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Structural characterization of tin doped indium oxide films prepared by magnetron sputtering

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The structural characteristics of transparent and conducting thin films of tin doped indium oxide (ITO) have been studied by X-ray diffraction and electron microscopy. The ITO films have been prepared by radio frequency sputtering employing a planar magnetron configuration. The effects of variation of substrate temperature and annealing have been studied. Films deposited at substrate temperatures up to 230° C show a marked ⟨1 1 0⟩ preferred orientation, whereas those deposited at 330° C are preferentially oriented in the ⟨3 1 1⟩ direction. Transmission electron micrographs of ITO films deposited on KCl crystals show the possible effects of strain on the structure, which are minimized to a great extent by annealing.

1. Introduction

Films of indium oxide and tin doped indium oxide (ITO) have been used as transparent conducting layers in many sophisticated devices such as solar cells, solar photothermal conversion devices, liquid crystal displays, etc. Extensive research has been done and is still being carried out for the improvement of electrical and optical properties of these films [1]. The main stress in research has been on the improvement of sheet resistance and transmittance of the films. These properties are also dependent on the structure of the film. Although several studies of ITO films report on some of the structural aspects [2–12], a concerted, systematic study of structural characterization does not appear to exist.

In an earlier paper [13] we reported the results of our studies on the electronic and optical properties of indium tin oxide (ITO) films prepared by the radio frequency (r.f.) magnetron sputtering method.

In this paper we have reported the results of our studies on the structural aspects of ITO films by X-ray diffraction and transmission electron microscopy. Since in our earlier study the properties of ITO films were found to be most sensitive to the substrate temperature, we have mainly varied this parameter in our structural studies.

2. Experimental procedures

ITO films were deposited by r.f. sputtering employing a planar magnetron configuration (CVC Inc., USA). The target employed was a disc of hot pressed powder (8 inch diameter, 1/4 inch thick) with a composition of 90% In_2O_3 and 10% SnO_2 by weight (supplied by CERAC Inc., USA). The r.f. power supplied to the target was 200 W. Unless specifically mentioned, the argon pressure employed was 4.5×10^{-3} torr. The other experimental details are described in [13].

For the X-ray diffraction studies, the films were deposited on Corning 7059 glass substrate. The deposition rate was of the order of

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TABLE I The relative intensity I/I_{max} (%) of X-ray profiles from ITO films

Film ITO	(*h k l*)																							
	211	222	321	400	411	420	332	422	431	521	440	611	620	541	622	631	543	640	721	642	732	800	811	820
As deposited at 50° C	–	–	–	94	15	–	–	–	17	–	100	15	8	11	34	11	–	–	–	–	–	–	–	–
Deposited at 50° C and annealed in air at 400° C	10	40	–	95	15	–	–	–	26	–	100	11	–	11	44	12	–	–	–	–	–	–	–	–
Deposited at 230° C	43	91	7	32	12	3	10	4	29	–	100	9	–	12	50	11	5	–	5	–	8	–	–	–
Deposited at 230° C and annealed in air at 400° C	42	93	8	31	9	3	9	5	29	3	100	9	–	12	51	9	3	–	5	3	7	–	–	–
Deposited at 330° C	32	12	5	37	24	6	–	4	20	9	45	13	3	5	100	19	–	3	10	5	4	4	6	5
In_2O_3 powder ASTM data	14	100	2	30	8	2	6	2	10	4	35	6	2	4	25	6	2	2	4	2	4	4	4	2

10 nm min^{-1}. The films were prepared at substrate temperatures of 50, 230 and 330° C. Films in the thickness range 600 to 850 nm were studied. X-ray line profiles were recorded using a Philips Geiger Counter Diffractometer (PW1050, 1051) with monochromatic Cu$K\alpha_1$ radiation from a Philips X-ray generator (PW1130). The line profiles were chart recorded at a speed of 1° per minute. All the measurements were carried out at room temperature (300 K).

Transmission electron microscopy (Hitachi HU-11F model operating at 75 kV) was performed on a few samples deposited on KCl single crystals and glass. The thickness of the ITO films was in the range 15 to 40 nm (required for Transmission Electron Microscopy) which is much lower than that of the films used for X-ray diffraction. Both bright field imaging and selected area diffraction studies were done to supplement the X-ray diffraction data on the structural aspects of the ITO films.

The thicknesses of the films was measured by a stylus type thickness measuring apparatus (Planer Products, UK). The dark conductivity has been measured by the van der Pauw technique and Hall effect has been studied by the four probe method with an electromagnet having a maximum field strength of 7.6 kG.

3. Results and discussion

X-ray diffraction measurements have been carried out on as-deposited ITO films and also on films annealed for one hour in a vacuum at 350° C and in air at 400° C. Typical results of X-ray diffraction measurements have been summarized in Table I. Intensities have been reported in terms of peak heights. In order to check the effects of line broadening, the line areas of the first and second most intense peaks have also been calculated and compared with the results in terms of peak heights (Table II). Both give virtually the same result.

All the lines in the diffraction patterns can be assigned to the cubic Tl_2O_3 (bixbyte) structure of In_2O_3 [14]. There is no evidence of the presence of a crystalline phase of SnO_2 in the X-ray diffractometer traces in any of the films examined. It may be mentioned here that Lehman and Widmer [6] could not detect the presence of SnO_2 in co-sputtered ITO films from X-ray diffraction traces, up to 40 mol % SnO_2 concentration. Fan *et al.* [5] and Itoyama [7] have also reported the absence of SnO_2 or Sn_3O_4 peaks in the diffraction patterns of their r.f. sputtered films.

TABLE II The relative intensity I/I_{max}(%) and the relative area A/A_{max}(%) of X-ray profiles from ITO films (two most intense peaks considered)

Film ITO	hkl	I/I_{max}(%)	A/A_{max}(%)
Deposited at 50° C	(4 4 0)	100	100
	(4 0 0)	94	96
Deposited at 230° C	(4 4 0)	100	100
	(2 2 2)	91	96
Deposited at 330° C	(6 2 2)	100	100
	(4 4 0)	45	47

The texture of a film depends upon the surface free energy and the most preferred alignment is of the set of planes with minimum surface free energy. The actual alignment depends strongly upon the deposition conditions and in our case changes substantially with a change in the substrate temperature.

For films deposited at 50° C, the two peaks (4 4 0) and (4 0 0) appear prominently, indicating the existence of both ⟨1 1 0⟩ and ⟨1 0 0⟩ textures. The (6 2 2) peak is third in order of intensity (Fig. 1a). Itoyama [7], for his as-deposited magnetron sputtered ITO films (substrate temperature ~ 140 to 180° C) obtained an amorphous like X-ray diffraction pattern. Only on annealing in air or in N_2 at 400° C, the ITO films became crystalline. In the present work, the samples, even those that were as-deposited, show well-developed crystallinity.

These films, when annealed in vacuum, show no remarkable change. However, when annealed in air for one hour at 400° C, the films also develop a ⟨1 1 1⟩ texture as shown by the presence of (2 2 2) peak. The intensity of the (4 4 0), (4 0 0) and (6 2 2) peaks also increase, indicating enhanced crystallinity (Fig. 1b). This is also corroborated by Hall effect measurements. For a film deposited at 50° C, the room temperature mobility is about 29 cm^2 V^{-1} sec^{-1}. On annealing in air at 400° C for 1 h, the mobility is found to be doubled (~ 58 cm^2 V^{-1} sec^{-1}), which could be attributed to an increased crystallinity.

For the films deposited at 230° C, the (4 4 0) peak is still the most prominent one (Fig. 2). However, the intensity of the (4 0 0) peak diminishes and that of the (2 2 2) peak increases,

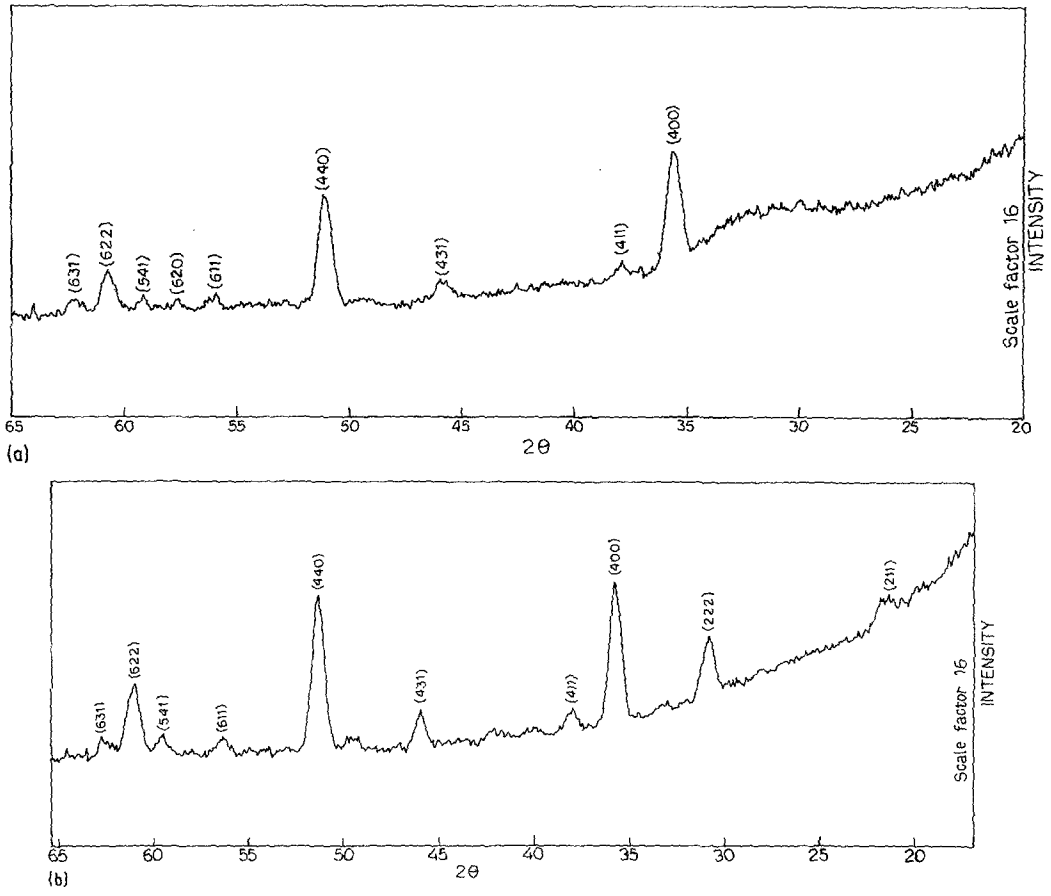

Figure 1 X-ray diffraction patterns for In_2O_3: Sn films: (a) deposited at 50° C; (b) deposited at 50° C and annealed in air at 400° C.

showing a ⟨1 1 1⟩ preferred orientation. The (6 2 2) peak also is more prominent. In the case of films deposited at 330° C, more high angle peaks are detectable compared with films deposited at lower temperatures (Fig. 3). The (4 4 0) peak diminishes and the most prominent peak is (6 2 2), showing a ⟨3 1 1⟩ texture.

Overall, there is an increase in the degree of crystallinity of ITO films with increasing substrate temperature. The resistivity also decreases from 3.1×10^{-4} to $7.4 \times 10^{-5}\,\Omega$cm as the substrate temperature is increased from 50 to 330° C. As reported in our earlier paper [13], there is an increasing trend in the conductivity,

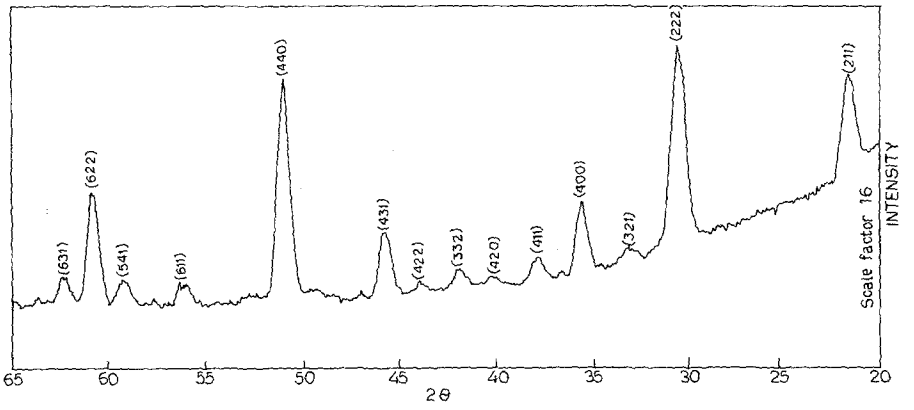

Figure 2 X-ray diffraction pattern for In_2O_3: Sn film deposited at 230° C.

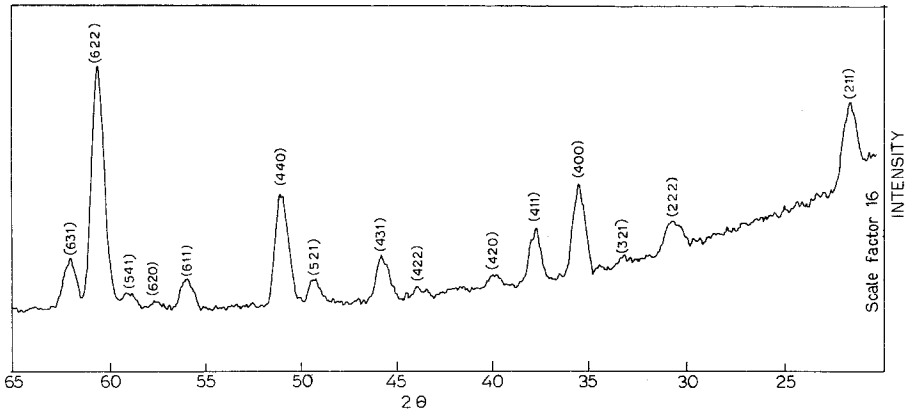

Figure 3 X-ray diffraction pattern for In_2O_3: Sn film deposited at 330° C.

carrier concentration and mobility with increase in the substrate temperature for deposition.

The effect of annealing in air at 400° C, for ITO films deposited at 230 and 330° C is not quite discernible in the X-ray profiles as in case of films deposited at 50° C (Table I). Perhaps, with a higher annealing temperature the change could have been prominent.

It may be mentioned here that X-ray diffraction studies on ITO films deposited by different sputtering techniques revealed either a ⟨1 1 1⟩ or ⟨1 0 0⟩ preferred orientation, depending upon the deposition parameters and also post-deposition annealing [2–9].

The lattice constant, a, of the ITO films increases with the deposition temperature, though not linearly. For films deposited at 50° C, a = 1.010 nm; for those deposited at 230° C, a = 1.011 nm; and for films deposited at 330° C, a = 1.012 nm. The value for a from ASTM data for In_2O_3 powder is 1.0118 nm. Kulaszewics [15] has also reported an increase in the lattice constant of ITO films, prepared by spray pyrolysis, as the spraying temperature of the substrate is increased.

As a supplement to the X-ray studies, the effects of deposition temperature on the microstructure and crystallinity of ITO films were studied by transmission electron microscopy. The as-deposited ITO films prepared at 50° C do not show very well developed crystallinity (Fig. 4). The films consist of poorly crystalline regions of the size ~10 to 20 nm. With the increase in substrate temperature there is a gradual increase in this size up to ~20–50 nm. Fig. 5b shows the typical micrograph for a film deposited on a substrate at 330° C. The selected area diffraction pattern however, still contains only a few slightly diffuse rings (Fig. 5a). It may be mentioned here that Nath *et al.* [11] reported TEM studies on In_2O_3 (Sn) films and observed that with the increase in deposition temperature, the crystallite size also increased.

The apparent difference between the degree of

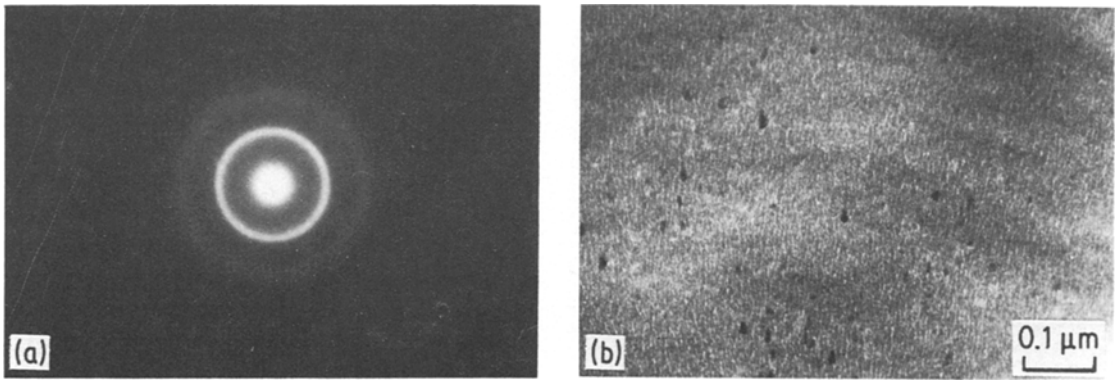

Figure 4 (a) Electron diffraction pattern and (b) TEM micrograph for In_2O_3: Sn film deposited at 350° C.

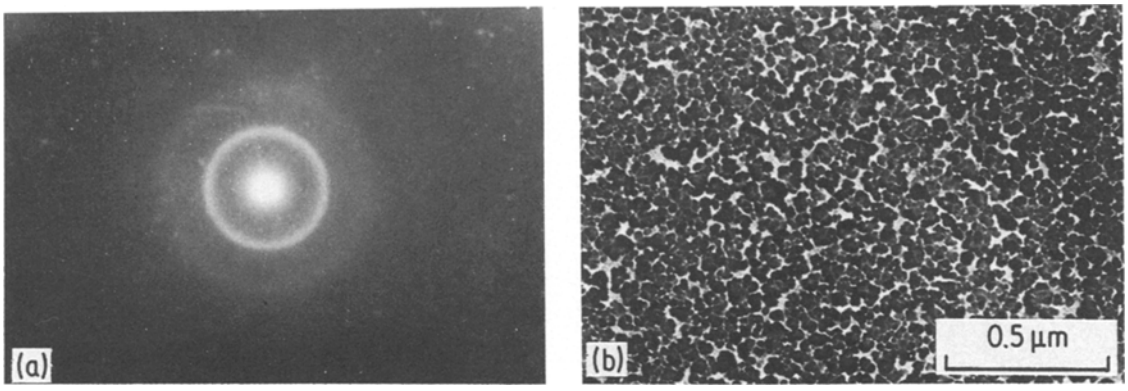

Figure 5 (a) Electron diffraction pattern and (b) TEM micrograph for In_2O_3: Sn film deposited at 330° C.

crystallinity of ITO films observed by the X-ray diffraction technique and TEM studies may be attributed to strain effects. These effects could arise due to the small thickness (15 to 40 nm) of the films used for TEM studies. The effect of substrate was checked by depositing ITO on glass at 50° C. TEM studies showed no significant change in these samples than those deposited on KCl.

To probe further into the results obtained by transmission electron microscopy, the effects of annealing on the ITO films were studied. For films deposited at 50° C, the selected area diffraction patterns show remarkable recovery effect on annealing both in vacuum and in air (Figs. 6a and 7a). There is no apparent increase in the crystallite size under vacuum annealing, yet the strain effects are removed. As a check, the resistivity of 15 nm thick ITO film deposited at 50° C was measured. The resistivity of the as-deposited film was $5.6 \times 10^{-4} \Omega$cm. After annealing in vacuum at 350° C for one hour, the resistivity decreased to $2.1 \times 10^{-4} \Omega$cm. A thicker film (140 nm) did not show any change in resistivity after similar treatment. The decrease in the resistivity of the thin film on vacuum annealing, could be attributed to the removal of strain effects, which are not prominent in thicker films. When annealed in air on the other hand, micrographs of films deposited at 50° C reveal regions of large grains ~ 150 nm, with a good degree of crystallinity (Fig. 7b). The resistivity of the sample increases by one order of magnitude on air annealing. This is due to the diffusion of oxygen into the ITO film, which reduces the concentration of oxygen vacancies. However, the mobility increases, as already mentioned in the discussion for X-ray diffraction studies. For films deposited at higher substrate temperatures, vacuum annealing does not show any prominent recovery effect. Annealing in air however shows significant recrystallization of the films (Fig. 8).

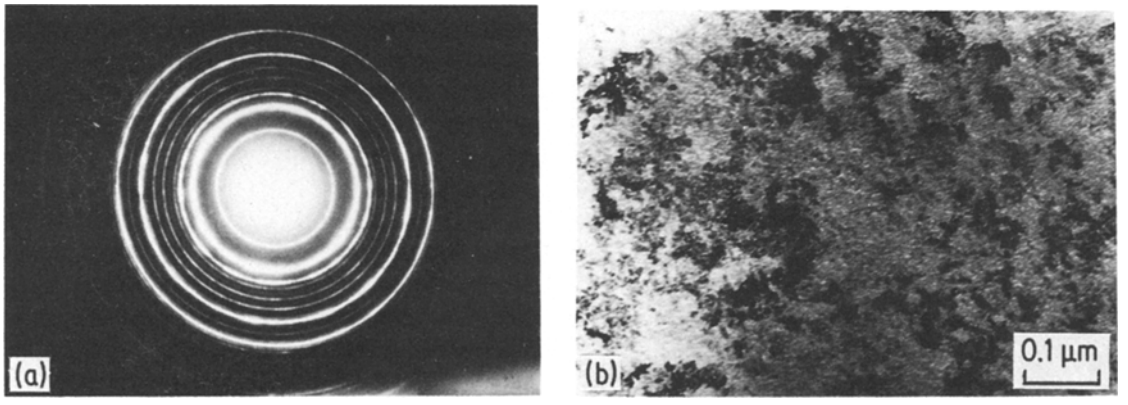

Figure 6 (a) Electron diffraction pattern and (b) TEM micrograph for In_2O_3: Sn film deposited at 50° C and annealed in vacuum at 350° C.

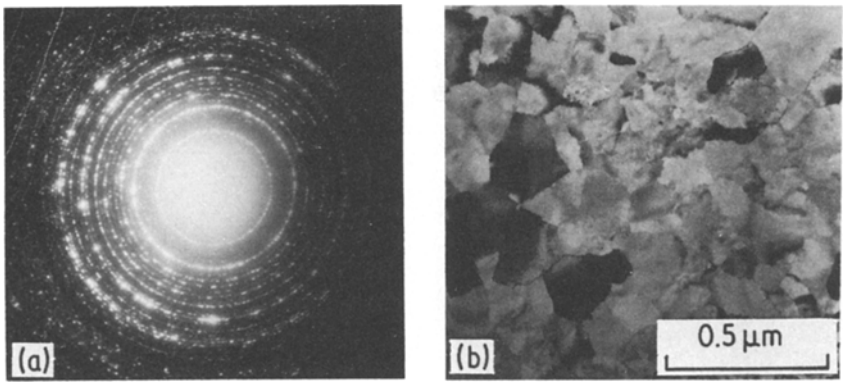

Figure 7 (a) Electron diffraction pattern and (b) TEM micrograph for In_2O_3: Sn film deposited at 50° C and annealed in air at 400° C.

To check whether strain effects are minimized by a slower rate of deposition, TEM studies were performed on ITO samples prepared at high argon pressure (12.5×10^{-3} torr) during sputtering. The substrate temperature was 230° C. As the argon pressure was increased from 4.5 to 12.5×10^{-3} torr during sputtering, the rate of deposition dropped to about one third of the previous value. (Therefore the TEM samples were prepared at argon pressure of 12.5×10^{-3} torr). The selected area diffraction pattern shows excellent crystalline structure even for the as-deposited films (Fig. 9). In contrast, as already stated, for films deposited at 4.5×10^{-3} torr, good crystalline structure is obtained only after annealing. Thus, slower rate of deposition minimizes strain effects and improves the microstructure considerably.

4. Conclusions

A gradual change from ⟨1 1 0⟩ to ⟨3 1 1⟩ texture is observed in X-ray profiles for ITO films prepared on glass by r.f. magnetron sputtering as the deposition temperature is increased from 50 to 330° C. Films deposited at 50° C show better cystallinity when annealed in air at 400° C. Films deposited at higher substrate temperatures (230° C, 330° C) do not show prominent annealing effects.

Transmission electron microscopy studies on much thinner specimens on KCI crystals show a different microstructural characteristic which does not change with higher deposition temperature. Annealing treatment under different environment has a significant effect on the structure of these films. Slower rate of deposition at increased argon pressure during sputtering produces good crystalline structure even without annealing.

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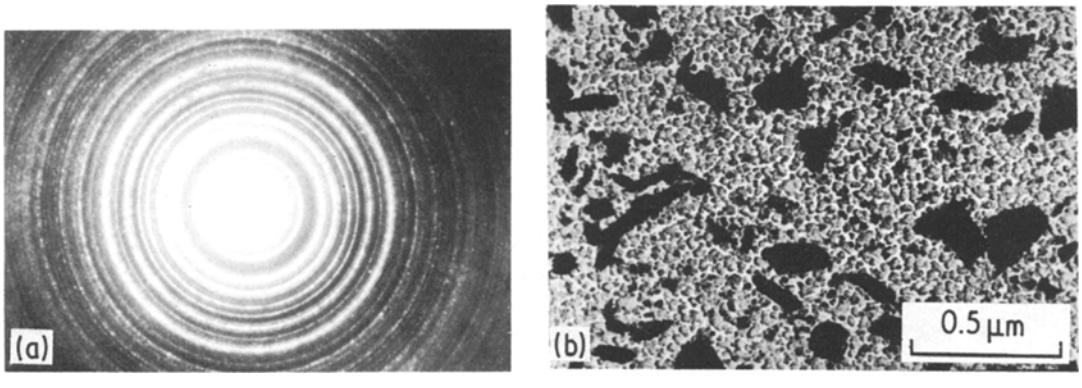

Figure 8 (a) Electron diffraction pattern and (b) TEM micrograph for In_2O_3: Sn film deposited at 330° C and annealed in air at 400° C.

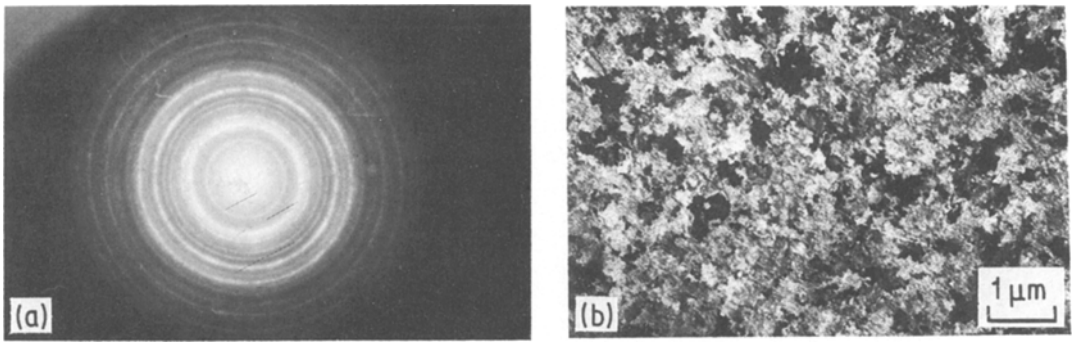

Figure 9 (a) Electron diffraction pattern and (b) TEM micrograph for In_2O_3: Sn film deposited at high argon pressure (12.5×10^{-3} torr).

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