TRANSPARENT CONDUCTIVE FILMS OF In$_2$O$_3$ Sn PREPARED BY THE PYROLYSIS METHOD

L A RYABOVA, V S SALUN AND I A SERBINOV

Institute of Radio Engineering and Electronics, Academy of Sciences of the U S S R, Moscow (U S S R)

Transparent conductive In$_2$O$_3$ Sn films 0 1–1 µm thick were deposited onto glass, mica and sapphire substrates by the pyrolytic decomposition of indium and tin acetylacetonates in a carrier gas (N$_2$) flow The films had a low resistivity ($\rho = (1\,6\text{–}1\,8) \times 10^{-4}$ Ω cm) and a high transparency in the visible region of the spectrum ($T = 90\%\text{–}95\%$) The optical properties of the In$_2$O$_3$ Sn films were studied at wavelengths in the range 0 3–20 µm, and the major light absorption mechanisms were determined The effect of post-deposition annealing on the composition and the structure of the films was investigated by electron X-ray microprobe analysis, Auger electron spectroscopy combined with depth profiling, X-ray diffractometry and scanning electron microscopy The resistivity decreased by a factor of 3–5 after annealing, and this behaviour was related to an increase in the homogeneity of the film

1 INTRODUCTION

In$_2$O$_3$ Sn films are of interest because they have a low resistivity (of the order of 10^{-4} Ω cm) and a high transparency to visible light (transmittances of at least 90%), and they reflect IR radiation effectively[1] Thus these films can be used as transparent current electroheaters and antistatic layers and also in a number of optoelectronic devices such as highly sensitive photodetectors and indicator devices based on liquid crystals and electrochromic materials In$_2$O$_3$ Sn films are also widely used in solar energy devices as transparent electrodes in solar cells[2], as degenerate n-type semiconductors for solar cells based on heterojunctions[3] and as spectral selective coatings (materials with selective reflectivity) in devices which utilize the photo-thermal conversion of solar energy[2,4]

At present In$_2$O$_3$ Sn films are prepared by the hydrolysis of chlorides[5,6], by the reactive sputtering of In–Sn alloys[7,8], by the r f sputtering of oxide targets[9,10], by magnetron sputtering[11,12] or by activated reactive evaporation[13] However, the physical vapour deposition techniques require expensive equipment, and films prepared by hydrolysis usually have a lower transparency in the visible region of the spectrum[1] Blandenet *et al*[14] have prepared In$_2$O$_3$ Sn films by the "pyrosol" method which is based on the pyrolytic decomposition of an aerosol produced by the ultrasonic agitation of the initial materials

In the present work In_2O_3 Sn films of high quality were prepared by the pyrolysis of vapours of indium and tin acetylacetonates These vapours were produced by heating the solid compounds in a carrier gas flow The films deposited had a very low sheet resistance, a high transparency in the visible region and marked reflectance selectivity The chemical composition, structure, electrical properties and optical properties of the In_2O_3 Sn films were investigated The effect of heat treatment on the properties of the deposited films was also studied

2 EXPERIMENTAL RESULTS

2 1 Preparation of the films

The apparatus used to deposit the In_2O_3 Sn films is shown schematically in Fig 1 In the quartz tube (reactor), which was 95 mm in diameter, two temperature zones were produced by two resistance furnaces the evaporation zone ($T_1 = 150-200\,°C$) where quartz boats containing the reactants were placed, and the reaction zone ($T_2 = 350-450\,°C$) where the substrates were located on a rotary holder Vapours from the reactants were transported into the reaction zone by the carrier gas (N_2) at a flow rate of 450 ml min^{-1} Indium and tin acetylacetonates mixed in the ratio 43 wt % to 57 wt % were used as the reactants It is known that In_2O_3 Sn films containing 5–20 at % Sn have optimal properties[7][9][13] According to X-ray microprobe analysis data, the films deposited from the chosen reactant mixture contained the optimum atomic concentrations of indium and tin ($C^{at}_{Sn}/C^{at}_{In} = 0\,08$) The films were deposited onto glass, mica and α-Al_2O_3(0001) substrates The sapphire substrates were annealed in a vacuum of about 10^{-2} Torr at 900–1000 °C before the film was deposited The highest quality In_2O_3 Sn films were those deposited onto sapphire, and all the results reported here were obtained for these films The film thickness was determined from the increase in the sample weight (the accuracy of weighing was 10^{-5} g) and varied from 0 1 to 1 µm The growth rate of the film was about 10–15 Å min^{-1} The films were annealed in a vacuum of about 10^{-2} Torr at 400 °C for 30–45 min to decrease their resistivity
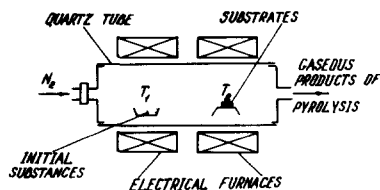

Fig 1 Schematic diagram of the experimental apparatus for the pyrolytic deposition of In_2O_3 Sn films

2 2 Properties of the films

The resistivity of the films was measured by the four-probe technique The concentration and the mobility of the charge carriers were obtained from measurements of the Hall coefficient The optical properties of the film (the transmission coefficient T and the reflectivity R) were measured at wavelengths in the range 0 3–20 µm The crystal structure of the films was studied by X-ray diffractometry using Co $K\alpha$ irradiation, and the surface morphology was investigated by scanning electron microscopy The film composition was determined

by X-ray electron microprobe analysis using a Camebax microanalyser and by Auger electron spectroscopy using an LAS-2000 spectroscope

The results of our investigations show that post-deposition heat treatment produces a substantial decrease in the film resistivity (by a factor of 3–5) The values of ρ for all annealed In_2O_3 Sn films was $(1\ 6–1\ 8) \times 10^{-4}\ \Omega$ cm, and the value of the sheet resistance R_s was determined from the film thickness d Thus for $d = 0\ 95\ \mu m$ the value of R_s was $1\ 9\ \Omega/\square$ The value of the transmission coefficient T at a wavelength λ of $0\ 5\ \mu m$ was 95% for this film The decrease in the film resistivity was caused by an increase in the charge carrier concentration from $4\ 3 \times 10^{20}$ to $8\ 8 \times 10^{20}$ cm^{-3} and by an increase in the Hall mobility from 25 to 43 cm^2 V^{-1} s^{-1}

The spectral dependence of the transmission coefficient of an In_2O_3 Sn film with $d = 0\ 95\ \mu m$ and $R_s = 1\ 9\ \Omega/\square$ is shown in Fig 2 It is known that the sharp decrease in the transparency of the film in the UV and IR regions is caused by fundamental light absorption and by free-carrier absorption respectively The parameters of these processes can be determined from the spectral dependence of the absorption coefficient α The dependence of α on λ can be obtained by measuring the transmission of the film at various thicknesses and using the well-known correlation[15] between T, R and α

$$T = (1 - R)^2 \exp(-\alpha d) \tag{1}$$

which is correct for the condition

$$\exp(2\alpha d) \gg R^2 \tag{2}$$

If the values of T for two films of different thicknesses are known, then α can be obtained from eqn (1)

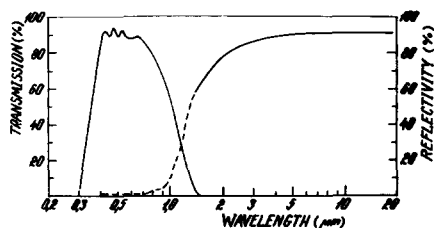$$\alpha = \frac{1}{d_2 - d_1} \ln\left(\frac{T_1}{T_2}\right) \tag{3}$$

Fig 2 The spectral dependence of the transmission coefficient and the reflectivity of an In_2O_3 Sn film with $R_s = 1\ 9\ \Omega/\square$ and $d = 0\ 95\ \mu m$

We used eqn (3) to calculate α_1, α_2 and α_3 using transmission data for the following three pairs of films of various thicknesses $d_1 = 0\ 15\ \mu m$, $d_2 = 0\ 30\ \mu m$, $d_1 = 0\ 30\ \mu m$, $d_2 = 0\ 60\ \mu m$, $d_1 = 0\ 95\ \mu m$, $d_2 = 1\ 9\ \mu m$ These calculations were carried out in the wavelength range $0\ 3–1\ 4\ \mu m$ The similarity of the values of α_1, α_2 and α_3 was taken as the criterion for the applicability of eqn (3) in a given spectral range From condition (2), the values of α_3 were taken as the best approximation to the true value of α in those regions of the spectrum where α showed a wide variation The dependence of α on λ obtained in this way is shown in Fig 3 Analysis of this

dependence showed that in the wavelength range 0 3–0 43 μm the light is absorbed by direct and indirect interband transitions (ΔE_1 and ΔE_2 were 3 78 eV and 2 6 eV respectively) These values of ΔE_1 and ΔE_2 are in good agreement with data reported previously[16] for the energy values for direct (3 75 eV) and indirect (2 69 eV) interband transitions in In_2O_3 and also with the energy values for the direct band gap in In_2O_3 doped with various quantities of tin (3 55–3 8 eV)[17] At wavelengths in the range 0 55–1 1 μm, α is proportional to λ^2 A dependence of this type is characteristic of light absorption by free carriers

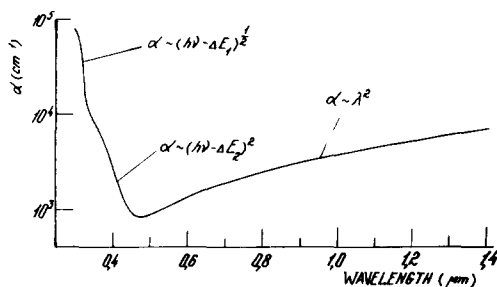Fig 3   The spectral dependence of the absorption coefficient of an In_2O_3 Sn film

The spectral dependence of the reflectivity of an In_2O_3 Sn film 0 95 μm thick with $R_s = 1\ 9\ \Omega/\square$ is shown in Fig 2 In the wavelength range 0 4 $\mu m \leqslant \lambda \leqslant 1\ 4\ \mu m$ where the film transparency is high, direct experimental determination of the precise value of R for the film is difficult because of the existence of multiple reflections at the film–air and the film–substrate interfaces Thus we determined values of R for a given wavelength range by using eqn (1) together with experimental data for the film transmission coefficient (Fig 2) and the film absorption coefficient (Fig 3) The dependence of R on λ in this part of the spectrum is shown by the broken curve in Fig 2 At $\lambda > 1\ 4\ \mu m$ where the In_2O_3 Sn film is almost opaque and thus the multiple reflectance can be neglected, the reflectivity was measured experimentally (full curve in Fig 2) At $\lambda = 1\ 4\ \mu m$ the experimental value of R coincided with that calculated using eqn (1) with an accuracy to 5%

In the examination of the film composition by electron X-ray microprobe analysis indium 99 999% pure and stoichiometric SnO_2 were used as the standards The error in the determination of the weight concentrations of the elements was $\pm 2\%$ All the samples, both annealed and non-annealed, were of the same composition 76 wt % In, 6 wt % Sn and 18 wt % O However, it is known that, for film thicknesses less than 1 μm, the X-ray microprobe analysis technique allows only mean values of the element concentrations throughout the film thickness to be determined To obtain the dependence of the film composition on the film thickness we used Auger electron spectroscopy combined with depth profiling The dependence on the etching depth of the ratio of the Auger peak intensity of indium (404 eV) to that of tin (430 eV) is shown in Fig 4 for non-annealed (full curve) and annealed (broken curve) samples A strong modulation of the composition with the film thickness is apparent in the non-annealed sample During annealing an equalization of the composition with the film depth is observed This is caused by diffusion of the dopant (tin) in the matrix (In_2O_3)
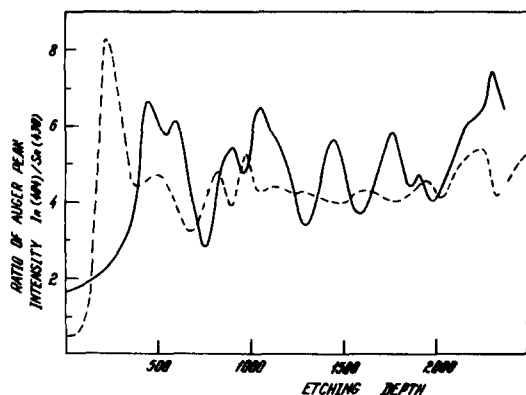
Fig 4   The dependence on the etching depth of the ratio of the Auger peak intensity of indium (404 eV) to that of tin (430 eV) ——, non-annealed sample, - - -, annealed sample

X-ray diffraction studies were also carried out on non-annealed (Fig 5) and annealed (Fig 6) samples Both diffraction patterns show strong In$_2$O$_3$ peaks and weak peaks characteristic of Sn$_3$O$_4$ The films were preferentially oriented in the (100) plane parallel to the substrate surface There were no marked changes in the crystal structure of the films after annealing, and only a slight change in the preferred orientation Examination of the samples in the scanning electron microscope showed that the films had very smooth surfaces. The mean grain size was of the order of parts of a micron and did not change during annealing
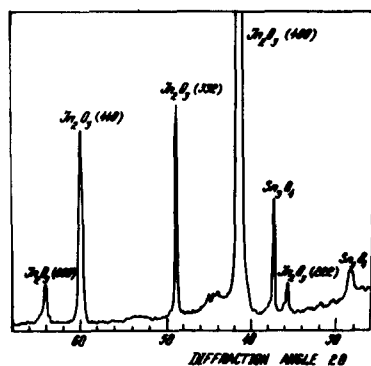

Fig 5   X-ray diffraction pattern of a non-annealed In$_2$O$_3$ Sn film

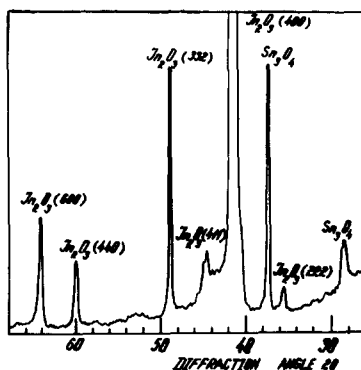Fig 6   X-ray diffraction pattern of an annealed In$_2$O$_3$ Sn film

3   DISCUSSION AND CONCLUSION

A decrease in the film resistivity was observed after post-deposition annealing This decrease is caused by an increase in the concentration and mobility of the charge carriers An increase in the charge carrier concentration in such cases is usually connected with an increase in the number of oxygen vacancies, and an increase in the charge-carrier mobility is usually explained in terms of the formation of or increase in a preferential orientation or by an increase in the grain size In our

case there was no significant difference between the structures of the non-annealed and the annealed samples However, annealing produced an increase in the homogeneity of the film as a result of the diffusion of tin atoms in the In_2O_3 matrix We suggest that a consequence of this homogenization is a decrease in the degree of disorder of the In_2O_3 lattice which leads to a decrease in the charge carrier scattering and hence to an increase in the mobility in annealed films

In_2O_3 Sn films prepared by the pyrolysis of indium and tin acetylacetonates have a resistivity of $(1\ 6\text{--}1\ 8) \times 10^{-4}\ \Omega$ cm, a charge carrier concentration of about 9×10^{20} cm^{-3} and a Hall mobility of about 43 cm^2 V^{-1} s^{-1} The film transparency in the visible range was more than 90%

To prepare high quality films it is necessary to carry out post-deposition heat treatment which produces an increase in the homogeneity of the films The optical properties of the films were investigated in a wide spectral range, and the major light absorption mechanisms were determined

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