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Effect of annealing parameters on thermal emissivity of sol - gel derived ITO films on glass

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ABSTRACT

Tin doped indium oxide (ITO) thin film was deposited on sodalime silica glass substrate by sol-gel dipping technique. Three different concentrations, 6, 8 and 10 wt% equivalent mixed In_2O_3 and SnO_2 maintaining In : Sn = 90 : 10 atomic ratio were prepared starting from inorganic salt precursor. Total thermal emissivity of the deposited films in wavelength range 0.25-18μm were measured by Integrating sphere method. For films derived from 6 wt % sol emissivity decreases from 0.91 to 0.61 after four deposition steps, whereas for 8 and 10 wt % sol the decrease were from 0.91 to 0.59 and from 0.88 to 0.16 respectively after three layer deposition. Instead of increasing physical thickness, emissivity could be lowered by simply optimizing the annealing atmosphere and time. Reducing atmosphere in this regard proved to be fruitful while annealing time of 3.5 h caused a significant decrease of thermal emissivity value.

KEYWORDS

ITO;
Thin film;
Thermal emissivity;
Annealing time.

INTRODUCTION

Transparent conducting oxides or more popularly known as TCOs are one of the most essential building materials nowadays for its heat reflecting behaviour without losing visible transparency when deposited as thin film form on window glass[1-5]. Such low–ε window glass (ε = thermal emissivity) has great impact to energy savings[6] of modern development as the present rate of energy consumption is alarming in view of the rapid depletion of existing conventional resources. Among a wide variety of TCO materials such as tin doped indium tin oxide (ITO)[7], antimony doped tin oxide[8], cadmium stannate[9], aluminium doped zinc oxide[10] etc, ITO is most popular. Although there are several conventional chemical and physical deposition techniques for ITO thin films but the sol–gel processing is a unique one for deposition of homogeneous films on relatively large substrate in cost effective way and for easy tailoring of dopant level[11]. It has been observed that optical and electrical properties of sol–gel ITO films depend on the crystallization behaviour. Again, annealing temperature, time and atmosphere play important roles in grain growth of ITO film material[12-14]. It is a common practice to deposit films of relatively high thickness (0.3 to 0.5 μm) to achieve desired property without improving the crystallization and / or grain growth of the deposited films. But, enhancement in the physical thickness of the films inevitably results surface inhomogeneity and loss of visible transmittance. Thus, in the present work thrust has been given to improve the crystallization of the deposited ITO films by optimizing various annealing parameters, mostly, annealing atmosphere and time. Moreover, the films were characterized by measuring thermal emmisivity values which is relatively less reported[15, 16] in the available literature.

EXPERIMENTAL

Preparation of precursor

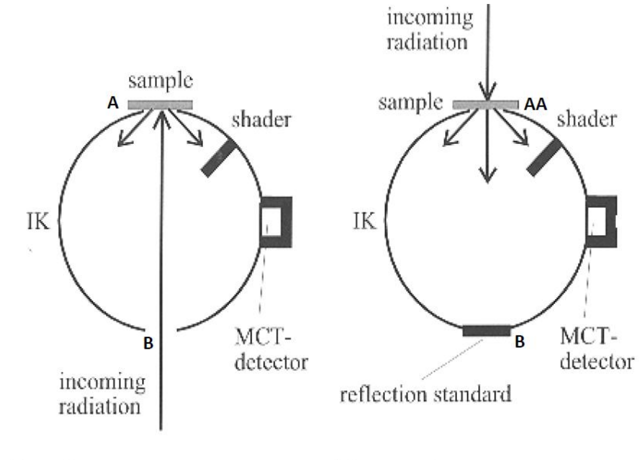
The starting materials of the precursor sols of ITO layers were indium metal ingots (99.9%, Sisco Research Laboratory) and hydrated stannic chloride ($SnCl_4$,$5H_2O$, 98% GR, Loba Chemie). Indium nitrate salt was prepared by dissolving indium metal in nitric acid to form indium nitrate. Excess nitric acid was evaporated off and liberated indium nitrate crystals were dissolved in measured amount of water. Sols corresponding to 6, 8 and 10 wt.% equivalent In_2O_3–SnO_2 maintaining In : Sn atomic ratios as 90 : 10 were prepared by mixing required amount of indium nitrate solution with few ml of equimolar solvent mixture of 1- propanol (for synthesis, E Merck India Ltd.) and 2 – methoxy ethanol (for synthesis, s. d. fine chem. Ltd.). The solution was stirred for 10 min. Then, required amount of acetylacetone (Extrapure AR, Sisco Research Laboratory Pvt. Ltd, India) (In : acetylacetone = 1 : 1, by mole) was mixed with the solution and the solution was stirred for 15 min. Next required amount of acetic acid (GR, E Merck India Ltd.) (In : acetic acid = 1 : 1, by mole) was mixed with the same solution. Both acetyl acetone and acetic acid are used as complexing agent. After 15 mins of stirring required amount of $SnCl_4$, $5H_2O$ (98% GR, Loba Chemie) was dissolved in the same mixed solvent and added to the solution of indium nitrate. Concentration of the solution was maintained by further addition of required amount of solvent mixture which was stirred for 1 h more. The solution was aged for 16 h for coating.

Deposition of ITO films

Soda lime silica (SLS) glass substrate (dimensions: 75 mm x 25 mm x 3 mm) was cleaned ultrasonically for 15 min in an aqueous Extran solution (2% v/v) followed by further ultrasonication for 15 min in distilled water. The substrates were then thoroughly washed with water followed by acetone and dried thereafter. Ultrasonically cleaned glass substrates are dipped into the prepared precursor sol and withdrawn at a speed of 10cm / min. The green coating was cured in air oven at ~500^{o}C for ½ h. The process was repeated several times to increase the physical thickness of the films. After final deposition the films were annealed under different annealing conditions.

CHARACTERIZATION

The hemispherical transmittance (T_h) and hemispherical reflectance (R_h) of the coated glass was determined at ambient temperature by the integrating sphere (IS) method. Two different equipments, Perkin Elmer λ9 UV-VIS-NIR double beam spectrophotometer, λ range, 0.18-3.2 μm and Brucker 66 evaccuable FTIR spectrometer, λ range, 1.40 – 500 μm (7000 - 20 cm^{-1}), each equipped with an integrating sphere, have been used for the measurement of optical spectra in the UV-VIS-NIR and MID-IR regions from 0.25 to 18 μm. The FTIR is equipped with KBr beam splitter, KBr windows and MCT (mercury cadmium telluride) detector. The internal surface of the integrating sphere (IS) is coated with a high reflecting sheath, which reflects the radiation diffusely. Barium sulphate and gold are the coated materials in the IS to be used as high reflecting sheath taken as the standard ones for the measurements of spectral density in the UV – Visible – NIR and MIR regions respectively. The IS has two apertures Figure 1. For measuring reflectance, the sample is placed at one aperture (position A) while the incoming radiation is passed through the aperture B and reflected from the sample. In the case of measuring transmittance the incoming radiation is passed through the same aperture A where the sample has been placed and the aperture B is kept closed by a reflection standard.



(a) reflectance measurement (b) transmittance measurement

Figure 1:Measurement set up with IS (integrating sphere)(a) measurement of the hemispherical reflectance and (b) measurement of the hemispherical transmittance

The hemispherical emittance (ε, radiation under investigation is contained in a hemisphere above the radiating surface) was calculated from the eqn. (1)

$$\varepsilon(\lambda, \theta=0°, T=T_{amb}) = 1 - R_h(\lambda, \theta=0°, T=T_{amb}) - T_h(\lambda, \theta=0°, T=T_{amb}) \quad (1)$$

Where é = angle of incidence, T = temperature in Kelvin, R_h and T_h are hemispherical reflectance and transmittance respectively.

For non-transparent samples in the blackbody radiation region at ambient temperature (5.0 μm to 50 μm) $T_h = 0$ and then the hemispherical emittance, $\varepsilon_{,}$ can be calculated from equation (2).

$$\varepsilon(\lambda, \theta=0°, T=T_{amb}) = 1 - R_h(\lambda, \theta=0°, T=T_{amb}) \quad (2)$$

As the window glass is not transparent in the infrared region[17] Figure 2, the eqn. (2) has been used in an Easy plot program to evaluate total thermal emissivity by integrating all hemispherical emittance values from the plot of R_h and T_h in the wavelength range 0.25-18μm.

RESULTS AND DISCUSSION

TABLE 1 shows total thermal emissivity values of ITO coatings deposited on SLS glass substrate by dipping technique and derived from 6, 8 and 10 wt% of mixed In_2O_3 and SnO_2 precursor sol maintaining In : Sn = 90 : 10 atomic ratio. After final deposition each film was cured in O_2 upto 300°C and from

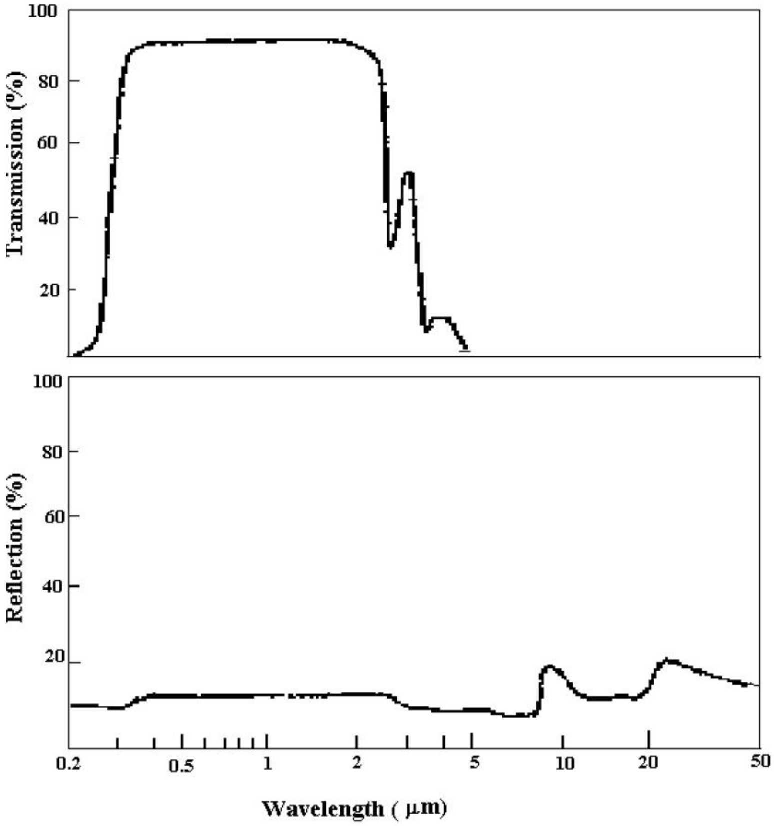


Figure 2 : Transmission and reflection spectra of soda lime silica (SLS) glass in the UV-VIS-NIR-IR region

TABLE 1 : Sample number, concentration of precursor sol, number of coating operations, total emissivity and surface nature of the ITO films (In : Sn = 90 : 10) deposited on SLS glass

Sample No.	Wt% equivalent of mixed oxide	Number of coating operation	Total thermal emissivity (? $_{20}{}^{o}{}_{C}$)	Nature of surface as observed in naked eye
ITA1	6	1	0.91	Homogeneous
ITA2	6	2	0.86	Homogeneous
ITA3	6	3	0.83	Homogeneous
ITA4	6	4	0.61	Homogeneous
ITB1	8	1	0.91	Homogeneous
ITB2	8	2	0.80	Homogeneous
ITB3	8	3	0.59	Homogeneous
ITB4	8	4	0.65	Inhomogeneous
ITC1	10	1	0.88	Homogeneous
ITC2	10	2	0.79	Homogeneous
ITC3	10	3	0.16 – 0.49$^{\#}$	Inhomogeneous
ITC4	10	4	0.21– 0.26$^{\#}$	Inhomogeneous

 # emissivity values vary within a range.

300°C to 500°C in reducing atmosphere of (Ar + H_2). Next, the films were kept in the reducing atmosphere at 500°C for ½ h. Initial curing in O_2 atmosphere helps in oxide formation whereas reducing atmosphere is necessary for creating oxygen vacancy in the host oxide. It is well known that anion or oxygen vacancy may be inherent as well as can be created under highly reducing condition. Each oxygen vacancy 17, 18] results in occurrence of two electrons of the oxygen ion left in the crystal as described in equations 3 and 4 using KrÖger-Vink (K-V) notation.

$$\mathbf{In_2O_3 \rightarrow In_2O_{3-x}(V_O^{\cdot\cdot})_x\ e'\ _{2x}} \qquad (3)$$

$$\mathbf{{}_O{}^x \rightarrow ½\ O_2\ (g) + V_O^{\cdot\cdot} + 2e'} \qquad (4)$$

Where $V_O^{\cdot\cdot}$ denotes doubly charged oxygen vacancy and e' denotes electron which are needed for charge neutrality on a macroscopic scale.

These electrons may be localized or one or both of them may have enough excitation energy to move away from the vacancy leaving an effective positive charge to the vacant position. Thus creation of oxygen vacancy enhances carrier concentration or in other words, reduces the specific resistance of the materials, which in turn decreases the thermal emissivity as depicted in equation 5[19, 20].

$$\boldsymbol{\varepsilon = 1 - R = 4\ (\pi \varepsilon_o C_o \rho\ /\lambda)^{1/2}} \qquad (5)$$

Where ε_o being the permittivity of free space, C_o denotes velocity of light, ⇧ is specific resistance and R being the reflection at wavelength λ.

In the process of making one or more electrons available for conduction the positively charged vacancy becomes an electron-trapping site. Hence, too much anion vacancy must be avoided for conduction to be effective. Therefore, optimization of annealing atmosphere and time is necessary.

Total thermal emissivity of the samples (TABLE 1) clearly shows a steady decrease with increasing number of coating operation (i.e. increasing physical thickness) of the film Figure 3. Although this is the normal trend but few exceptions are there. Beyond third operation films deposited from 8 and 10 wt% precursor sol (ITB4 and ITC4 respectively) showed an unusual increase in the emissivity values which may be attributed to the inhomogeneity of the films because of much higher physical thickness. As mentioned in TABLE 1, emissivity values for the samples ITC3 and ITC4 are different at different position of the films due to inhomogeneity although in the plot Figure 3 the minimum value has been considered. The above findings once again established the requirement for optimization of annealing parameters so that a desirable thermal emissivity value can be achieved for a homogeneous film of relatively low physical thickness.

As mentioned earlier that both oxidising and

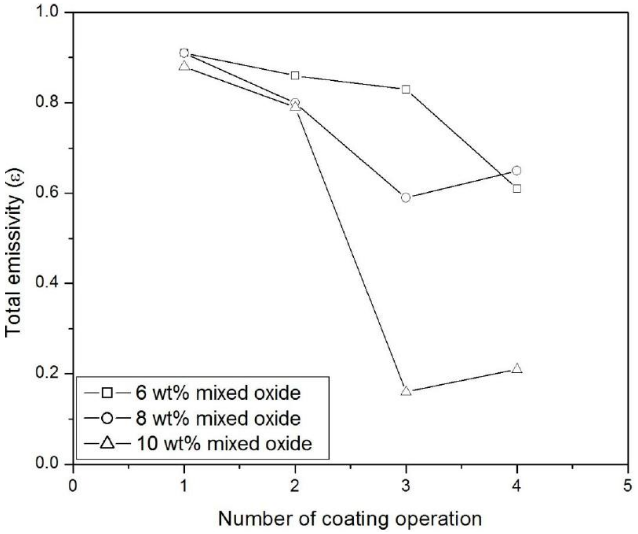


Figure 3 : Variation of total emissivity of ITO filmswith number of coating operation

reducing atmosphere are necessary during annealing treatment of the films for oxide formation and oxygen vacancy generation respectively, therefore a balance between these two are required at optimized condition. For this purpose sample ITB4 are cut into four pieces and each of them were re-annealed at different annealing conditions TABLE 2.

It is evident from TABLE 2 that emissivity of all four pieces of ITB4 decreased further from its original value of 0.65 TABLE 1 when they are re-annealed. But, most significant decrease happened in case of piece no. 2 (ε = 0.29) which was re-annealed in reducing atmosphere for 3.5h. But emissivity value is not that low for piece no. 3(ε = 0.32) which was re-annealed in the same reducing atmosphere for 7h. This might be due to development of too much of anion vacancy that act as electron trapping site resulting hindered conduction. On the other hand overheating even in absence of reducing atmosphere (piece no.1; ε = 0.61) could not produce much lowering of emissivity value. All the above arguments suggested that annealing in reducing atmosphere is essential but the time of annealing should be optimized. As it was already established from TABLE 2 data that 7h annealing resulted too much of anion vacancy hence annealing time was optimized by varying it from 0.5h to 5h. TABLE 3 shows the emissivity values of ITO films after annealing in reducing atmosphere for different periods of times. The effect was studied over films derived from both low (6 wt% mixed oxide) and high (10 wt% mixed oxide) concentration precursor sol.

In order to avoid inhomogeneity in the relatively thick films only two depositions were carried out. It

TABLE 2 : Total thermal emissivity values of ITO films deposited from 8 wt% equivalent mixed oxide precursor sol (In : Sn = 90 : 10) and annealed under different conditions

Sample number	Atmosphere			Annealing time (Step)	Total thermal emissivity ($\varepsilon_{20^{o}C}$)
	Step-1 (Temp)	Step-2 (Temp.)	Step-3 (Temp.)		
ITB4 (piece no. 1)	Air (500°C)	-	-	3.5h (Step 1)	0.61
ITB4 (piece no. 2)	O_2 (300 °C)	Ar+H_2 (500°C)	-	3.5h (Step 2)	0.29
ITB4 (piece no. 3)	O_2 (300 °C)	Ar+H_2 (500°C)	-	7.0h (Step 2)	0.32
ITB4 (piece no. 4)	Air (500°C)	O_2 (300°C)	Ar+H_2 (500°C)	7.0h (Step1 & 3)	0.58

TABLE 3 : Total thermal emissivity values of ITO films deposited from 6 and 10 wt% equivalent mixed oxide precursor sol (In : Sn = 90 : 10) and annealed in reducing atmosphere for different times

Wt% equivalent of mixed oxide	Number of coating operation	Total hemispherical emissivity ($\varepsilon_{20^{o}c}$)			
		Annealing time 0.5h	Annealing time 2h	Annealing time 3.5h	Annealing time 5h
6	2	0.86	0.85	0.82	0.87
10	2	0.79	0.77	0.71	0.74

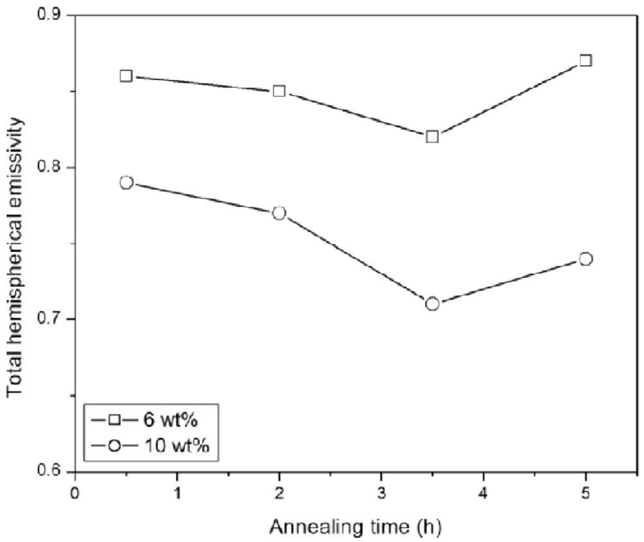


Figure 4 : Variation of total emissivity of ITO films with annealing time

was found that minimum emissivity was achieved after 3.5 h annealing in reducing atmosphere Figure 4. Beyond that time, enhancement of emmisivity values occurred possibly due to development of too much of anion vacancy. It is interesting to note that emissivity of the film derived from 6 wt% precursor sol can be lowered upto the value of 0.82 TABLE 3 which is even lower than the value obtained after three depositions (sample no. ITA3; $\varepsilon = 0.83$, TABLE 1).

CONCLUSIONS

ITO films from 6, 8 and10 wt% equivalent mixed oxide precursor sols were deposited on soda lime silica glass substrate by sol-gel dipping technique. Thermal emissivity values showed gradual decrease with increasing number of deposition upto three times. Reducing atmosphere during annealing treatment was essential for generation of oxygen vacancy. But, presence of too much anion vacancy was avoided by optimizing the annealing time. In the present work 3.5 h annealing in reducing atmosphere resulted minimum thermal emissivity value which is generally achieved by simply increasing the physical thickness of the film.

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