A Determination of Thin Oxide Film Thickness by Integrated Intensity Measurements

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The thicknesses of thin single-crystal oxide films are determined by integrated intensity measurements in absolute units. The method is illustrated with measurements of Cu_2O films grown on copper single crystals. Thicknesses determined from two different Bragg maxima agree well with each other, and are reasonably consistent with the thicknesses determined from the line shapes.

An X-ray diffraction study of thin oxide films grown on copper single crystals has revealed that with properly refined techniques one may detect the Bragg maxima of such films when they are as thin as 100 Å. The experimental technique and a method for the interpretation of the shapes of the Bragg reflections in terms of thickness and strain present in the films has been previously reported (Borie, 1960). Described here is a second method for measuring film thickness which is independent of the line shapes. It provides a valuable supplement to information obtained from an interpretation of the line contours and promises to be among the more accurate methods to measure film thickness.

Films of Cu_2O grown at 250 °C. in one atmosphere of oxygen on a 110 face of a copper single crystal were used. Under such conditions the film grows as a single crystal with the 110 direction of its cubic lattice normal to the film surface (Lawless & Gwathmey, 1956).

The method consists of a classical integrated intensity measurement in absolute units. From several points of view the measurement is made under ideal circumstances: For single crystals so thin, the problem of extinction is unimportant even for the strongest low angle reflections; and a knowledge of the absorption coefficient is unnecessary since for all practical purposes the film is transparent to X-rays.

The experimental arrangement is as follows: A monochromatic beam of X-rays (Cu $K\alpha$) impinges on a flat oxidized copper single crystal. The crystal is oriented so that the planes parallel to the single crystal surface will diffract (in our case $hkl = 110$ or 220), and the face of the crystal is large enough so that the entire incident beam is intercepted. The detector is a crystal scintillation counter with a large uniformly sensitive face. It is fixed at the scattering angle of the diffracting planes, and it intercepts a solid angle sufficiently large that it will detect all of the diffracted radiation.

Let the sample be rotated through a small angle α about an axis normal to the plane of the incident and diffracted beam, and let $P(\alpha)$ be the power detected by the counter at that orientation. There then exists the relation

$$\int P(\alpha)\,d\alpha = \frac{I_0 e^4}{m^2 c^4}\, \frac{\lambda^3 F_{hkl}^2 \exp\left[-2M\right]}{v_a^2}$$
$$\times \frac{V}{\sin 2\theta}\, \frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{1 + \cos^2 2\theta_m}\,. \quad (1)$$

The integral is carried out over the entire range of α for which diffraction occurs. The incident beam intensity is I_0, e and m are the electronic charge and mass, c the velocity of light, λ the wavelength of the X-rays, and $F_{hkl}^2 \exp\left[-2M\right]$ is the structure factor squared times the Debye–Waller temperature factor. The volume of the crystal irradiated and the volume of a unit cell are given by V and v_a, and the Bragg angle of the diffracting planes is θ. Since the incident beam is partially polarized, the polarization factor contains the Bragg angle of the crystal monochromator, θ_m. This well known result presumes that the crystal is so small that there is no extinction and that absorption is negligible.

Since the diffracting planes are parallel to the surface, if the cross sectional area of the beam is A, then the area of the film irradiated is $A/\sin\theta$, and the volume irradiated $V = AT/\sin\theta$ where T is the thickness of the film. Hence,

$$I_0 V = P_0 T / \sin\theta\,, \quad (2)$$

where P_0 is the total power in the primary beam. We measure P_0 indirectly by measuring the scattering from an amorphous sample. For this situation, with a flat sample of polystyrene (C_8H_8) making equal angles with the incident and scattered beams and large enough to intercept the entire incident beam, the scattered intensity is given by

$$I_s = \frac{P_0 e^4}{m^2 c^4}\, \frac{I_{\text{eum}}}{2M_s R^2 (\mu/\varrho)}\, \frac{1 + \cos^2 2\theta_m \cos^2 2\theta_s}{1 + \cos^2 2\theta_m}\,, \quad (3)$$

where $2\theta_s$ is the scattering angle, μ/ϱ the mass absorption coefficient, R the specimen to detector distance, and M_s the mass of one molecule of polystyrene. The total coherent and incoherent scattering in electron units per molecule is given by I_{eum}. It is assumed that the sample is infinitely thick, and, since θ_s is chosen in the back reflection region, that its atoms scatter randomly with respect to each other. In such a case, I_{eum} may be accurately calculated from tabulated atomic form factors. There is available a recent precision measurement of μ/ϱ for carbon (Chipman, 1955).

Equations (1), (2), and (3) may be combined to give

$$T = \frac{v_a^2 I_{\text{eum}} \displaystyle\int P(\alpha)\,d\alpha}{2 I_s R^2 F_{hkl}^2 \exp\left[-2M\right] \lambda^3 M_s (\mu/\varrho)}$$
$$\times \sin\theta \sin 2\theta \, \frac{1+\cos^2 2\theta_m \cos^2 2\theta_s}{1+\cos^2 2\theta_m \cos^2 2\theta}. \quad (4)$$

The quantity $F_{hkl}^2 \exp\left[-2M\right]$ was measured in absolute units from bulk Cu_2O powder in a separate experiment. The details of that experiment will be reported elsewhere; we here quote only the result that $F_{110}^2 \exp\left[-2M\right]=175$ and $F_{220}^2 \exp\left[-2M\right]=4220$.

We illustrate the method by applying it to the 220 reflection from a particular film of Cu_2O. Tabulated below are the various constants which, for our diffractometer and this reflection, enter equation (4).

$\lambda = 1{\cdot}54$ Å	$I_{\text{eum}} = 65{\cdot}4$
$\theta_s = 50°$	$M_s = 1{\cdot}73 \times 10^{-22}$ g.
$\theta_m = 22{\cdot}5°$	$\mu/\varrho = 3{\cdot}87$ cm.^{2}/g.
$\theta = 30{\cdot}2°$	$F_{220}^2 \exp\left[-2M\right] = 4220$
$v_a = 77{\cdot}8$ Å^3	$R = 16{\cdot}77$ cm.

Their insertion into equation (4) gives

$$T = 2{\cdot}70 \times 10^{-5}\ \text{cm.}^{-1} \int P(\alpha)\,d\alpha/I_s. \quad (5)$$

Shown in Fig. 1 is the measured curve of $P(\alpha)$ for the 220 reflection for one of the films studied. This curve is measured with the entire sensitive area of the detector exposed, and since the entire diffracted beam is intercepted, $P(\alpha)$ has units of power, or counts per second. The value of $\int P(\alpha)\,d\alpha$ determined from the area under the curve of Fig. 1 is 5·57 c.p.s.

With the specimen replaced by a flat sample of polystyrene, at $2\theta_s = 100°$, and with a 2·70 cm.^{2} window before the detector, a count rate, corrected for air scattering, of 126·3 c.p.s. was observed. Hence, $I_s = 46{\cdot}8$ c.p.s./cm.^{2}.
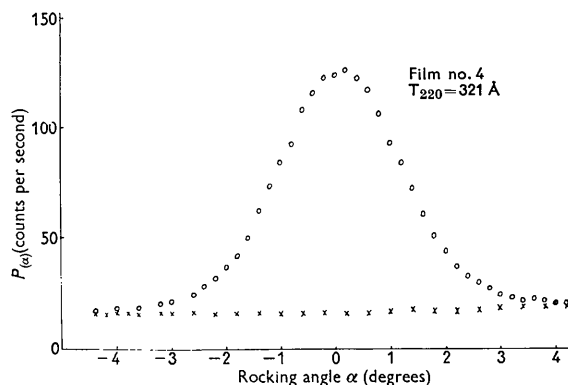

Fig. 1. The total diffracted power $P(\alpha)$ as a function of the rocking angle α for the 220 reflection of a film of Cu_2O. Crosses show back-ground determined by repeating the measurements with the oxide film removed.

From equation (5), with the above values of $\int P(\alpha)\,d\alpha$ and I_s, there results $T = 321$ Å.

Table 1. *Measured oxide film thicknesses*

Film no.	T_{110}	T_{220}	T_s
1	152 Å	146 Å	140 Å
2	218	219	190
3	285	275	230
4	319	321	280
5	499	501	440

The results of five such thickness measurements are summarized in Table 1. The film used in the above illustration is film 4. Included in the table are the thickness measurements T_s determined from the line shapes by the method described by Borie (1960). In general the integrated intensity thickness determinations are probably more accurate. Non-uniformity in the film thickness undoubtedly will contribute to error in the value of T_s. Incoherent low angle boundaries which would affect the line shapes but not the integrated intensities probably account for the fact that T_s is slightly but systematically smaller than T_{110} or T_{220}.

References

Borie, B. (1960). *Acta Cryst.* **13**, 542.
Lawless, K. R. & Gwathmey, A. T. (1956). *Acta Met.* **4**, 153.
Chipman, D. R. (1955). *J. Appl. Phys.* **26**, 1387.