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A Diffraction Measurement of the Structure of Cu_2O Films Grown on Copper

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A method for the detection of the Bragg maxima of very thin (100–500 Å) oxide films grown on metals is described. The shapes of the maxima are interpreted to give the strain present in the film and its thickness. The method is illustrated by its application to Cu_2O grown on a 110 face of a copper single crystal.

1. Introduction

With the hope of contributing to the understanding of the growth mechanism and structure of oxide films formed on metal surfaces, a series of diffraction experiments were undertaken to determine whether it is possible, during the very early stages of the life of such films (200 Å thick or less), to detect their presence by means of X-rays and, if so, to attempt to interpret the diffraction maxima associated with the oxide film in terms of its thickness and the deviations from crystalline perfection it may experience as it grows. The experiments have been performed with cuprous oxide grown on flat surfaces of copper single crystals at 250 °C. in one atmosphere of oxygen. Attention has been limited to films grown on (110) faces of the metal crystal. Lawless & Gwathmey (1956) have shown that for this face, there is a simple epitaxial relation between the oxide and the copper substrate: their cube axes are parallel.

Cuprous oxide grown on copper recomends itself because of the uncomplicated well-known cubic crystal structure of the oxide, and the facility with which oxidized metal crystals may be prepared. The conditions for its growth were chosen to avoid contamination with cupric oxide and to obtain a film of uniform thickness. Details of the technique for preparing the films have been described by Young, Cathcart & Gwathmey (1956).

Reported here is a simple X-ray diffraction tech-

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nique for the measurement of the shapes of the Bragg maxima of such films, and a method for the interpretation of their contours in terms of the thickness and strain distribution.

2. Experimental arrangement

Fig. 1 illustrates schematically the arrangement of the diffractometer. X-rays from essentially a point source impinge on a doubly bent LiF monochromator. The radii of bending are chosen so that Cu $K\alpha$ radiation is diffracted over the angular range α and so that vertically the diffracted beam converges at the specimen which is a flat copper single crystal appropriately oxidized. The scattered radiation must pass through the slit S before striking the face of a scintillation counter. The specimen and detector are mounted on a conventional General Electric diffractometer table so that parafocusing geometry is maintained as the counter scans through 2θ.

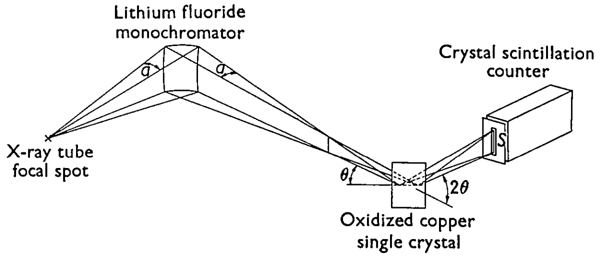

Fig. 1. Arrangement of diffractometer for line contour measurements from thin surface films.

Though for the sake of clarity, the monochromator and sample are shown in Fig. 1 in parallel positions, they were arranged antiparallel to each other for our measurements. As Guinier (1956) has pointed out, over a limited range of 2θ one thus obtains an achromatization of the $K\alpha_1$–$K\alpha_2$ doublet, causing them to superimpose on the 2θ scale of the counter. Hence, contributions to the line shapes from sources other than the imperfections present in the sample are greatly minimized.

Ambiguities in the establishment of background under the Bragg peaks were avoided by scanning the 2θ range of interest with an unoxidized copper sample. Since for practical purposes a 200 Å film of Cu_2O is transparent to Cu $K\alpha$ radiation, there results an objective and accurate determination of the tails of the broadened reflections.

Fig. 2 shows the 110 and 220 Bragg maxima for a Cu_2O film approximately 180 Å thick as measured by a polarizing spectrometer. The success of the method depends on the use of strictly monochromatic radiation which ensures a very low background. It is probably also necessary that the film be substantially a single crystal, so that most of its irradiated volume may contribute to the diffracted beam to be measured.

3. Diffraction theory

Warren & Averbach (1950) have shown that if the shape of a Bragg maximum $00l$, broadened because of strain and small partial size, is represented by the Fourier series

$$I(h_3) = \sum_n C_n \exp\,[2\pi i n h_3]\,,$$

then the coefficients C_n may be related directly to the

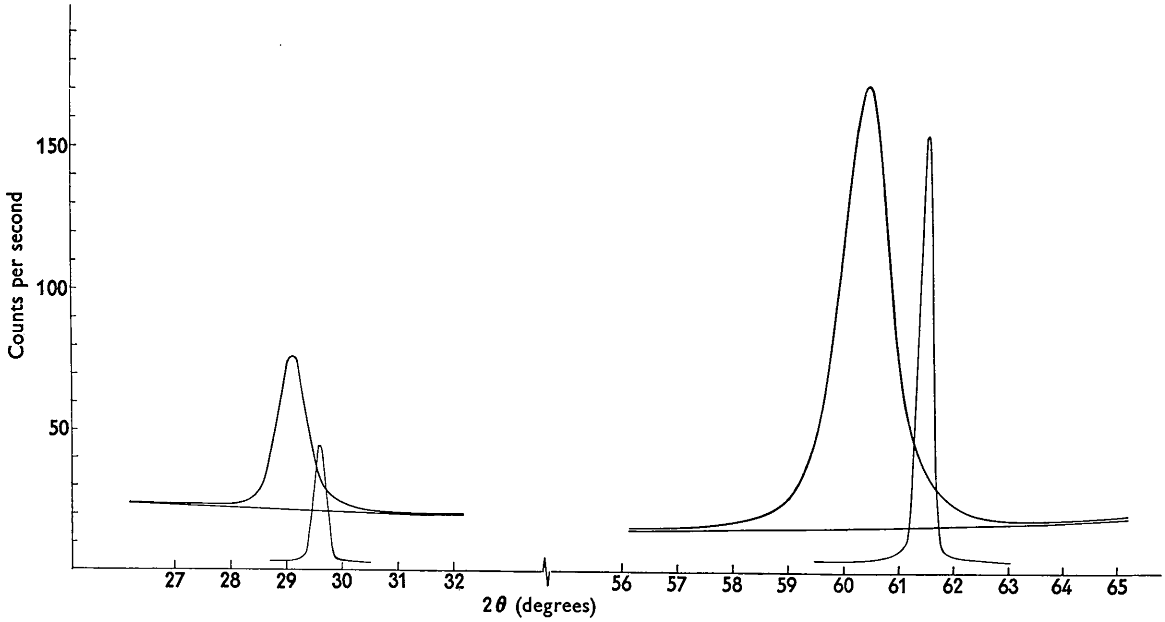

Fig. 2. The 110 and 220 Bragg maxima for a thin Cu_2O film (broad lines). The sharper lines show the positions and shapes of the corresponding reflections measured from bulk Cu_2O and are not to scale.

particle size and strain distribution present in the sample. The continuous variable h_3 is related to the scattering angle 2θ by

$$h_3 = 2|a_3| \sin \theta/\lambda \,,$$

where $\mathbf{a}_3$ is a vector normal to the diffracting planes along a unit-cell edge (the cell is assumed to be orthogonal). At the center of the diffraction peak, h_3, takes on the value l. It was shown by Warren & Averbach that

$$C_n = N_n/N \langle \exp [2\pi i l Z_n] \rangle \,, \qquad (1)$$

where N is the total number of unit cells in the crystal and N_n is the number of unit cell pairs which may be formed in such a manner that the vector between the cells is $n\mathbf{a}_3$. If the crystal is strained, then the vector between cells is given by $n\mathbf{a}_3 + Z_n\mathbf{a}_3$. The average indicated in equation (1) is taken over all such pairs which may be formed in the crystal. The area under the Bragg peak is normalized so that C_0 is unity.

To specialize the Warren–Averbach result for the case of an oxide single crystal film adherent to a metal surface, we assume that the film is of uniform thickness and that the strain in the film is uniform in a plane parallel to the metal surface and varies only in a direction normal to the surface. In such a case the average of equation (1) need be taken only over a single column of unit cells parallel to the diffraction vector, the direction of which is the film normal. Let the film be M unit cells thick and let them be labeled from zero to $M-1$. Then equation (1) may be written

$$MC_n = \sum_{m=0}^{m=M-n-1} \exp [2\pi i l (Z_{m+n} - Z_m)] \,. \qquad (2)$$

Here the subscript on Z is always relative to the unit cell at the origin.

We consider the variation of Z_n as a function of n. We may take Z_0 to be zero, and if $\mathbf{a}_3$ is chosen to correspond to the center of gravity of the diffraction peak, we have that $Z_{M-1} = 0$. We discuss the simplest nontrivial relation between Z_n and n which satisfies these boundary conditions:

$$Z_n = An(M-1-n) \,. \qquad (3)$$

As will be seen, the constant A is related to the strain in the film. Then

$$Z_{m+n} - Z_m = An(M-1-n) - 2Amn = Z_n - 2Amn$$

and equation (2) may be written

$$MC_n = \exp [2\pi i l Z_n] \sum_{m=0}^{m=M-n-1} \exp [-4\pi i l Amn] \,.$$

This series may be summed and the result simplified to give

$$MC_n = \sin 2\pi l An(M-n)/\sin 2\pi l An \,. \qquad (4)$$

In general $2\pi l An$ is a very small angle, hence the denominator in (4) may be replaced by the angle. It is more convenient to represent the Fourier coefficient of equation (4) in terms of the distance $L = n|a_3|$. Let $B = A/|a_3|^2$ and the oxide film thickness $T = M|a_3|$. We may then write the Fourier coefficient in terms of the parameters T and B and the variable L:

$$C_L = \sin 2\pi B l L (T-L)/(2\pi B l L T) \,. \qquad (5)$$

Since the Fourier coefficients given by (4) or (5) are real, it follows that the diffraction line contour which they represent must be symmetrical. This restriction is a consequence of the relation (3). Any less simple assumption would complicate considerably the summation of equation (2), though, as is here shown, some such more general representation of Z_n is necessary to account for any asymmetry in the shape of the Bragg maxima.

4. Comparison of theory with experiment

Since the diffraction maxima for the Cu_2O film of Fig. 2 are quite symmetrical, it is presumed that they may be described by the simple theory discussed above. The line contours of both the film and of bulk Cu_2O were resolved into Fourier coefficients with the aid of Beevers–Lipson strips. Those of the bulk material were used to correct for instrumental contributions to the line shapes for the films by the method of Stokes (1948). A new tetragonal unit cell for the oxide may be chosen so that the two reflections may be indexed 001 and 002, in order to obtain reflections of the type $00l$, as assumed by the theory.

In attempting to fit the theory, it is useful to consider the function LC_L which is given by

$$LC_L = \sin 2\pi B l L (T-L)/(2\pi B l T) \,. \qquad (6)$$

As L increases, this function increases from zero and passes through a maximum. The maximum may be of two kinds, depending on the magnitudes of the parameters Bl and T. If they are such that for some L, $BlL(T-L) = \frac{1}{4}$, then this point corresponds to the

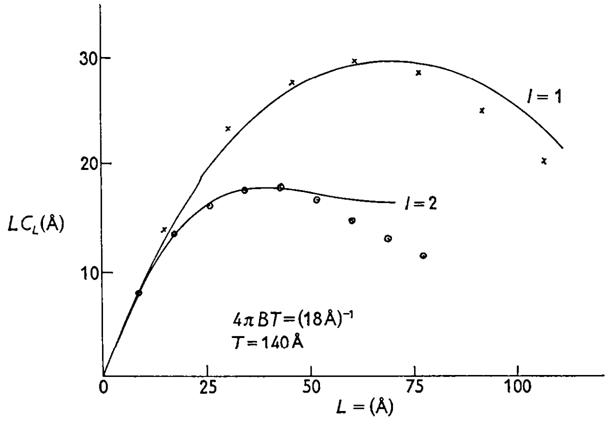

Fig. 3. Comparison of theoretical (solid lines) and experimental values of LC_L for a thin Cu_2O film.

maximum and $LC_L(\text{max.})=(2\pi BlT)^{-1}$. The function then decreases slowly, and it is not symmetrical about its maximum. On the other hand, if Bl and T are such that $BlL(T-L)<\frac{1}{4}$ for all L, then the maximum value of LC_L occurs at $L=T/2$ and the function is symmetrical about its maximum.

Fig. 3 is a plot of the experimentally measured values of LC_L as a function of L for $l=1$ and 2. The Fourier coefficients are those determined from the line shapes of Fig. 2. It is clear from the shapes of these curves that 002 has a maximum of the first kind, from which may be determined BT, while 001 is symmetrical about its maximum, thus determining the thickness T of the film. The experimental measurements are compared in Fig. 3 with values of LC_L computed from equation (6). The values of B and T as determined from the maxima were slightly modified to obtain the best fit to both curves.

5. Discussion

To interpret the meaning of B, let the interplanar spacing at the nth unit cell be given by $d_n=d(1+\varepsilon_n)$ where d is the average interplanar spacing as determined by the center of gravity of the peak. Then from the definition of Z_n,

$$\begin{aligned}\varepsilon_n &= Z_n - Z_{n-1}\\ &= An(M-1-n)-A(n-1)(M-n)=AM-2An\ .\end{aligned}$$

The interplanar spacing varies linearly from one interface to the other. We let $\Delta d=d_0-d_M$ and obtain

$$\Delta d/d=2AM=2BlTd\ .$$

For the film used here as an illustration, $d=3\cdot068$ Å for $l=1$, and from Fig. 3 $4\pi BT=(18\text{ Å})^{-1}$, hence $d_0=3\cdot110$ Å and $d_M=3\cdot027$ Å. This interplanar spacing for bulk Cu_2O is 3·019 Å.

Throughout its entire thickness the interplanar spacing of the film is larger than that of the bulk material, though at one interface the spacing is almost normal. It is not possible from the X-ray experiment to know whether this is the metal–oxide or oxide–gas interface.

There is a discrepancy between the film thickness as measured by X-rays and that determined by the polarizing spectrometer. A possible reason for this may be that the spectrometer measures the *total* thickness while the diffraction line contour is sensitive only to that portion of the film which is a single crystal throughout its thickness. At present it is not clear what the part of the film which may not be a single crystal is. It may be a polycrystalline layer of Cu_2O, though this possibility does not appear to be consistent with electron-diffraction photographs of similar films stripped from the metal single crystal (Cathcart, 1959). In any case, recent work (Cathcart, 1959) has thrown considerable doubt on the reliability of the polarizing spectrometer measurements, so that the diffraction thickness measurement may well be the more accurate of the two.

Though the comparison of Fig. 3 of experiment with theory is reasonably satisfactory, at large values of L there is some discrepancy. Since these points are associated with small, high order Fourier coefficients, they undoubtedly suffer most from experimental error. They are also the points most affected by deviations from the assumption that the film is of uniform thickness.

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