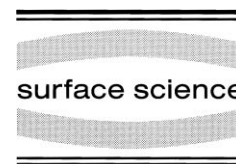




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Surfactant properties of chemisorbed oxygen in Fe/Fe(001) homoepitaxy: a He diffraction study

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Abstract

He diffraction measurements show that preadsorption of an $O(1 \times 1)$ phase on Fe(001) promotes two-dimensional growth of Fe at temperatures below 400 K, in contrast to the island growth observed on the bare Fe(001) surface. Oxygen floats at the surface, acting as a surfactant. After repeated cycles of film annealing and Fe re-deposition, a beat is observed in the pattern of He reflectivity measured as a function of deposition time. The beat is assigned to the growth on surface domains characterized by a different surfactant efficiency. © 2000 Elsevier Science B.V. All rights reserved.

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Ultra-thin iron films have been extensively studied for their importance in the field of magnetic systems of reduced dimensionality and small-scale magnetic devices. Many different substrates have been considered so far, often with the declared aim to ‘design’ films with unusual properties. However, deposit/substrate intermixing processes impose, on many substrates, severe constraints on the choice of the temperature of deposition; low temperatures, kinetically limiting or even inhibiting intermixing, usually lead to films of poor morphological quality. An appealing method by which to obtain elementally pure and smooth films, developed in studies on semiconductors heteroepitaxy [1], is provided by surfactant species. Indeed, there has recently been a continuous effort towards elucidating the atomistic processes responsible of

surfactant-assisted growth, from both the experimental [2–4] and theoretical point of view [5–7].

In this respect, the measurement of the intensity of He diffraction (HeD) peaks as a function of exposure time [in brief, ‘deposition curves’ or $R(t)$] is a well established tool with which to characterize the growth front in real time [8–10]; HeD deposition curves have also been exploited to investigate quantum size effects affecting film growth [11–13] and, more recently, to study the surfactant effect [4,14,15].

In this work, HeD is used to demonstrate the surfactant properties of an ordered layer of atomic oxygen in the Fe/Fe(001) growth. Interestingly, a well-defined beat is observed in the deposition curves under determined growth conditions. Indeed, beats have already been reported in RHEED experiments [16], but their origin is still not completely understood. We will discuss the origin of the observed beat in terms of a local efficiency of the surfactant action.

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The experiments have been carried out in a UHV apparatus (base pressure of the order of 5×10^{-11} mbar), fully described in previous papers [17].

The Fe(001) surface (orientation $\pm 0.5^\circ$) has been prepared through a great number of cycles of sputtering and annealing (a few μA of Ne^+ at 3 keV for several hours followed by heating up to 700 K); frequent exposures in UHV at high temperature to O_2 and H_2 were used to lower the quantity of segregating impurities (mainly sulfur). Annealings have been monitored by HeD to look at surface long-range order and by ARUPS to control surface purity. After preparation, HeD patterns showed an intense specular peak and faint first-order diffraction peaks; the specular peak width turned out to be approximately three times larger than the instrumental resolution, indicating a typical domain size of the order of 100 Å. ARUPS results were in agreement with data in the literature [18].

Iron was deposited by an electron bombardment source. The chamber pressure, during typical depositions (5–20 ML at 1 ML/min) remains below 5×10^{-10} mbar.

We first studied Fe/Fe(001) growth without surfactant. $R(t)$ curves measured in antiphase conditions under different substrate temperatures (T_s) are shown in Fig. 1. The data are representative of a more extended series of measurements, taken at several deposition rates.

At room temperature (RT, Fig. 1A), weak damped oscillations are superimposed upon a strongly decaying average intensity, indicating that the roughness of the growing front increases rapidly [19], in agreement with RHEED data for Fe homoepitaxy on whiskers [20]. The growth mode moves towards a two-dimensional (LbL) regime at higher T_s , always in agreement with Ref. [20]. At 415 K (Fig. 1B), however, oscillations are still damped, suggesting that the system is far from LbL growth. Concerning growth at $T_s = 415$ K, we attempted an estimate of the interface width, W , as a function of the exposure time, t . The specular intensity as a function of perpendicular momentum transfer was measured after stopping deposition at the fourth, fifth, seventh, and 10th maximum of $R(t)$ and was analyzed according

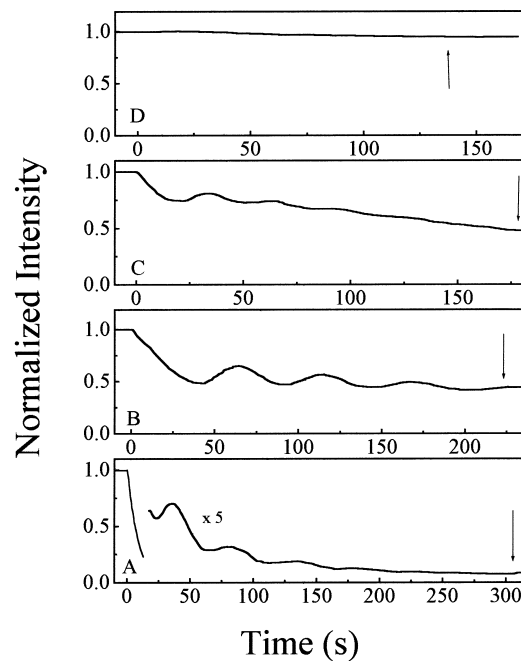


Fig. 1. He ($k_i = 5.87 \text{ \AA}^{-1}$) reflectivity measured as a function of time during Fe growth on Fe(001). Arrows indicate shutter closure. (A) $T_s = 300$ K; deposition rate: 1.5 ML/min; (B) $T_s = 415$ K; deposition rate: 1 ML/min; (C) $T_s = 500$ K; deposition rate: 0.5 ML/min; (D) $T_s = 715$ K; deposition rate: 1 ML/min.

to the model developed in Ref. [21]; three exposed layers were enough for a satisfactory analysis, which indicates that in the 4–10 ML range, W increases as t^β with $\beta = 0.22$, close to the value (0.18) obtained in simulations applied to describe STM data of the Fe/Fe(001) growth [22]. At higher T_s values (500 K, Fig. 1C), the system evolves towards a step flow regime, fully appreciable in Fig. 1D ($T_s = 715$ K). The step flow regime at high T_s values is to be related to the step density of our sample, which is two orders of magnitude larger than that reported on whiskers of Ref. [20].

In order to study the effect of oxygen on film growth, we prepared a well-ordered $\text{O}(1 \times 1)$ phase; the overlayer was formed by exposure of the Fe surface, after a light sputtering, to O_2 (3–4 L at room temperature), followed by annealing at 800 K. The phase has been characterized by HeD and ARUPS. The $\text{p}(1 \times 1)$ He diffraction pattern exhibits a specular peak slightly broader

than the instrumental resolution and intense first- and second-order diffraction peaks. The specular intensity as a function of the incidence angle (not reported) shows well-defined minima, assigned to the well-known diffraction-mediated selective adsorption resonances (DMSAR) [23], induced by the exchange of (10), (01), and (11) surface reciprocal lattice vectors. The sharpness and deepness of the DMSAR structures instil confidence that the oxygen phase is well ordered and that the diffractive coupling is strong. ARUPS measurements are in agreement with the results of Ref. [24].

We measured numerous He deposition curves at various T_s values and deposition rates. Up to the onset (~ 500 K) of the step flow regime, all the measured $R(t)$ present regularly spaced, cuspidated oscillations, as shown in Fig. 2, both in antiphase and in in-phase conditions. After an initial rapid decay, the $R(t)$ continues to oscillate about a nearly constant level, indicating that the thickness of the growing front remains essentially constant, as in LbL growth [25]. We note that in the case of surfactant-assisted growth close to RT, the intensity of $R(t)$ at the 10th maximum is still $\sim 18\%$ of the initial intensity (and $\sim 50\%$ of the intensity at the first maximum); under comparable experimental conditions but without surfactant, the intensity decreases and is practically indistin-

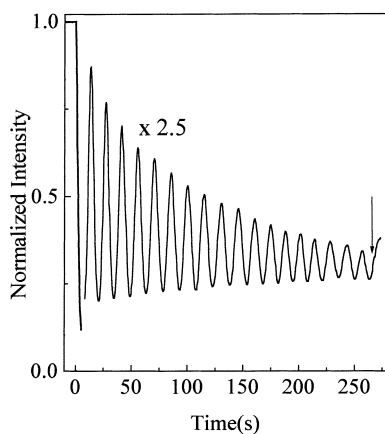


Fig. 2. He ($k_i = 5.87 \text{ \AA}^{-1}$) reflectivity measured as a function of time during Fe growth upon a freshly prepared $O(1 \times 1)$ -Fe(001) phase; $T_s = 350$ K; deposition rate 4.21 ML/min. The arrow indicates shutter closure.

guishable from background signal already at an exposure corresponding to five oscillations.

The intensity of the first-order diffraction peaks oscillates during deposition as well. Further, after completion of 10 layers, the measured DMSAR patterns present the same structures found prior to deposition. All these findings indicate that oxygen floats on the surface during growth, maintaining the (1×1) structure and corrugation, thus assuring the continuity of the surfactant action. This conclusion is in agreement with a parallel experiment on the surface magnetism of Fe films deposited on a $O(1 \times 1)$ -Fe(001)/MgO(001) system; in fact, an analysis of the surface electronic density of states reveals that the surface composition remains practically unchanged, passing from a minimum to a maximum of the He deposition curve [26].

After deposition, the annealing at 650 K induces a substantial recovery of the diffraction intensities measured on the freshly prepared oxygen phase. Interestingly, after repeated cycles of film annealing and re-deposition, the damping of oscillations increased, and the $R(t)$ curves showed a modulation that looked like a beat. As an example, in Fig. 3 an $R(t)$ obtained after five cycles of growth of 10 ML and annealing is reported. The seventh

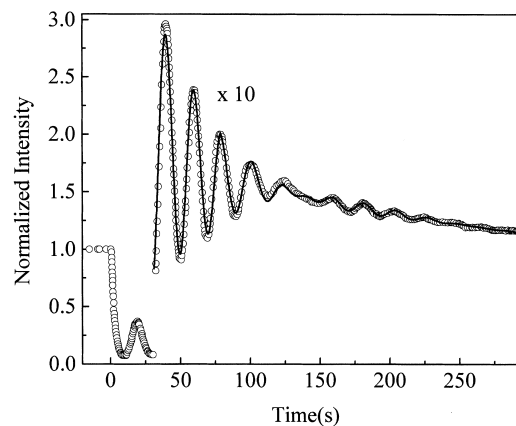


Fig. 3. Comparison between Eq. (1) (solid line) and the He reflectivity measured during oxygen-assisted Fe growth ($T_s = 350$ K; deposition rate ~ 3 ML/min) after several annealing/re-deposition cycles (see text for details on the fit). In order to aid comparison, the experimental curve is represented here by open circles.

maximum is missing, and after this vacancy, a moderate recovery in the oscillation intensity can be appreciated. The same modulation was observed, also varying the deposition rate in the 0.5–5 ML/min range.

The power spectrum of the $R(t)$ curve of Fig. 3 shows a single broad peak. The shape of the peak and its width, approximately three times larger than the peak found in the power spectrum of the $R(t)$ of Fig. 2, is compatible with a convolution of narrower peaks located at two slightly different frequencies. We then resorted to a fit, adopting the following empirical formula:

$$R(t) = A \exp(-\alpha_1 t) \times \{\cos(2\pi\nu_1 t) + \cos(2\pi\nu_2 t)\} + B \exp(-\alpha_2 t) + C. \quad (1)$$

A , α_1 , B , α_2 , and C control the amplitude and the exponential decay of the oscillations superimposed upon an average intensity that decays exponentially; ν_1 and ν_2 are the key parameters responsible for the beating. A satisfactory fit (line in Fig. 3) is obtained with $\nu_1 = 0.0482$ Hz and $\nu_2 = 0.0515$ Hz.

According to mean field models, as the growth mode moves from ideal LbL towards non-diffusive growth, the position of the maxima in $R(t)$ curves becomes shifted with respect to the integral average film thickness [19]. As the beating occurs after several deposition/annealing cycles, it is therefore tempting to assign the oscillation at the higher frequency, ν_2 , to domains where the oxygen action is fully efficient, while ν_1 could be related to domains where the surfactant efficiency has been reduced after surface treatments. In this respect, it is useful to consider the model proposed in a recent work on the growth of Cu on Pb/Cu(111) [4]. Comparing HeD and STM data with simulations, it is shown that easy incorporation of incoming Cu below the Pb layer inhibits intralayer diffusion, while interlayer transport, promoting LbL growth, still occurs by exchange with atoms at the borders of nucleated islands. As stressed in Ref. [4], the model implies a strictly ‘local’ surfactant action; the quality of films is therefore directly related to the compactness of the surfactant layer. The atomistic processes involved in the model of Ref. [4] are rather general and could therefore

work also in our system. In this view, the loss of surfactant efficiency could be due to an inhomogeneous quality of the overlayer resulting from repeated surface treatments. Oxygen vacancies seem to be plausible faults locally affecting the quality of the $O(1 \times 1)$ phase and, as a consequence, the surfactant efficiency. Vacancies could result from the kinetic failure of the Fe/O exchange mechanism [27], occurring both during re-depositions and in annealing stages, finally leading to the trapping of oxygen into the film.

In conclusion, preadsorption of an $O(1 \times 1)$ overlayer on Fe(001) promotes LbL growth of Fe below 400 K, in contrast to the island growth observed on the bare Fe(001) surface. Oxygen floats at the surface and acts as a surfactant by promoting the interlayer Fe transport through an exchange mechanism. A modulation of the deposition curves measured on the oxygen-covered film after a few cycles of annealing and Fe re-deposition, due to the presence of two slightly different frequencies, is assigned to the presence of faulty domains where the surfactant effect is less efficient. We have considered a compact oxygen phase, of easy and highly reproducible formation; an interesting development of this work could be the study of the surfactant properties of a less compact oxygen layer, such as the $c(2 \times 2)$ phase reported in the literature at a lower coverage [28].

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