An X-ray Cylindrical Texture Camera for the Examination of Thin Films

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An X-ray cylindrical texture camera has been constructed for the examination of thin polycrystalline films. Information about the type and degree of preferred orientation can be obtained. In certain cases the thickness of the film can be measured, and the order of deposition determined where more than one layer is present.

1. Introduction

X-ray diffraction cameras in which the diffraction pattern is recorded on a cylindrical photographic film coaxial with the incident beam have previously been used to make measurements of preferred orientations in polycrystalline materials by Kratky (1930), Wooster (1948), Mackay (1953) and Richards (1964). The diffraction cones of constant 2θ intersect the recording film in straight lines. These may then be scanned with a linear densitometer to yield intensity distributions characteristic of the preferred orientation, allowing for the effects of X-ray absorption in the specimen. The uniaxial textures of continuously rotated drawn wires and graphite specimens, mounted normal to the camera axis, have been studied by Mackay (1953) and Richards (1964). The more complex moving-film method of Wooster (1948) has been used to plot the pole figures of rolled sheets.

The cylindrical texture camera described here employs a flat specimen inclined to the incident X-ray beam, which, as in the above cases, is along the cylinder axis. The camera is particularly applicable to the crystallographic examination of thin crystalline films deposited on flat substrates. It is capable of detecting and identifying very thin deposits and of characterizing the type of preferred orientation that may have occurred. For cases where orientation effects are not pronounced, consideration of the specimen absorption factors provides information about layer thickness and order of deposition when more than one layer is present.

2. Description of the camera

The camera uses a cylindrical cassette of 5.73 cm diameter (allowing for the thickness of the photographic film) and 12.5 cm long. Collimator and beam-stop tubes, concentric with the camera axis, are mounted at each end of the cassette on discs which act as radiation shields. The flat specimen is mounted on a disc perpendicular to a motor shaft, which can if required rotate the specimen continuously in its own plane. (The experimental arrangement is shown in Fig. 1.) The angle between the motor shaft and the camera axis is continuously variable to give the specimen plane any desired angle of inclination, i, up to 45°, to the incident beam. The position of the specimen along the camera axis is also variable, and since the finite length of the cassette cuts off the diffraction pattern at both ends of the 2θ scale, by altering the position of the specimen the whole diffraction pattern may be shifted along the axis so that either the low-2θ or high-2θ regions may be recorded on the film.

Since the relative positions of the powder diffraction lines are unaffected by movement of the specimen along the camera axis or motor shaft or variation in i, the only essential alignment is that of the incident beam accurately coincident with the cylindrical axis. Accurate positioning of the specimen is necessary only if the absolute positions of the powder diffraction lines need to be recorded relative to a fiducial mark on the recording film, or if a specific point on the specimen is to be isolated for examination. In the latter case, if the specimen is rotated it is necessary that its position along the motor shaft be accurately set so that the specimen surface coincides with the intersection of the incident beam and the rotation axis. If the specimen surface is out of alignment or if the two axes do not intersect, the irradiated area describes an annulus on the specimen surface, so that a diffraction pattern more representative of the specimen may be obtained in this manner.

A second mode of operation is employed in which the specimen is mounted across the beam stop normal to the incident beam and remains stationary during the exposure. In this case a back-reflexion photograph is

formed of powder diffraction lines for which 2θ exceeds 90°.

3. Applications of the camera to crystalline thin films

The powder diffraction patterns of both thin films and substrates in the cylindrical camera (radius R) may be interpreted by measuring the positions of the lines, y, along the camera axis and deriving the corresponding values of 2θ, given by the relation \( y = R \cot 2\theta \), and interplanar spacing, d, from Bragg's law. Fig. 2 shows the relation between d and y for a number of commonly used radiances, with 2R = 5.73 cm. If ϕ is the angle between the planes, parallel to the camera axis, containing the diffracted beam and the specimen surface normal, then the x coordinate is equal to Rϕ. Part of the diffraction pattern is excluded from the photograph by absorption of the diffracted radiation in the substrate. The cut-off or specimen shadow is given by the intersection of the specimen plane with the recording film and is a cosine curve described by the equation

\[ y = R \cot i \cos (x/R) \]

i.e.

\[ \cos \varphi = \tan i \cot 2\theta \]  

The angle of inclination, i, sets a lower limit to the range of 2θ values which may be recorded.

If there is no fiducial mark to determine the position \( y = 0 \), the uncertainty in the absolute values of y may be resolved in one of the following ways. If the powder pattern of the substrate or any component of the layer is known, the film may be calibrated using the calculated values of y. If the substrate is a single crystal, complete rotation of the specimen generates a diffraction pattern in which the spots still lie on lines of constant 2θ or y characteristic of the powder diffraction pattern, which are independent of the alignment of the crystal lattice. If the surface is a lattice plane, the corresponding Laue spot will be recorded at the point \((0, R \cot 2\theta)\). Alternatively the specimen shadow may itself be used to calibrate the photograph, whether or not i is known accurately, from the positions of greatest and zero slope of the cut-off curve. The position \( y = 0 \) is characterized by a 180° extent of the pattern along the x axis.

For very thin films, glancing-angle electron diffraction with a penetration depth of 100–200 Å is the most common analytical technique. X-ray diffraction patterns of such systems tend to be dominated by the substrate, making identification of the thin-film pattern difficult. The sensitivity of X-ray diffraction to very thin films can be enhanced by reducing the accelerating voltage, and thus the amount of scattered and fluorescent radiation generated in the substrate by the more penetrating high-energy incident radiation. (In this respect larger improvements can be achieved using a monochromator, e.g. pyrolytic graphite.) A second method of increasing the sensitivity is to make use of the photoelectric attenuation of the characteristic radiation. As the angle, r, between the diffracted beam and the surface approaches zero there is a rapid decline in intensity because of the increasing path length through the sample. A further effect is to introduce a contrast between the thin film or films and the substrate. Near the cut off, the thin-film diffraction lines are diminished by absorption in the thin film itself. However the substrate diffraction lines, which are likewise diminished by substrate absorption, suffer an additional attenuation on passing obliquely through the thin film. The result is that although both sets of powder diffraction lines are attenuated as the cut off is approached, the intensities of the thin-film lines are enhanced relative to those of the substrate. For the same reason, if more than one layer is present, the attenuation of the lines of each phase is more rapid the deeper the layer below the surface. The actual surface layer is distinguished by diffraction lines suffering the least attenuation towards the cut off.

The increased visibility of the diffraction patterns of thin films near to the specimen shadow over a wide range of 2θ accounts for the sensitivity of this camera, and inspection of this region of the pattern enables film and substrate, and the order of deposition of different films, to be distinguished, provided that intensity gradients associated with preferred orientation effects are not too strong. By contrast the conventional Debye-Scherrer powder photograph, in which only a limited zone of the diffraction pattern is recorded, suffers in that reduction of the angle of incidence, i, leads to excessive broadening of the diffraction lines [except in the region where a degree of focusing is attained (Peiser, Rooksby & Wilson, 1955)].

For the purpose of demonstrating the technique a specimen was prepared consisting of a flat molybdenum plate on which were electro-deposited successive layers of gold, copper and zinc in that order. The thickness of the films was chosen to be of the order of a small fraction (≤ 0.1) of the mean absorption depth for the material of copper Kα radiation. (The values of \( \mu^{-1} \), where \( \mu \) is the linear absorption coefficient, for Zn, Cu, Au ~ 23, 20, 2.5 μm respectively). The specimen was mounted in the cylindrical camera inclined

![Fig. 2. Relationship between d and y for Cu Kα, Co Kα and Cr Kα radiances.](image-url)
at 30° to a beam of nickel-filtered copper radiation and continuously rotated during the exposure. The X-ray tube was operated at 20 kV in order to reduce the proportion of fluorescent and high-energy polychromatic radiation registered on the emulsion. The diffraction pattern thus obtained is reproduced in Fig. 3.

The diffraction lines of each phase have been identified and indexed with the aid of the chart shown in Fig. 2. The diffraction pattern of the Mo substrate is characterized by a strong ‘arcing’ of the lines due to the rolling texture. The diffraction pattern of the surface layer can be immediately recognized, being formed from those lines which maintain their intensity closest to the cut off. Thus it is confirmed that the surface layer consists of zinc. Similarly it can be verified that the copper layer lies below the zinc, and the gold layer below the copper. The effect of order of deposition is illustrated most vividly by inspection of the four adjacent lines Zn 1013, Cu 220, Au 311 and Zn 1122, where they meet the cut off. This region, inset in Fig. 3, is shown magnified in Fig. 4. Methods for analysing the intensity profiles are given in § 4.

Preferred-orientation effects are commonly exhibited by thin films and are revealed by arcing or intensity modulations of the powder diffraction lines along the x axis. Uniaxial or fibre textures, having cylindrical symmetry about the surface normal, may be developed during the growth or deposition of the films as there is a tendency for crystallites having certain lattice planes aligned with the surface to grow preferentially. Fig. 5 shows the uniaxial texture pattern of a thick (~200 μm) deposit of polycrystalline Si formed by decomposition of SiHCl₃ on an oxidized Si crystal at 1050°C. The surface was inclined at 30° to a beam of Cu Kα radiation and continuously rotated. The information obtained in such patterns is sufficient to identify the nature of the preferred orientation present, and the plane (or planes) which are preferentially aligned with the surface. Quantitative measurements of the degree of preferred orientation can be obtained from the intensity profiles. Methods of interpreting these profiles are outlined in § 5.

Biaxial or sheet textures may be exhibited by thin films when the orientation of the crystallites within the surface plane is constrained, either by a marked deviation of the growth conditions from cylindrical symmetry or the use of a crystallographically anisotropic substrate such as a single crystal. The information obtained from a cylindrical texture camera photograph, recorded under conditions of continuous specimen rotation, is restricted to identification of planes parallel to the surface. The lack of isotropy about the surface normal is evident in patterns obtained with the specimen stationary, and is unambiguously displayed in back-reflexion patterns (beam normal to surface). Again there are a number of advantages in using the cylindrical camera. The glancing reflexions in the neighbourhood of the specimen shadow at y=0, 2θ=90° cannot be recorded in the conventional flat-film method, which is thus less sensitive to thin films. Secondly the sensitivity of the intensity profiles to preferred orientation of the crystallites within the surface plane increases with the angle, α, between the Bragg plane and the surface. The cylindrical camera is potentially more sensitive than the flat-film method because powder diffraction lines are recorded with a
higher limit on the value of $\alpha$ at $45^\circ$. An example of a cylindrical back-reflexion photograph of a biaxial texture is reproduced by Richards, Scobey & Wallace (1974; Fig. 4). The sample is an oriented film of PtSi formed in a substrate of single crystal silicon by reaction of a deposited Pt layer. By contrast the Si deposit represented in Fig. 5 of the present paper gave perfectly uniform diffraction lines in back reflexion, indicating a uniaxial texture.

4. The effect of photoelectric absorption

Provided that the crystallite size is such that the diffraction lines are continuous, the variations in diffraeted intensity with $x$ along the lines are governed by three factors: preferred orientation, photoelectric absorption, and refraction. Let us assume the crystallites to be perfectly random in orientation and, ignoring the small refraction effect, calculate the effect of photoelectric attenuation. Because the only movement of the specimen during the exposure is a rotation in its own plane, the irradiated volume is the same for every part of the diffraction pattern and is equal to $A t$, where $A \sin i$ is the incident-beam cross section and $t$ the thickness of material. If the integrated intensity in any element $d\varphi$ of a powder diffraction line is given by $I(\varphi)d\varphi$, $I(\varphi)$ is proportional to a constant $K$ multiplied by an attenuation factor exp $(-mz/t_0)$ integrated over the irradiated volume. $K$ takes account of the beam intensity and divergence, and the structure and polarization factors (the Lorentz factor being unity for this camera). $t_0=1/\mu$ is the mean absorption depth and $m=m(i, \theta, \varphi)$ is the ratio of the total beam path length to the depth $z$ below the surface, and is given by the expression

$$m(i, \theta, \varphi) = \frac{1}{\sin i} + \frac{1}{\sin r}$$

where

$$\sin r = \cos i \sin \theta \cos \varphi - \sin i \cos 2\theta.$$  (3)

The integrated intensity for a surface film is then given by

$$I(\varphi) = AK \frac{t_0}{m} \left[1 - \exp \left(-mt/t_0\right)\right].$$  (4)

From equation (4) it is clear that it is possible in principle to determine the film thickness, $t$, from the intensity profile $I(\varphi)$ in relation to the absorption depth $t_0$. $1/t_0$ may be determined by multiplying the mass absorption coefficient for the material ($\mu/\rho$) by the density. If however the density of the film cannot be assumed to be the same as the theoretical bulk value, then the same method effectively measures the mass per unit area $gt$ in terms of the mass absorption coefficient.

A simple method of computation is first to determine the constant $AK$ from the form of the profile close (within a few degrees of $\varphi$) to the cut off where $m \approx \csc r$ is large and all the radiation is effectively absorbed by the film. $\varphi_c$, the cut-off value of $\varphi$ for which $\sin r = 0$, is given by equation (1). For $\varphi$ close to $\varphi_c$, exp $(-mt/t_0)$ $\ll 1$ and the intensity is given approximately by

$$I(\varphi) \approx AK t_0 \left[\sin (2\theta + i) \sin (2\theta - i)\right]^{1/2}(\varphi_c - \varphi).$$  (5)

Thus $I(\varphi)$ descends to zero linearly as $\varphi$ approaches $\varphi_c$, with slope given by:

$$-\left(\frac{\partial I}{\partial \varphi}\right)_c = AK t_0 \left[\sin (2\theta + i) \sin (2\theta - i)\right]^{1/2}.$$  (6)

The thickness is then determined from the intensity at the centre, $I(0)$, using the formula

$$t_0 = \frac{-1}{m(0)} \log_e \left[1 - \frac{I(0)m(0)}{AK t_0}\right]$$

where

$$m(0) = \frac{1}{\sin i} + \frac{1}{\sin (2\theta - i)}.$$  (8)

It is important that the attenuation in the film at $\varphi=0$ should be relatively small. In this case the intensity should reach a wide central plateau in which it is effectively controlled by the film thickness. Further, if $t \ll t_0/m$, then $I(\varphi) \approx AK t$ and the thickness is given by the formula

$$t = \frac{I(0)}{m(0)} \left(\frac{\partial}{\partial \varphi}\right)_c \left[\sin (2\theta + i) \sin (2\theta - i)\right]^{-1/2}.$$  (9)

Fig. 6. Densitometer trace of 1012 Zn diffraction line of Fig. 3 after elimination of background.

Fig. 7. Cylindrical texture camera photograph of PbO deposit. Cu $K\alpha$ radiation at $\theta = 33^\circ$. 

Fig. 8. Cylindrical texture camera photograph of PbO deposit. Cu $K\alpha$ radiation at $\theta = 33^\circ$. 

-60 -40 -20 0 20 40 60

\[ \varphi \]
Equation (5) takes a particularly simple form when the angle of incidence $i=30^\circ$. Then

$$I(\varphi) \simeq \frac{1}{2} AK_t [2 \cos 4\theta + 1]^{1/2} (\varphi_c - \varphi).$$

(10)

For a reliable estimate of film thickness to be made using this method, there should be no significant distortion of the intensity profiles due to preferred orientation. As a result of preferred orientation effects different values of $t$ would be derived from several diffraction lines and the spread of values is a measure of the error from this source. Also, although it is important that $t < t_0$, the value of $t/t_0$ should still exceed the angular divergence of the beam and the angular deviation of the film surface due to its roughness. If the film is perfectly smooth, anomalous intensity effects may be observed within a fraction of a degree from the cut off due to refraction.

The intensity profile $I(x)$ integrated over the width of the diffraction line is measured using a microdensitometer, after subtracting the background which is taken to be the average of two profiles obtained at equal distances, $\delta y$, either side of the diffraction line, assuming $\delta y$ is small enough for linear interpolation. The powder lines of the Zn layer shown in Fig. 3 are relatively free from preferred orientation effects. Fig. 6 shows the profile of the Zn 1012 line of Fig. 3 after elimination of the background, and it is clear that intensity modulations due to orientation are not more than a few per cent. The Zn layer is therefore amenable to thickness determination by this method. The values of $\varphi t$ and $t$ (assuming the theoretical density) derived from three Zn profiles are given in Table 1 and a total spread of about 10% is obtained.

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<th>Table 1. Values of $\varphi t$ and $t$ derived for an electrodeposited Zn layer</th>
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Therefore the average values of $\varphi t$ and $t$ can be quoted with an accuracy of the order of 10%. The method is thus capable of yielding a good estimate for the thickness of surface films relatively free from preferred orientation.

### 5. The analysis of uniaxial textures

In a uniaxial or fibre texture, the polar distribution by volume of each Bragg plane may be expressed as a function of the angle, $\alpha$, between the Bragg plane and the specimen surface. For each point on the diffraction line the corresponding value of $\alpha$ may be calculated for the crystallites contributing to the reflexion, with the formula

$$\cos \alpha = \sin \theta \sin i + \cos \theta \cos i \cos \varphi.$$  

(11)

For any given angle of incidence there is an upper and lower limit to the values of $\alpha$ which may be recorded for each diffraction line. The upper limit is set by the specimen cut off and is given by

$$\cos \alpha_{\text{max}} = \frac{1}{2} \sin i \sin \theta.$$  

(12)

A lower limit is reached at $\varphi=0$ and is equal to $\alpha_{\text{min}} = |\theta - i|$. A partial polar distribution may thus be derived within these limiting values of $\alpha$ for each Bragg plane. Values of $\alpha$ down to zero are registered only if the angle of incidence is set equal to the Bragg angle. The upper limit is then $\alpha_{\text{max}} = 60^\circ$, while equation (11) takes the form

$$\sin \alpha/2 = \cos \theta \sin \varphi/2.$$  

(13)

The intensity profiles along $x$ may be interpreted as follows. Let us suppose the intensity profile $I(\varphi)$ of equation (4) is multiplied by a modulating factor $P(\varphi)$ representing the effects of preferred orientation. Then $AKP(\varphi)$ is obtained from the densitometer trace after subtraction of the background level and division by the attenuation factor of equation (4). Then if $G(\alpha)$ is the proportion by volume of Bragg planes inclined to the surface at an angle between $\alpha$ and $\alpha + \delta \alpha$, the angular distribution function is derived from

$$G(\alpha) = \frac{1}{2} P(\varphi) \cos \theta \cos i |\sin \varphi|.$$  

(14)

where $\varphi(\alpha)$ is given by equation (11).
Most thin films are characterized by one or more planes that are preferentially aligned parallel to the surface. To record the polar distribution and thus quantify the degree of preferred orientation, it is necessary to set \( i = 30^\circ \) equal or very close to one of the Bragg angles for the preferred plane. The diffraction pattern of a relatively thick (20 \( \mu \)m) layer of PbO evaporated onto SnO\(_2\)-coated glass is reproduced in Fig. 7 by way of illustration. The plane preferentially aligned with the surface is (110) in the tetragonal (litharge) form of PbO, and the beam of Cu K\( \alpha \) radiation is incident at the Bragg angle for the 220 reflexion, \( i = 33.9^\circ \). The litharge pattern is indexed in Fig. 7; other diffraction lines represent hydrocerussite, Pb\(_3\)(CO\(_3\))\(_2\)(OH)\(_2\), formed after exposure of the layer to the atmosphere. Fig. 8 shows the densitometer trace of the central part of the 220 diffraction line (-30° < \( \varphi \) < 30°) after subtraction of the mean background level. Because the attenuation factor varies little with \( \varphi \) across the profile, this curve is an adequate representation of \( P(\varphi) \).

If there is no peak in intensity at \( \varphi = 0 \) in a diffraction line for which \( \theta \) is close to \( i \), the nature of the orientation texture may be deduced from the values of \( \zeta \) corresponding to intensity peaks in all the diffraction profiles except those occurring at \( \varphi = 0 \). Peaks at \( \varphi = 0 \) may be taken to indicate a preferred value of \( \alpha \) lying between zero and \( \theta - i \), or overlapping of peaks with small \( \varphi \). From the preferred values of \( \zeta \) for each Bragg plane may be deduced, by means of spherical trigonometry or stereographic projection, the preferred direction(s) of the surface normal with respect to the axes of the crystal lattice, which correspond to the peaks of the inverse pole figure. From the information obtained from cylindrical texture patterns it is possible to distinguish the different orientation types in multiple textures which frequently occur in thin films, and to estimate their relative proportions and degree of alignment.

A simple aid to the interpretation of the patterns is a chart from which the peak values of \( \zeta \) can be read off for a given value of \( i \). Choosing arbitrarily \( i = 30^\circ \) a chart has been constructed with lines of constant 2\( \theta \) (parallel to \( x \)) and constant \( \alpha \) which is reproduced in Fig. 9. [An analogous chart for \( i = 0 \) is given by Mackay (1953), Fig. 2]. With the use of this chart the cylindrical texture pattern of Fig. 5 can be shown to be basically consistent with a preferred orientation of (110) type. An additional minority texture, not unambiguously identified, is represented by the lesser peaks on the 220, 400, 440 profiles arrowed in Fig. 5.

If a principal crystallographic axis, of repeat unit \( e \), is aligned preferentially normal to the surface, the intensity peaks will lie on layer lines which are lines of constant angle of reflexion, \( r \), given by Laue's equation

\[
\sin r + \sin i = n\lambda/e = \zeta
\]

(15)

where \( \sin r \) is given by equation (3). The specimen shadow is itself a layer line of index \( \zeta = \sin i \). The row lines are derived from the relation

\[
\zeta = 2 \sin \theta \sin \alpha
\]

(16)

where \( \alpha \) is given by equation (11). Bernal charts may be constructed for the cylindrical camera for any value of \( i \). That for \( i = 30^\circ \) is reproduced in Fig. 10. Values of \( \zeta \) can be recorded between 0.5 (at the cut-off) and 1.5. The intensity peaks of Fig. 5 can all be shown to lie on lines of constant \( \zeta \) and \( \xi \) in the Bernal chart consistent with the (110)-type orientation, except for those arrowed which clearly belong to a distinct minority texture.

6. Conclusions

The cylindrical powder diffraction camera described above has been successfully applied to the analysis of the following film/substrate systems; PtSi/Si (Richards, Scobey & Wallace, 1974), ZnS/SnO\(_2\)/glass, PbO/SnO\(_2\)/glass, ZnO/Al\(_2\)O\(_3\). The technique can be applied when the layer as well as the substrate is monocrystalline, for example in the NiAs/GaAs system (Scobey, Wallace & Ward, 1973). The development of further X-ray diffraction techniques especially for the characterization of heteroepitaxial layers (i.e. monocrystalline layers grown on single crystal substrates of alien material) will be described in a separate paper by the present authors (Wallace & Ward, 1975).

References


