

INFLUENCE OF ANNEALING ON THE PHASE COMPOSITION, TRANSMISSION AND RESISTIVITY OF SnO_x THIN FILMS

G. BEENSH-MARCHWICKA, L. KRÓL-STĘPNIEWSKA AND A. MISIUK *

Institute of Electron Technology of Wrocław, Technical University, Janiszewskiego 11–17, 50-372 Wrocław (Poland)

(Received March 7, 1983; accepted January 9, 1984)

Undoped and antimony-doped tin oxide films were prepared by d.c. reactive ion sputtering in an argon atmosphere with oxygen partial pressures ranging from 0 to 50%. The films were annealed in air, nitrogen and a vacuum in the temperature range 570–750 K. The influence of thermal annealing on the structural properties, electrical resistance and optical transmittance is described.

1. INTRODUCTION

Optically transparent electrically conducting films have been used for many years as electrodes or resistive elements^{1–3}. Recently, they have been applied to semiconductor devices as transparent gates on charge injection devices and charge-coupled devices and as transparent barrier layers on solar cells⁴. The materials used for such applications are tin oxide (SnO_2), antimony-doped tin oxide and tin-doped indium oxide. These films have been deposited by chemical vapour deposition, sputtering, evaporation and spraying^{1,2,5}. Temperature stability and reproducibility of the film properties are important for device reliability. The films are exposed to heat during the preparation and operation of the devices, and this may cause structural changes and influence their electrical and optical properties. The effects of annealing are complex, and various phenomena may be observed. For example, the grain size may increase, the antimony interstitials may move into lattice sites, the oxygen vacancy density may decrease, the tin and antimony may out diffuse, and chemisorption and desorption of oxygen from the grain boundaries may occur^{2,6–8}.

The effect of heat treatment on the phase composition is described in this paper, and the properties of undoped and antimony-doped tin oxide films prepared by reactive d.c. low energy ion sputtering under various conditions are presented.

2. EXPERIMENTAL DETAILS

Tin oxide (SnO_x) thin films were prepared by reactive sputtering of tin or

* Present address: High Pressure Research Centre, Polish Academy of Sciences, Sokołowska 29, 01-142 Warsaw, Poland.

Sn–10wt.%Sb alloy in an O₂–Ar atmosphere. A d.c. triode low energy sputtering system⁹ was used in the pressure range 10^{-4} – 5×10^{-4} Torr. The sputtering parameters were as follows: arc discharge voltage V_{AC} , 18–50 V; arc discharge current I_{AC} , 6 A; magnetic coil current I_{MC} , 7 A (corresponding to a field of about 76 G). The total gas pressure p_t was 5×10^{-4} Torr, while the residual pressure p_r was 2×10^{-6} Torr. The oxygen content K in the gaseous mixture was defined as the ratio of the oxygen partial pressure to the total pressure. The value of K was varied from 0 to 50%. The targets were water-cooled copper discs faced with tin or Sn–Sb alloy. The negative ion extraction voltage U_T was limited to 200 V so that the tin did not melt. The SnO_x films condensed on a borosilicate glass (Corning 7059) substrate in the temperature range 300–523 K. The film thickness was 50–600 nm. The thin film properties were characterized from measurements of the resistance, transmittance and phase composition before and after annealing. The transmittance was measured in the wavelength range 330–850 nm. The film structure was investigated using X-ray diffraction with Cu K α radiation. The X-ray diffraction patterns of the films were compared with data from a powder sample which in turn was compared with published results^{10,11}.

3. RESULTS AND DISCUSSION

3.1. Undoped films

All undoped films deposited at a substrate temperature T_s of 300 K and oxygen contents greater than 10% were amorphous.

The diffraction patterns of thin films deposited at $T_s = 423$ K are presented in Fig. 1. The diffraction pattern of an SnO₂ powder standard, which was of spectral purity, is also shown for comparison. Four strong reflections are visible for the powder standard. The d values observed match those accepted for tetragonal SnO₂^{10,11}, although the intensity ratios are slightly different and some weak reflections are absent.

Films prepared in a pure argon atmosphere consisted of tetragonal β -Sn with the lattice constants $a = 0.5825 \pm 0.0005$ nm and $c = 0.3178 \pm 0.001$ nm. The films prepared at $K = 5\%$ consisted of β -Sn and SnO, whereas amorphous material was obtained at $K \approx 10\%$. The films deposited at higher oxygen contents contained the SnO₂ phase in which the crystallite orientation was either almost random ($K = 15\%$) or preferential ($K \geq 20\%$). The intensity of the ($hk0$) reflections of these films was much higher than that of the (hkl) reflections for $l \neq 0$. This indicates that the c axes of most of the crystallites are parallel to the substrate surface. The well-known Scherrer equation gives a value of about 50 nm for the average crystallite dimension.

Films 450 nm thick deposited at $T_s = 523$ K exhibited diffraction patterns similar to those in Fig. 1. However, the amorphous films were obtained over a wider range of oxygen concentrations ($15\% \leq K \leq 25\%$).

After deposition, the films were annealed in a vacuum, nitrogen or air at temperatures in the range 600–750 K for periods of 4–20 h. Vacuum annealing ($p = 10^{-5}$ Torr; $T_a = 623$ K) and dry nitrogen annealing (in a gas flow furnace at $T_a = 650$ K) for 4 h did not cause any significant changes in the film structure. However, decreases in the film resistance were often observed. The changes in the

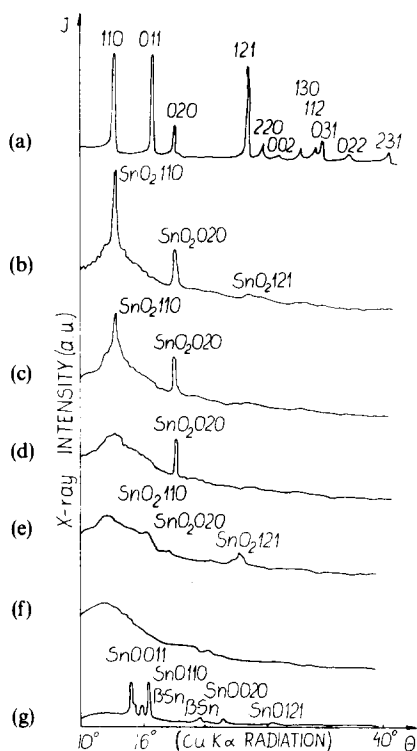


Fig. 1. Diffraction patterns of samples sputtered from a tin target in atmospheres with various oxygen contents K (film thickness, 400 nm) (sputtering conditions: $T_s = 423$ K; $U_T = -150$ V): (a) SnO_2 standard; (b) 50% O_2 ; (c) 40% O_2 ; (d) 30% O_2 ; (e) 15% O_2 ; (f) 10% O_2 ; (g) 5% O_2 .

resistance of films about 100 nm thick containing the SnO_2 phase after aging in a vacuum are presented in Fig. 2.

Annealing in air has a significant effect on the film structure as well as on the electrical and optical properties. This effect depends on the sputtering parameters, and particularly on the oxygen partial pressure during film condensation. The films deposited in a pure argon atmosphere underwent partial oxidation during annealing in air ($T_a = 623$ K) for 4 h. β -Sn, SnO and traces of SnO_2 were observed. The films deposited at $K = 5\%$ oxidized to SnO (Fig. 3) which was stable and did not oxidize further during prolonged annealing at 623 K. The amorphous films deposited at $K \approx 10\%$ crystallized to SnO and SnO_2 with random crystallite orientation. The films initially consisting of the SnO_2 phase (deposited at oxygen contents K in the range 15%–50%) did not change their phase composition during annealing. However, a substantial increase in the integral reflection intensities (up to a factor of 4) was observed. This increase is related to the crystallization of the initially amorphous material. The diffraction peaks of samples annealed in air became much broader, and in the θ range investigated additional reflections appeared only at θ values between 18.2° and 19.8° . This effect is probably related to the effect of the orientation of the existing crystallites on further crystallization of the initially amorphous part of the deposited film. Some diffraction lines, particularly (020), not only became more intense and broader but sometimes appeared to split (Fig. 4). The

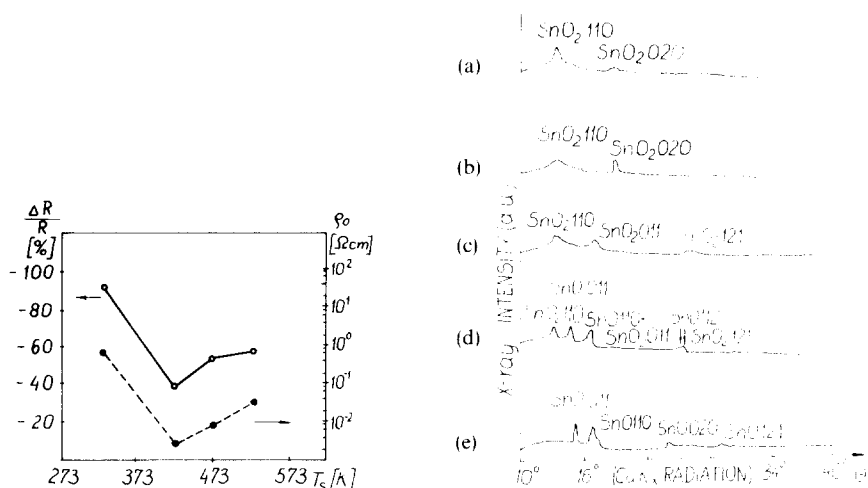


Fig. 2. Resistivity ρ_0 before annealing and changes in resistance after vacuum annealing at $T_a = 623$ K for 4 h plotted against the substrate temperature during sputtering (sputtering conditions: $K = 33^\circ$; $U_T = -150$ V).

Fig. 3. Diffraction patterns of samples annealed in air at 623 K for 4 h (the patterns obtained before annealing are shown in Fig. 1): (a) 40% O_2 ; (b) 30% O_2 ; (c) 15% O_2 ; (d) 10% O_2 ; (e) 5% O_2 .

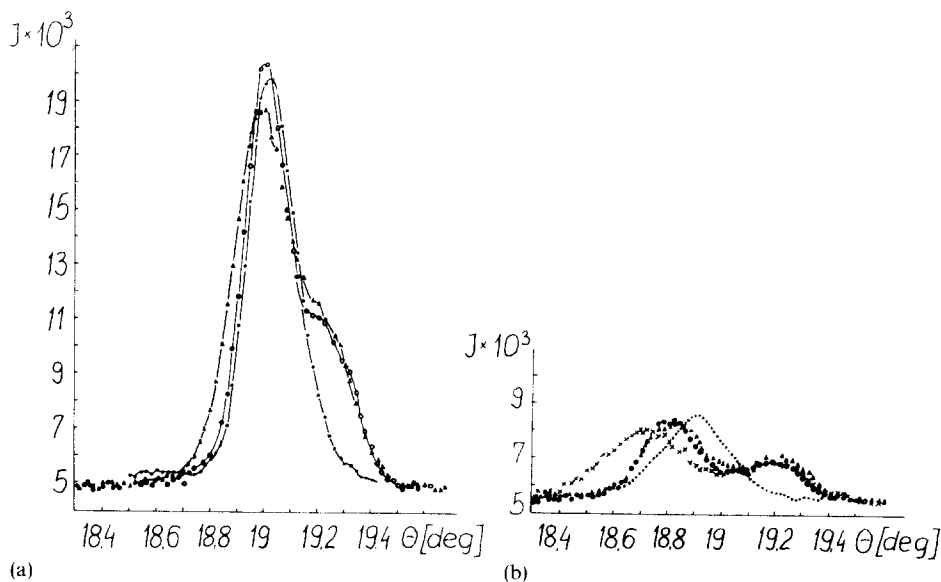


Fig. 4. Diffraction patterns of SnO_x films measured with θ in the range 18.2° – 19.8° : \bullet , before annealing; \times , after aging in air at 623 K for 4 h; \circ , after aging in air at 623 K for 4 h and at 673 K for 20 h; \blacktriangle , after aging in air at 623 K for 4 h, at 673 K for 20 h and at 743 K for 10 h. The films were deposited at K values of (a) 25% and (b) 40%, $T_s = 423$ K and $U_T = -150$ V.

lower angle line then had almost the same intensity and angle position as that in the unannealed film, whereas the additional line was shifted to a higher angle. The intensity of the additional peak tended to decrease with decreasing oxygen content

in the gaseous mixture during sputtering. Prolonged annealing of the samples at the higher temperatures (up to 20 h at 673 K) did not appreciably change the position and intensity of such lines. A (111) SnO_2 line of comparatively low intensity has been reported for an SnO_2 standard in the 18.2° – 19.8° range where this additional line is seen¹¹. The angular shift of this line relative to the (020) line is about 0.45° .

The angular shift in line positions between the (020) line and the additional line in the diffraction patterns of tin oxide thin films is in the range 0.1° – 0.4° . The position of an assumed (111) line calculated from the (110), (020) and (121) peak positions is displaced by about 0.1° – 0.3° towards higher angles relative to the position of the additional peak. Therefore it appears that the additional line cannot be attributed to the (111) SnO_2 line. According to the data¹¹ this peak does not correspond to other tin oxides, particularly Sn_3O_4 , $\text{SnO} \cdot \text{SnO}_2$ and tin oxide hydrate^{12,13}. We thus postulate that the additional line can be indexed as (020) and attributed to the SnO_{2-x} material crystallized under the influence of annealing. The lattice constants are slightly less than those of stoichiometric SnO_2 (Fig. 5) and increase with increasing oxygen content during the deposition of the unannealed films. The value of a for the material crystallized during annealing was less than that of the material deposited during sputtering and was almost independent of the deposition parameters.

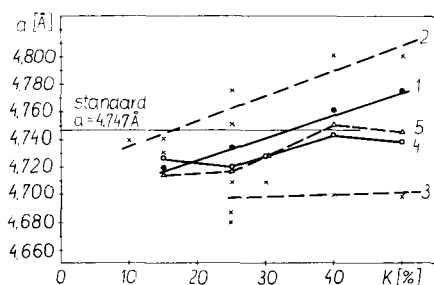


Fig. 5. The lattice constant a of the SnO_2 phase before and after annealing in air at 623 K for 4 h as a function of the oxygen concentration during sputtering: line 1, undoped as-deposited films; line 2, annealed undoped films; line 3, annealed undoped films (the value calculated from the additional peak assuming that it is the (020) SnO_2 peak); line 4, antimony-doped as-deposited films; line 5, annealed antimony-doped films. The data for the powder specimens are as follows: $a = 0.474$ nm (ref. 10); $a = 0.4738$ nm (ref. 11).

The optical transmittance of all the samples aged in air at 623 K for 4 h increased (Fig. 6). The greatest changes were obtained after the first thermal aging cycle. Subsequent annealing cycles did not change the transmittance appreciably (Fig. 6(b)).

The resistance of films with thicknesses in the range 100–150 nm increased by about three orders of magnitude after annealing in air or nitrogen containing a small percentage of oxygen (Fig. 7). A decrease in the resistance after annealing was sometimes observed for films sputtered at high oxygen concentration ($K = 50\%$). More complicated changes in resistance on annealing were observed for films with thicknesses of about 500 nm, for which the resistance may increase substantially, increase slightly or decrease. The large increases in resistance can be attributed to oxidation of the film, but the small increases and decreases are difficult to explain.

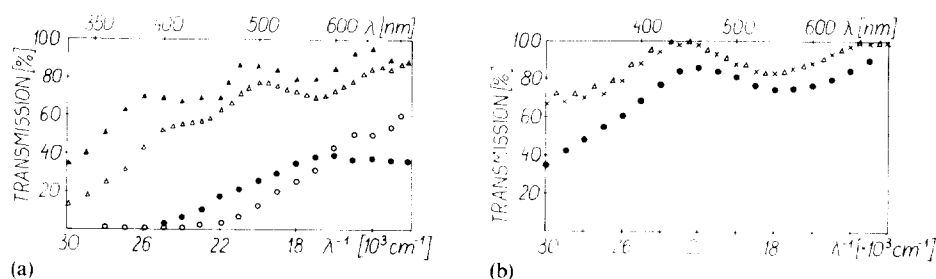


Fig. 6. Optical transmission as a function of wavelength for films about 400 nm thick deposited at various oxygen doping levels: (a) before (\circ , $K = 10\%$; \triangle , $K = 15\%$) and after (\bullet , $K = 10\%$; \blacktriangle , $K = 15\%$) aging in air at 623 K for 4 h; (b) before (\bullet) and after (\times , 4 h at 623 K; \triangle , 20 h at 673 K and 10 h at 743 K) prolonged annealing ($K = 40\%$).

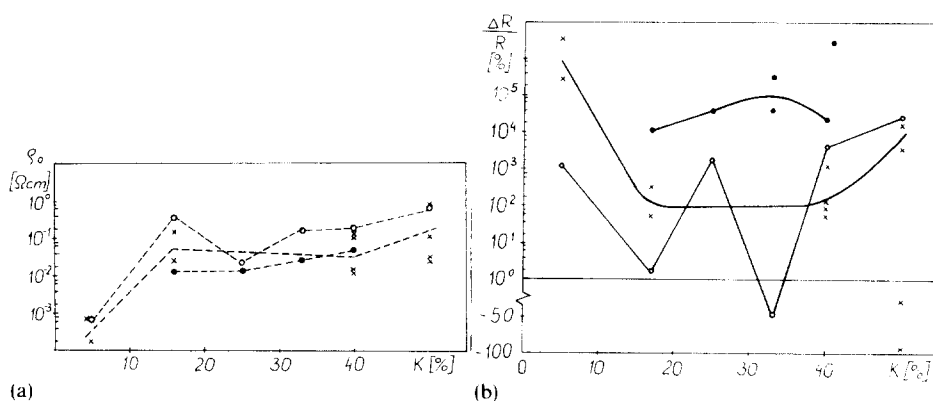


Fig. 7. (a) Resistivity ρ_0 before annealing and (b) the average change in the resistance of the films after aging ($T_a = 523$ K) vs. the oxygen doping level during sputtering: \times , films 150 nm thick sputtered at $U_T = -200$ V and aged in air for 10 h at 573 K; \bullet , films 100 nm thick sputtered at $U_T = -150$ V and aged in nitrogen containing a small amount of oxygen for 4 h at 650 K; \circ , films 500 nm thick sputtered at $U_T = -150$ V and aged in nitrogen containing a small amount of oxygen for 4 h at 650 K.

They may be due to ordering of the film structure. However, an increase in the width of the (020) peak is observed for the annealed films, and this can be interpreted in terms of additional crystallization of SnO_2 to form small crystallites (dimensions less than 50 nm) or it may be due to stresses generated during annealing. We also observed stresses, which sometimes decreased during annealing, in the as-deposited films. When the stress decreases during annealing the resistivity decreases simultaneously¹⁴.

3.2. Doped films

Diffraction patterns of thin films sputtered from a 90%Sn–10%Sb target are presented in Fig. 8. The films sputtered in a pure argon atmosphere consisted of the β -Sn and antimony phases.

The films deposited at $K = 10\%$ – 15% were amorphous or polycrystalline with random crystallite orientation. The addition of antimony to the target material changed the texture of the films obtained at $K = 30\%$ – 50% . The (110) diffraction peaks were the strongest whereas in undoped films the (020) peak was the strongest

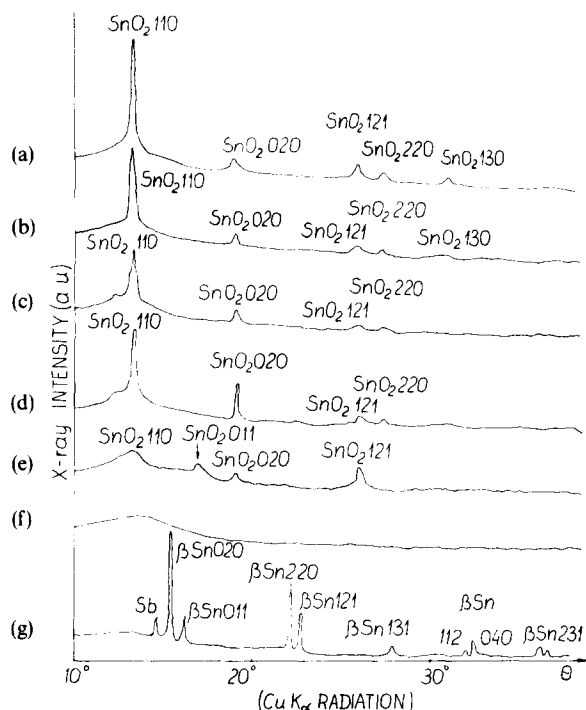


Fig. 8. Diffraction patterns of samples sputtered from a 90%Sn-10%Sb target in atmospheres with various oxygen contents (sputtering conditions: $T_s = 423$ K; $U_T = -150$ V): (a) 50% O_2 ; (b) 40% O_2 ; (c) 30% O_2 ; (d) 25% O_2 ; (e) 15% O_2 ; (f) 10% O_2 ; (g) 0% O_2 .

or was comparable with the (110) peak. The diffraction patterns of the films sputtered at $K = 25\%$ were similar for the films obtained from both targets.

The diffraction patterns of antimony-doped films which had been annealed in air are shown in Fig. 9. The films deposited in an argon atmosphere oxidized in the same way as the undoped films. β -Sn, SnO , SnO_2 and Sb_2O_4 phases were detected. The structure of the films deposited at $K = 5\%$ – 50% was much more stable during annealing than was that of the undoped films. The films which were initially amorphous remained ($K = 10\%$) amorphous. The diffraction peak intensities increased slightly (up to about 30%) in the films deposited at higher oxygen concentrations. The initial texture was preserved. The (020) peaks showed an insignificant split.

The dependence of the lattice constants of as-deposited and aged antimony-doped films on the oxygen concentration during sputtering is presented in Fig. 5.

The transmittance of the antimony-doped films before and after annealing in air is presented in Fig. 10. Annealing produced an increase in the transmittance of films deposited at low oxygen concentrations ($K = 0\%$ – 15%) similar to that observed in undoped films. However, the transmittance measured at optical wavelengths greater than 400 nm decreased slightly for films sputtered at high oxygen concentrations ($K = 40\%$ – 50%).

The changes in the resistance after annealing in dry nitrogen and in air are shown in Fig. 11. The thickness of the films aged in dry nitrogen was about 100 nm.

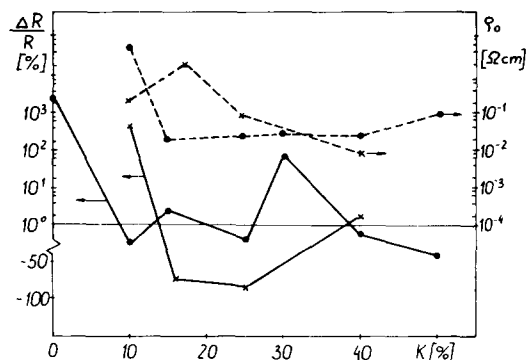


Fig. 11. Resistivity ρ_0 before annealing and the average change in the resistance of antimony-doped films (10% Sb) after aging vs. the oxygen doping level during sputtering ($U_T = -150$ V): x, films sputtered at $T_s = 473$ K and aged in nitrogen for 5 h at 650 K; ●, films sputtered at $T_s = 423$ K and aged in air for 4 h at 623 K.

4. CONCLUSIONS

The effects of annealing on the properties of sputter-deposited undoped and antimony-doped tin oxide films were investigated for various values of oxygen partial pressure in the sputtering atmosphere.

As-deposited doped and undoped films contained partially oriented SnO_2 crystallites as well as amorphous material. The preferred orientation of the SnO_2 crystallites in the undoped films was (020). This orientation has been reported elsewhere¹³. The preferred orientation in antimony-doped films is (110). The orientation is preserved after annealing in both cases.

When the sputtering was performed in an atmosphere containing 10% O_2 amorphous films were obtained from both doped and undoped targets. Annealing the undoped films in air resulted in the appearance of (011) and (110) reflections of the SnO phase and (011), (110) and (121) reflections of the unoriented SnO_2 phase. The antimony-doped films remained amorphous after annealing.

As-deposited films sputtered in atmospheres with K in the range 15%–50% contained the SnO_2 phase which was still present after annealing in air. An increase of up to a factor of 4 in the reflection intensity was observed after annealing the undoped films in air, indicating that crystallization of the initially amorphous material had taken place. This was accompanied by a marked increase in the optical transmittance. Splitting of the (020) line was observed in the undoped films after annealing. An additional peak which appeared on the high θ side of the (020) peak was attributed to an SnO_{2-x} phase which crystallized during annealing in air. The antimony-doped films showed only a slight increase in the reflection intensity after annealing in air and the additional peak was not detected. Annealing in a vacuum or in a nitrogen atmosphere did not alter the diffraction pattern and changed the optical transmittance only slightly.

The electrical resistance of undoped films 150 nm thick increased by several orders of magnitude on annealing in air or an N_2 – O_2 mixture.

The increase in the reflection intensity, the optical transmittance and the resistance of the undoped films on annealing in the presence of oxygen is attributed

to a more complete oxidation of the films involving out-diffusion of oxygen vacancies and oxidation of tin interstitials. The smaller increases observed on annealing the antimony-doped films, compared with those of the undoped films, are believed to be due to the lower free energy of the antimony-doped tin oxide which results in increased oxidation during sputtering.

REFERENCES

- 1 Z. M. Jarzebski and J. P. Marton, *J. Electrochem. Soc.*, **123** (7) (1976) 199C-205C.
- 2 S. M. Jarzebski and J. P. Marton, *J. Electrochem. Soc.*, **123** (9) (1976) 299C-310C.
- 3 Z. M. Jarzebski and J. P. Marton, *J. Electrochem. Soc.*, **123** (10) (1976) 333C-346C.
- 4 D. K. Schroder, *IEEE Trans. Electron Devices*, **25** (2) (1978) 90-97.
- 5 K. L. Chopra, S. Major and D. K. Pandya, *Thin Solid Films*, **102** (1983) 1-47.
- 6 A. G. Sabnis and L. D. Feisel, *IEEE Trans. Parts, Hybrids Packag.*, **12** (4) (1976) 357-360.
- 7 S. Shanthi, A. Banerjee, V. Dutta and K. L. Chopra, *Thin Solid Films*, **71** (1980) 237-244.
- 8 A. G. Sabnis, *J. Vac. Sci. Technol.*, **15** (4) (1978) 1565-1567.
- 9 E. Mendrela, M. Szreter, M. Tancula and K. Wieckowski, *Pr. Nauk. Inst. Technol. Elektron. Politech. Wroclaw.*, **21** (13) (1978) 109-115.
- 10 L. S. Mirkin, *Spravochnik po Rentgenostrukturnomu Analizu Polikristalov*, Gosudarstvennoe Izdatielstwo Fiziko-Matematicheskoi Litieratury, Moscow, 1961, pp. 522-523.
- 11 *Powder Diffraction File*, ASTM, Philadelphia, PA, 1967, Cards 21-1250, 20-1293, 25-1259, 24-1342, 14-140, 25-1303, 18-1386, 11-694, 6-0395 (revised), 7-195 (revised).
- Powder Diffraction File*, Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Swarthmore, PA, 1972, Card 13-111.
- Powder Diffraction File*, Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Swarthmore, PA, 1974, Card 16-737.
- 12 E. Leja, T. Pisarkiewicz and A. Kolodziej, *Thin Solid Films*, **67** (1980) 45-48.
- 13 N. S. Murty and S. R. Jawalekar, *Thin Solid Films*, **100** (1983) 219-225.
- 14 M. Just, N. Maintzer and I. Blech, *Thin Solid Films*, **48** (1978) L19-L20.