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Epitaxic Growth of Iron on Alkali Halides

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Studies of the epitaxic growth of iron on various alkali halides reveal that single-orientation (100) iron films may be grown readily on potassium chloride and potassium iodide. With most other halides examined, there is usually a tendency to form a mixture of two orientations. Film structures and decoration effects are observed on air-cleaved and vacuum-cleaved potassium iodide surfaces. Differences are observed which underline the pitfalls of too direct an interpretation of such features.

Introduction

The general features of the epitaxic growth of iron on alkali halides, observed by Brück (1936), Shirai (1937, 1938), Collins & Heavens (1957) and Heavens, Brown & Hinton (1959) are as follows. Above a certain minimum temperature, termed the epitaxic temperature, one or more complete three-dimensional orientations of the deposit material are observed. At sufficiently large (~1000–1200 Å) thicknesses of deposit, practically continuous films form for which the density lies close to that of bulk iron. The epitaxic temperatures reported lie in the range 440 °C to 520 °C for the following substrates: sodium chloride, potassium chloride, potassium bromide, potassium iodide. The above experiments have been carried out at pressures of the order 10^{-5}–10^{-4} torr, on substrates which were either cleaved, for cube faces, or polished and thermally etched. In all the above cases, the crystal surfaces had been exposed to air before the films were deposited. Recent work of Sella & Trillat (1964) and of Honjo (1964) show that epitaxic growth may occur on freshly prepared surfaces, which have not been exposed to air, at temperatures very much lower than those previously observed for air-exposed surfaces. These findings are confirmed in the results reported in this paper, which deals with the growth of iron on air-cleaved and vacuum-cleaved substrates and which reports the occurrence of decoration features on air-cleaved surfaces which, however, are absent on surfaces which are prepared *in vacuo*. This would appear to introduce some uncertainties in the usual interpretation of decoration patterns.

An ulterior motive of the investigation was to prepare continuous films of single orientation, for studies of the magneto-optical properties of the films. These results will be reported elsewhere. Earlier difficulties in obtaining single-orientation (100) iron films have been overcome, as described below.

Experimental

The evaporation source consisted of a pendant drop on the end of a Specpure iron rod, heated by electron bombardment. By suitable arrangement of shields (Heavens, 1959) contamination from the filament was avoided, as was also the risk of impurities from a crucible. The source rod was outgassed before use and no pressure rise was observed during the evaporation.

The surface temperature of the substrate was measured in terms of the reading of a thermocouple at the back of the slab. Calibration was effected in terms of the surface temperature by observing the melting of fine metallic grains on the substrate surface. The validity of this procedure was checked by noting the reading of very fine thermocouple wires embedded in the substrate surface.

On the basis of these experiments, it is clear that previous estimates of the temperature required for epitaxic growth of iron on rocksalt surfaces (prepared by cleavage in air) are too high. Complete orientation was observed at 330 °C for rates of deposition in the range 50–300 Å min^{-1}.

Films were grown on the (100) faces of various alkali halide crystals under the following conditions:

(*a*) On surfaces produced by cleavage in air.

(*b*) On cleavage surfaces which had been polished and annealed at the temperature stated for one hour (beyond which time no further change was observed in surface structure or film structure).

(*c*) On surfaces produced by cleavage in vacuum (10^{-5} torr) during the evaporation process. The substrate temperature is as stated. At the rates of deposition used, the incidence of contamination by the residual gas is very small.

Results

General features

The form of microstructure displayed by films grown under epitaxic conditions followed that shown by

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films of silver and gold in so far as growth occurred by accretion of atoms to initially isolated nuclei. However, the surface density of nuclei remained substantially constant with increasing film thickness suggesting that, for iron deposits, migration of whole nuclei, as observed for gold in the cinemicrographs of Pashley, does not occur.

The degree of orientation of the iron films was found to improve as the thickness was increased. No signs were observed of the lacework patterns obtained by Heavens, Moss, Miller & Anderson (1961) for films of nickel grown under the same conditions.

In general, similar behaviour was observed for films grown under conditions (*a*) and (*b*); for films produced on surfaces cleaved during deposition, marked differences were observed, both in orientation and in microstructure.

Growth on air-cleaved surfaces

Films were grown on substrates of sodium chloride, sodium bromide, potassium bromide, potassium chloride and potassium iodide which had been first cleaved and then polished and annealed. No significant differences were observed for these two surface treatments.

On (100) substrates of NaCl at 330°C, the usual double orientation of (100) Fe films was observed:

$$\langle 001\rangle \text{ Fe} \parallel \langle 001\rangle \text{ NaCl}$$
$$\text{and } \langle 011\rangle \text{ Fe} \parallel \langle 001\rangle \text{ NaCl}$$

for rates of deposition up to about 200 Å min^{-1}. At higher rates, however, (>300 Å min^{-1}) the first-mentioned orientation persisted and the second did not occur.

Deposition under similar conditions on sodium bromide crystals at 330°C produced the same mixed orientation of (100) films together with the following:

$$\text{Fe } (110)\ \langle 001\rangle \parallel \text{NaBr } (100)\ \langle 001\rangle$$
$$\text{Fe } (110)\ \langle 110\rangle \parallel \text{NaBr } (100)\ \langle 001\rangle\,.$$

The latter is an unusual orientation. Study of the relative atomic positions in the apparently juxtaposed faces yields no plausible explanation. This is not very surprising – this kind of approach is only rarely fruitful.

On (100) faces of potassium bromide, parallel orientation of iron was observed, usually with the two orientations at 45°, as in sodium chloride and sodium bromide. Occasionally, the (100) films of iron were observed to grow with the iron cube directions inclined at 30°. On potassium chloride, however, deposition under most conditions yielded single-orientation films. At low rates of deposition a faint sign of the second orientation was sometimes discernible, but at 300 Å min^{-1}, single-orientation films, with $(100)\langle 011\rangle$ Fe $\parallel$ (100) $\langle 001\rangle$ NaCl, were produced without difficulty. Generally similar behaviour was observed with substrates of potassium iodide. As this material was selected for the investigations on vacuum-cleaved surfaces, results with this material will be discussed below.

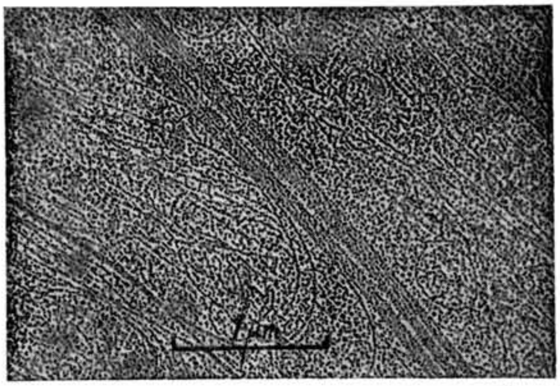

Fig. 1. Iron deposit on potassium iodide surface at 70°C. Substrate cleaved *in vacuo* and briefly exposed to air.

It thus appears that the earlier difficulties which prevented the use of this technique for the production of single-crystal (100) iron films of single orientation may be overcome by the appropriate choice of substrate and rate of deposition.

Comparison of films on air-cleaved and vacuum-cleaved surfaces

It has been clear for some time that in very few studies of epitaxy have the arriving atoms enjoyed unrestricted access to the force fields of the surface atoms of the substrate used. Not only have surfaces been exposed to the atmosphere, and generally mutilated to produce the desired crystal face, but most experiments have been conducted in what must now be described as dirty vacua. Recent work with the field-ion microscope serves to indicate for how short a time after preparation a contamination-free surface will exist. There are two ways in which the effects of contamination may be avoided. One is to work under ultra-high vacuum conditions whilst the other, adopted in this work, is to prepare a fresh surface of the substrate during the course of the deposition. Except at very low rates of deposition, the extent of contamination of the crystal surface is reduced to negligible proportions. This method is necessarily restricted to the study of film growth on cleavage surfaces: it has been used here to study the microstructure of iron deposits on potassium iodide cleavages.

Optical examination (phase contrast) of the cleaved potassium iodide surface reveals the usual strain lines radiating from the point of cleavage. Gobeli & Allen (1960) have successfully used an L-shaped crystal, cleaved at the end of the shorter arm, to produce surfaces which are free of such strain lines. This method was quite unsuccessful with the potassium iodide crystals used in these experiments, probably because of the large strains present in the crystals.

The film structures observed on air-cleaved and on vacuum-cleaved-and-exposed surfaces were similar to those observed by Sella & Trillat for silver on rocksalt, except that the development of etch figures along

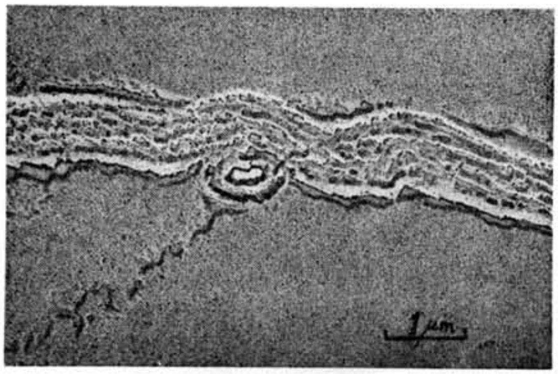

Fig. 2. As in Fig. 1. Temperature 100 °C.

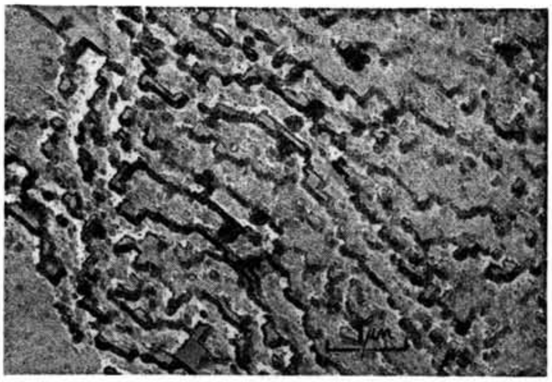

Fig. 3. As in Fig. 2. Temperature 120 °C.

Fig. 4. Iron deposit on potassium iodide surface cleaved during deposition at 300 Å.min^{-1}. Substrate temperature 120 °C.

cleavage steps occurred at much lower temperature for potassium iodide than for sodium chloride. Thus a typical area of a potassium iodide surface which has been cleaved *in vacuo* at a temperature of 70 °C and briefly exposed to air produces an iron film showing the features of Fig. 1. Figs. 2 and 3 show the film structures obtained from similar surfaces at temperatures of 100 °C and 120 °C respectively. Aggregations in the iron film reveal etch patterns on the crystal surface.

In sharp contrast to the etch patterns revealed in the surfaces prepared as described above were those obtained on surfaces which were cleaved during the evaporation procedure. Thus Fig. 4 was obtained from a surface cleaved at 120 °C during deposition of iron at a rate of 300 Å min^{-1}. Cleavage steps appear, with signs of conchoidal fracture in some regions, but there is no sign of the etch figures characteristic of the air-exposed surfaces. It appears therefore that the well-marked etch patterns of Figs. 2 and 3 may be associated with the exposure to air of the crystal surface before deposition of the film. Potassium iodide is highly hygroscopic and it is probable that adsorption of water is associated with the observed etching. It would thus appear that circumspection is needed in associating the surface features revealed by the deposited film with topographical features of the virgin surface.

Decoration effects with gold and iron deposits

Decoration effects on potassium iodide were observed when iron was used as deposit material, and were found to be similar in general form to those observed by Bassett (1958), Sella, Conjeaud & Trillat (1958) using gold. These effects show best when the mean thickness of the deposited material is much less than 100 Å. As in the experiments described above, no decoration features were observed, either with gold or with iron, on surfaces cleaved *in vacuo* during the deposition process. This behaviour differs completely from that of heated sodium chloride on which excellent decoration features were observed (Sella & Trillat, 1963) with gold and silver.

A comparison of the decoration patterns by Au and Fe on surfaces cleaved *in vacuo* and exposed to air is seen in Figs. 5 and 6. Cleavage steps are revealed in both patterns but the crystallite size in the iron patterns is substantially smaller than that of the gold pattern, suggesting that the surface mobility of the iron atoms is lower than that of gold atoms. Around the aggregated crystallites in Fig. 5 are seen denuded patches on the surface of the order 1000 Å across. In the higher magnification pattern of Fig. 7 for the iron deposit the denuded regions beside the cleavage steps are seen to be only 200 Å wide. Close inspection of the apparently curved lines on Fig. 6 reveals that these are in fact formed of fine zigzags, with lines in the directions of the cube axes. Signs are also observed of aggregation of the crystallites into line features (Fig. 8) which do not, however, follow the crystal axis dir-

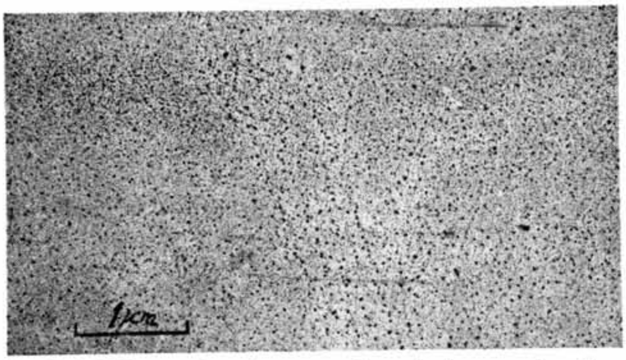

Fig. 5. Gold decoration of vacuum-cleaved, air-exposed surface of potassium iodide at room temperature.

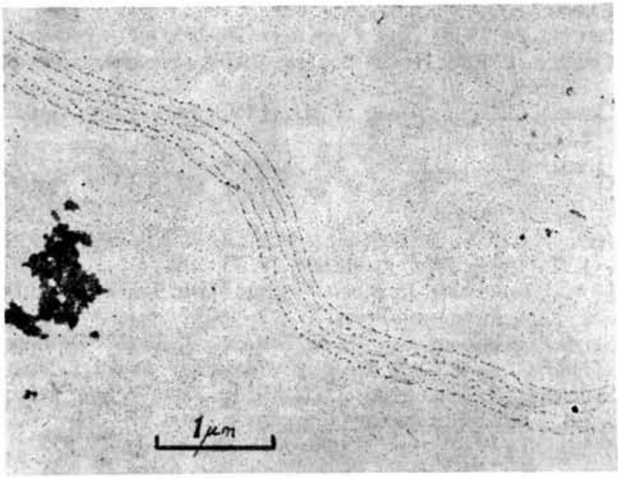

Fig. 6. Surface prepared as for Fig. 5 and carrying iron deposit.

ections. In places a suspicious periodicity in the formation of small aggregates is evident. It is possible that this represents an early stage of development of lacework patterns, such as are observed with nickel deposits on sodium chloride. The tendency to align approximately in one direction may indicate forces of magnetic origin, since stray magnetic fields would be present in these experiments.

A variation in the condensation coefficient for surfaces under different conditions has been observed, *e.g.* by Sella & Trillat, for glass surfaces exposed to air or broken in vacuum. These authors observed a similar difference in the behaviour of air-cleaved and vacuum-cleaved sodium chloride, which is also found to be the case for iron on potassium iodide. However, a variation was also observed in these experiments in different parts of the *same* film (Fig. 9) despite the facts that (*a*) the potassium iodide crystal exhibited no serious misorientation and (*b*) the iron deposits were well oriented. This suggests a mosaic structure in the underlying crystal in which different regions were in slightly different states of strain. Very large variations in condensation coefficient are seen in regions close to the clamp which holds the crystal (necessarily rather

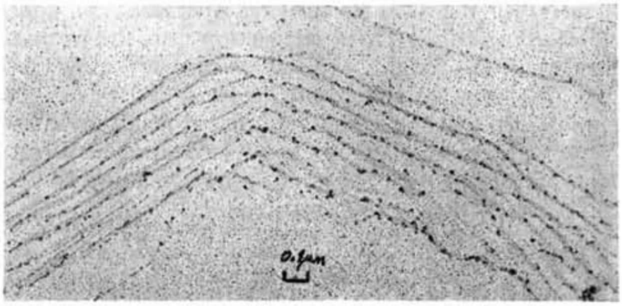

Fig. 7. As for Fig. 6 at higher magnification.

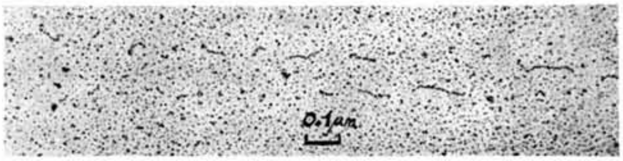

Fig. 8. Linear aggregation of iron nuclei on potassium iodide surface vacuum-cleaved and air-exposed at room temperature.

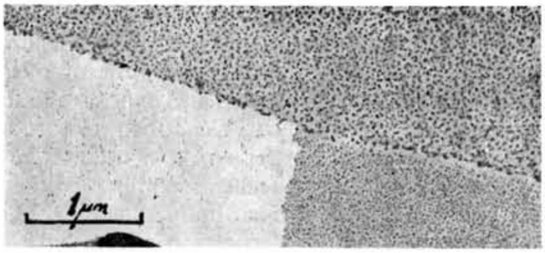

Fig. 9. Variation of condensation coefficient in different parts of same film on potassium iodide surface.

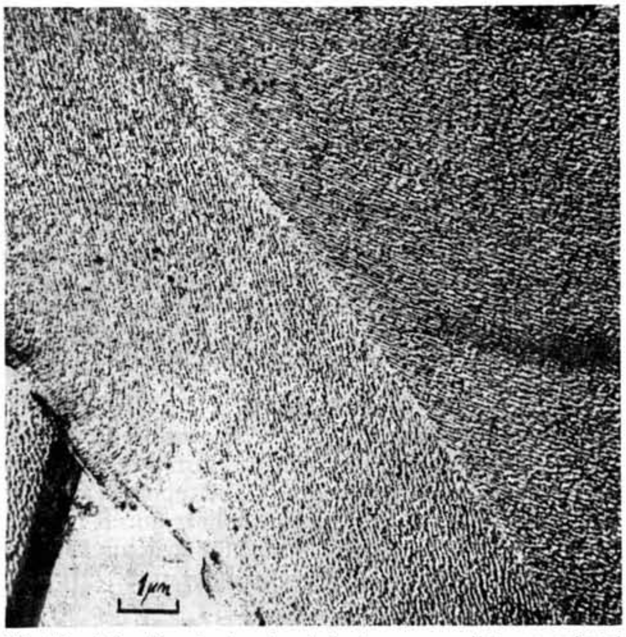

Fig. 10. Directional structural features, possibly associated with strain, on iron film on potassium iodide surface.

fiercely) for the vacuum cleavage operation. In addition to the variation in condensation rate, the form of deposit in the neighbourhood of mosaic boundaries may also vary, as shown in Fig. 10. It must again be emphasized that the crystallographic orientation in the film of Fig. 10 was very highly developed. The directions of the furrows appeared quite unrelated to the directions of the deposit crystal axes.

Conclusion

By choice of suitable substrate, deposition temperature and rate of deposition it has proved possible to grow films of iron in single orientation. Potassium chloride and potassium iodide are particularly suitable, at 330 °C and at a deposition rate of the order 300 Å.min^{-1}.

The structure of the iron deposit obtained depends on whether or not the substrate has been exposed to air. As has been previously observed, epitaxic growth takes place on vacuum-cleaved surfaces at significantly lower temperatures than for surfaces which have been exposed to air. Whereas a temperature of 320 °C is required for complete orientation of iron on air-cleaved potassium iodide, a temperature of 260 °C suffices for the vacuum-cleaved material. Deposition during the act of cleaving the crystal ensures a minimum of interference from residual gas atoms and exposes the deposit material more strongly to the substrate forces. In contrast, however, to earlier work, a qualitative difference is observed in the decoration effects of the iron nuclei compared with those obtained with gold. Although generally similar decoration effects have been observed as with gold, such decoration was obtained only on surfaces which had not been exposed to air. Strong etch figures developed on air-exposed surfaces under conditions for which no trace of etching was observed on the vacuum-cleaved surface. Although this suggests a powerful effect of the adsorbed air, or probably water and carbon dioxide, on the surface, it is not clear how the initial adsorbed layer can result in etching to the very substantial depths observed.

The mobility of iron atoms on the potassium iodide surface appears to be lower than that generally observed for silver and gold on halide surfaces, leading to decoration patterns of somewhat higher resolution than is possible with the noble metals.

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The Crystal Structure of High-Pressure UO_3*

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The high pressure modification of uranium trioxide is orthorhombic with $a = 7{\cdot}511 \pm 0{\cdot}009$, $b = 5{\cdot}466 \pm 0{\cdot}008$, and $c = 5{\cdot}224 \pm 0{\cdot}008$ Å. The unit cell contains four formula weights and the space group is $P2_12_12_1$. Each uranium atom is bonded to seven oxygen atoms leading to shared $[UO_7]$ configurations. Two short bonds of 1·80 Å and 1·85 Å are nearly equal and collinear and are identified as uranyl bonds. The five secondary bonds form a puckered pentagonal coordination about the uranyl groups. The formula may thus be written as $(UO_2)O$. Bond distances vary considerably but are consistent with published bond strength–bond length values.

Introduction

Six crystalline forms of UO_3 and one amorphous modification are known. The high pressure type described here is the seventh polymorph to be reported and was produced at a pressure of 30 kilobars and a temperature of 1100 °C. Crystals suitable for structural studies were prepared at pressure and temperature.

Crystallographic data

The symmetry is orthorhombic with

$$a = 7{\cdot}511 \pm 0{\cdot}009 \text{ Å}$$
$$b = 5{\cdot}466 \pm 0{\cdot}008$$
$$c = 5{\cdot}224 \pm 0{\cdot}008$$
$$D_{\text{X-ray}} = 8{\cdot}85 \text{ g.cm}^{-3}$$
$$D_{\text{meas.}} = 8{\cdot}62 \text{ g.cm}^{-3}.$$
$$Z = 4$$

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.