가열분무법으로 제조한 F-doped SnO_2 박막의 특성비교

은 희 태, 고 용 식
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Comparison of F-doped SnO_2 films obtained by spray pyrolysis technique

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Introduction

The high transmittance in the visible spectral region in combination with a high conductivity, and a high reflectance in the IR region of non-stoichiometric and doped films of oxides of tin is still of wide interest due to their broad applications in electronic and optical devices and heating elements in aircraft and car windows for defogging and deicing[1]. These coatings have been deposited by various methods such as CVD, RF sputtering, evaporation, spray pyrolysis and sol-gel process[2]. Spray pyrolysis is widely used due to its simplicity and commercial viability. Final film properties depend on various growth parameters, nature of the substrate, the carrier gas, and atmosphere.

In the last decade there has been a great deal of interest in the production of inexpensive thin films of tin oxide. Because a wide bandgap semiconductor such as tin oxide can be made highly conducting when sufficiently doped, it has the desirable property of being transparent through most of the visible spectrum while reflecting a great deal of the IR. A thin film of conducting tin oxide on glass can be used to improve building insulation(greenhouse effect) or as the heating element in anti-frost windshields. It can be used as the front contact in the manufacture of a wide variety of solar cells and undoped tin oxide can be used to add strength to glass containers[3,4]. It is well known that the conductivity of tin oxide films can be enhanced by appropriate doping. It was observed that F-doped tin oxide films have a higher conductivity, transmissivity and infrared reflection than the undoped films[5].

In this work, F-doped tin oxide films(FTO) were prepared by spray pyrolysis technique on flat borosilicate glass substrates at 500～550℃ and investigated with respect to their electrical and optical properties of FTO films with different spraying solutions and dopant agents.

Experimental

1. Preparation of spraying solutions

Tin(Ⅳ) chloride pentahydrate(99.8%, Fluka), ammonium fluoride(98%, Fluka) and hydrofluoric acid(48%, Aldrich) were used as starting materials of SnO_2 and F, respectively. Three different solutions were prepared and used for the spraying experiments to obtain F-doped SnO_2 coatings as follows;

In the case of a solution of $SnCl_4 \cdot 5H_2O$ in ethanol doped with NH_4F, different dopant concentrations of NH_4F in $SnCl_4 \cdot 5H_2O$ with F/Sn ratios in the range from 0.5 to 5% were produced and investigated. For a solution of $SnCl_4 \cdot 5H_2O$ in ethanol doped with HF, a concentration of 3.14 atomic percent(F/Sn ratio) was used. The third solution is organic solution which is a commercially available ethanolic solution(OTN 3-5, Goldschmidt AG) of

monobutyltintrichloride(MBTC) doped with 3 wt% HF.

2. Spraying process and characterization

The heating of the substrate was done with a ceramic heating plate with embedded electrical heating wires. The maximum set temperature of the heater measured inside with a thermocouple was 800℃. The resulting temperature on the surface of the substrate was measured with a pyrometer (Heimann KT 19.43, 7.5-8.2㎛). The maximum substrate temperature which we were able to achieve with full heating power was 550～555℃. A borosilicate glass of 3mm thickness and the size of 12×12cm size was used as the substrate.

The spraying process was done with a conventional hand spray gun (SATA Mini Jet) equipment with a 0.5mm Nozzle. Compressed air with a pressure of 1 or 2 bar was used as a carrier gas. For a number of experiments oxygen was used as a carrier gas with a pressure of 2bar. The opening of the valve for the liquid flow was set near to the lower limit of the possible range. A solution flow rate was 13～17㎖/min, typically. The spraying process was done in an interrupted made with 3s spraying and subsequent waiting for 1min to avoid a too strong cooling of the substrate during the deposition process due to the cooling effect of the carrier gas.

The film thickness, t, was measured with a Tencor P10 profilometer and the sheet resistance, $R_{\square}$, was measured with the Van der Pauw method(MMR Technologies, Inc.). The electrical resistivity, ρ, was determined by the relation $\rho = R_{\square} t$. Transmission and near normal(7°) reflection of the sprayed layers were measured with a Cary 5E spectrometer from 300nm to 3㎛ and the reflection in the IR from 3 to 20㎛ IR range with a Brucker 66v FTIR spectrometer.

Results and Discussion

1. FTO films prepared with NH_4F doped $SnCl_4$ solutions

Fig. 1 shows the resistivity of samples sprayed with NH_4F doped $SnCl_4$ solutions as function of the F/Sn concentration under air condition for the same spraying time of 60s. The resulting layer thickness for all these investigated layers was in the range of 7～9 nm/s. As can be seen in Fig. 1 the dopant concentration of 3.1% or more(up to 5.0%) resulted in the lowest values of the resistivity of 1.3 ～ 1.5×10^{-3} Ωcm. For this reason we have taken a dopant concentration of 3.1% for all further experiments with NH_4F doped $SnCl_4$ solutions and have chosen a substrate temperature of 500℃. For comparison the same F/Sn ratio was used for the HF doped solution and the same substrate temperature of 500℃.

Fig. 2 shows the resulting sheet resistance($R_{\square}$) as function of the film thickness of samples sprayed with the NH_4F doped $SnCl_4$ solutions containing a F/Sn concentration of 3.1%. The solutions were sprayed with compressed air at 500℃ for a spraying time of 60s (nozzle size 0.5㎜, flow rate 15㎖/min) resulting in a deposition rate of 4.6～6.5nm/s. Fig. 2 shows a strong decrease of the sheet resistance values with increasing thickness for spraying condition of air and oxygen. The resistivity of 2.0 ～ 2.7×10^{-3} Ωcm for all investigated samples sprayed with air condition is showed whereas the samples sprayed with oxygen are slightly higher values of 2.7～3.3 × 10^{-3} Ωcm[6].

The transmission curves and the corresponding reflection curves of the air sprayed films are showed. The transmission droped with increasing thickness whereas the reflectivity for longer wavelengths increased slightly with increasing thickness. The reflectivity obtained at a wavelength of 3000nm was relatively low. The values were in the range of 15% for both carrier gases but will increase to higher values for longer wavelengths.

2. FTO films prepared with HF doped $SnCl_4$ solutions

The resulting sheet resistance and the corresponding resistivity of samples sprayed with 3.1% HF doped $SnCl_4$ solutions under forming gas at 500℃ are showed. In both cases a nozzle size of 0.5mm was used for all experiments. The flow rate was 15㎖/min for the air sprayed films resulting in a deposition rate of 5.1～7.3nm/s. The resistivities varied within the range of 0.9 to 1.5×10^{-3} Ωcm for the films having thickness ranging from 400～600nm. The resistivities of both sets of oxygen sprayed films were higher than those of the air sprayed films but quite a difference lies in the resistivities of the oxygen sprayed films themselves.

The measured transmission curves and the corresponding reflection curves of the air sprayed films with different film thickness ranging from 440 to 614nm are showed. As can be seen, the overall transmission did not drop continuously with increasing film thickness in all cases and the reflectivity for longer wavelengths also did not represent a systematic behavior. The reason for this will be the strong variations in the resistivity of the films. Since the height of the value of reflection intensity for longer wavelengths than the plasma wavelength is directly dependent from the electrical data(carrier density and mobility), a varying IR reflection behavior with increasing layer thickness has to be expected for varying electrical properties of the coatings[7].

3. FTO films prepared with HF doped monobutyltintrichloride(MBTC) solutions

The sheet resistance and the corresponding resistivity samples sprayed with 3% HF doped monobutyltintrichloride(MBTC) solution under forming gas at 500℃ are showed. A flow rate of 15㎖/min was used for the air sprayed films with the 0.5mm size nozzle resulting in a deposition rate of 15.5～18.8nm/s. This deposition rate is comparable with the rates resulting for the deposition of this sol under compressed air using the same flow rate. However, these deposition rates are much higher than those used for the spraying experiments of the NH_4F- and HF-doped tin oxide films.

The resistivities investigated for thicknesses from about 500 to 1500nm decreased from 4.5 to 3.6×10^{-4} Ωcm for the air sprayed films with increasing thickness. The resulting low value of about 3.5×10^{-4} Ωcm for layers thicker than 400nm is comparable with the values we have found earlier for ITO coatings before they were reduced in a forming gas treatment at 400℃[8].

The transmission and reflection curves of the sprayed FTO coating with monobutyltintrichloride solutions for different thickness are showed. As expected the transmission in the visible region is significantly lowered with increasing layer thickness. The reflectance is increased for thicker thicknesses but reaches a nearly identical curve at wavelengths longer than 1500nm for layers having thicknesses of 720nm to 1380nm. This means that the average depth of penetration of light with wavelengths longer than 1500nm is in the near of the thickness of these two layers. Therefore an increasing thickness will not result in an increasing IR reflection[9,10]. This explanation will be clear by the fact that the two thickness coatings which shows nearly no transmission for wavelengths larger than 1500nm, indicating that the thick coatings are nearly totally absorbing at 1500nm since the reflection is still low. The small values for the resistivity of SnO_2 : F coatings obtained by spray pyrolysis of monobutyltintrichloride solutions show that this material is appropriate to produce coatings with good electrical conductivity. For a possible technical application, the optical properties especially the transmission in the optical range must also be regarded as an important factor.

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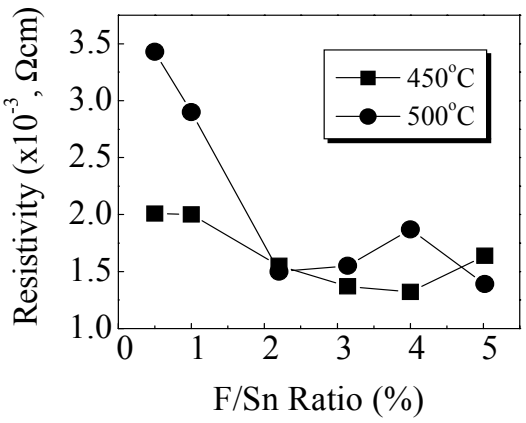

Fig.1. Resitivity of NH_4 doped SnO_2 films with different F/Sn ratios under air condition.

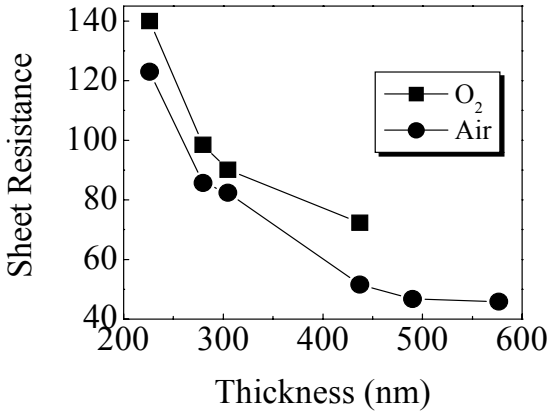

Fig.2. Sheet resistance of sprayed SnO_2 coating doped with 3.1% NH_4F versus film thickness under forming gas at 500°C.