Development of a Spray Pyrolysis Coating Process for Tin Oxide Film Heat Mirrors

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Abstract

This research studies heat mirror preparation, at a lab scale, on 2.5 x 7.5 cm glass substrates by a spray pyrolysis method. Tin oxide (SnO_2) and fluorine doped heat mirror films (SnO_2:F) were deposited on the substrate in a horizontal reactor designed and constructed for research under the following conditions : substrate temperature (400, 450, 500 °C), initial solution concentration ($SnCl_4$:H_2O ratio=3:1), pneumatic force of spray nozzles (pneumatic transducer, pressure 5 bar), fluorine concentration in the initial solution (F:Sn atom ratios= 1:4, 1:2, 1:1, 2:1 and 4:1) and spray time (120 s). The film spectral transmission are 82, 74 and 58 % in the wavelength regions of 300 - 760 nm and 70, 68 and 56 % in infrared wavelength regions of 760 - 3200 nm. The fluorine doping films were studied using substrate temperature at 450 °C and 0.4 μm film thickness. The average transmittance of film of F:Sn atom ratio 1:1 and undoped films were 81 and 74 % in the wavelength regions of 300 - 760 nm. In the infrared wavelength regions of 760 - 3200 nm, it was 59 and 68 % respectively. For the F:Sn atom ratio of 1:4, 1:2, 1:1, 2:1 and 4:1, the average transmittance of films were 69, 78, 81, 76 and 68 % respectively in the wavelength regions of 300 - 760 nm and 65, 60, 59, 54 and 52 % respectively in infrared wavelength regions of 760 - 3200 nm.

1. Introduction

Tinoxide (SnO_2) coatings are well known as infrared-reflecting coating [1]. The use of tinoxide coatings as heat mirrors for windows is emphasized in this paper. Properties needed for heat mirrors are high solar transmittance and high infrared reflectance, as shown in Fig.1 [2]. There are many techniques that have been used to prepare the tinoxide films. Spray pyrolysis is a reliable and cheap method. It is a known technique that is closely related to chemical vapour deposition (CVD). A chemical spray deposition process can be described with six parameters [3] : temperature of the gaseous environment, flow of carrier gas, distance between nozzle-substrate, droplet radius, solution concentration and solution flow. The diagram of equipment for chemical - and spray deposition are depicted in Fig.2. The CVD process needs fine droplets to react on the heated substrate. In many cases large droplets of the solution do not vaporize before reacting to deposit on the substrate. They hit the surface (possibly as a result of the choice of transducer) and form a powdery deposit. If it strikes at a high enough velocity, the droplet will splatter and form a dispersed powdery layer. As mentioned above, the droplet cannot completely vaporize before it hits the surface and for this reason, true CVD film growth cannot occur. Fig.3 shows the types of trajectories that are expected to occur in the spraying of a solution on hot glass substrate. The fogging system can be of different types : pneumatic, piezoelectric etc. The pneumatic is preferable because it is cheap and easy to use. The design of the reactor chamber is horizontal. The distance in the horizontal direction can screen droplet size. Fig.4 shows the principal concept of droplet size selection. The big droplet will drop near the transducer nozzle and very fine droplet will go to the heating zone in substrate placement.

The described results are obtained by preparing coatings by spray pyrolysis while varying different process parameters. An analysis of the optical properties gives information about the coating properties.

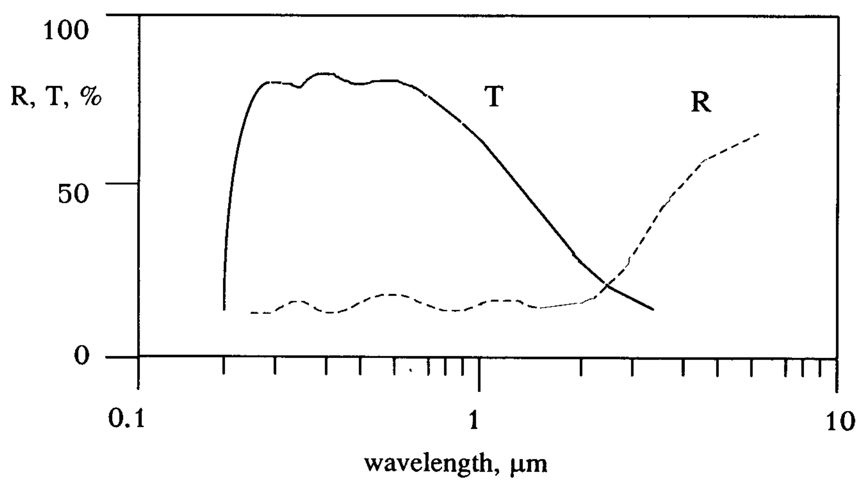


Fig. 1 Transmittance and Reflectance of SnO_2 films.

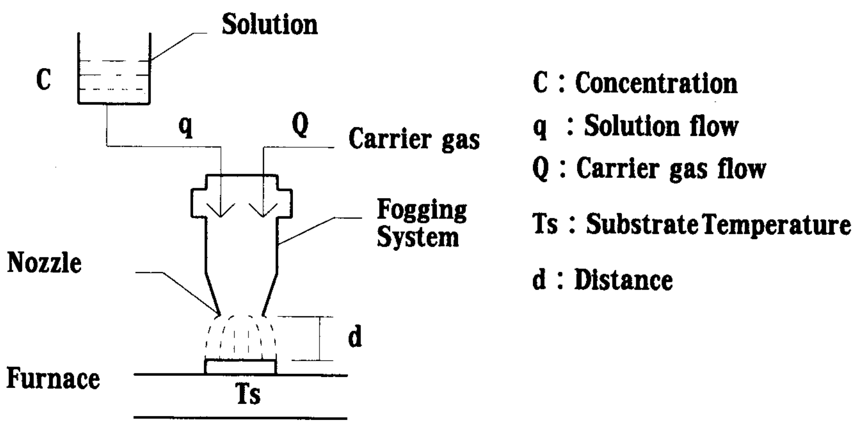


Fig. 2 Diagram of equipment for chemical spray deposition.

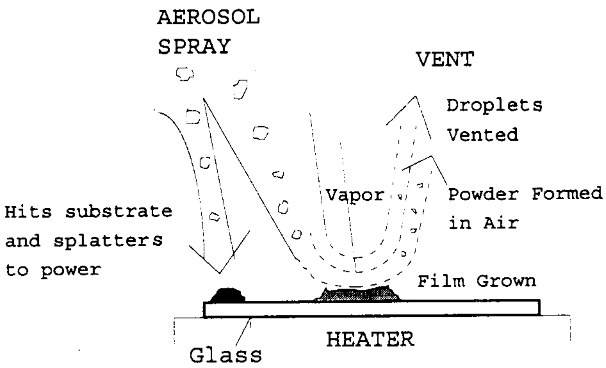


Fig. 3 The interaction of an aerosol spray with a hot substrate showing a proposed mechanism of film growth.

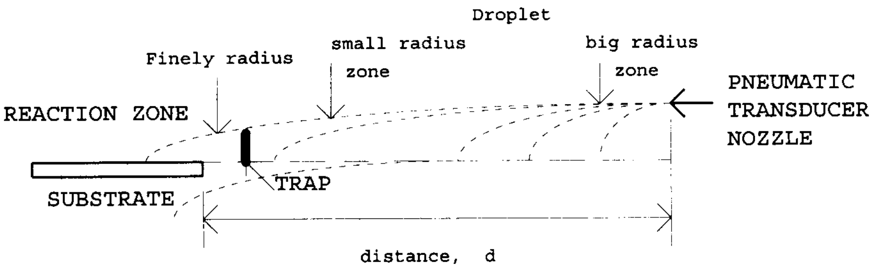


Fig. 4 The horizontal droplet size confined reactor.

2. Experimental techniques and procedures

The coating was prepared by the spray pyrolysis method on a 2.5x7.5 cm microscope slide glass. The spray solution used was a solution of tinchloride in water and alcohol with NH_4F as a dopant. A block diagram of the reactor and associated equipment evaluating is shown in Fig. 5. In the spraying process, we divided the quality of films into 3 types : good, fair and poor. The good film is the clearest while the fair has some misty area on the film and the poor is the worst film on which most area is misty. Film samples were prepared and the properties determined under the following conditions: the surface temperature (400, 450 and 500 °C), solution concentration (alternative ratio of tin chloride and water were 2, 2.5 and 3), spray time and fluorine doping (Sn:F atom ratio were 4:1, 2:1, 1:1, 1:2 and 1:4).

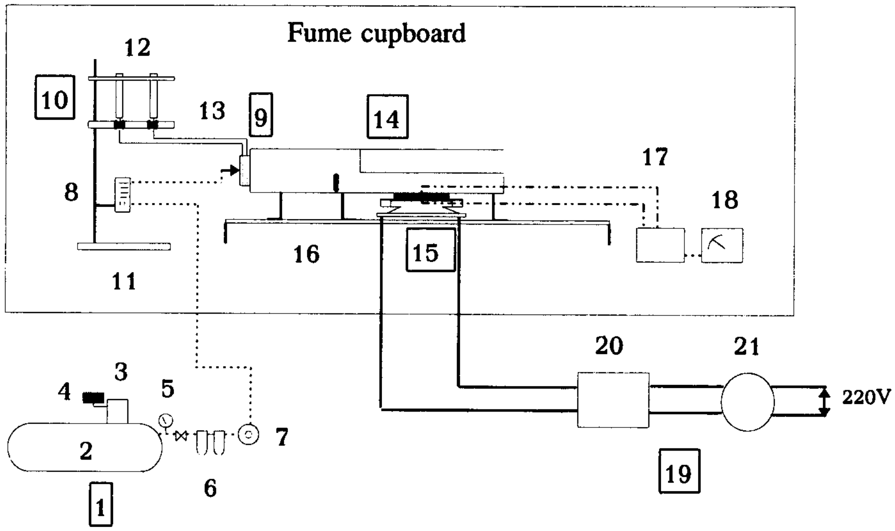
Good samples of tin oxide films are determined as follows :

1. Optical properties of films

The films were tested for their optical properties, transmittance and reflectance, using a Shimadzu UV-VIS-NIR Recording Spectrophometer UV-3100. The wavelength tests were 300 nm to 3200 nm under air baseline. We tested 3 points in many zones, i.e. near edge, center and far edge zones on the substrate.

2. Films thickness evaluation

A scanning electronmicroscope (SEM) was used for thickness determining. We approximated the film thickness by cross section of films. The thickness was determined at 3 points, i.e. near edge, center and far edge zones, the same as the optical properties.



Air line — Thermocouple wiring — Solution line — Cable wiring

(1) Air compressor
(2) Storage tank
(3) Piston air pump
(4) Air filter
(5) Pressure gauge
(6) Water trap
(7) Regulator
(8) Rotameter
(9) Nozzle block
(10) Solution feeder
(11) Stand
(12) Solution cylinder
(13) Glass & silicone tube
(14) Reactor
(15) Substrate heater
(16) Reactor support
(17) Selector switch
(18) Display thermocouple
(19) Electrical source
(20) Secondary transformer
(21) Primary transformer

Fig. 5 Diagram of apparatus of the Spray Pyrolysis Process.

3. Results and discussion

The most important factor of the pyrolysis process is the substrate surface temperature, that is the surface/air interface temperature. It is hard to measure when the process is in operation. The chemical droplets which are sprayed against the surface are the principal cause of temperature drop. More details of temperature distribution on the surface of the substrate are shown in Fig.6, which show more variation. This effect would be influenced by the reaction temperature.

The basic solution that most literature references use to prepare the SnO_2 film coating is a standard solution. At First, we used the standard solution for the spraying process. The greatest film thickness was approximately 0.1 μm. This result may occur especially in a reactor of our design. We prepared solutions with a high ratio of tin. With a spray time of 30 s, 400 °C and solution ratio 3:1, the amount of tin in the film was 0.0008 g and the film thickness was approximately 0.15 μm, which indicated that the process should be operated at this ratio. Other reasons that determined the choice of this ratio were the high solubility ratio of tin chloride in water and a larger amount of tin for analyzing. The ratio of tin in the solution can be reduced if needed.

The sample of SnO_2 films which were prepared at conditions : 450 °C, solution ratio 3:1, 120 sec spray time and 0.4 μm thickness is chosen to illustrate the fluorine doping effects. We selected 5 ratios of tin and fluorine by atoms, 4:1, 2:1, 1:1, 1:2 and 1:4 in the initial solution. The fluorine atom in the SnO_2 films affected the optical property of the films, as shown in Fig.8.

The average transmittance of 300 - 3200 nm wavelength of ordinary glass, undoped SnO_2 films and ratio doping 1:1 SnO_2 films are 86, 72 and 61 % respectively. The average reflectance can be calculated by neglecting the small absorbence term. The average reflectance is then equal to 100 minus the average transmittance. The SnO_2 films and 1:1 ratio doped SnO_2 films can reduce infrared ray transmittance approximately 12% and 50 % respectively.

The 5 samples of fluorine doped tin chlorine solutions were prepared. Ratios of tin and fluorine atom were; 1:4, 1:2, 1:1, 2:1 and 4:1. The tin chloride solution was prepared with a ratio of tin chloride ($SnCl_4$) to water (H_2O) of 3:1. We calculated the concentration of fluorine atom in the ammonium fluoride solution (NH_4F) and doped in the selected tin chloride solution. The spray condition of F-doped tin chloride solution was the same as for pure tin chloride solution.

The high ratio gives the most optical effect, as illustrated in Fig.9. The average transmittance are *70, 65, 61, 54* and *48 %* for the ratio 4:1, 2:1, 1:1, 1:2 and 1:4 respectively.

The substrate temperature influences the fluorine doping in SnO_2 films. The transmittance of fluorine doped SnO_2 films at any study area on the substrate which have different temperature, is shown in Fig.10. The temperature was 430, 450 and 430 °C at near edge, center and far edge area respectively. The center area transmittance curve shows greater average transmittance than the far area and near curve respectively. This transmittance curve also shows the same pattern at any fluorine doping ratio. The transmittance curve of pure SnO_2 films at such substrate temperature conditions does not show the pattern of the fluorine doped SnO_2 films. Fig. 11 shows the supposed fluorine atom flow on the 450 °C substrate which may occur by the influence of temperature and characteristic flow of carrier gas.

The pattern of X-ray diagrams of F-doped SnO_2 films at any ratio were seen to be similar to the pattern of undoped SnO_2 films (Fig.12). It does not show the preferential peak that indicates the effect of fluorine atom in the films or the number of fluorine atom may be too low for detection, as shown in Fig.13. The efficiency of stannic mass transfer was less than 0.1 %. The opportunity of fluorine, which is more volatile than stannic chloride, to deposit in the structure of SnO_2 films was small. This may be the reason for the lack of fluorine in the SnO_2 films.

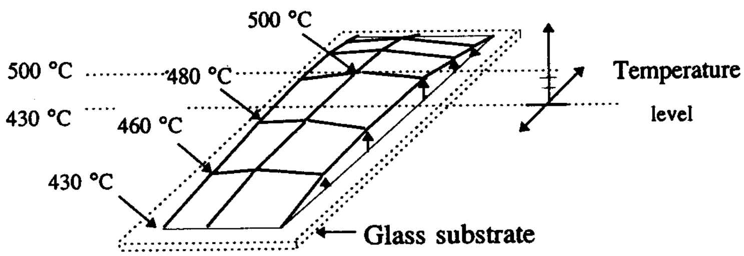


Fig. 6 Temperature distribution on the substrate.

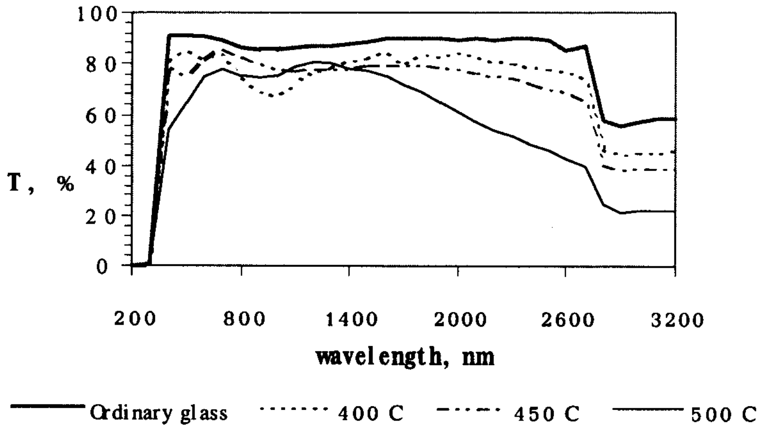


Fig. 7 Transmittance of SnO_2 film at substrate temperature 400, 450 and 500 °C, Spray time 120 s, solution ratio 3:1 and no doping.

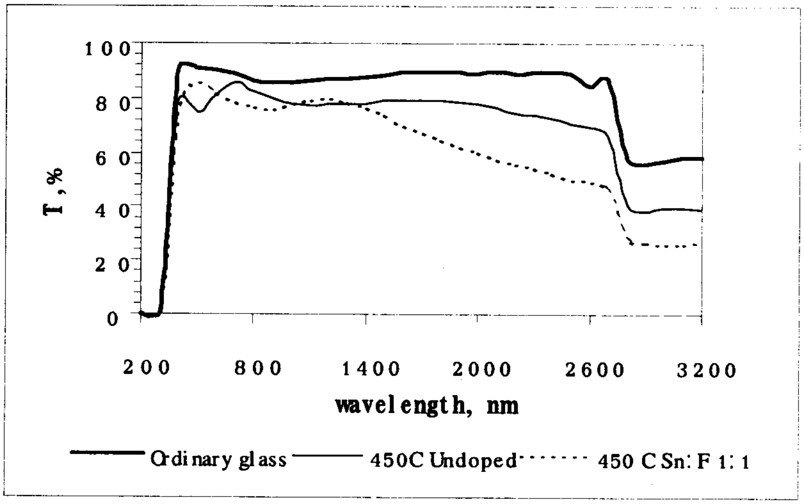


Fig. 8 The transmittance of glass substrate, SnO_2 films at substrate temperature 450 °C, undoped and ratio of doping 1:1.

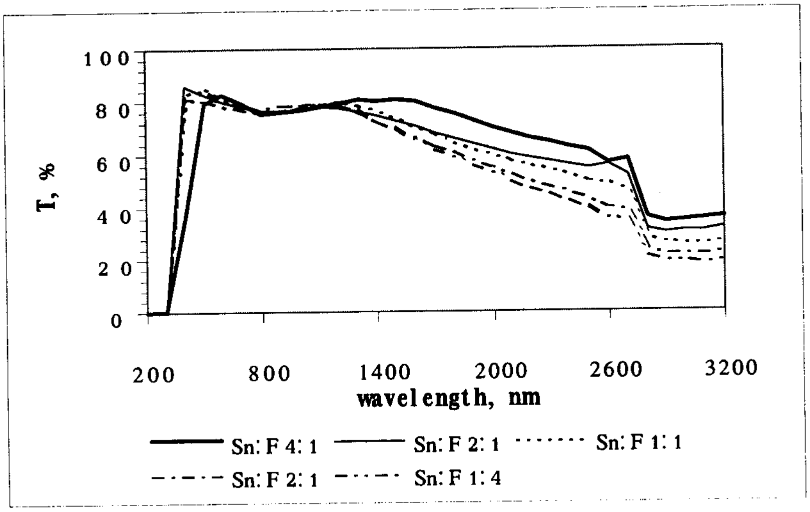


Fig. 9 The transmittance of SnO_2 films at substrate temperature 450 °C, ratio of doping 4:1, 2:1, 1:1, 1:2 and 1:4.

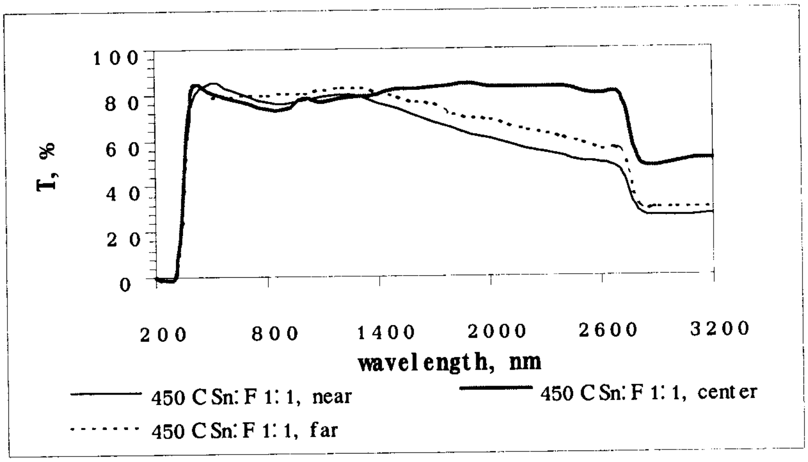


Fig. 10 The transmittance of fluorine doped SnO_2 films, ratio of doping 1:1, substrate temperature 450 °C, plot of any area on the substrate.

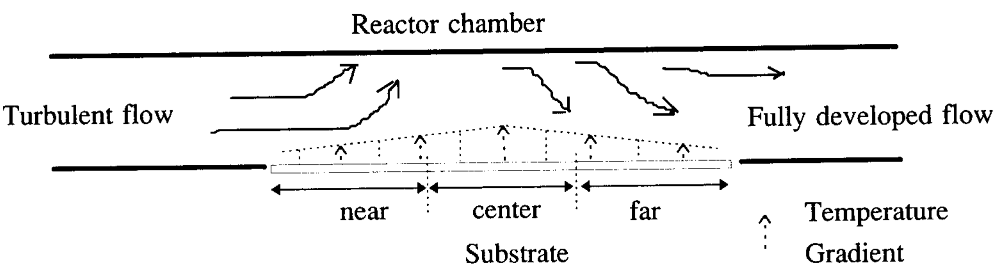


Fig. 11 The supposed fluorine atom flow on the substrate.

4. Conclusions

The spectral transmittance and reflectance of SnO_2 films were considered in two wavelength regions, namely, visible and infrared regions. It is required that the transmittance in the infrared region should be made low by controlling process parameters. Some difficulties and inconclusive results are encountered, especially the amount of F atoms in doped films. The following can be concluded.

1. The substrate temperature is the most important parameter that should be controlled when spraying. Before spraying, the temperature distribution as shown in Fig.6 contributes to the non-uniformity of deposits on the substrate.

2. The X-ray diffraction of F-doping SnO_2 films can not provide conclusive results of the effect of fluorine atoms in the film. It could be either that there are no F atoms incorporated in the SnO_2 films or they are present in a very small and undetectable amount. This is not too surprising as the calculated efficiency of stannic mass transfer is less than 0.1 % whereas F and F-compounds are quite volatile and could readily evaporate and not deposit on the substrates.

3. The average transmittance of F-doping SnO_2 films in the visible region are larger than the undoped SnO_2 films as shown in Fig.8.

4. Among all Sn:F ratios, the highest ratio shows the lowest average transmittance in the infrared region as shown in Fig.9.

5. The heat mirror index of the films,that is,the ratio of average transmittance in visible region to average transmittance in solar infrared region, is one indicator for comparing the optical properties of films. The high valve shows the more heat reflection. The result of heat mirror index in wavelength 320-2200 nm of undoped and F-doped films is shown in Fig.14 and Fig.15. The lowest index is shown at high temperature (500 °C), in Fig.14. It means poor heat reflection. Thus, the request substrate temperature is 450 °C, Fig.15. The high doping ratio shows a high index because the impurity in the film increases optical properties.

5. Acknowledgements

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6. References

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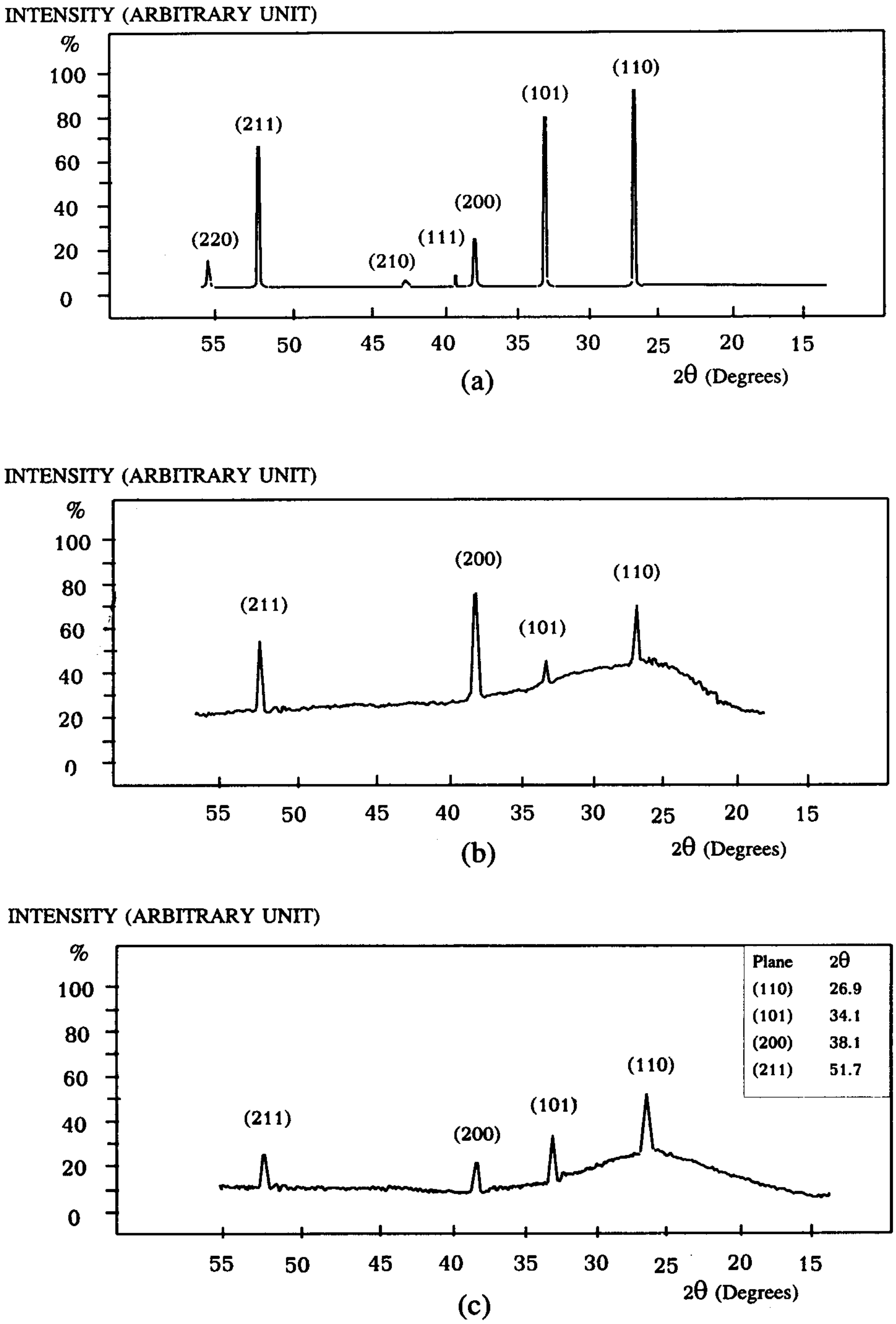

Fig. 12 X-ray diagrams for SnO_2 : (a) SnO_2 powder pattern : (b) SnO_2 film on a glass substrate : (c) SnO_2 film from experiment (thickness of film, d = 0.2 μm)

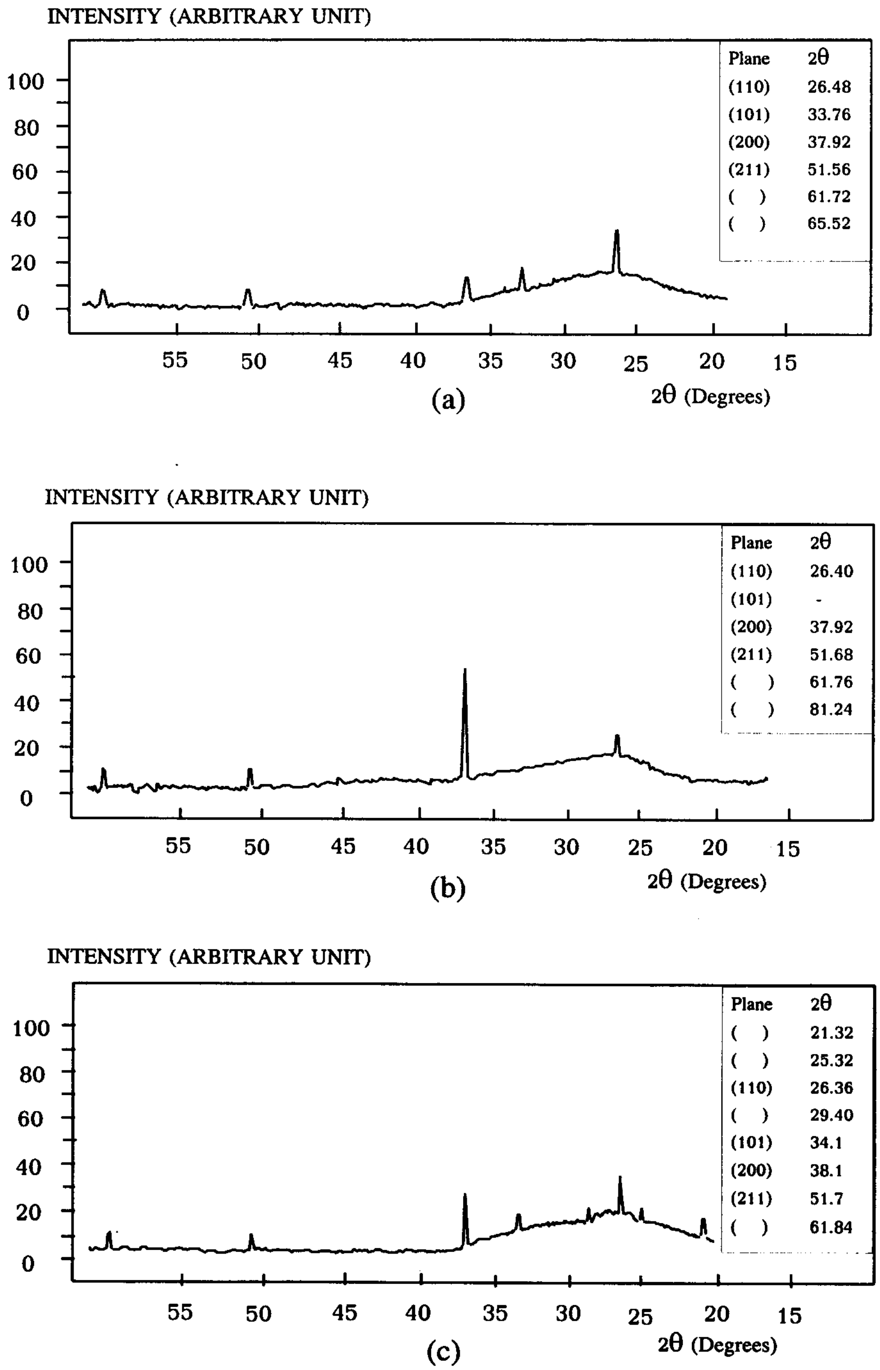

Fig. 13 X-ray diagrams for F-doped SnO_2 : (a) Sn:F ratio* 4:1 : (b) Sn:F ratio* 1:1 : (c) Sn:F ratio* 1:4 (thickness of all film, d = 0.4 μm)

*** ratio in the initial spray solution.**

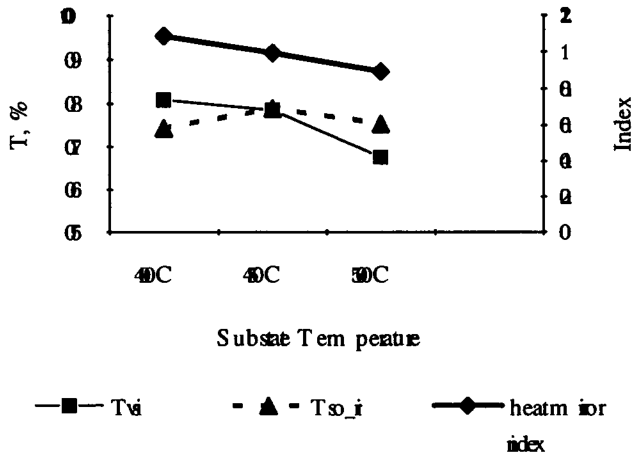

Fig. 14 Heat Mirror index of undoped SnO_2 films.

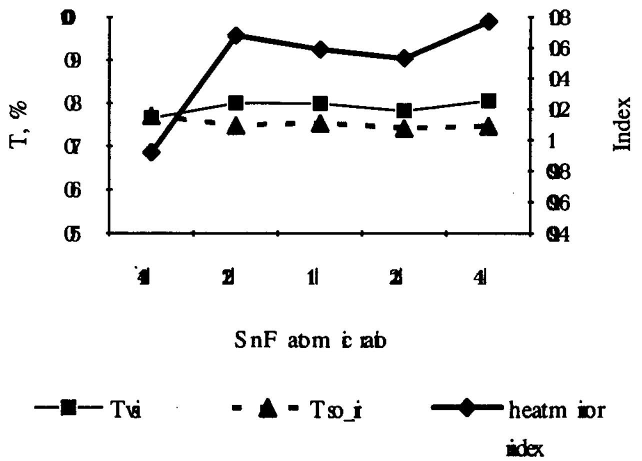

Fig. 15 Heat Mirror index of F-doping SnO_2 films.