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A Synthetic and Spectroscopic Study of the Mechanism of Atomic Layer Deposition of Tin Dioxide

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Supporting Information Placeholder

ABSTRACT: This study details the surface reaction chemistry relevant to the vapor deposition mechanism of SnO₂ thin films by atomic layer deposition. The mechanism was elucidated by combining different spectroscopic studies. Initial nucleation of cyclic N²,N³-di-*tert*-butyl-butane-2,3-diamido tin(II) (**1**) consists of surface SiOH protonation of ligands as shown by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). This SiO₂-surface-bound stannylene was further characterized by X-ray absorption (XAS) and resonance Raman spectroscopy. XAS, DRIFTS and Raman spectroscopy were then used to follow the further reaction of the surface-bound stannylene with different oxygen sources and a second equivalent of **1**. It was observed that water does not oxidize the initial surface bound tin site and a well-defined, three-coordinate tin(II) species, with two surface oxygen bonds and coordinated water molecule, was characterized. Treatment of the surface stannylene with protic oxidants such as H₂O₂ or *t*BuOOH fully oxidizes tin to 4+ and coordination of additional oxygen ligands is observed. When a second equivalent of **1** is added to surface bound Sn⁴⁺, the resulting surface tin is also found to be in the +4 oxidation state, contrary to the nonoxidative nucleation step. As such, surface peroxide species provide a probable growth mechanism of SnO₂ through oxidation, while nucleation occurs through protic ligand exchange.

INTRODUCTION

The controlled synthesis of well-defined materials for catalytic¹ and electronic² applications is dependent on intimate knowledge of chemical processes. This is particularly challenging for gas-solid reactions, such as in the rapidly growing field of atomic layer deposition (ALD), where sequential, stoichiometric reactions of gaseous metal and non-metal sources are used to grow a material. By far the most common strategy for deposition relies on proton transfer followed by ligand dissociation as the synthetic pathway; e.g. oxides, sulfides, and nitrides prepared from metal precursor and corresponding protic reagents H₂O, H₂S and H₃N.³ In addition to water, other oxygen sources such as molecular oxygen, ozone, and hydrogen peroxide, have been used to prepare metal oxide films. In general, little attention has been paid to the role that the non-metal ‘precursor’ (reagent) plays in the chemistry beyond whether it is acting as a proton-containing reagent or an oxidant. However, utilizing more complicated chemistry for ALD processes requires a detailed understanding the impact of metal and nonmetal reagents upon both nucleation and growth mechanisms.

One new synthetic strategy for growth by ALD is controlled oxidation of a lower-valent metal starting material. This is advantageous because the nature of the oxidant can control the

resulting metal oxide species, has been shown in the case of iron oxides.⁴ Furthermore, lower valent complexes require fewer ligands and therefore *can* be more volatile, which has been demonstrated by our group for iron⁴ and tin oxides.⁵ In the case of tin, a low valent tin(II) precursor (Figure 1) has

Figure 1. Stannylene, N₂,N₃-di-*tert*-butyl-butane-2,3-diamido tin(II) (**1**), previously reported to be ALD precursor for growth of SnS with H₂S and SnO₂ with H₂O₂.

been shown to be quite versatile for the synthesis of tin chalcogenides. This tin(II) compound (**1**) can be used with H_2S as an ALD partner to grow the photovoltaic material SnS by a protonation ALD mechanism.⁶ Also, **1** can be used with H_2O_2 to grow SnO_2 by an oxidation mechanism. Interestingly, SnO does not grow when H_2O is used as an ALD partner.⁵

Since stannylenes show reactivity through oxidation as well as ligand exchange, mechanisms for ALD growth are not simple to predict. Issues arise from the ability to anticipate whether a stannylene will react through oxidative addition *versus* protolytic ligand transfer, as outlined in Scheme 1. Intuitively, it is anticipated that a more acidic proton would induce protolytic ligand transfer and more basic compound could induce oxidative addition. However, Power and co-workers have established that reactivity of diarylstannylenes depends less on the $\text{p}K_a$ of the reagent or the steric bulk of the arene groups, but rather the thermodynamic stability of the products and kinetics of the reaction. For instance, the bulky stannylene $\text{Sn}(\text{Ar}^{\text{Me}_6})_2$, [$\text{Ar}^{\text{Me}_6} = \text{C}_6\text{H}_3-2, 6- (\text{C}_6\text{H}_2-2, 4, 6-(\text{CH}_3)_3)_2$] undergoes arene elimination with H_2 and NH_3 ($\text{p}K_a = 10.5$) to remain $2+$ ⁷ and oxidative addition with HBF_4 ($\text{p}K_a = -0.44$) and $\text{H}(\text{SO}_3\text{CF}_3)$ ($\text{p}K_a = -14.1$) to form $\text{Sn}(\text{IV})$ compounds.⁸ Complicating the matter further, stannylenes have shown a wide range of additional reactivity; coordination via the lone pair to transition metals⁹ or as Lewis acid-base pairs with carbenes,¹⁰ insertion,¹¹ reduction (disproportionation to Sn metal), cycloaddition,¹² and substitution¹³ reactions.

ALD of SnO_2 films has been successful using a wide range of precursors,³ however recent use of stannylenes have been found to grow films with superior quality and electrical properties.^{5, 14} Clean, stoichiometric reactivity is absolutely necessary for ALD of quality materials, most prominently at interfaces. The stoichiometric nature of an ALD reaction, where a maximum of one mono-layer of precursor can react with the active surface species during each half-cycle, allows for the growth mechanism, in theory, to be studied with traditional solution chemistry.¹⁵ Thus the chemistry of **1** provides an ideal setting to study the solution and surface coordination chemistry of stannylenes with oxidants and hydroxide ($-\text{OH}$) bonds. We wish to report the discovery of the deposition mechanism reaction of a cyclic stannylene with H_2O_2 .

RESULTS AND DISCUSSION

While the successful deposition of SnO_2 from N^2, N^3 -di-tert-butyl-butane-2, 3-diamido tin(II) (**1**) and H_2O_2 has been performed for years,⁵ the mechanism, specifically how and when tin is oxidized, has yet to be studied in detail. Generally,

Scheme 1. Potential pathways for low valent stannylene compound with protic species. Path A is protonation reaction, Path B is Lewis acid/base coordination and Path C is oxidative addition.

Figure 2. N^2, N^3 -di-tert-butyl-butane-2, 3-diamido tin(II) (**1**) molar loading levels of (a) 0 molar%, (b) 1.5 molar%, (c) 3.0 molar%, and (d) 4.5 molar% on SiO_2 .

stannylenes have access to different reaction paths, as shown in Scheme 1, depending on the geometry and availability of the tin p-type orbitals. Low coordinate heterocyclic stannylenes show similar reactivity to the general class of stannylene mentioned above; however **1** does not have the stability of additional nitrogen π -donors to mitigate the reactivity of the unfilled p-orbital. As such, coordinately unsaturated compounds similar to **1** are expected to undergo more facile oxidative addition compared to ligand transfer/protonation or acid/base donor chemistry. Foley et. al. showed facile protonation chemistry of bis(dimethylamido) tin(II) with ethanol to give $\text{Sn}(\text{OR})_2$ ¹⁶ and Tolman and coworkers showed the conversion and isolation of a bis(amidinate)tin(II) compound to the monosubstituted alcohol was aided by the steric bulk of the reactants.^{13b} Additionally, Neumann remarks how dialkyl stannylenes are expected to make Lewis acid-base donor pairs with small Lewis bases, such as H_2O ;¹⁷ unfortunately the authors are not aware of any single molecule examples of this type of Lewis acid-base compound to date. Recently, Power and coworkers found that diarylgermylenes and diarylstannylenes exhibit oxidative addition behavior with Brønsted acids. For example, Ar_2Sn oxidizes to $\text{Sn}(\text{IV})$ with HBF_4 .⁸ These works outline three distinct pathways for reaction with protic oxygen sources, as shown in Scheme 1; substitution through protonation, coordination of a Lewis base to the empty p-orbital of the Sn and oxidative addition to generate a $\text{Sn}(\text{IV})$ species.

Access to the different mechanisms of stannylene reactivity is observed in ALD literature as these types of coordinately unsaturated precursors will grow SnS ^{14c} with H_2S and SnO_2 with H_2O_2 .⁵ Interestingly, these cyclic stannylenes do not appreciably grow SnO with H_2O under ALD conditions. This disparate behavior is worthy of further investigation. In solution, **1** reacts with H_2O and H_2O_2 to form an insoluble solid. Further investigative reactions with triphenylsilanol gave a mixture of products that were difficult to characterize by ^1H NMR and, in our hands, did not produce an isolable product.

To overcome the difficulty faced in solution with **1**, we produced a material that contains isolated stannylene species on dehydrated high surface-area silica (SiO_2). Synthesis of **1** with SiO_2 proceeded quickly in organic solvents at room temperature where an orange solution of **1** reacts with white SiO_2 to give light orange **2**, as shown in Figure 2b-d. The clear mother

Figure 3. (a) XANES spectra of N^2, N^3 -di-tert-butyl-butane-2, 3-diamido tin(II) (**1**) with as deposited **2** and (b) the first derivative of the same XAS data.

liquor was devoid of starting material by ^1H NMR at this point and heating **2** in benzene- d_6 to 60°C for 30 minutes showed just under an equivalent of free ligand in solution, compared to an internal standard, and was observed across molar loading on the SiO_2 surface. Molar loading was kept at 1.5 mol% for all further investigations. Loss of ligand around the Sn center is further supported by X-ray absorption near edge structure (XANES) spectroscopy, the excitation energy for the 1s electron or edge position is the same for the SnO standard (tabulated in the Supporting Information, Table S1), but shape is drastically different from **1**, as shown in Figure 3. The change in shape is due to the difference in orbital contribution to the LUMO on Sn between two NR_2 ligands and two OSi^* (OSi^* indicates a surface species) ligands. Ligand exchange is also confirmed with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Material **2** shows a decrease in the band associated with the surface hydroxyl of high surface area silica (3743 cm^{-1})¹⁸ after addition of the Sn(II) precursor (**1**), as shown in SiO_2 background subtracted spectrum in Figure 4. Additionally, the spectra show the existence of protonated ligand on the surface of the SiO_2 , where the NH stretch was observed at 3310 cm^{-1} , close to the published value of 3307 cm^{-1} .¹⁹ No nitrogen was observed in the films grown by Gordon and co-workers⁵ and the NMR data showed release of a full equivalent of protonated ligand, it is assumed that free ligand does not interfere with the surface growth chemistry and is removed during growth conditions. To ensure isolated Sn species, we maintained a low molar loading, 0.015 moles (1.5 molar%) of Sn/moles of surface hydroxyls (Figure 2b). The single site nature of **2** is confirmed by Raman spectroscopy, shown in Figure 5, through the absence of a peak at 580 cm^{-1} associated with SnO_2 clusters,²⁰ and X-ray absorption fine structure (XAFS), where approximately two first shell scattering paths (both Sn-O bonds) and no higher ordered scatters are present (Figure S1 in the Supporting Information). The lack of large clustering shown by these samples is in accord with Scotti and coworkers research on tin doped glass; a loading of less than 0.03 moles of Sn/moles of surface hydroxyls (3 mole%) produces a material with isolated SnO_2 sites.²⁰ From these data we can infer that the isolated Sn species remains in the 2+ oxidation state, are approximately two coordinate and that **2** should have reactivity similar to a stannylene. Thus, we infer that **1** undergoes substitution through protonation with two neighboring surface silanol groups, generating

free ligand in the process, similar to Path A in Scheme 1. To the best of the author's knowledge, this is the first observation of a surface bound stannylene by X-ray absorption spectroscopy (XAS).

After establishing the isolated nature of **2**, that material was treated with water to produce a new orange material, **3**, as seen in Scheme 2. By XAFS, the coordination number of **3** increased from two to three as the bond length increased from $2.05(17)$ to $2.11(21)\text{ \AA}$. It was determined through a difference fit that a full coordination of water is responsible for this lengthening of average bond-length. This result implies a picture where two Sn-OSi^* bonds of $2.05\text{ \AA}$, one Sn-OH_2 bond of $2.15\text{ \AA}$, along with the Sn lone pair, fill the coordination sphere of the surface stannylene in a Lewis acid-base type reaction, shown in Scheme 2. This distance is in agreement with other sterically hindered stannylene-water Lewis acid-base compounds such as $[\text{Sn(18-crown-6)(H}_2\text{O)}][\text{BF}_4]_2 \cdot 2\text{H}_2\text{O}$, where the apical water is at a distance of $2.150(7)\text{ \AA}$.²¹ Since the reactivity with H_2O is a Lewis acid-base type, as shown as Path B in Scheme 1, and not a protonation/deprotonation or oxidative addition type, the surface stannylene nature of **2** is further supported. One would also predict that **3** would be unreactive to further Sn(II) precursor and would not grow SnO by ALD.

Figure 4. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of unreacted silica (black) and the product of **1** with silica (**2**) with SiO_2 as a background shown in red.

Figure 5. Raman spectra of materials **2**, **4**, **5** which were taken directly after the conclusion of each reaction. Spectra are offset for clarity.

When **3** was exposed to a second molar equivalent of **1** (Scheme 2), there was no change in the XAS or Raman spectra, simply a darkening in the color of the material, further discussed below.

Exposure of **2** with strong oxidant sources, H_2O_2 and $t\text{BuOOH}$, gave two new white materials, **4** and **5** respectively, as characterized by XAS. The judicious choice of oxidants provides a comparison of oxidants with similar strength, but with and without the presence of H_2O . As expected, both peroxides fully oxidized **2** to the 4+ state, as shown by a shift of 3.94 eV in the XANES spectrum (Table S1 of the Supporting Information). Additionally, the coordination number was found to be approximately six for **4** and **5**, which are in line with the Sn-O coordination of bulk SnO_2 and significantly greater than that of SnO. Additionally, the Sn-O bond length stays 2.05 (17) Å which is only marginally longer than bulk SnO_2 (2.042 Å) and much shorter than bulk SnO (2.231 Å). The structural similarities between **4** and **5** shows that the

presence of water does not affect the proposed growth mechanism, since care was taken to exclude water in the synthesis of **5**, and that **3** undergoes oxidative addition with peroxides. From Raman data we know that peroxide species exist on the surface of the high surface area silica for both **4**, 874 cm^{-1} , and **5**, 895 cm^{-1} (Figure 5 above and Figures S7 and S8 of the Supporting Information). These values are in good agreement with the published values of the ν O-O mode²² but the resolution was not sufficient to distinguish between SiO-OR or SnO-OR species. From XAFS data we also see an emergence of higher shell, Sn-O-Sn, scattering after peroxide treatment, as seen in Figures S3 and S4 of the Supporting Information. This is associated with Sn agglomeration; the amount of Sn-O-Sn in **4** was calculated to be 0.24(0.32) and 3.49(1.37) in **5**. While the uncertainty is substantial, the tin clustering is confirmed with Raman data as a peak emerging around 580 cm^{-1} .²⁰ The distance between Sn atoms is 3.23 (0.01) Å for **4** and 3.30 (0.14) Å for **5**, which is longer than the bulk value of 3.17 (0.01) Å for SnO_2 . From these data, we infer a mechanism similar to Path C from Scheme 1, where oxidative addition occurs across the hydrogen oxygen bond, generating surface bound Sn(IV) species **4** and **5**, from Scheme 2, with at least one peroxide ligand.

With the nucleation and oxidation chemistry consisting of protonation followed by tin oxidation, we then added a second dose of tin precursor to the well-characterized Sn(II) **2** and **3** and the Sn(IV) **4** and **5** materials to elucidate the probable ALD growth mechanism. In the same fashion as the reaction with high surface silica, **2** and **3** react with a molar equivalent of **1** quickly in organic solvent where the orange solution turns clear as the silica becomes deeper orange/brown, as seen in the higher molar loading (3.0%) in Figure 2c. These materials showed no change in the XAS or Raman spectra, consistent with the observation that bulk SnO is not grown from the tin precursor **1** and H_2O by ALD. Unlike the Sn(II) counterparts, the Sn(IV) materials, **4** and **5**, showed novel reactivity by XAS and Raman spectroscopy. The white material of **4** and **5** was added to an orange solution of **1** and in less than 10 minutes,

Scheme 2. Reaction pathways for **2** with various oxygen sources as well as a second molar equivalent of N^2 , N^3 -di-tert-butyl-butane-2, 3-diamido tin(II) (**1**). Si-O* denotes a surface bound species.

the solution became clear-colorless while the material remained white. These new materials, **6** and **7**, showed only Sn(IV) by XANES, with no Sn(III) or Sn(II) apparent, but with an increase in the overall amount of Sn compared to **4** or **5**. The XAFS spectra of **6** and **7** were essentially unchanged with respect to bond distances and coordination with respect to **4** and **5**. This means that the surface peroxide species observed in **4** and **5** are responsible for the complete oxidation of all newly introduced **1** to Sn(IV) and an excess of protons (from H_2O_2 or $t\text{BuOOH}$) is responsible for the removal of the di-amido ligand. Disappearance of the ν O-O mode in the Raman spectrum of **6** and **7** further supports the peroxide driven mechanism purposed (Figures S7 and S8 Supporting Information). Thus it appears that a low coordinate stannylene will react with surface peroxide species (Sn or Si) in a manner similar to Path C in Scheme 1 faster than a proton transfer in Path A. Unlike the initial nucleation by the protic ligand transfer mechanism, the steady state growth mechanism likely involves the newly introduced stannylene insertion into a O-O bond of the peroxide, as shown on the left side of Scheme 2, and requires more peroxide to generate a reactive surface species which allows for ALD type growth. Thus, the mechanism for ALD growth of SnO_2 is as follows. First, **1** undergoes ligand exchange, by protonolysis, with surface hydroxyls to form a two coordinate surface stannylene (**2**). Then a peroxide molecule oxidizes the surface stannylene, while excess H_2O_2 regenerates reactive surface peroxide species (**4**). Further vapor phase stannylene molecules react with the surface peroxide species, oxidatively inserting into the O-O bond and creating all Sn(IV) surface species (**6**). This insertion and oxidation occurs at a rate much faster than protonolysis and ALD growth temperatures would limit the thermal lifetime of the surface bound peroxide species.

CONCLUSIONS

In summary, we have mapped the likely deposition mechanism of a low-coordinate stannylene molecule, N^2 , N^3 -di-*tert*-butyl-butane-2, 3-diamido tin(II) (**1**), which successfully grows SnO_2 but not SnO by ALD with high surface-area silica and three oxygen sources. X-ray absorption spectroscopy (XAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Raman spectroscopy show that the initial nucleation of **1** with the surface is nonoxidative. The surface stannylene contains isolated Sn(II) species that bind water without change in oxidation state. This new material, **3**, provided an example of a H_2O -stannylene Lewis acid-base complex. The surface stannylene reacts via well-defined oxidative addition with both aqueous and nonaqueous peroxide sources to yield surface Sn(IV). A "second dose" of **1** did not produce a reaction with the water-coordinated tin(II) stannylene but surface peroxide groups bound to tin (IV) fully oxidized the second dose of tin precursor to 4+ without the observance of tin deposition in lower oxidation states. The thermal stability of the surface-bound tin(IV) peroxide is likely process-limiting for the growth of ALD SnO_2 with precursor **1**.

EXPERIMENTAL SECTION

General consideration: All chemical manipulations were carried out using standard Schlenk techniques or in a glove box (Vacuum Atmosphere) in a dry nitrogen atmosphere, with the exception of H_2O and H_2O_2 treatments. Pentane, diethyl ether, tetrahydrofuran (THF), toluene, benzene and hexane were dried by argon assisted movement

over two columns (one neutral alumina column and one copper (II) oxide-Q5 column for pentane, toluene, benzene, and hexane and two neutral alumina for diethyl ether and THF), stored over 4 Å molecular sieves and tested periodically with sodium benzophenone ketyl.²³ Synthesis of N^2 , N^3 -di-*tert*-butyl-butane-2, 3-diamido tin(II) (**1**) was performed according to literature procedures.⁵ Hydrogen peroxide (30% in water from Sigma Aldrich), *tert*-butyl hydroperoxide (5 M in decane from Sigma Aldrich) and deionized water were deoxygenated with a moderate N_2 flow for a minimum of 15 minutes directly prior to use. High surface-area silica (Sigma Aldrich 250-500 μm , 35-60 mesh, 1.15 cm^3 pore volume, 150 Å pore size) was heated to 150°C under reduced pressure (~ 25 mtorr) for over five hours to remove chemisorbed water. All other reagents were obtained from commercial suppliers and used as received. IR data were taken in diffuse reflection mode on a BRUKER FTIR model ALPHA-R spectrophotometer in DRIFT mode with a gold sample holder. Surface Raman measurements were taken with a red laser (785 nm) on a Renishaw spectrophotometer in a back scattering configuration, using a Renishaw CCD camera and a 1200 nm slit. ^1H (300 MHz) NMR spectra were recorded on a Bruker 300, at ambient temperature and referenced to internal protio resonances.²⁴ NMR solvent was received from Cambridge Isotopes and dried over 4 Å molecular sieves for a minimum of 48 hours prior to use.

Sn(II)@SiO₂ (2**).** Absorption of **1** on high surface area silica was performed by dissolving 77 mg (0.243 mmol) of **1** in 10 ml pentane or hexane with a Teflon stir bar in a scintillation vial. Slowly, 1 g high surface area silica was added and the orange solution was allowed to stir for one hour. The solution turned colorless within 10-30 minutes with a simultaneous color change of the silica to light orange. After this time, the solvent was removed under reduced pressure. This combination gave 2.9 wt% or 1.5 mol% of the desired product. Removal of free ligand was observed by ^1H NMR when a small amount of **2** was heated to 60°C in 1 ml C_6D_6 .

Oxygen source treatment of **2.** Reactions were carried out on **2** with different oxygen sources; H_2O (**3**), H_2O_2 (**4**), and $t\text{BuOOH}$ (**5**). An indicative example with is given below.

A 100 ml round bottom flask with Teflon stir bar and 15 ml pentane was charged with 960 mg of **2** then capped with a rubber stopper. Under nitrogen flow, 0.45 ml of *tert*-butyl hydroperoxide in decane (5.0 M, 2.25 mmol) was added and the mixture was allowed to stir for one hour. The solid turned colorless immediately. Volatile components were removed under reduced pressure and **5** was further dried with 5 ml toluene.

3 and **4** were synthesized in the same fashion with de-oxygenated water as the solvent and without the toluene drying step.

Addition of second diamido (1**) treatment to **3**, **4** and **5**.** Deposition of additional molar equivalent of **1** was performed on all three oxygen source treatments to give two new materials **6** from H_2O_2 , and **7** from $t\text{BuOOH}$. A control was performed by addition of a second molar equivalent of **1** to **2**. A typical experiment is outlined below.

In a scintillation vial with Teflon stir bar was added 12 mg (0.037 mmol) of **1**, then 5 ml pentane. Then, 288 mg of **5** is added slowly and the mixture is allowed to stir for one hour. The orange solution turned colorless immediately for both **4** and **5** while the solid stayed colorless. With **2** and **3** the solid darkened in orange-red color as the solution became colorless.

X-ray absorption spectroscopy experiments and data fitting techniques

All x-ray experiments were carried out in Sector 10 at hutch 10-BM of The Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS). References and samples were pulverized in a mortar and pestle, in the amount of approximately 0.024 mmol of Sn, loaded and pressed into sample holders in an air-tight reactor, with kapton window, while under nitrogen atmosphere in a glove box. To ensure sufficient volume of sample, boron nitride was used for **1** and silica was used to supplement for all other samples. X-ray absorption spectroscopy (XAS) measurements were carried out around the Sn K edge ($E_0 - 29.2$ keV) and collected in transmission mode using ionization gas chambers filled with only argon. Energy of X-ray photons was calibrated using a Sn metal foil, which was placed between the second and third gas chambers. Spectra were

taken from -250 eV below to 800 eV above the absorption edge. X-ray absorption near edge structure (XANES) data were processed with the ATHENA program.

Extended X-ray absorption fine structure spectroscopy (XAFS) data curve fitting was performed in ATREMIS (version 0.8.014) and IFEFFIT software (version 1.2.11) by the FEFF program (0.8.061)²⁵ and by WinXAS (version 1.1). Scattering paths were calculated from SnO₂²⁶ and SnO²⁷ crystallographic information, as well as “quick first shell approximations” by FEFF for comparison. Data had the pre-edge and postedge backgrounds subtracted and then normalized to edge height. Background removal was accomplished through a seven domain cubic-spline with *k*-weight of two. To determine the phases and amplitudes, those data were Fourier transformed (FT) into R space, then back-Fourier transformed into *k* space. Amplitude reduction factors (*S*₀²) were determined by using four scattering paths generated in IFEFFIT for SnO and SnO₂ while setting the coordination number of the scatters to the known crystal structures. These values were determined to be 0.97 for Sn(IV) species and 1.16 for the Sn(II) species (due to SnO₂ contamination) and thus set to 1. Coordination numbers of shells in unknown samples were then determined by setting *S*₀² and allowing the coordination number of the paths to vary independently. The disorder factor ($\Delta\sigma^2$), coordination number (*N*) and scattering distance (*R*) were then generated in this fashion from the experimental data (full tabulated data can be found in the Supplementary Information).

WinXAS fits were performed as followed. After normalization, in the same fashion as before, and XANES analysis by inspection of the first derivative of the Sn *K* edge position, phase and amplitude references were extracted from the published crystal structure for the Sn-O path in SnO₂²⁶. Once these parameters were experimentally determined, chemically realistic fits were attempted using a basic least-squares refinement. This was accomplished by allowing the program to find a best fit, then setting the $\Delta\sigma^2$ to provide realistic coordination numbers for the Sn-O path (full tabulated data can be found in the Supplementary Information).

ASSOCIATED CONTENT

Supporting Information

Athena and WinXAS fit information table for compounds 2-7 with standards and XAFS figures for compounds 2-5, Raman spectroscopy data for compounds 2-7 and controls and Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data for compounds 3 and 5 is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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Table of Contents artwork:

Supporting Information for: A Synthetic and Spectroscopic Study of the Mechanism of Atomic Layer Deposition of Tin Chalcogenides

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S1. ATHENA AND WINXAS FIT INFORMATION TABLE FOR COMPOUNDS 2-7 WITH STANDARDS AND XAFS FIGURES FOR COMPOUNDS 2-5

Table S1: Data for Artemis fits and amplitude reduction factor determination for unknown and reference compounds (values in bold were not allowed to vary).

Compound	Path	amp	R (Å)	N	σ^2 (Å)	ΔE_o (eV)	Chi ² (reduced)	R-ractor (%)	Edge Jump (eV)
SnO ₂	Sn-O	0.96 (0.15)	2.031 (0.009)	4.000	0.0018 (0.0017)	3.04 (1.73)	11598.00	6.60	29206.048
	Sn-O		2.064 (0.009)	2.000	0.0015 (0.0017)				
	Sn-Sn		3.170 (0.009)	2.000					
	Sn--O		3.567 (0.009)	4.000					
SnO	Sn-O	1.16 (0.15)	2.231 (0.008)	4.000	0.0087 (0.0024)	6.81 (0.96)	2900.00	7.30	29202.028
	Sn-Sn		3.554 (0.008)	4.000	0.0066 (0.0016)				
	Sn-O-O		3.580 (0.008)	8.000					
	Sn--Sn		3.706 (0.008)	4.000					
	Sn---Sn		3.815 (0.008)	4.000					
2	Sn-O	1.000	2.05 (0.178)	2.64 (0.15)	0.0084 (0.0010)	3.57 (0.66)	30.21	5.20	29201.052
3	Sn-O	1.000	2.07 (0.154)	3.01 (0.17)	0.0070 (0.0009)	3.93 (0.63)	44.89	5.20	29202.028
4	Sn-O	0.970	2.05 (0.015)	5.42 (0.39)	0.0056 (0.0010)	4.23 (0.79)	94.23	13.50	29204.996
	Sn-Sn		3.23 (0.013)	0.24 (0.32)	0.0032 (0.0073)				
5	Sn-O	0.970	2.05 (0.018)	6.38 (0.38)	0.0062 (0.0009)	4.57 (0.61)	58.19	8.70	29204.996
	Sn-Sn		3.30 (0.135)	3.49 (1.37)	0.0126 (0.0039)				
3 with 2nd addition of 2	Sn-O	1.000	2.08 (0.143)	2.89 (0.13)	0.0063 (0.0007)	4.94 (0.51)	38.23	3.65	29201.052
6	Sn-O	0.970	2.049 (0.007)	5.76 (0.35)	0.0057 (0.0008)	3.81 (0.71)	101.36	8.82	29204.996
	Sn-Sn		3.25 (0.091)	1.49 (0.90)	0.0086 (0.0045)				
7	Sn-O	0.970	2.04 (0.011)	6.11 (0.26)	0.0065 (0.0006)	4.86 (0.47)	38.21	3.54	29204.020
	Sn-Sn		3.28 (0.111)	3.41 (0.89)	0.0124 (0.0026)				
2 with 2nd addition of 2	Sn-O	1.000	2.03 (0.203)	2.21 (0.18)	0.0076 (0.013)	1.78 (0.94)	32.89	9.70	29201.089

Table S2: Data for WinXAS fits for unknown and reference samples (uncertainty is approximately 10%).

Compound	Edge Energy (keV)	Oxidation State	Scatter	N	R (Å)	$\Delta\sigma^2$ (x 10 ³)	E _o (eV)
SnO ₂	29.2046	IV	Sn-O	6	2.05	0.0	0.2
1	29.1994	II					
2	29.2003	II	Sn-O	2.3	2.05	3.0	-3.1
3	29.2000	II	Sn-O	2.9	2.11	4.0	2.0
3 (difference Fit)	-	-	Sn-O (H ₂ O)	1.0	2.15	1.0	3.4
4	29.2031	IV	Sn-O	4.9	2.05	3.0	-3.3
5	29.2040	IV	Sn-O	6.0	2.03	5.0	-5.2
				5.4	2.03	3.0	-5.2
3 with 2nd Addition of 2	29.2000	II	Sn-O	2.9	2.09	4.0	-1.1
6	29.2034	IV	Sn-O	4.9	2.06	3.0	-2.3
7	29.2037	IV	Sn-O	6.0	2.03	6.0	-5.6
				5.0	2.03	3.0	-5.3
2 with 2nd addition of 2	29.1997	II	Sn-O	2.0	2.03	3.0	-4.0

Figure S1: XAFS data in R and k space for **2** with corresponding fit calculated in the Artemis program.

Figure S2: XAFS data for R and k space for **3** with corresponding fit calculated in the Artemis program.

Figure S3: XAFS data in R and k space for **4** with corresponding fit calculated in the Artemis program.

Figure S4: XAFS data in R and k space for **5** with corresponding fit calculated in the Artemis program.

S2. RAMAN SPECTROSCOPY DATA FOR COMPOUNDS 2-7.

Figure S5. Raman spectroscopy data for untreated silica and compound 2.

Figure S6. Raman spectroscopy data for **2**, **3**, and **3** with 2nd addition of **1**.

Figure S7. Raman spectroscopic data for **2**, **4**, and **6**.

Figure S8. Raman spectroscopic data for 2, 5, and 7.

S3. DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY (DRIFTS) DATA FOR COMPOUNDS 3 AND 5.

Figure S9. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data for **3** with background subtractions of high surface area silica and **2**.

Figure S10. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data for **5** with background subtractions of high surface area silica and **2**.