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High quality ITO thin films for application as conductive transparent electrodes

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A detailed study of structural, electrical and optical properties of ITO films, obtained under various deposition conditions by RF sputtering in pure Ar gas atmosphere, has been performed. The relationship between sheet resistance and optical transmittance of the films studied was followed through the variation of sputtering voltage, substrate temperature and film thickness. The figure of merit of these films, which is a measure of their quality as transparent conductive electrode, was evaluated. It is established that the deposition of ITO films at higher sputtering voltages leads to a considerably lower sheet resistance, better optical transparency and lower roughness of the films. The investigation of the film microstructure by X-ray diffraction (XRD) analysis showed that the prepared ITO films are polycrystalline with preferred (111) orientation. The AFM study performed revealed the formation of smooth films at higher V_s, with nanosized grains and uniformally distributed electrical current. Besides, smooth uniform ITO films with low resistance of 8 Ω/sq and average transmittance above 82% in the visible range 400-800nm were obtained on glass substrates without additional annealing of films. Thus, the possibilities of producing high quality ITO films by the RF sputtering method used at the established optimal experimental conditons have been demonstrated.

Keywords: ITO films, RF sputtering, structural, optical and electrical properties

INTRODUCTION

Indium tin oxide (ITO) is one of the most widely used transparent conducting oxides due to its excellent combination of high optical transmission, high electrical conductivity and good chemical stability [1]. Nowadays thin films from ITO are widely used as transparent electrodes in such advanced applications as photovoltaic cells [2, 3] organic light emitting diodes (OLEDs) [4] and flat panel displays (PDPs) [5, 6]. However, due to the complexity of starting ITO materials the thin film properties are strongly dependent on the deposition processes. So far various deposition methods such as RF and DC sputtering, thermal evaporation, chemical vapour deposition, sol–gel method, spray pyrolysis, etc. have been applied for achieving a suitable compromise between low electrical resistivity and high transmittance of the films in the visible spectral range [1-2, 7]. Among them, DC and RF sputtering are the most attractive techniques because of their high deposition rate, good reproducibility and possibility of using available large area commercially sputtering systems [8-11]. Many research groups have studied the effects of the deposition conditions, such as substrate temperature, RF/DC power, oxygen-to-argon ratio, deposition pressure, substrate-to-target distance and bias voltage on the properties of ITO films [10-13]. However, most of the reports in this area were devoted to reactive sputtering and relatively little papers reported on sputtering in pure Ar gas without oxygen mixing [14-16]. Depending on the sputtering system and plasma discharge mode used, an essential difference of optimum sputtering conditions (discharge power, pressure, oxygen concentration, etc.) was observed, as well as a difference in the crystalline structure and morphology of the formed layers [9].

In the present paper the results of a systematic investigation of the structural, electrical and optical properties of the ITO films as a function of the sputtering voltage, substrate temperature and film thickness are presented. The purpose of our study was to obtain ITO films with both high transmittance and low sheet resistance applying RF sputtering of ITO target with RF power supply at 2 MHz in pure Ar gas atmosphere. In order to simplify the growth process we did not introduce oxygen gas during the film deposition.

EXPERIMENTAL

The ITO films were prepared by a commercial

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sputtering system HZM-4 with RF power supply at 2.5 MHz and diode electrode configuration. A 20 cm diameter sintered ceramic target with 99.9% purity, containing 90 wt.% of In_2O_3 and 10 wt.% of SnO_2 (supplied by Leadmat Advanced Material Co. Ltd.) was used for the deposition of the films. The system was first pumped down to a base pressure of $1.3x10^{-6}$ mbar. ITO sputtering was carried out in a pure Ar atmosphere without oxygen at a constant pressure of $7x10^{-3}$ mbar. The argon gas flow was controlled by MKS mass flow controller. A pre-sputtering of ITO target for 15 min was necessary for preparing homogeneous films with reproducible properties. The sputtering voltage employed during deposition was varied from 800 V to 1400 V which corresponds to sputtering power density from 0.5 Wcm^{-2} to 2.45 Wcm^{-2}. The target to substrate distance was kept constant at 6 cm. The film thickness was varied by adjustment of the deposition time. The film thickness was measured by thin film analyzer (F20, Filmetrics) with accuracy of ± 5nm. The temperature of the substrate was measured by a K-type thermocouple attached directly to the substrate surface and was controlled with 1% measurement accuracy.

ITO films were deposited on polished Corning glass substrates, preliminary ultrasonically cleaned in isopropyl alcohol and de-ionized water baths.

The structural properties of the films were analyzed by X-ray diffraction using a Philips (PW 1710) apparatus with Cu-Kα radiation separated by a graphite focusing monochromator. The intensity and full width at half maximum (FWHM) of an (hkl) plane were determined by profile fitting procedure, using an Gaussian or pseudo Voigt peak shape after baseline correction and Kα2 stripping procedure. Scherer's equation was used to estimate the average crystallite size. This estimate has excluded the effects of peak broadening due to the instrument used and any effect of residual stresses in the ITO films.

The surface morphology of the films was studied by an atomic force microscope (AFM, MFP-3D, Asylum Research, Oxford Instruments). The grain size was determined by Gwyddion mask segmentation function applied to a preprocessed image [17]. The function is based on the classical Vincent algorithm for watershed in digital spaces. The mean size was calculated by averaging the equivalent square size of one grain [17].

The transmittance (*T*) of the samples were measured at normal light incidence in the spectral range λ = 400-800 nm by a Cary 5E spectrophotometer with an accuracy of ±0.5%.

The sheet resistance of the films was determined by four-point probe method. The set-up consisting of Keithley 220 Programmable Current Source and Agilent 3458A multimeter was controlled by a Labview program.

RESULTS

It has been well established that the electrical properties of ITO films depend both on film thickness and deposition parameters such as applied sputtering power, substrate deposition temperature, etc. [1, 2]. The sputtering power is a product of sputtering voltage (V_s) and sputtering current (I_s). We have found that more expressed dependences are obtained using V_s instead of power, most probably due to observed little instabilities in I_s at constant sputtering pressure.

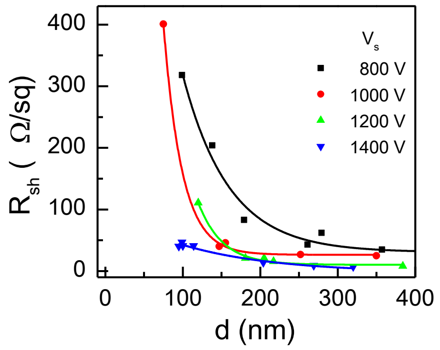


Fig. 1. Sheet resistance of ITO films as a function of the thickness of the films deposited at various sputtering voltages.

Fig.1 shows the influence of sputtering voltage V_s at constant sputtering pressure of $7x10^{-3}$ mbar on the sheet resistance (R_{sh}) of ITO films with different thickness (d). It can be seen that the R_{sh} decreases considerably with the increase of V_s from 800 V to 1400 V and film thickness from 80 nm to 400 nm, which is in good accordance with the literature data [11]. As seen, the films with thickness 300 nm, deposited at V_s of 1300 – 1400 V have minimum sheet resistance of 8 Ω/sq. Simultaneously, a dramatic rise of R_{sh} is observed for films thinner than 100 nm, which were deposited at V_s lower than 1200 V.

The results from numerous investigations performed have shown that the deposition of ITO without heating the substrate results in the formation of amorphous films with high resistance. are [1, 3]. On the contrary, crystalline ITO films with low resistivity were obtained by raising substrate temperature during deposition or by post annealing of the films at temperatures above 250 °C

[2, 3, 16]. It should be noted here that the results presented in Fig. 1 were obtained without additional heating of the glass substrates during sputtering or after deposition. Nonetheless, we have found that the surface of the substrate is heated during the deposition process in which the sputtered particles condense on the substrate surface and give up energy. Most probably, the substrate heating arises not only from the condensation energy of the depositing adatoms, but also from the high kinetic energy of the depositing particles, particularly at low pressures where the particles have not been thermalized. The substrate heating can also arise from plasma effects such as radiant heat of the target and the bombardment by high energy secondary electrons or energetic neutral [18]. Fig.2 shows the change of the substrate temperature (T_s) with deposition time at different sputtering voltages. For comparision the time for depositing 300 nm thick ITO film at 1200 V was 9.3 min and 8.5 min at 1400 V. It is seen from Fig. 2 that for these deposition times the substrate temperature rised up to 480 °C at 1200 V and respectively to 620 °C at 1400 V without need for additional substrate heating. On the one hand this temperature effect is favourable for preparing crystalline films with low resistivity. On the other hand it limits the range of usable voltage up to 1200 V- 1300 V and the deposition time at those voltages up to 10 min.

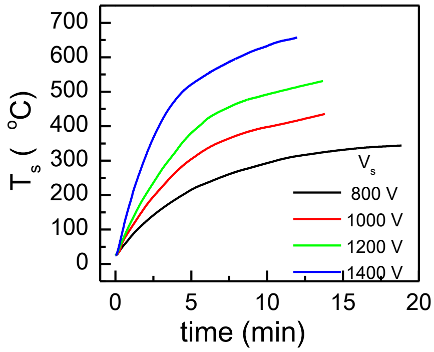


Fig. 2. Variation of the substrate temperature T_s with the deposition time at indicated sputtering voltages.

The X-ray diffraction patterns of ITO films, deposited on different sputtering voltages, are given in Fig. 3. The XRD data show that the deposited films have the cubic bixbyite structure of In_2O_3. Besides, the spectra of all films exhibit an intense (222) peak of In_2O_3, indicating a preferred orientation in the (111) direction, which takes place when T_s increases over 300 °C (see Fig. 2). This result is consistent with data of other authors, who have obtained the same (222) prominent peak [19, 20]. Furthermore, the (400) peak indicating the coexistence of the (111) and (100) textures, is observed only in the spectra of films, deposited at 800 V. As seen from the figure, the crystallinity of the ITO films increases with rising sputtering voltage, most probably due the the elevated substrate temperature. No systematic change in orientation was observed with variation of film thickness in the range 50≤d≤ 350 nm. Applying the Scherrer formula, it was found that the crystallite size range from 10 to 20 nm. Fig. 4 presents crystallite size determined by half peak width of the (222) peak as a function of the sputtering voltage. It is seen that the size decreases with increasing V_s up to 1300V.

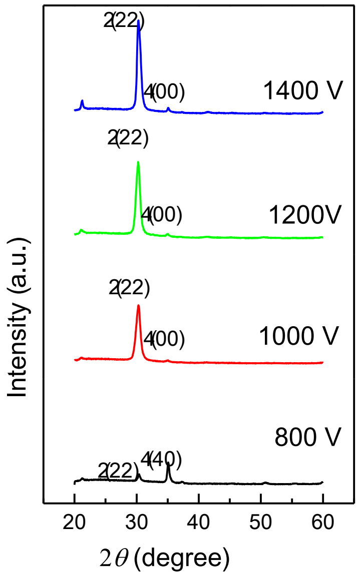


Fig. 3. X-ray diffraction patterns of 180 nm thick ITO films, deposited at indicated sputtering voltage.

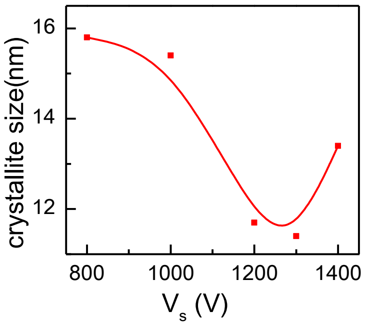
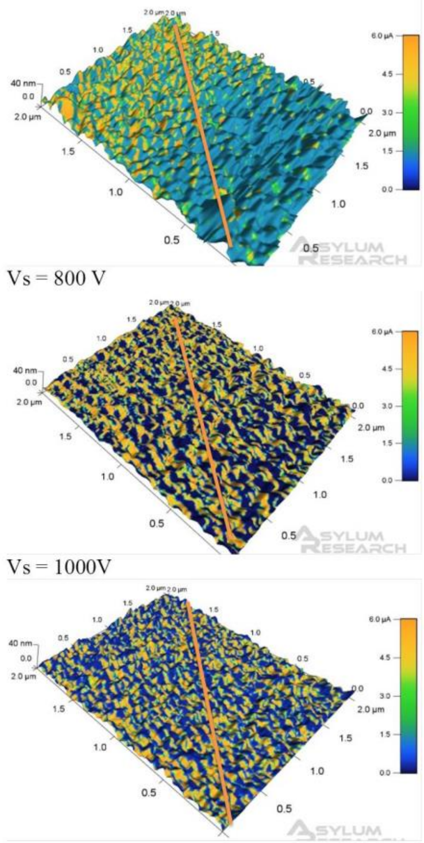


Fig. 4. Crystalite size of 180 nm thick ITO films as a function of sputtering voltage.

In the literature a low resistivity of ITO films was found to be related to a big grain size, which is attributed to less scatting at grain boundaries [3, 21]. Obviously, the established by us decrease of R_{sh} with V_s could not be explained only on the base of the better crystallinity and larger grain size.

The results obtained by AFM study showed that apart from the grain size, the surface of the films had a significant impact on the sheet resistance values. Figs. 5 presents 3D topography and current map AFM images of 180 nm thick films deposited at different sputtering voltage. The corresponding height and current section across line on the images are shown in Fig. 6. The surfaces of ITO films seem to be formed by small nanosized grains with current uniformally distributed in the grains of films deposited at higher V_s. However, the presence of areas with big peaks and valleys, where the current has very low value was detected on films deposited at low V_s.

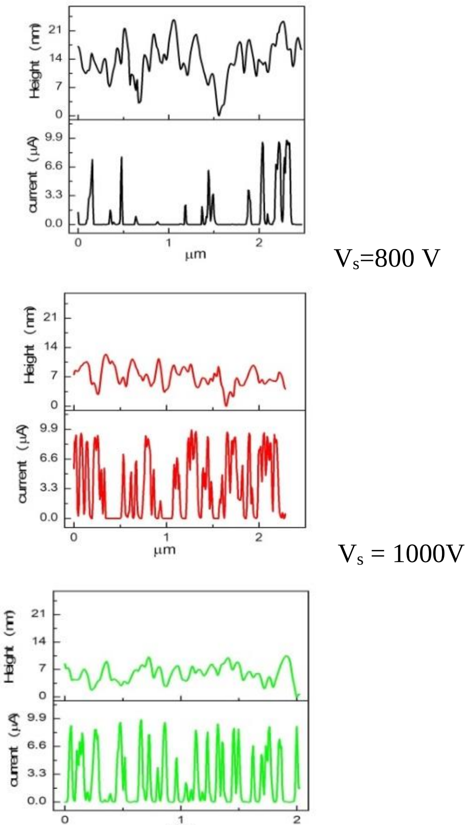


Vs = 800 V

Vs = 1000V

Vs = 1200V

Fig. 5. 3D AFM images (contact mode) of the 180 nm thick ITO films deposited at indicated V_s. The topography is shown in z-scale of 40 nm, while the colour is the measured current, overlaid on the surface. A bias of +100 mV was applied to the sample surface during measurements.



V_s=800 V

V_s = 1000V

V_s = 1200V

Fig. 6. Height and current section acrros the line shown in Fig. 5

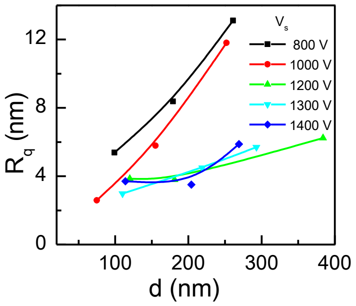


Fig. 7. Standard deviation R_q of surface roughness as a function of the thickness of ITO films, deposited at indicated V_s.

It is known that in quantitative analyses on AFM images the surgface roughness is most commonly described by amplitude parameters including the average deviation R_a, root mean square (R_{RMS}) and the standard deviation R_q. These parametes have units of length with higher values indicating greater height variation. R_{RMS} and R_q are more sensitive than R_a to occasional hight and lows. Fig. 7 shows the standard deviation R_q of surface roughness as a function of the thickness of ITO films deposited at different V_s. It can be seen that the height roughness decreases with increasing the sputtering voltage and hence the deposition power. The ITO thin films, deposited at Vs up to 1000 V have larger clusters and further become rougher with increasing their thicknesses, while the R_q of films deposited at high V_s (1200 V- 1400 V) changes slightly with the thickness. As known, the average energy of adatoms is considered to be determined by the kinetic energy of the sputtered atoms, controlled by sputtering voltage just before arriving at the substrate. Simultaneously, the substrate heating imparts a thermal energy to the heated atoms thus enhancing the adatom mobility. Consequently, more uniform ITO films with small roughness are deposited at high voltages.

Fig.8 shows the lateral grain size obtained from surface profiles. As a whole, the values derived are larger than the values for crystallite sizes obtained by XRD (see Fig. 4). Most probably this stemps from the fact that the Scherer's equation used is only an approximation, which did not include any effect of residual stresses in the films along with the effects of peak broadening due to the instrument used. However, in accordancane with the XRD results the same tendency of the grain size reduction with the increase of sputtering voltage was obtained. On the contrary, at a given V_s the grain sizes became larger in films with increased thicknesses.

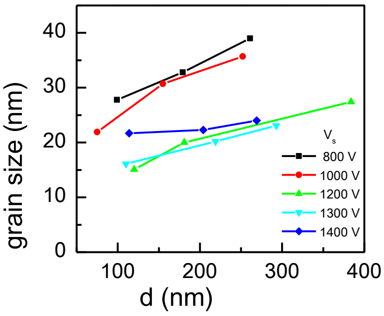


Fig. 8. Grain size, calculated by AFM images as a function of the thickness of ITO films deposited at indicated V_s.

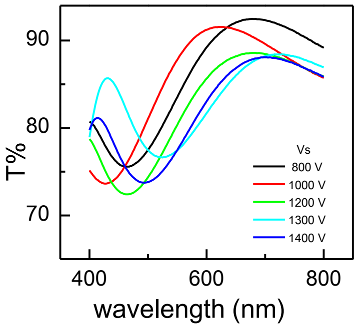


Fig. 9. Transmittance spectra of 180 nm thick ITO films, deposited at indicated V_s.

The resistivity of intrinsic n-type of ITO films strongly depends on the oxygen vacancy amount, Sn dopant and microstructure [1, 22]. It has been supposed that the carrier density is determined mainly by oxygen vacancies while the carrier mobility by the grain size, respectively [22]. On the basis of this assumption we can suppose that the existence of a minimum resistance of films deposited at high sputtering voltage is determined mainly by enhanced oxygen vacancies and hence, the increased carrier density in films, obtained in atmosphere of oxygen deficiency. At a given V_s further drop in R_{sh} with the film thickness most probably is due to the larger grain sizes that leads to the enhanced electron mobilities in the films.

The optical properties of ITO thin films along with the resistivity are known to depend strongly on the growth techniques, deposition parameters and microstructure. Fig. 9 illustrates the transmittance spectra of 180 nm thick ITO films, deposited on glass substrates at different sputtering voltages. It is seen that the films prepared at higher V_s have lower transmittance, but as a whole the average transmittance (T_a) is above 82 % in the spectral range 450–800 nm. Since T and R_{sh} are inversely related in order to determine the best trade-off between electrical and optical properties, a figure of merit $\phi = T_a^{10}/R_{sh}$ as suggested by Haake for transparent conductive layers, was calculated [23].

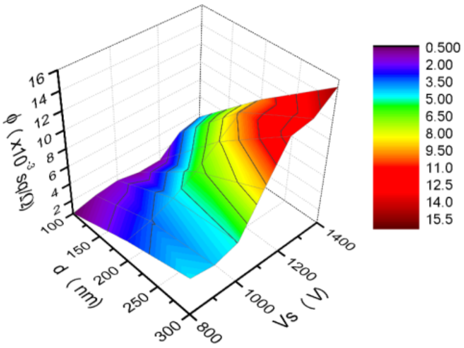


Fig.10. Figure of merit as a function of the film thickness and the sputtering voltage.

The variation of the calculated figure of merit with sputtering voltage and film thickness is presented in Fig. 10. It is evident that the highest value of ϕ ($15.5\ \mathrm{x}10^{-3}$sq/Ω) is obtained for 300 nm thick ITO films deposited at sputtering voltage of 1300 V.

CONCLUSION

The present work represents a systemathic investigation of electrical, structural and optical properties of ITO thin films, prepared by RF sputtering in pure Ar atmosphere, aimed at assessing their potentiality as transparent conductive electrodes. A big difference in sheet resistance R_{sh} of ITO films, obtained at different sputtering voltages V_s has been observed. It is established that samples deposited at high sputtering voltage have much lower sheet resistance. Besides, further drop in R_{sh} of the films has been measured whith increasing their thickness. Simultaneously, the analysis of XRD spectra show that the crystallinity of the ITO films increases with increased sputtering voltage. Strong (222) peak and preferred orientation in the (111) direction was detected for low resistance samples, obtained at high V_s. Furthermore, the surface of the films appeared to have a significant impact on the sheet resistance values. The results from AFM study revealed the formation of smooth films at higher V_s, with nanosized grains and uniformally distributed electrical current. The presence of areas with high roughness, where the current has very low value has been detected in films deposited at low V_s.

Summarizing the above, it is worth to highlight the most important results of the study, which demonstrate the possibities of preparing high quality ITO films by RF sputtering deposition at high V_s of 1300 V with thickness of 300 nm, the lowest sheet resistance of 8 Ω/sq and the highest figure of merit 15.5 x10^{-3}sq/Ω, without of necessity of additional annealing of films.

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ТЪНКИ ITO ФИЛМИ КАТО ПРОВОДИМИ ПРОЗРАЧНИ ЕЛЕКТРОДИ

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(Резюме)

В работата са представени резултатите от подробно изследване на структурни, електрически и оптични свойства на индиево-калаени (ITO) филми с различна дебелина. Филмите са отложени при различни условия на RF разпрашване на ITO таргет в чиста атмосфера от Ar газ в отсъствие на кислород. Изследвана е зависимостта на листовото съпротивление (R_{sh}) и оптичната пропускливост (T) на получените ITO филми от приложеното напрежение на разпрашване, температура на подложката и дебелина на филма. Направена е оценка за качеството на отложените филми като прозрачни проводящи електроди. Резултатите от проведеният рентгеноструктурен анализ (XRD) показват, че получените ITO тънки слоеве притежават поликристална струйтура с предпочитана (111) ориентация. Установено е, че филмите, отложени при по-високи напрежения на разпрашване са с по-ниска грапавост, значително по-ниско листово съпротивление и по-висока оптична пропускливост. Гладки и равномерни филми с ниско R_{sh} = 8 Ω/sq и средна пропускливост над 82% във видимия диапазон 400-800 nm са получени при отлагането на ITO върху стъклени подложки без тяхното допълнително отгряване.