

Crystal Growth and Orientation in Deposits Condensed from the Vapour

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The nature of the crystal orientation in deposits of Zn, Cd, Sb, Bi, Fe, NaCl, NaF and PbS, condensed from the vapour upon smooth substrates initially at room temperature, is investigated by electron diffraction. The effects of substrate roughness, vapour-stream obliquity, deposit thickness, crystal habit and mobility of the deposit atoms are investigated.

Materials (Zn, Cd, Sb, Bi, NaCl) having high atomic mobility have initially a densely populated plane on the average parallel to the mean substrate plane. Further limitation of azimuthal orientation and slight inclination of the mean axis from the substrate normal is found at the surface of thick deposits, resulting from the preferred growth of those crystals whose main faces are most nearly normal to the oblique vapour stream.

Materials (Fe, NaF, PbS, CaF₂, Al) with low mobility have little or no orientation in thin layers, and at oblique vapour incidence, as the deposit thickness increases, develop one-degree orientation with an oblique axis. It is concluded this oblique orientation originates from the fine-scale roughness of the deposit surface, followed by attainment of appreciable atomic mobility, leading to preferred growth of those crystals having free surfaces in the form of characteristic faces.

1. Introduction

Deposits condensed from the vapour upon substrates of various kinds have recently become much used in industry and research for many purposes. Many electron-diffraction results have shown that the crystals in such deposits on a smooth amorphous or inactive crystalline substrate tend to grow in preferred orientations. The crystals have then, on the average, a densely populated net plane of a certain type parallel to the (macroscopic) substrate surface, but there is more or less spread from the mean. The interpretation now generally accepted is that such a 'one-degree' orientation originates from the tendency of the atoms (or ions or molecules), when their mobility is sufficient on the substrate at the condensation temperature, to aggregate first in close packing to form plane sheets of monatomic or monomolecular thickness on the substrate.

In a few cases, however, where experiments have been made with a stream of vapour incident obliquely on the substrate, a one-degree orientation has been found but with the orientation axis inclined away from the substrate normal, towards the vapour stream but not to full parallelism with it (Burgers & Dippel, 1934 (CaF₂); Burgers & Ploos van Amstel, 1936 (Ba); Beeching, 1936 (Al); Nelson, 1937 (Fe)). This type of orientation has not yet been investigated in much detail experimentally, nor have the available results been satisfactorily interpreted. Burgers & Dippel suggested that the orientation axis was inclined because the crystals developed plane facets. They considered that, of the initially-formed random crystals, those orientated with such a facet more or less perpendicular to the incident vapour stream must

tend to grow sideways (parallel to the facet plane) more rapidly than crystals not so orientated; they thus acquire a larger and larger share of the incident atoms and predominate in the upper parts of the deposit. These authors suggested that the only partial inclination of the orientation axis towards the vapour stream might be due to a greater rapidity of lateral extension of such facets in crystals orientated with these facets inclined at low angles to the substrate surface, which they considered only as an ideal plane. This explanation was also quoted by Beeching (1936), Thomson & Cochrane (1939, pp. 167-9) and Thomson (1948) without further clarification.

The experiments outlined below now lead to (i) recognition that the degree of mobility of the atoms (or ions or molecules) on the substrate and deposit surface is the ultimate factor which decides whether the one-degree orientation axis is normal to or inclined to the substrate surface; (ii) a demonstration of the effects caused on the orientation by substrate roughness and facet development on the deposit crystals; (iii) new observations on the inclined type of orientation, supporting a new interpretation of its origin; (iv) an explanation of Schulz's (1949) results from LiF; (v) examples of new methods of interpretation of electron-diffraction patterns from materials of low crystal symmetry.

2. Experimental

The deposits were prepared in a pyrex test-tube 20 cm. long and 4 cm. in diameter, closed by a rubber stopper through which passed a 1 cm. diameter glass tube leading, by a wide-bore glass tap, to a Cenco 'Hyvac'

rotary oil pump capable of reducing the pressure to 10^{-3} mm. Hg. Two brass rods passed through the stopper nearly to the far (sealed) end of the tube and carried a filament electrically heated by a.c. regulated by a series resistance.

Zn, Cd, Bi, NaCl and NaF were vaporized from a small localized quantity of the material on a 0.012 in. diameter tungsten filament about 2 cm. long, while Sb and PbS were evaporated from a small piece of the material enclosed in a nickel gauze strapped between the brass rods. Iron was in some cases evaporated directly from an electrically-heated high-purity iron wire, but more conveniently from thin iron wire wound round a tungsten filament, the iron evaporating at a suitable rate when the tungsten was white hot. A slight initial evaporation was always carried out to remove surface impurities, before using the evaporation assembly to prepare deposits.

Deposits of the above materials were prepared *in vacuo* on glass substrates which consisted of portions of microscope slides about 2 cm. long, 0.5 cm. broad and 1.5 mm. thick. These were placed about 0.5–0.8 cm. from the vapour source, which was nearly above one end of the glass, so that the effect of vapour-stream obliquity could be investigated in each specimen. The glass substrates were first washed in benzene, then placed in a mixture of alcohol and nitric acid, next washed with distilled water and finally dried on a clean filter paper, thus providing a grease-free surface. In the case of Zn and Fe, deposits were also prepared on fresh cleavage faces of rocksalt and muscovite mica and on liquid glycerol surfaces to test the effect of substrate roughness on the deposit orientation. The metal deposits were practically opaque (several thousand Å thick) in the region of normal incidence, and transparent or translucent (~ 200 – 500 Å thick) where the vapour was incident at about 70° to the normal. They were prepared on substrates initially at room temperature and unheated except by radiation from the hot source of vapour.

The deposits were examined by electron diffraction in a Finch-type camera (Finch & Quarrell, 1933;

Finch & Wilman, 1937), using 50–65 kV. electrons and a camera length of approximately 50 cm. For interpretation of the photographs the methods described by Wilman (1952) were used.

3. Results

For brevity i and δ denote the inclination of the vapour stream and the orientation axis, respectively, to the substrate normal; and the A and B azimuths of the electron beam denote the directions along and perpendicular to the plane of incidence of the vapour stream, respectively. Of the materials investigated, Zn and Cd are close-packed hexagonal with $c/a=1.856$ and 1.88 respectively; Sb and Bi are referred to the pseudo-cubic face-centred-rhombohedral cells with $a'=6.22$ Å, $\alpha'=87^\circ 26'$ and $a'=6.56$ Å, $\alpha'=87^\circ 33'$ respectively; Fe is body-centred-cubic; and NaF, NaCl and PbS are face-centred-cubic. The results are shown in Table 1 and Figs. 1–19.

Under the conditions described in § 2 the crystals, in deposits of each material investigated, consistently

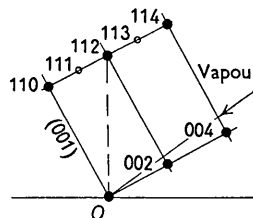


Fig. 3 (b).

developed in an orientation of one or other of the two following types, with more or less spread from the mean: (i) a one-degree orientation about a common axis normal to the substrate or practically so, but at oblique vapour incidence developing a strong azimuthal limitation in the uppermost regions when the deposit thickness was increased to a few hundred or thousand Å; or (ii) a one-degree orientation about a common axis inclined away from the substrate normal towards,

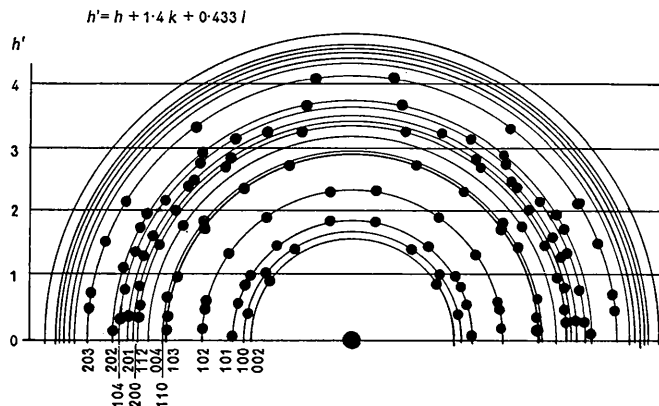


Fig. 4 (b). Theoretical pattern from Zn in $\{135\}$ orientation.

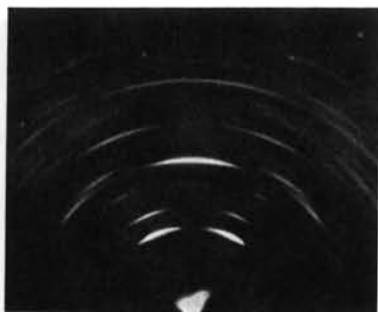


Fig. 1. Zn, {112}; $i = 0^\circ$.
(+faint ZnO, {112}.)



Fig. 2. Zn, {112}; $i = 14^\circ$.
(+faint ZnO, {112}.)

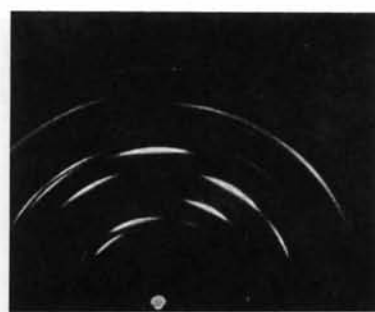


Fig. 3 (a). Zn, {112}; $i = 54^\circ$.
(+faint ZnO, {112}.)

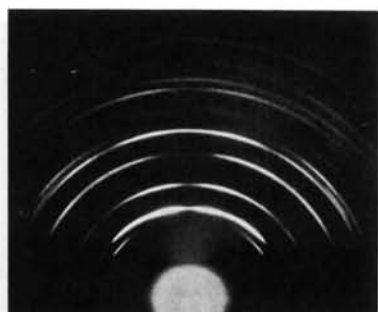


Fig. 4 (a). Zn, {135}; $i = 0^\circ$.



Fig. 5. Zn, {101}; $i = 0^\circ$.
(+faint ZnO, {101}.)



Fig. 6. Zn, {201}; $i = 0^\circ$.



Fig. 7. Zn, {001} and {100},
possibly associated with rapid
deposition.



Fig. 8. Zn, {112} on NaCl
cleavage face.

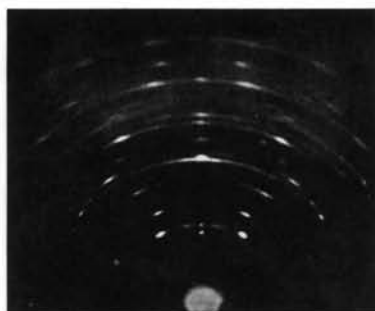


Fig. 9. Zn, {112} (+{100}+{101})
on mica cleavage face.

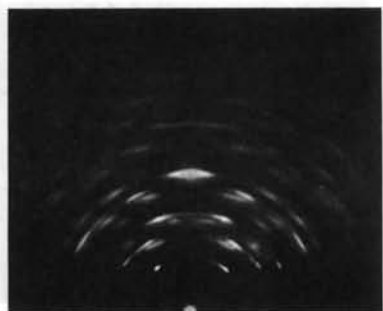


Fig. 10 (a). Sb, $\{21\bar{1}\}$ and $\{211\}$;
 $i = 0^\circ$.

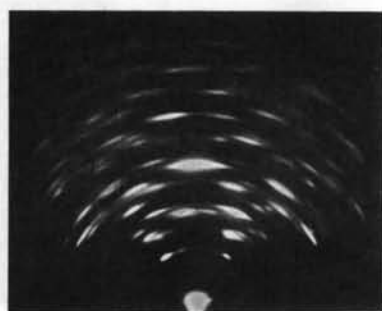


Fig. 11. Sb, $\{21\bar{1}\}$ and $\{211\}$;
 $i = 20^\circ$.

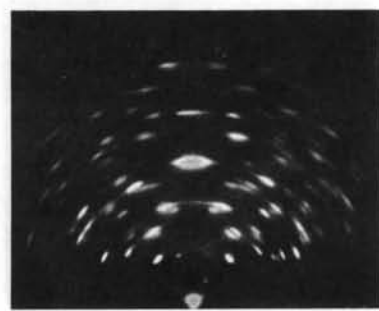


Fig. 12. Sb, $\{21\bar{1}\}$ and $\{211\}$;
 $i = 58^\circ$.



Fig. 13. Bi, $\{11\bar{1}\}$ and $\{100\}$;
 $i = 0^\circ$.

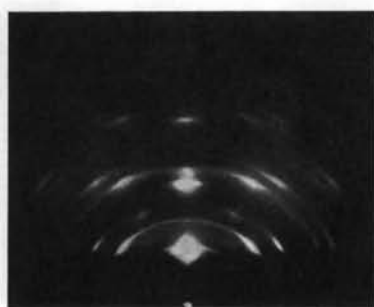


Fig. 14. NaCl, $\{001\}$; $i = 0^\circ$.

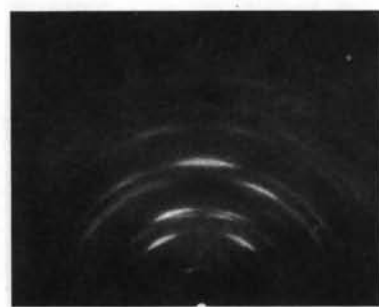


Fig. 15 (a). NaCl, $\{211\}$; $i \sim 30^\circ$.

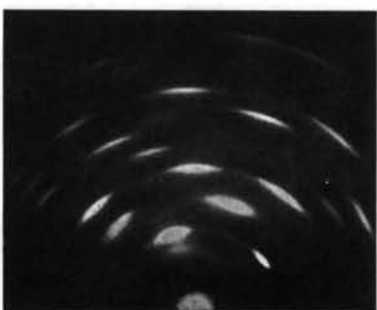


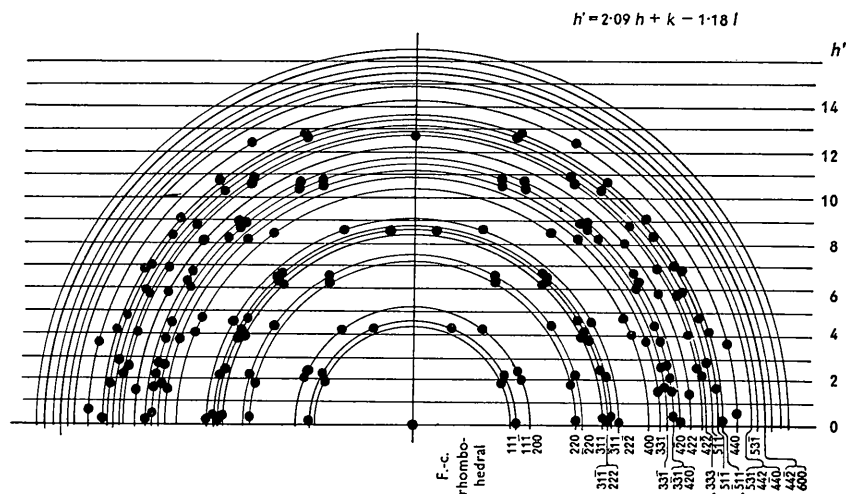
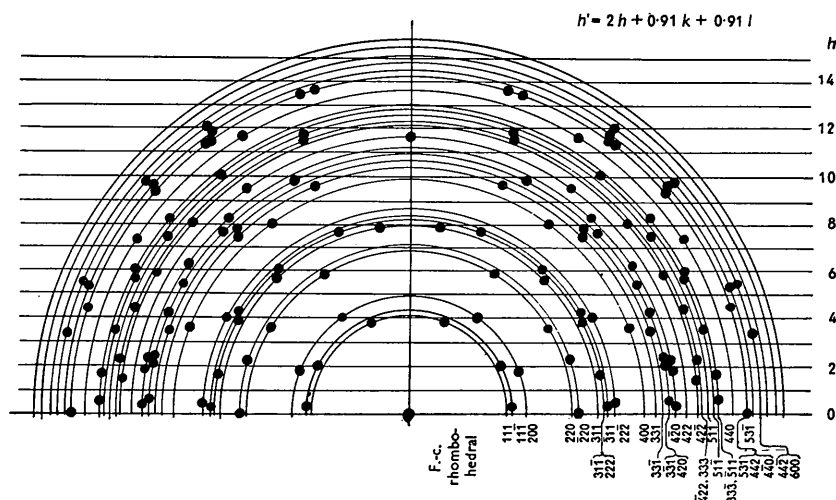
Fig. 16. Fe, $\langle 111 \rangle$; $i = 37^\circ$.



Fig. 17. Fe, $\langle 110 \rangle$ on glycerol;
 $i = 45^\circ$.



Fig. 18. PbS, $\langle 100 \rangle$ and $\langle 110 \rangle$;
 $i = 56^\circ$.

Fig. 10 (b). Theoretical pattern from Sb in $\{2\bar{1}1\}$ orientation.Fig. 10 (c). Theoretical pattern from Sb in $\{211\}$ orientation.

though not as far as, the incident vapour-stream direction, but with no marked azimuthal limitation of the orientation about the common axis even in deposits several thousand Å thick.

The electron-diffraction patterns from the type-(i) deposits normally contain arcs which, both at $i = 0$ and $i \neq 0$ in all azimuths, are symmetrically disposed relative to the plane of incidence of the electron beam, as in Fig. 1, those centred on the plane of incidence corresponding to the Bragg reflexions from the net plane $\{HKL\}$ which tends to lie parallel to the substrate. The surface regions of thick deposits, however, yield where $i \neq 0$ (sometimes even at i as small as $2-3^\circ$), in the B azimuth, patterns such as Figs. 2 and 3(a), in which the arcs of each symmetrically-disposed pair have different intensities, thus showing that the initial one-degree orientation is then further limited to a certain azimuthal range. In the $\{11\bar{2}\}$ -orientated Zn and Cd deposits both the

arc intensities and the strong optical sheen observed in defined directions due to reflexion from minute facets indicated the nature of this limitation. It is thus concluded that crystals in azimuths such that the (0001) faces were more or less facing the vapour stream (with wide scatter about the mean) had grown preferentially and predominated in the surface regions. In the $\{211\}$ -orientated NaCl a development of a $\{100\}$ habit accounted for the azimuthal limitation shown by the arc intensities, while in the $\{21\bar{1}\}$ -orientated Sb a $\{100\}$ habit appeared to be the origin.

In deposits where there is much spread from the mean one-degree orientation, as in Figs. 1-3(a), this preferential growth of favourably disposed crystals (having a face normal to the vapour stream or nearly so) leads in general, except at a certain i value, not only to the azimuthal preference of orientation but also to a mean orientation axis inclined by a few degrees from the substrate normal, so that in the B azimuth

the (*HKL*) Bragg reflexion arcs lie on a radius slightly inclined to the plane of incidence of the electron beam. At appropriate *i* values this inclination is *away from* the vapour-stream direction, as in Fig. 2, and it may be concluded that Schulz's (1949) $\langle 111 \rangle$ -orientated LiF deposit having a small inclination of the orientation axis away from the vapour stream at $i \neq 0$ originated in this way from a type-(i) orientation, not as a typical oblique type-(ii) orientation.

In the Zn patterns of Figs. 2 and 3(a) the arcs of 111 and 113 type, normally forbidden by structure factor, are probably due to secondary elastic scattering. There is also a fainter and more diffuse arc pattern due to the normal ZnO formed in $\{11\bar{2}\}$ orientation (relative to the substrate) on the Zn surface during its transference in air to the electron-diffraction camera (cf. Finch & Quarrell, 1933), and this is closely similar to the Zn pattern except for the lower axial ratio (1.602), and is likewise asymmetric in intensities relative to the plane of incidence.

Patterns similar to Fig. 4(a) (at $i=0$) were obtained at all azimuths from one deposit, and calculation by method (3) of Wilman (1952) led to estimation of the orientation as $\{135\}$ approximately. The theoretical diffraction positions calculated by method (1), Fig. 4(b), support this conclusion. The occasional modification of the initial $\{11\bar{2}\}$ orientation, in the surface of thick deposits, to a roughly $\{135\}$ type or even further, in the region where $i \simeq 0$, appears to be due to the effect of gradual preponderance of extensive $\{101\}$ facets on the crystals instead of $\{001\}$ facets as above. This would lead to more rapid lateral growth of those crystals having $\{101\}$ faces normal to the vapour-stream direction or nearly so, and thus cause progressive change of the mean orientation from $\{112\}$ towards $\{101\}$ by such preferred growth within the initial $\pm 20^\circ$ or more spread from the mean, shown by the arc lengths. A point two-thirds of the way from $[[112]]^*$ to $[[011]]^*$ has coordinates $[[\frac{1}{3}1\frac{2}{3}]]^*$ in the reciprocal lattice; thus a $[134]^*$ direction, which is near to the estimated $[135]^*$ orientation axis, could be an intermediate orientation between the initial $[112]^*$ and a final $[101]^*$ orientation axis such as Fig. 5 shows. The presence of the 101 arcs near to the plane of incidence, corresponding to Bragg reflexions from the planes parallel to the main $\{101\}$ faces, must then be explained as due to these faces being stepped, i.e.

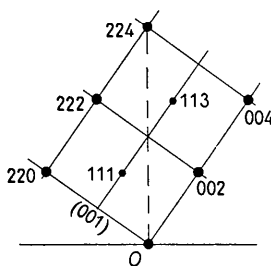


Fig. 15 (b).

built up of terraced layers some of which were laterally small enough for the electron beam to pass through. On the other hand, the 100 beams which should have given rise to the uppermost pair of 100 arcs in Fig. 4(a) would be directed at a low angle into the more massive main plate-like body of the $\{135\}$ -orientated crystals. Thus their absence in Fig. 4(a) is evidently due to absorption, as in the more usual case of weakened 00*l* diffractions. The 101 arcs nearest the plane of incidence are in fact slightly broadened, especially on their inner side, as would result from refraction at crystal faces which were at least partly tending to consist of plane $\{101\}$ faces.

The type-(ii) deposits, of Fe, PbS and NaF, all had the same type of variation of δ with *i*, as in Fig. 19. Thus with Fe, $\delta \simeq i$ up to about $10\text{--}20^\circ$ but then remained practically constant or decreased slightly as *i* increased up to 70° . In this range of *i* between 0° and 70° the local mean thickness decreased from between 5000 and 10000 Å to several hundred Å (translucent). Within the wide range of rates of deposition explored, from about 100 Å thickness/min. during $1\frac{1}{2}$ hr. to 20000 Å/min. during 0.5 min., there was no marked variation of results with rate of deposition of the Fe. Roughening the glass by light abrasion on 0000 emery or by etching in 10% HF solution also did not cause noticeable change in the nature of the deposits. The patterns from Fe on NaCl, mica or glycerol were closely similar to those from Fe on glass, and the variation of δ with *i* was also similar. On the glycerol the deposit was highly reflecting and microscopically structureless, but developed slight macroscopic wrinkling (cf. also Hast, 1948). The Fe crystals were about 50–100 Å in diameter in all these deposits.

4. Discussion

4.1. The effect of atomic mobility and deposit thickness

Taking the above results with those for Ba and CaF_2 (Burgers & Dippel, 1934; Burgers & Ploos van Amstel, 1936) and for Al (Beeching, 1936), it is clear that the materials which developed type-(i) orientation (Zn, Cd, Sb, Bi, NaCl) have relatively low melting points (419, 321, 630, 271 and 801°C .) while those developing type-(ii) orientation (Fe, PbS, NaF, Ba, CaF_2 and Al) have mostly much higher melting points (1535, 1114, 1000, 850, 1360 and 660°C .) except for Al. The inference that the type-(i) materials are characterized by high, and type-(ii) by low, atomic or molecular mobility on the substrate and the growing deposit is supported by two main classes of data. First there is the direct observation of the small crystal size and low degree of migration and aggregation of metals such as Cr (m.p. $\sim 1850^\circ\text{C}$.), (see Wyckoff, 1949); and the larger crystals and extensive migration of low-melting metals like Zn, Cd, Sb and Bi on substrates at or near room temperature (Volmer, 1921; Estermann, 1923; Gen, Zelmanoff & Schalnikow, 1933; Germer, 1939; Picard & Duffendack, 1943; Levinstein,

Table I. *Results*

Material (and substrate*)	No. of deposits	Orientation	Crystal habit	Fig. No.	Further data†
Type-(i) deposits ('normal' orientation)					
Zn (1)	21	{112}	{001}	1, 2, 3(a), (b)	1, 2, 5
	2	Not quite {112}	{001}		5
	1	{135}	{001}, {101}	4(a), (b)	—
	1	{101}	{101}?	5	—
	1	{201}	{001}?	6	—
	1	Weak {105}	—	—	—
	3	{001} + {100}	—	7	—
Zn (2)	3	Mainly {112}	{001} + ?	8 (cf. 1(b))	—
Zn (3)	3	Mainly {112}, some {100} + {101}	{001} + ?	9	—
Zn (4)	3	—	—	—	3
Cd (1)	5	{112}	{001}	—	1, 2, 5
Sb (1)	1	{211}, trace of {211}, no {211}	{100}	10(a)-(c), 11, 12	1
	1	Weak {211}	—	—	—
	1	{111}, no {111}	{100}	—	—
	1	Mainly {111}, some {110}, no {110}	—	—	1
Bi (1)	3	{111}	—	—	1
	1	{111} + some {100}	{111}	13	1, 4
NaCl (1, 5)	4	{100}	{100}	14	4
	2	{211}	{100}	15(a), (b)	4, 1
Type-(ii) deposits ('oblique' orientation)					
Fe (1)	10	<111>	{111}	16, 19	4
	1	<110>	{110}	As 17	—
Fe (2, 3)	4	<111>	{111}	As 16	4
Fe (4)	1	<110>	—	17	4
PbS (1)	2	<100>, some <110>	—	18, 19	—
NaF (1)	3	<111>	{111}?	—	4

* 1 = glass; 2 = fresh NaCl cleavage; 3 = fresh mica cleavage; 4 = glycerol; 5 = polished stainless steel.

† 1 = marked azimuthal limitation to orientations such that a main face is more or less facing the vapour stream; 2 = optical sheen observed in directions corresponding to main facets, strongest in region where vapour was normal to these faces; 3 = no condensation except at edges; 4 = strong refraction of electron diffraction beams by main facets; 5 = very weak 001 diffractions indicate {001} plate habit.

1949). Secondly there are many electron-diffraction results showing small crystal size (or even amorphous structure) in deposits on substrates at temperatures which are low relative to the melting point, larger random crystals at higher temperatures, and still larger crystals orientated on the substrate at still higher temperatures.

We thus conclude (a) that the type-(ii) (oblique) orientation is characteristic of a degree of mobility intermediate between that leading to random small crystals and that giving large crystals in type-(i) orientation; (b) that when the atomic mobility is so high that extensive plates are developed, (cf. Volmer, 1921; Straumanis, 1931, 1932; Stranski, 1949) a characteristic modification of the type-(i) orientation occurs as the deposit becomes thicker (e.g. of Zn, Cd, Sb, Bi or NaCl), leading to further (mainly azimuthal) limitation of orientation where the vapour stream is incident obliquely, and at normal incidence a modified one-degree orientation tending gradually towards that with the face normal to the vapour stream. The present results for Zn and Cd may also be compared with those of Matthewson & Phillips (1927), Straumanis (1931, 1932), Kaischew, Keremidtschiew & Stranski (1942) and Finch, Wilman & Yang (1948).

An analogous effect of the formation of plane faces on crystals leading to preferred growth of favourably orientated crystals is also important sometimes in the case of two-degree-orientated crystals growing epitaxially on a single crystal. Thus, this has been observed strongly (Wilman, unpublished) both in {211}-orientated NaCl and {111}-orientated Ag deposits on heated muscovite mica cleavages. Of the geometrically equivalent azimuthal {211} NaCl orientations, which had <011> of the NaCl parallel to one of the pseudo-equivalent mica axes of length 5.17 Å, in any part of the deposit only those NaCl crystals occurred in the one azimuthal orientation such that a cube face was most nearly facing towards the vapour stream, which came from a small source.

4.2. The effect of substrate roughness on the orientation

In Zn the type-(i) deposits on the highly smooth though stepped rocksalt appeared to have mainly a much narrower spread of orientation about the mean than in deposits on glass, which is moderately smooth though slightly wavy (cf. Backus & Williams, 1949; Schulz, 1949), and this was still less on the still more predominantly flat mica. The high perfection of orientation in Au deposits on liquid mercury may also

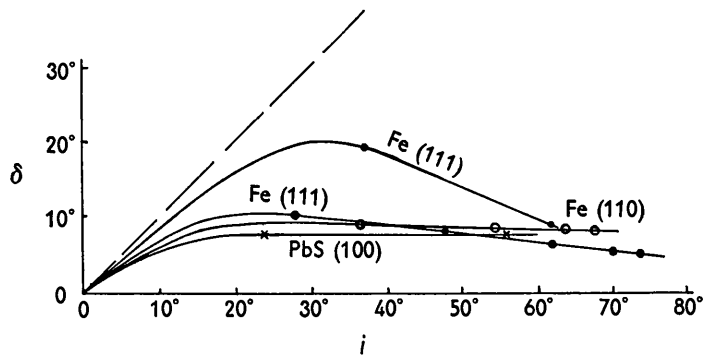


Fig. 19.

be cited (Bailey, Fordham & Tyson, 1938; cf. also Jenkins, 1935).

Iron deposits in type-(ii) orientation were closely similar on all the substrates, showing that orientation of this type is not conditioned by marked roughness of the substrate.

If highly oxidisable materials are deposited in an inadequate vacuum an initial usually rough oxide layer (cf. Stahl, 1949) will be deposited, and in the case of Ba and Al this may assist development of the oblique type-(ii) orientation (cf. §§ 4.3 and 4.1).

4.3. The nature and development of the oblique orientation

The following considerations show that since type-(ii) orientation can be developed even in deposits formed on atomically smooth substrates, it must be due to a fine-scale surface roughness of the growing deposit, though this may be increased if rough substrates are used.

First we concluded above that it must be a consequence of low atomic mobility, and conversely that high atomic mobility leads initially to type-(i) orientation with further modification if extensive plate-like habit is developed. This makes it clear that type-(ii) orientation cannot be due to such extensive outward-growing plate-like habit as occurs in Zn, Cd, Sb, Bi and NaCl. The low atomic mobility during the formation of type-(ii) deposits is shown both by the usually much smaller crystal size than that in type-(i) deposits, and by the tendency to form randomly disposed crystals in the initial stages of deposition. Thus, Nelson (1938) sometimes obtained nearly random Fe deposits, and Burgers & Dippel (1934) found that the oblique {111} orientation in CaF_2 developed only after a random layer about 500 Å thick had been deposited. This may be taken as evidence that it is the progressive heating of the deposit by radiation from the hot source of vapour* which causes sufficient increase of atomic mobility on the deposit crystals

for the arriving atoms to take up preferred positions (of low potential energy) on suitably disposed crystals.

The patterns from the type-(ii)-orientated iron deposits usually show, by refraction broadening of the arcs, that the crystals have highly smooth surface elements approximating to the plane which lies normal to the orientation axis. We therefore conclude that this appreciable mobility promotes lateral growth, along the local surface elements, of those crystals out of the random initial deposit which have a certain type of net-plane parallel to the local free surface of the deposit, this being of fine-scale roughness. This is in effect a tendency to reduce the surface energy to a minimum (cf. surface tension) and involves also a tendency to develop the preferred net plane as a more or less smooth face at the free surface of the deposit if the temperature is high enough. On the other hand, proof that the *deposit* surface is rough on a fine scale at all stages of the deposition is provided by the low background intensity in the electron-diffraction patterns, as Nelson (1938) indeed pointed out (cf. also the electron micrograms of König & Helwig, 1950).

We have therefore only to show that the above conclusions can explain the observed difference of δ and i and the variation of δ with i . Qualitatively this can be shown as follows:

For the rough surface of the deposit at the initial random stage a function $f(\varphi)$, represented by a curve such as that marked in Fig. 20, in general represents the relative proportion of the deposit surface inclined at different angles φ to the mean substrate plane ($f(\varphi) \cdot d\varphi$ represents the surface area inclined at angles between φ and $\varphi + d\varphi$), and this curve must be symmetrical in the region of normal vapour incidence ($i = 0$) and is likely to be substantially so even when i is large. The orientation of the crystals at these surface elements must also be random. If the mobility of the atoms arriving on the deposit surface is negligible before they lose their initial kinetic energy, then deposition from the vapour stream must cause all parts of the surface (except those in the 'shadow' of other projecting regions) to advance at the same rate along the reversed vapour-stream direction. Surface elements inclined at φ to the mean substrate plane

* Experiments by Wilman (1942) and Mutucumarana (1948) show that even with the tungsten filament about five times as far from the substrate as in the present experiments, the substrate surface may reach 200° C. or more above the initial temperature as deposition continues.

acquire per sec. per cm.² only $\cos(\varphi-i)$ times the amount of material acquired by elements which are normal to the vapour stream.

The curve showing the amount of material deposited on the surface elements at these inclinations φ is therefore, at $i = 0$, the curve marked $f(\varphi) \cdot \cos \varphi$ in Fig. 20, obtained from $f(\varphi)$ by multiplying the ordinates

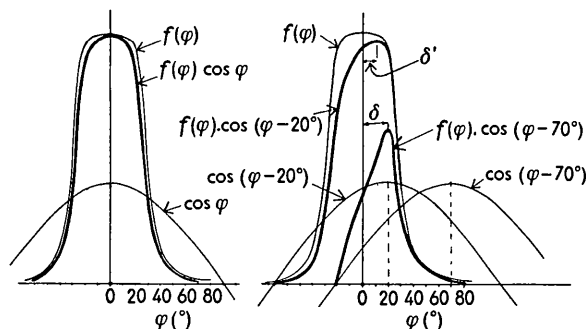


Fig. 20.

by $\cos \varphi$. At $i \neq 0$ the conditions become rather complex, but if we consider first a simpler case where the surface elements are all normal to the plane of incidence of the vapour relative to the mean substrate plane, then the corresponding curve (Fig. 20) is obtained from the $f(\varphi)$ curve by multiplying its ordinates by those of $\cos(\varphi-i)$, where i is the particular angle of incidence under consideration; and also by a factor less than unity expressing the effect of the greater distance of these regions from the vapour source. In this case the curve is clearly asymmetrical and qualitatively as shown in Fig. 20 for $i = 20^\circ$ and $i = 70^\circ$.

If now the surface mobility of the deposit atoms is sufficient to favour faces of a certain type as the free-surface form, then this curve will tend to represent also the proportional distribution (by volume) of crystals in the surface regions of the deposit (accessible to the electrons) as a function of φ . From Fig. 20 it will be seen that on this basis most of the crystals would be expected to be disposed at or near an orientation with the normal to the preferred boundary face in the plane of incidence of the vapour stream and inclined at an angle δ from the normal of the mean substrate plane towards the vapour stream, δ being less than i . The angle δ will increase continuously as i increases, according to this picture (cf. Fig. 20), but actually as i increases the curve must have a narrower peak than that for $i = 0$, because the surface of the thinner parts of the deposit must be correspondingly less rough, and this might well cause a reduction of δ with increasing i , and may even lead to an actual decrease of δ with increasing i , as observed in § 3 (Fig. 19). If these qualitative conclusions are correct, it follows that the shape of the experimental curve of δ against i indicates the degree of roughness of the surface of the growing deposit at the stage when

the preferred orientation begins to be developed. The upper curve in Fig. 19 from $\langle 111 \rangle$ -orientated iron would thus correspond to a rougher surface than that giving the lower curve.

Taking also into account the presence of surface elements tilted by a range of angles φ about axes lying in the surface and inclined at all angles η to the plane of incidence of the vapour clearly leads again to the above qualitative conclusions.

The limited penetration of the electron beam below the mean deposit surface on which it impinges at grazing incidence may in some cases affect the interpretation of the electron-diffraction results, but this is difficult to allow for, except by multiplying the $f(\varphi) \cdot \cos(\varphi-i)$ curves by a further factor which decreases as φ increases. If the projections of the rough surface have only a height of the order of 50 Å this limited penetration will not cause much change in the pattern, but if the surface is more coarsely rough then mainly only the tips of the projections will contribute to the pattern, and in that case the pattern will correspond to the finer-scale roughness of surface of the coarse projections.

4.4. Relation of other previous work to the present results

Many electron-diffraction investigations have shown that deposits of Zn, Cd, Sb and Bi condensed from the vapour on substrates at room temperature are often orientated (Kirchner, 1932, 1934; Prins, 1933; Finch & Quarrell, 1933; Dixit, 1933; Gen, Zelmanoff & Schalnikoff, 1933; Bound & Richards, 1939; Hass, 1938, 1942; Was, 1939a, b; Ruedy, 1941; Lotmar, 1945, 1947; Keogh & Weber, 1948; Levinstein, 1949). The nature of the orientation has in most cases not been elucidated, except that a $\{111\}$ (rhombohedral) orientation was concluded to occur in Sb (Kirchner, 1932; Hass, 1938, 1942; Ruedy, 1941; Lotmar, 1945, 1947) and also in Bi (Bound & Richards, 1939). In the present results, based more critically on reflexion patterns and recent techniques of interpretation (Wilman, 1952), no $\{111\}$ orientation of Sb was observed, but $\{11\bar{1}\}$ and $\{21\bar{1}\}$ (relative to pseudocubic rhombohedral axes) were found.

The asymmetrical reflexion patterns obtained from Zn by Finch & Quarrell (1933) are now seen to correspond to a medium-strong $\{11\bar{2}\}$ orientation, further limited azimuthally as in § 3 owing to $\{0001\}$ face development. The Zn reflexion pattern published by Dixit (1933) also shows such an obvious asymmetry, characteristic not of orientation on a smooth substrate, caused by recrystallisation during heat treatment, but of the type of facets developed during the initial formation of the deposit. His results for Zn cannot therefore be regarded as supporting his theory of the relation of crystal orientation to the substrate temperature.

In the case of PbS deposits the simultaneous presence of $\langle 100 \rangle$ and $\langle 110 \rangle$ orientations was also observed

frequently by Wilman (1948), but occasionally other oblique orientations, such as $\langle 311 \rangle$, were noticed.

4.5. Relation of the observed type-(i) orientations to the crystal structure

The strong preference of Zn and Cd for growth in $\{11\bar{2}\}$ orientation is at present difficult to understand in terms of the crystal structure, since this is not a particularly densely-populated plane, nor have faces of this type been observed microscopically on Zn or Cd crystals grown by condensation from the vapour.

On the other hand, the $\{21\bar{1}\}$ pseudocubic orientation and $\{100\}$ habit in Sb matches well the $\{211\}$ orientation and $\{100\}$ habit of NaCl, since the Sb structure is not very different, in its atomic positions, from that of NaCl with Sb replacing both the Na and the Cl. In NaCl both the $\{001\}$ and $\{211\}$ orientations are such that the net plane formed parallel to the surface contains equal numbers of anions and cations and consists of alternate parallel $\langle 110 \rangle$ rows of these, thus allowing easy and stable growth of these monatomically thick initial sheets from the condensed NaCl molecules.

In the deposits which developed in oblique orientation it is significant that there, also, the plane normal to the orientation axis is by no means always the most densely-populated plane, since it is mostly $\langle 111 \rangle$ in Fe (cf. also Ba), and $\langle 100 \rangle$ and $\langle 110 \rangle$ in PbS.

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