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TEMPERATURE PROGRAMMED DESORPTION OF F-DOPED SnO_2 FILMS DEPOSITED BY INVERTED PYROSOL TECHNIQUE

S. Aukkaravittayapun[1*], *C. Thanachayanont*[1], *T. Theapsiri*[2], *W. Veerasai*[2], *Y. Sawada*[3], *T. Kondo*[3], *S. Tokiwa*[4] *and T. Nishide*[4]

[1]National Metal and Materials Technology Center (MTEC), 114 Paholyothin Road, Klong 1, Klong Luang
Pathumthani 12120, Thailand
[2]Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Rd., Bangkok 10400, Thailand
[3]Department of Industrial Chemistry, Graduate School of Engineering, Tokyo Polytechnic University, Iiyama
Atsugi 243-0297, Japan
[4]Department of Materials Chemistry and Engineering, College of Nihon University, Tamura, Koriyama 963-8642, Japan

Fluorine-doped tin dioxide (FTO) films were deposited on silicon wafers by inverted pyrosol technique using solutions with different doping concentration (F/Sn=0.00, 0.12, 0.75 and 2.50). The physical and electrical properties of the deposited films were analyzed by SEM, XRF, resistivity measurement by four-point-probe method and Hall coefficient measurement by van der Pauw method. The electrical properties showed that the FTO film deposited using the solution with F/Sn=0.75 gave a lowest resistivity of $3.2\cdot10^{-4}$ ohm cm. The FTO films were analyzed by temperature programmed desorption (TPD). Evolved gases from the heated specimens were detected using a quadruple mass analyzer for mass fragments m/z, 1(H^+), 2(H_2^+), 12(C^+), 14(N^+), 15(CH_3^+), 16(O^+), 17(OH^+ or NH_3^+), 18(H_2O^+ or NH_4^+), 19(F^+), 20(HF^+), 28(CO^+ or N_2^+), 32(O_2^+), 37(NH_4F^+), 44(CO_2^+), 120(Sn^+), 136(SnO^+) and 152(SnO_2^+). The majority of evolved gases from all FTO films were water vapor, carbon monoxide and carbon dioxide. Fluorine (m/z 19) was detected only in doped films and its intensity was very strong for highly-doped films at temperature above 400°C.

Keywords: *F-doped SnO_2, inverted pyrosol, temperature programmed desorption*

Introduction

Fluorine-doped tin dioxide (F-doped SnO_2 or FTO) is well known as one of the most common transparent conducting oxides (TCOs) used in many applications, for example thin film solar cell, infrared reflective glass and transparent electrode of other optoelectronic devices. Although FTO glass has been commercially available for very long time, its price is still too high for widely-spread applications. Cheaper or easier process is always desired. An inverted pyrosol technique, which has a potential to produce large area of good quality FTO films on glass at low cost, was invented [1] and used for FTO deposition. The uniqueness of this technique is that fine droplets, in a narrow range of size distribution generated by ultrasonic, are brought upward by a carrier gas and deposited on a substrate which is placed upside down. A heating element is placed above the substrate. This technique is able to select the size of the droplets for film formation by varying the flow rate of a carrier gas.

As is considered to be one of the spray CVD techniques [2–4], inverted pyrosol technique also pyrolyzes the raw materials provided as liquid solution (droplet) and forms a solid film on hot surface. Unlike a physical route, normally a chemical route would leave some residues or unwanted by-products on the surface or inside of the film. As often found on glass substrate, fresh films look fine but after exposure to environment for a few hours, some dendrites form on the surface and they disappear during contacting with water or humidity. This is a typical evidence for the existing of residues on the surface of films.

In order to understand more about the residues on the films fabricated by the inverted pyrosol technique, temperature programmed desorption (TPD) was used to reveal this problem which was not much addressed in the literature. Moreover, it was proved that the TPD can determine the quality of the TCOs films. For example, TPD results showed some correlation between the film quality and type/amount of the evolved gases from ITOs (Indium Tin Oxides) fabricated by several techniques [5, 6].

Therefore, in this study, we carried out the TPD of FTO films fabricated by inverted pyrosol technique with different fluorine doping concentration in order to reveal the nature of residues as well as the correlation between doping amount and the film's quality and resistivity.

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[*] Author for correspondence: suparerk@mtec.or.th

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

In order to be investigated by TPD up to elevated temperature, fluoride-doped SnO_2 (FTO) films were fabricated on cleaned (001) silicon substrates (instead of glass) by a cheap laboratory-scale inverted pyrosol system as shown in Fig. 1. The solution was a mixture of $SnCl_2\cdot 2H_2O$ in a solvent containing 5% deionized water and 95% ethanol with different amount of NH_4F (F/Sn=0.00, 0.12, 0.75 and 2.50) as a fluorine doping agent. A small amount of hydrochloric was added into the solution to increase solubility. A commercial ultrasonic mist generator with a frequency of 1.7 MHz was adopted to generate fine solution droplets with mean diameter of approximately 2–3 μm for ethanol solution [7]. The aerosols were atomized from the precursor solution at a rate of 1 mL min^{-1}. The temperature of a substrate, which was placed underneath the inverted heater, was set at 450°C. The aerosols were brought up to the substrate by air at a flow rate of 1 L min^{-1}. The deposition time was 10 min. The physical and electrical properties of the deposited films were analyzed by SEM, XRF, resisitivity measurement by four-point-probe method and Hall coefficient measurement by van der Pauw method.

Temperature programmed desorption (TPD) of bare silicon substrate and FTO films on silicon substrates were carried out with the same manner as previously reported [5, 6]. A schematic illustration of the TPD apparatus (ESCO EMD-WA1000S) is shown in Fig. 2. Each FTO film was cut to more or less the same size around 1 cm^2. The system was evacuated to $\sim 1.0\cdot 10^{-8}$ Pa by a turbo molecular pump. The specimen (film-deposited silicon wafer) was placed on a quartz stage directly using a manipulator system. Radiation from a halogen lamp was guided via a quartz rod and the quartz stage to the uncoated surface of the Si substrate. A thermocouple was pressed on the film surface to monitor and control the heating rate at 20°C min^{-1}. Gas evolved from the specimen was analyzed with a quadruple mass analyzer (QMS) with an ionization voltage of 70 V. The mass detected (m/z) are 1(H^+), 2(H_2^+), 12(C^+), 14(N^+), 15(CH_3^+), 16(O^+), 17(OH^+ or NH_3^+), 18(H_2O^+ or NH_4^+), 19(F^+), 20(HF^+), 28(CO^+ or N_2^+), 32(O_2^+), 37(NH_4F^+), 44(CO_2^+), 120(Sn^+), 136(SnO^+) and 152(SnO_2^+).

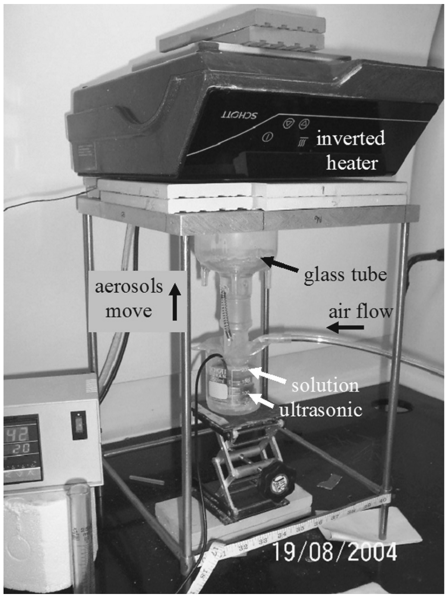

Fig. 1 Inverted pyrosol deposition system

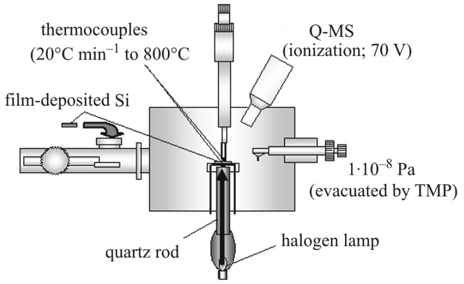

Fig. 2 Schematic illustration of the TPD apparatus

Results and discussion

The obtained FTO films deposited using the solutions with different doping ratios (F/Sn=0.00, 0.12, 0.75 and 2.50) are shown in Fig. 3. The thickness of FTO films was determined by XRF (fundamental parameter method) and plotted in Fig. 4a). As seen in Fig. 4a, thickness of the FTO films was not the same although the deposition condition was kept the same except the doping ratio. The carrier concentration was increased as increasing doping ratio and saturated after F/Sn>1.0 as seen in Fig. 4b while the mobility improved by adding slight amount of fluorine but deteriorated at high doping level as shown in Fig. 4c. As a result, the resistivity of the FTO films decreased to a minimum point, $3.2\cdot 10^{-4}$ ohm cm, at F/Sn=0.75 and slightly increased at higher doping as illustrated in Fig. 4d. These data indicated that FTO film with low resistivity in order of $(3–5)\cdot 10^{-4}$ ohm cm can be obtained from this cheap inverted pyrosol technique with a flexible F/Sn ratio in a range of 0.5–1.0 where carrier concentration is approaching a saturated value and mobility does not much deteriorate.

It was found that the majority of evolved gases from all FTO films was water vapor as m/z 18(H_2O^+), m/z 17(OH^+) [8] and m/z 1(H^+) were dominated among all TPD spectra and they all synchronized to each others as typically illustrated in Fig. 5 for the films deposited using the solution with F/Sn=0.00. The second majority of evolved gases were carbon dioxide (m/z 44(CO_2^+), m/z 28(CO^+) and m/z 16(O^+) [9])

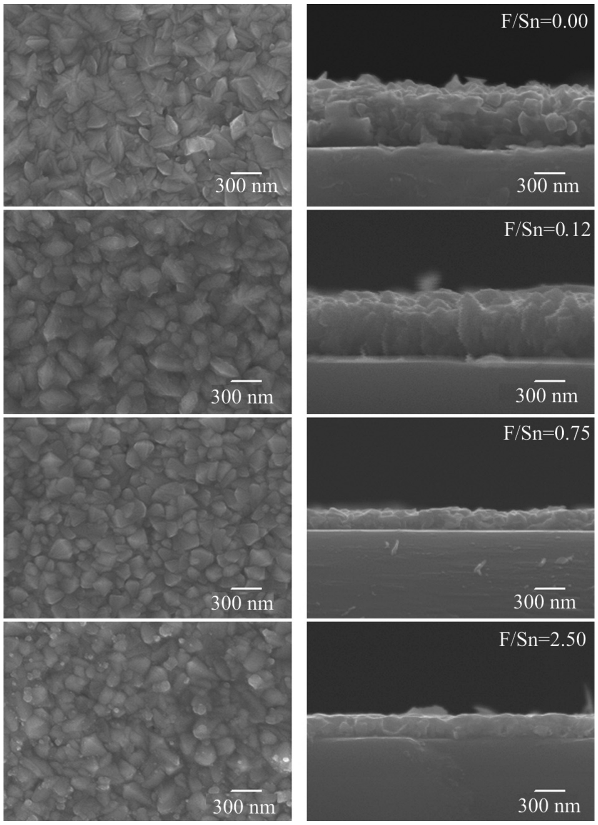

Fig. 3 SEM images of FTO films

and carbon monoxide (m/z 28($\mathrm{CO^+}$), m/z 12($\mathrm{C^+}$) and m/z 16($\mathrm{O^+}$) [10]) which all synchronized to each other as illustrated in Figs 6 and 7 for the films deposited using the solution of F/Sn=0.00 and 0.75, respectively. The rises of water vapor and carbon dioxide signals also synchronized to the rise of total pressure (measured with a BA gauge) at the corresponding temperatures. The m/z 16($\mathrm{O^+}$) signal synchronized to the evolution of water vapor, carbon dioxide and carbon monoxide as seen in Figs 5 and 6. It should be noted that the m/z 2($\mathrm{H_2^+}$) [11] was also another major signal from all samples including uncoated silicon substrate and its spectra and intensity was almost the same as that of the uncoated silicon substrate. The m/z 14($\mathrm{N^+}$) [12] spectra of all films was almost undetectable (intensity $<1\cdot10^{-12}$ A); this suggested that the amount of nitrogen was negligible in the present specimens. The m/z 15($\mathrm{CH_3^+}$) was detected very weakly ($2–4\cdot10^{-12}$ A) at around 150–450°C in all samples but there was no systematic tendency of spectra. The m/z 32($\mathrm{O_2^+}$) signal did not synchronize to others and its intensity raised rapidly after 750°C (from below $1\cdot10^{-12}$ A to several 10^{-12} A after 750°C). For m/z 120($\mathrm{Sn^+}$) and m/z 136($\mathrm{SnO^+}$), they were detected very weakly ($<1\cdot10^{-12}$ A) at high temperature around 650–750°C whereas m/z 152($\mathrm{SnO_2^+}$) was not detectable; this suggested that evaporation of tin dioxide occurred by the reduced species (Sn and SnO).

To compare the quality of film and the effect of fluoride doping from the TPD data, the TPD intensity were normalized by the volume of the film (film thickness x area). Figure 8 shows the normalized signal of m/z 18 ($\mathrm{H_2O^+}$) of different doping ratio. As seen in Fig. 8, the amount of water vapors evolved per unit volume of FTO film tends to increase for higher F/Sn ratios. The total number of evolved water vapor throughout the TPD measurement (50 to 800°C) was calculated based on the integration of the TPD intensity. The total number of evolved water vapor were $2.57\cdot10^{-4}$, $3.21\cdot10^{-4}$, $4.75\cdot10^{-4}$ and $4.44\cdot10^{-4}$ mol cm^{-3} for the film with F/Sn=0.00, 0.12, 0.75 and 2.50 respectively. Clearly, more evolved water vapor was found in more doping film. According to [5, 6] the

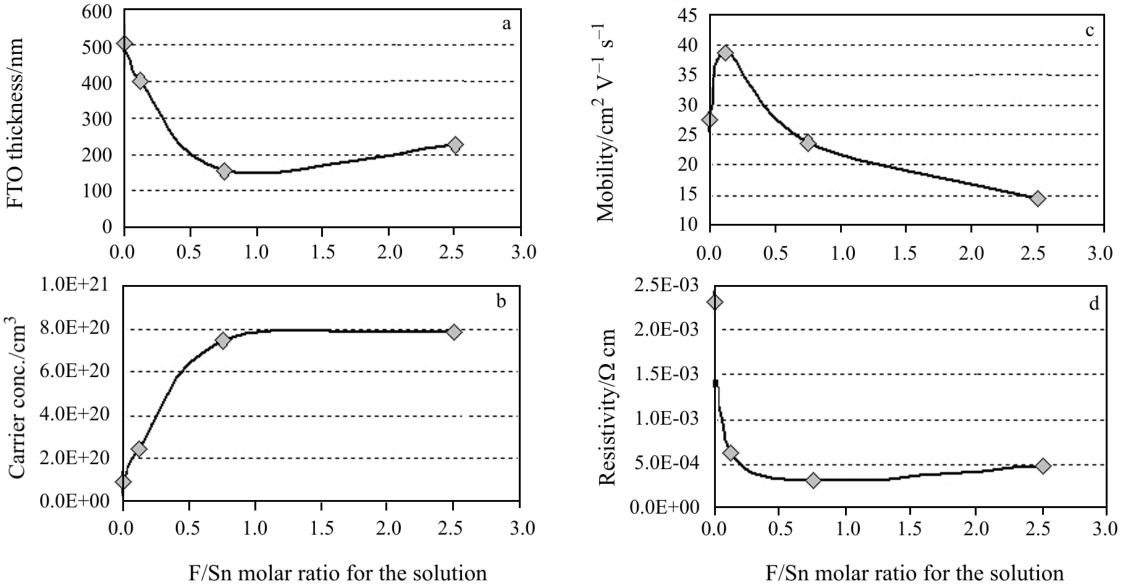

Fig. 4 Thickness and electrical properties of FTO films

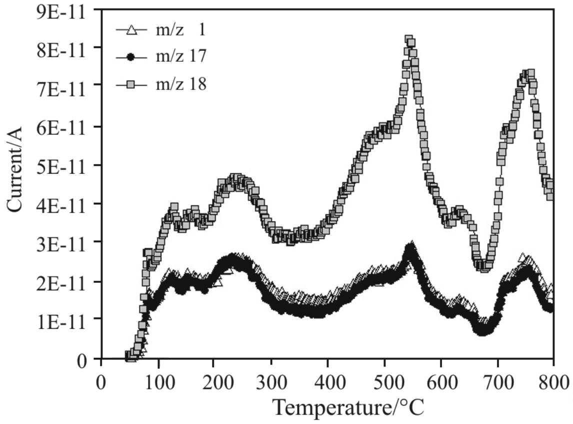

Fig. 5 TPD results of FTO film with F/Sn=0.00 for *m*/*z* 1(H^+), *m*/*z* 17(OH^+) and *m*/*z* 18(H_2O^+)

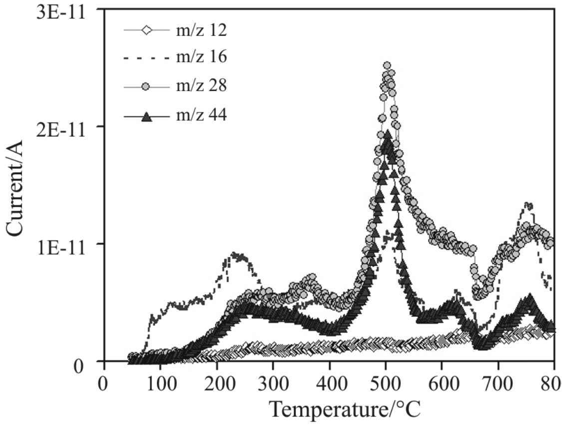

Fig. 6 TPD results of FTO film with F/Sn=0.00 for *m*/*z* 12(C^+), *m*/*z* 16(O^+), *m*/*z* 28(CO^+) and *m*/*z* 44(CO_2^+)

higher amount of water vapors evolved from the film implied the poorer quality of the film (more porous). This means that fluoride doping results deteriorated film although it promotes electrical conductivity. The degradation of film quality was more severe for heavy doping (F/Sn>0.5). As a consequence, mobility and conductivity decreased. TPD spectra of F/Sn=0.75 and 2.50 were more or less than same except at about 100°C where signal of F/Sn=0.75 was much stronger. For *m*/*z* 19 (F^+), the normalized TPD signal of different doping ratio are shown in Fig. 9. It was very clear that the amount of F^+ evolved from undoped film was almost undetected. However, it can be detected for slightly doped film (F/Sn=0.12) whose intensity increased following the increasing of the sample temperature. However, for the high doping films (F/Sn=0.75 and 2.50) the rapid jump of TPD signal started at 400°C has been observed. It is possible that the excessive F^+ came from the interior of film; for example at the grain boundaries where is the usual location for segregation and accumulation of impurity whose amount is over than solubility limit of materials. Thus, when the temperature of the sample was raised up to the temperature where the film was originally formed by pyrolysis (450°C), the film may undergo recrystallization and releases the fluorine tapped at the grain boundaries, yielding the jump of

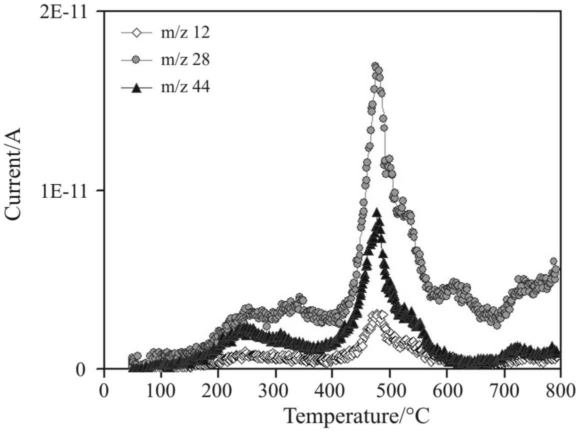

Fig. 7 TPD results of FTO film with F/Sn=0.75 for *m*/*z* 12(C^+), *m*/*z* 28(CO^+) and *m*/*z* 44(CO_2^+)

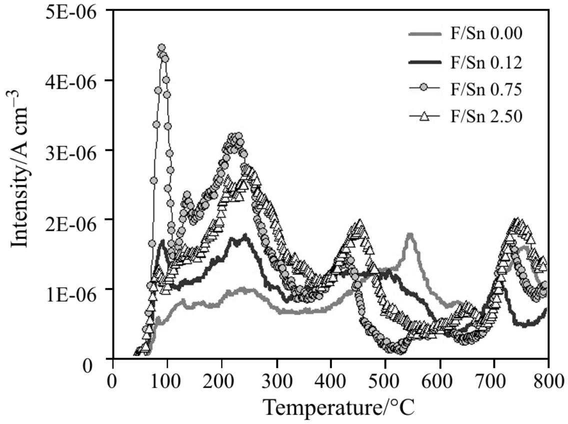

Fig. 8 Normalized TPD results for *m*/*z* 18(H_2O^+) of FTO films with different doping ratio

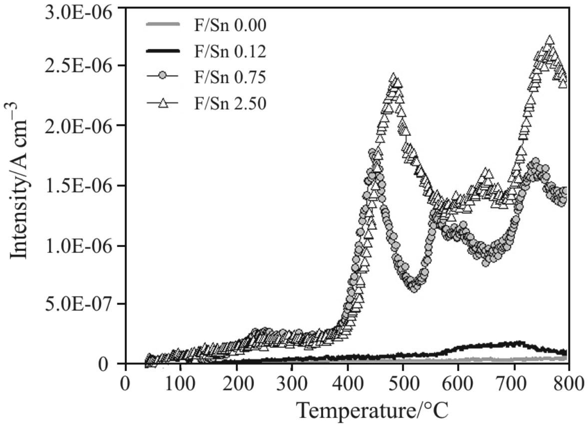

Fig. 9 Normalized TPD results for *m*/*z* 19(F^+) of FTO films with different doping ratio

the intensity. For *m*/*z* 20(HF^+) and *m*/*z* 37(NH_4F^+), their TPD signals were very weak ($<1\cdot10^{-12}$ A). However, the TPD signal of *m*/*z* 20 synchronized with that of *m*/*z* 19(F^+) whereas the TPD signal of *m*/*z* 37(NH_4F^+) did not synchronized with those of *m*/*z* 19 and *m*/*z* 20. The highest intensity was observed at around 200–300°C and there was no systematic trend of the spectra due to the doping.

Conclusions

FTO film with low resistivity in order of $(3–5)\cdot10^{-4}$ ohm cm can be obtained from a cheap inverted pyrosol technique with a flexible F/Sn ratio which is in a range of 0.5–1.0. The thickness of all FTO films was not the same, depending on doping ratio. The carrier concentration of FTO film increased as increasing doping ratio and saturated after F/Sn>1.0 while the mobility seemed to be deteriorated at high doping level. By the TPD investigation, it was found that the major of evolved gases from all FTO films were water vapor and carbon dioxide. F^+ (*m*/*z* 19) was detected only in doped films. Its intensity was very strong for highly doped films particularly at temperature above 400°C which was approximately the same as the deposition temperature. The big jump of F^+ signal above this temperature was attributed to the releasing of fluorine from the grain boundaries when the sample undergoes recrystallization during TPD measurement. Apart from water vapor and carbon dioxide, other evolved gases were very little detected which means that FTO films by inverted pyrosol technique were reasonable high quality with low residues on the surface (dendrites also were not observed on the film). The only main residue was fluorine whose amount depended on the amount of doping. To avoid this problem and also to use the dopant precursor effectively, doping not excess F/Sn=0.75 is recommended.

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