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Surface characterization of sol–gel derived indium tin oxide films on glass

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Abstract. Indium tin oxide (ITO) films containing different In : Sn atomic ratios, viz. 90 : 10, 70 : 30, 50 : 50, 30 : 70, were deposited on two types of glass substrates by sol–gel spinning technique. XPS analysis of the films was done under as-received and after-sputtering conditions. The narrow spectra obtained for the Na1*s*, In3*d*, Sn3*d* and O1*s* have been discussed. Oxygen was found to exist in three chemical environments in as-received samples due to the existence of (i) environmental hydroxyl (–OH) group, (ii) crystalline ITO and (iii) amorphous ITO; but it was in two chemical environments, (ii) and (iii), after surface cleaning by sputtering. The presence of both tin metal and tin oxides was confirmed by the peak analysis of Sn3*d*. The In : Sn atomic ratio taken in the precursor sols did not change considerably in the case of developed films of low Sn content, but considerable change was observed in the films having high Sn content.

Keywords. Indium tin oxide (ITO); sol–gel film; resistivity; XPS.

1. Introduction

Indium tin oxide (ITO) coating on glass is an important item in the field of optoelectronic devices such as solar cells (Barua and Banerjee 1992), electrochromic systems, light-emitting diodes, etc for its large band gap (Ohhata *et al* 1979; Balasubramanian and Subramanyam 1989) and special optical and electrical (Frank *et al* 1981; Kostlin 1982; Biswas *et al* 2000; Cho *et al* 2000; Kim *et al* 2001) properties. These properties are greatly influenced by oxygen stoichiometry and dopant concentration. Usually in ITO, maximum free carrier concentration is obtained with the dopant concentration, 5–10 at.% Sn (Christian and Shatynski 1983; Naseem and Coutts 1986; Karasawa and Miyata 1993; Mori *et al* 2002). The crystalline bixbyite phase of In_2O_3 exists even in high concentration of Sn due to very high solid solubility of tin in In_2O_3 (Kostlin *et al* 1975). On the other hand, Parent *et al* (1992) reported that the ITO network is disordered at higher dopant concentration. Hence, it is noteworthy to carry out basic research on the bonding behaviour of different elements in ITO of relatively high dopant concentration. This knowledge can be gained by XPS study as the binding energy of the elements present in ITO would differ with change in environments. Extensive work (Kobayashi *et al* 1992; Ishida *et al* 1993; Mori *et al* 2002) on the study of surface characterization of PVD developed ITO films has been done for its wide use in thin film form, but the study on the above properties with wide variation of dopant concentration is scanty (Kulkarni and Knickerbocker 1992; Cao *et al* 1998). The present report focuses on surface characterization of ITO films deposited on soda lime silica (SLS) glass. As the sol–gel technique is cost effective and produces relatively homogeneous films (Arfsten *et al* 1984; Furusaki and Kodaira 1991; Takahashi *et al* 1992, 1997; Gallagher *et al* 1993; Cao *et al* 1998; Atashbar *et al* 1999), it can be utilized for the development of homogenous ITO films on glass of relatively large dimensions. Since the diffusion of Na^+ ion of SLS substrates occurs towards the deposited films during thermal curing, the electrical conductivity of ITO decreases resulting in decrease in efficiency of functional properties of ITO. If silica barrier layer be deposited on SLS substrate then it may inhibit the Na^+ ion diffusion in the film and the modified substrate can be used for ITO deposition. This work deals with surface characterization of sol–gel ITO films of relatively high dopant concentration, deposited on bare and silica barrier layer coated SLS glass substrates by XPS study.

2. Experimental

2.1 *Preparation of precursors*

2.1a *ITO system*: The starting materials of the precursor sols of ITO layer were hydrated stannic chloride ($SnCl_4·5H_2O$, 98% GR, Loba Chemie) and indium metal ingot (99·9%,

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Sisco Research Laboratory) derived hydrated indium nitrate. Concentration of the sols was 6 wt% equivalent In_2O_3–SnO_2 having In : Sn atomic ratios of 90 : 10, 70 : 30, 50 : 50 and 30 : 70. The sol was prepared in two steps. First, required amount of indium nitrate solution was mixed with mixed solvent (1 : 1 by volume) of 1-propanol and 2-methoxyethanol and then the required amount of acetic acid (E. Merck India Ltd. GR; In : acetic acid = 1 : 1) and acetyl acetone (*acac*) (SRL, GR; In : *acac* = 1 : 1) were added to the above solution with stirring. The second step was to dissolve the required amount of $SnCl_4·5H_2O$ in the same mixed solvent which was added to the initial solution and stirred for ~ 1 h. The final solution was aged for 16 h for coating.

2.1b *Silica system*: Precursor sol of 6 wt% equivalent SiO_2 prepared from tetraethylorthosilicate (TEOS) was used for the deposition of silica layer as barrier layer. The detailed preparative procedure of polymeric SiO_2 precursor was given in our earlier paper (Kundu *et al* 1989).

2.2 *Deposition of thin films*

2.2a *Cleaning of substrate*: Soda lime silica glass (dimension, 5 × 5 cm, 3 mm thickness) was cleaned (Atta *et al* 1990) following a number of steps. The glass substrates were first immersed in a solution of Extran pure (E. Merck India Ltd.) (2·0 vol%) in water for 1 h and then treated ultrasonically for 40 min. The substrates were then washed with distilled water several times. Ultrasonic treatment (for about 30 min) in 0·01 M HCl or HNO_3 medium was again followed. The substrates were then washed thoroughly with distilled water followed by washing with GR grade acetone (E. Merck India Ltd.), wiping carefully with Whatman lens cleaning tissue paper and subsequent air drying in a relatively dust-free room.

2.2b *Silica films*: Some of these cleaned substrates were used for the deposition of silica layer of around 200 nm thickness. Spinning technique (rate, 1200–1500 rpm) was followed for the deposition of sol layer. Next, the layer was heated at 450 ± 5°C with a soaking time of 0·5 h to transform it to oxide layer.

2.2c *ITO films*: The salt (In- and Sn-) derived indium tin oxide (ITO) coatings of different In : Sn atomic ratios (90 : 10, 70 : 30, 50 : 50 and 30 : 70) were deposited on two types of substrates: (i) soda lime silica glass (SLS), where the samples prepared from the corresponding precursors are designated as WS-1, WS-2, WS-3, WS-4 and (ii) ~ 200 nm thick SLS glass where the samples prepared from the corresponding precursors are designated as S-1, S-2, S-3, S-4, respectively. The detailed preparative procedure is given elsewhere (Biswas *et al* 2000, 2003). The coatings were annealed at 500 ± 5°C in H_2O vapour atmosphere where carrier gas was nitrogen. The annealing time was about 30 min. Indium tin oxide layers of about 100–500 nm thicknesses containing different atomic ratios of In : Sn were prepared in this way. Single operation yielded a layer of 100–150 nm physical thickness. To increase physical thickness number of operations was increased; after each operation the samples were cured at 500 ± 5°C in air with 30 min soaking. The curing was chosen at the above temperature as the softening point of soda lime silica (SLS) glass was ~ 550°C. Annealing in water vapour was carried out after attaining the requisite thickness. Only two operations were followed for bare SLS substrates while four operations were followed for silica barrier layer coated SLS substrate, because, for bare substrate there is a possibility of Na^+ ion diffusion into the film with increasing number of heating.

2.3 *Characterization*

The physical thickness of the films was measured by stylus method (Tencor's Alpha-Step 200). Crystallinity of the samples was examined with Siemens D5005 goniometer (20–70°, 0·60°/min) using nickel filtered CuK_a radiation. The electrical conductivity of the films were measured at room temperature following four-probe van der Pauw method. The X-ray photoelectronic spectroscopic (XPS) characterization was done by introducing the samples into an UHV chamber equipped with helium (He) discharge lamp for UPS, MgK_a X-ray source for XPS, heating and Ar^+ sputtering cleaning facilities. The Ar^+-sputtering was continued for 30 min maintaining a current density of 6–8 $\mu A\ cm^{-2}$ with a kinetic energy of 1 keV. The base pressure of the chamber was $6·67 \times 10^{-8}$ Pascal. For the XPS analysis the energy resolution was 0·1 eV for the MgK_a line at 1253·6 eV. The XPS study of the samples was done under two conditions: (i) as-received and (ii) after-sputtering. The XPS spectra of the elements present in the film were fitted by Voigt fit-function with corresponding FWHM and linear background. The quantitative analyses were performed by using Hartree–Slater sensitivity factors of elements for integral peak intensity with reference to Briggs and Seah (1990) and Scofield (1976). During XPS experimentation, charging was not observed on the ITO samples.

3. Results and discussion

The thickness of ITO films deposited on bare SLS glass substrate (sample nos. WS-1 to WS-4) was in the range 260–320 nm (± 25 nm), while that deposited on silica barrier layer coated SLS glass substrates (sample nos. S-1 to S-4) varied from 400 (± 25 nm) to 560 nm (± 25 nm). X-ray diffraction pattern of the deposited films shows (figure 1) broad background with relatively broad diffraction peaks indicating presence of amorphous nature along with

Table 1. Sample designation, chosen In : Sn in the precursors, nature of substrate, electrical resistivity and the evaluated In : Sn of ITO film by XPS study.

Sample designation	In : Sn in precursor sol	Nature of substrate	Resistivity (ohm.cm) $(\times 10^{-3})$	In : Sn evaluated from XPS (after sputtering)
S-1	90 : 10	Silica coated soda lime silica glass	1·5 ± 0·3	88 : 12
S-2	70 : 30	-do-	1·4 ± 0·2	87 : 13
S-3	50 : 50	-do-	3·5 ± 0·6	52 : 48
S-4	30 : 70	-do-	2700 ± 500	42 : 58
WS-1	90 : 10	Soda lime silica glass	5·0 ± 0·9	92 : 8
WS-2	70 : 30	-do-	2·3 ± 0·4	72 : 28
WS-3	50 : 50	-do-	3·9 ± 0·7	71 : 29
WS-4	30 : 70	-do-	410 ± 70	44 : 56

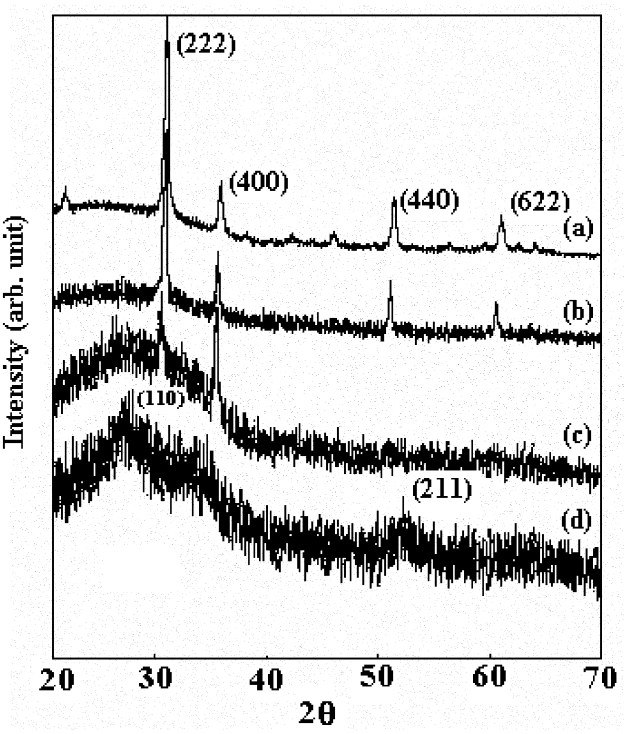


Figure 1. X-ray diffraction patterns of ITO films deposited on silica coated soda lime silica glass substrate from the precursor sols of different In : Sn ratios: (a) 90 : 10 (cubic In_2O_3 phase), (b) 70 : 30 (cubic In_2O_3 phase), (c) 50 : 50 (cubic In_2O_3 phase) and (d) 30 : 70 (cassiterite SnO_2 phase).

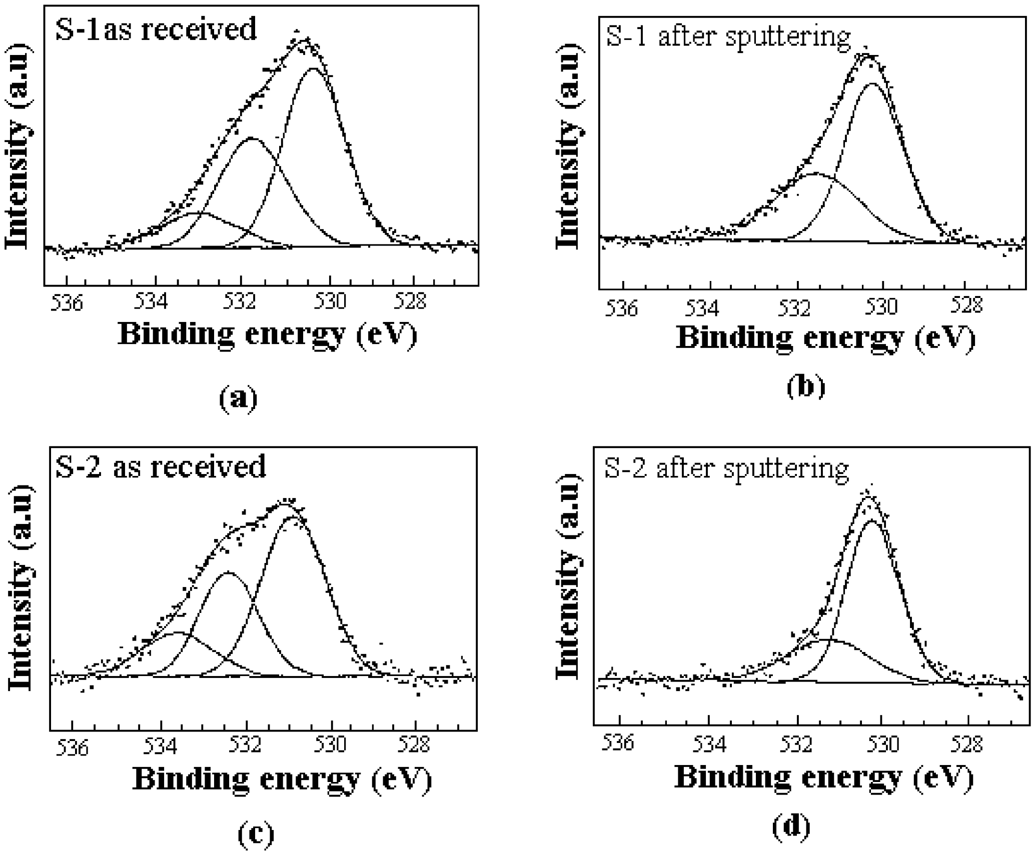
some definite crystalline phases. Although we have observed cubic indium oxide phase even for the system of In : Sn = 50 : 50, but it would be prudent to state the formation of a mixture of indium oxide and tin oxide and small amount of tin doped indium oxide has occurred as the content of tin is relatively high for the S-2 to S-4 and WS-2 to WS-4 samples. The films are electrically conducting and its resistivity (*r*) (table 1) increases with increase in Sn concentration (> 30%) possibly due to change in coordination numbers of In and Sn in ITO network. Resistivity of the S-1, S-2 and S-3 samples were relatively low with respect to those of the WS-1, WS-2, WS-3 samples and the variation of *r* with change in substrate was not much. But there was a large variation in values of *r* for S-4 and WS-4 samples although the In : Sn ratio obtained from XPS study showed almost similar composition. Kostlin *et al* (1975) reported that there are Sn ions at close proximity to each other due to incorporation of higher % of tin. At this stage there is a large possibility of reduction of Sn(IV) to Sn(II) by the free electrons generated due to the creation of oxygen vacancy which occurs during the processing of ITO films under reducing condition. Hence, the Sn(IV) ions are associated with Sn(II) by an electrostatic force. This association forms a defect complex whose average electrical charge is 3^+. Thus the associated Sn ions do not contribute to the electrical conduction (Kostlin *et al* 1975; Alam and Cameron 2002). In addition, Sn(II) or Sn(IV) forms interstitial bond with oxygen in ITO and exists as SnO or SnO_2. Accordingly, it has a valency of 2+ or 4+ respectively. The lower valence state results in a net reduction in carrier concentration since a hole is created which acts as a trap and reduces conductivity. On the other hand, predominance of the SnO_2 state means Sn^{4+} acts as an *n*-type donor releasing electrons to the conduction band.

If the above mechanism prevails in the film, then it may be presumed that the WS-4 sample has relatively high content of SnO_2 and relatively less content of SnO assuming the concentration of the defect complex in WS-4 was same as in S-4. The relatively high content of SnO_2 in WS-4 results in higher conductivity than that of S-4 sample.

The change in coordination number of In and Sn was also observed by EXAFS study of ITO with maximum Sn content, 39% (Parent *et al* 1992). The knowledge of contribution of oxygen to In and Sn may be visualized by XPS experiments of the samples as the binding energy of oxygen will be different with change in environments such as crystalline or amorphous.

XPS experiments were carried out with the as-received samples as well as after cleaning the film surface by Ar^+ sputtering and the obtained data were compared. The wide scan spectra (from 200–600 eV, not shown here) exhibit the peaks at ~ 530·0, 493·0, 486·0, 452·0, 444·0 and 285·0 eV for O1*s*, Sn3$d_{3/2}$, Sn3$d_{5/2}$, In3$d_{3/2}$, In3$d_{5/2}$ and C1*s*, respectively. In addition, the XPS spectra from 1050–1150 eV (not shown here) exhibit peak at ~ 1078 eV due to Na1*s*. Composition of ITO layer for a specific sample was determined from the area intensities of the XPS peaks appearing for different elements. It was observed that the atomic ratios of In : Sn of the films obtained by this analysis differed (table 1) in some cases from those taken in the precursors.

The XPS peaks in the regions of O1*s* measured at two different conditions exhibit the existence of oxygen in different environments in ITO. Under as-received condition the peaks at around 530·5 eV, 531·5 eV and 532·5 eV for O1*s* suggested the existence of three different environments while the peak at 532·5 eV disappeared when the surface was cleaned (figure 2, table 2). The peak at ~ 532·5 eV may be attributed due to the oxygen of free hydroxyl groups which were etched out by sputtering. The existence of this oxygen is possibly due to environmental moisture trapped in the film surface. In addition, contamination of carbon from environment cannot be ruled out. As hydrogen atoms have higher electronegativity than indium atoms, oxygen atoms in the In–O–H species are less negatively charged than those in indium oxide where oxygen atoms are bound to six indium atoms. This implies that O1*s* binding energy in In–OH species is higher than that in indium oxide (Ishida *et al* 1993). The removal of the above peak at around 532·5 eV after Ar^+ ion etching implies low density of the films. This is also evident from the remarkable change of O_{tot}/In ratio after sputtering (table 3). The peak at around 530·5 eV may be assigned as due to lattice oxygen in lattice crystal (Ishida *et al* 1993) and the other peak at around 531·5 eV may be due to the oxygen atoms in an amorphous ITO phase. Thus, it can be inferred that the films contain both crystalline and amorphous phases. Fan and Goodenough (1977) also suggested that the peak, ~ 531·5 eV, might be due to O^{2-} in an oxygen deficient region. In most of the cases the ratio of intensity of ~ 530·5 eV to ~ 531·5 eV peaks after sputtering condition was relatively high (table 2) with respect to that under as-received condition. This may be due to the condensation of two –OH groups of two In–OH entities producing relatively high crystalline environment in ITO.



(a) (b) (c) (d)

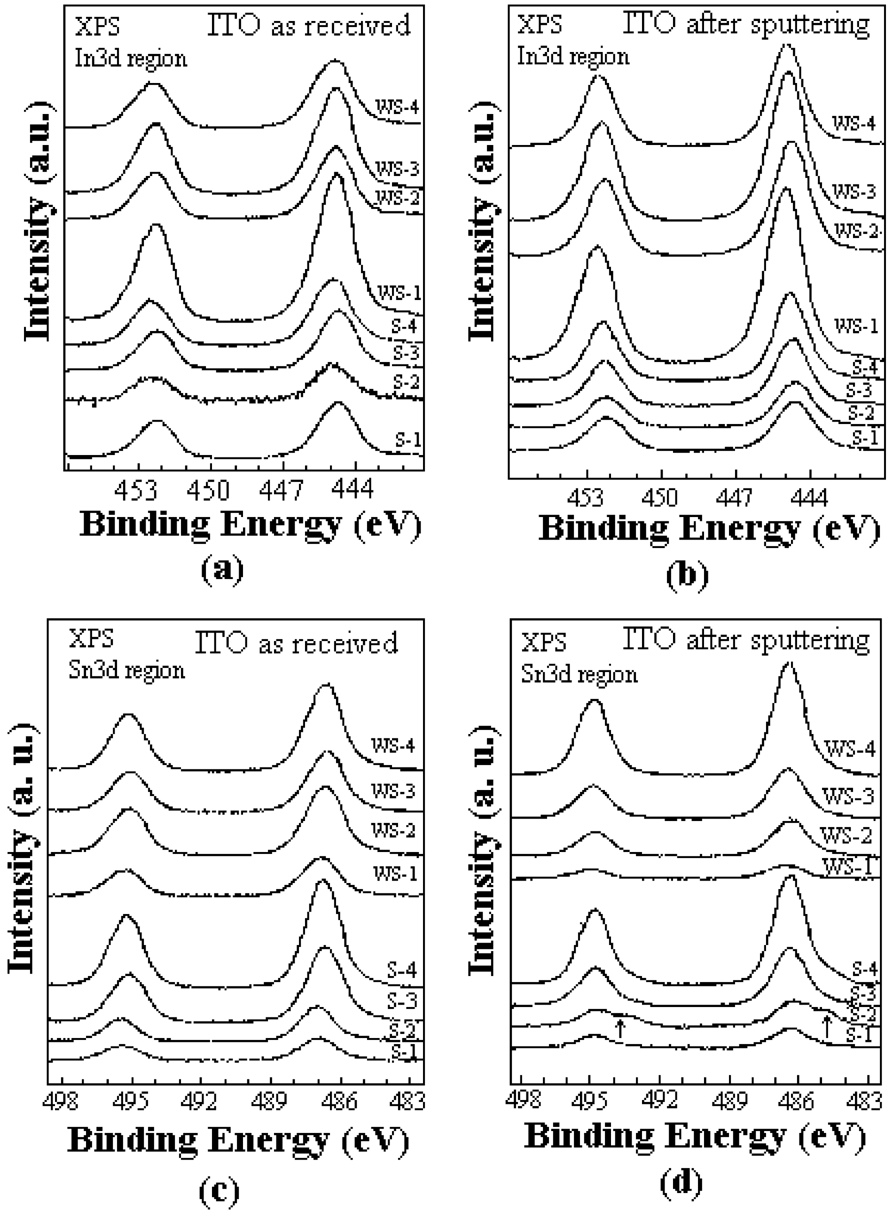
Figure 2. Results of peak analysis of O1*s* narrow XPS spectra measured in two conditions before (as-received) and after sputter (cleaned) treatment (a), (b) for S-1 (In : Sn = 90 : 10) and (c), (d) for S-2 (In : Sn = 70 : 30) samples. The original spectra (points) and fitting curves (lines) are shown.

Table 2. The XPS peaks of O1*s* due to its existence in different environments in ITO films, their full widths at half-maximum (FWHM) and the intensity ratio of oxygens present in crystalline (~ 530·5 eV) and amorphous (531·5 eV) states.

	Experimental condition			
	As-received		After sputtering	
Sample no.	Peak value (eV) (relative peak intensity)	FWHM (eV)	Peak value (eV) (relative peak intensity)	FWHM (eV)
S-1	530·31	1·67	530·17	1·63
	531·70	1·90	531·43	2·61
	(1·7 : 1·0)		(2·0 : 1·0)	
	532·90	2·32		
S-2	530·83	1·76	530·21	1·51
	532·42	1·75	531·54	2·03
	(1·4 : 1·0)		(1·4 : 1·0)	
	533·89	1·57		
S-3	530·14	1·55	530·18	1·46
	531·00	1·72	530·79	2·56
	(3·2 : 1·0)		(4·6 : 1·0)	
	532·18	2·55		
S-4	530·51	1·69	530·22	1·41
	531·96	1·49	530·91	2·67
	(2·7 : 1·0)		(2·2 : 1·0)	
	533·04	1·93		
WS-1	530·23	1·52	530·30	1·50
	531·27	1·67	531·50	2·10
	(3·1 : 1·0)		(3·7 : 1·0)	
	532·13	2·31		
WS-2	530·27	1·61	530·11	1·51
	531·80	1·81	531·45	1·80
	(2·6 : 1·0)		(5·6 : 1·0)	
	533·37	2·02		
WS-3	–	–	530·21	1·37
			530·74	2·59
			(2·1 : 1·0)	
WS-4	530·33	1·61	530·21	1·40
	531·52	2·10	530·63	2·28
	(1·0 : 3·2)		(3·6 : 1·0)	
	532·21	2·93		

Table 3. Ratios of oxygen (O) to indium (In) at different environments of oxygen present in ITO layers determined from the area intensities of XPS spectra in the regions of O1*s* and In3*d*.

		After-sputtering condition		
Sample no.	O_{tot}/In (calc.)	$O_{\sim 530\cdot 5}$/In (%)	$O_{\sim 531\cdot 5}$/In (%)	O_{tot}/In
S-1	1·71	1·00	0·78	1·78
		(56)	(44)	
S-2	2·32	1·63	0·45	2·08
		(78)	(22)	
S-3	3·44	1·28	1·10	2·38
		(54)	(46)	
S-4	6·02	1·71	0·70	2·41
		(71)	(29)	
WS-1	1·71	1·03	0·39	1·42
		(86)	(14)	
WS-2	2·32	1·22	0·29	1·51
		(81)	(19)	
WS-3	3·44	0·83	0·73	1·56
		(53)	(47)	
WS-4	6·02	1·83	0·83	2·66
		(69)	(31)	



(a) (b) (c) (d)

Figure 3. In3*d* and Sn3*d* XPS narrow spectra of all samples before (a), (c) and after (b), (d) sputtering; the arrows at 493·13 eV and 484·71 eV indicate the peak position for BE of Sn3$d_{3/2}$ and Sn3$d_{5/2}$, respectively due to SnO/Sn.

In the case of as-received samples (S-1 and S-2) deposited on barrier silica layer the binding energy (BE) for O1*s* of amorphous and crystalline states of ITOs has been increased by 0·72 and 0·52 eV, respectively with increase of Sn content from 10–30%. This positive shift of BE implies substitution of In atom by Sn in In_2O_3 network resulting in In–O–Sn linkage. The increment in BE is due to more covalent character of Sn–O bond because of relatively high polarization effect in Sn–O bond than in In–O bond. The higher polarization of Sn–O is caused by higher charge density in Sn^{4+}. With further increase in Sn content (50%, S-3), the corresponding BE decreased by 1·42 eV and 0·69 eV in the amorphous and crystalline states, respectively; this behaviour may be caused by the non-formation of In–O–Sn linkage favouring formation of mixed oxides of In_2O_3 and SnO_2. On further increase in Sn content (70%), only initial behaviour was observed although casseterite SnO_2 phase with more amorphous nature was the main crystalline phase. On the contrary, crystalline state remains constant even up to 70% Sn of ITO on bare glass. The trend of non-formation of In–O–Sn linkage is present in the WS sample of > 30% Sn. In the case of cleaned surface, the crystalline state was constant even up to 70% Sn indicating In–O–Sn linkage was fixed. On the other hand, the linkage deteriorates in the case of amorphous state with increasing tin content as evident from the negative shift (0·63–0·75 eV) of binding energy for O1*s*. Similar behaviour was obtained for ITO films coated on bare substrate.

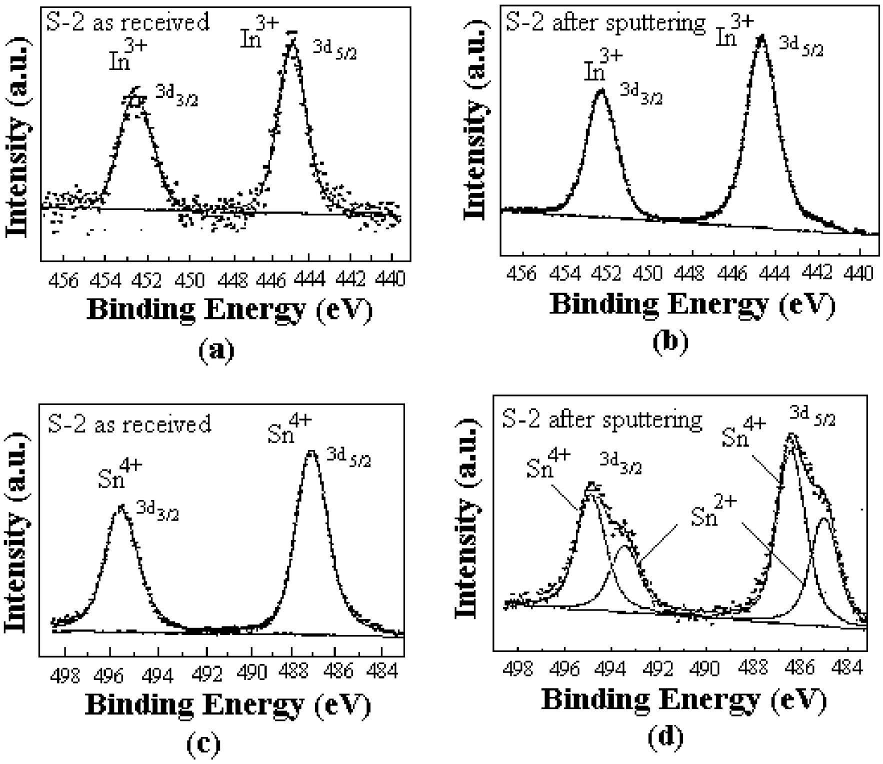


Figure 4. Peak fitting results of In3*d* and Sn3*d* narrow XPS spectra of S-2 (In : Sn = 70 : 30) sample before (a), (c) and after (b), (d) sputter treatment. After sputtering two Sn3*d* doublets for Sn^{4+} and metal Sn/Sn^{2+} species are resolved.

Table 3 shows the ratios of the amount of total oxygen to that of indium in ITO films along with the contribution of oxygen to indium at different environments. These ratios were determined from the area intensities of the In3$d_{5/2}$ and O1*s* peaks. The O_{tot}/In ratio maintains tentatively the increasing order as followed in the case of precursor sols.

Figures 3a and b show XPS spectra of ITO films in the In3*d* region measured under as-received and after-sputtering conditions, respectively. In each case, the intensities of WS-1–WS-4 samples were relatively high with respect to those of S-1–S-4 samples. Two peaks were observed at ~ 452 eV and ~ 444 eV due to In3$d_{3/2}$ and In3$d_{5/2}$, respectively with respective FWHM being in the range 1·54–1·91 eV and 1·54–1·93 eV. In the case of bare glass substrate, the peak intensity due to In3*d* decreased with decrease in In content, but the opposite effect was observed in S-1–S-4 samples.

Figures 3c and d show XPS spectra in the Sn3*d* region for ITO films recorded at two conditions with almost similar spectral feature. Two peaks were observed at ~ 495 eV and ~ 486 eV due to Sn3$d_{3/2}$ and Sn3$d_{5/2}$, respectively. Intensity of the peaks increased with increase in Sn content. In this case, deposition of barrier layer (S-1–S-4) did not change the peak intensities significantly but an inflexion was observed for Sn3$d_{5/2}$ in S-2 sample after sputtering.

Figures 4a and b show typical well resolved XPS spectra of indium in the In3*d* region recorded under as-received and sputtering conditions. The In3$d_{3/2}$ and In3$d_{5/2}$ were observed at 452·47 eV and 444·91 eV with FWHM of 1·83 eV and 1·78 eV, respectively under as-received condition. These values were close to that (2·0 eV) of vacuum evaporated ITO (Fan and Goodenough 1977) of In : Sn = 95 : 05. After sputtering, the peaks for the two *d*-states appeared almost in the same positions with separation of energies remaining almost constant. But, FWHM decreased from 1·83 to 1·54 eV for In3$d_{3/2}$ and from 1·78 to 1·54 eV for In3$d_{5/2}$ with increasing Sn contents (not shown here).

Figures 4c and d show typical well resolved XPS spectra of tin in the Sn3*d* region recorded under as-received and sputtering conditions. The peak analysis of typical S-2 sample exhibited Sn3$d_{3/2}$ and Sn3$d_{5/2}$ of Sn^{4+} in SnO_2 at 494·70 eV and 486·24 eV, respectively along with two additional peaks at 493·13 eV and 484·71 eV. These two additional peaks are due to the presence of Sn metal or Sn^{2+} (Ishida *et al* 1993; Yamaguchi *et al* 2004; Pujilaksono *et al* 2005) as reduction of Sn^{4+} by sputtering is not unlikely as oxygen may be removed from the surface during Ar^{+} sputtering. Their full widths at half-maximum (FWHM) also suggest the existence of Sn metal or Sn^{2+} of SnO in the films. For the other films (S-1, S-3, S-4, WS-1, WS-2, WS-3 and WS-4), its existence could not be resolved.

The diffusion character of sodium ion from the bare as well as from the barrier layer (silica) coated soda lime silica glass substrate was also analysed by XPS. Sodium content in the modified substrate decreased by the application of silica layer on SLS substrate as evident from the peak analysis due to Na1*s* (BE, ~ 1078 eV) in the typical sample, WS-1 (Na, 4%) and S-1 (Na, 3%). This implies that the application of barrier layer of 200 nm thickness could not inhibit the diffusion of sodium ion into the film significantly. However, the barrier layer inhibited the diffusion of Na^+ in ITO to some extent as evident from the decrease in electrical resistivity of ITO coatings (table 1) having cubic crystalline phase.

4. Conclusions

Indium tin oxide (ITO) films with wide variation of Sn content (10%, 30%, 50% and 70%) were deposited on bare as well as on barrier layer (SiO_2) coated soda lime silica glass, and XPS studies of the films were done to understand the behaviour of In–O–Sn linkage in amorphous and crystalline states. Oxygen was found to exist in three chemical environments under as-received condition while it was in two chemical environments in the case of after-sputtering condition. With increasing Sn content (> 30%), the In–O–Sn linkage is not favoured resulting in the disordered nature of the species. The FWHM of $In3d_{3/2}$ and $In3d_{5/2}$ were relatively less with respect to those values usually observed for In : Sn = 95 : 05. This discrepancy is possibly due to the large variation of Sn content in the film. For a specific chosen composition, In : Sn = 70 : 30, Sn metal/SnO was found to exist along with SnO_2 if the films are sputtered. Application of ITO on silica barrier layer shows relatively low electrical resistivity due to inhibition of Na^+ ion diffusion but this was not visualized by XPS study possibly due to low thickness of silica layer (around 200 nm).

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References

Alam M J and Cameron D C 2002 *Thin Solid Films* **420–421** 76

Arfsten N J, Kaufmann R and Dislich H 1984 *Ultrastructure processing of ceramics, glasses and composites* (eds) L L Hench and D R Ulrich (New York: John Wiley & Sons) p. 189

Atashbar M Z, Gong B, Sun H T, Wlodarski W and Lamb R 1999 *Thin Solid Films* **354** 222

Atta A K, Biswas P K and Ganguli D 1990 *J. Non-Cryst. Solids* **125** 202

Balasubramanian N and Subramanyam A 1989 *J. Phys. D: Appl. Phys.* **22** 206

Barua A K and Banerjee R 1992 *New materials* (eds) S K Joshi *et al* (New Delhi: Narosa Publishing House) p. 96

Biswas P K *et al* 2000 *Photonics-2000* (eds) S K Lahiri *et al* (New Delhi: Allied Publishers Limited) **2** p. 636

Biswas P K, De A, Pramanik N C, Chakraborty P K, Ortner K, Hock V and Korder S 2003 *Mater. Lett.* **57** 2326

Briggs D and Seah M P 1990 *Practical surface analysis* (New York: John Wiley & Sons) **1**

Cao X, Cao L, Yao W and Ye X 1998 *Thin Solid Films* **317** 443

Cho J-S, Koh S-K and Yoon K H 2000 *J. Electrochem. Soc.* **147** 1065

Christian K D J and Shatynski S R 1983 *Thin Solid Films* **108** 319

Fan J C C and Goodenough J B 1977 *J. Appl. Phys.* **48** 3524

Frank G, Kauer E and Kostlin H 1981 *Thin Solid Films* **77** 107

Furusaki T and Kodaira K 1991 *High performance ceramic films and coatings* (ed.) P Vincenzini (Amsterdam: Elsevier Science Publishers) p. 241

Gallagher D, Scanlan F, Houriet R, Mathieu H J and Ring T A 1993 *J. Mater. Res.* **8** 3135

Ishida T, Kobayashi H and Nakato Y 1993 *J. Appl. Phys.* **73** 4344

Karasawa T and Miyata Y 1993 *Thin Solid Films* **223** 135

Kim H, Horwitz J S, Kushto G P, Qadri S B, Kafafi Z H and Chrisey D B 2001 *Appl. Phys. Lett.* **78** 1050

Kobayashi H, Ishida T, Nakamura K, Nakato Y and Tsubomura H 1992 *J. Appl. Phys.* **72** 5288

Kostlin H 1982 *Festkorperprobleme* **XXII** 229

Kostlin H, Jost R and Lems W 1975 *Phys. Status Solidi* **A29** 87

Kulkarni A K and Knickerbocker S A 1992 *Thin Solid Films* **220** 321

Kundu D, Biswas P K and Ganguli D 1989 *J. Non-Cryst. Solids* **110** 16

Mori N, Ooki S, Masubuchi N, Tanaka A, Kogoma M and Ito T 2002 *Thin Solid Films* **411** 6

Naseem S and Coutts T J 1986 *Thin Solid Films* **138** 65

Ohhata Y, Shinoki I and Yoshida S 1979 *Thin Solid Films* **59** 255

Parent Ph, Dexpert H and Tourillon G 1992 *J. Electrochem. Soc.* **139** 276, 282

Pujilaksono B, Klement U, Nyborg L, Jelvestam U, Hill S and Burgard D 2005 *Mater. Charact.* **54** 1

Scofield J H 1976 *J. Electron Spectrosc. & Rel. Phenom.* **8** 129

Takahashi Y, Hayashi H and Ohya Y 1992 *Mater. Res. Soc. Symp. Proc.* **271** 401

Takahashi Y, Okada S, Tahar R B H, Nakano K, Ban T and Ohya Y 1997 *J. Non-Cryst. Solids* **218** 129

Yamaguchi M, Ektessabi A I, Nomura H and Yasui N 2004 *Thin Solid Films* **447–448** 115