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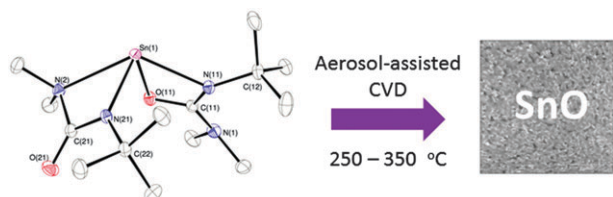
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Exclusive formation of SnO by low temperature single-source AACVD†

Thomas Wildsmith,[a] Michael S. Hill,*[a] Andrew L. Johnson,*[a] Andrew J. Kingsley[b] and Kieran C. Molloy[a]

An easily synthesised Sn(II) bis(ureide) derivative is shown to be a single-source precursor for the aerosol-assisted CVD of SnO, providing unprecedented levels of oxidation state control at temperatures as low as 250 °C.

High natural abundance and durability combined with low electrical resistance and excellent optical transparency have resulted in the adoption of stannic oxide, SnO_2,[1] as the wide band gap (3.6 eV) transparent oxide of choice in numerous optoelectronic applications *e.g.* solar control glazing,[2] in gas sensing,[3] as an electrode material in solar cells[4] and as a blue emitter in light-emitting diodes.[5] Despite this impressive utility, and in common with all other widely used transparent conducting oxide (TCO) materials, primarily indium tin oxide and zinc oxide, SnO_2 displays native n-type character.[6] The realisation of high performance p-type oxide materials, a requisite for the fabrication of transparent p–n heterojunctions, has, thus, become a major research goal in materials science.[7] While p-type behavior has been described for a variety of ternary delafossite (MM′O₂: M = Cu, Ag; M′ = B, Al),[8] spinel ($NiCo_2O_4$)[9] and oxy-chalcogenide materials,[10] examples of simple binary oxides that display inherent p-type semiconduction have been effectively restricted to NiO and Cu_2O. Group 15 doping of ZnO[11] and similar group 13 substitution in SnO_2 has also been reported to provide p-type behavior,[12] although the veracity of these latter reports has been questioned or, in the case of a recent theoretical exploration, all but discounted.[13] Although the achievement of 'all tin oxide' heterojunction devices based entirely on SnO_2 would, thus, appear to be doubtful, this appealing prospect may yet be realised through the recent emergence of SnO, stannous oxide, containing tin in its lower Sn(II) oxidation state, as a potential p-type candidate material.[14]

While thin films may be prepared by electron beam evaporation,[15] pulsed laser deposition[16] and RF magnetron sputtering of the bulk oxide,[17] vapour phase chemical deposition of SnO from reactive inorganic or metalorganic precursors presents formidable challenges. The maintenance of low or intermediate oxidation states during the chemical vapour deposition (CVD) of any metallic oxide requires stringent control of the oxygen-containing process stream and, for the specific case of SnO, is further complicated by a tendency toward disproportionation to Sn(0) and SnO_2 at temperatures reportedly as low as 200 °C.[1] For example, while Gordon has described the cyclic Sn(II) amide precursor (I) for the atomic layer deposition (ALD) of SnO_x, the use of hydrogen peroxide as co-reagent ensured that the tin centres within the resultant thin film materials were ostensibly in the +4 oxidation state.[18] In contrast, SnO in nanoparticle or nanowire form has been prepared with some level of oxidation state and morphological control through use of well-defined Sn(II)-centred precursors,[19] while a recent report from this laboratory has described the first use of a stannous single-source precursor, the cage molecule $Sn_6O_4(OSiMe_3)_4$ (II), for the liquid injection CVD of SnO.[20] Although these latter observations highlight the feasibility of maintaining the +2 oxidation state of tin during a CVD process, deposition could only be achieved at high temperature (450 °C) above which the constitutional integrity of the oxide was apparently compromised by the aforementioned lability of SnO toward disproportionation. In this contribution we address these issues and describe a simple and practical single-source precursor approach which provides exceptional oxidation state control for the CVD of phase-pure SnO at unprecedentedly reduced process temperatures.

Although Sita and Kemp have demonstrated that stannous derivatives of silylated amide ligands react with heteroallenes such as CO_2 and organic isocyanates through insertion into the Sn–N bond, these reactions were deliberately intended to continue with subsequent silicon-to-oxygen migration and extrusion of the respective silyl-isocyanate or -carbodiimide products.[21,22] The non-silylated
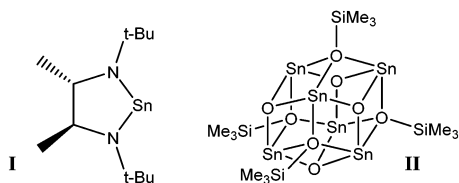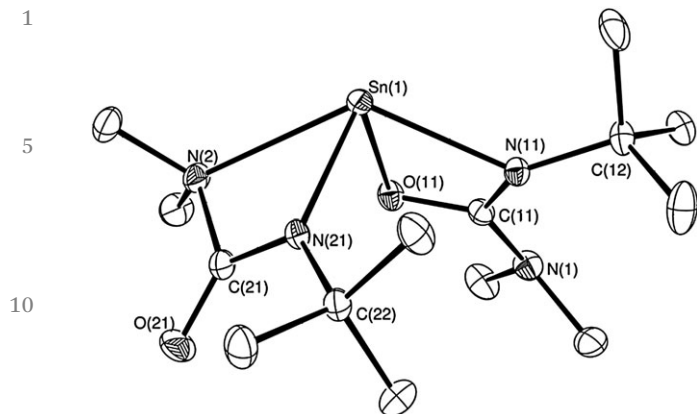

I

II

Fig. 1   ORTEP representation (50% probability ellipsoids) of compound **1**. Hydrogen atoms removed for clarity. Sn(1)–O(11) 2.1688(11), Sn(1)–N(21) 2.1715(13), Sn(1)–N(11) 2.3151(13), Sn(1)–N(2) 2.4839(13), O(11)–C(11) 1.3058(19), O(21)–C(21) 1.220(2) Å; O(11)–Sn(1)–N(11) 59.15(4), N(21)–Sn(1)–N(2) 57.90(5)°.

stannous ureide precursor compound (**1**) was, thus, synthesised in high yield by the addition of 2 molar equivalents of *tert*-butyl isocyanate to a toluene solution of the stannous alkylamide [Sn(NMe$_2$)$_2$]$_2$. Compound **1** was isolated in effective stoichiometric yield by crystallisation from the reaction solution and characterised by solution NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy. X-ray diffraction analysis performed on single crystals of compound **1** confirmed that a four-coordinate mononuclear constitution is adopted in the solid state. The results of this analysis are shown in Fig. 1 and illustrate the distorted square pyramidal geometry enforced at the Sn(II) centre through a combination of the stereochemically active lone pair and the narrow bite angles of the two ureide ligands, which adopt contrasting κ^2-*N*,*N*′ and κ^2-*N*,*O* coordination modes. Evidence for solution anisobidenticity could be discerned through ^{1}H NMR studies, in which the signal assigned to the *tert*-butyl signal of **1** split into two singlet resonances below 238 K. Although the solution dynamics of compound **1** were not further examined we surmise that this process is due to facile ($\Delta G^{\ddagger} = 46$ kJ mol^{-1}) intramolecular exchange between κ^2-*N*,*N*′ and κ^2-*N*,*O* coordination modes in solution. No directly analogous Sn(II) ureide derivatives appear to have been reported previously, however, the ^{119}Sn{^{1}H} NMR spectrum of compound **1** provided a single resonance at δ −357 ppm in d$_8$-toluene, a value which is comparable to previously reported stannous, bis-(iso-ureide),[22] bis(amidinate)[23] and bis(guanidinate)[24] derivatives.

These latter compounds are unambiguously 4-coordinate in solution and we, thus, deduce that compound **1** maintains its structural integrity and displays a similar coordination geometry in hydrocarbon solution.

Thermogravimetric analysis (TGA) (Fig. S1, ESI†) performed on compound **1** provided a single mass loss event with an onset temperature of *ca.* 100 °C. A stable residue was obtained at 190 °C (with <0.5% further mass loss to a high temperature limit of 525 °C), which provided a residual mass of *ca.* 5%, considerably lower than expected for either SnO (37.1%) or tin metal (29.2%). Although such apparent material loss by sublimation indicates that compound **1** is likely to be applicable to low pressure direct vapour phase delivery, a combination of high solubility and potentially higher mass transport and deposition rates led us to employ aerosol-assisted chemical vapour deposition (AACVD) for initial film growth studies.[25] Accordingly, pale yellow, non-hazy and adherent films could be grown by AACVD of compound **1** from toluene solution (0.1 M) employing either hot or cold wall conditions onto glass or silicon substrates over a 250 °C to 350 °C temperature range. Tetragonal SnO (*P4/nmm*) was identified by PXRD as the only crystalline phase present at temperatures above 300 °C with no evidence for disproportionation to Sn(0) and SnO$_2$ even at the highest temperature (Fig. 2a). In contrast to our earlier report of SnO CVD utilising compound **II**, the major diffraction lines [(101), (110)] were identical to those reported in SnO powder, with no evidence for any preferentially-oriented growth.[20] These data were corroborated by Raman spectroscopy performed on samples prepared under the full range of growth and temperature conditions, all of which displayed characteristic B$_{1g}$ and A$_{1g}$ modes at 109 cm^{-1} and 209 cm^{-1} respectively as the only observable vibrations (Fig. 2b).[26] Importantly, the lower crystallinity samples prepared at 250 and 275 °C were confirmed as SnO and, again, no evidence for disproportionation to Sn(0) and SnO$_2$ or to intermediate phases with Sn$_2$O$_3$ or Sn$_3$O$_4$ compositions could be discerned even for the samples prepared at 350 °C. Microscopic analysis of films grown on both glass and silicon substrates by FE-SEM and AFM showed them to be continuous and to consist of tightly packed platelets, typical of SnO films deposited by physical and evaporative techniques.[15–17,19] The platelets are uniform in both size and shape (approximate width 50 nm) and are interleaved across the planar surfaces, becoming more densely packed with increasing deposition temperature (Fig. 3).

Although high hole mobility in metallic oxides is difficult to achieve due to the formation of deep and localised O 2p-based valence
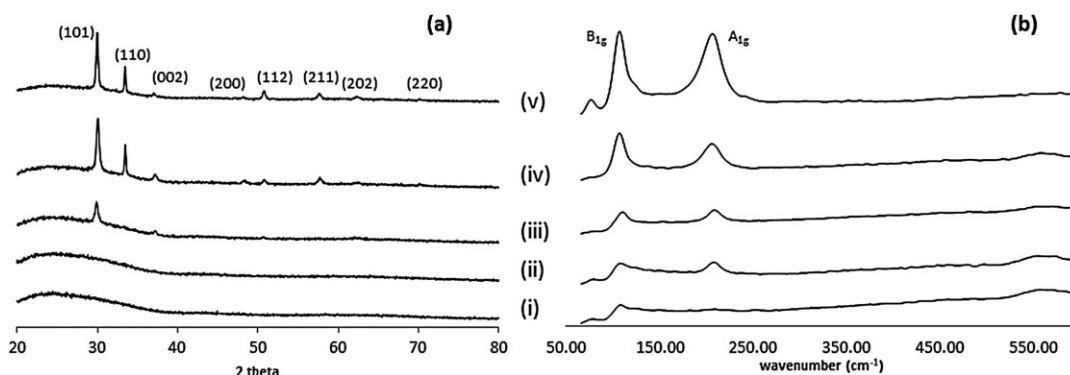

Fig. 2   PXRD patterns (a) and Raman spectra (b) of films deposited at (i) 250, (ii) 275, (iii) 300, (iv) 325 and (v) 350 °C.
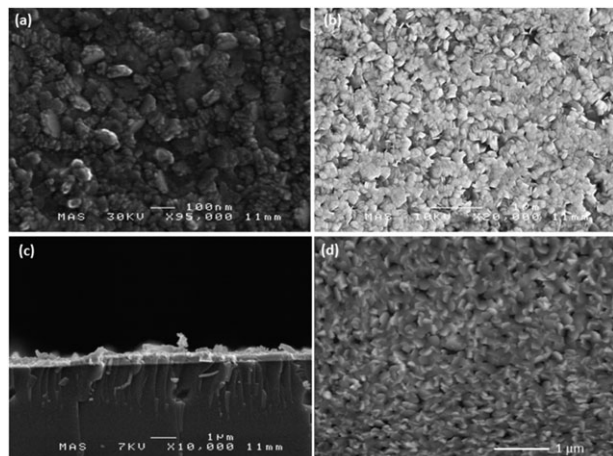
Fig. 3 SEM images of SnO films prepared on glass at (a) 300 and (b) 325 °C. (c) Cross section SEM of SnO film prepared on Au-coated glass at 350 °C. (d) AFM image of SnO film prepared on glass at 350 °C.
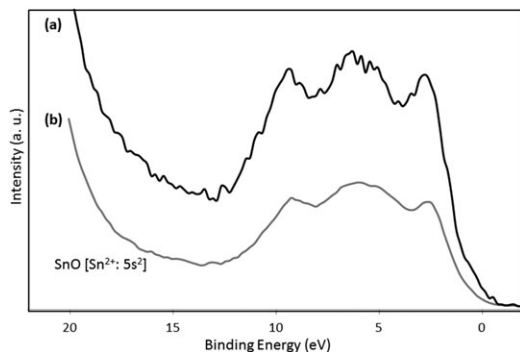

Fig. 4 (a) Valence band XPS spectrum of AACVD film of SnO deposited on glass; (b) valence band XPS spectrum of SnO reference standard (Thermo Fisher Scientific Knowledge Viewer).

band maxima (VBM),[27] the presence of the pseudo-closed shell $5s^2$-orbitals of the Sn(II) centres in SnO has been reasoned to provide a mechanism for oxide rehybridisation and consequent advantageous modification of the VBM.[28] Consistent with this rationale, SnO_2 does not exhibit any 5s character in the VBM and the observation of XPS features in pristine SnO samples with binding energies of 2 eV and 9 eV have, thus, been ascribed to the formation of antibonding and bonding Sn(II) $5s$-O_{2p} states, respectively.[29] Although evidence for some surface oxidation to Sn(IV) was observed, valence band XPS spectra recorded after argon etching of samples deposited from compound **1** on glass revealed a prominent underlying Sn(II) component with a leading valence band energy of *ca.* 2 eV (Fig. 4).

In conclusion, we have demonstrated that the provenance of the Sn(II) centres in thin films of AACVD-deposited SnO may be directly attributed to the use of a simple single-source stannous bis(ureide) precursor. Notably, deposition may be achieved at temperatures approaching those that will be tolerated by less thermally stable substrates than glass and silicon and no evidence for Sn(II) dispro-portionation is observed even at the highest deposition temperature. Although the decomposition mechanism of compound **1** is yet to be deduced, our initial supposition is that the production of SnO with this system may be viewed as the kinetic outcome of a sequence of well-defined elimination reactions similar to those observed during the production of inorganic sulfide materials from metalorganic xanthate precursors.[30] We are continuing to elaborate this hypothesis and to devise routes to similarly metastable oxide and heavier chalcogenide materials through judicious molecular design.

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