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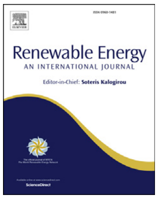

The controllable deposition of large area roll-to-roll sputtered ito thin films for photovoltaic applications

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ABSTRACT

In the present study, using a large area roll-to-roll DC magnetron sputtering system deposition of ITO thin films on polyethylene terephthalate (PET) substrates were achieved. In order to investigate the effect of growth conditions on the film properties all through the deposition process, optical emission spectroscopy (OES) analysis have been accomplished in a governable way. The consequences of Oxygen partial pressure and film thickness on electrical, and optical properties of the films were determined. It was shown that the intensity of optical emission peaks are subjected to the discharge power and as well as the O_2/Ar flow ratio. Large area, uniform ITO films with relatively high transparency and low electrical resistivity ($R_s < 50\ \Omega$/sqr) were succesfully deposited on PET substrates. The significance of both the figure of merit (FOM) and the optical band gap values on the performance of different TCO thin films were addressed. In this work, the obtained results suggest that the overall performance is sufficient to implement the ITO films in photovoltaic and OLED applications.

1. Introduction

Since Indium-tin oxide (ITO) has exceptional operational properties namely low electrical resistivity and high transparency across the solar spectrum region with respect to other transparent conducting oxide (TCO) materials [1] it has been extensively employed as transparent electrodes in photovoltaic (PV) instruments.

Although even staying transparent in the visible and near-infrared wavelength region, the virtually common TCOs (ZnO, CdO, In_2O_3, SnO_2) can be doped up to carrier concentrations of the order of 10^{21} cm^{-3}. In between the TCOs, CdO displays the highest mobility and lowest resistivity of the order $3 \times 10^{-5}\ \Omega$ cm however the disfavour of CdO is the comparatively low band gap value 2.3 eV alone, on the other hand for ITO this value is 3.8 eV. Even though ITO is the most extensively employed transparent conductive oxide (TCO), in various applications zinc oxide (ZnO) and associated structures are favoured opponents, Zinc oxide is a hexagonal wurtzite-type semiconductor having a wide direct band gap with a value of 3.37 eV. When primary characteristics of zinc oxide and Indium tin oxide are compared, it is observed that apparently ITO displays a lower resistivity with respect to ZnO. Furthermore, ZnO is more sensitive to Oxygen in comparison to ITO, and management of the procedure is demanding to a great extent. Some other TCO option at least equiavalent to ITO having a resistivity value of $< 1 \times 10^{-4}\ \Omega$ cm, has been established with ZnO:Al (AZO) deposited by PLD technique [2]. On the other hand, in the case of large area substrates PLD is not regarded as a appropriate deposition process. Appreciable improvement has been achieved in advancing robust process control and scaling to large area substrates in the development of AZO films by DC and RF magnetron sputtering however the achieved resistivity is approximately 3×10^{-4} or higher [2,3]. As it is well established that, method of cleaning has a significant influence on the work function and chemical structure of ITO at its surface which implies that ITO is unstable in the oxidation process. This reality emerges evidently when fluorine doped tin oxide (FTO) does not display similar dependence. Regrettably, in almost all

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electrically conducting FTO thin film deposited using magnetron sputtering methods the value of $7.0\times 10^{-3}\ \Omega$ cm has been accomplished [4]. Electrical property is the most significant property in comparison with the optical transparency which indicates a lower sheet resistance, together with improved stability and adhesion. In this context, since ITO can be developed over substrates with a larger area, at a comparatively lower handling temperatures in comparison to FTO coatings, and ITO coatings are much smoother, it will operate more efficiently.

In the previous years, along with TCOs transparent electrode materials have also emerged, namely atom-thick graphene layers have been employed since they maintain equivalent superb optical transmission properties, possess exceedingly high electron mobilities coupled with low carrier concentration (10^3–10^4 cm^2, V^{-1} s^{-1}, ~10^{13} cm^{-2}) and own good mechanical flexibility [5]. On the other hand, in order to compare the sheet resistance of graphene with ITO at least four monolayers of graphene are involved but this leads to a substantial loss of optical transmission in the graphene. Moreover, at angle of incidence of light greater than approximately ~300, optical transmission in the graphene decreases seriously. This feature will adversely affect the efficiency of information displays as well as the efficiency of photovoltaic devices. Hereby ITO virtually stays as the effective electrode material, which essentially does not display drop-off in transmission from an increased angle of incidence.

Due to their solitary characteristic properties such as flexibility and lightweight, recently flexible electronic devices are appealing growing attention in the field of photovoltaics, thin-film transistors (TFTs) and integrated circuits [6–11]. Moreover, this interest is in connection with the reality that when the flexible films are used as substrates the utilization of roll to roll processing is accomplished which initiate extremely significant gains in manufacturing productivity and economy [12]. Thin metal foil, plastic materials or paper can be used in place of the flexible substrate as the support material in the flexible electronic devices. In photovoltaic devices, polyethylene terephthalate (PET), polycarbonate (PC), polyarylate (PAR), polyethersulfone (PES), polyimide (PI) and polyolefin are usually utilized as plastic substrate materials. As a substrate in flexible display operations, PET included among the above mentioned materials which has outstanding optical property as well as low cost comes to the forefront as an encouraging prospect. Current commercial tendency is in the direction of increasingly developed flexible solar cells with a corresponding requirement for ITO films coated on plastic substrates [13]. Plastic substrates in comparison with glass substrates, provide a good deal of superiority namely low weight, durability and an easy scale up to a large format [14,15]. The flexibility property of these materials permits the modification of the device shape with the purpose of optimizing visibility and prohibit reflections. On the other hand, since ITO is a natural fragile material, strength of ITO thin films is an important problem, which must be taken into account in the advancement of flexible optoelectronic technology. In DC magnetron sputtering method it is feasible to control very strictly the thickness of the films which is an important advantage compared to other numerous deposition methods and consequently all the deposition parameters to accomplish required properties in ITO thin films could be taken under control consistently [16–21]. Hence, when the ITO films are produced by sputtering they are extremely uniform and free from impurities, and also exhibit superior mechanical and adhesion characteristics. Nowadays, in order to achieve extremely conductive and transparent ITO film with outstanding uniformity and desirable adhesion to a flexible substrate by means of the sputtering technique, various efforts have been performed [22,23]. Moreover, in the fabrication it is accessible to large-scale coating of high quality ITO films on glass. In between the methods, since sputtering technique supplies high deposition rates where it is straightforward to control sputtering parameters and able to deposit on a large area of substrates with good thin films quality, this technique is mainly used to deposit the ITO thin films.

Remarkable results on roll to roll processed large area modules with high device efficiencies have been established in flexible substrates where ITO is introduced as transparent electrode [24–26]. On the other hand, in specific ITO utilization namely for flexible optoelectronic devices, owing to the low thermal resistance of the polymer substrates, high substrate temperatures or high post-deposition annealing temperatures are unacceptable. After all, numerous works with a conventional sputtering chamber and small ITO target have been reported. It is believed that in the manufacturing, process circumstances are expected to be entirely distinct since the processing will be carried out on a large substrate where a relatively large cathode under a moving-state substrate is employed (the so-called in-line process). Aforesaid discrete processes will generate substantially different results on film properties for qualifications such as power, pressure, and gas ratio, etc.

The properties of the out coming films are instantly associated to the species in the plasma that are emitted from the target and thus a plasma-monitoring technique in place would permit the adjustment of the deposition parameters which consequently lead to the control of the characteristics of the deposited thin film.

In plasma monitoring, one of the adopted techniques is optical emission spectroscopy (OES) which is usually employed as a real time spectroscopy technique in deposition processes [27–30]. In the present work, with the purpose of monitoring all light emitting species in the plasma; for the deposition of large area ITO thin films on PET substrates by roll to roll industrial dc magnetron sputtering system, OES is utilized for the first time to the best of our knowledge. In an effort to specify the mechanism of Oxygen partial pressure in the ITO thin film quality, OES has been employed in the process of the entire deposition for controlling deposition parameters and the optical emission data were correlated with the properties of the thin films.

2. Experimental

In the deposition of the ITO thin films a large area roll to roll magnetron sputtering coating system was used. In Fig. 1 (a), the schematic representation of the large area magnetron sputtering coating system is presented. The system was provided with unwind and rewind rollers and a rotational feed through mechanism. By the movement of unwind and rewind rollers in the system the flexible substrate is gently moved under the target with the help of the feed through mechanism. The film thickness depends on the applied power and angular velocity of the feed through and the ITO film can be continuously deposited on large area flexible substrates. The PET substrate with the dimensions of 400 mm width, 0.075 mm thickness were installed on unwind and rewind roller thereafter put into the vacuum chamber. A rough pump backing a turbo-molecular pump is employed in order to evacuate the large area system to below 3.30×10^{-6} mbar.

Subsequently, the vacuum chamber was evacuated, high purity Ar and O_2 were introduced through independent mass flow controllers. With the purpose of investigating the influence of Oxygen partial pressure, the Oxygen flow rate was varied from 1.5 to 4.5 sccm while keeping the Argon flow rate at 40 sccm. Afterwards, in order to generate the plasma on the 50×20 cm^2 ITO target (purity of 99.99% and a weight percent of 10–90 for SnO_2 and In_2O_3) 1.66 kW DC power (ADL Maris, 10 kW) was introduced. Using the rotational feed through, the loaded PET substrate was rolled one end to the other, ITO large area films were deposited with different

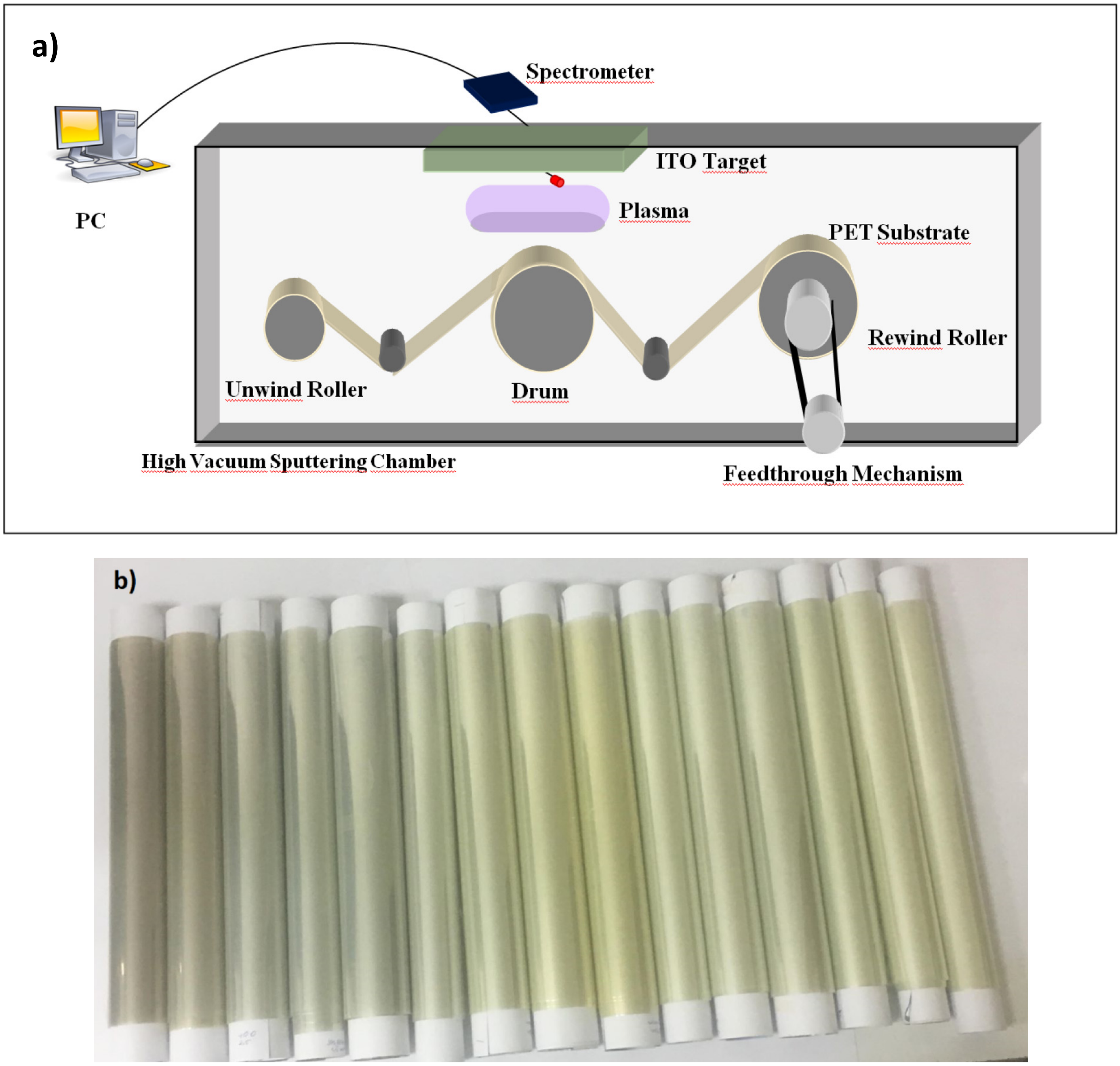

Fig. 1. (a) Schematic representation of our large area magnetron sputtering coating system.

Ar/O_2 ratio and roll to roll speed (18, 22, 27, 29 cm/min) for every 10 m of substrate. ITO thin films in different thicknesses were obtained by the variation of the roll to roll speed. The total number of samples produced is 16 (4 for each 4 set of roll to roll speed) and in Table 1, detailed sample descriptions and the sputtering parameters employed in this investigation are presented. In order to investigate the effect of growth conditions on the film properties, optical emission spectroscopy (OES) analysis has been accomplished in a governable manner in the course of the deposition process. The Stellar Inc. EPP2000 Fiber optic spectrometer system consisted of a UV–vis SMA905 optical fiber, a UV enhanced 2048 pixel CCD detector (wavelength range 200–1100 nm) and computer control system for processing and analyzing the optical data were introduced. The optical fiber was pointing to the middle of the 11 cm distance between the target and the substrate holder, and was placed 15 cm away from the plasma which was confined above the ITO target. Allocation of atomic lines was accomplished on the base of information tabulated in NIST Atomic Spectral Database. Using the cross-sectional SEM images, the films thicknesses were measured (Fig. 2).

The optical properties of the ITO thin films were measured by a spectrophotometer (PerkinElmer Lambda 950 UV/Vis/NIR Spectrophotometer) in the 200–2600 nm wavelength range. Using a Keithley 2420 instrument with the help of the four point probe method, the sheet resistances (R_S) of ITO thin films were measured.

3. Results and discussion

3.1. Optical emission spectroscopy (OES) analysis

Using annealing processes for ITO thin films, the electrical properties of the films can be developed furthermore. On the other hand, when handled for heating process flexible PET substrates are not long-lasting and thus in order to attain the high quality ITO films the deposition parameters must cautiously be optimized. The Oxygen partial pressure is the best sputter parameter to ascertain the properties of the films. Consequently, for each treatment (plasma excitation, temperature, sputter pressure, base pressure) determination of the optimum value is very important. In the present study, the foremost endeavor was given to the prediction

Table 1
The detailed sample descriptions, sputtering parameters and the sheet resistance values of the ITO films.

Roll to roll speed (cm/min)	Argon/Oxygen Flow (sccm)	DC Power (kW)	DC Power Density (W/cm^2)	Sheet Resistance (ohm/sqr)
18	40/1.5	1.66	2.20	55
18	40/2.5	1.66	2.20	49
18	40/3.5	1.66	2.20	122
18	40/4.5	1.66	2.20	145
22	40/1.5	1.66	2.20	72
22	40/2.5	1.66	2.20	65
22	40/3.5	1.66	2.20	150
22	40/4.5	1.66	2.20	157
27	40/1.5	1.66	2.20	181
27	40/2.5	1.66	2.20	71
27	40/3.5	1.66	2.20	120
27	40/4.5	1.66	2.20	185
29	40/1.5	1.66	2.20	78
29	40/2.5	1.66	2.20	75
29	40/3.5	1.66	2.20	101
29	40/4.5	1.66	2.20	332

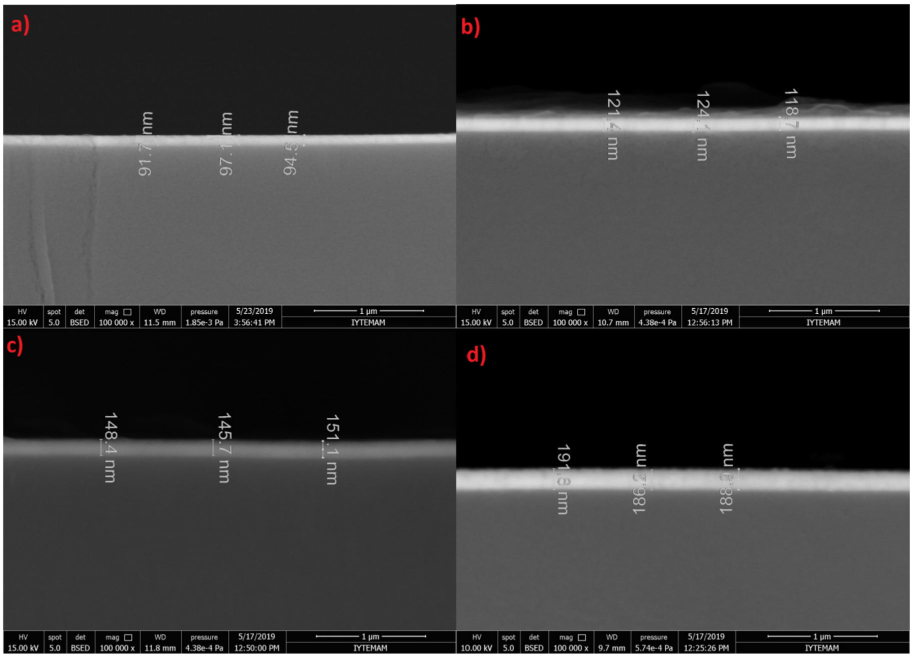

Fig. 2. The cross sectional SEM images of the ITO films with (a) 29 cm/min (b) 27 cm/min (c) 22 cm/min and (d) 18 cm/min roll to roll speeds (40 sccm Argon flow, 2.5 sccm Oxygen flow).

and manipulation of parameters in ITO thin films specifically resistivity and transparency by in-situ measuring of the plasma emission spectra by the OES method. In Fig. 3, characteristic OES lines achieved in the deposition process of large area ITO films in Ar plasma under the sputtering conditions of 1.5 sccm O_2 flow with 40 sccm Ar flow at 18 cm/min roll to roll speed are presented. The adopted notations (ionization stage) are: In I – excited Indium, In II – ionized Indium, etc. The magnetron plasma emission spectra is consisted from the excited Argon (Ar I), Indium (In I), Oxygen (O I) and ionized Argon (Ar II), Indium (In II), tin (Sn II) lines. It was established that the intensity of peaks are subjected to the discharge power and as well as to O_2/Ar flow ratio. On some occasion, the dominant O line at 777 nm cannot be observed and moreover there might be species that could be established) depending on the low concentration or the necessity of higher potentials for excitation and overlapping with emission lines of other species. Hence, detecting a good deal of weak Oxygen emission lines must be due to the fact that Oxygen involves higher energy for excitation.

There is a powerful relation between the plasma parameters and thin film properties. Anticipation and conduction of thin film parameters are provided by in-situ measurement of the plasma properties. It is believed that the quality and quantity of the species in plasma are very much subjected to sputtering used (DC, RF or magnetron), to the geometrical configuration of the chamber (large area) and, naturally, to the deposition parameters and especially on the gases used. In magnetron sputtering for target surface cleaning, presputtering is predominantly the favoured option. On the other hand, since it is not feasible to integrate a shutter on a movable feed through this is not conceivable in the present system and a few meters of PET substrate is deposited at the beginning for presputtering. In the course of the whole presputtering process, optical emission data is recorded and presented in Fig. 4 (a),(b).(c), namely the beginning of the sputtering, following first 10 and 20 min respectively. In this kind of industrial large area systems, another critical issue is to establish a stable plasma and pressure. An

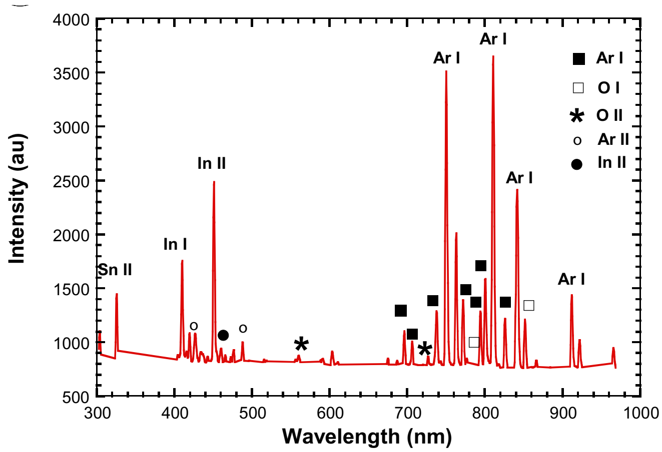

Fig. 3. The optical emission spectroscopy of large area ITO films in plasma under the sputtering conditions of 1.5 sccm O_2 flow with 40 sccm Ar flow at 18 cm/min roll to roll speed.

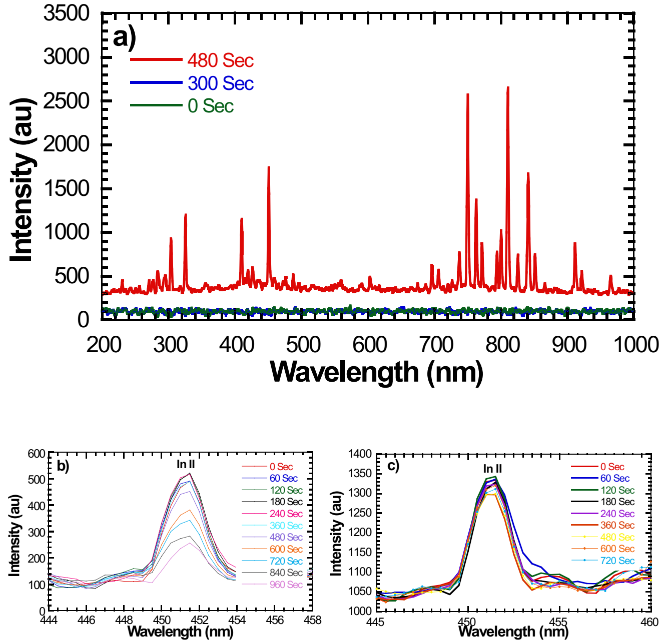

Fig. 4. The optical emission spectroscopy analysis (a) in the beginning of the sputtering, (b) during the first 10 min and (c) 20 min after.

arbitrary increase in the intensity of In lines is observed in the first 10 min. When the plotted graphs are investigated it is observed that at least 20 min presputtering time is necessary to make sure that most of the impurities on the target surface were removed and suitable, stable conditions are obtained before proceeding to the thin film growth. In this manner, for photovoltaic applications the deposition of high quality transparent conductive electrodes which are uniform over a large area can be supplied. Moreover, the intensities of Indium (wavelength 450.48 nm), and Argon (wavelength 811.08 nm) peaks are investigated as a function of the Oxygen flow rate and discharge power. In Fig. 5, the identified emission lines, and their intensities are given which originate from the target during deposition of the ITO films at different DC power.

The deposition rate was correlated to the In II species emission intensities in the plasma, and the higher intensity values of the In species in the Ar plasma gives rise to a higher deposition rate of the ITO films. The optimization of the sputtering power is substantial since the electrical and optical properties of ITO films are intimately connected to the film crystalline quality. The crystalline quality of ITO films are governed by the sputtering rate due to the fact that sputtered atom on PET substrate customarily has low mobility.

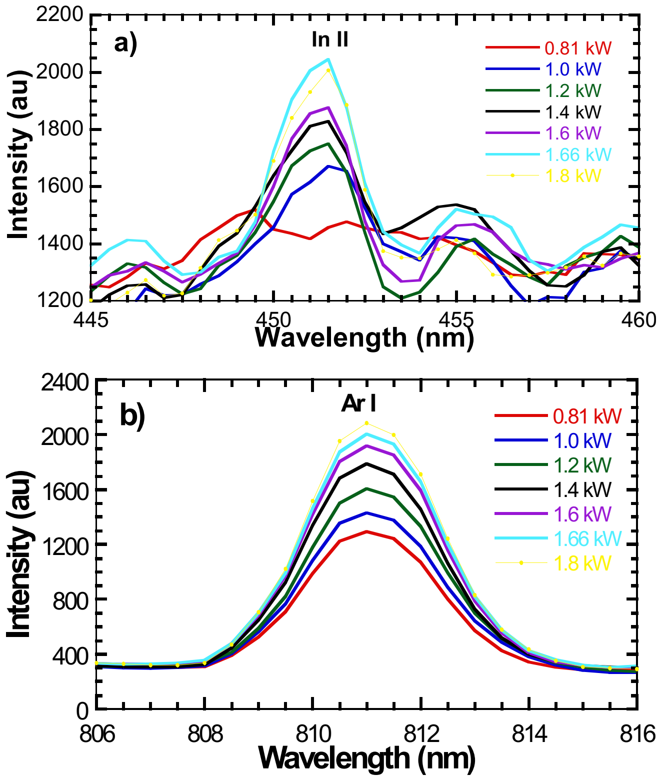

Fig. 5. The intensities of (a) Indium (wavelength 450.48 nm), (b) and Argon (wavelength 811.08 nm) peaks as a function of the discharge power (18 cm/min roll to roll speed. 40 sccm Ar, 2.5 sccm O_2 flow rate).

In the present investigation, depending on our recent results and making use of the OES analysis 1.66 kW optimized dc power is utilized for all of the samples. Fig. 6 (a), (b), (c), (d), exhibit the dependence of In, Sn, Ar species intensities to Oxygen rate for 18 cm/min roll to roll speed (the OES measurement were carried out for 1.5, 2.5, 3.5, 4.5 sccm Oxygen flow rate to search the optimum level). It is clearly observed that the intensities of In (II), Sn (II), In (I), Ar (I) peaks increase with the increase of O_2 flow rate from 1.5 sccm to 2.5 sccm and decrease with the increase of O_2 flow rate from 2.5 sccm to 3.5 and 4.5 sccm.

On the other hand, lowest sheet resistance values are obtained from the ITO films that are deposited with 2.5 sccm Oxygen flow hence the electrical measurements and the OES analysis demonstrate that the 2.5 sccm Oxygen flow is an optimum value to reduce the resistivity of the films in this study.

3.2. Electrical characterization of ITO thin films

Since for photovoltaic applications it is substantial to accomplish low sheet resistance values, in Table 1 sheet resistances (R_s) of the ITO films on PET substrates are presented. There is a powerful relation between the amount of Oxygen vacancies together with the microstructure and the sheet resistances of the ITO thin films [30–32].

Due to the fact that the carriers in ITO films come to existence as a result of the creation of Oxygen vacancies, the electrical properties are influenced by the Oxygen partial pressure in the DC

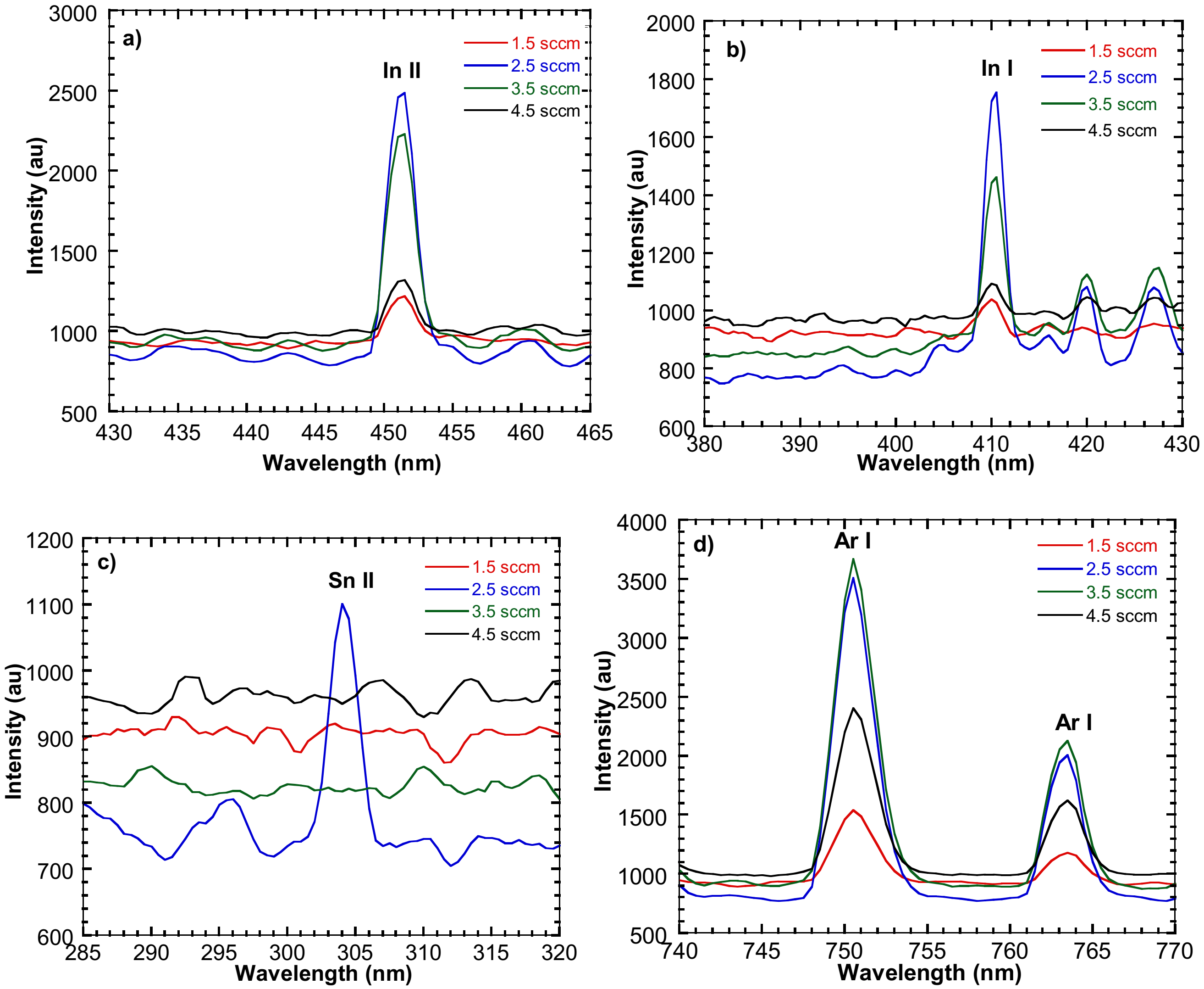

Fig. 6. The dependence of (a) In II, (b) In I, (c) Sn II, (d) Ar I species intensities to Oxygen rate for 18 cm/min roll to roll speed (40 sccm Ar, 1.5, 2.5, 3.5, 4.5 sccm O_2 flow).

magnetron sputtering. A decrease in the electrical resistance in ITO coated PET samples is observed which is a consequence of the diminution of the Oxygen amount in the sputter gas. As aforesaid, since one vacancy produces two electrons on the conduction band to assure the charge neutrality, it is known that the conductivity of ITO is related to the Oxygen vacancies in the material. Oxygen vacancies in the deposited material is demanded to increase when the Oxygen partial pressure decreases, accordingly accomplishing the films to be less stoichiometric or more metallic, which increases the conductivity and the number of charge carriers in the layers. Hence, deducing that a decrease in the Oxygen flow rate leads to an enhanced conductivity and detecting a slight increase in the transmittance values is anticipated.

3.3. Optical characterization of ITO thin films

In Fig. 7, optical transmittance at a visible wavelength from 200 to 2600 nm in the ITO films which are deposited with variable Oxygen flow for each roll to roll speed is presented in order to compare with the associated bare PET substrate. The transmission, reflection and absorption characteristics of the samples for 2.5 sccm O_2 flow are given on the same graph, the inset of Fig. 7. The graphs indicates that the increase in the transmittance is complemented by the decrease in the reflectance. The reflection increase of near-infrared region is due to the decrease of resistivity. The absorbance graph of the films shows one distinct peak, which is due to the plasma resonance, is around %68. The bandgap absorption is obtained below 450 nm. ITO is the most well known TCO that absorb both the UV and the IR due to the excitation of free charge carriers.

In the visible range, the transmittance of the ITO films on PET substrates are observed to be lower than that of the bare PET substrate however the variation is not substantial. In spite of the fact that, in the growing process substrate heating or post-annealing was not adopted, a sharp absorption edge can be detected. In order to control the optical properties of ITO films, an important role was taken by Oxygen gas flow. In Fig. 7, the decrease of optical transmission while the Oxygen gas flow rate increases from 1.5 to 4.5 sccm is presented whereas increasing film thickness also leads to a decrease of transmission. Thus, it is concluded that when excessive Oxygen was included in the films the electrical conductivity together with the optical transmission of the films decreased. When Oxygen flow are at higher rates, due to Oxygen adsorption the excess Oxygen is likely to accumulate on the grain boundary or surface which behaves as light scattering centers and this situation leads to the decrease in transmission of the films).

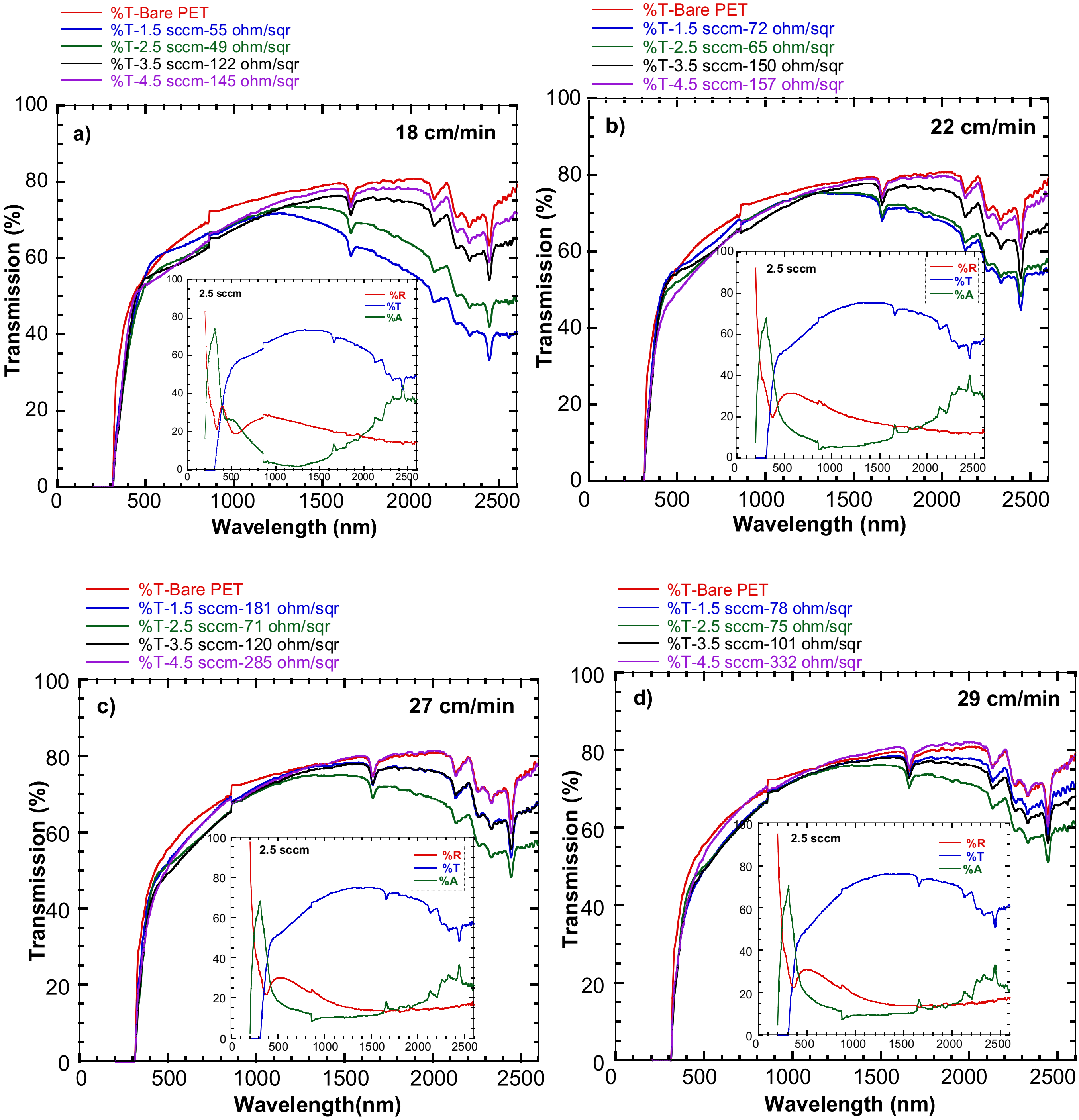

Fig. 7. The optical transmittance analysis of the ITO films which are deposited with variable Oxygen flow rates for (a) 18 cm/min, (b) 22 cm/min, (c) 27 cm/min and (d) 29 cm/min roll to roll speeds. The reflection, transmission and absorption analysis for 2.5 sccm O_2 flow (on the same graph) are shown in the inset figures.

Once the optical characteristics of ITO deposited onto PET substrates at different Oxygen partial pressure were compared, a substantial variation on infrared optical transmittance was observed, however in the visible transmittance values an insignificant change was detected.

In the case of degenerate semiconductors namely ITO, when the near infrared region is considered the transmittance loss is associated to the plasma frequency where the transition between transparent to reflectance behavior takes place. The effective mass of the free electrons and the concentration of charge carriers in the film determine the plasma frequency.

In practice, TCO thin films involve maintaining high optical transmission and low sheet resistivity simultaneously but it is not always feasible. Consequently, the electrical and optical properties must be optimized to the excellent feasible limit. In order to compare the performance of different TCO thin films the figure of merit (FOM) for each thin film was adopted.

The transmission and electrical properties of the thin films are compared at the same time by the FOM values [31] where a better performance of the deposited material is indicated by a higher figure of merit.

$$\Phi_{TC} = T^{10}/R_s \tag{1}$$

where Φ_{TC} is FOM, T is the transmittance and R_s is the sheet resistivity. The FOM values of our samples are calculated by the above given formula. Our calculations show that for the sample grown at 18 cm/min roll to roll speed and 1.5 sccm Oxygen flow the highest value is attained. On the other hand, the least value is achieved for the films that is grown at 29 cm/min roll to roll speed and 4.5 sccm Oxygen flow.

Once more proceeding with the trend in electrical and optical properties, the FOM gets better with the film thickness and reducing Oxygen flow from 4.5 to 1.5 sccm, and this result is in agreement with our recent conclusions. The previous studies reported that the low transmittance value of the ITO thin films is a consequence of the low value of the Tauc gap. In the present study, we succeed to achieve transmittance values closer to bare PET substrates transmittivity. Since in most of the optoelectronic applications high energy gap value for ITO thin films is required, the Tauc method was adopted to calculate the energy gap of the samples. In the existing study, in order to estimate the band gap energy of the ITO thin films the absorption coefficient, α^2 versus photon energy (hf; h is planck constant and f is frequency) plot was employed (Fig. 8).

In the calculation of absorption the following equation is used

$$\text{T-R} = e^{-\alpha t} \tag{2}$$

where T and R denote the transmittance and reflectance, respectively, and t is the thickness of the film. Since the reflectance of the films have a relatively low value it is ignored and then the absorption coefficient takes the simple form

$$\alpha^2 = \ln\,(T)^2/t^2. \tag{3}$$

Recalling that Indium doped tin oxide has a direct transition, namely,

$$\alpha hv = A(hv\text{-}E_g) \tag{4}$$

The band gaps of the fllms are derived (where α, v, A, and Eg are absorption coefficient, light frequency, proportionality constant, and band gap) using the extrapolation of the linear plots of α^2versus hv. In Fig. 8, the direct optical band-gap values of large area ITO thin films for different roll to roll speeds and Oxygen flow rates are given. When PO_2 decreased, we notice that there is a small shift towards higher band gap energy values ranging from 3.50 to 3.56, 3.60 to 3.68, 3.60 to 3.76 and 3.78–3.86 eV for the roll to roll speeds of 18, 22, 27, 29 cm/min respectively (Table 2.). The above mentioned difference may be attributed to the higher carrier concentrations in the samples with lower Oxygen concentration. On the other hand, the above given values are in the range of other

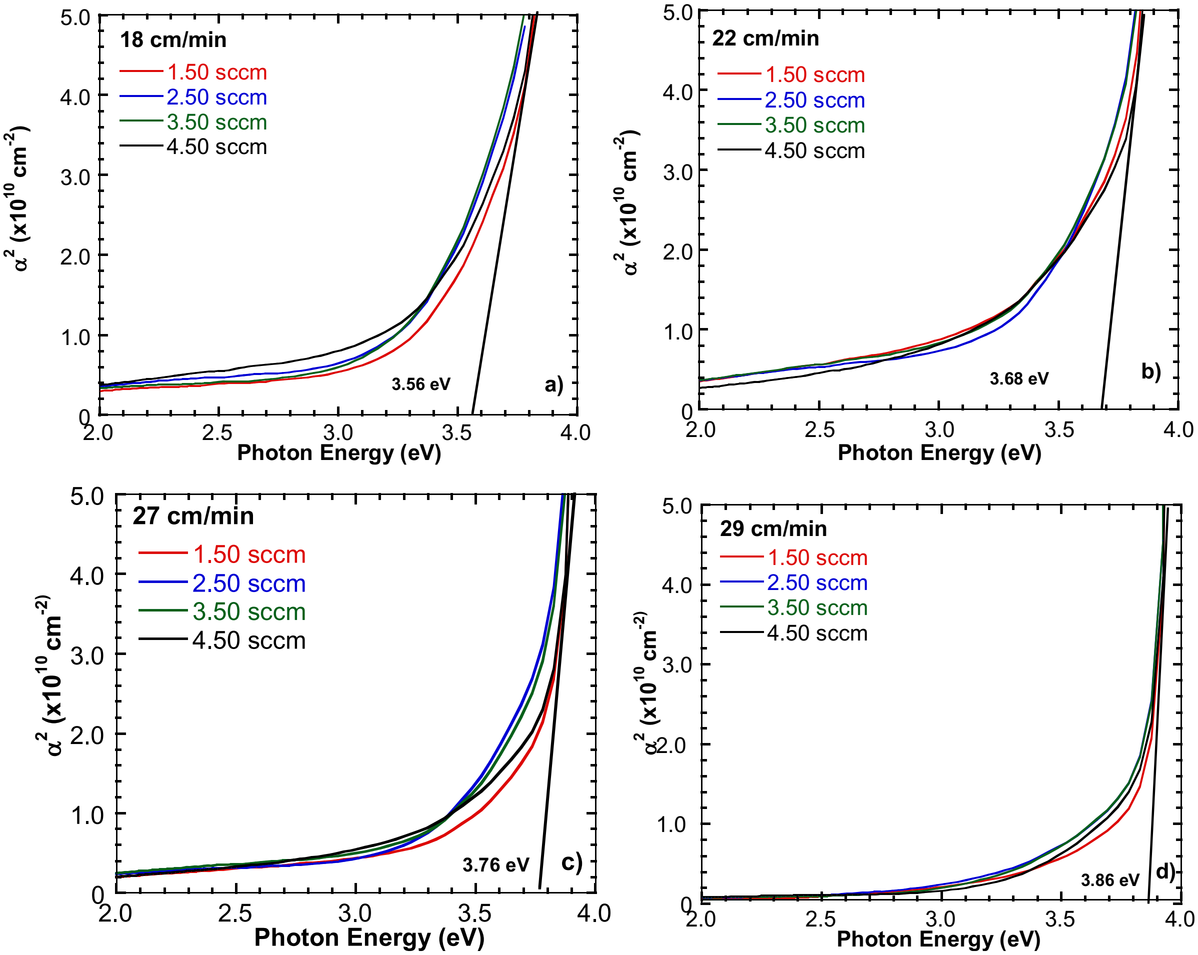

Fig. 8. α^2 Versus Photon Energy (hv) curves of the ITO films deposited with variable Oxygen flow rates for (a) 18 cm/min, (b) 22 cm/min, (c) 27 cm/min and (d) 29 cm/min roll to roll speeds.

Table 2
The E_g and calculated FOM values of the ITO films.

Roll to roll speed (cm/min)	Argon/Oxygen Flow (sccm)	E_g (eV)	FOM (1/ohm)
18	40/1.5	3.56	1.3×10^{-4}
18	40/2.5	3.50	6.1×10^{-5}
18	40/3.5	3.54	2.4×10^{-5}
18	40/4.5	3.52	1.4×10^{-5}
22	40/1.5	3.68	5.0×10^{-5}
22	40/2.5	3.60	3.2×10^{-5}
22	40/3.5	3.63	1.6×10^{-5}
22	40/4.5	3.66	1.0×10^{-5}
27	40/1.5	3.76	1.3×10^{-5}
27	40/2.5	3.60	1.2×10^{-5}
27	40/3.5	3.74	1.2×10^{-5}
27	40/4.5	3.72	8.8×10^{-6}
29	40/1.5	3.86	1.8×10^{-5}
29	40/2.5	3.78	2.3×10^{-5}
29	40/3.5	3.85	1.9×10^{-5}

investigations reported by Refs. [17–34].

A correlation between the band-gap and R_s values for all of the ITO thin films is obviously observed which implies that a decrease of resistivity leads to an increase in band-gap with respect to the increase in the carrier concentrations. In order to give an explanation to this band gap widening the Burstein–Moss effect is introduced where the lowest states in the conduction band are occupied and only transitions to higher states are allowed. Nevertheless, band gap narrowing may be observed at very high carrier concentrations as a result of the scattering at the electron and electron-impurity level.

In Fig. 9(a) and Fig. 9(b), optical band gap and sheet resistance values of the ITO films deposited with different Oxygen flows are given on the same graphs. From Fig. 9(c), it is observed that the FOM values of the ITO films enhanced with both the film thickness and with reduction of Oxygen flow from 4.5 to 1.5 sccm for the films with a roll to roll speeds of 18 and 22 cm/min (Table 2.).

New technologies emerge due to the requirements of extremely thin, entirely strong mechanical properties and flexible transparent conductive electrodes that lead to fast development of new devices in the past years. The enhancement of the optical and electrical characteristics of Indium tin oxide (ITO) layers is maintained to accomplish a higher efficiency in its application as frontal electrical contacts in thin film photovoltaic devices.

In the present work, resistivity and transparency parameters of ITO thin films are forecasted and controlled which is admitted by the study of the correlation in-situ measuring of plasma emission spectra. It is acknowledged that, a high performance electrode should preserve a low sheet resistance and a high optical transmittance, conforming to a high value of FOM.

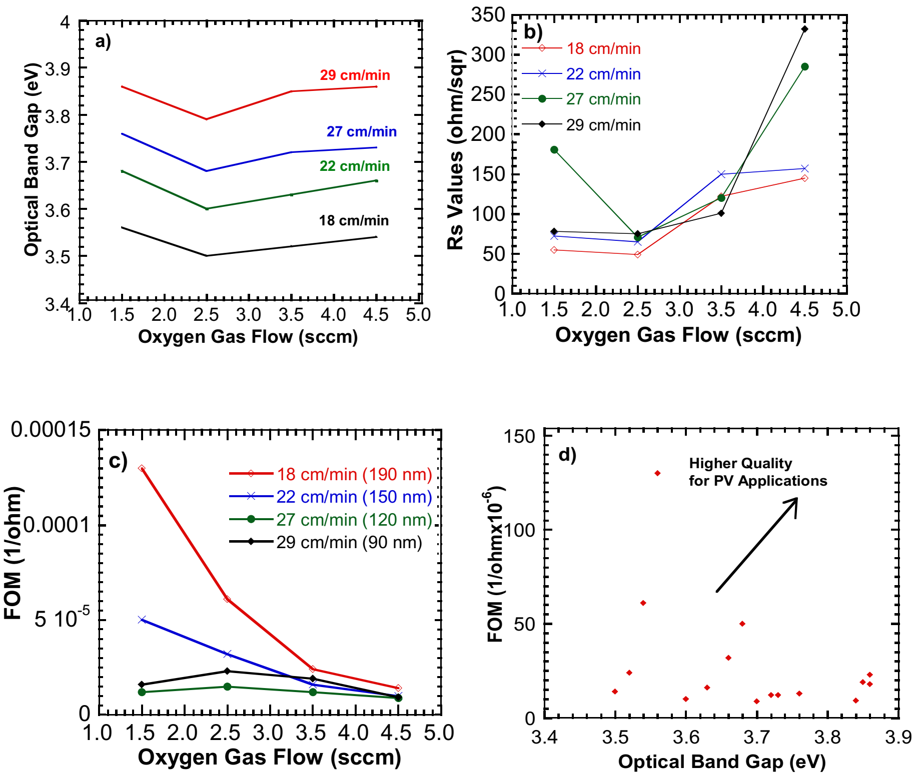

Fig. 9. (a) Optical band gap (eV) versus Oxygen flow rate (b) R_s values versus Oxygen flow rate (c) Figure of Merit versus Oxygen flow rate (d) Figure of Merit versus Optical band gap (eV) curves of ITO films deposited with different roll to roll speeds are plotted on the same graph.

In contesting ITO with sheet resistance, optical transparency and FOM values, large area ITO thin films have demonstrated a hopeful expectation. For additional development, the highest optical transmittance has to be accomplished with the lowest electrical resistance (Fig. 9(d)).

Traditionally, the electrical properties of thick films are customarily better in comparison to thin films. This fact is assigned to a change in the microstructure of the film in the growing process with more extra Oxygen integrated during the beginning stage of film growth. Primarily, thick ITO film deposition is required in order to obtain high transmittance and low resistance. Merely, high optical transmittance similar to that of ITO as well as very low sheet resistance (lesser than that of ITO) can be accomplished provided that a thin metallic layer (Ag, Au.) is introduced between two thin ITO layers. When the thicknesses of ITO and metallic layers are cautiously altered solar spectrum transmittance and reflectance of the ITO/Metal/ITO multilayer can be accommodated.

4. Conclusion

In the presented study, using a roll to roll large area DC magnetron sputtering system, coating of ITO thin films on PET substrate without heating were accomplished. During the deposition process, in order to control the effect of growth conditions on the film properties, specifically resistivity and transparency, OES analysis have been carried through. The intensities of Indium, Oxygen and Argon peaks were investigated as a function of the Oxygen flow rate and discharge power. It was demonstrated that the deposition rate was correlated to the In II species emission intensities in the plasma. Moreover, it is obvious that the intensities of In (II), Sn (II), In (I), Ar (I) peaks increase with the increase of O_2 flow rate from 1.5 sccm to 2.5 sccm and decrease with the increase of O_2 flow rate from 2.5 sccm to 3.5 and 4.5 sccm. The investigation of the effect of Oxygen partial pressure and film thickness on electrical, and optical properties of the large area ITO films have been realized. The decrease of transmission while the Oxygen gas flow rate increases from 1.5 to 4.5 sccm is obtained since when excessive Oxygen was included in the films the electrical conductivity together with the optical transmission of the films decreased. In addition to the electrical and optical properties, the FOM gets better with the film thickness and reducing Oxygen flow from 4.5 to 1.5 sccm.

Minimum resistivity was accomplished at a 2.5 sccm Oxygen flow by increasing the Oxygen ratio from 1.5 to 4.5 sccm no matter how highest FOM values were attained at Oxygen flow of 1.5 sccm. So, the electrical measurements and the OES analysis demonstrate that the 2.5 sccm Oxygen flow is an optimum value to reduce the resistivity of the films in this study.

The deposited films can be adopted as a transparent electrode in flexible displays and solar cells. In our progressing and prospective investigations, for additional developement of structural and functional properties of these transparent electrodes we are planning to deposit ITO/Ag/ITO multilayers.

(b) ITO deposited flexible Polyethylene terephthalate (PET) films (7 cm rolled, 40 cm width, 10 m long for each process parameter).

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