

Reactivity of hydrogen on ultra-thin FCC iron films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 SB161

(<http://iopscience.iop.org/0953-8984/1/SB/027>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:11

Please note that [terms and conditions apply](#).

Reactivity of hydrogen on ultra-thin FCC iron films

Chikashi Egawa and Elaine M McCash

Cavendish Laboratory, Department of Physics, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

Received 21 April 1989

Abstract. We report LEED, AES and TDS for hydrogen adsorption–desorption on iron films of various thicknesses in the range from 0 to 12 monolayers (ML) grown on Cu(100), and discuss these in the light of previous published work on hydrogen adsorption on BCC iron single crystals. The results were critically dependent on the growth conditions of the iron films. Below 3 ML, film growth did not appear to be epitaxial. Growth at 120 K and annealing to 300 K produced three and four ML films exhibiting a (4×1) LEED pattern and 5 ML films exhibiting (5×1) LEED patterns, with a corresponding shift down to 310 K in peak desorption temperature. Film growth at 290 K gave 3–5 ML films which exhibited a (4×1) LEED pattern and 6–10 ML films exhibiting a $p(2 \times 2)$ – $p4g$ superstructure. The heat of adsorption of hydrogen on well ordered films was found to be the order of 71 – $76 (\pm 1) \text{ kJ mol}^{-1}$, which is considerably less than those found for the low-indexed faces of BCC iron (typically 88 – 109 kJ mol^{-1}). This observation is particularly important with regard to catalytic activity.

1. Introduction

The reactivity and properties of iron surfaces have long been of interest because of the importance of this metal in a large number of catalytic processes, including ammonia synthesis and the Fischer–Tröpsch synthesis of hydrocarbons from hydrogen and carbon monoxide.

For some time, physicists have been investigating the properties of iron films grown on a variety of single-crystal substrates [1–3]. They have found that films deposited on copper grow with a face-centred cubic crystal structure (FCC), which is dictated by the underlying copper lattice, rather than the ‘usual’ body-centred cubic form. These FCC films exhibit unusual magnetic, electronic and sometimes structural properties depending on the film thickness, growth conditions and the specific face of the underlying copper substrate.

We have investigated the chemical properties of these films by studying the adsorption–desorption of hydrogen as a function of iron film thickness on the Cu(100) substrate. Hydrogen is an ideal adsorbate for this work as, in spite of its being technically difficult to work with, is an important ‘probe’ of the surface, and from a catalytic point of view it is one of the major starting materials for many reactions of industrial importance.

2. Experimental

Experiments were performed in a stainless steel UHV system equipped for thermal desorption spectroscopy (TDS), Auger electron spectroscopy (AES), low-energy electron

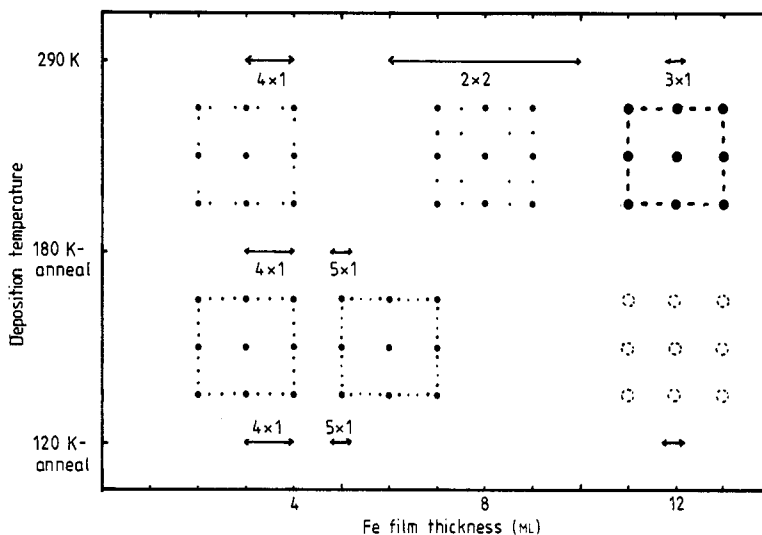


Figure 1. Low-energy electron diffraction patterns for iron films grown under different conditions.

diffraction (LEED) and work function measurements ($\nabla\phi$). The base pressure was less than 1×10^{-10} mbar.

The copper crystal was prepared by mechanical polishing and chemical etching followed by several cycles of argon ion bombardment and annealing at 450 °C in UHV. The iron source was a resistively heated tungsten boat containing iron wire. The maximum pressure during evaporation was less than 2×10^{-10} mbar. The iron uptake was monitored from the ratio of the normalised peak-to-peak Auger intensities of iron (47 eV) and copper (63 eV). Iron deposition rate was controlled by monitoring the iron partial pressure during deposition.

3. Results and discussion

Figure 1 summarises the LEED patterns for iron films prepared at copper substrate temperatures in the range from 120–290 K. LEED patterns were observed after deposition at the given temperature, annealing to 300 K and cooling to 120 K. Figure 2 shows hydrogen thermal desorption spectra (TDS) from comparable iron films as a function of iron film thickness, after exposure to 6 L and 1.8 L of hydrogen at 180 K or less.

After iron deposition at 290 K, a $p(1 \times 1)$ LEED pattern was observed up to 2 ML iron coverages. This pattern was also observed after deposition at 120 K and annealing to 300 K. Above 3 ML of iron, deposited at 290 K, additional spots were observed due to a (4×1) superstructure. These spots became sharper at 4 ML of iron but were streaky at 5 ML, suggesting a continuous surface structural change due to the internal stress of the iron films.

Iron films deposited at 120 K and annealed to 300 K gave rise to a much sharper (4×1) LEED pattern at 3–4 ML coverages, with each superlattice spot being clearly visible. Further increase in iron coverage caused streaking in the (4×1) structure and gave a sharp (5×1) pattern at 5 ML iron coverages. This observation of the dependence of the superstructure formed on the substrate temperature during deposition is consistent with recent XPS forward scattering results [3].

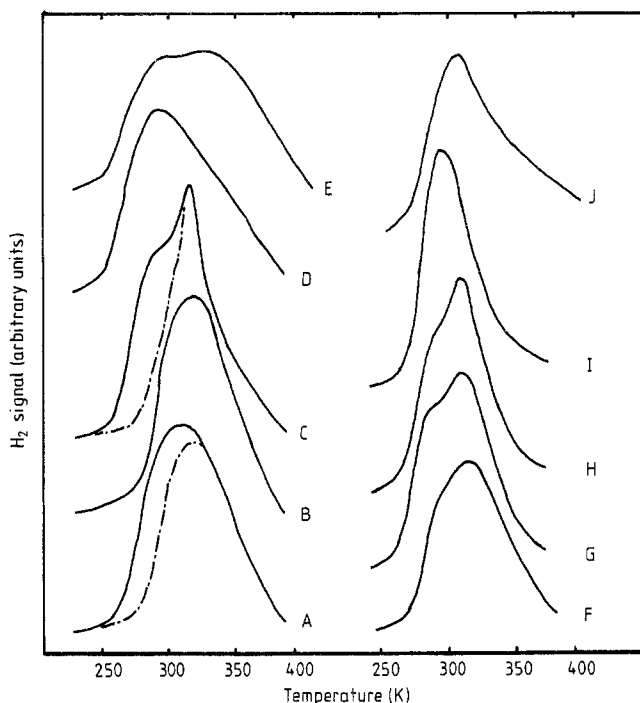


Figure 2. Thermal desorption spectra for hydrogen adsorbed on iron films as a function of iron coverage. Films grown at 120 K and annealed to 300 K: A, 3 ML; B, 4 ML; C, 5 ML; D, 8 ML; E, 12 ML. Films grown at 290 K: F, 3 ML; G, 4 ML; H, 5 ML; I, 8 ML; J, 12 ML. The chain curve indicates desorption of an initial exposure of 1.8 L of hydrogen; the full curves indicate desorption of an initial exposure of 6 L of hydrogen.

Changes in the LEED patterns were accompanied by corresponding changes in the thermal desorption spectra. For the annealed films, the change in LEED pattern was accompanied by an increase in desorption peak intensity and a shift down to 310 K, giving a heat of adsorption of $76 (\pm 1) \text{ kJ mol}^{-1}$. In particular, the desorption observed from the 5 ML film (figure 2(c)) gave a very narrow desorption peak, particularly apparent at low (1.8 L) coverages of hydrogen, indicating that the surface had a high degree of long-range order and flatness. However, above 8 ML of iron, annealed films did not give a well-ordered structure, with correspondingly broad thermal desorption peaks. Films grown at 180 K and annealed to 300 K gave identical results to those which were grown at 120 K and annealed to 300 K.

For films grown at 290 K a similar correlation was observed in that, as the (4×1) superstructure developed above 3 ML of iron, the hydrogen desorption peak shifted to lower temperature with iron coverage until at 8 ML a single desorption peak was observed at 290 K. This resembled the desorption peaks observed for the $\text{H}_2\text{-Fe}(100)$ BCC system [4] where very high hydrogen exposures were used. At low exposures, such as those in these experiments, the desorption peak from BCC Fe(100) was found to be at 400 K. For the 8 ML film grown at 290 K the desorption energy is found to be $71 (\pm 1) \text{ kJ mol}^{-1}$, compared to the values in the range $88\text{--}109 \text{ kJ mol}^{-1}$ for the low-indexed faces of BCC iron.

For 6–10 ML iron films grown at 290 K a two-fold LEED pattern was obtained as shown in figure 1. The pattern appeared as a weak (2×1) pattern, but systematic absences

occurred at $(h + \frac{1}{2}, 0)$ and $(0, k + \frac{1}{2})$; thus we denote it $p(2 \times 2)$ - $p4g$. This pattern became more intense on adsorption of hydrogen, the effect of which was most marked at 8 ML iron coverages, the role of hydrogen being to stabilise the surface reconstruction. This has been discussed in detail elsewhere [5].

The well ordered LEED patterns observed in this study can be compared to the superstructures reported for thinner films by Daum *et al* [2]; they reported the (5×1) pattern for 1 ML films and the (2×1) pattern for 2–3 ML films. We account for these differences in terms of the growth conditions, surface defects and roughness. Daum *et al* grew their films at 350 K, while ours were grown at either 290 K or at 120 K and annealed to 300 K. Recently it has been shown [6] that a high degree of interdiffusion takes place at high growth temperatures, but our TDS peaks occurred at temperatures below which significant structural changes and interdiffusion takes place.

Iron films grown at 290 K at thicknesses in excess of 10 ML gave streaky (3×1) LEED patterns with high backgrounds. Adsorption of hydrogen increased the streaking and gave even higher backgrounds. Correspondingly, the thermal desorption spectra began to show the formation of a higher-temperature thermal desorption extending up to 400 K—typical of a low-indexed BCC iron surface. This indicates the onset of disorder, possibly due to the formation of microfacets of BCC iron.

4. Conclusions

This work illustrates the critical dependence of the properties of the iron films on their growth conditions. At film thicknesses between 3 and 5 ML, FCC films exhibiting long-range ordering and flatness can be produced by growth at 120 K and annealing to 300 K. Above 5 ML, this growth method results in disordered layers. Thicker ordered films can be grown at 290 K, the most highly ordered being of 8 ML of iron.

The changes in the observed thermal desorption spectra corresponded well to changes in the surface structure observed by LEED.

The heat desorption of hydrogen on the flattest, most highly ordered films are in the range 71–6 kJ mol⁻¹, which is considerably lower than those observed from BCC iron crystals (88–109 kJ mol⁻¹), indicating a lower activation energy barrier for hydrogen on the FCC surface. This is of particular interest for studies of catalytic activity.

Acknowledgments

We thank SERC for a Post-Doctoral Research Assistantship (CE) and a Post-Doctoral Fellowship (EMcC).

References

- [1] Clarke A, Rous P J, Arnott M, Jennings G and Willis R F 1987 *Surf. Sci.* **192** L843
- [2] Daum W, Stuhlmann C and Ibach H 1988 *Phys. Rev. Lett.* **60** 2741
- [3] Steigenwald D A, Jacob I and Egelhoff W F Jr 1988 *Surf. Sci.* **202** 472
- [4] Bozso F, Ertl G, Grunze M and Weiss M 1977 *Appl. Surf. Sci.* **1** 103
- [5] Egawa C, McCash E M and Willis R F 1989 *Surf. Sci. Lett.* **215** L271–8
- [6] Arnott M and Allison W 1989 *Physica B* at press