Precursors for the formation of tin(IV) oxide and related materials

Kieran C. Molloy*

Department of Chemistry, University of Bath, Bath BA2 7AY, UK

Molecular precursors for the formation of tin oxide and related materials by chemical vapour deposition or sol-gel routes are reviewed.

Keywords: tin oxide, precursor, chemical vapour deposition, sol-gel

Tin oxide is one of the most widely exploited metal oxides. As a catalyst, usually in combination with a transition metal, it is effective in a number of key protocols (oxidation, hydrogenation and dehydrogenation, cracking, isomerisation). As a ceramic it has been used for centuries as a glaze, but it is as a coating on glass that it has been most widely exploited in recent years. These coatings can impart structural rigidity to the surface of, for example, bottles, act simply to decorate the surface of the glass, or as a functional coating. Stoichiometric tin oxide is an electrical insulator (resistivity *ca* 10^5 Ωcm), 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; FTO), though Group 15 elements (particularly antimony) have also been widely studied; indium tin oxide (ITO) is related but has a dominant indium content. Applications for tin oxide 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,[1] which, like the catalysts mentioned above, generally require a second metal to introduce selectivity. Smoke alarms based on tin oxide are the most generally available for such a device based on a metal oxide. More details on all these applications can be found in general books on tin chemistry[2,3] and included in recent reviews on thermochemical and mechanistic aspects of tin oxide chemical vapour deposition (CVD).[4,5]

This review attempts to bring together the molecular approaches to the formation of tin oxide and related materials. A selective approach has been necessary for such a disparate collective of data, and will thus focus primarily on CVD and sol-gel routes, at the exclusion of other techniques such as dip-coating, chemical bath deposition, sputtering etc, all of which are important in their own right. The emphasis will be on where molecular chemistry can impart new directions in tin oxide materials chemistry and, if only by omission, indicate areas for further study where precursor chemistry can play a role in developing novel materials.

CVD precursors

The key issues of volatility (for atmospheric pressure or low-pressure chemical vapour deposition, APCVD/LPCVD), solubility (aerosol-assisted or liquid injection chemical vapour deposition, AACVD/LICVD) and decomposition processes need to be addressed when choosing a suitable precursor chemical. In addition, the choice between a dual-source approach (in this case, separate precursors for tin and oxygen) and a single-source (one precursor delivering all elements of the final film) needs to be considered. The vast majority of work on the deposition of SnO_2 thin films is based on APCVD using dual-sources, in which the oxygen source is usually O_2 or H_2O, though alternative reagents *e.g.* MeOH, MeC(O)OEt have been reported. The focus of this review is the tin precursor, which is one of three broad compound classes: inorganic compounds (*e.g.* tin halides), organometallics (possessing at least one Sn–C bond) and metal-organics (no direct Sn–C bond but where one or more ligands have a hydrocarbon component).

Relatively few inorganic tin compounds have sufficient volatility for CVD purposes. $SnCl_4$, a liquid, is paramount among these and has been used in conjunction with O_2 and/or H_2O to form SnO_2 films by APCVD, at typical substrate temperatures of 450–550 °C;[6-9] SnO has also been observed at lower temperatures.[8] Even with volatile $SnCl_4$, however, several groups have reverted to a spray pyrolysis techique (effectively AACVD), rather than conventional APCVD.[10,11] Reliable comparisons between studies are impossible, as parameters other than simply the precursor *e.g.* reactor configuration, also play a part. However, typical results suggest that grain size is generally uniform and increases (0.1 to 0.5 nm) as the temperature of deposition increases from *ca* 430 to 580 °C, and films deposited at 480 °C have the highest conductivity, with no haze and transmission in the visible range larger than 80%.[9] The addition of water significantly lowers the temperature of SnO_2 formation by *ca* 250 °C.[4] Both this reaction, and that of $SnCl_4$/MeOH,[12] probably involve adduct intermediates as well as direct reaction with water to form chloro-hydroxides *e.g.* $Cl_3Sn(OH)$.

By contrast, solid $SnCl_2$ has found less favour, though reactive thermal evaporation has been found to produce good quality films for electrodes in electronic devices, albeit at the relatively elevated temperature of 550 °C.[13] SnO_2 films with preferred (200) orientation have been deposited by reaction of $SnCl_2$ with O_2, with an optimum deposition temperature range of 450–500 °C generating films with typical resistivity of 10^{-4} Ωcm, among the lowest reported for undoped SnO_2.[14] Sb:SnO_2 has recently been deposited by APCVD from hydrated $SnCl_2/SbCl_3/O_2$ in the range $350 < T < 420$ °C, though optical transmission and conductivity of the films are inversely related, so while 0.88% Sb-doping showed the lowest resistivity (6×10^{-4} Ωcm) it only has *ca* 40% transmission in the visible region.[15]

Anhydrous $Sn(NO_3)_4$ is the only reported single-source inorganic precursor for tin oxide, and the lack of inherent carbon makes it particularly attractive. Glassy, oxygen-rich tin oxide was deposited from this precursor at 500 °C, which became more stoichiometric on annealing at 700 °C.[16] Subsequently, the same precursor has been used with analogous anhydrous Zr and Hf nitrates to deposit a compositional spread of ternary Sn/Ti/Hf mixed oxides *via* an elegant combinatorial CVD approach.[17-20]

Organotins, with weaker intermolecular interactions and thus generally higher volatilities, have been the precursors of choice in the majority of dual-source CVD processes (O_2 co-reactant, H_2O has little impact on growth rate). Me_4Sn dominates these reports across a variety of conditions (APCVD,[8,21] LPCVD[22-26]), though Et_4Sn also figures.[27,28] Many of these studies have measured reaction kinetics, and a complex reaction mechanism involving 96 reactions and 27 gas-phase species proposed, of which Me_3SnOH is suggested as a key intermediate.[26] Surprisingly therefore, the latter does not appear to have been explored as a precursor in its own right.

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* E-mail : k.c.molloy@bath.ac.uk

Typical films produced by LPCVD of Me_4Sn/O_2 are deposited at rates as high as 120 Åmin^{-1}, are polycrystalline with a refractive index of 2.00–2.10, have visible-light transmission of 84% and resistivity of 0.6 Ωcm.[22] One area which has been relatively overlooked is plasma-assisted CVD of SnO_2, in which a tin precursor (typically Me_4Sn or Et_4Sn) is oxidised by rf plasma-activated O_2.[29-33] Deposition temperatures as low as 30 °C have been reported, which accommodates coating of temperature-sensitive substrates such as plastics. This is likely to be a growth area in coming years.

Organotin halides represent something of a compromise between the extremes of $SnCl_4$ and R_4Sn and have been widely studied, particularly Me_2SnCl_2 and $BuSnCl_3$. The gas phase chemistry of the reactions between these organometallics and oxygen sources (O_2, H_2O and their mixtures) has been reviewed.[4,5] GC/MS detection of the gas-phase by-products in the oxidation of Me_2SnCl_2 include H_2, CO_2, CO, CH_4, C_2H_6 and CH_3Cl, formed by a complex mechanism in which both surface and gas-phase radicals are involved; similarities in the mechanism with that between Me_4Sn and O_2 have been noted.[34] An *in situ* study of the oxidation Me_2SnCl_2, using optical sensors based on Fourier transform IR spectroscopy (FTIR) and tunable diode laser spectroscopy (NIR-DLS), has been reported, in which the gas phase directly above the growing layer has been monitored.[35]

Less well-studied is the mechanism of the reaction between $BuSnCl_3$ and H_2O/O_2. The reaction rate increases with the addition of water, with intermediates involving hydrolysis of the Sn-Cl bond seemingly important; interestingly, unlike $SnCl_4$, only carbon is deposited from the reaction of $BuSnCl_3$ and water in the absence of O_2.[4] Heats of reaction and bond energies derived from theoretical models suggest that all the organometallic precursors described above react by initial Sn-C bond cleavage, with potential contributions (where possible) from gas-phase hydrolysis. Thermochemical calculations also suggest $SnCl_2$ is a common intermediate in the formation of SnO_2 from both Me_2SnCl_2 and $BuSnCl_3$.[4] From an environmental perspective the toxicity of organotins used in CVD has been raised,[36] however there is no evidence that either $BuSnCl_3$ or Bu_2SnCl_2 disproportionate to generate more toxic Bu_3SnCl, at least at 200–300 °C in the liquid phase.[37]

Beyond the organotin halides, other functionalised organotins as precursors have been largely overlooked, though $Me_2Sn(NMe_2)_2$ does deposit high purity (101)-oriented films,[38] suggesting this is an approach which merits further evaluation. $Bu_2Sn(O_2CMe)_2$ also deposits tetragonal SnO_2 though mixed with amorphous phases (coatings of 800–5000 Å have resistivities of 5×10^{-3}– 9×10^{-2} Ωcm and visible transparency of 90–95%); O_2 and H_2O are required co-reactants.[39] Under AACVD, $Bu_2Sn(O_2CMe)_2$ (0.1 mol l^{-1} in butanol) has produced dense films with good optical transparency at low temperatures by a surface-mediated process (*ca*. 450 °C) while more textured films suitable for gas sensing applications occur *via* mass transport control at $T > 550$ °C.[40] In conjunction with $SbCl_5/O_2/H_2O$, Sb:SnO_2 has been deposited which, at dopant levels of 0.6–2.7%, show good transmission (85–91%) but modest resistivity (1.5×10^{-3}–3.2×10^{-3}Ωcm).[41] The results are consistent with AACVD using $SnCl_2$ mentioned earlier, in which good conductivity is at the expense of low optical transmission and *vice versa*.[15] These data are also very similar to Sb:SnO_2 produced by dip coating $[Sn(OPr^i)_4/Sb(OEt)_3$/triethanolamine/$H_2O/^iPrOH$].[42]

Tin alkoxides, β-diketonates and carboxylates comprise the classes of metal-organic precursor used to deposit SnO_2. Both Sn(II) and Sn(IV) alkoxides have been exploited, though the lower oxidation state gives rise to hybrid materials incorporating both Sn^0 and tin oxides, and are discussed later in this review. $Sn(OBu^t)_4$ acts as a single-source precursor for SnO_2 nanowires at 550–750 °C by a vapour–liquid–solid (V–L–S) growth mechanism using gold particles as templates. The diameter of the nanowires is determined by the diameter of the gold particles, while only granular films are seen at lower deposition temperatures (< 525 °C).[43] The gas-sensing properties of Pt:SnO_2, deposited from (in part) $Sn(OBu^t)_4$, have been explored and found to exceed those of films deposited by sputtering.[44] SnO_2 films have also been deposited by APCVD from various tin(II) β-diketonates (acac,[45] tfac, hfac[46]) in either air or O_2. Initially thin, polycrystalline films deposited from $Sn(acac)_2$ develop a preferred (002) orientation at over 1000 nm thickness; typical deposition rates are 20–600 Åmin^{-1}.

$Sn(O_2CMe)_2$, in combination with O_2 or just in air, also deposits SnO_2 by a photo-assisted CVD route in which a low-pressure mercury lamp (λ = 235.7 nm) was used to irradiate the substrate. Amorphous films accrued at $150 < T < 200$ °C, which became polycrystalline on heating at above 300 °C. The deposition rate was enhanced over simple thermal CVD by the irradiation.[47]

The tin amide $Sn(NMe_2)_4$, synthesised from $SnCl_4$ and $LiNMe_2$, is a volatile liquid which is thermally stable and only moderately air-sensitive, and has been used in APCVD experiments with O_2 to yield SnO_2 at temperatures lower than described above for $SnCl_4$ (250–400 °C). Growth rate increases with both temperature and oxidant flow rate, though the mechanism of film deposition is unknown and the film resistivities can be relatively high (10^{-1}– 10^{-3} Ωcm).[48]

Sol-gel precursors

The hydrolysis of tin alkoxides is among the earliest attempts to use precursors to control the formation of ceramic tin oxide materials.[49] Though not alone as precursors –tin halides and carboxylates have also been studied– the fundamental solution chemistry and characterisation of reaction intermediates is most widespread for the alkoxides. While this hydrolysis and condensation *i.e.* sol-gel chemistry, is most commonly used to produce bulk materials, in combination with spin-coating it can also be used to form thin films. For example, spin-casting solutions of $Sn(OMe)_2$ or $Sn(OPr^i)_4$ mixed with valeric acid and water (to generate a tin oxo-valerate polymer *in situ*) has lead, after oxidation by either H_2O_2 at room temperature or aerobic calcination at 400 °C, to transparent, amorphous tin(IV) oxide films.[50] However, it offers an inferior alternative to conventional CVD in large-scale and/or continuous coating processes but is probably superior for deposition onto temperature-sensitive substrates, though low-temperature plasma-assisted CVD is likely to challenge this position in the future.

The synthesis and structural chemistry of tin alkoxides has been reviewed, both specifically[51] and as part of wider reviews of homo- and hetero-metallic systems.[52,53] Several reports relate to the structural characterisation of tin oxo-alkoxide intermediates from the hydrolysis of these precursors *e.g.* $Sn_6(O)_4(OCH_2CH_2NMe_2)_4$,[54] $Sn_5(O)_2(ONeo)_6$[55] and $Sn_3(O)(OBu^i)_{10}.2^iBuOH$,[56] (Fig. 1a–c) though aggregates are smaller than observed from the hydrolysis of organotin(IV) trihalides *e.g.* $(^iPrSn)_9(O)_8(OH)_6Cl_5$,[57] $(^iPrSn)_{12}(O)_{14}(OH)_6Cl_2$.[58] $(RSn)_8(O)_{14}(OH)_8(SnOH)_4$ (R = 2,4,6-$^iPr_3C_6H_2$).[59] These structural studies offer insights into the evolution of the final oxide material in a way that is impossible for gas-phase CVD chemistry.

Hydrolysis of monomeric $Sn(OBu^t)_4$, dimeric $[Sn(OPr^i)_4.HOPr^i]_2$ or polymeric $[Sn(OEt)_4]_n$ has afforded spherical cassiterite SnO_2 particles of diameter 70–250 nm.[60] Some control over the rate of hydrolysis of tin alkoxides can be gained by the incorporation of chelating ligands,[61] though fundamental studies in this area are sparse. This, though, offers a route to materials of controlled architecture, such as the formation of mesoporous

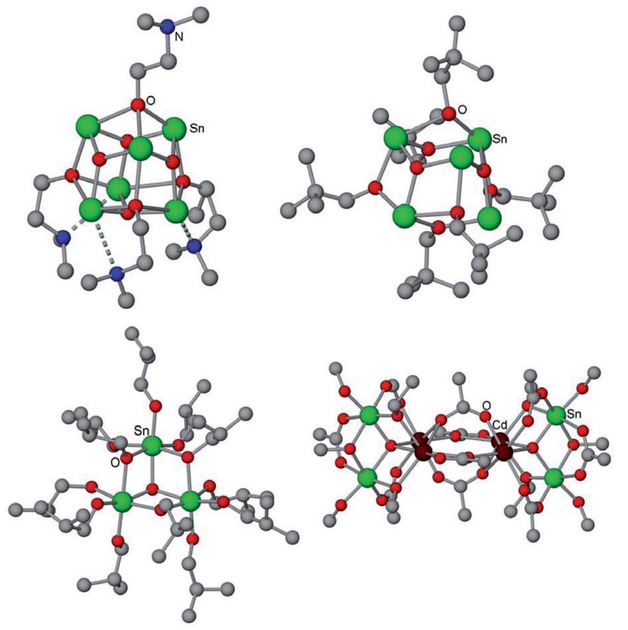


Fig. 1 The structures of (top left) (a) $Sn_6(O)_4(OCH_2CH_2NMe_2)_4$,[54] (b) $Sn_5(O)_2(ONeo)_6$,[55] bottom left (c) $Sn_3(O)(OBu^i)_{10}.2^iBuOH$,[56] and (d) $Cd_4Sn_4(\mu\text{-}O)_2(OAc)_{10}(ONeo)_{10}$ (only α-C of the Neo groups shown for clarity).[113]

SnO_2 from controlled hydrolysis of $Sn(acac)_2(OAm^t)_2$. Variation in both hydrolysis ratio and calcination temperature have been used to prepare SnO_2 powders of variable surface area.[62] The structural characterisation of $Sn_4(O)_2(\mu\text{-}OEt)_4(OEt)_6(acac)_2$, from hydrolysis of $Sn(acac)_2(OEt)_2$, gives an insight into this process.[63]

The most significant alternative sol-gel precursor to tin alkoxides has been developed by Jousseaume and Toupance, who have exploited the hydrolytic sensitivity of Sn-alkyne bonds to furnish a radically different class of precursor. While these precursors have been extensively used to form $F:SnO_2$ materials (*see below*), the basic principals can be appreciated from undoped materials. The precursors, $RSn(C{\equiv}CR')_3$, act effectively in the same way as $RSn(OR)_3$ but are generally far easier to handle.[64] When ditin precursors $(RC{\equiv}C)_3Sn(spacer)Sn(C{\equiv}CR)_3$ are hydrolysed in a similar manner, hybrid materials $[O_{1.5}Sn(spacer)SnO_{1.5}]_n$, in which Sn-O sheets are linked by the organic spacer [*e.g.* $(CH_2)_4$, $CH_2C_6H_4CH_2$, $CH_2(C_6H_4)_2CH_2$], are generated (Scheme 1).[65]

When xerogels derived from hydrolysis of $O_{1.5}SnC_6H_4SnO_{1.5}$ are calcined in air at 400–500 °C, the bridging phenylene group is easily removed resulting in nanocrystalline nanoporous cassiterite SnO_2 with tunable surface area.[66] An analogous strategy has been used to elaborate and functionalise the surface of SnO_2 particles, by hydrolysis of $XSn(C\ldots CR)_3$ in the presence of the nanoparticles, which resulted in attachment of XSn to the oxide surface. In this way, fluorinated chains [$X = (CF_2)_7CF_3$] or dyes [$X = (CH_2)_n$perylene, $n = 2, 4$], for applications in self-cleaning coatings and photovolataic devices, respectively,[67,68] have been prepared.

F-doped tin oxide

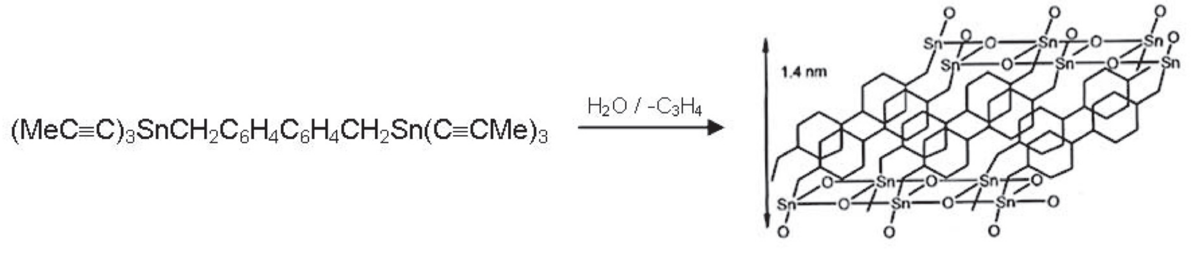
Of all the dopants which have been added to tin oxide, fluorine has received the most attention as it generates films of high conductivity and optical clarity.[69-72] This is particularly pertinent in the coating of architectural glass, where $F:SnO_2$ has been widely exploited as a solar control coating to reduce energy loss from buildings, and in which the doped tin oxide film acts by being transparent to visible wavelengths but reflective in the IR. The optimum doping level is *ca* 3% of the halogen which generates films of resistivity *ca* 2×10^{-4} Ωcm, 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.[69,72] Other dopants which should, however, be noted include the Group 15 elements (P,[73,74] As,[75] Sb[76,77]), while indium tin oxide (ITO) is predominantly indium. Some comments of the deposition of $Sb:SnO_2$ have been made earlier.[15,41]

CVD is the method of choice for large-scale coatings, though other methods (*e.g.* rf sputtering) have also been employed. Of these alternative techniques, only precursors to $F:SnO_2$ used in sol-gel processes have been included in this review.

In dual-source CVD procedures, one of the tin precursors discussed above [Me_4Sn, $SnCl_4$, $SnCl_2$, $Sn(NMe_2)_4$] along with either F_2,[78] NH_4F,[79,80] HF,[70,81] $BrCF_3$[69] and other fluorocarbons,[73] or CF_3CO_2H[82] as sources of fluorine have been reported. However, the "activity" of the fluorine within the oxide lattice is sometimes variable and dependent on deposition conditions.[69] Typical film properties *e.g.* from $Me_4Sn/O_2/O_3/HF$ at below *ca* 350 °C by thermal-CVD and photo-CVD respectively, include resistivities of 3.4 and 4.5×10^{-4} Ωcm, and transmittances of 70% and 80% at 550 nm.[70] Plasma-assisted CVD of $F:SnO_2$, by adding SF_6 to a Me_4Sn/O_2 mix, yielded films whose conductivity was dependent on SF_6 flow rate, as doping and etching of the film become competing processes.[83]

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. Thus, solutions to this problem have been sought through precursors which deliver the halogen to tin as part of the deposition process.

Fluoroalkyltin compounds $R_{4-n}Sn(R_f)_n$ (R = Me, Et, Bu, $R_f = C_4F_9$, $n = 1$; R = Bu, $R_f = C_4F_9$, $n = 2, 3$; R = Bu, $R_f = C_6F_{13}$, $n = 1$) deliver 0.79–2.02% fluorine to the SnO_2 film at deposition temperatures of *ca* 550 °C under APCVD conditions, with the surprising exception of the most fluorinated ligand, $Bu_3SnC_6F_{13}$ (< 0.05%); oxygen was added to the system to aid film growth. The gas-phase structure of $Me_3SnC_4F_9$ was determined by electron diffraction to gain insights into the mechanism of fluorine transfer, and among the four conformations present in the gas phase, fluorine



Scheme 1 Reprinted with permission from ref. 65. Copyright (2004) American Chemical Society.

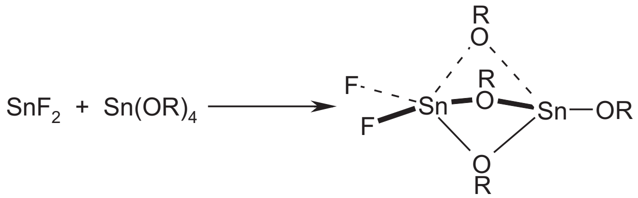
attached to γ- or δ-C of the R_f chain seemed most suitably oriented.[84] By analogy with the β-H elimination mechanism common in CVD processes, however, the β-C might also be anticipated to be important. In the only other related study, $(BuC{\equiv}C)_3SnCH_2CH_2CF_3$ has delivered fluorine from the γ-C in a sol-gel approach (*see below*).[85,86]

While the synthesis of the fluoro-alkyltin compounds (above) is problematic, fluorocarboxylates, $R_{4\text{-}n}Sn(O_2CR_f)_n$, are potentially more viable synthetically and offer the possibility of generating $R_{4\text{-}n}Sn(R_f)_n$ *in situ* by the well-known decarboxylation process. Both $Sn(O_2CCF_3)_2$[87] and $Bu_2Sn(O_2CCF_3)_2$[88] have been assayed in APCVD experiments. The organotin compound delivers increasing fluorine content with increasing temperature (up to 0.015 F:Sn at 490 °C), and better transparency (> 75%) but higher resistivity (8.2 × 10^{-4} Ωcm) than the film from the Sn(II) derivative (5.92 × 10^{-4} Ωcm). From a broader range of $R_3SnO_2CR_f$ (R = Me, Et, Bu; R_f = CF_3, C_2F_5, C_3F_7, C_7H_{15}), $Et_3SnO_2C_2F_5$ gave the highest quality films and fastest deposition rate. In comparison, $Me_2Sn(O_2CCF_3)_2$ gave a film with much higher F-content (4.8 *vs* ~ 1%), higher than seen for $Bu_2Sn(O_2CCF_3)_2$, but with diminished overall physical properties. That the fluorine content of the films across the series $R_3SnO_2CR_f$ studied was largely constant suggests a common decomposition pathway, which mass spectral evidence from data on $Me_3SnO_2CC_2F_5$ suggests is by loss of CO_2 and C_2F_4 *i.e.* β-F transfer to tin.[89]

Two fluorinated tin alkoxides of differing oxidation state have also been evaluated. $Sn[OCH(CF_3)_2]_4.2HNMe_2$, synthesised by amine elimination from reaction of $(CF_3)_2C(H)OH$ and $Sn(NMe_2)_4$, generated $F{:}SnO_2$ films with good transparency (> 85%) but relatively high resistivity (2.1 × 10^{-3} Ωcm) using LPCVD. In contrast, LPCVD using the divalent tin analogue, $Sn[OCH(CF_3)_2]_2.HNMe_2$ in air or water vapour afforded non-conductive $SnO_{0.9\text{-}1.3}F_{0.1\text{-}0.4}$, suggesting hydrolysis, rather than oxidation, was driving film deposition.[90]

Sol-gel routes to $F{:}SnO_2$ follow a complementary strategy to those described above, in which now a Sn–F bond is established in the precursor before hydrolysis takes place; lack of volatility due to any possible intermolecular F:→Sn interactions is not an issue here. Under hydrolysis conditions, the robust Sn–F bond is maintained and introduces fluorine to the final material, while incorporation of fluorine into, for example, a fluorocarboxylate ligand, would result in loss of the fluorinated ligand through $Sn–O_2CR_f$ bond cleavage. Several closely related precursors involving fluorinated β-diketonate ligands, alkoxides and fluorine have been investigated, namely $(tfac)_2Sn(OAm^t)_2$,[91] $(acac)_2Sn(F)(OAm^t)$[91] and $F_2Sn(acac)_2$.[85] The studies show that hydrolysis leads initially to soluble oxo-tin oligomers or polymers which retain the Sn–F and Sn–(β-diketonate) moieties, but that fluorine is lost during pyrolysis except when a pre-established Sn–F bond is present. Precursors meeting this requirement generate cassiterite powders which incorporate typically 4–8% fluorine and show enhanced conductivities over undoped analogues.[91] Their resistivities are, however, generally higher than typical CVD (or spray pyrolysis) films,[91] even when cast into a thin film by spin coating;[85] residual carbon and excess fluorine have been suggested as possible causes,[92] though the authors also point out that for certain electrochemical applications carbon-rich $F{:}SnO_2$ has advantages.[85]

In a novel variation on these themes, mixed valence adducts between SnF_2 and $Sn(OR)_4$ (R = Bu^t, Am^t) have been prepared by simple mixing of the two components in the absence of solvent, though crystallographic confirmation of the structure is outstanding.[93]



Hydrolysis maintains the Sn:F ratio but removes most of the alkoxy groups; thermolysis removes most of the residual carbon and some fluorine (14% remaining), so that at 550 °C the optimum resistivity (0.7 Ωcm) is reached. While this is inferior to thin film $F{:}SnO_2$, it is three times lower than that of $Sb{:}SnO_2$ powders. The application of this material as an anode in lithium batteries has been described.[94,95]

An imaginative variation which takes the best of many of the strategies described in this section has been used to generate carbon-free $F{:}SnO_2$ by a sol-gel route. Tetraorganotins $(C_4H_9C{\equiv}C)_3SnR_f$ (R_f = C_6H_4F-2, $CH_2CH_2CF_3$), whilst requiring a three step synthesis, can be purified by column chromatography, an advantage over thermally labile liquid tin alkoxides which require distillation for purification. The alkynyl groups are preferentially hydrolysed and fluorine is delivered to tin from the β- or γ-C of the remaining aryl or alkyl group, respectively. After calcination at 550 °C, the resulting $F{:}SnO_2$ have the cassiterite structure, about 4% F-doping, residual carbon of 3% [cf: 12% from $(acac)_2Sn(F)(OAm^t)$] and conductivities approaching an order of magnitude higher than from the latter amyloxy-precursor.[85]

More complex systems

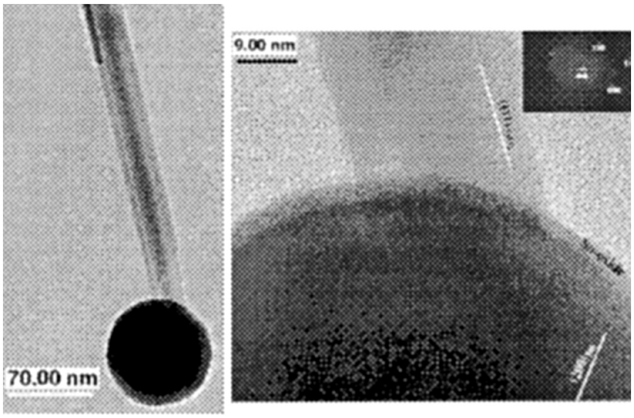
The decomposition of tin(II) alkoxides has proved a valuable entry into the formation of more complex materials. $Sn(OBu^t)_2$ thermally decomposes at *ca* 400 °C *via* a disproportionation to Sn^0 and Sn^{4+}, to form spherical core-shell materials in which a metal core is coated in an oxide layer *i.e.* $SnO_2@Sn$.[96,97]

$$2Sn(OR)_2 \longrightarrow Sn^0 + Sn(OR)_4$$

Partial hydrolysis of $Sn(ONeo)_2$ affords the oxo-alkoxides clusters $Sn_6(O)_4(ONeo)_4$ and the rarer penta-tin cluster $Sn_5(O)_2(ONeo)_6$ (Neo = CH_2CMe_3; Fig. 1b), each of which have been found to be sufficiently volatile for LPCVD.[98] $Sn(ONeo)_2$, like $Sn(OBu^t)_2$, forms mixtures of Sn^0 and various tin oxides (SnO, SnO_2, Sn_3O_4), in approximately equal amounts at low temperatures but with Sn^0 dominating at T > 350 °C. The penta-tin has more complex behaviour, forming mainly Sn^0 at low and high temperature, but in the intermediate range (*ca* 380 °C) tin oxide wires growing on a spherical Sn^0 seed are seen (Fig. 2); the hexa-tin has broadly similar behaviour, also forming wires and ribbons of oxide on a metal seed.[98]

Heterobi-metallic tin(II) alkoxides similarly provide an entry to mixed-metal materials. $MSn_2(OBu^t)_6$ (M = Ca, Sr, Ba) decompose to give a Sn^0 core with a mainly $BaSnO_3$ shell (Fig. 3).[96] More complex behaviour is seen from $Ni_2Sn_2(OBu^t)_8$ in a LPCVD experiment, which deposited thin films of Ni_3Sn_4 dispersed in a SnO_2matrix.[99] At lower temperature the process is dominated by the disproportionation of Sn^{2+}, as described above; at T > 550 °C, redox reactions become responsible for the formation of the Ni–Sn alloy phase.[99]

The two most targeted binary TCOs containing tin are ITO and the cadmium stannate Cd_2SnO_4. The former presents a problem from a single-source precursor prospective, because of the non-stoichiometric nature of the material which is predominantly indium. Various dual-source approaches have been followed[100] which allow greater control over In:Sn ratio, including $In(acac)_3$ with $Sn(acac)_2$[101] or $Sn(OBu^t)_4$,[102] though, as the latter paper discusses, control of particle morphology remains a challenge. Single-source precursors are far more



(a) (b)

Fig. 2 HRTEM of the deposit from $Sn_5(O)_2(ONeo)_6$ at 380 °C, showing (a) a single SnO_2 rod on an Sn^0 spherical seed and (b) a higher magnification view of the interface between the two materials, showing a thin layer of tin oxide on the metal surface. Reprinted with permission from ref. 98. Copyright (2003) American Chemical Society.

limited, though the use of $R_2InOSnBu_2R'$, prepared from $R_2R'In$ and Bu_2SnO (R = R' = Bu; R = Bu, R' = $EtCO_2$),[103] has successfully formed ITO *via* a solution pyrolysis route.[104-106] Surprisingly few compounds with an In:Sn > 1 are known, limited to $Me_2Sn(CH_2InMe_2)_2$ and $Me_2Sn[CH_2In(OCH_2CH_2NMe_2)_2]_2$:[107]

$$Me_2Sn(CH_2Li)_2 + 2Me_2InCl \xrightarrow{-2LiCl} Me_2Sn(CH_2InMe_2)_2$$

$$Me_2Sn(CH_2Li)_2 + 2(Me_2NCH_2CH_2O)_2InCl \xrightarrow{-2LiCl} Me_2Sn[CH_2In(OCH_2CH_2NMe_2)_2]_2$$

For comparison, tin-rich $(Me_3SnCH_2)_nInR_{3-n}$ (R = Me, n = 1, 2; R = Bu^t, n = 1) have also been synthesised, by treating Cl_nInR_{3-n} with Me_3SnCH_2Li.[108] There is clearly scope for further work in this general area.

Deposition of Cd_2SnO_4, a low-cost alternative to ITO, represents another relatively fertile area for further work. Thin films have been prepared by co-evaporation of SnO_2 and Cd,[109] by co-precipitation from the metal chlorides,[110] or by dip-coating (sol-gel) using a tin alkoxide/cadmium acetate mixture,[111,112] the latter containing species such as $Cd_4Sn_4(\mu\text{-}O)_2(OAc)_{10}(ONeo)_{10}$ (Fig. 1d).[113] However, only relatively recently has a viable CVD route to Cd_2SnO_4 been reported, involving a dual-source approach with $Cd(hfac)_2$.TMEDA and $Bu_2Sn(O_2CCF_3)_2$ as precursors. Films of comparable charge transport properties to commercial ITO were achieved.[114] In contrast, the single-source precursor $[Sn(OCH_2CH_2NMe_2)_2Cd(acac)_2]_2$ formed only tin oxide, with cadmium levels at or below the limit of detection. Separation of the adduct into its components, $Sn(OCH_2CH_2NMe_2)_2$ and $Cd(acac)_2$, and preferential decomposition of the tin alkoxide was suggested as an explanation for the observed behaviour.[54]

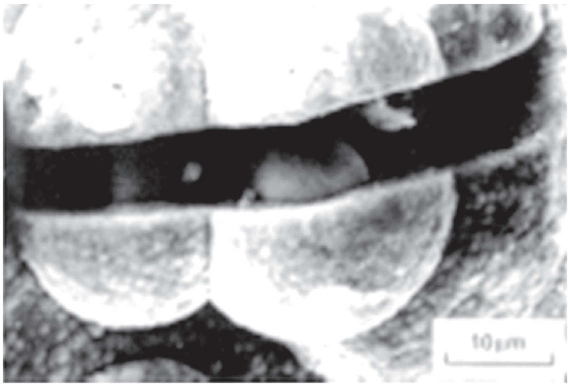


Fig. 3 Scanning Auger microscope image of an Sn^0 core surrounded by a (mainly) $BaSnO_3$ shell. The spherical metal core is evident at the centre of the image. The nanospheres were frozen at –195 °C to cause fracture. Reproduced with kind permission from Springer Science and Business Media and reference 96.

$ZnSnO_3$ has been prepared from calcination of $ZnSn(OH)_6$, itself formed by base condensation of the bi-metallic alkoxide $ZnSn(OEt)_6$. Morphological control of both the intermediate and the final $ZnSnO_3$ could be achieved by variation of the reaction solvent.[60] $CdSnO_3$ has also been prepared by a co-precipitation method.[115]

Other complex materials which have received passing attention include the APCVD of VO_2/SnO_2 from $VOCl_3/SnCl_4/H_2O$,[116] and SnO/GeO by closed-circuit CVD using the single-source precursor $Bz_2Sn[O_2CCH(Me)CH_2GePh_3]_2$.[117]

Concluding remarks

The deposition of SnO_2 is now a well established process. Numerous precursors are now available, all of which are capable of forming films with acceptable visible transmission and conductivity. The choice for the user will be made on the material to be coated (size, thermal sensitivity) and hence the choice of technique to be adopted (AP- *vs* LP- *vs* AA-CVD). This will also dictate the choice of precursor, and the attendant properties of volatility or solubility, along with synthetic accessibility and aerobic sensitivity/ease of handling. Similar comments can be made about $F:SnO_2$, while other doped systems *e.g.* $Sb:SnO_2$ do not appear to offer any major advantages which merit significant further research effort. ITO remains something of a challenge, though the increasing cost of indium is driving a search for alternative, cheaper TCOs for, for example, large-scale photovoltaic applications. Conversely, the impact of bespoke precursors on the synthesis of hitherto unknown core-shell materials *e.g.* $SnO_2@Sn$, or unusual morphologies of known materials *e.g.* SnO_2 wires, should be a significant incentive for more research at this interface between molecular and materials chemistries.

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