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Section 9: Thin films and multilayers

CHARACTERIZATION OF ITO THIN FILMS PREPARED BY SPINNING DEPOSITION STARTING FROM A SOL-GEL PROCESS

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ITO thin films were deposited by spin coating method starting from indium and tin propoxide in the frame of a sol-gel process. Films with the thickness corresponding to 68 nm for one layer deposition were produced and characterized by X-ray diffraction, transmission electron microscopy and infrared reflection spectroscopy. Low conductivity polycrystalline films exhibiting cubical structure (bixbyite-type) and good adherence were obtained.

Keywords: ITO, Thin films, Sol-gel process, Spin coating, X-ray diffraction, TEM, IR reflection spectroscopy

1. Introduction

Tin-doped indium oxide (ITO) thin films are being extensively studied because of the interesting properties they could have, such as a low resistivity, transparency in the visible region of the electromagnetic spectrum and high infrared reflectivity. These properties make them good candidates for many applications such as infrared reflectors, antireflection coatings, thin film resistors [1].

Several methods have been used to get ITO films: reactive evaporation [2], the spray pyrolysis [3], chemical vapor deposition (CVD) [4], dc and rf magnetron sputtering [5,6] and last but not least sol-gel method.

The application of sol-gel processing is widespread and certain applications, such as coating on window glass are being used on commercial basis. The use of In_2O_3-SnO_2 and SnO_2-CdO systems are currently noticed as electron conductors in various applications [7].

Because of the awkward problems that appear during drying and sintering (cracking, warping, shrinkage) the sol-gel route has seen little use for the fabrication of the monolithic ceramics. Instead it has seen considerable use for the fabrication of films, fibers and powders.

Two main sol-gel techniques have been used for producing thin films: (i) dip coating, where the object to be coated is lowered into the solution and withdrawn at a suitable speed and (ii) spin coating, where the solution is dropped on the object, which is spinning at a high speed.

For dip coating, the most currently used method, the thickness of the liquid film depends on the viscosity of the solution and the speed and the speed of the withdrawal of the objected.

The physics of spin coating is different from that of dip coating. The thickness of the films prepared by spin coating varies inversely as $\omega^{2/3}$, where ω is the angular velocity of the spin coater, and as $\eta^{1/3}$, where η is the viscosity of the solution.

The sol-gel derived, transparent, electrically conducting tin-doped In2O3 films system, where only air baking is required, has been developed by Mattox [8]. In this paper we used the spin coating method to produce ITO thin films starting from indium and tin propoxides. The films were characterized as regarding the structural and electro-physical properties.

2. Film preparation

Indium and tin propoxides, $In(OC_3H_7)_3$ and $Sn(OC_3H_7)_4$, supplied by InorgChem (England) were dissolved in isopropylalcohol and ethyl alcohol.

The concentration of each propoxide was 0.05 mol/l and the Sn/In ratio was 9 %. The solutions were mixed under controlled atmosphere (nitrogen) with the aim to avoid the rapid hydrolysis reaction. The difficulties related to the rapid hydrolysis reaction have been avoided by using unhydrolysed or partially hydrolyzed metal-alkoxide solutions of the coating precursor. The stability of the sol was obtained by the addition of triethanolamine as complexing agent.

The films were deposited on silicon wafers.

After spin coating at room temperature, and at a speed of 1000 rot/min, the coated wafers were dried 15 minutes at 150 ^oC. The formation of ITO films by removing the organic component followed by structural rearrangement was performed by annealing the coated wafers for one hour at the temperature of 550 ^oC in ambient atmosphere.

The deposition procedure was repeated 2 times and 5 times for every support.

3. Thermal analysis of the polymeric precursor

The heat treatment of the films after deposition is important for the final film properties. Therefore, the behaviour of the solution used for spin coating, as a function of temperature is in an important property to be studied before preparing the ITO films.

The thermal evolutions of the polymeric mixture of indium-tin propoxides were followed by thermogravimetry (TG) and differential thermal analysis (DTA).

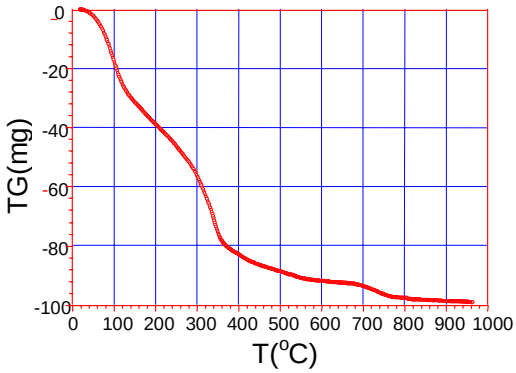

Fig.1. Thermogravimetric curve of In-Sn of indium-tin propoxide solution.

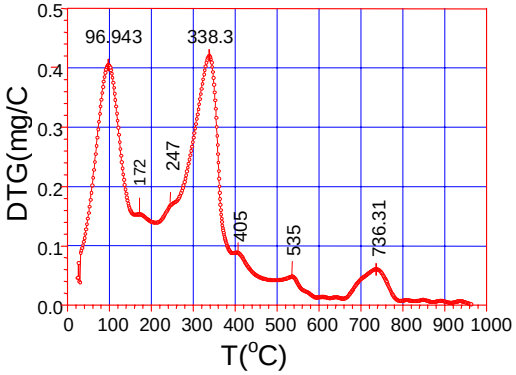

Fig. 2. Differential thermogravimetric curve of indium-tin propoxide solution.

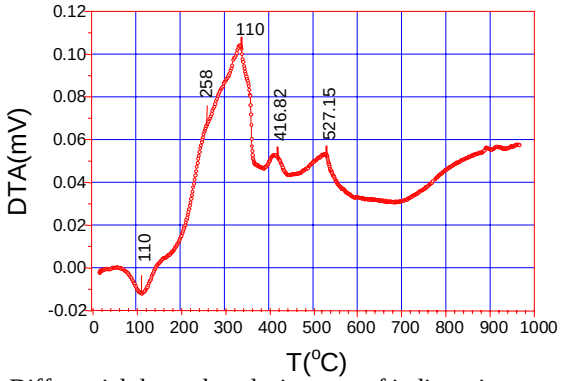

Fig.3. Differential thermal analysis curve of indium-tin propoxide polymer.

Fig. 1 shows the thermogravimetric curve of ITO precursor. Three exothermal effects accompanied by large weight loss are evidenced. The DTG curve depicted in Fig. 2 point out high

peaks corresponding to large losses of material around 100 and 340 ^{o}C that can be scribed to the loss of water and of organic ligands, respectively.

The DTA curve (Fig. 3) exhibits two endothermic peaks situated at 110 ^{o}C and at ~180 ^{o}C related to the elimination of the water in different state of binding (physical and chemical, respectively). The exothermal main peak situated at 335 ^{o}C is undoubtedly related to the decomposition of indium propoxide. Burning of residues are possibly related to the DTA peaks at 416 ^{o}C and 527 ^{o}C because the appearance of these peaks is accompanied by weight losses (see Fig. 2). The broadened peak at 527 ^{o}C can be related beside the elimination of some residues, to ITO crystallite formation and growth. Another peak appeared at ~736 ^{o}C on DTG curve due to significant weight loss at that temperature, and a broad negative energetic balance speak in favour of a strong transformation of the ITO films including the elimination of a certain amount of hydroxides remained in the films.

As a conclusion, annealing temperatures higher than 400 ^{o}C are needed to remove the major part of the organic ligands and more than 535 ^{o}C in order to get crystallized ITO films. Above 736 ^{o}C dehydration of $In(OH)_3$ occurs and ITO films become single phase.

4. Film characterization

4.1. X-ray diffraction.

X-ray diffraction measurements were carried out on ITO thin films deposited on silicon substrates and annealed at 550^{o}C. A TUR M62 diffractometer provided with nickel target tube and proportional counter was used to this purpose. The X-ray diffraction diagrams were recorded in the range $\theta = 10 - 35^{o}$ with the angular step 0.05^{o} and measuring time per angular position: 10 s.

Fig. 4 shows the X-ray diffraction pattern recorded on a film prepared with five successive depositions at the same spinning rate (1000 rot/min). A unique ITO phase with cubical symmetry (bixbyite-type) was identified in the diagram. The main peak (222) situated at $\theta \sim 16.5^{o}$, which is highly sensitive to the substitution of In^{3+} ions by larger Sn^{4+} ions, does not exhibit an anomalous shift or broadening. This confirm the formation of the homogeneous solid solution of indium and tin oxide with small tin content, as required by the initial Sn/In ratio used in the preparation of the precursor.

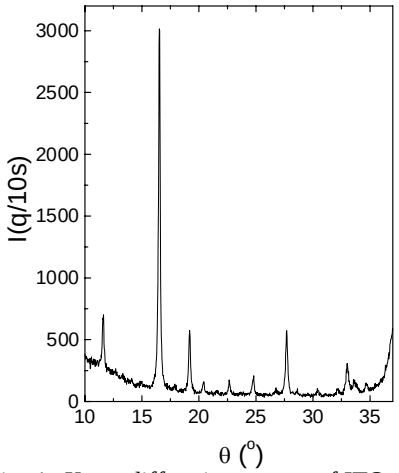

Fig. 4. X-ray diffraction pattern of ITO Film annealead at 550 ^{o}C.

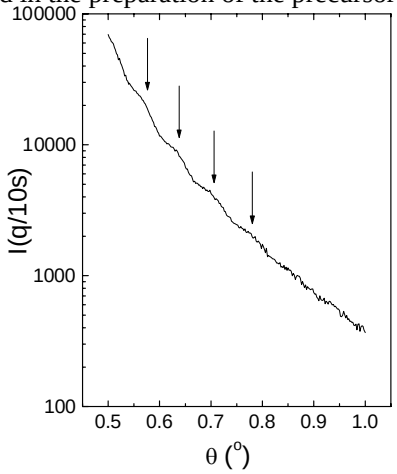

Fig. 5. Small angles X-ray diffraction pattern of the ITO film (one deposition).

Medium size crystallites are characteristic to the film. No preferential orientation of the crystallites was evidenced from the intensities ratios of different diffraction lines appeared on the diagram.

In order to get information on the film thickness of the films we have carried out X-ray diffraction measurements at small diffraction angles (SAXS-small angle X-ray scattering). Fig. 5 shows the SAXS pattern, which is characterized by the formation of Kiessig fringes. The distance

between two neighbouring fringes can be used to calculate the film thickness. For the sample with one deposition layer, the thickness of the film is 68.0 nm. This means that single spinning deposition process determine the formation of an ITO film with a thickness of 35 nm.

4.2. Transmission electron microscopy

TEM measurements were carried out in a JEM-200CX electron microscope by using a freestanding film expelled from a wafer substrate.

The ITO film is completely crystallized. Crystallites with the shape of regular prism and sizes in the range 42-52 nm are seen on the micrograph (Fig. 6).

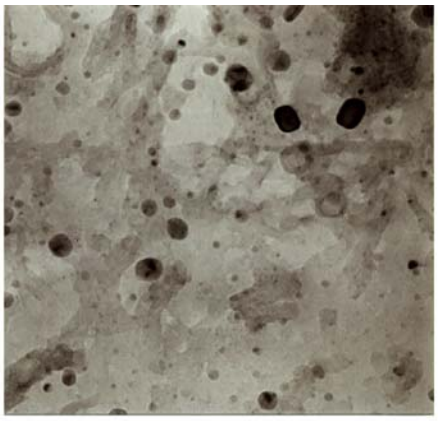

Fig. 6. The crystallite shape and size as revealed by transmission electron microscopy on annealed ITO film deposited on silicon wafer.

The mean crystallite size calculated form TEM pictures is 22 nm. The crystallites exhibit the tendency to connect themselves by side and to form aggregates. TEM and electron diffraction pictures reveal the formation of the ITO crystalline phase (as regular prisms) and a small amount of irregular, transparent crystallites of composition $In(OH)_3$.

4.3. IR reflection measurements

A Spekord 75 IR (Zeiss) spectrometer with electronic acquisition was used in measurements. A special reflection device was used. The infrared reflection spectrum of the annealed ITO film was recorded in the range 400 – 1200 cm^{-1} is shown in Fig. 7.

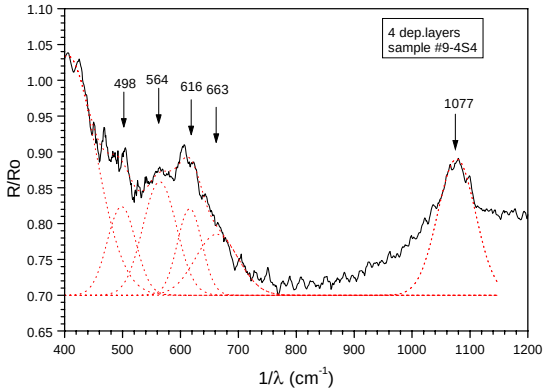

Fig.7. Infrared reflection spectrum of ITO film deposited on silicon wafer.

The IR reflection spectrum reveals several peaks, which can be ascribed to vibration modes of different bonds in the ITO film. For the identification of the vibration peaks we have used the IR absorption tables published by Nyquist and Kagel [9]. The peaks situated at 420 cm^{-1} and 558 cm^{-1} confirms the existence of In-O-In bonding. The Sn-O and Sn-O-Sn bonds are evidenced by the peaks situated at 498 cm^{-1} and 616 cm^{-1}, respectively. The large peak situated at 1077 cm^{-1} is given by the Si-O-Si vibration at the interface wafer-film.

5. Discussion

ITO thin films have been prepared with good homogeneity and adherence to silicon substrate.

The electrical resistivity of the ITO films was measured by the direct current four-probe method at room temperature. The electrical conductivity of our films for the case of three layer deposition is $\sigma = 34\ \Omega^{-1}cm^{-1}$ while for five layer deposition is $33\ \Omega^{-1}cm^{-1}$. These values are higher than that reported by Yamamoto and Sasamoto [10] for the case of indium tin oxide thin films (doped by 9 at.% Sn) prepared by thermal decomposition of ethylene glycol solution and treated at 600 ^oC: $\sigma = 2 \times 10^{-4}\ \Omega^{-1}cm^{-1}$. Nevertheless the resistivity deserves the use of ITO films in applications.

6. Conclusions

Thin polycrystalline films with ITO composition ($In_2O_3 - SnO_2$) were successfully deposited by spinning of indium-tin propoxide solution obtained by a sol-gel process.

ITO solid solution ($In_{2-x}Sn_xO_3$) keeps the cubic symmetry of the In_2O_3 crystal in a compositional range at least till 9 at.% Sn.

In the spin coating procedure based on a sol-gel process, good adherence films with nanometric size and low electrical resistivity values have been obtained.

The easy control of the spin coating from a drop of solution derived from a sol-gel method, followed by a single heat treatment in air, makes the technique suitable for large applications.

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