J Electroceram (2009) 23:506–511
DOI 10.1007/s10832-008-9522-2

Electrical and optical properties of fluorine-doped tin oxide (SnOx:F) thin films deposited on PET by using ECR–MOCVD

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Received: 24 May 2007 / Accepted: 5 May 2008 / Published online: 6 June 2008

Abstract The electrical, optical, structural and chemical bonding properties of fluorine-doped tin oxide (SnO_x:F) films deposited on a plastic substrate prepared by Electron Cyclotron Resonance–Metal Organic Chemical Vapor Deposition (ECR–MOCVD) were investigated with special attention to the process parameters such as the H_2/TMT mole ratio, deposition time and amount of fluorine-doping. The four point probe method, UV visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic emission spectroscopy (AES), X-Ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to characterize the films. Based on our experimental results, the characteristics of the SnO_x:F thin films were significantly affected by the process parameters mentioned above. The amount of fluorine doping was found to be one of the major parameters affecting the surface resistivity, however its excess doping into SnO_2 lead to a sharp increase in the surface resistivity. The average transmittance decreased with increasing film thickness. The lowest electrical resistivity of 5.0×10^{-3} Ω·cm and highest optical transmittance of 90% in the visible wavelength range from 380 to700 nm were observed at an H_2/TMT mole ratio of 1.25, fluorine-doping amount of 1.3 wt.%, and deposition time of 30 min. From the XRD analysis, we found that the SnO_x:F films were oriented along the (2 1 1) plane with a tetragonal and polycrystalline structure having the lattice constants, a=0.4749 and c=0.3198 nm.

Keywords SnOx:F · PET · Electrical conductivity · Optical transmittance · ECR–MOCVD

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1 Introduction

Fluorine-doped tin oxide (SnOx:F) is one of the advanced ceramic materials used for various optical and electronic applications, due to its high transparent and conductive properties [1–3]. SnOx:F film, therefore, has been employed in organic optoelectronic devices such as electrodes in thin film solar cells, gas sensors, electronic devices and flat panel displays [4–8]. SnOx:F films can be prepared by various deposition techniques such as spray pyrolysis, reactive thermal evaporation, chemical vapor deposition (CVD) and sputtering [9–11]. The employment of a plastic substrate instead of glass for SnOx:F film deposition has many advantages, due to its light weight, small volume, low cost and flexible shape. The optical and electrical properties of SnOx:F film are highly dependent on the deposition process and its parameters in the CVD system.

In this work, the effects of the process parameters on the characteristics of the SnOx:F film were investigated. The process parameters studied are the H_2/TMT mole ratio, deposition time and the amount of fluorine-doping. We also study the SnOx:F film properties such as the crystal structure, lattice parameters, electrical resistivity, transmittance, atomic concentration and occupancy ratios of related bondings.

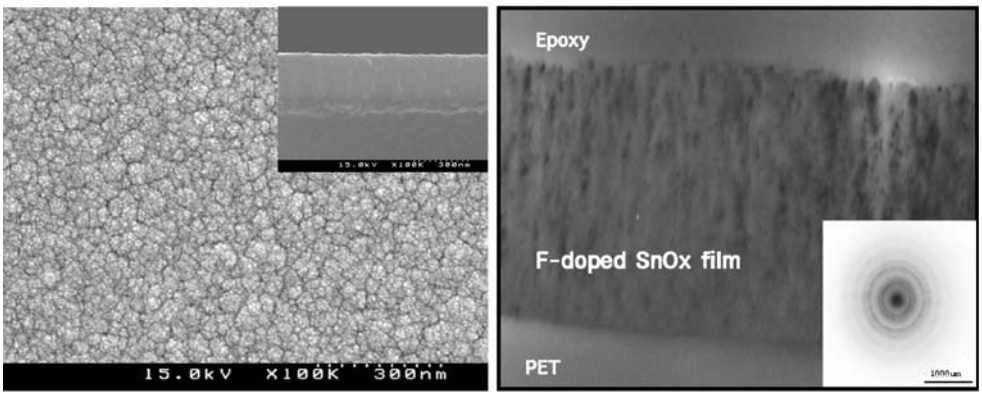


Fig. 1 Scanning electron micrograph (**a**) and electron diffraction pattern in cross section (**b**) of SnOx:F film on PET substrate prepared by ECR–MOCVD

2 Experimental

The Electron Cyclotron Resonance–Metal Organic Chemical Vapor Deposition (ECR–MOCVD) system for SnOx:F thin film deposition was described in detail in previous work [12]. Microwaves at a frequency of 2.45 GHz under a magnetic flux density of 875 G were introduced through a rectangular guide into the plasma chamber to generate the plasma. A PET (Polyethylene Terephthalate) film with dimensions of 17×36 cm^2 used as the substrate is rolled during the SnOx:F film deposition. An ECR plasma system was employed to carry out the experiments. It consisted of two separate regions i.e., the plasma zone and the deposition zone. It was pumped down to a base pressure of 1×10^{-6} Torr with a turbo-molecular pump, supported by a rotary mechanical pump and a roots blower pump.

Tetra-Methyl Tin (TMT) and SF_6 were used as the precursors for tin and fluorine, respectively. The working gases were fed into the chamber through the mass flow controllers. The TMT was then introduced into the deposition chamber using argon as a carrier gas. The argon gas flowed through the bypass line of the TMT bubbler until the reactor was stable; then it flowed through the TMT bubbler, which was maintained at room temperature in order to carry TMT vapor into the reactor. The deposition conditions were an argon flow rate of 3 sccm, distance from the magnet to the TMT feeding point of 8 cm, distance from the TMT feeding point to the substrate of 10 cm, and a working pressure of 10 mTorr. The structural properties of the SnOx:F thin films were studied using SEM, TEM and XRD. The optical and electrical properties were evaluated by measuring the transmittance and resistivity using UV visible spectroscopy and a four point probe, respectively. The composition depth profile of the SnOx:F film was observed with Auger electron spectroscopy/Scanning auger microscopy (AES/SAM, Perkin-Elmer, Ψ-670). The chemical composition of the films was examined by X-ray photoelectron spectroscopy (XPS).

3 Results and discussion

3.1 Characteristics of SnOx:F film

3.1.1 Structure

Figure 1(a) shows the scanning electron micrographs of the surface and cross sectional SnOx:F films on the PET substrate prepared by ECR–MOCVD. SnOx:F film with a grain size of 40~60 nm and thickness of 250 nm was obtained at an H_2/TMT mole ratio of 1.25, fluorine-doping amount of 1.3 wt.% and deposition time of 30 min. Figure 1(b) shows the electron diffraction pattern in the cross section (Mag. 6100) of the SnOx:F films on the PET substrate. The diffraction pattern of the SnOx:F film reveals the characteristic 110, 101, 200, 211 and 301 ring patterns of the polycrystalline structure.

Figure 2 shows the X-ray diffraction pattern of the prepared SnOx:F film. The SnOx:F films were found to have a partially amorphous nano-crystalline structure. In

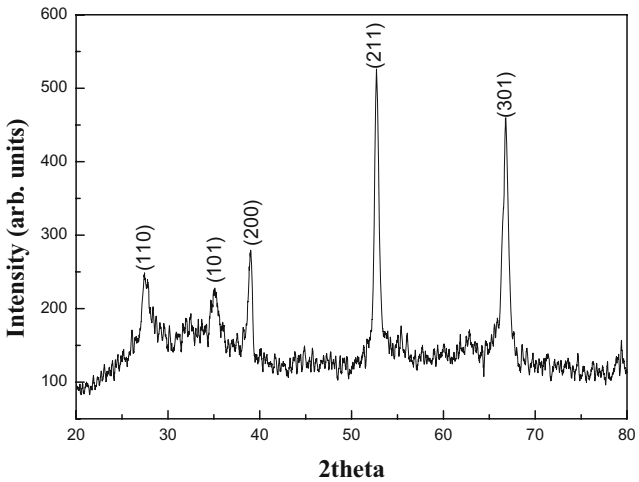


Fig. 2 X-ray diffraction pattern of optimized SnOx:F films on PET substrate prepared by ECR–MOCVD at room temperature

this work, we also found that the SnOx:F films that were prepared have (211) as their preferred orientation along with the largest crystalline size. The obtained lattice constants were found to be a=0.4749 and 0.3198 (c/a= 0.6734). The polycrystalline SnOx:F thin film having two strong preferred orientation of (211) and (301) diffraction peak, which showed good optical and electrical properties, was prepared at an H_2/TMT mole ratio of 1.25, amount of fluorine doping of 1.2 wt.% and deposition time of 30 min.

3.1.2 Optical transmittance and electrical resistivity

Figure 3 shows the relationship between the thickness and electrical resistivity for the SnOx:F film. The partial pressure of TMT, which can be determined from the bubbler pressure, was used to control the film thickness for the same deposition time. In this work, the bubbler pressure was varied from 50 to 80 Torr. The other deposition conditions were fixed as follows: an H_2/TMT mole ratio of 1.25, deposition time of 30 min and fluorine-doping amount of 1.3 wt.%. As shown in this figure, the electrical resistivity decreases with increasing thickness, while the average transmittance value remains constant, up to a thickness of 200 nm, but slowly decreases when the film thickness is further increased. Thus, the compromise between the optical transparency and the electrical properties was made on a thickness of 250 nm.

3.1.3 Composition

Figure 4 shows the AES (Auger Electron Spectroscopy) depth profiles for the SnOx:F film. The C peak observed at the initial sputtering time was due to contamination, which

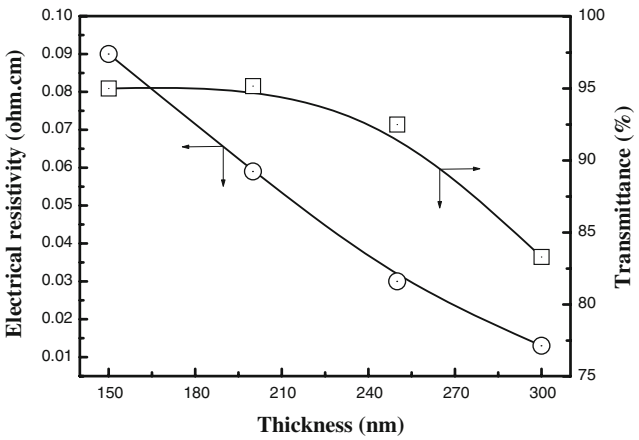


Fig. 3 Variation of the electrical resistivity and optical transmittance with the thickness of the SnOx:F thin film. The film thickness was controlled by the bubbler pressure (Torr). The deposition conditions were as follows: H_2/TMT mole ratio of 1.25, bubbler pressure of 50~80 Torr, deposition time of 30 min and fluorine-doping amount of 1.3 wt.%

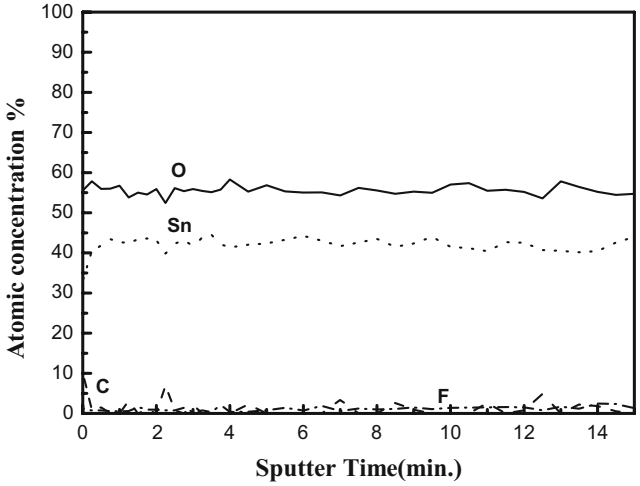


Fig. 4 AES depth profile for fluorine-doped tin oxide (SnOx:F) film on PET substrate

was probably caused by the deposition of decomposed TMT. This may affect the optical and electrical properties of the thin film. As the sputtering time is further increased, two major profiles for Sn and O are observed. The amount of F is too small to observe in the composition of the SnOx: F film. The Sn/O ratio through the film remained almost constant at 0.8 with increasing sputtering time.

In order to determine the contents of oxygen and fluorine, we employed the approximation equation (1), wherein the atomic concentration C_A (%) of an element A in a sample is given by

$$C_A\% = \left\{ \left(I_A / I_A^{\infty} \right) \Big/ \left[\sum_i \left(I_i / I_i^{\infty} \right) \right] \right\} \times 100 \qquad (1)$$

where I_A is the intensity of the Auger signal from the specimen and I_A^{∞} is that from a pure standard recorded under identical conditions. The summation was carried out for the corresponding intensity ratios from all other elements in the sample. The values for I_A^{∞} and the corresponding values of the other elements in the film, I_i^{∞}, in equation (1) were obtained from handbooks of Auger spectroscopy [13]. Table 1 shows the contents of fluorine and carbon depending on the H_2/TMT mole ratio. The amount of carbon decreases with increasing H_2/TMT mole ratio due to the higher reactivity of TMT. The highest fluorine content was observed at an H_2/TMT mole ratio of 1.25, which is closely related to the electrical resistivity of the SnOx:F thin film. The content of fluorine decreases at an H_2/TMT mole ratio of 1.5, due to the higher reactivity of hydrogen with fluorine.

3.2 Chemical bonding

The chemical bonding of the surface of the SnOx:F film prepared by ECR–CVD was analyzed by XPS. The four

Table 1 Oxygen and fluorine atomic concentration % normalized with respect to the SnOx:F films with the different H_2/TMT mole ratios.

H_2/TMT mole ratio	Electrical resistivity (Ωcm)	Optical transmittance (%)	F (%)[a]	C (%)[a]
0.75	0.033	87	0.43	0.7
1.0	0.007	88	0.75	0.5
1.25	0.005	90	1.17	0.4
1.50	0.011	80	0.96	0.3

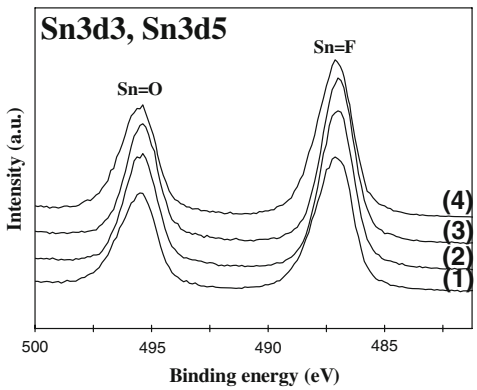
[a] The film atomic concentration% of F and C from AES is expressed in atomic concentration %: $C_A = \left\{ \left(I_A / I_A^{\infty} \right) \Big/ \left[\sum_i \left(I_i / I_i^{\infty} \right) \right] \right\} \times 100$

spectra with different H_2/TMT mole ratios for the Sn doublet 3d3 and 3d5, F1s, and C1s are shown in Fig. 5(a), (b) and (c), respectively. The components of the tin precursor, $(CH_3)_4Sn$, were incorporated into the surface structure of the films. Figure 5(a) showed the Sn doublet, 3d3 and 3d5, spectrum for the tin film deposited by ECR–MOCVD, which consisted of two distinct peaks: Sn=O (495.1 eV) and Sn=F (486.7 eV). Figure 5(b) shows the C1s spectrum for the tin film, which consisted of three distinct peaks: C=H (284.58~284.64 eV), C=F (287.0 eV), and C=O (288.60 eV). Figure 5(c) shows the F1s spectrum for the tin film, which consisted of two distinct peaks: C=F (687.3 eV) and C_9F (685.7 eV). The components having a bonding energy between 285 eV and 287 eV can be assigned to the inductive effect of the C=F bonds. They correspond to the C atoms that are indirectly bound to fluorine atoms. The F1s spectrum can be deconvoluted into two peaks, C=F and C_9=F. The peak at c.a. 685.7 eV is assigned to the C_9=F bond and the peak at 687 eV is assigned to the C=F bond [14]. The transition of the F1s peak was observed with increasing H_2/TMT mole ratio, as can be seen in Fig. 5(c).

Figure 6 shows the variation of the relative occupancy of the C=C/C=H, Sn=F/Sn=O and C/F bonds with the H_2/TMT mole ratio which was obtained from the XPS analysis by comparing the area intensity ratios corrected by the ratios of the sensitivity factors. Figure 6(a) shows that the relative ratio of C=C/C=H is the lowest at an H_2/TMT mole ratio of 1.25. Figure 6(b) shows that the occupancy of Sn=F/Sn=O is the highest at an H_2/TMT mole ratio of 1.25. Figure 6(c) shows that the lowest occupancy of C/F is observed at the same H_2/TMT ratio. These results indicate that the amount of hydrogen relative to that of TMT plays an important role in determining the surface composition of the SnOx:F thin film, which is closely related to its optical and electrical properties. The relationship between the process parameters and characteristics of the thin film will be explained in detail in the following section.

3.3 Effect of process parameters on electrical and optical properties

SnOx:F films are known as typical n-type conductive semiconductors. Their electrical resistivity and optical transmittance would be expected to increase with increasing H_2/TMT mole ratio, deposition time and fluorine doping amount. The fluorine contributes to the generation of free electrons in the film, thereby lowering the electrical



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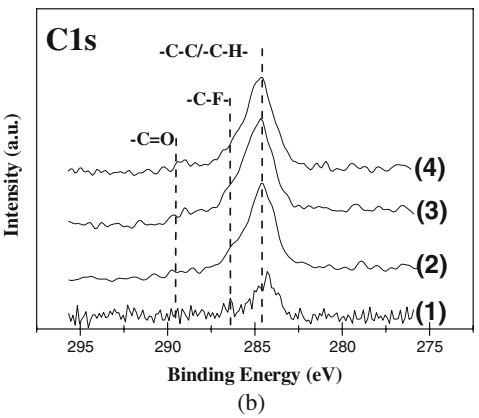

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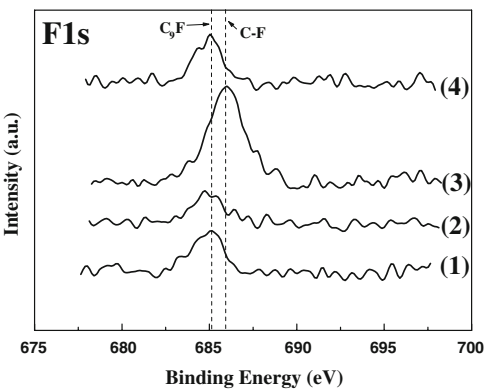
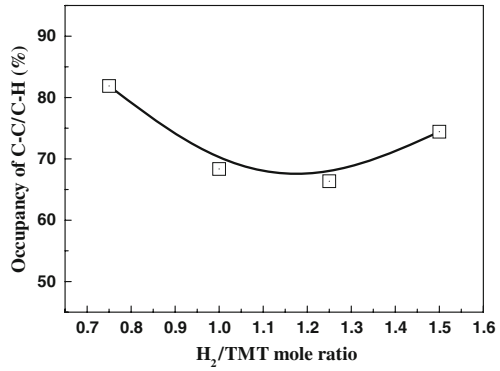


(c)

Fig. 5 (**a**) Sn doublet 3d3, 3d5, (**b**) C1s and (**c**) F1s XPS spectra obtained at the surface of the SnOx:F films. XPS spectra of SnOx:F films deposited on PET by ECR–MOCVD with H_2/TMT mole ratios of (*1*) 0.75, (*2*) 1.0, (*3*) 1.25, (*4*) 1.5



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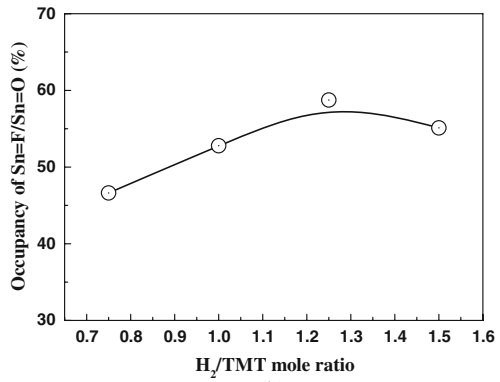

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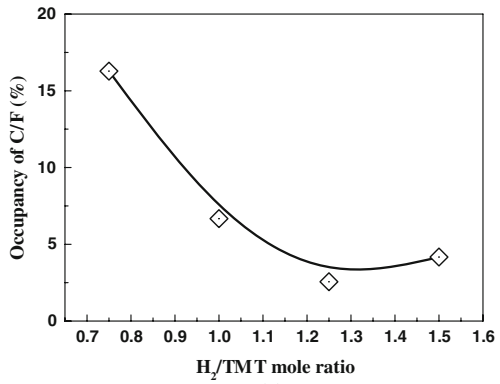
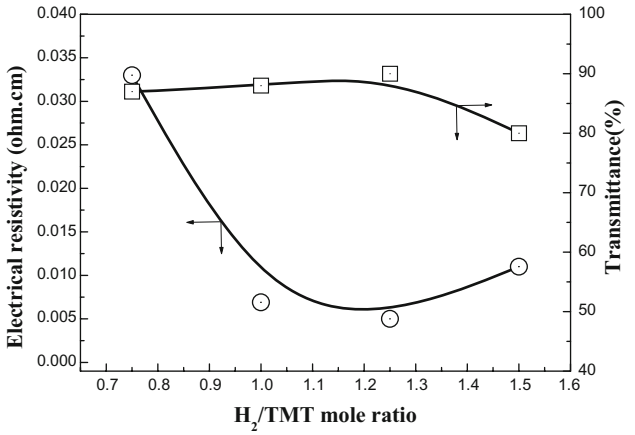


(c)

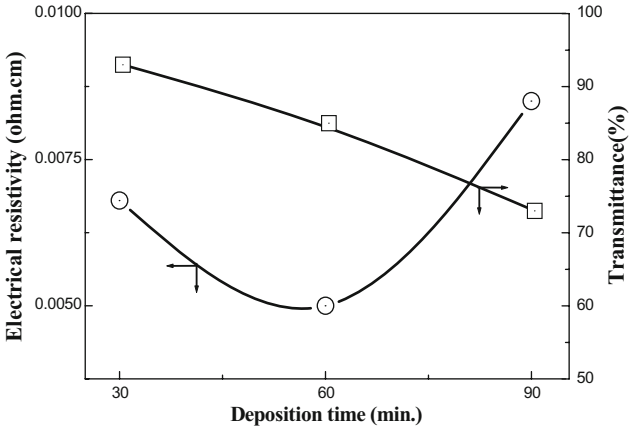
Fig. 6 (**a**) Occupancy of C=C/C=H (%), (**b**) occupancy of Sn=F/Sn=O (%) and (**c**) occupancy of C/F (%) with the change of H_2/TMT mole ratio for SnOx:F films deposited on PET by ECR–MOCVD

resistivity or reducing the grain boundary gap or activation energy of chemical bonding. The incorporation of fluorine into the tin oxide plays an important role in reducing the grain boundary gap and activation energy of chemical bonding of the tin oxide. However, for the heavily fluorine doped SnOx:F film, the electrical resistivity increases. The estimated optical transmittance values due to lattice, polar, ionized impurity, neutral impurity and grain boundary scattering are closely related to the electrical resistivity and optical transmittance properties of the SnOx:F films [15–18]. Therefore, we investigated the effects of the process parameters on the properties of the film with special attention to the H_2/TMT mole ratio, the amount of fluorine doping and deposition time.

Figure 7(a) shows the electrical resistivity and optical transmittance of the film deposited on the PET substrate in the visible range of 380–780 nm. As the H_2/TMT mole ratio increases from 0.75 to 1.25, the electrical resistivity



(a)



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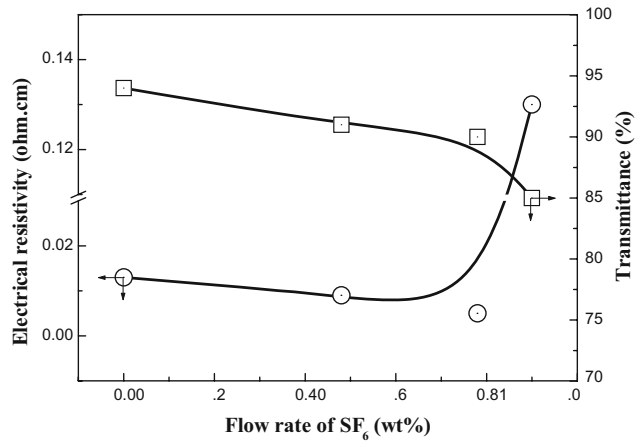

(c)

Fig. 7 Electrical and optical properties analysis of SnOx:F film prepared at (**a**) influence of H_2/TMT mole ratio, (**b**) deposition time and (**c**) flow rate of SF_6 (wt.%)

decreases from 3.3×10^{-2} to 5.0×10^{-3} Ωcm, while the transmittance remains almost constant in the range of visible wavelength. The increment of the H_2/TMT mole ratio results in an increase of the chemical bonding and composition, because the increase in the H_2/TMT mole ratio leads to an increase in the electron path and raises the possibility of inelastic collisions. The C/F mole ratio of the films decreases up to 1.25 H_2/TMT mole ratio. The reason for these results can be explained by the increase in working pressure of hydrogen in the plasma that generates of the more hydrogen ions through the inelastic collisions in the plasma. These hydrogen ions lead to the formation of stable volatile organic compounds such as CH_4, C_2H_4, C_2H_6, CO, CO_2, OH, etc., by a gas phase substitution reaction with TMT. These chemical bonding and composition, arriving at the surface with a high energy, can sufficiently import momentum to the surface atoms of the growth film. Thus, the excellent electrical resistivity and optical transmittance of the deposited film result from the formation of tightly packed columns. Figure 7(b) shows the effect of the deposition time on the electrical resistivity and optical transmittance of the SnOx:F film. As shown in the figure, the lowest electrical resistivity of 5.3×10^{-3} Ωcm was observed at a deposition time of 60 min. The average transmittance decreases with decreasing deposition time, while the lowest electrical resistivity was observed at a deposition time of 60 min. Figure 7(c) shows the effect of the flow rate of SF_6 (wt.%) on the electrical resistivity and optical transmittance of the SnOx:F film. The flow rate of SF_6 (wt.%) of the films showed that the doped film composition ranged from 0 to 0.9 wt.% which corresponds to the feeding rate of the fluorine precursor, SF_6. As shown in the figure, the electrical resistivity and transmittance decreases with increasing flow rate of SF_6 (wt.%). A sharp increase in the electrical resistivity and decrease in the transmittance were observed at an SF_6 flow rate of 0.9, probably due to the excessive formation of HF.

4 Conclusion

Fluorine-doped tin oxide films were prepared on PET substrates by ECR–MOCVD at room temperature and the effects of the process parameters on the characteristics of the films were investigated. Polycrystalline SnOx:F thin films with good optical and electrical properties having a (211) diffraction peak were prepared at an H_2/TMT mole ratio of 1.25, amount of fluorine doping of 1.2 wt.% and deposition time of 30 min. It was observed that the electrical and optical properties of the non-stoichiometric SnOx:F film were better than those of the stoichiometric film. In our experimental range, the lowest electrical resistivity of the SnO_x:F films was 5.0×10^{-3} Ωcm and their average optical transmittance and reflectance were 90% in the wavelength range of 380–780 nm at an H_2/TMT mole ratio of 1.25, fluorine-doping amount of 1.3 wt.%, and deposition time of 30 min where the lowest content of carbon was also observed.

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