

STRUCTURAL DETERMINATION OF INDIUM OXIDE THIN FILMS ON POLYESTER SUBSTRATES BY TRANSMISSION ELECTRON MICROSCOPY

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The variation of structure with bias voltage, created by an r.f. discharge directed towards the substrate, of magnetron-sputtered films of indium oxide was determined by transmission electron diffraction techniques and showed a preferred (222) orientation parallel to the substrate. A technique for the reliable separation of thin films from a polyester substrate is described.

1. INTRODUCTION

We have studied indium oxide (In_2O_3) and indium-tin oxide (ITO) films on polyester in this laboratory with a view to developing heat mirror techniques¹. One particularly successful preparation technique has been ion plating from a planar magnetron-sputtering source. Ion plating leads to strong adhesion², and the magnetron sputtering produces stable structures, normally only found in sputtered and annealed systems, when the usual secondary-electron heating is suppressed by the magnetic field. This suppression is, of course, essential for deposition on polyester. The film thickness of interest (approximately 50 nm) is such that the film will remain coherent when stripped and will be sufficiently transparent to electrons in a conventional electron microscope to give simple micrographs. Scanning electron microscopy (SEM) does not have the resolution required to indicate the size of the grains (approximately 10 nm). Therefore it has been necessary to develop routine stripping techniques and to extract information from electron diffraction experiments.

2. SAMPLE PREPARATION

Initial attempts to dissolve the Melinex† from the films were made by heating very gently the samples which were dropped into *o*-chlorophenol (OCP). The applied heat was increased very slowly but currents still appeared within the liquid at about 52°C. The Melinex dissolved slightly above 65°C and thermal currents fragmented the film unless the temperature was raised very gently. Once the correct

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†Registered trade mark for ICI Ltd. for their polyethylene tetrathalate (polyester) film.

heater power was found to bring the OCP to 65 °C (or just above), a more routine "production line" was possible. A small square of the film was placed, Melinex down, on a copper mesh grid. This grid was then positioned, film up, on a fine stainless steel wire mesh which rested horizontally on a heated glass container filled to the brim with OCP. Since OCP fumes are toxic the whole apparatus was contained within a fume cupboard. Power was switched on at a level which gave an asymptotic temperature rise towards, for example, 70 °C. (A temperature slightly higher than 65 °C was required. However, the thicker the Melinex, the longer dissolution takes and higher temperatures may be more practicable.) The critical point was the OCP level which was always in contact with the stainless steel mesh so that surface tension drew it into contact with the copper grid and then again up to the Melinex itself. Since OCP vaporizes rapidly at these temperatures it had to be continually replenished. At 70 °C, a 23 μm film took about 1 h to dissolve, but samples may be safely left longer provided the deposited film does not react quickly with OCP. The In_2O_3 films, for example, thinned down very slowly. If the deposited film has no lateral strength it may be carbon coated beforehand. With the method described it was possible and preferable to prepare many samples simultaneously.

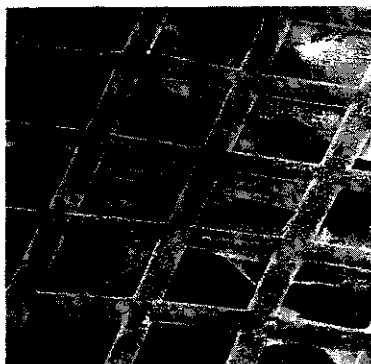


Fig. 1. A scanning electron micrograph of the film breakup on a copper grid caused by Melinex swelling. (Magnification 250 \times .)

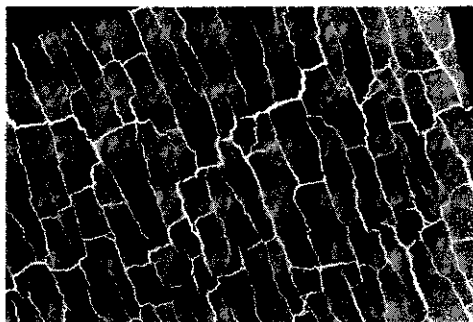


Fig. 2. A transmission electron micrograph of the film breakup on a copper grid caused by Melinex swelling. (Magnification 800 \times .)

(An attempt to use hexafluoroisopropanol (HFIP) as a cold solvent was abandoned. The room temperature reaction was too violent and the HFIP vaporized too rapidly for economy.) The mechanism of dissolution of Melinex in OCP led to a characteristic fragmentation of the deposited film (Figs. 1 and 2). The OCP was actually absorbed by the Melinex which swelled slightly causing the thin film to crack along the stress axes of the Melinex.

3. FILM STRUCTURE

An example of the polycrystalline structure of the In_2O_3 film is shown in Fig. 3 and the corresponding electron diffraction pattern is shown in Fig. 4. Although the sample film was only 50 nm thick, too much confusion was still produced in the

transmission photograph to directly measure the sizes of the crystallites. Thinner films would not be structurally similar to the 100–200 nm thickness required for optical applications. Therefore the crystallite size must be determined by Debye–Scherrer broadening of the electron diffraction rings for In_2O_3 films of thickness 50 nm. Ring widths vary for different lattice planes, but not in the regular manner which is indicative of stress effects. The ring spacings correspond precisely to those of body-centred cubic In_2O_3 , so that deficiencies must be confined to the grain boundary regions if the films are not stoichiometric. No element other than indium or oxygen was found below the surface layer by Auger analysis.

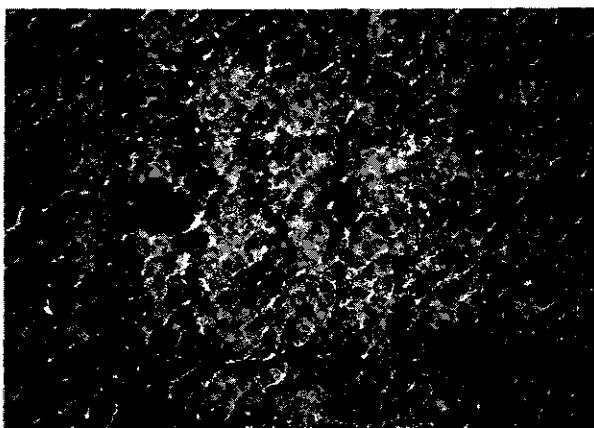


Fig. 3. A transmission electron micrograph of the In_2O_3 film. (Magnification 100 000 \times .)

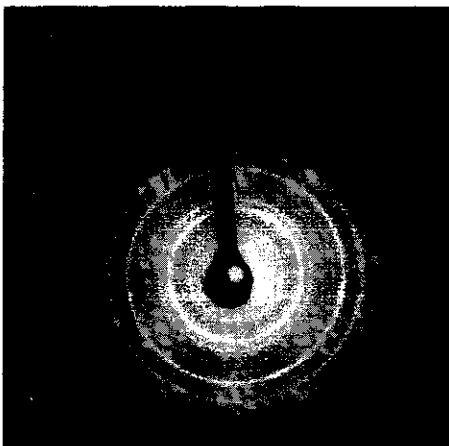


Fig. 4. The electron diffraction pattern of the In_2O_3 film shown in Fig. 3.

Ring intensities and halfwidths were determined from the negatives by means of a scanning photometer system which was precalibrated. The results are shown in Figs. 5 and 6. Figure 5 presents crystallite dimensions d perpendicular to the substrate and determined for each set of planes. In Figs 5 and 6 “strong” and “weak”

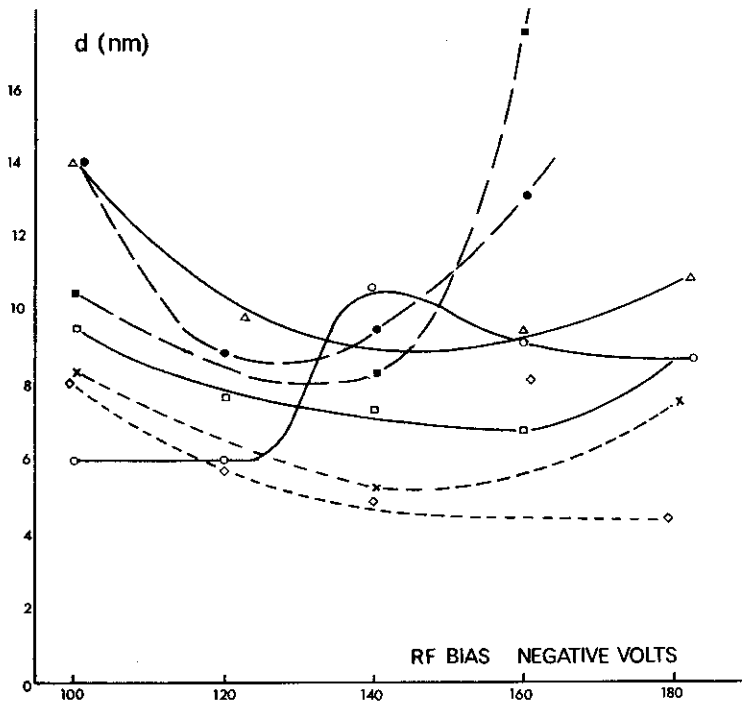


Fig. 5. The variation of crystallite dimensions perpendicular to the substrate with r.f. sputtering bias: Δ , (211); \circ , (222); \square , (400); \bullet , (332); \blacksquare , (431); \times , (440); \diamond , (632); —, strong linear; ----, weak non-linear; — · —, strong non-linear.

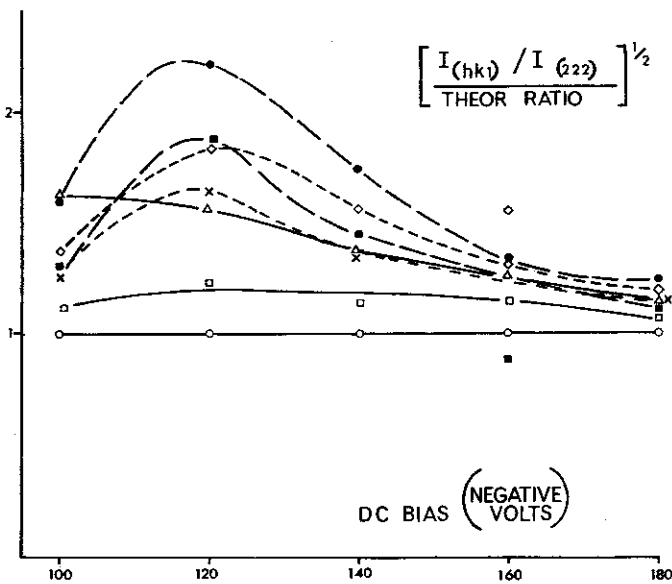


Fig. 6. The intensity anomaly as a function of the r.f. sputtering bias: Δ , (211); \circ , (222); \square , (400); \bullet , (332); \blacksquare , (431); \times , (440); \diamond , (632); —, strong linear; ----, weak non-linear; — · —, strong non-linear.

refer to the relative line intensities (*i.e.* signal magnitude) and "linear" and "non-linear" differentiate between peaks which were or were not wholly confined to the linear region of the photometer measurement system. Thus the data for the (211), (222) and (400) rings are expected to be more reliable than those for the (332) or (431) rings. The strongest ring is the (222) which is unique in its variation with the d.c. bias voltage developed in the r.f. sputtering system. The (222) planes are maximally close packed and normally control crystal growth. When the measured diffraction intensities are compared with theoretical values³, the (222) intensity is (with one exception) considerably less than that predicted. The intensities are related to the total number of crystal planes (*i.e.* the number of crystallites times the crystallite size) and the deviations from the theoretical (plotted in Fig. 6) may be taken to indicate the preferred (222) orientation parallel to the substrate.

Two points must be made in relation to the results.

(1) Both the (222) crystallite size and the preferred orientation variations with bias, peak within the same bias range as the electron mobility in In_2O_3 films prepared in the same way on glass⁴. (In fact, the product of the two curves would peak at approximately the same bias value as the mobility peaks.)

(2) A variety of preferred orientations have been noted for In_2O_3 films prepared in different ways but (222) orientation parallel to the substrate is normally only produced by annealing at high temperatures (400 °C)⁵. Such annealing is, of course, impossible for films on polyester substrates. Therefore the original proposition that the magnetron-sputtered ion-plating process would produce films at low temperatures with the properties of films otherwise obtainable only at high temperatures is confirmed. This conclusion is also supported by recent mobility measurements on ITO films⁴.

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