

Growth mode and atomic structure of ultrathin Fe films on Rh{001} determined by quantitative low-energy electron diffraction

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The epitaxial growth of Fe on Rh{001} at room temperature is studied by means of quantitative low-energy electron diffraction and Auger electron spectroscopy. The Fe films are pseudomorphic to the substrate and grow in the layer-by-layer mode for at least three layers—no attempts were made to determine the growth mode above this thickness. The spacing between Fe and Rh at the substrate-film interface remains approximately the same (about 1.75 Å), within experimental error, when the Fe films grow from one to two and three layers. The Fe-Fe interlayer spacing in the bilayer films is also about the same (1.73 Å), but in the three-layer film the first two interlayer spacings collapse to about 1.65 Å. Thicker (eight- to ten-layer) Fe films have bulk spacings of 1.56 Å and a 5.8%-expanded surface interlayer spacing (1.65 Å). These films have a compressive strain in the film plane (the misfit to Rh{001} is -6.3%) and have a body-centered-tetragonal structure. Elastic strain analysis shows that the equilibrium (i.e., the unstrained) phase is bcc Fe; the bulk interlayer spacing in the films is expanded by 8.7% over the equilibrium value of bcc Fe (1.43 Å) as a consequence of the epitaxial strain in the plane of the layers, and the atomic volume is reduced by 4.5%.

I. INTRODUCTION

In the study of ultrathin epitaxial films two properties are of particular interest: how the films grow (i.e., what the growth mode is) and how large a strain they have (if any). Ultrathin films are defined here as films with thicknesses up to a few tens of atomic layers—they are therefore not self-supporting, but must be supported by the substrate on which they are grown. We briefly summarize below the present situation, first with regard to studies of the growth mode in epitaxial systems and second with regard to investigations of strains in ultrathin films.

Growth mode. There is not yet a single well-tested technique which allows unambiguous determination of the growth mode, and perhaps for this reason there is much controversy over the mode of growth in several epitaxial systems. Three techniques are usually employed for this purpose: Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and reflection high-energy electron diffraction (RHEED).

A widespread tendency in the literature is to declare that growth occurs layer by layer (in the so-called Frank-van der Merwe, or FvM, mode) if and when the Auger signal from the film (or substrate) material increases (or decreases) in a piecewise-linear manner with increasing deposition time, thus exhibiting the so-called Auger breaks. Each Auger break is then assumed to be associated with the completion of one atomic layer of the film. This conclusion, however, is not necessarily correct, because Auger breaks can occur for reasons other than FvM growth.^{1,2} Similarly, the conclusion, often reached

in the literature, that FvM growth occurs if and when a 1×1 LEED pattern is observed in the early stages of growth is also not necessarily correct, because 1×1 LEED patterns can also be produced by other mechanisms, e.g., by pseudomorphic flat multilayer islands of the growing film. Finally, the widely accepted notion that the occurrence of oscillations of the specular intensity in the RHEED spectra (so-called RHEED oscillations) signals the occurrence of FvM growth is also not necessarily correct, because there is more than one reason for RHEED oscillations to occur in any given epitaxial system.³

The safe statement to make about the use of AES, LEED, and RHEED in this kind of study is that Auger breaks, 1×1 LEED patterns, and RHEED oscillations are necessary but not sufficient indications of FvM growth in pseudomorphic epitaxial systems. To confirm the occurrence of FvM growth it is advisable to seek the *additional* help of less ambiguous techniques, such as, e.g., scanning tunneling microscopy (STM—e.g., a recent STM study of homoepitaxy of Fe on Fe{001} has provided evidence for island growth despite the observation of RHEED oscillations⁴), or *quantitative* LEED—the word *quantitative* implying that diffracted intensities [more precisely, intensities *versus* voltage or $I(V)$ curves] are measured and used for comparison either with other experimental intensities or with calculated intensities for purposes of identification.

A 1×1 LEED pattern may be observed in the early stages of epitaxy even when the film grows by way of small islands, as in this case the bare areas of the substrate are the ones responsible for producing the LEED pattern. Measurement of $I(V)$ curves and comparison

with those measured on the clean substrate is usually sufficient to establish this fact, at least in the cases where monolayer islands of the growing film would be expected to alter the $I(V)$ curves perceptibly.⁵ (These are the cases in which substrate and film atoms are at least one row apart from one another in the Periodic Table of the elements.) If the $I(V)$ curves measured in the early stages are different from those of the clean substrate, then the possibility of FvM growth exists, but direct confirmation is necessary. Such confirmation requires fulfillment of two conditions: (i) Knowledge of *when* an integral number of atomic layers of the film is completed (a difficult thing to do experimentally), and measurement of the $I(V)$ curves at those junctures; and (ii) fitting of the experimental data by curves calculated for models involving completed layers. In the work reported here these two conditions were reasonably well satisfied, as will be shown below.

The controversies over growth modes are also complicated by problems of reproducibility in surface preparation and ambient conditions between different laboratories, e.g., presence or absence of impurities, temperature of the samples,⁶ purity of the sources of film material, growth rates, etc. It would be very desirable, in this respect, to be able to conduct growth experiments with more than one unambiguous technique in the same experimental chamber, but this condition has not been fully met so far. Typical examples of contrary assertions that have been made about growth modes are Fe/Cu{001} (Refs. 7 and 8), Fe/Ag{001} (Refs. 5 and 9), and Fe/Au{001} (Refs. 10–12). Note that a theoretical study of the probability of FvM growth based on surface free-energy considerations¹ discounted FvM growth for all the above systems, but considered the Co/Cu{001} system “borderline.” Experimentally, Co/Cu{001} exhibits very good LEED patterns, RHEED oscillations, and Auger breaks,¹³ but a different study with angle-resolved x-ray photoemission spectroscopy (ARXPS) indicates two-layer islands in the zero- to two-layer regime.¹⁴ The Cr/Au{001} system was considered to “favor” FvM growth¹⁵ despite the fact that no Auger breaks were observed, but a later study¹⁶ showed alloying.

Strains. When an epitaxial film grows pseudomorphically it is generally either compressed or expanded in two directions in the plane of the interface, because pseudomorphism forces the growing film to assume the lattice parameters of the substrate surface. This in-plane strain, or parallel strain, or epitaxial strain, is produced by, and is equal to, the misfit between the mesh constant of the substrate surface on one hand and the mesh constant of the equilibrium (i.e., the unstrained) phase of the film on the other. As a consequence of this epitaxial strain the interlayer spacing in the bulk of the film will be altered (i.e., expanded or compressed) from the value prevailing in the equilibrium phase, i.e., a perpendicular strain will be produced. To determine this perpendicular strain one needs to determine the interlayer spacing in the bulk of the film and one needs to know the equilibrium phase of the growing film. The ratio of perpendicular to parallel strain, the so-called strain ratio, can be calculated from ratios of the elastic constants of the film's equilibrium

phase within the limits of linear elasticity theory¹⁷ and can then be compared with the strain ratio measured experimentally.

How do we measure the interlayer spacing in an ultrathin film? In principle, there are a few experimental techniques which can do this kind of measurement, e.g., medium-energy ion scattering, quantitative LEED, and perhaps surface x-ray diffraction. But in practice only quantitative LEED has been repeatedly used for this purpose in recent years (see, e.g., Ref. 17). This technique is particularly suited for this purpose because the penetration depth of low-energy electrons is limited to four or five atomic layers in most materials, and hence, when a film is thicker than five or six layers LEED can probe both the bulk and the surface of such a film without complications arising from the out-of-reach substrate-film interface.

We report here the results of an extensive study of the growth of Fe on one of the few transition-metal surfaces so far not commonly utilized, viz., fcc Rh{001}. We shall show that Fe grows epitaxially and pseudomorphically on Rh{001}, and that the growth mode is very probably layer by layer, within experimental error, in the coverage regime in which quantitative LEED can be definitive (zero to three layers).

The room-temperature lattice constant of Rh{001} is 3.80 Å (hence the edge of the primitive unit mesh is 2.69 Å), whereas that of bcc Fe is 2.87 Å, corresponding to a misfit of –6.3%, and that of fcc Fe is 3.59 Å (Ref. 18), which corresponds to a misfit of +5.8%. The latter mismatch is the smallest from among all of the fcc transition-metal substrates, apart from the two on which fcc Fe has been observed to grow, i.e., Ni{001} (–1.9%) and Cu{001} (+0.5%). Rh is also one of the few metals whose surface free energy (2.8 J/m²) is nearly equal to that of Fe (2.9 J/m², data from Ref. 19), a condition that favors wetting.² Only Ru, Os, and the refractory metals have higher surface free energies than Fe.

Previous reports on the growth of ultrathin films of metals on Rh{001} include the following: a field-ion microscopy study of Fe on Rh (Ref. 20), which reports islands of Fe on Rh{001} after laser pulsing to 600 K, with the Fe atoms arranging themselves in a square pattern “. . . as expected of an epitaxial growth . . .”; a LEED and AES study of Cu on Rh{001}, which claims pseudomorphic FvM growth up to three layers, although the quality of the LEED pattern is described as poor;²¹ an XPS study also of Cu on Rh (Ref. 22); and a LEED and AES study of Ag on Rh (Ref. 23). The LEED study of Ag/Rh{001} holds relevance for our work since the mismatch of Fe and Ag is less than 1%. Peebles *et al.*²³ found that the growth mode of Ag is temperature dependent—at 300 K it is layer by layer, but at 640 K it is Stranski-Krastanov.

The present paper is organized as follows: In Sec. II we give experimental details, in Sec. III we describe the observations, in Sec. IV we present the LEED intensity analyses pertinent to Fe films of increasing thickness, in Sec. V we carry out the strain analysis of a thick [8-LE (layer equivalent)] epitaxial Fe film, and in Sec. VI we discuss the results and the conclusions.

II. EXPERIMENTS

The experiment was done in an UHV chamber with a typical pressure of 1×10^{-10} Torr. The Rh{001} sample was cleaned *in situ* by cycles of sputtering (with 500-eV argon ions at a typical pressure of 5×10^{-5} Torr for several hours) followed by anneals of about 1 h at temperatures of 600 °C. The resulting Rh surface was free of any impurities to within about 2% of a monolayer, as verified by AES via a double-pass cylindrical mirror analyzer (CMA), and exhibited very bright 1×1 LEED patterns up to our maximum beam energy of 512 eV.

The iron source was a 99.999 at. %-pure wire wound on a tungsten spiral which was heated resistively and extensively outgassed before each deposition. The source and the surrounding chamber walls were air-cooled from the outside in order to minimize oxygen and carbon contamination of the sample. During deposition of Fe the tungsten spiral was heated typically to about 1300–1400 °C (as measured with an infrared pyrometer). Deposition rates were kept roughly constant at about 0.3 Å/min, leading to pressures in the chamber of about 3×10^{-10} Torr. During deposition the Rh substrate was neither heated nor cooled—the substrate temperature was monitored with an infrared pyrometer and was never found to be above the minimum temperature measurable by this instrument (~ 150 °C). Previous experiments with identical sources and sample-temperature monitoring by thermocouple showed that the substrate temperature did not rise above 50 °C during deposition.

The film thicknesses were determined from AES by using the peak-to-peak heights of the Fe (651 eV) and Rh (302 eV) signals. This standard process has been well documented before.²⁴ The inelastic mean free paths used in the calibration were taken from Tanuma, Powell, and Penn.²⁵ 13.8 Å (Fe) and 6.0 Å (Rh). The thicknesses thus obtained are quoted, according to our standard procedure, in terms of the LE. The conversion from Å to LE was done using the relevant lattice spacings deduced by analysis of the $I(V)$ curves (see below). The overall error in this thickness calibration is estimated to be $\pm 50\%$, mostly derived from the determination of the inelastic mean free paths. Further complications of the calibration process may come from Auger electron diffraction (less important for a CMA that integrates the signal over a large angular range), and from the band-structure changes associated with the structural changes as the film grows, but they were not taken into account in this work.

Deposition of Fe was done in small installments to allow for AES and LEED tests: after each deposition the film thickness was calibrated by AES, the LEED pattern was scrutinized, and $I(V)$ curves were collected. The system used for collection of $I(V)$ spectra consists of a rear-view LEED optics and a standard SIT TV camera linked via a digitizer card to a microcomputer.²⁶ The software typically allows for the collection of all of the 10, 11, 20, 21, and 22 spectra within about 1 h for good statistics. The LEED patterns and associated $I(V)$ spectra were all totally reproducible for similar film thicknesses on different occasions and for different deposition rates.

III. OBSERVATIONS

As Fe was deposited up to about 9 LE, the LEED patterns showed only slight progressive changes from the very sharp 1×1 pattern seen at zero coverage. The sharpness of the diffracted beams tended to decrease with coverage, while the background increased. Consequently, the pattern at 4.3 LE was still quite a bright 1×1 , but

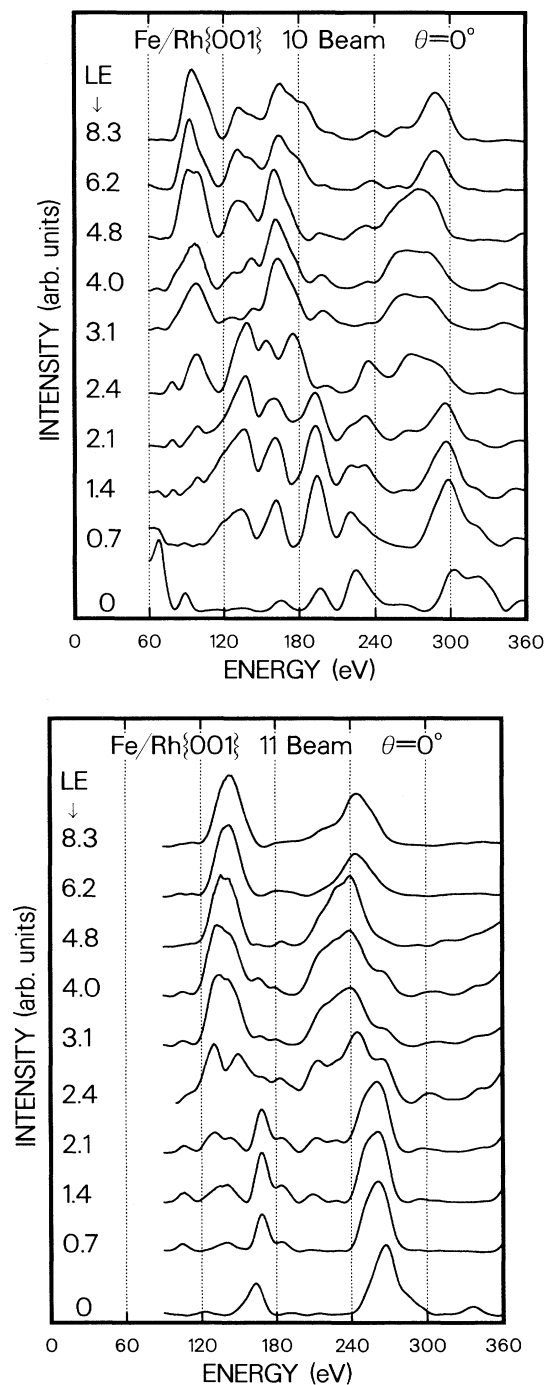


FIG. 1. Evolution of the 10 and 11 LEED spectra from Fe on Rh{001} with increasing film thickness given in layer equivalents (LE).

with slightly diffuse beams and a noticeable background. For even higher coverages the pattern worsened more appreciably until the beams were rather broad on a high background. The signal-to-background ratio was too low to take sensible $I(V)$ data above about 8 LE.

Figure 1 shows the evolution of the 10 and 11 spectra with increasing thickness of the Fe film in LE. A few observations about this figure are noteworthy. The curves from the clean Rh{001} substrate (curves labeled 0 LE in the figure) compare perfectly with those taken in a previous experiment using the same sample and with curves taken from very thick films of unstrained Rh on Au{001}.²⁷ They are also in good agreement with an investigation of clean Rh{001} by Oed *et al.*²⁸ The curves for near monolayer thickness (labeled 0.7 and 1.4 LE), are quite similar to one another and are notably different from those of the clean Rh{001} substrate. This observation tells us that the deposited Fe does contribute to the LEED signal already in the earliest stages. Hence the Fe islands are flat and, given the unchanged geometry of the 1×1 pattern, they are also epitaxial and pseudomorphic, although their thickness is not known at this time. Subsequent curves in Fig. 1 also exhibit progressive changes with coverage up to about 6 LE, above which they remain stabilized (very similar curves of inferior statistics from films of 9 LE were collected, but are not shown here). Thus, the progressive changes of the curves in Fig. 1, coupled with the persisting good quality of the 1×1 LEED pattern, tend to indicate pseudomorphism up to about 8 or 9 LE. Whether or not the growth mode is layer by layer (which requires that the second layer does not start until the first layer is completed, and so on) remains to be proven.

IV. LEED INTENSITY ANALYSES

In view of the changes exhibited by the LEED $I(V)$ curves with increasing nominal thickness of the Fe film, it is worthwhile testing whether some of the curves can be fitted to intensity calculations with models involving complete layers. In the course of these tests, it is good to keep in mind that the coverages determined by AES (and listed on the left in Fig. 1) could perhaps be in error by about $\pm 50\%$, and that the analysis is best carried out in steps, starting with the first layer and proceeding to two and more layers progressively. All intensity calculations were done with Jepsen's full-dynamical CHANGE program²⁹ using Rh and Fe potentials taken from the collection of Moruzzi, Janak, and Williams,³⁰ 8 phase shifts and 69 beams up to 500 eV, inner potential $V_0 = -(10 + 4i)$ eV (real part adjustable in the fitting process), and isotropic root-mean-square amplitude of thermal vibrations of 0.15 Å. Evaluation of the agreement between theory and experiment was done both visually and by R -factor analysis using the Van Hove-Tong R_{VHT} (Ref. 31), the Zanazzi-Jona r_{ZJ} (Ref. 32), and the Pendry R_p (Ref. 33) factors.

The first layer. The theoretical model consists of a single complete pseudomorphic layer of Fe at variable distance from the Rh{001} substrate. After an initial search, which bracketed the value of the interlayer spac-

ing between 1.70 and 1.75 Å, in the final refinement the interlayer spacing was varied from 1.62 through 1.78 Å in steps of 0.02 Å. The calculated $I(V)$ curves were compared with *both* the 0.7- and the 1.4-LE experimental curves. The best agreement was found between a calculation with interlayer spacing $d_{\text{Fe-Rh}} = 1.74 \pm 0.03$ Å and the $I(V)$ curves for the 1.4-LE film, giving reliability factors $R_{\text{VHT}} = 0.25$, $r_{\text{ZJ}} = 0.10$, and $R_p = 0.38$. The quality of the fit is good, as can be judged from Fig. 2.

This result does not imply that the experimental curves labeled 1.4 LE stemmed *exactly* from a single and full atomic layer of Fe (it is doubtful that this kind of analysis could detect differences between 100% and, say, 90% or 110% coverage of the substrate surface by monolayer islands of Fe), but it does say that the Fe film did "wet" the substrate and was very close to a full layer.

The second layer. The $I(V)$ curves depicted in Fig. 1 do not change much when the nominal coverage increases from 1.4 to 2.1 LE, but they do so significantly for the 2.4-LE film. It is therefore reasonable to try and fit the 2.4-LE data with a model involving two pseudomorphic layers of Fe. The problem is to identify both the first- and the second-interlayer spacing, i.e., $d_{\text{Fe-Fe}}$ and $d_{\text{Fe-Rh}}$, respectively. We varied $d_{\text{Fe-Fe}}$ from 1.4 through 1.75 Å in steps of 0.05 Å in the initial stages and from 1.65 through 1.775 Å in steps of 0.025 Å in the refinement stage; and for each value of $d_{\text{Fe-Fe}}$ we varied $d_{\text{Fe-Rh}}$ from 1.6 through 2.0 Å in steps of 0.05 Å in the initial stages and from 1.74 through 1.82 Å in steps of 0.01 Å in the refinement stage. The contour plots for all three R factors used to evaluate the fit are shown in Fig. 3, and

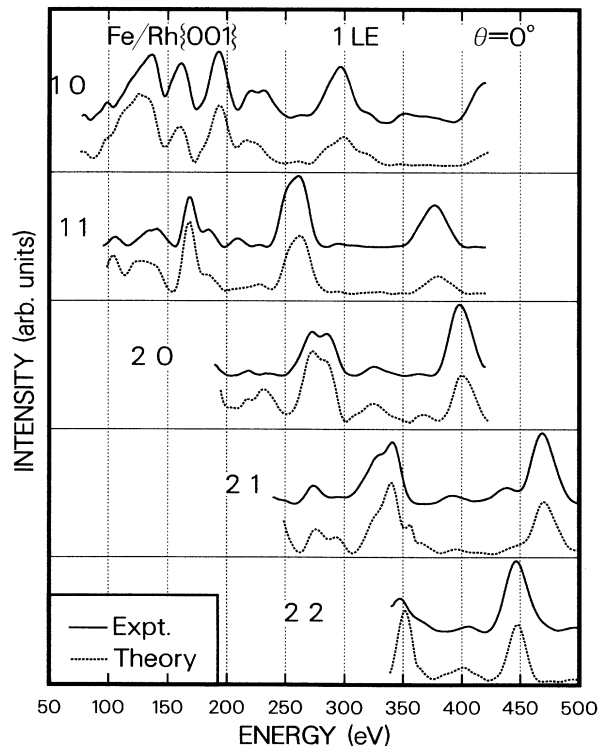


FIG. 2. Experimental (solid lines) and theoretical (dotted lines) $I(V)$ spectra for a pseudomorphic monolayer of Fe on Rh{001}.

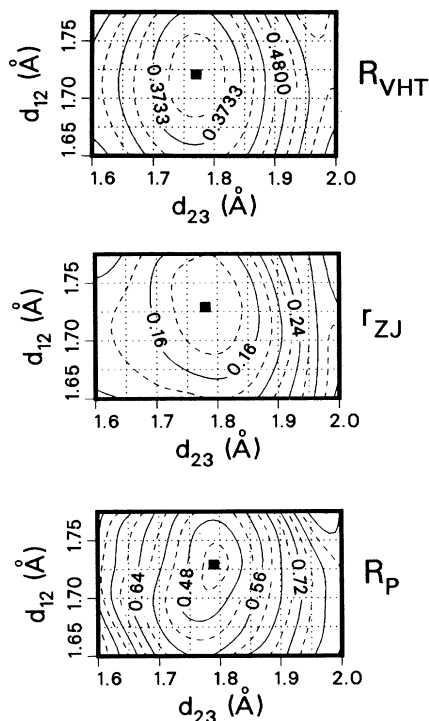


FIG. 3. R -factor contour plots in the plane of interlayer spacings $d_{12}=d_{\text{Fe-Fe}}$ vs $d_{23}=d_{\text{Fe-Rh}}$ for a two-layer film of Fe on Rh{001}. See the text for the best-fit parameter values.

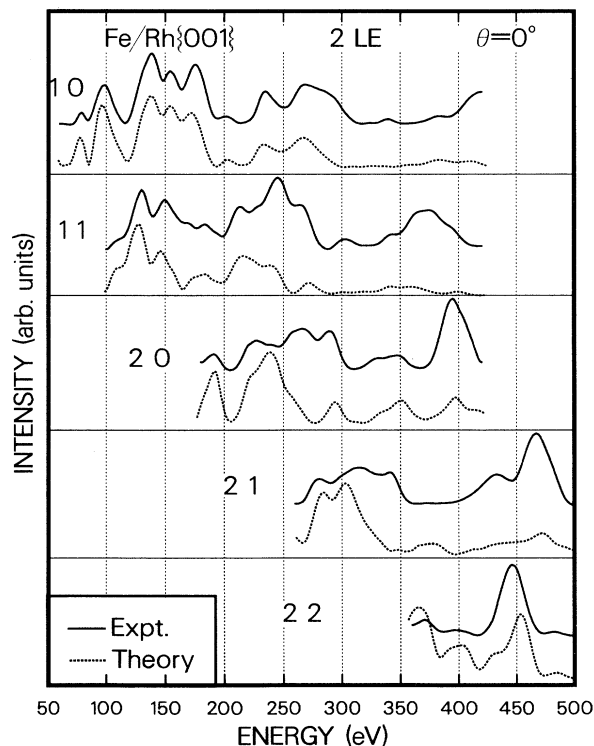


FIG. 4. Experimental (solid lines) and theoretical (dotted lines) $I(V)$ spectra for a pseudomorphic two-layer film of Fe on Rh{001}.

the $I(V)$ curves calculated with the average values of the parameters that minimize the R factors are depicted in Fig. 4.

The fit to experiment is acceptable: the corresponding R factors are $R_{\text{VHT}}=0.33$, $r_{\text{ZJ}}=0.12$, and $R_P=0.42$, and the best-fit parameters are $d_{\text{Fe-Fe}}=1.73\pm 0.03$ Å and $d_{\text{Fe-Rh}}=1.78\pm 0.03$ Å. These results indicate that by the time the surface coverage reached the nominal value of 2.4 LE a bilayer of Fe was very nearly completed. It is puzzling to note, in Fig. 1, that the $I(V)$ curves measured on the 2.1-LE film are more similar to those from the 1.4-LE film than to those from the 2.4-LE film (one and two full Fe layers, respectively), indicating either an unexpected lack of internal consistency in the AES-derived film thicknesses or some other unknown phenomenon.

The third layer. Upon further deposition above 2.5 LE, the LEED $I(V)$ curves again develop gradually but significantly, see Fig. 1. The difficulty in seeking a model of three full layers of Fe that would produce $I(V)$ spectra in agreement with experiment lies in the fact that one must identify three interlayer spacings correctly, namely, $d_{12}=d_{\text{Fe-Fe}}$, $d_{23}=d_{\text{Fe-Fe}}$, and $d_{34}=d_{\text{Fe-Rh}}$, a problem that requires an extensive search. Fortunately, a satisfactory solution was found relatively fast. We varied d_{12} from

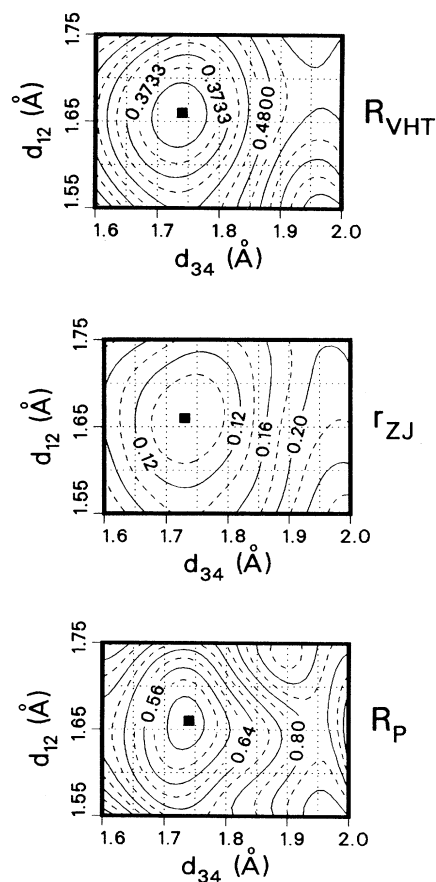


FIG. 5. R -factor contour plots in the plane of interlayer spacings $d_{12}=d_{\text{Fe-Fe}}$ vs $d_{34}=d_{\text{Fe-Rh}}$ for a three-layer film of Fe on Rh{001}. See the text for the best-fit parameter values.

1.55 through 1.75 Å in steps of 0.05 Å with $d_{23}=1.60$, 1.65, and 1.70 Å and with d_{34} varying between 1.6 and 2.0 Å. A best fit to the experimental 3.1-LE $I(V)$ curves was achieved with the following triad: $d_{12}=1.66$ Å, $d_{23}=1.64$ Å, and $d_{34}=1.74$ Å (all ± 0.03 Å). The three R factors used are all consistent in the choice of the best-fit parameters: we show as an example, in Fig. 5, three contour plots in the d_{12} - d_{34} plane for constant $d_{23}=1.65$ Å. Figure 6 shows that the agreement between theory and experiment is satisfactory, especially in view of the rather large changes in the $I(V)$ curves between two and three full layers (nominal 2.4 and 3.1 LE in Fig. 1).

The thick film. Intensity calculations were done for a semi-infinite film of Fe{001} with the in-plane mesh constant of Rh{001}, i.e., $a=2.69$ Å, for comparison with the $I(V)$ curves measured on an 8-LE film. In this case the focus of attention is on the determination of the *bulk* interlayer spacing d_{bulk} , which depends upon the plane epitaxial strain at the interface. The calculations were done in the first stage for d_{bulk} between 1.1 and 1.9 Å, in the second stage for d_{bulk} between 1.40 and 1.7 Å, and in the final stage for d_{bulk} from 1.50 through 1.70 Å in steps of 0.025 Å. The R -factor minima on the average values: $d_{\text{bulk}}=1.56\pm 0.03$ Å and $d_{12}=1.65\pm 0.03$ Å, for $R_{\text{VHT}}=0.26$, $r_{\text{ZJ}}=0.10$, and $R_{\text{P}}=0.42$. R -factor contours are shown in Fig. 7 and the $I(V)$ curves, both experimental and theoretical, are depicted in Fig. 8.

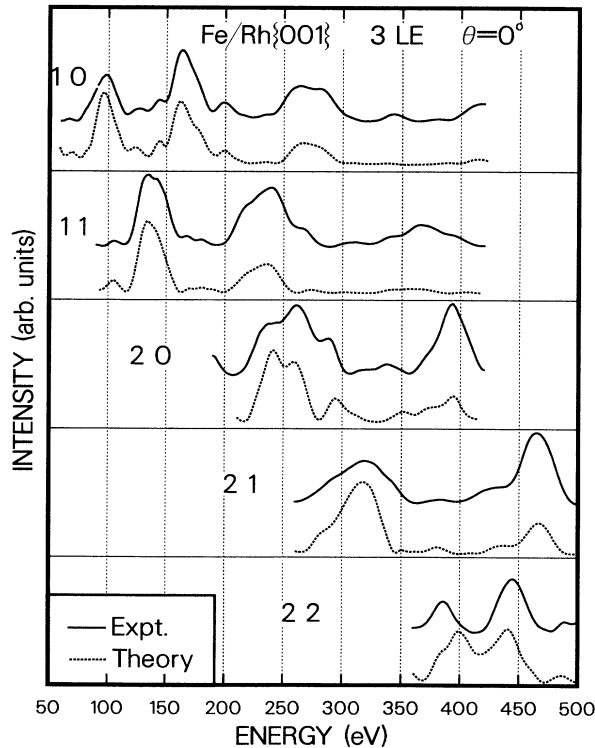


FIG. 6. Experimental (solid lines) and theoretical (dotted lines) $I(V)$ spectra for a pseudomorphic three-layer film of Fe on Rh{001}.

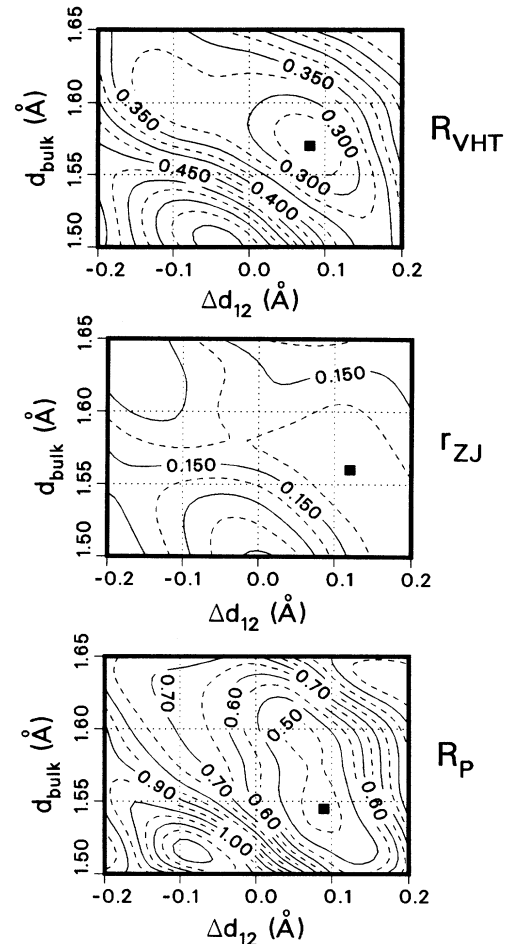


FIG. 7. R -factor contour plots in the plane of interlayer spacings d_{bulk} vs d_{12} for an eight-layer film of Fe on Rh{001}. See the text for the best-fit parameter values.

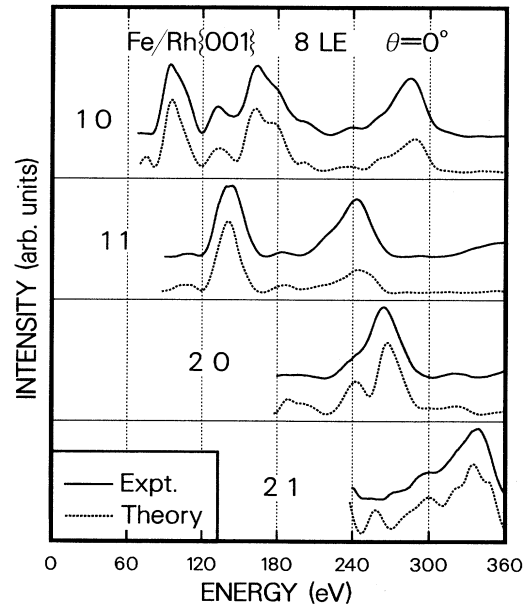


FIG. 8. Experimental (solid lines) and theoretical (dotted lines) $I(V)$ spectra for a pseudomorphic three-layer film of Fe on Rh{001}.

V. STRAIN ANALYSIS

The purpose of the strain analysis of the thick film is to determine both the strain in the film and the equilibrium phase of the film material. The structure of the film is obviously no longer cubic, but rather body-centered tetragonal (bct), with $a = 2.69 \text{ \AA}$ (imposed by the Rh substrate) and $c = 3.12 \pm 0.06 \text{ \AA}$ [i.e., $2 \times d_{\text{bulk}} = 2 \times (1.56 \pm 0.03) \text{ \AA}$]. The quantity of interest is the strain ratio $r_s = \epsilon_3 / \epsilon_1$ between the strain ϵ_3 in the perpendicular direction and the linear strain ϵ_1 in the plane of the film.

In order to calculate r_s we need to know what the film is strained from, i.e., the equilibrium phase, as

$$r_s = \frac{(c - c_{\text{eq}})/c_{\text{eq}}}{(a - a_{\text{eq}})/a_{\text{eq}}}, \quad (1)$$

where c_{eq} and a_{eq} are the lattice parameters of the equilibrium phase. If we assume that the equilibrium phase is bcc Fe ($a_{\text{eq}} = c_{\text{eq}} = 2.87 \text{ \AA}$), then $r_s^{\text{exp}} = -1.39 \pm 0.33$. If we assume that the equilibrium phase is fcc Fe [$a_{\text{eq}} = c_{\text{eq}} = 3.59 \text{ \AA}$ (Ref. 18)], then $r_s^{\text{exp}} = -2.24 \pm 0.29$.

We can also calculate the value of the strain ratio expected from linear elasticity theory, i.e., from the elastic constants of the equilibrium phase. For cubic {001} surfaces we find that $r_s = -2c_{12}/c_{11}$ with c_{12} and c_{11} being the elastic constants.¹⁷ Hence, the theoretical value for bcc Fe [$c_{11} = 2.3310$, $c_{12} = 1.3544$ in units of 10^{12} dyn/cm^2 , Ref. 34] is $r_s^{\text{theor}} = -1.16$, whereas that for fcc Fe [$c_{11} = 1.54$, $c_{12} = 1.22$ in units of 10^{12} dyn/cm^2 at $1155 \text{ }^\circ\text{C}$ (Ref. 35), but we assume the same values at room temperature] is $r_s^{\text{theor}} = -1.58$ (-1.64 if the elastic constants are corrected to room temperature by comparison with the known temperature dependence of the elastic constants of bcc Fe).

Comparison between theoretical and experimental strain ratios shows that, taking into account the experimental error, the equilibrium phase is bcc Fe. It is plausible that the experimental strain ratio differs from the theoretical one because of nonlinear effects, as the strains involved here are very large. But in any case it is safe to conclude that the equilibrium phase of the films grown on Rh{001} in this work is that of stable bcc Fe.

VI. DISCUSSION

This is the first time, in our experience, that a metallic layer-by-layer growth mode has been confirmed by quantitative LEED, at least up to a thickness of three layers. This result is somewhat surprising because after the first Fe layer has been formed, further deposition causes the growth of Fe on Fe, but the homoepitaxy of Fe on Fe{001} was reported to occur by way of multilayer islands, in a combined STM and RHEED study, despite the occurrence of RHEED intensity oscillations.⁴ The only difference between true Fe on Fe{001} homoepitaxy and the growth of the second and the third Fe layers in the present work is of course the presence of the Rh substrate underneath and the fact, very probably important,

that the Fe layers are strained. It would indeed be very desirable to carry out a joint LEED, RHEED, and STM experiment on the Fe/Rh{001} system.

There are no other metal-on-metal systems, to our knowledge, in which layer-by-layer growth has been confirmed by quantitative LEED. The Co/Cu{001} system, which is to date the most widely acknowledged layer-by-layer growth system,¹³ was studied by quantitative LEED by Clarke *et al.*,³⁶ but no attempt was made either to show the evolution of the spectra with coverage, or to model the two-layer film. Actually, the Co/Cu system is not well suited to quantitative LEED studies because Co and Cu are very close to one another in the Periodic Table and therefore practically indistinguishable by LEED.

The main problem in trying to determine layer-by-layer growth with quantitative LEED, assuming of course that the $I(V)$ curves are found to change with increasing film thickness, lies in the difficulty of preparing films with an integral number of atomic layers. This difficulty stems from the imprecision in the determination of surface coverage—an imprecision that is common to all techniques used for this purpose, but is particularly true for AES, owing to the uncertainties in the values of inelastic mean free paths. In the present work the $\pm 50\%$ error bars on the coverages determined by AES are presumably the reason why the theoretical monolayer and bilayer films are best matched to films of thicknesses of 1.4 and 2.4 LE, respectively.

We note that the separate $I(V)$ analyses for the monolayer, the bilayer, and the three-layer films show the following trends: (i) The layer spacing at the interface between substrate and film remains approximately the same, within the experimental error of $\pm 0.03 \text{ \AA}$, for the first (1.74 \AA), the second (1.78 \AA), and the third (1.74 \AA) atomic layer; (ii) in the two-layer film the spacing between the two Fe layers (1.73 \AA) is also about the same as the spacing at the interface with the substrate; but (iii) in the three-layer film the first two interlayer spacings suddenly collapse by about 5% of what they were to about 1.65 \AA ; and (iv) in the thick film the bulk spacing is further collapsed to 1.56 \AA , which is still 8.7% larger than in the equilibrium phase (1.435 \AA).

It is also interesting to see, from the strain analysis, that the equilibrium phase of these ultrathin films is bcc Fe, even though it has a somewhat larger and a compressive misfit to Rh{001} (-6.3%) when compared to fcc Fe ($+5.8\%$). It is remarkable (although already observed in other epitaxial systems¹⁷) that films as thick as eight or ten layers can be grown under such large strains. The occurrence of substantial compressive strain is understandable because the bcc{001} surface is not close packed, hence the atoms can move in the surface plane; such movements occur, for example, in the reconstruction of the W{001} surface.³⁷ We have not measured the magnetization of the film directly, but we can infer that the film has a magnetic moment from the volume per atom, which is substantially greater than for a nonmagnetic phase. The atomic volume is 11.29 \AA^3 in the bulk of the strained film, and even larger in the surface layers, to be compared with 11.82 \AA^3 in equilibrium ferromagnetic bcc

Fe and 11.57 \AA^3 in ferromagnetic fcc Fe ($a_0 = 3.59 \text{ \AA}$). However, nonmagnetic fcc Fe ($a_0 = 3.44 \text{ \AA}$, see Ref. 38) has an atomic volume of 10.2 \AA^3 , 11% less than the film, indicating that the film is magnetic. Since bulk bcc Fe does not have a stable antiferromagnetic phase³⁹ one expects that the film is ferromagnetic.

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