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Pyrosol process for deposition of fluorine-doped tin dioxide thin films

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Transparent low-resistance SnO_2:F films, suitable as a low-emissivity and conducting coating, have been deposited on silica-coated soda lime glass substrates by pyrosol process. $SnCl_4{\cdot}5H_2O$ and NH_4F dissolved in solvent of 50% C_2H_5OH/50% H_2O served as the starting solution. With the parameters such as substrate temperature of 450°C, distance between the nozzle and substrate of 60mm, carrier gas flow rate of 8L/min and deposition time of 5min, the optimized SnO_2:F films having a sheet resistance of about 2Ω/□, were deposited repeatedly. The relationship between sheet resistances and infrared transmission spectra of SnO_2:F films is shown schematically.

Keywords: pyrosol deposition, tin dioxide, conducting coating
PACC: 6150C, 4225B

1. Introduction

Transparent conducting films such as SnO_2 doped with fluorine are of widespread interest because of their unique properties. These include: high electrical conductivity, good transmittance in visible spectrum region and high reflectance in infrared wavelengths, excellent chemical, mechanical and thermal stabilities. The above-mentioned properties make them very useful in many fields of applications: transparent electrodes for silicon and CdS/CdTe solar cells,[1−4] display devices, high sensitive gas sensors[5,6] and high-insulation low-emissivity glasses.

There are many processes in the deposition of SnO_2 films, but spray pyrolysis and pyrosol deposition processes are fairly simple and inexpensive. Several years ago atmospheric pressure chemical vapour deposition (APCVD) was mostly used as deposition process for oxide thin films in industrial application, and pyrosol process was a laboratorial technique only. Recently, pyrosol process has developed rapidly and will definitely find application in industry in the near future.

The fluorine-doped SnO_2 films(SnO_2:F films) have been produced for the improvement of the optical and electrical properties, especially for decreasing the electrical resistance, but the mechanism concerning fluorine doping is reported very few up to now.

The purpose of the present paper is to demonstrate how to deposit a good-quality fluorine-doped film, including tin precursor solution preparation, solvent composition, carrier gas and deposition temperature.

The mechanism of fluorine doping is discussed on the basis of experimental results, and the relationship between the sheet resistances and infrared transmission spectra of SnO_2:F is shown in the present paper.

2. Experiment

The tin precursor used in the present work was $SnCl_4{\cdot}\ 5H_2O$, in analytical purity. The solvent was a mixture of C_2H_5OH–H_2O. The starting solution for SnO_2:F deposition consisted of $SnCl_4$ of 0.5–0.9 mol·L^{-1} dissolved in the C_2H_5OH–H_2O mixture. NH_4F was added as a dopant with F/Sn ratio of 0–1.2.

The experimental set-up for deposition of SnO_2:F films is shown in Fig.1.

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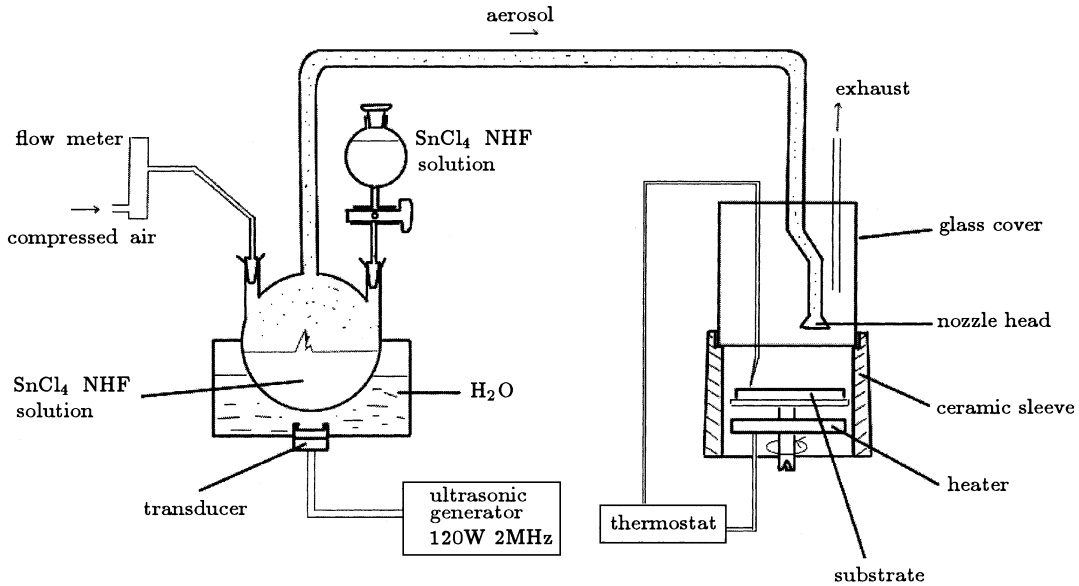


Fig.1. Experimental set-up used for deposition of fluorine-doped SnO_2 films by the pyrosol process.

It consists of an ultrasonic atomizer and a deposition reactor. A glass flask containing $SnCl_4$ solution was used for generation of aerosol by a transducer installed under the bottom of the flask. The ultrasound generated by the transducer penetrates the water, glass bottom and slightly focused nearby the $SnCl_4$ solution surface to raise up a "geyser". The droplets generated by a transducer working at 2MHz in our system are 3–4μm of diameter and are suitable for pyrosol process.[7] Compressed air was used as carrier gas to carry the mist to deposition reactor. The outer covering of the reactor consists of an upper glass cover and a lower ceramic sleeve which is located nearly to the heater. The substrate holder is a rotating plate mounted above the heater. The nozzle has a flat bill of 60mm in width, 50mm in length, and 1.5mm in thickness on the inside and is fixed at a height of 50–60mm above the rotating plate. The temperature of the substrate was measured by using a thermocouple and the signal was fed to a thermostat to control the temperature of the substrate.

All the SnO_2:F film deposition processes were carried out on silica-coated soda-lime glass substrates (10cm×10cm). The film thickness was determined by transmission spectra in the visible region measured with a TU-1901 UV-VIS spectrophotometer of Beijing Purkinje General Instrument Co., Ltd. and an ellipsometer for comparison. The infrared transmission spectra was measured with Hitachi U–4100 spectrophotometer up to 2500nm.

The sheet resistance of the SnO_2:F film was measured with a four-point probe.

3. Results and discussion

Up to the present, methanol and ethanol have been used for most research works in the pyrosol process. But alcohol solvents have a serious weakness of flammability especially nearby a high-temperature substrate in air. In this work we have chosen $SnCl_4 \cdot 5H_2O$ as precursor of SnO_2 film and NH_4F as dopant. For the purpose of safety, an increase of water content in the solvent is desired. According to the deposition mechanism of pyrosol process, the deposition parameters are critical under the influence of solvent volatility. A preliminary study showed that a greater distance between the nozzle and substrate, and a higher substrate temperature were needed for $50\%C_2H_5OH/50\%H_2O$ mixture solvent in accordance with low volatility of water.

3.1. Solvent composition

Experimental results obtained using different solvent compositions are listed in Table 1. The deposition parameters such as substrate temperature of 450°, distance between nozzle and substrate of 60mm, carrier gas flow rate of 8L/min were fixed. The solution containing 0.7M $SnCl_4 \cdot 5H_2O$ and 0.4M NH_4F was used in the experiments.

Table 1. Solvent composition, operability, film aspect, and sheet resistance of the deposited SnO_2:F films.

solvent composition Vol/Vol	operability (flammability)	film aspect	sheet resistance (three measurements with the same sample) /(Ω/□)
95%C_2H_5OH/5% H_2O	flammable	milky	19,22,84
80% C_2H_5OH/20% H_2O	flammable	transparent or milky	16,18,42,
60%C_2H_5OH/40% H_2O	weakly flammable	transparent	7,10,8
50%C_2H_5OH/50% H_2O	nonflammable	transparent	2,2,1
25% C_2H_5OH/75% H_2O	nonflammable	milky	2,4,5

Transparent deposits with a sheet resistance of about 2Ω/□ by using the 50% C_2H_5OH/50% H_2O solvent show that this solvent is not only nonflammable, but also suitable for deposition of SnO_2:F films.

3.2. Measurement of film thickness

Film thickness is an important parameter that influences the performance of SnO_2:F film. In the present paper, we use two methods to measure the thickness of the film. One is the method of transmission spectrum and the other is to measure by an ellipsometer. Although the method of transmission spectrum is not very precise, it is quite convenient by using a spectrophotometer for measuring both thickness and refractive index of the film. When the film is relatively uniform, a thin-film interference appears, because of the interference of light waves reflecting off the top surface of the SnO_2:F film with the waves reflecting from the bottom surface. To obtain the extrema of interference in transmission spectrum, the film thickness has to be on the order of wavelength according to the basic expression

$$2nd = m\lambda, \tag{1}$$

where n is the refractive index, d is the film thickness, λ is the wavelength of light and m is the order.

When we use the data of two adjacent maxima (or minima), we can obtain the thickness by the following expression:

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}, \tag{2}$$

where λ_1 and λ_2 are the wavelengths of two adjacent maxima (or minima), n_1 and n_2 are corresponding refractive indices, which can be calculated by the following formula[8]

$$n = \sqrt{N + \sqrt{N^2 - S^2}}, \tag{3}$$

$$N = 2S\frac{T_M - T_m}{T_M T_m} + \frac{S^2 + 1}{2}, \tag{4}$$

where S is the refractive index of the substrate, T_M is the maximum and T_m is the corresponding minimum for the same wavelength.

To measure the transmission spectrum we used the TU-1901 UV–visible spectrophotometer in which the computer program is compiled by C^{++} Builder. The measurement of thickness by ellipsometer is more accurate. The results of film thickness measured by the two methods are summarized in Table 2 and their corresponding transmission spectra are shown in Fig.2. The computer-simulated curves of T_M and T_m for sample 1 are shown in Fig.3.

Table 2. Measured thickness of SnO_2:F film by the method of transmission spectrum and by ellipsometer.

	thickness measured by transmission spectrum/nm	thickness measured by ellipsometer/nm
sample 1	319±10	369.2
sample 2	649±10	571.7
sample 3	253±10	272.3

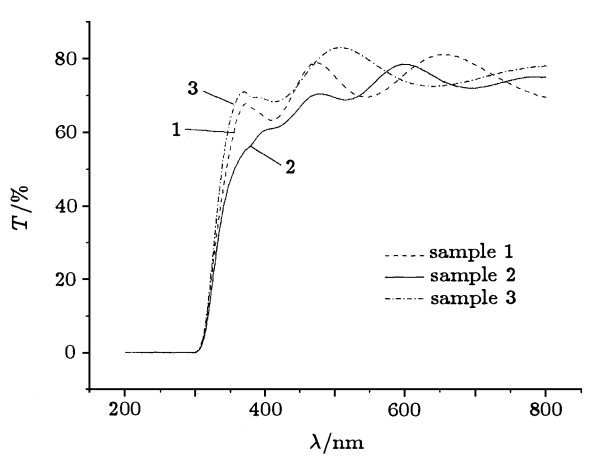


Fig.2. Optical transmission of the SnO_2:F films deposited on glass substrates.

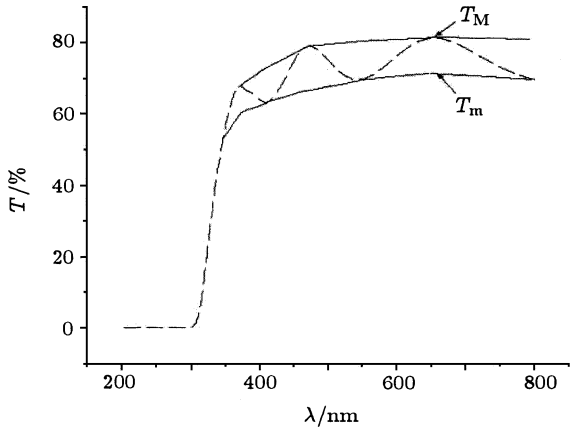


Fig.3. The computer-simulated curves of T_M and T_m for sample1.

3.3. Fluorine doping content.

The data in Table 3 show the dependence of sheet resistances of SnO_2:F films of approximately the same thickness (about 400nm) on different concentrations of NH_4F in starting solutions. The distance between nozzle and substrate is 60mm, substrate temperature is 450°C, carrier gas flow rate is 8L/min and deposition time is 5min.

At a fluorine concentration of 0.3–0.5mol NH_4F and 0.7mol $SnCl_4 \cdot 5H_2O$ in starting solution, the sheet resistances are low and the film aspect is good, corresponding to highly conducting and proper fluorine doping contents in the SnO_2:F films. It is possible to observe in Table 3 that when F:Sn is small, the amount of fluorine incorporated into the film increases significantly. However, at higher F:Sn in starting solution the fluorine is not efficiently incorporated into the film.

Table 3. Sheet resistances of deposited SnO_2:F films for different fluorine concentrations in starting solutions.

tin precursor, $SnCl_4 \cdot 5H_2O$ concentration /mol·L^{-1}	dopant NH_4F concentration /mol·L^{-1}	sheet resistances of deposited films (three measurements with the same sample)/(Ω/□)	film aspect
0.7	0	12,14,28	transparent or milky
0.7	0.1	4,9,11	transparent
0.7	0.2	3,6,8	transparent
0.7	0.3	2,3,7	transparent
0.7	0.4	2,3,5	transparent
0.7	0.5	3,6,8	transparent
0.7	0.6	4,12,20	transparent

The reflectance of the SnO_2:F film is very important for the study of low-emissivity glass, but publications concerning this subject have been limited up to now.

Figure 4 shows the infrared transmission spectra of SnO_2:F films for different sheet resistances deposited under conditions shown in Table 3. It is clearly indicated that sample A with sheet resistance of 12Ω/□ has higher transmittance in the near-infrared region, corresponding to lower reflectance as compared with samples B (6Ω/□) and C (2Ω/□). According to the sheet resistance of a SnO_2:F film we can imagine approximately the shape of its infrared reflection spectrum. Sheet resistance is very easy to measure with a simple, inexpensive instrument, the four-point-probe.

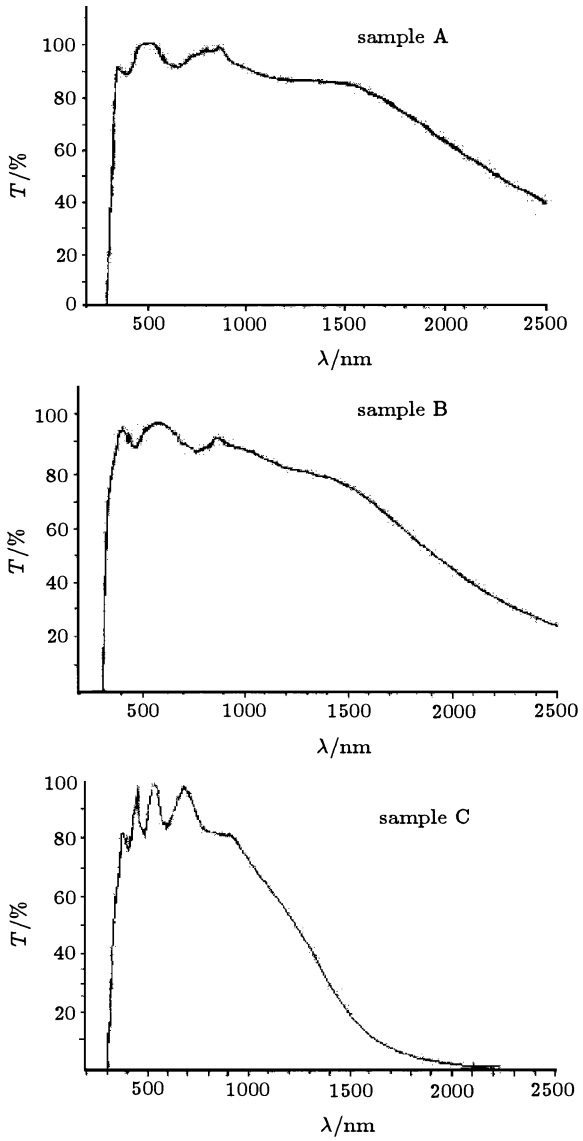


Fig.4. Infrared transmission spectra of SnO_2:F films for different resistances.

Low-emissivity coatings such as SnO_2:F, transmit visible light while reflecting the long-wave infrared light. The reflectance in the infrared region is dependent on the refractive index, thickness, but primarily on the free carrier concentration of the film. The SnO_2 films without doping have very low conductivity, close to an insulator. When NH_4F is added to the starting solution, in the process of deposition fluorine ions occupy oxygen positions and create free carriers, moving freely in the crystal lattice. With increasing doping content of fluorine in the SnO_2:F films, the sheet resistance decreases gradually, reaches a minimum, and then increases with subsequent increase of fluorine content. We have observed a sheet resistance minimum in the range of (F)/(Sn)=0.3–0.4 in starting solution. This minimum of sheet resistance can be explained by an increase in donor concentration and carrier mobility. When the ratio (F)/(Sn) continues to increase over the minimum, the Fermi level of SnO_2 can enter the conductive band, part of F ions sit in the gap of crystal lattice, but not the substitutional oxygen position. These dopant ions cannot provide carriers. Furthermore, if the concentration of F ions is too high, the carrier mobility could be decreased, and the conductivity of SnO_2:F films can be made worse.

4. Conclusions

(1) A nonflammable alcohol solvent system has been developed for pyrosol deposition of transparent conducting SnO_2:F films. It consists of a 50%C_2H_5OH/50% H_2O mixture and is a good solvent for both $SnCl_4 \cdot 5H_2O$ and NH_4F.

(2) Under the optimum condition, the transparent SnO_2:F films could be deposited repeatedly with sheet resistance of about $2\Omega/\square$.

(3) By using the transmission spectrum, the film thickness measurements were proceeded successfully with a spectrophotometer and the measured results of thickness are reasonably good as compared with the results measured by using an ellipsometer. For a good-quality SnO_2:F film, it seems that its thickness should be around 200–400nm.

(4) The relationship between the sheet resistance and infrared transmission spectra of SnO_2:F films has been given experimentally.

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