

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Peter Dowben Publications

Research Papers in Physics and Astronomy

May 1986

Epitaxial growth of iron iodide films on Fe(110)

D.R. Mueller

Cornell University

T.N. Rhodin

Cornell University

Peter A. Dowben

University of Nebraska-Lincoln, pdowben@unl.edu

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsdowben>



Part of the [Physics Commons](#)

Mueller, D.R.; Rhodin, T.N.; and Dowben, Peter A., "Epitaxial growth of iron iodide films on Fe(110)" (1986).
Peter Dowben Publications. 130.

<https://digitalcommons.unl.edu/physicsdowben/130>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Epitaxial growth of iron iodide films on Fe(110)

D. R. Mueller and T. N. Rhodin

School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853

P. A. Dowben

Department of Physics, Syracuse University, Syracuse, New York 13244

(Received 9 October 1985; accepted 11 November 1985)

The interaction of iodine vapor on an Fe(110) single crystal surface at room temperature has been investigated primarily through the use of LEED and UPS. Both a series of chemisorbed overlayers and an epitaxial iodide layer are observed. Iodide formation proceeds through an island growth mechanism with the iodide basal plane parallel to the Fe(110) surface. Evidence is presented that the defects introduced on the surface during argon ion sputtering may be important as nucleation sites for iodide growth. The results are compared with the results of previous studies.

I. INTRODUCTION

Halogen interaction with transition metal surfaces is a subject of current research interest partly because of the importance of halogen species as catalyst moderators^{1,2} and partly because the halogens are well suited to the study of trends in chemisorption and epitaxial growth.³ Halide growth sometimes occurs readily at room temperature under UHV conditions as in the case of Cl on Hf.⁴ In other cases (e.g., Cl on Ru)⁵ only the formation of a chemisorbed overlayer is reported. That different surfaces of different metals show differing reactivities toward the halogens is a result that might very well be expected. Sometimes, however, as in the case of Cl/Ag(111)^{1,6-7} or Cl/Fe(100)⁸⁻⁹ different workers have come to different conclusions about the behavior of a specific surface/adsorbate system. Both the exposure level⁹ and the temperature^{6,10} are important factors in determining whether or not halide formation is observed. We found that the sample preparation procedure is also of importance.

Room temperature exposure of a Fe(110) single crystal surface to iodine vapor under UHV conditions can result in the formation of various chemisorbed overlayers, an epitaxial iodide layer or a surface covered by detectable regions of both the iodide and a chemisorbed overlayer. When a freshly sputtered sample was annealed for 2 min at 825 to 875 K and subsequently, after cooling, exposed to 300 L iodine vapor (uncorrected gauge pressure), extensive iodide formation was observed. If the sample was annealed at 975 K instead, no iodide formation was found. When the sample was given the same sputtering and 975 K anneal treatment followed by a very brief sputter treatment, extensive iodide formation was observed after only 4 L exposure.

II. EXPERIMENTAL

Data were collected in two different UHV chambers. One was a modified Vacuum Generators ADES400 system used primarily for ARUPS at the Tantalus Storage Ring of the University of Wisconsin at Madison. It was equipped with a 150° hemispherical analyzer with 4° angular resolution, a single pass CMA, a four grid LEED optics system, a mass spectrometer, and an ion gun. Pumping was by means of a

150 l/s turbomolecular pump, a 400 l/s ion pump and a titanium sublimation pump.¹¹ More detailed LEED observations and photography were carried out in a second chamber equipped with a four grid LEED system which doubled as a retarding field analyzer, a mass spectrometer, and an ion gun. This chamber was pumped by a 400 l/s liquid nitrogen trapped oil diffusion pump, a 100 l/s ion pump, and a titanium sublimation pump.¹²

Iodine adsorption was accomplished by admitting iodine vapor to the chamber through a standard leak valve at pressures up to 1×10^{-6} Torr. The vapor was in equilibrium with resublimed solid iodine held at room temperature in an otherwise evacuated bottle. Initial exposure of either vacuum chamber to iodine resulted in the desorption of carbon monoxide from the chamber walls. To prevent contamination of the surface during the experiments, the chambers were first dosed with iodine vapor in 300 or 600 L exposures until admitting iodine resulted in no significant rise in the carbon monoxide partial pressure. The base pressure of either chamber after the iodine dosing procedure was 2×10^{-10} Torr.

One sample was used for the photoemission work, while the LEED patterns were observed from a second Fe(110) surface as well. The initial sample preparation and cleaning procedure was lengthy and is described elsewhere.¹³ Before collecting a set of photoemission data or making LEED observations, the resistively heated sample was held at 750 K while it was sputtered for 30 min with 700 eV argon ions at 5 μ A beam current. Annealing the sample for 2 min at 825 to 875 K after sputtering produced a surface that gave a sharp bcc (110) LEED pattern. Contamination levels as estimated from Auger were 2% or less. No electron beam induced effects were observed even for prolonged exposure to the electron beam (4 h) either through changes in the LEED patterns or in the Auger peak height ratio. This was the case for both the iodide and the chemisorbed structures.

III. RESULTS

When the sample surface is prepared as described above and subsequently exposed to iodine vapor, LEED patterns A through E (see Fig. 1) may be observed sequentially with

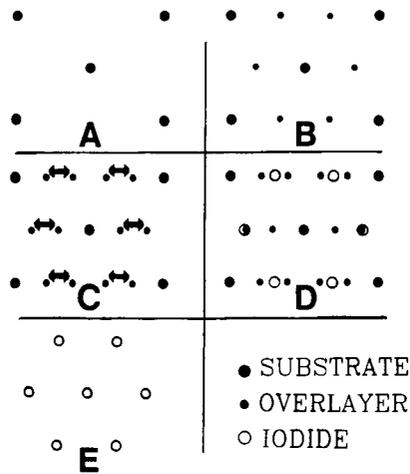


FIG. 1. Sequence of LEED patterns observed as a clean, room temperature, Fe(110) surface is exposed to increasing amounts of iodine vapor. The arrows in C are to indicate that the overlayer spots shown in B split continuously with increasing coverage until pattern C is observed. A: clean Fe(110); B and C: chemisorbed overlayer patterns; D: chemisorbed overlayer and iodide; E: iodide.

increasing iodine exposure. The pattern shown in B is sharp after 0.6 L exposure (uncorrected gauge pressure). Upon further exposure to iodine vapor, the overlayer spots elongate and split along the $\langle 100 \rangle$ azimuth. The split spots separate continuously with increasing coverage as is shown in Part C. Splitting is complete after about 5 L exposure. The Auger electron peak ratio $I(511)/Fe(651)$ for the chemisorbed overlayer increases from 0.27 to 0.45 as the spot splitting increases from zero to its maximum value. Additional iodine adsorption weakens the LEED reflections and increases the background intensity. After about 20 L exposure faint new features first appear as represented by the open circles in D. With subsequent exposure these weak new features gradually intensify at the expense of the substrate and original overlayer spots until after 300 to 1000 L exposure only a hexagonally symmetric pattern remains (E).

Note that the pattern formed by the "ring" of overlayer spots around the (0,0) beam in B is not identical to the pattern in E. Pattern E is truly hexagonal while in B the two edges that are parallel to the $\langle 100 \rangle$ azimuth are shorter than the other edges. If a surface that produces LEED pattern E is annealed at temperatures above 560 K, pattern C is restored. Annealing the sample to higher temperatures reduces the overlayer spot splitting until pattern B is recovered after a 710 K anneal. Restoration of the iron substrate spots is accompanied by an abrupt decline in the Auger peak height ratio $I(511)/Fe(651)$ from a value of 2.0 to 0.45.

Dramatic changes in the photoemission spectra accompany changes in the LEED patterns. Curve c in Fig. 2 shows a photoelectron energy distribution curve from a surface that gives LEED pattern B. Under the conditions for which the spectrum was obtained, only a single peak with a binding energy of 5.6 eV with respect to the Fermi level appears. Curve b is from a surface characterized by LEED pattern E. There appear to be six peaks in addition to a strongly attenuated iron d-band, with binding energies of 1.4, 2.2, 3.5, 4.2, 5.8, and 6.7 eV with respect to the Fermi level. These peaks

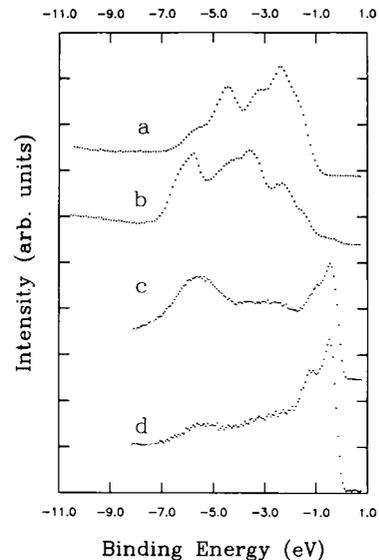


FIG. 2. ARUPS electron energy distribution curves from molecularly adsorbed iodine: (a) an epitaxial iodide layer; (b) a dissociatively chemisorbed iodine overlayer; and (c) nearly clean Fe(110) with a small quantity of chemisorbed iodine adsorbed from the background during data acquisition (d). The vertical scale has been purposefully omitted as it is not identical for each curve. The curves have been offset for clarity. The incident radiation was 20 eV energy. The incidence angle was 45° . Electrons were collected in even geometry with an emission angle 30° along the $\langle 1\bar{1}0 \rangle$ azimuth for spectra (a) and (b) and along the $\langle 100 \rangle$ azimuth for spectra (c) and (d).

do not disperse greatly with k_{\parallel} .¹⁴ Curve a in Fig. 2 shows photoemission from a surface covered with molecular iodine at 100 K. Molecular iodine will adsorb on Fe(110) under UHV conditions at temperatures below 150 K after forming a chemisorbed layer as is described elsewhere.¹⁵

The exposure level required before the extra features (open circles in Fig. 1 D) appear in the LEED pattern is sensitive to the sample preparation procedure. When the sample was annealed to 975 instead of 875 K while the rest of the preparation procedure remained the same, the open circles in Fig. 1 D did not appear even for exposure levels of 1000 L. A sample given the same 975 K anneal treatment followed by 120 s of sputtering at 0.05 μA beam current and 700 eV still showed a good substrate LEED pattern. After exposure to as little as 4 L iodine vapor, the LEED pattern from this surface appeared as in Fig. 1 E. Annealing the sample to 975 instead of 875 K did not introduce additional surface contamination.

IV. DISCUSSION

Continuous splitting of overlayer induced LEED reflections (Fig. 1 B,1 C) has been observed in many halogens on transition metal systems. Examples include Br/Cr(110),¹⁶ Br/W(100),¹⁷ Cl,Br,I/Fe(100),⁸ I/Ni(100),¹⁸ and Cl/Ru(100).⁵ For some of these systems low pressure halide formation is also observed at higher exposure levels.^{16,19} The variable low coverage LEED patterns have most often been explained in terms of double diffraction between the substrate and an incommensurate variable coverage overlayer net. In most cases an alternate explanation based on antiphase domain boundaries must be rejected because it requires unrealistically small adatom-adatom spacings. We

also interpret the LEED patterns observed for chlorine, bromine, and iodine adsorbed on Fe(110) at low coverages in terms of incommensurate dissociatively chemisorbed overlayers as is described in detail elsewhere.²⁰ The photoemission evidence (Fig. 2, curve c) is consistent with an interpretation in terms of a dissociatively chemisorbed overlayer. Atomic chemisorption systems involving nonmetallic adsorbates generally show a few photoemission peaks derived from the adsorbate p levels and the metal orbitals 2 to 8 eV below the Fermi level. Under the conditions for which curve c in Fig. 2 was obtained, emission is observed predominantly from the iodine $4p_z$ derived level 5.6 eV below the Fermi level.

At higher exposure levels (300 L), however, the evidence points toward iodide formation. When measurements are carried out on photographs of LEED pattern E, the spot separations are found to correspond to $1.77 \pm 0.05 \text{ \AA}^{-1}$. Transforming the reciprocal space lattice vectors yields a real space separation of $4.16 \pm 0.14 \text{ \AA}$ between units of the diffracting structure parallel to the surface. FeI_2 crystallizes in the Cd(OH)_2 structure. This is a hexagonal structure with one molecule per unit cell and can be regarded as a close packing arrangement of the anions with the cations in sheets between alternate layers of anions. For FeI_2 the separation between unit cells parallel to the iodide basal plane is 4.04 \AA (that is, $a = 4.04 \text{ \AA}$),²¹ in good agreement with the $4.16 \pm 0.14 \text{ \AA}$ derived from the LEED pattern. The pattern of Fig. 1 E is therefore explained if we assume that FeI_2 grows epitaxially on the Fe(110) surface with its basal plane parallel to the surface.

Although FeF_3 , FeCl_3 , and FeBr_3 all exist, FeI_3 is not commonly observed. In any event FeI_3 formation on an Fe sample under UHV conditions is very unlikely because of the presence of unreacted iron. Formation of the dihalide as opposed to the trihalide has been observed for the low pressure interaction of chlorine and bromine with V(100) and Cr(100).³ The authors of that report note that "the reaction $M(s) + 2MX_3(s) \rightarrow 3MX_2(s)$ is highly exothermic and so a combination of low incident flux and intimate contact with the underlying metal substrate favors the dihalide." The same argument applies in the case of iron.

If we adopt the view that the LEED pattern of Fig. 1 E is due to diffraction from an epitaxial layer of FeI_2 restoration of the pattern in Fig. 1 C after a 560 K anneal can be explained by assuming that the iodide evaporates leaving a chemisorbed overlayer on the iron surface after such an anneal treatment. In a recent study²² on the electronic structure of gaseous FeI_2 the workers evaporated FeI_2 at temperatures of 560 to 720 K. This range is consistent with vaporization of a thin FeI_2 film at 560 K.

The photoemission data are also consistent with FeI_2 formation at high exposure levels. Curve b in Fig. 2 is qualitatively similar to vapor phase He I photoelectron spectra of FeCl_2 and FeBr_2 .²³ The width of the energy range over which our peaks occur ($\approx 6 \text{ eV}$) is broader than the width of the gas phase data for the related compounds ($\approx 4 \text{ eV}$). A wider distribution of energy levels in a solid as opposed to a gas of the same material is generally observed because of overlap between the orbitals in different molecules. Ishii *et*

*al.*²⁴ have investigated the extreme ultraviolet photoelectron spectra of FeCl_2 . They observe a valence bandwidth of approximately 8 eV and a weak feature at higher binding energy that they attribute to a multielectron satellite feature.

McConville and Woodruff have studied the valence band photoemission from a surface layer of NiI_2 grown under UHV conditions.¹⁹ They observe iodide bands from 2 to 6 eV below the Fermi level which is similar to the range reported here for FeI_2 . Grade *et al.*²⁵ have examined the He I photoemission spectra of solid FeI_2 . They deconvolute their spectrum into six peaks with the binding energies are quite different from ours. Both our study and the study of Grade *et al.*²⁵ examined emission from the iodide basal plane. Only a single iodide spectrum is shown in Fig. 2; however, we have collected numerous spectra under a wide variety of incidence and emission angle conditions. Although the relative intensities of the peaks change and there may be some weak dispersion, we do not observe features more than 7 eV below the Fermi level. The discrepancy between our results and those of Grade *et al.* is therefore unlikely to be a consequence of the differing angular resolution of the analyzers used. Charging effects should not be a problem for thin overlayers such as the ones studied here. Nevertheless, we tested for this by taking spectra with the monochromator slits wide open and with the slits nearly closed. Only changes due to altered resolution were observed. While photoemission from a thin FeI_2 layer grown *in situ* at low pressure was studied here, Grade *et al.*²⁵ examined photoemission from a bulk FeI_2 sample grown in the presence of excess iodine. Perhaps the discrepancy in the valence bandwidth is a consequence of excess iodine retained in the bulk sample.

The coexistence of iodide induced diffraction features and chemisorbed LEED spots as shown in Fig. 1 D can only be explained if the surface is covered by regions of both iodide and chemisorbed iodine. At higher exposure levels a larger fraction of the surface is covered by iodide and thus the iodide induced diffraction features intensify with increased exposure at the expense of the chemisorbed overlayer spots. FeI_2 formation on Fe(110) therefore occurs via an island growth mechanism. Epitaxial halide growth also occurs by an island growth mechanism for chlorine and bromine interaction with V(100) and Cr(100) surfaces.³ This observation suggests that nucleation sites are of importance in the initiation of halide growth.

A chemisorbed overlayer differs from the halide in that the chemisorbed overlayer consists of a single layer of halogen atoms on top of a semi-infinite number of metal atom layers while in the halide double halogen atom layers alternate with layers of the metal. Perhaps defects on the surface are important in providing sites at which the halogen atoms "can get under" layers of the metal. If this is the case the observation of rapid iodide formation on the damaged Fe(110) surface and the lack of iodide growth on the well-annealed surface can be explained easily. It is of interest to note that chloride growth has been observed on a polycrystalline tungsten specimen of mainly (100) orientation,²⁶ while it was not observed for a W(100) single crystal surface.²⁷ The grain boundaries of the polycrystalline sample might act like nucleation sites for halide formation.

V. SUMMARY

(1) Both a series of chemisorbed overlayers and an epitaxial layer of FeI₂ can be produced through low pressure interaction of iodine vapor and an Fe(110) single crystal surface at room temperature.

(2) Conditions can be controlled so that the surface is either covered predominantly by the iodide or covered only with a chemisorbed overlayer.

(3) Iodide formation proceeds through an island growth mechanism with the iodide basal plane parallel to the Fe(110) surface.

(4) Defects on the sample surface produced during argon ion sputtering may be important as nucleation sites for iodide formation.

ACKNOWLEDGMENTS

This work was supported by the Cornell Materials Science Center (NSF DMR No. 8217227-A01). The support of the staff and use of the facilities at the Tantalus I Storage Ring at the University of Wisconsin, Madison (NSF DMR No. 7721888) are also greatly appreciated.

¹Yung-Yi Tu and J. M. Blakely, *J. Vac. Sci. Technol.* **15**, 563 (1978).

²C. T. Au and M. W. Roberts, *Surf. Sci.* **149**, L18 (1985).

³A. P. C. Reed and R. M. Lambert, *Vacuum* **33**, 707 (1983).

⁴M. P. Cox, J. S. Foord, and R. M. Lambert, *Surf. Sci.* **129**, 375 (1983).

⁵N. J. Gudde and R. M. Lambert, *Surf. Sci.* **134**, 703 (1983).

⁶M. Bowker and K. C. Waugh, *Surf. Sci.* **134**, 639 (1983).

⁷P. J. Goddard and R. M. Lambert, *Surf. Sci.* **67**, 180 (1977).

⁸P. A. Dowben and R. G. Jones, *Surf. Sci.* **88**, 348 (1979).

⁹A. P. C. Reed, R. M. Lambert, and J. S. Foord, *Surf. Sci.* **134**, 689 (1983).

¹⁰M. Grunze and P. A. Dowben, *Appl. Surf. Sci.* **10**, 209 (1982).

¹¹For a more detailed description of the apparatus, see Charles Ward Seabury, Ph.D. Thesis, Cornell University, 1980.

¹²For a more detailed description, see T. Weston Capehart, Ph.D. Thesis, Cornell University, 1979.

¹³E. S. Jensen and T. N. Rhodin, *Phys. Rev. B* **27**, 3338 (1983).

¹⁴D. R. Mueller, P. A. Dowben, and T. N. Rhodin (in preparation).

¹⁵D. Mueller, T. N. Rhodin, and P. A. Dowben, *Surf. Sci.* **164**, 271 (1985).

¹⁶J. S. Foord and R. M. Lambert, *Surf. Sci.* **138**, 258 (1984).

¹⁷K. J. Rawlings, G. G. Price, and B. J. Hopkins, *Surf. Sci.* **100**, 289 (1980).

¹⁸R. G. Jones and D. P. Woodruff, *Vacuum* **31**, 411 (1981).

¹⁹C. F. McConville and D. P. Woodruff, *Surf. Sci.* **152**, 434 (1985).

²⁰D. R. Mueller, T. N. Rhodin, and P. A. Dowben (submitted to *Ber. Bunsenges. Phys. Chem.*).

²¹Ralph Wyckoff, *Crystal Structures* (Interscience, New York, 1960).

²²M. Grade and W. Rosinger, *Surf. Sci.* **156**, 920 (1985).

²³J. Berkowitz, D. G. Streets, and A. Garritz, *J. Chem. Phys.* **70**, 1305 (1979).

²⁴T. Ishii *et al.*, *Phys. Rev. B* **12**, 4320 (1975).

²⁵M. Grade, W. Rosinger, and P. A. Dowben, *Ber. Bunsenges. Phys. Chem.* **88**, 65 (1984).

²⁶R. H. Prince and R. M. Lambert, *Chem. Phys. Lett.* **67**, 388 (1979).

²⁷G. G. Price, K. J. Rawlings, and B. J. Hopkins, *Surf. Sci.* **85**, 379 (1979).