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Atmospheric pressure deposition of F-doped SnO_2 thin films from organotin fluoroalkoxide precursors

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Five tributyltin fluoroalkoxides Bu_3SnOR_f [R_f = $CH(CF_3)_2$ (1), CH_2CF_3 (2), $CH_2C_2F_5$ (3), $CH_2(CF_2)_3CF_2H$ (4), CH_2CH_2F (5)] were synthesized and assessed as precursors for the APCVD of F-doped SnO_2. O_2 is required as co-reagent to produce hard, well-adhered coatings. Of the precursors assessed, 5 gave the best film incorporating 1.52 atom% fluorine, showing some (200) preferred orientation, resistivity of 1.30×10^{-3} Ω cm and 0.42% haze.

Keywords: tin oxide; CVD; fluoroalkoxide

Introduction

Tin oxide is one of the most widely exploited metal oxides. It has been used for centuries as a ceramic glaze while more recent applications include use as a catalyst, usually in combination with a transition metal, to effect a number of key processes (e.g. oxidation, hydrogenation).[1] However, it is as a coating on glass that it is now being most widely exploited, to impart structural rigidity to the surface of bottles, simply to decorate the surface of the glass or as a functional coating. Stoichiometric tin oxide is an electrical insulator (resistivity *ca* 10^5 Ω cm), but when non-stoichiometric, or by the introduction of dopants, it becomes an *n*-type semiconductor. The most common dopant is fluorine ($F:SnO_2$), although Group 15 elements (particularly antimony) have also been widely studied.[2–6] Applications for these coatings on glass include solar control windows (Pilkington K glass®) and self de-icing windscreens for aircraft. The electronic properties of tin oxide also make it a suitable basis for gas sensors,[7] which, like the catalysts mentioned above, generally require a second metal to introduce selectivity.

Chemical vapour deposition (CVD) is the method of choice for large-scale coatings, particularly at atmospheric pressure. In *dual-source* CVD procedures, a tin precursor (e.g. Me_4Sn, $SnCl_4$) is used along with either F_2, NH_4F, HF, $BrCF_3$ or other fluorocarbons, or CF_3CO_2H as sources of fluorine.[8] However, the 'activity' of the fluorine within the oxide lattice is sometimes variable and dependent on deposition conditions.[9] Approaches to $F:SnO_2$ from a *single-source* precursor are less common. Compounds with a direct Sn–F bond are likely to be insufficiently volatile, as such species commonly generate bridged oligomers/polymers through F: → Sn interactions, e.g. Ph_3SnF.[10] Thus, solutions to this problem have been sought through precursors which deliver the halogen to tin as part of the deposition process and include $Sn(O_2CCF_3)_2$,[11] $Bu_2Sn(O_2CCF_3)_2$[12] and our own work on organotin(IV) fluoroalkanes[13] and fluorocarboxylates.[14] Volatility is not an issue in sol–gel approaches to $F:SnO_2$, and precursors with a direct Sn–F bond have proved useful in this methodology.[15–18]

Surprisingly, despite the widespread use of metal alkoxides as CVD precursors to metal oxide films, the only such reports relating to $F:SnO_2$ are based on the purely inorganic systems $Sn[OCH(CF_3)_2]_4\cdot 2(HNMe_2)$ and $Sn[OCH(CF_3)_2]_2\cdot L$ (L = $HNMe_2$, C_5H_5N). The Sn(IV) species generated $F:SnO_2$ films with good transparency (>85%) but relatively high resistivity (2.1×10^{-3} Ω cm), while the divalent tin analogue, $Sn[OCH(CF_3)_2]_2.HNMe_2$ in air or water vapour afforded non-conductive $SnO_{0.9-1.3}F_{0.1-0.4}$, suggesting hydrolysis, rather than oxidation, was driving film deposition; both processes required low pressures (LPCVD) due to limited precursor volatility.[19] We now report our findings on the suitability of organotin fluoroalkoxides for $F:SnO_2$ film deposition.

Experimental

General

Elemental analyses were performed using an Carlo-Erba Strumentazione E.A. model 1106 microanalyser operating at 500 °C. ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-GX270 FT spectrometer, while ^{19}F and ^{119}Sn NMR spectra were recorded on a Jeol JNM-EX400 FT machine, all using saturated $CDCl_3$ solutions unless indicated otherwise; chemical shifts are in ppm with respect to Me_4Si, Me_4Sn or $CFCl_3$, coupling constants in Hz. Details of our Mössbauer spectrometer and related procedures are given elsewhere;[20] Mössbauer data are in mm s^{-1}. Dry solvents were obtained by distillation under inert atmosphere from the following drying agents: sodium-benzophenone (toluene, ether, THF), calcium hydride (CH_2Cl_2), sodium (hexane). Standard Schlenk techniques were used throughout. Starting materials were commercially obtained and used without further purification.

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Syntheses

*Tributyltin hexafluoroisopropoxide – $Bu_3SnOCH(CF_3)_2$ (**1**)*

Sodium hydride (1.00 g, 42 mmol) was suspended in dry ether (60 ml), and hexafluoroisopropyl alcohol (3.67 g, 22 mmol) added dropwise. After gas evolution had ceased the solution was stirred for a further 30 min and the excess sodium hydride separated by a canula transfer of the soluble material to a clean vessel in the strict absence of air. Tributyltin chloride (7.08 g, 22 mmol) was then added dropwise to the filtrate and a white precipitate rapidly formed. The mixture was subsequently refluxed for 1 h, cooled and the soluble material separated by a second canula transfer. The solvent was removed *in vacuo* and the residue distilled under reduced pressure to yield the product as a colourless oil (7.70 g, 93%), b.p. 105 °C/1.0 mm. Analysis: found (calcd for $C_{15}H_{28}F_6OSn$): C 39.7 (39.4)%; H 6.30 (6.45)%. ^{1}H NMR: 0.92 [9H, t, $CH_3(CH_2)_3$], $^{3}J(^{1}H-^{1}H) = 7$ Hz; 1.26 [6H, m, C_4H_9]; 1.34 [6H, m, C_4H_9]; 1.58 [6H, m, C_4H_9]; 4.40 [1H, sept, $Bu_3SnOCH(CF_3)_2$], $^{3}J(^{1}H-^{19}F) = 6$ Hz. ^{13}C NMR: 13.5 [$CH_3(CH_2)_3$]; 15.8 [$CH_3(CH_2)_2CH_2$]; 27.0 [$CH_3CH_2(CH_2)_2$]; 27.4 [$CH_3CH_2CH_2CH_2$]. $^{1}J(^{13}C-^{119}Sn) = 364$ Hz. C–F carbons not observed. ^{19}F NMR: −76.1 [d, CF_3], $^{3}J(^{19}F-^{1}H) = 6$ Hz. ^{119}Sn NMR: 151.9. Mössbauer: IS = 1.36; QS = 2.81.

*Tributyltin trifluoroethoxide – $Bu_3SnOCH_2CF_3$ (**2**)*

The same method as for (**1**) was used. Sodium hydride (2.40 g, 100 mmol) and trifluoroethanol (7.00 g, 70 mmol) were reacted together, followed by the addition of tributyltin chloride (11.50 g, 35 mmol). The product was isolated as a colourless oil (9.50 g, 81%), b.p. 100 °C/1.0 mm. Analysis: found (calcd for $C_{14}H_{29}F_3OSn$): C 44.0 (43.2)%; H 7.83 (7.53)%. ^{1}H NMR: 0.92 [9H, t, $CH_3(CH_2)_3$], $^{3}J(^{1}H-^{1}H) = 7$ Hz; 1.19 [6H, m, C_4H_9]; 1.36 [6H, m, C_4H_9]; 1.61 [6H, m, C_4H_9]; 4.01 [2H, q, CH_2CF_3], $^{3}J(^{1}H-^{19}F) = 9$ Hz. ^{13}C NMR: 13.6 [$CH_3(CH_2)_3$]; 15.2 [$CH_3(CH_2)_2CH_2$]; 27.2 [$CH_3CH_2(CH_2)_2$]; 27.8 [$CH_3CH_2CH_2CH_2$]; 64.4 [CH_2CF_3]. $^{1}J(^{13}C-^{119}Sn) = 358$ Hz. C–F carbon not observed. ^{19}F NMR: −77.7 [t, CH_2CF_3], $^{3}J(^{19}F-^{1}H) = 9$ Hz. ^{119}Sn NMR: 133.7. Mössbauer: IS = 1.34; QS = 2.56.

*Tributyltin pentafluoropropoxide – $Bu_3SnOCH_2C_2F_5$ (**3**)*

This was prepared as for (**1**) using sodium hydride (1.64 g, 70 mmol) and pentafluoro-1-propanol (5.13 g, 34 mmol). The sodium alkoxide was subsequently reacted with tributyltin chloride (10.20 g, 31 mmol) and the product isolated by distillation under reduced pressure to yield a colourless oil (10.20 g, 75%), b.p. 102 °C/1.0 mm. Analysis: found (calcd for $C_{15}H_{29}F_5OSn$): C 41.9 (41.0)%; H 7.27 (6.67)%. ^{1}H NMR: 0.92 [9H, t, $CH_3(CH_2)_3$], $^{3}J(^{1}H-^{1}H) = 7$ Hz; 1.18 [6H, m, C_4H_9]; 1.33 [6H, m, C_4H_9]; 1.60 [6H, m, C_4H_9]; 4.10 [2H, t, $CH_2CF_2CF_3$], $^{3}J(^{1}H-^{19}F) = 14$ Hz. ^{13}C NMR: 13.6 [$CH_3(CH_2)_3$]; 15.2 [$CH_3(CH_2)_2CH_2$]; 27.2 [$CH_3CH_2(CH_2)_2$]; 27.8 [$CH_3CH_2CH_2CH_2$]; 63.8 [$CH_2C_2F_5$]. $^{1}J(^{13}C-^{119}Sn) = 358$ Hz. C–F carbons not observed. ^{19}F NMR: −126.4 [m, $CH_2CF_2CF_3$], $^{3}J(^{19}F\text{-}^{1}H) = 14$ Hz; −83.7 [m, $CH_2CF_2CF_3$]. ^{119}Sn NMR: 132.4. Mössbauer: IS = 1.30; QS = 2.52.

*Tributyltin octafluoropentoxide – $Bu_3SnOCH_2(CF_2)_3CF_2H$ (**4**)*

Bis(tributyltin) oxide (11.44 g, 19 mmol) and a slight excess of octafluoro-1-pentanol (10.00 g, 43 mmol) were dissolved in dry toluene (100 ml) and refluxed for 2 h. The water formed was removed azeotropically using a Dean and Stark apparatus. The toluene was then removed *in vacuo* to yield a yellow oil which was distilled under reduced pressure to give the product as a colourless oil (13.70 g, 69%), b.p. 130°/1.0 mm. Analysis: found (calcd for $C_{17}H_{30}F_8OSn$): C 39.4 (39.2)%; H 5.94 (5.81)%. ^{1}H NMR: 0.92 [9H, t, $CH_3(CH_2)_3$], $^{3}J(^{1}H-^{1}H) = 7$ Hz; 1.19 [6H, m, C_4H_9]; 1.35 [6H, m, C_4H_9]; 1.60 [6H, m, C_4H_9]; 4.12 [2H, t, $CH_2(CF_2)_3CF_2H$], $^{3}J(^{1}H-^{19}F) = 9$ Hz; 6.14 [1H, tt, $CH_2(CF_2)_3CF_2H$], $^{2}J(^{1}H-^{19}F) = 52$ Hz, $^{3}J(^{1}H-^{19}F) = 6$ Hz. ^{13}C NMR: 13.5 [$CH_3(CH_2)_3$]; 15.0 [$CH_3(CH_2)_2CH_2$], $^{1}J(^{13}C-^{119}Sn) = 357$ Hz; 27.1 [$CH_3CH_2(CH_2)_2$]; 27.7 [$CH_3CH_2CH_2CH_2$]; 63.6 [t, $CH_2(CF_2)_3CF_2H$], $^{2}J(^{13}C-^{19}F) = 24$ Hz; 107.8 [tt, $CH_2CF_2(CF_2)_3H$]; $^{2}J(^{13}C-^{19}F) = 254$ Hz, $^{3}J(^{13}C-^{19}F) = 30$ Hz; 110.3 [m, $CH_2CF_2CF_2(CF_2)_2H$]; 111.3 [m, $CH_2(CF_2)_2CF_2CF_2H$]; 116.7 [tt, $CH_2(CF_2)_3CF_2H$], $^{2}J(^{13}C-^{19}F) = 254$ Hz, $^{3}J(^{13}C-^{19}F) = 30$ Hz. ^{19}F NMR: −138.4 [m, $CH_2(CF_2)_3CF_2H$]; −131.5 [m, $CH_2(CF_2)_2CF_2CF_2H$]; −127.1 [m, $CH_2CF_2CF_2(CF_2)_2H$]; −122.7 [m, $CH_2CF_2(CF_2)_3H$]. ^{119}Sn NMR: 133.9, Mössbauer: IS = 1.34; QS = 2.54.

*Tributyltin fluoroethoxide – $Bu_3SnOCH_2CH_2F$ (**5**)*

The synthetic method for (**4**) was followed using bis(tributyltin) oxide (16.69 g, 28 mmol) and a slight excess of 2-fluoroethanol (4.91 g, 77 mmol). A colourless oil was obtained (15.70 g, 79%), b.p. 130 °C/1.0 mm. Analysis: Found (calcd for $C_{14}H_{31}FOSn$): C 47.7 (47.6)%; H 8.89 (8.87)%. ^{1}H NMR: 0.92 [9H, t, $CH_3(CH_2)_3$], $^{3}J(^{1}H-^{1}H) = 7$ Hz; 1.15 [6H, m, C_4H_9]; 1.34 [6H, m, C_4H_9]; 1.61 [6H, m, C_4H_9]; 3.90 [2H, dt, CH_2CH_2F], $^{3}J(^{1}H-^{19}F) = 30$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz; 4.45 [2H, dt, CH_2CH_2F], $^{2}J(^{1}H-^{19}F) = 48$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz. ^{13}C NMR: 13.4 [$CH_3(CH_2)_3$]; 14.6 [$CH_3(CH_2)_2CH_2$]; 27.0 [$CH_3CH_2(CH_2)_2$]; 27.7 [$CH_3CH_2CH_2CH_2$]; 65.2 [CH_2CH_2F]; 85.6 [CH_2CH_2F]. $^{1}J(^{13}C-^{119}Sn) = 347$ Hz. ^{19}F NMR: −75.6 [CH_2CH_2F]. ^{119}Sn NMR: 114.2. Mössbauer: IS = 1.28; QS = 2.38.

Chemical Vapour Deposition

Details of our apparatus are given elsewhere.[13,21] In all cases, the substrate used was 4 mm glass which was undercoated with a thin film of SiCO to act as a 'blocking layer' to prevent sodium diffusion into the fluorine-doped tin oxide film. Approximately 10 g of precursor was used in each series of experiments; details of the relevant deposition conditions are given in Table 1.

Film Analysis

The X-ray diffraction equipment consisted of a Philips PW1130 generator operating at 45 kV and 40 mA to power a copper long fine-focus X-ray tube. A PW 1820 goniometer fitted with glancing-angle optics and proportional X-ray detector was used.

Table 1. Conditions for the CVD of fluorine-doped tin oxide using fluorinated organotin alkoxides

	Precursor					
	1	**2**	**3**	**4**	**5**	**5**[a]
Reactor temperature (°C)	554	554	554	544	554	467
Bubbler temperature (°C)	98	111	112	106	128	128
Heater tapes (°C)	200	200	200	200	200	200
Diluent flow (L min^{-1})	2.75	2.75	2.75	2.75	2.75	2.75
Carrier flow (L min^{-1})	1.0	1.2	1.0	1.0	1.2	1.2
Oxygen flow (cm^{3} min^{-1})	600	600	600	600	600	0
Run time (min)	25	30	30	20	20	35

[a] No oxygen used during deposition.

The non-focusing thin film optics employed a 1/4-degree primary beam slit to irradiate the specimen at a fixed incident angle of 1.5°. Diffraction radiation from the sample was collimated with a flat plate collimator and passed through a graphite flat crystal monochromator to isolate diffracted copper Kα peaks onto the detector. The equipment was situated in a total enclosure to provide radiation safety for the highly collimated narrow beams of X-rays. Data were acquired by a PW1710 microprocessor and processed using Philips APD VMS software. Crystalline phases were identified from the International Centre for Diffraction Data (ICDD) database. Samples of coating for XRD were of approximate dimensions 1.5×2.0 cm. Crystallite size was determined from line broadening using the Scherrer equation.[22] The instrumental effect was removed using the NIST SRM660 lanthanum hexaboride standard. These operating conditions were used in preference to conventional Bragg–Brentano optics for thin films to give an order of magnitude increase in count rate from a fixed volume of coating with little contribution from the substrate.

Film thickness was determined by etching a thin strip of the film with zinc powder and 50% HCl solution. This created a step in the film, which was measured with a Dektak stylus technique.

Haze was measured on a Pacific Scientific Hazeguard meter and with a barium fluoride detector. The calculation of haze was carried out by measurement of the specular light and diffusive light. Specular light is defined as light transmitted straight through the sample within $\pm 2.5°$ of normal incidence and the diffusive light is defined as light scattered beyond 2.5°. The initial measurement was carried out with the specular detector slot closed and therefore a value for the sum of the specular light and the diffusive light was obtained. The specular light slot was then opened and a measurement of the diffusive light was obtained.

Emissivity data (integral of total emittance between 5 and 50 µm divided by the integral from 5 to 50 µm of the total emittance of a blackbody at room temperature) were then calculated from the infra-red reflectance spectra, measured using a two-beam Perkin Elmer 883 machine and measured against a rhodium mirror standard.[23]

Sheet resistance was measured with a four-point probe on an electrically isolated scribed circle of film ($\square = 25$ cm^2) and corrected using a conversion factor, the value being dependent on the diameter of the scribed circle.

Fluorine was determined by XRF measurements made on a Philips PW1400 machine fitted with a scandium target X-ray tube. The penetration depth achieved was between 9 and 10 µm, so the result obtained was throughout the thickness of the coating. The analysis was performed on approximately 6 cm^2 of material.

Results and Discussion

Synthesis and Spectroscopy

A series of organotin fluoroalkoxides were prepared with a variation in the fluorinated component, which enabled the effect of different fluorine arrangements on the incorporation of the halogen into an SnO_2 film to be explored. All alkoxides synthesized were tributyltin derivatives, Bu_3SnOR_f, which was due to the cheap availability and lower degree of toxicity of the butyltin starting materials. The toxicity implications of organotin precursors for CVD have been discussed by others.[24] As we have previously reported with respect to perfluoroalkyltins[13] and organotin carboxylates,[14] the choice of hydrocarbon group on tin has been found to have little effect on the properties of the fluorine-doped tin oxide film deposited, although it can impact on film growth rates. Therefore, in this study, we have chosen to explore the effect of the fluorinated component of the alkoxides with an invariant R group on tin.

Two methods were utilized for the preparation of the tributyltin alkoxides which both used fluoroalcohols as the fluorine-containing source. The method chosen was dependent on the boiling point of the fluoroalcohol. With lower boiling alcohols the common method of using a sodium alkoxide to react with the organotin chloride was utilized. The appropriate sodium alkoxide was formed by reaction of the fluorinated alcohol with sodium hydride, then subsequent reaction with tributyltin chloride yielded the target tributyltin fluoroalkoxide. An excess of the sodium alkoxide was required to ensure complete reaction and prevent contamination of the product with unreacted tributyltin chloride, subsequent separation of the liquid reagent and product proving difficult.

$$R_fONa + Bu_3SnCl \xrightarrow{Et_2O} Bu_3SnOR_f + NaCl \qquad (1)$$

$$R_f = CH(CF_3)_2\ (\mathbf{1}), CH_2CF_3\ (\mathbf{2}), CH_2C_2F_5\ (\mathbf{3})$$

Distillation under reduced pressure produced colourless liquids in high yield (75–93%).

For alcohols with boiling points in excess of 90 °C, the alternative method of reacting the fluorinated alcohol with bis(tributyltin) oxide was utilized. The reaction was carried out in toluene and the water formed removed azeotropically using a Dean and Stark separator.

$$(Bu_3Sn)_2O + 2R_fOH \xrightarrow{\text{toluene}} 2Bu_3SnOR_f + H_2O \qquad (2)$$

$$R_f = CH_2(CF_2)_3CF_2H\ (\mathbf{4}), CH_2CH_2F\ (\mathbf{5})$$

Following distillation under reduced pressure, colourless liquids were obtained in yields of 69–79%.

The Mössbauer spectra of **1**–**5** have isomer shifts (IS) consistent with organotin(IV) compounds, as expected. The values obtained for the quadrupole splitting (QS = 2.38–2.81 mm s^{-1}) do not provide a conclusive determination of the structure adopted, owing to the similarity in the observed quadrupole splitting range for tetrahedral (1.00–2.40 mm s^{-1}) and *cis*-trigonal bipyramidal (1.70–2.40 mm s^{-1}) geometries.[25] Tetrahedral compounds would arise from monomeric entities, with a *cis*-trigonal bipyramidal arrangement $Bu_3Sn(OR_f)_2$ generated by association to a dimeric structure with a μ-OR_f group. Relatively high QS values are also influenced by the electronegative fluorine atoms, which cause additional asymmetry of the electronic field gradient around the tin. The effect of the fluorine atoms present on the first fluorinated carbon atom (γ with respect to tin) is clearly visible within the series of compounds synthesized. For example, $Bu_3SnOCH(CF_3)_2$ (**1**), which contains the largest number of fluorine atoms in this position, exhibits a very high QS value of 2.81 mm s^{-1}. At the other end of the scale, $Bu_3SnOCH_2CH_2F$ (**5**) with a single fluorine atom in the same location has the lowest QS value of 2.38 mm s^{-1}. Compounds **2**–**4** have very similar QS values which is broadly consistent with the presence of two (**3**, **4**) or three (**2**) fluorines on the γ-carbon in these compounds. The electron-withdrawing nature of the fluorine also reduces the basicity of the alkoxide and hence its tendency to bridge between metal centres. Thus, the Mössbauer QS data are probably indicative of tetrahedral metal environments.

^{1}H and ^{13}C NMR spectra are unexceptional and have the expected signals with the correct integrals for the proposed formulations. The ^{19}F NMR spectra displayed the expected resonances for all the fluorine atoms contained in the alkoxide ligands, and confirmed the presence of those ligands. The magnitudes of $^1J(SnC)$ (347–364 Hz) are in the appropriate region for four-coordinate tributyltin species, which are usually found in the range 327–387 Hz.[26] These data correspond to C–Sn–C angles of 109–111° based on the correlation derived by Holeček.[27] Very similar ^1J values (358, 357 Hz) were obtained for compounds **2**–**4**, which all possess fully fluorinated arrangements in the γ-position (i.e. the β-carbon). A slightly higher value (364 Hz) was observed for $Bu_3SnOCH(CF_3)_2$ (**1**), which can be explained by the presence of an additional CF_3 group in the γ-position which leads to a slightly higher demand for *p*-orbital character from tin by the ligand and hence a larger 5*s*(Sn) character within the Sn–Bu bond. Similarly, a slightly lower coupling constant was observed for $Bu_3SnOCH_2CH_2F$ (**5**, 347 Hz) owing to the presence of only one fluorine atom in the ligand, lowering its overall electronegativity.

A similar pattern is shown by the ^{119}Sn chemical shifts to that observed for the Mössbauer and $^1J(SnC)$ coupling constant data. Again, the highest value occurs for $Bu_3SnOCH(CF_3)_2$ (**1**, 151.9 ppm) and the lowest for $Bu_3SnOCH_2CH_2F$ (**5**, 114.2 ppm) with little deviation observed for the series **2**–**4** (132.4–133.9 ppm). All these chemical shifts are typical of tin with a coordination number of four. For example, a ^{119}Sn chemical shift of +129 ppm has been found for Me_3SnOMe, which is four-coordinate in solution.[28]

CVD Studies

All precursors were tested with oxygen gas as a co-reagent, although, in addition, **5** was also tested as a true single-source precursor. The deposition conditions used are given in Table 1. As all precursors are liquids, it was hoped that low bubbler temperatures would be sufficient to achieve a good transport of material in the vapour phase. However, as found with the liquid perfluoroalkyltin compounds,[13] reasonably high temperatures were again required, suggesting that the alkoxides are not remarkably volatile. It was generally found that a slightly lower bubbler temperature could be used for precursors containing more fluorine atoms. For example, for $Bu_3SnOCH(CF_3)_2$ (**1**) a bubbler temperature of 98 °C proved adequate, compared with 128 °C for $Bu_3SnOCH_2CH_2F$ (**5**).

Deposition was found to occur at the front end of the substrate directly after the inlet, and only coated the first 5–6 cm of the glass. All films were found to adhere well to the glass substrate, and could not be removed without relatively harsh treatment, with the exception of the film produced from **5** in the absence of O_2, which was extremely powdery and could easily be wiped from the glass.

Glancing angle X-ray diffraction studies confirmed the crystalline nature of the films and their composition as tin oxide, with the exception of that deposited from **3**, which was amorphous. The film from **1** showed preferred orientation along the (200) direction compared with a standard sample of SnO_2, as assessed as the by the ratio of the intensity of the 200 reflection compared with that of the total diffraction pattern (Fig. 1). A ratio of 25.5% was measured for the film from **1**, against a 7% ratio for a randomly oriented film; more randomly oriented films were obtained from **2** (9.9%), **3** (6.7%) and **4** (5.5%). SnO_2 films with (200) preferred orientation are believed to contain less structural defects and therefore exhibit better properties.[2]

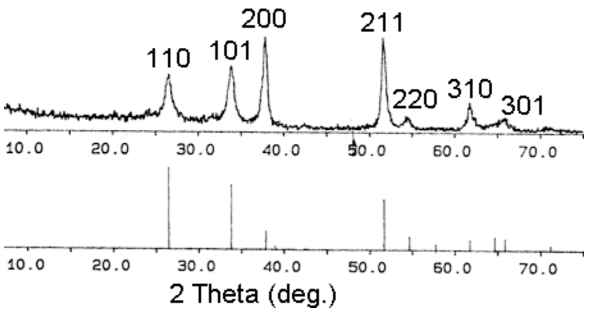


Figure 1. Powder XRD of the F : SnO_2 film deposited from precursor **1**. Shown below in Fig. 2 is the pattern for a randomly oriented samples of SnO_2 (cassiterite, PDF 21–1250).

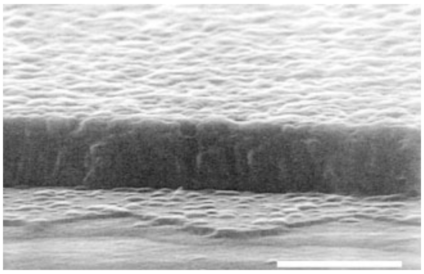


Figure 2. SEM of the film from $Bu_3SnOCH(CF_3)_2$ (**1**); bar = 600 nm.

From line broadening measurements of the (110) reflection it was possible to measure the approximate crystallite size of the samples using the Scherrer equation.[22] A representative crystallite size of 132 Å was measured for the film deposited from $Bu_3SnOCH(CF_3)_2$ (**1**).

Scanning electron microscopy (SEM) was performed to show the morphology of the film deposited from $Bu_3SnOCH(CF_3)_2$ (**1**) (Fig. 2). The image shows the SiCO undercoat (a blocking layer to prevent sodium diffusion from the glass) and the crystalline SnO_2 film which has subsequently been deposited.

For all films deposited in the presence of oxygen gas, thickness, haze, emissivity, sheet resistance, resistivity and fluorine content were measured and compared with the data for typical films produced industrially from separate tin and fluorine sources (Table 2).[29]

For use as a solar control coating, which reduces energy loss from buildings, the F : SnO_2 film acts by being transparent to visible wavelengths but reflective in the infrared. The optimum doping level is *ca* 3% of the halogen, which generates films of resistivity *ca* 2×10^{-4} Ω cm; however the amount of fluorine is not necessarily indicative of electronic properties as they depend on how it is incorporated into the tin oxide lattice.[9,30] Typically, films of *ca* 3000 Å are required for solar control purposes, which we were not able to achieve for precursors **2** and **3**, despite the quantities of precursor used (10 g), high bubbler temperatures and long run times. Furthermore, analysis of these two films reveals poor properties with extremely high emissivity and resistivity measurements, which can be associated with the low fluorine contents of both films but particularly that from **3** (<0.03%).

An unusual pattern can be observed from the fluorine contents determined for the films. It can be seen that precursors **2**, **3** and **4** achieved very little fluorine incorporation and hence extremely poor film properties. The arrangements of the fluorinated alkoxide ligands are very similar in these three precursors with a linear chain containing an increasing number of fluorine atoms in the fashion

Table 2. Analysis of fluorine-doped tin oxide films from fluorinated organotin alkoxide precursors

	Precursor						
	1	**2**	**3**	**4**	**5**	Standard[a]	$Et_3SnO_2C_2F_5$[b]
Thickness (Å)	3750	1815	1460	2910	2410	3000	3470
Haze (%)	0.74	0.54	0.27	0.61	0.42	<0.40	0.39
Emissivity	0.278	0.813	0.829	0.889	0.358	<0.150	0.167
Sheet resistance (Ω/□)	38	915	1035	220	54	15	16
Resistivity ($\times 10^{-3}$ Ω cm)	1.42	16.60	15.13	6.40	1.30	0.50	0.54
Fluorine content (atom%)	0.64	0.10	<0.03	0.14	1.52	2.00	1.16

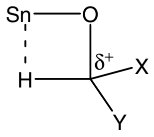
[a] Typical measurements for a good fluorine-doped tin oxide film derived from separate tin and fluorine sources.[29]
[b] Mahon *et al.*[14]

CF_3 (**2**), C_2F_5 (**3**) and $(CF_2)_3CF_2H$ (**4**), respectively. The common feature of the three compounds is the $Bu_3SnOCH_2CF_2$ segment, and it appears that the presence of additional fluorine in these ligands does not have a positive effect on the amount of resultant fluorine deposited in the doped tin oxide film.

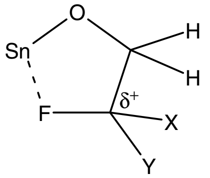
To explain the very low fluorine incorporation into these films, it seems likely that the decomposition pathway involved the loss of the fluorinated ligand in such a way as to prevent effective fluorine transfer to the tin during the CVD process. There are two feasible explanations for this. Firstly, the electron withdrawing effect of the fluorinated alkoxide ligands causes a weakening of the Sn–O bond [as shown by the trend in $^1J(SnC)$], which promotes elimination of the ligand as the parent alcohol:

$$Bu_3SnOR_f \xrightarrow{\text{- butene}} HSnOR_f \xrightarrow{O_2} SnO_2 + HOR_f \qquad (3)$$

However, this would seem unreasonable, as **1** has the strongest electron-withdrawing groups closest to the O–C bond [largest $^1J(SnC)$] yet incorporates more fluorine into the film than **2**–**4**. The second explanation for the low fluorine incorporation could be that a β-hydride elimination is more favourable than a γ-fluoride elimination, which would result in transfer of hydrogen rather than the desired fluorine:



(**I**)



(**II**)

A β-hydride elimination would explain the low fluorine levels determined for precursors **2**–**4**, which all contain two β-hydrogens and γ-fluorines. During the course of a β-hydride elimination, positive charge is developed on the carbon from which hydrogen is leaving, which is stabilized by electron-donating groups. Thus, the two γ-CF_3 groups in **1** would destabilize the transition state and work against this mechanism (**I**, X = Y = CF_3). This would explain the enhanced fluorine content of the film derived from **1** (0.64 atom%) relative to **2**–**4**, which results in much improved film properties, although overall they are still inferior to those found for the standard film deposited by the dual-source method. The presence of only one hydrogen atom on the β-carbon could also be significant, as statistically this would also work against β-H transfer.

It is interesting that the fluorine content determined for the film deposited from $Bu_3SnOCH_2CH_2F$ (**5**) was the highest from the precursors studied (1.52 atom%). This increased fluorine content resulted in improved film properties as expected, although they too were still inferior to the properties of the standard film grown from dual-source precursors. However, the film derived from precursor **5** was relatively thin (2410 Å).

The large difference in the fluorine content found for the films deposited from the two closely related precursors $Bu_3SnOCH_2CF_3$ (**2**) and $Bu_3SnOCH_2CH_2F$ (**5**) also requires comment. γ-F transfer will, like β-H transfer, build up positive charge on the associated carbon. In precursor **2** (and **1**, **3**, **4**), this centre will be destabilized by the two γ-F (**II**, X = Y = F) relative to **5** (**II**, X = Y = H). Additionally, it can be argued that the CF_3 group in **2** induces greater partial positive charge on the associated carbon even before γ-F transfer, strengthening each of the C–F bonds by an additional ionic component. Thus, it might be expected that the C–F bond of the CH_2F group in **5** would be weaker than any of the analogous bonds of the CF_3 group in **2**, thus also rationalizing the greater ability of **5** to transfer fluorine to tin.

In summary, the trend in fluorine incorporation can be rationalized by (i) precursors **2**–**4** having unfavourable γ-F transfer and the least unfavourable β-H transfer, thus the lowest incorporation, (ii) **1** having substituents which make β-H transfer less likely but which also work against γ-F transfer, thus it produces a film intermediate in its fluorine content; finally, (iii) **5**, which ironically has the lowest fluorine content in the ligand, generating the film with the highest halogen content by having a γ-F transfer mechanism which, it appears, competes favourably with β-H transfer and plausibly incorporates the weakest C–F bond.

Conclusions

Based on the data reported in this study, the F : SnO_2 films produced from organotin alkoxides are generally inferior in overall properties to those generated by dual-source approaches (Table 2), with generally very little fluorine incorporation achieved. Modest results were obtained from only one compound, $Bu_3SnOCH_2CH_2F$ (**5**), which implies that it is the environment of fluorine in the ligand with respect to other substituents (H, F), rather than simply the quantity of halogen, which determines the level of its incorporation into the oxide film, i.e. for the linear fluoroalkoxides (**2**–**5**) simply increasing the fluorine content of the ligand does not appear to increase the fluorine content of the F : SnO_2 film deposited. Further comparison with other tin-fluoroalkoxides is limited. $Sn[OCH(CF_3)_2]_4.2HNMe_2$ generated films with good transparency (>85%) but relatively high resistivity (2.1×10^{-3} Ω cm) by LPCVD,[31] while $Sn[OCH(CF_3)_2]_2.2HNMe_2$ in combination with air and water vapour produced films of $SnO_{0.9-1.3}F_{0.1-0.4}$, suggesting hydrolysis rather than oxidation drives film formation.[19] The Sn(IV) species incorporates between 0.6 and 2.4% fluorine depending on temperature (200 and 450 °C), similar to but somewhat higher than **1** at a comparable temperature. However, direct comparison should be treated with caution as the two formulations are sufficiently different to make meaningful comparisons; similar comments apply to the Sn(II) analogue, where film formation is reported to accrue by a different mechanism.

As a precursor class, the organotin fluoroalkoxides, at least those studied here, perform poorly in comparison with organotin fluoroalkyls (R_3SnR_f),[13] and particularly organotin fluorocarboxylates ($R_3SnO_2CR_f$), data for which are also included in Table 2.[14] The latter, being cheap, easy to synthesize and air-stable, offer the best combination of properties from the three families of organometallic precursors for use as APCVD precursors for F : SnO_2. Fluoroalkyltin compounds do generate good quality films (e.g. $Bu_3SnC_4F_9$: 1.48% fluorine, 0.64% haze, resistivity 0.85×10^{-3} Ω cm), but are limited by the synthetic protocols required to produce them.[13] Comparisons relating the fluorine incorporation from the fluoroalkoxides with that from these fluoroalkyltins have to be qualified by the fact that the ligands are not identical. However, like **2**–**5**, $Bu_3SnC_6F_{13}$ incorporates very little halogen, while $Bu_3SnO_2CCF(CF_3)_2$, which is probably converted to $Bu_3SnCF(CF_3)_2$ by CO_2 elimination, incorporates a similar quantity of fluorine (0.88%) to **1**. However, none of the fluoalkyltins nor the fluorocarboxylates contain β-hydrogens with which F-transfer has to compete.

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