

Atmospheric-pressure chemical vapor deposition of fluorine-doped tin oxide thin films

Seigi Suh^a, Zuhua Zhang^b, Wei-Kan Chu^b, David M. Hoffman^{a,*}

^aDepartment of Chemistry and Materials Research Science and Engineering Center, University of Houston, Houston, TX 77204, USA

^bTexas Center for Superconductivity, University of Houston, Houston, TX 77204, USA

Received 30 June 1998; accepted 11 September 1998

Abstract

Fluorine-doped tin oxide films were deposited on silicon, glass and quartz substrates at 370–490°C by atmospheric-pressure chemical vapor deposition from $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ and oxygen. Backscattering spectra indicate the films are stoichiometric with O/Sn ratios of 1.9–2.0. Nuclear reaction analysis (NRA) for fluorine gives F/Sn ratios of 0.005–0.015 with the amount of fluorine in the films increasing with increasing deposition temperature. The films are transparent in the visible region (>75%) and have resistivities as low as $8.2 \times 10^{-4} \Omega \text{ cm}$. X-ray diffraction studies indicate the films deposited on glass are polycrystalline. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chemical vapour deposition; Tin oxide; Fluorine-doped

1. Introduction

Doped SnO_2 films are used as transparent conductors in liquid crystal displays, thin-film solar cells and other optoelectric device applications [1,2]. Fluorine is a preferred dopant because it gives films with high transparency and conductivity [3].

Deposition methods for fluorine-doped SnO_2 ($\text{SnO}_2:\text{F}$) films include spray pyrolysis [4–8], pyrosol processing [9] and chemical vapor deposition (CVD) [3,10–12]. In the CVD processes, fluorine is typically introduced into the films by including a fluorocarbon or some other fluorine-containing molecule in the precursor mixture during deposition. For example, CVD $\text{SnO}_2:\text{F}$ has been successfully deposited by using $\text{Sn}(\text{CH}_3)_4$, oxygen, and the fluorine dopant BrCF_3 at deposition temperatures >440°C [3] and $\text{Sn}(\text{CH}_3)_4$, oxygen containing 5 mol% O_3 , and HF at 350°C [13]. Other reported CVD fluorine dopants include fluorocarbon iodides [14], difluoroethane [11], CCl_3CF_3 [15] and $\text{CF}_3\text{CO}_2\text{H}$ [9,16].

To circumvent the need for a separate fluorine dopant, precursors having fluorinated ligands have been used to prepare $\text{SnO}_2:\text{F}$ films. Maruyama and Tabata [17], for example, have used a trifluoroacetate tin(II) complex, $\text{Sn}(\text{O}_2\text{CCF}_3)_2$, and we have used the hexafluoroisopropoxide

tin(IV) compound $\text{Sn}(\text{OCH}(\text{CF}_3)_2)_4(\text{HNMe}_2)_2$ [18]. Interestingly, however, our use of a related hexafluoroisopropoxide tin(II) complex, $\text{Sn}(\text{OCH}(\text{CF}_3)_2)_2(\text{HNMe}_2)_2$, gave poor quality, oxygen-deficient films. Motivated by these results, we became interested in attempting to deposit $\text{SnO}_2:\text{F}$ from other types of tin(IV) precursors having fluorinated ligands. In this paper we report the successful atmospheric-pressure CVD of transparent, conductive $\text{SnO}_2:\text{F}$ films from $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ and O_2 .

2. Experimental

2.1. Thin film depositions

Depositions were performed in an atmospheric-pressure laminar-flow rectangular glass reactor that has been described elsewhere [19]. The solid precursor was loaded with exclusion of air into a glass container that was then connected to the CVD apparatus via a VCO[®] fitting. Ultra high purity argon was used as the carrier gas. After the substrate was loaded, the reactor was heated and simultaneously flushed with a 600 sccm flow of argon for 0.5 h prior to each deposition to remove water. The precursor container and feed lines were maintained at 70°C and 120°C, respectively, during depositions. The argon carrier gas flow rate through the precursor container was 250 sccm. The oxygen (200 sccm) was diluted in argon (350 sccm) before entering the reactor. The films were left under the

* Corresponding author. Tel.: + 1-713-743-3255; fax: + 1-713-743-2787.

E-mail address: hoffman@uh.edu (D.M. Hoffman)

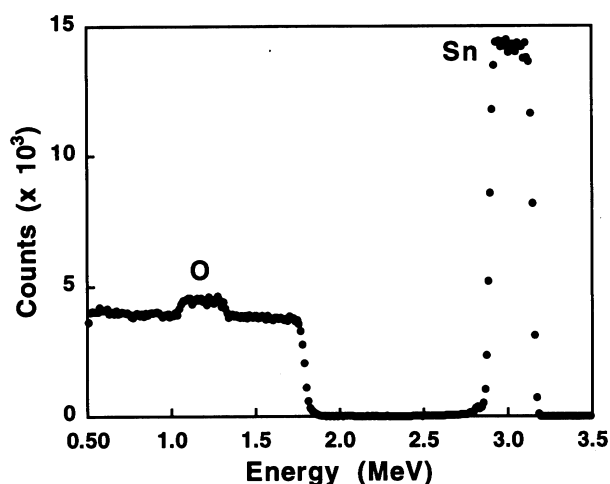


Fig. 1. Backscattering spectrum for a fluorine-doped tin oxide film deposited on silicon at 490°C. Beam 3.59-MeV $^4\text{He}^{2+}$.

O_2/Ar flow for 5 min at the deposition temperature after the precursor feed was stopped. The films were then cooled to 300°C under the same O_2/Ar flow, after which the flow was switched to argon (140 sccm) and the films were cooled slowly to room temperature.

The silicon substrates were degreased by rinsing them in hexanes and methanol. The substrates were then immersed in a $\text{HF}:\text{H}_2\text{O}$ (1:2) solution for 30 s, and subsequently rinsed in deionized water before blow-drying with nitrogen. Borosilicate glass and quartz microscopic slides were degreased with soap, rinsed with deionized water, and then rinsed with methanol before blow-drying with nitrogen.

2.2. Film characterization

Ion beam analyses were carried out at the Texas Center for Superconductivity using a 1.7-MeV tandem accelerator manufactured by NEC. The backscattering spectra of a 3.59-MeV $^4\text{He}^{2+}$ beam were used to determine the stoichiometries of the tin oxide films. The Si detector was set at 165° with respect to the beam. The deviation of the scattering cross section of 3.59-MeV $^4\text{He}^{2+}$ on oxygen from the Rutherford cross section was taken into account. The data were analyzed and moduled by using the program RBX. Nuclear reaction analyses for the detection of fluorine

were performed using 1.53-MeV H^+ beam ($^{19}\text{F}(\text{p},\alpha)^{16}\text{O}$). X-ray diffraction studies were carried out using Siemens diffractometers (models D5000 and GADDS; $\text{Cu K}\alpha$ radiation). Resistivities were measured by the Van der Pauw method [20] for films deposited on silicon (the substrate resistivity was 30 Ω cm). The film thicknesses used in the calculations were obtained from the backscattering spectra. Transmittance spectra were collected on a Hewlett-Packard 8452A diode array spectrophotometer.

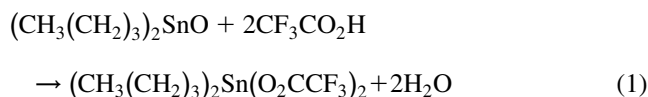
2.3. Synthesis of $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$

The following procedure, which is based on a patent method [21,22], was used to prepare the tin precursor: $\text{CF}_3\text{CO}_2\text{H}$ (6.70 g, 59.0 mmol) was added slowly to a suspension of $(\text{CH}_3(\text{CH}_2)_3)_2\text{SnO}$ (7.00 g, 28.1 mmol) in benzene (100 ml). The suspension changed rapidly to a pale yellow solution. After the reaction mixture was stirred for 1 h, an atmospheric pressure distillation was carried out under argon to remove the benzene solvent and water reaction product (benzene and water form an azeotrope). The resulting residue, a light gray solid, was extracted with benzene (1 \times 30 ml), and the extract was filtered through a Celite pad. The benzene was vacuum distilled from the filtrate to give the product as a colorless solid (yield 11.6 g, 90%).

3. Results and discussion

3.1. The precursor $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$

The precursor $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ was prepared by the reaction shown below (Eq. (1)) in high yield from commercially available reagents. The crude product was purified by vacuum sublimation ($\approx 70^\circ\text{C}$ at 0.06 Torr) or by dissolving it in benzene, filtering, and then drying under vacuum. Both methods gave pure compound as judged by ^1H NMR spectra ($>98\%$). $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ can be handled briefly in air without noticeable decomposition. We routinely handled the compound under an inert atmosphere, however.



3.2. CVD studies

Atmospheric-pressure CVD using $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ and dry O_2 gave films at substrate temperatures of 370–490°C. On a typical substrate that was 2 cm by 2 cm, the films covered uniformly an area approximately 1 cm wide by 1.5–2 cm long, where the latter measure is in the direction of the gas flow. Optimization of the film coverage was not attempted due to deficiencies in the reactor design and delivery system. Film analyses were

Table 1
Composition of films deposited on silicon from $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ and oxygen

Deposition temperature ($^\circ\text{C}$)	O/Sn ^a	F/Sn ^b
370	2.0	0.005
400	2.0	0.007
430	2.0	0.010
460	2.0	0.012
490	1.9	0.015

^a From backscattering spectra. The error is estimated to be ± 0.1 .

^b From NRA. The error is estimated to be ± 0.002 .

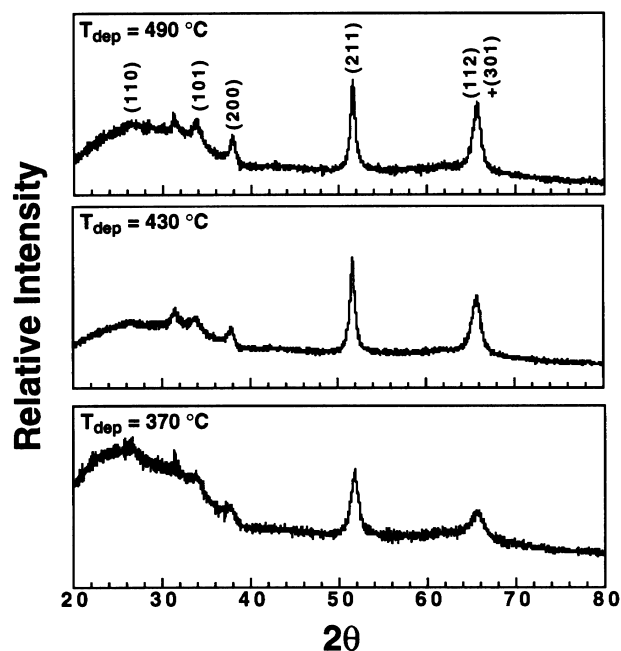


Fig. 2. X-ray diffraction patterns for films deposited on glass at 370 (a), 430 (b) and 490°C (c).

typically performed on a section approximately .75 cm by .75 cm that was cut from the interior of the substrates.

Backscattering spectra (e.g. Fig. 1) indicate the films are stoichiometric with O/Sn ratios of 1.9–2.0 (Table 1). Carbon and fluorine peaks are not observed in the spectra, indicating low levels of these elements in the films (<2 at.%). Nuclear reaction analysis (NRA) for fluorine gives F/Sn ratios of 0.005–0.015 with the amount of fluorine in the films increasing with increasing deposition temperature (Table 1). The fluorine content in the films is generally lower than the amounts in films prepared from $\text{Sn}(\text{O}_2\text{CCF}_3)_2/\text{O}_2$ (F/Sn 0.027) [17] and $\text{Sn}(\text{OCH}(\text{CF}_3)_2)_4(\text{HNMe}_2)_2/\text{air}$ (F/Sn 0.025) [18]. According to Gordon, for $\text{SnO}_2\text{:F}$ films obtained from $\text{Sn}(\text{CH}_3)_4$, oxygen and BrCF_3 the highest

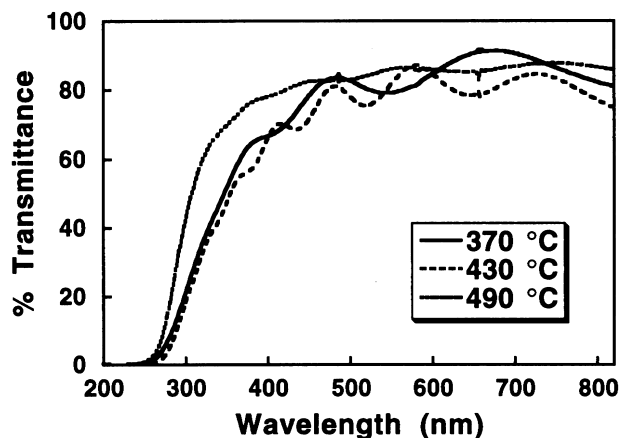


Fig. 3. Transmittance spectra for films deposited on quartz at 370, 430 and 490°C.

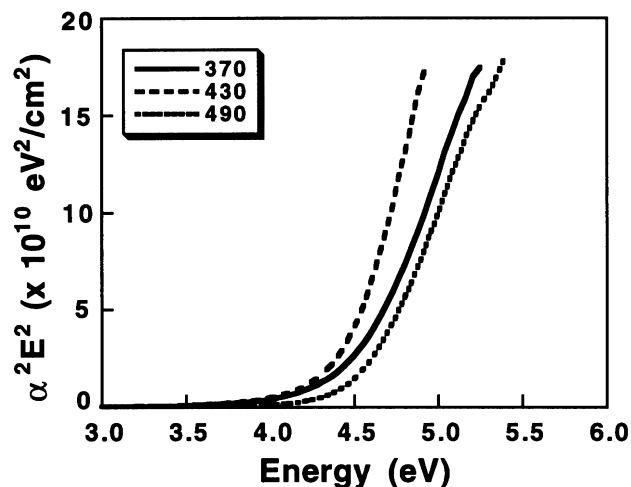


Fig. 4. Plots to determine band gaps for tin oxide films deposited on quartz at 370, 430 and 490°C.

conductivity is typically obtained when F/Sn is 0.02–0.04 [3,23].

Film thicknesses obtained from the backscattering spectra give a growth rate of 180 Å/min at 370°C which increases to ≈200 Å/min at deposition temperatures >400°C. Higher growth rates were observed when the precursor container temperature was increased, but we did not attempt to optimize the rates. The observed growth rates are lower than the reported growth rates of other CVD fluorine-doped tin oxide films. Maruyama and Tabata, for example, reported a growth rate of around 400 Å/min at 500°C using $\text{Sn}(\text{O}_2\text{CCF}_3)_2/\text{O}_2$ [17] and Proscia and Gordon observed 36000 Å/min at 600°C using $\text{Sn}(\text{CH}_3)_4$, oxygen and BrCF_3 [3].

X-ray diffraction studies for ≈10000 Å films deposited at 370, 430 and 490°C on borosilicate glass show the presence of polycrystalline tetragonal SnO_2 (Fig. 2). The most intense peaks are (211) and a combination of (112) and (301), which are merged into one broad peak [24]. The source of the diffraction peak observed at $2\theta = 31.4^\circ$, corresponding to a plane spacing of 2.85 Å, could not be identified but it could arise from cubic fluorite-type SnO_2 [25] or a suboxide such as Sn_3O_4 , Sn_3O_8 or Sn_2O_3 [9,24,26]. The mean grain sizes obtained by Scherrer's formula [27] from the (211) diffraction peak are approximately 120 (370°C), 160 (430°C) and 170 Å (490°C).

Selected transmission spectra for 7500–8000 Å films grown on quartz are shown in Fig. 3. All the films examined show over 75% transmittance in the visible and near-IR regions. This is lower than the reported transmittances of >85% for CVD films deposited at >250°C from $\text{Sn}(\text{OCH}(\text{CF}_3)_2)_4(\text{HNMe}_2)_2$ and air by Suh et al. [18] but it is comparable to the >75% transmittances for films deposited at 621–677°C from $(\text{CH}_3(\text{CH}_2)_3)\text{SnCl}_3$ and $\text{CF}_3\text{CO}_2\text{H}$ [16] and at >250°C from $\text{Sn}(\text{O}_2\text{CCF}_3)_2/\text{O}_2$ [17].

Optical band gaps were calculated from the absorbance data by plotting $\alpha^2 E^2$ versus E and extrapolating the linear

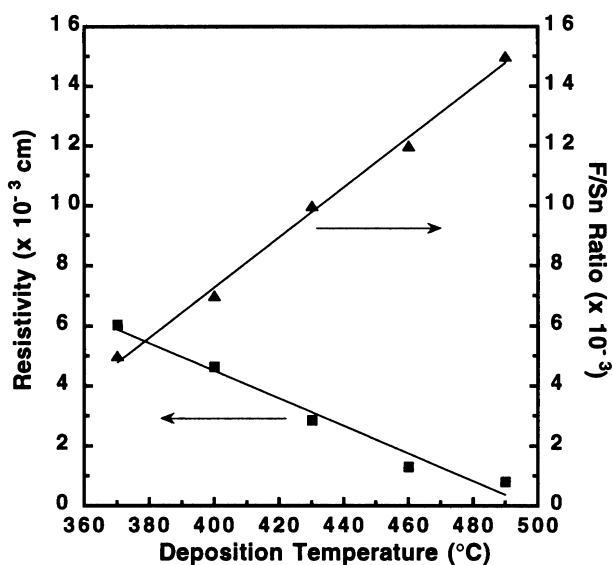


Fig. 5. Plot of resistivity and F/Sn versus deposition temperature for films deposited on silicon.

portion of the curve to $\alpha^2 E^2 = 0$, where α is the absorption coefficient and E is the photon energy. At 370, 430 and 490°C the band gaps are 4.4, 4.4 and 4.5 eV, respectively (Fig. 4). These values are slightly higher than those reported for other CVD fluorine-doped SnO_2 films (3.7–4.3 eV) [12,13].

Resistivities for the films deposited on silicon, which were measured by the van der Pauw method, ranged from 6×10^{-3} to $8 \times 10^{-4} \Omega \text{ cm}$ (Fig. 5). The resistivities decreased with increasing deposition temperature. Since the grain size did not change appreciably with deposition temperature, the trend of decreasing resistivity with increasing deposition temperature is probably due to the increase in the amount of fluorine in the films with increasing deposition temperature (Fig. 5). This interpretation should be taken with caution because the changes in fluorine content are small and the error bars in the fluorine analysis are large. If the correlation is correct, however, a further increase in fluorine content of our films should give films with lower resistivities, assuming fluorine incorporated beyond what is already there will contribute to the conductivity. The observed trend of increasing fluorine content with increasing deposition temperature (Table 1 and Fig. 5) suggests that higher deposition temperatures are needed to incorporate more fluorine, but the maximum attainable deposition temperature of our current apparatus is around 500°C. The resistivity values for our films are higher than those reported ($(3\text{--}6) \times 10^{-4} \Omega \text{ cm}$) for fluorine-doped SnO_2 films prepared by Ishida et al. [13], Gordon et al. [3] and Maruyama and Tabata [17].

4. Conclusion

Atmospheric pressure chemical vapor deposition using

$(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ and O_2 gave fluorine-doped tin oxide films at substrate temperatures of 370–490°C. The films are highly transparent in the visible region ($>75\%$) and electrically conductive. A film deposited at 490°C with a F/Sn ratio of 0.015 had the lowest resistivity ($8.2 \times 10^{-4} \Omega \text{ cm}$). $(\text{CH}_3(\text{CH}_2)_3)_2\text{Sn}(\text{O}_2\text{CCF}_3)_2$ and O_2 comprise a new precursor system for the low temperature deposition of transparent conductive tin oxide films.

Acknowledgements

This work was supported in part by the Environmental Institute of Houston (DMH, SS), the MRSEC Program of the National Science Foundation under Award Number DMR-9632667 (DMH, SS) and by the State of Texas through the Texas Center for Superconductivity at the University of Houston.

References

- [1] K.L. Chopra, S. Major, D.K. Pandya, *Thin Solid Films* 102 (1983) 1.
- [2] S.J. Lavery, H. Feng, P. Maguire, *J. Electrochem. Soc.* 144 (1997) 2165.
- [3] J. Proscia, R.G. Gordon, *Thin Solid Films* 214 (1992) 175.
- [4] C. Agashe, B.R. Marathe, M.G. Takwale, V.G. Bhide, *Thin Solid Films* 164 (1988) 261.
- [5] J. Bruneaux, H. Cachet, M. Froment, A. Messad, *Thin Solid Films* 197 (1991) 129.
- [6] G.C. Morris, A.E. McElnea, *Appl. Surf. Sci.* 92 (1996) 167.
- [7] D.R. Acosta, E.P. Zironi, E. Montoya, W. Estrada, *Thin Solid Films* 288 (1996) 1.
- [8] E. Shanthi, A. Banerjee, V. Dutta, K.L. Chopra, *J. Appl. Phys.* 53 (1982) 1615.
- [9] J.-M. Laurent, A. Smith, D.S. Smith, J.-P. Bonnet, R.R. Clemente, *Thin Solid Films* 292 (1997) 145.
- [10] G.H. Lindner, U.S. Patent 4,696,837 (1987).
- [11] L. Mao, R.E. Benoit, J.W. Proscia, *Mater. Res. Soc. Symp. Proc.* 317 (1994) 181.
- [12] A.K. Saxena, R. Thangraj, S.P. Singh, O.P. Agnihotri, *Thin Solid Films* 131 (1985) 121.
- [13] T. Ishida, O. Tabata, J. il Park, S.H. Shin, H. Magara, S. Tamura, S. Mochizuki, T. Mihara, *Thin Solid Films* 281–282 (1996) 228.
- [14] R.G. Gordon, U.S. Patent, 4,146,657 (1979).
- [15] D. Bélanger, J.P. Dodelet, B.A. Lombos, J.I. Dikson, *J. Electrochem. Soc.* 132 (1985) 1398.
- [16] P.R. Athey, F.K. Urban III, P.H. Holloway, *J. Vac. Sci. Technol. B* 14 (1996) 3436.
- [17] T. Maruyama, K. Tabata, *J. Appl. Phys.* 68 (1990) 4282.
- [18] S. Suh, D.M. Hoffman, L. Atagi, D.C. Smith, J.-R. Liu, W.-K. Chu, *Chem. Mater.* 9 (1997) 730.
- [19] R. Fix, R.G. Gordon, D.M. Hoffman, *Chem. Mater.* 3 (1991) 1138.
- [20] L.J. Van der Pauw, *Philips Res. Rep.* 13 (1958) 1.
- [21] V. Peruzzo, G. Tagliavini, *J. Organomet. Chem.* 66 (1974) 437.
- [22] J.E. Dewnurst, J.D. Nicholas, A.C.L. Savoca, U.S. Patent 5, 308,880 (1994).
- [23] R.G. Gordon, *Mater. Res. Soc. Symp. Proc.* 335 (1994) 9.
- [24] J.C. Manifacier, *Thin Solid Films* 90 (1982) 297.
- [25] L. Liu, *Science* 199 (1978) 422.
- [26] N. Srinivasa Murty, S.R. Jawalekar, *Thin Solid Films* 100 (1983) 219.
- [27] B.D. Cullity, *Elements of X-Ray Diffraction*, 2nd edn., Addison-Wesley, CA, 1978 p. 102.