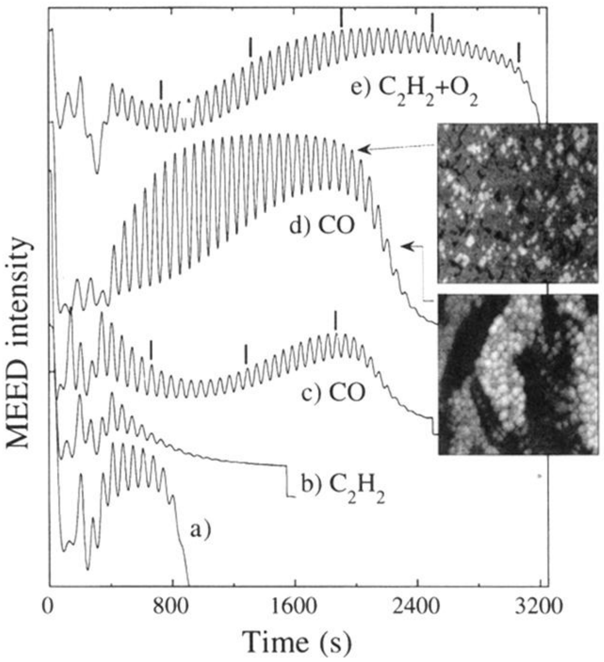

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