identifying the correct pair of mirror orientations). They will certainly provide for simpler calculation procedures. Nevertheless the present treatment has not that special advantage of the treatment of Fong where, provided there are four sufficiently precise \{111\} trace directions, a more expeditious solution arises from the fact that two quartic equations in a common unknown \(y\) (the counterpart of \(x\) in the present work) could then be established by considering first one set of three trace directions and then a second set from the four available trace directions. In this way \(y^4\), \(y^3\), and \(y^2\) may be eliminated between the two quartic equations and a linear equation in \(y\) results so that \(y\) is readily and uniquely obtained without having to solve a quartic equation.

References


Skew-Reflection X-ray Microscopy of the Vapor-Growth Surface of an Al$_2$O$_3$ Single Crystal

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The most commonly used geometry for the Berg-Barrett X-ray microscopy uses the zero-layer reflections as described by Newkirk. It can be shown that non-zero-layer reflections, skew-plane reflections, can be used equally well to obtain X-ray micrographs. The analysis of the stereographic representation of the skew-reflection geometry demonstrates the many usable reflections and gives the conditions for minimum image distortion. In these X-ray micrographs the contributions to diffraction contrast from shadowing and sub-boundaries can be identified. An estimate of the height of steps occurring on the crystal surface can also be made.

Introduction

Armstrong (1965) has shown that the Berg–Barrett X-ray technique can be utilized to give information on both the surface topography and the dislocation substructure threading the underlying crystal volume of a vapor-condensed zinc crystal. Zero-layer reflections, as originally described by Newkirk (1959), were employed to obtain the Berg–Barrett micrographs. Because growth processes determine the crystal-surface orientations and it is desired that these surfaces not be damaged by cutting and polishing procedures, there is no guarantee that suitable zero-layer reflections will be available to study the ‘as-grown’ surface features. The macroscopic vapor-growth surface of an Al$_2$O$_3$ crystal grown along the \{0001\} direction is such an example (Farabaugh, 1972). For these reasons non-zero-layer (Juleff, Lapierre & Wolfson, 1966; Turner, Vreeland & Pope, 1968), i.e. skew reflections, have been employed here to investigate the surface topography and the dislocation substructure of this crystal. The study has involved the following items: a stereographic-projection method for determining favorable skew reflections; an assessment of the surface shadowing or enhancement of diffracted X-ray intensity which occurs at surface steps; and, an analysis of image distortion which occurs within skew reflections.

Experimental details

The Al$_2$O$_3$ crystal was produced by a vapor-transport technique previously described by Parker & Harding (1970). The crystal was grown at 1750°C at a total pressure of 4 torr according to the reaction:

\[2\text{AlCl}_3(g) + 3\text{CO}_2(g) + 3\text{H}_2(g) \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{HCl}(g) + 3\text{CO}(g).\]

Under these conditions, the average deposition rate was 80 mg h$^{-1}$ cm$^{-2}$. A growth period of 30 h resulted in a crystal 20 mm long and 15 mm in diameter. The crystal-growth surface was found to be macroscopically composed of numerous steps and terraces. Measurements by optical goniometry and optical microscopy led to identification of the terraces as being nearly parallel to \{0001\} planes and the steps to be nearly parallel to \{10\bar{T}4\} planes; thus the step edges run parallel to \{11\bar{2}0\}. The largest steps were estimated to be of 50 \(\mu\)m in height.
The crystal and the recording film were supported on a horizontal table rotated on a vertical axis in the conventional Berg–Barrett geometry (Newkirk, 1959; Webb, 1962). A cobalt tube was used, operated at 25 kV and 14 mA, with an iron filter placed between crystal and film. Ilford L-4 nuclear emulsion (25 μm thickness) was used to record the diffraction images. Exposure times from 10 to 14 min were required to obtain suitable images.

Fig. 1 is a (0001) stereographic projection for the trigonal \( \text{Al}_2\text{O}_3 \) structure. The projection includes certain planes which proved useful for giving Berg–Barrett skew plane reflections. The obtainment of zero-layer and skew-plane reflections with the Berg–Barrett technique may be understood on the basis of the stereographic projection given in Fig. 2. The plane of the stereographic projection is approximately parallel to the average (0001) growth surface of the crystal. The X-ray source is at the western direction on the equator so that the X-ray beam is incident onto the crystal from the left. For particular lattice planes, circles of reflection, centered on the X-ray source, are drawn with radius \([\pi/2]-\theta_p\) where \(\theta_p\) is the Bragg angle for that plane and the characteristic cobalt radiation. The circles are drawn as bands corresponding to the 2° divergence in the incident X-ray beam. Rotation of the crystal about the vertical axis, \(AA'\), can bring different plane normals into contact with their reflecting circles thus allowing diffraction to occur. A small rotation will bring (2028) into contact with its reflecting circle. In this example, Fig. 2, the rotation axis is roughly parallel to the \(a_3\) axis. This case is termed a zero-layer reflection because the incident beam, the diffracted beam and the diffracting-plane normal, all in the plane of incidence, are perpendicular to the crystal rotation axis. However, it is observed in Fig. 2 that a slightly smaller rotation would bring the (2116) plane normal into contact with its reflection circle. This would produce a non-zero-layer (skew) reflection because the incident beam, the diffracted beam, and the diffracting-plane normal are not all perpendicular to the crystal-rotation axis. For \(\text{Al}_2\text{O}_3\), 2028 is a very weak reflection and nearly impossible to observe compared to 2116. It will be shown that in such a case the non-zero layer reflection, 2116, can be effectively used to obtain the desired X-ray micrographs.

**Experimental results**

A print of an X-ray micrograph taken using the (2116) skew reflection is shown in Fig. 3. The area of the Figure corresponds to approximately \(\frac{1}{3}\) of the total crystal surface. The X-ray image is limited by the natural extent of the crystal and by those subgrain boundaries for which the adjacent crystal regions are rotated away from the circle of reflection (Wu, Armstrong & Armstrong, 1971). The X-ray beam, which is incident from the left of the figure, produces (A) enhanced intensity (black on the micrograph) and (B) surface-shadowing (white on the micrograph) effects as a result of the steps and terraces on the crystal-growth surface. Other dislocation subgrain boundaries are observed within the X-ray image mainly as white or dark bands of (C) underlapping or (D) overlapping X-ray intensities according to the relative misorientation of adjacent subgrains. There are narrow dark edges generally associated with the (C) white bands. Individual dislocations are not observed. This is probably because their images are obscured by the very significant surface shadowing and enhancement of intensity effects. The surface effects even obscure, in several instances, the X-ray contrast of the subgrain boundaries.
The causes of the major contrast effects which are observed in Fig. 3 are illustrated in Fig. 4. Low density in the X-ray micrograph corresponds to portions of the specimen surface which are shielded from the incident beam. The high-density regions on the X-ray film result from the enhanced diffracted radiation due to the reduced projected width of the diffracting surface as described by Newkirk (1959). Fig. 4 also shows the combined contrast effects associated with dislocation subgrain boundaries. In the case illustrated, the relative misorientation is such that underlapping of diffracted intensities occurs, resulting in a white image of the boundary. The reduction in primary extinction due to the strain field associated with the dislocations comprising the boundary results in an increase in diffracted intensity on both sides of the boundary, evidenced by black borders on the white boundary image. All of these effects are observed in a detailed examination of the structure in Fig. 3.

It is interesting to consider the information which may be obtained by comparing the enhancement of the intensity versus the shadowing effect associated with a single surface step as viewed from opposite directions as indicated in Fig. 5. For the geometry whereby the incident X-ray beam from the left causes enhancement of the diffracted X-ray intensity, the effect is measured by the width, $W_b$, parallel to the incident beam $I_0$. Neglecting the minor consideration (in this case) of the thickness of the X-ray emulsion and assuming that the X-ray penetration depth is much less than the step heights, one finds that $W_b$ corresponds directly to the width of the blackened image of the step recorded on the X-ray film when the film is placed parallel to the direction of $I_0$. By the relationships between the angles $\alpha$, $2\theta_B$ and $(2\theta_B-\alpha-\psi)$ in the plane of incidence, $W_b$ is related to the step height, $h$, by

$$W_b = \frac{h \sin (2\theta_B-\alpha-\psi)}{\sin 2\theta_B \sin \psi},$$  \hspace{1cm} (1)$$

where $\theta_B$ is the Bragg angle for the reflection, $\alpha$ is the angle between the incident beam and its projection on the terrace, and $\psi$ is the apparent angle between the step surface and the terrace.

For the reverse direction, the shadowed width $W_w$, measured parallel to the incident beam, is given by

$$W_w = \frac{h}{\sin \alpha_w},$$  \hspace{1cm} (2)$$

where $\alpha_w$ is the angle between the incident beam and its projection on the terrace. It is important to note that equation (2) is independent of the Bragg angle. Combining equations (1) and (2) gives the ratio of the step widths observed in the two X-ray images as

$$\frac{W_w}{W_b} = \frac{\sin 2\theta_B \sin \psi}{\sin \alpha_w \sin (2\theta_B-\alpha-\psi)}. \hspace{1cm} (3)$$

Since the angle $\psi$ is measured in the plane of incidence for the X-ray beam as indicated for Fig. 5, $\psi$ is related to the true angle, $\psi'$, between the step surface and the terrace, by the relationship

$$\psi' = \tan^{-1} (\cos \gamma_b \tan \psi),$$  \hspace{1cm} (4)$$

where $\gamma_b$ is measured in the terrace plane as the angle between the projected direction of the incident beam and the normal to the terrace edge. Substitution for $\psi'$ from equation (4) into equation (3) gives the final result

$$\frac{W_w}{W_b} = \frac{\sin 2\theta_B \sin [\tan^{-1} (\cos \gamma_b \tan \psi)]}{\sin \alpha_w \sin (2\theta_B-\alpha-\tan^{-1} [\cos \gamma_b \tan \psi])}. \hspace{1cm} (5)$$

![Fig. 3. Skew-reflection X-ray micrograph, 2Ti6 reflection, Co Kx radiation, 12 min exposure.](image-url)

![Fig. 4. Illustration of enhanced intensity, surface-shadowing and subgrain-boundary-contrast effects in Berg-Barrett X-ray micrographs.](image-url)
The indication, then, from these equations is that the features in the X-ray image are related directly to the geometry of the step-and-terrace structure on the crystal surface. This means, for example, that \( \psi \) and \( h \) could be determined from X-ray results.

Fig. 6 shows two X-ray micrographs from the same surface region of the crystal for which independent measurements of \( \psi \) and \( h \) were made. Fig. 6(a) is a 2\( \bar{1} \)6 reflection taken in the intensity-enhancement geometry with \( \alpha_b = 4^\circ \). Fig. 6(b) is an unidentified reflection taken in the reverse direction, for which \( \alpha_w = 21^\circ \) after the crystal was rotated \( 216^\circ \) about its axis. The measured ratio of step widths in the two micrographs was found to be independent of the step height, thus illustrating the validity of equation (5). For a particular set of steps in Fig. 6 having \( \gamma_b = 40^\circ \), \( \psi = 36^\circ \), \( \alpha_b = 4^\circ \) and \( \alpha_w = 21^\circ \), \( (W_w/W_b) \) was calculated to be 2-1 which compares favorably with the measured ratio of 2-2 \( \pm 0 \cdot 3 \).

It is of special interest, when one compares either different X-ray micrographs or the features of a micrograph with the actual details of the crystal surface, to consider the image distortion which may possibly occur. This consideration was found experimentally to be a minor factor in analyzing the features of Fig. 6; however, the general situation for a skew reflection may be discussed in terms of the 2\( \bar{2} \)04 reflection as indicated in Fig. 7. In this figure, \( N_c \) is the crystal-surface normal, \( H \) is the direction of the horizontal diameter on the crystal surface, \( N_b \) is the diffracting-plane normal and \( R \) is the direction of the diffracted beam. The X-ray film is taken parallel to the plane of the projection and \( T, -T \) is the trace of the horizontal diameter of the crystal on the X-ray film. The crystal and thus \( N_c, H \) and \( N_b \) have been rotated about the axis \( AA' \) through an angle \( \alpha \) to bring (2204) into a diffracting position. The angle \( \alpha' \) relates the direction \( H \) to that of \( -T \) and \( \phi \) is the angle between \( R \) and \( H \). From the geometry of Fig. 7, the length, \( d' \), of the horizontal diameter projected onto the X-ray film is related to the actual horizontal diameter of the crystal, \( d \), by the relation

\[
d' = d(\cos \alpha' - \sin \alpha' \cot [\phi + \alpha']). \tag{6}
\]

Inspection of equation (6) indicates that the distortion vanishes, \( i.e. \), \( d = d' \) when \( \tan \phi = \cot (\alpha'/2) \). It may be seen for a zero-layer reflection \( (\alpha = \alpha' \) and \( \phi = 2\theta_b - \alpha \) \) that equation (6) takes the simpler form

\[
d' = d \sin (2\theta_b - \alpha) \sin 2\theta_b, \tag{7}
\]

which has been given by Newkirk (1959). Except for the special case which has been mentioned the general form of equation (6) indicates that, as for the zero-layer case, the distortion can be minimized by making \( \alpha' \) as small as possible. It may be seen in Fig. 7 that if the crystal were rotated about \( N_c \) to bring (2204) as close as possible to its reflecting circle, then a smaller rotation angle \( \alpha \) about \( AA' \) would be required to bring (2204) into a diffraction position. The net effect of these manipulations would be to reduce the angle \( \alpha' \) and thus reduce the image distortion. When \( \alpha' \) and \( \alpha \)
are decreased in this manner, both smaller image distortion and greater resolution are achieved. These effects have been observed in the present investigation on micrographs taken with the same diffracting plane but different pairs of \( \alpha \) and \( \alpha' \) values. The calculated image distortion is in agreement with that which was measured. The distortion of the X-ray image normal to \( d \) or \( d' \) is generally negligible because the change in image dimension in this direction is only affected by the vertical divergence of the X-ray beam.

**Discussion**

The use of skew reflections offers several advantages in studying single-crystal materials by X-ray microscopy. The number of diffracting planes available to examine the substructure of the material is greatly increased. This provides, in some cases, a choice between a more intense skew reflection and a less intense zero-layer reflection in the obtainment of an X-ray micrograph. There is only minor image distortion introduced by employing skew reflections and even this can be minimized. Inspection of equation (6) shows that by manipulating the crystal so as to reduce \( \alpha \) and \( \alpha' \) to their smallest possible values the image distortion is decreased.

The surface topography of a vapor-growth surface of \( \text{Al}_2\text{O}_3 \) has been studied using these features of the skew reflections. The contrast due to enhanced intensity and shadowing effects has been related to the steps and terraces on the growth surface. In the derivation of the ratio \( W_w/W_b \) we have assumed a small penetration depth for the X-rays. An increased depth of penetration would reduce the apparent width of the shadowed X-ray image, thus also reducing the ratio \( W_w/W_b \). The reasonable agreement in this present study between the measured and calculated \( W_w/W_b \) ratios indicates that the assumption of negligible penetration effect is valid.

The well-defined surface topography of this vapor-grown \( \text{Al}_2\text{O}_3 \) crystal yielded sharp X-ray images comparable to those reported for a vapor-condensed zinc crystal (Armstrong, 1965). Both of these results may be contrasted with very faint observations of surface roughness for a chemically etched zinc crystal (Armstrong & Schultz, 1968). It is apparent that the etching process for the zinc crystal produced rounded step edges which were revealed in the X-ray images by less pronounced contrast effects.

**Conclusion**

The skew-reflection geometry for the Berg–Barrett technique has been used to reveal the crystal-surface topography and the subgrain-boundary structure in the vapor-growth surface of an \( \alpha \)-\( \text{Al}_2\text{O}_3 \) single crystal. Skew reflections contribute to a greater choice of diffracting planes with which to examine the crystal microstructure. The surface structure of steps and terraces is related to contrast effects observed in the X-ray images. The results of this study indicate that measurements of these features in X-ray images may be utilized to determine actual step heights of crystal terraces and to determine the angular relationships between steps and terraces. The distortion in the skew X-ray image, which is no more worrisome than in a zero-layer reflection, can be described in terms of the parameters that govern the diffraction conditions. On this basis, the skew X-ray geometry may be designed so as to minimize the distortion.

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