

molecules necessarily possess the symmetry $m=C_s$. The bond lengths and angles, together with their estimated standard deviations, are given in Table 3. The accuracy

Table 3. *Bond lengths and angles*

Se-C	1.86 Å	with $\sigma=0.10$ Å
C-N	1.42 Å	with $\sigma=0.15$ Å
Se-C-N	177°	with $\sigma=6^\circ$
C-Se-C	119°	with $\sigma=6^\circ$

of these values is so low that no conclusions about the nature of the bonding can be drawn. The closest approach between neighbouring molecules is between selenium and nitrogen atoms (close approaches shown by dotted lines in Fig. 1); the distance between these is 2.35 Å, with standard deviation 0.10 Å, which is significantly shorter than the sum of the van der Waals radii (3.5 Å).

The calculations were carried out on the Durham University Pegasus Computer with programs devised by Cruickshank & Pilling (1961) and Samet. The atomic scattering factors used were those of Thomas & Umeda

(1957) for selenium, and Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and nitrogen.

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References

- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 CRUICKSHANK, D. W. J., PILLING, D. E. & (in part) BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
 FEHÉR, F., HIRSCHFELD, D. & LINKE, K.-H. (1963). *Acta Cryst.* **16**, 154.
 FOSS, O. (1956). *Acta Chem. Scand.* **10**, 136.
 THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

Acta Cryst. (1963). **16**, 844

Electron-diffraction evidence of an outward growth tendency in electrolytic crystal growth.

By A. K. N. REDDY* and H. WILMAN, *Applied Physical Chemistry of Surfaces Laboratory, Chemical Engineering Department, Imperial College, London, England*

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The present authors have systematically studied, by electron diffraction, the structure and growth of iron electrodeposits on copper (100), (110) and (111) single-crystal substrates. The work has been described in detail elsewhere (Reddy, 1958; Reddy & Wilman, 1959). The purpose of this short communication is to describe an interesting observation made on iron electrodeposits on the copper (110) face.

Results

The epitaxy of iron on the copper (110) face corresponded to Fe (211) || Cu (110) with Fe $[\bar{1}11]$ || Cu $[1\bar{1}0]$. This orientation relationship only stipulates that two crystal axes of iron are fixed relative to the copper substrate lattice. The third axis can take up one of two possible positions. Thus the iron deposit crystals can grow on the copper (110) face in two crystallographically equivalent ways without violating the requirements of epitaxy. Corresponding to each of these orientations there is a particular electron diffraction pattern. With the electron beam along the Cu $[1\bar{1}0]$ azimuth the hexagonal patterns from the two possible orientations coincide with each other. When, however, the beam is along the Cu $[001]$ azimuth, each orientation contributes a distinct rectangular spot pattern (the sides of the rectangle being in the ratio 1:½) with the 211 spot in the plane of incidence (Figs. 1 and 4).

The interesting feature of patterns with the beam

* Present address: The Electrochemistry Laboratory, University of Pennsylvania, Philadelphia 4, Pennsylvania, U.S.A.

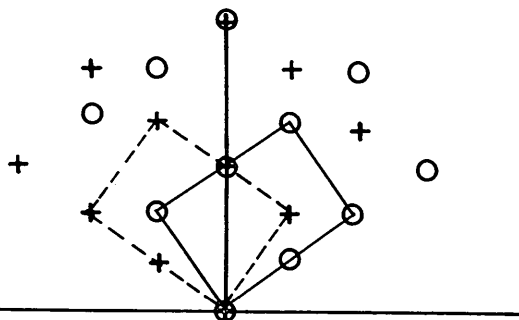


Fig. 4. Theoretical pattern based on Fe (211) || Cu (110) and Fe $[\bar{1}11]$ || Cu $[1\bar{1}0]$ with beam parallel to Cu $[001]$ azimuth.

along the Cu $[001]$ azimuth concerns the *intensity* of the component $\sqrt{2}$ -rectangle patterns. Figs. 1, 2 and 3, for example, are patterns obtained from 1000 Å thick iron deposits from a ferrous ammonium sulphate (350 g.l⁻¹) — sulphuric acid (2.5 g.l⁻¹) bath with a current density of 25 mA.cm⁻² at room temperature (20 °C). They show that the two component patterns are equal in intensity only in Fig. 1, which has been taken with the electron beam grazing the flat middle part of the single-crystal surface. At the curved edges of the specimen, where the surface deviates slightly from the Cu (110) plane, Figs. 2 and 3 show that one of the component patterns is much more intense than the other. That component pattern is more intense in which the line joining the 000 and 011 spots makes a smaller angle

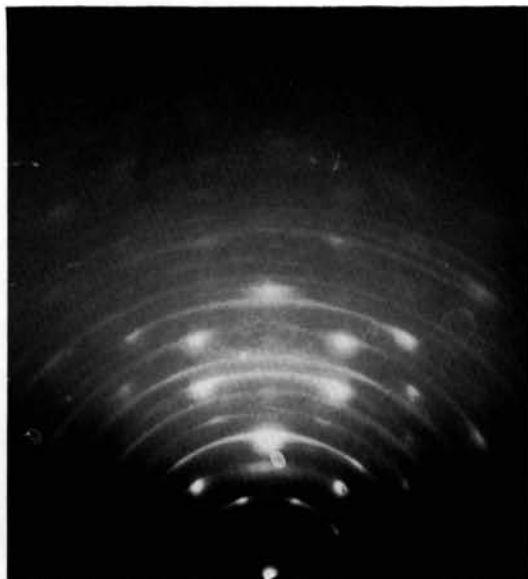


Fig. 1. Electron diffraction pattern of 1000 Å thick Fe electrodeposited on Cu (110) face. Beam along the Cu[001] azimuth. Pattern obtained from middle of crystal surface.

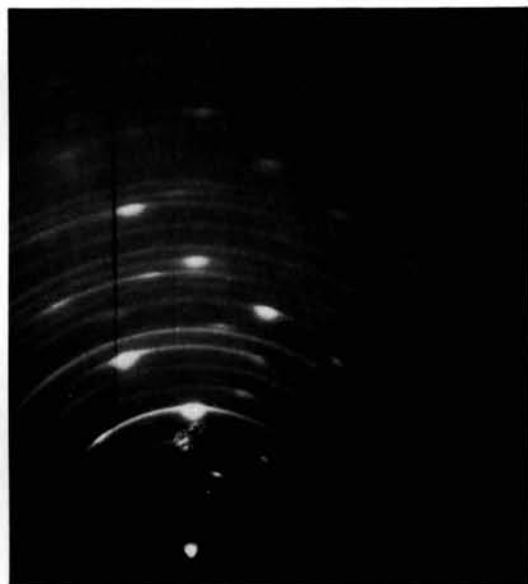


Fig. 2. Electron diffraction pattern obtained from LEFT edge of crystal surface. Same deposit as in Fig. 1.

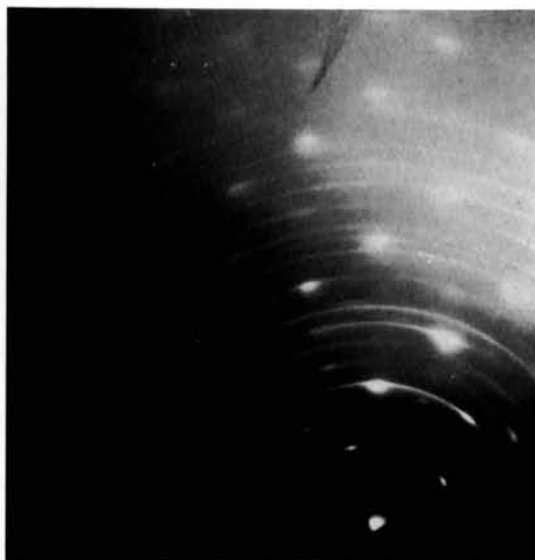


Fig. 3. Electron diffraction pattern obtained from RIGHT edge of crystal surface. Same deposit as in Fig. 2.

with the normal to the surface (the surface being defined by the shadow edge).

The relative intensities of the component patterns depend on the proportion of deposit crystals in the corresponding orientation. When the relative intensities of the component patterns are equal, it can be concluded that both the crystallographically equivalent orientations are equally adopted for growth. *At the edges of the substrate surface, therefore, electron-diffraction examination indicates that there is a preferential growth of crystals in one of the two crystallographically equivalent orientations.*

Discussion

Electron-diffraction studies (Finch, Wilman & Yang, 1947; Setty & Wilman, 1955), have established the stage-wise growth of electrodeposits, each stage having a characteristic orientation of the deposit crystals. The first stage is marked by a strong substrate influence on the orientation of the deposit crystals. Where single-crystal substrates are used, epitaxial orientations are observed in the first stage.

If the atomic forces that induce epitaxy were the only ones operating, then the two crystallographically equivalent orientations of Fe on Cu (110) should be equivalent from the point of view of growth also. The observation that deposit crystals show, under certain circumstances, a preference for one of the two equivalent orientations clearly points to the operation of another force which will be considered below.

Finch, Wilman and co-workers have discussed the two main modes of growth adopted by compact electrodeposits, *viz.* outward and lateral growths. Outward growths are characterized by columnar, dendritic, needle-like crystals, *i.e.* crystals with greater height than girth.

The origin of outward and lateral growths has been considered recently (Rajagopalan & Reddy, 1960). It has been pointed out that the mode of transport of the depositing ion is an important factor. When the metal-bearing ion is transported to the cathode by migration under the influence of the electrical field, there is a tendency for deposition on to peaks with the result that deposit crystals have a velocity of outward growth, V_O , (in a direction normal to the substrate surface, *i.e.* parallel to the current lines) which is greater than the lateral growth velocity, V_L , (in a direction parallel to the substrate surface).

In the bath which has been used for the electrodeposition of iron, the current is carried mainly by ferrous ions whose mode of transport is, therefore, essentially by migration. Hence, apart from the deposit crystals fulfilling epitaxial requirements, they must also grow under the influence of an outward growth tendency with $V_O > V_L$.

In the middle of the substrate surface, both the equivalent orientations achieve the same rate of outward growth in the direction of the current lines (Fig. 5(a)). Thus, the diffraction patterns corresponding to them would be equally intense (Fig. 5(b)). This is not the case, however, at the edge of the substrate surface. The outward velocity of growth of deposit crystals in one of the crystallographically equivalent orientations would

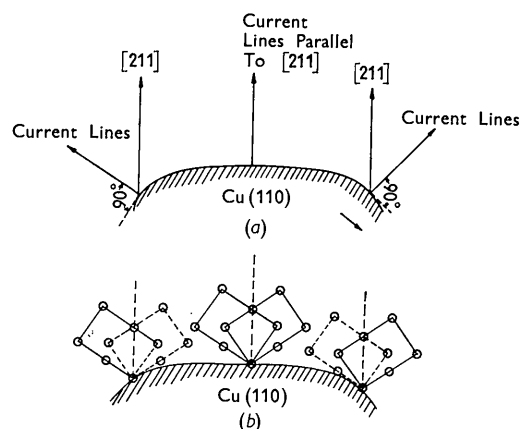


Fig. 5. (a) Relative disposition of current lines and Fe [211] direction normal to Cu (110)—in the left, middle and right edges of deposit surface. (b) Relative intensities of two crystallographically equivalent Fe (211) orientations parallel to Cu (110).

————— bright pattern; ----- weak pattern.

differ from that of the other, leading to the preferential growth of crystals in that orientation (of the two equivalent orientations) which ensures the maximum rate of outward growth. The diffraction pattern corresponding to this favoured orientation would be more intense (Figs. 5(a), (b)). In the case of Fe (211) || Cu (110) with Fe [111] || Cu [110], the preference would be for that orientation wherein the [011] lattice direction makes a smaller angle with the normal to the substrate surface, *i.e.* with the current lines.

Conclusion

The outward-growth tendency had hitherto been mainly inferred from optical microscopic observation of large crystals in fairly thick electrodeposits. In these deposits the tendency was manifested by the fact that the crystals had greater height than width. Electron-diffraction observations on 1000 Å thick iron electrodeposits have here demonstrated the outward-growth tendency leading to the preferential growth of crystals in one of two crystallographically equivalent orientations. This is apparently the first evidence for the outward-growth tendency in thin electrodeposits.

References

- FINCH, G. I., WILMAN, H. & YANG, L. (1947). *Disc. Faraday Soc.* **1**, 144.
 RAJAGOPALAN, S. R. & REDDY, A. K. N. (1960). Paper read at the First Seminar on Electrochemistry, held at Karaikudi in April, 1960.
 REDDY, A. K. N. (1958). Ph.D. Thesis, University of London.
 REDDY, A. K. N. & WILMAN, H. (1959). *Trans. Inst. Metal Finishing*, **36**, 97.
 SETTY, T. H. V. & WILMAN, H. (1955). *Trans. Faraday Soc.* **51**, 984.