# **Supporting Information**

# Atmospheric atomic layer deposition of SnO<sub>2</sub> thin films with Tin(II) acetylacetonate and water

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## 1. Geometrical parameters of precursors

Table S1: Calculated geometrical parameters of presursors shown in Figure 1 in the main text. The corresponding molecular structures with numbered atoms are shown in Figure S1. The values in parentheses are experimetal or other computational data

Prec.	Bond (Å) DFT (Exp./Cal.)		Angle (°) DFT (Exp./Cal.)		Ref.
P1	Sn-N	2.05	N-Sn-N	103-113	1
	N-C	1.45 (1.46)	Sn-N-C	111-113	1
			C-N-C	112-113	1
				(111.4/112.6)	
P2	Sn-O	2.00 (1.946/1.949)	O-Sn-O	107-112	2
				(105.06-115.83)	
	C-0	1.46 (1.447)	Sn-O-C	124-128	2
				(124.09-125.03)	
			O-C-C	104-112	2
				(104.9-111.2)	
P3	Sn-O1/Sn-O2	2.14 (2.147)	Sn-O1-C-O4	0.32 (0)	3
			(dihedral angle)		
	Sn-O3/Sn-O4	2.58/2.60 (2.597)	Sn-O2-C-O3	1.22 (0)	3
			(dihedral angle)		
	C-O1/C-O2	1.306 (1.308)			3
	C-O3/C-O4	1.26/1.25 (1.249)			3
P4	Sn-O1/Sn-O3	2.20	O1-Sn-O4/O2-Sn-O3	80	4
	Sn-O2/Sn-O4	2.29	O1-Sn-O2/O3-Sn-O4	79	4
	C-0	1.29 (1.30)	Sn-O-C	122-125	4
	C-C	1.40 (1.39)	O-C-C/O-C-CH <sub>3</sub>	125/116	4
				(127/114)	
	C-CH <sub>3</sub>	1.51 (1.51)	C-C-C	126 (127)	4
P5	Sn-N	2.15	N-Sn-N	105	
	Si-N	1.75	Sn-N-Si/ Si-N-Si	118/124	
	Si-C	1.89	C-Si-C	104-109	
P6	Sn-O	2.25	01-Sn-O2/O3-Sn-O4	85	
	Sn-C	2.17	O1-Sn-O4/O2-Sn-O3	95	
	C-0	1.28	Sn-O-C	124-127	



Figure S1: Geometrical optimization of different conformers and the corresponding energies of precursors P3 and P6. The lowest energy conformers are highlighted in bold.

# 2. Prices of some tin precursors

Table S2: Price of some tin metalorganic precursors used for ALD (values consulted from different suppliers in Oct.2021: Sigma-Aldrich, Strem Chemicals, Santa Cruz Biotechnology, etc. ). Data consulted in November 2021.

Precursor	Name	Price for 5 g
P1	Tetrakis(dimethylamido)tin(IV)	240 - 280 \$
P2	Tin(IV) tert-butoxide	200 - 250 \$
P3	Dibutyltin diacetate	80 - 120 \$
P4	Tin(II) acetylacetonate	140 - 160 \$
P5	Bis[bis(trimethylsilyl)amino]tin(II)	60 - 80 \$
P6	Dibutyltin bis(acetylacetonate)	2 - 5 \$
P7	Tetrakis(diethylamido)tin(IV)	320 - 350 \$
P8	Tin(II) hexafluoroacetylacetonate	300 - 350 \$

# 3. AP-SALD injection head used and COMSOL Multiphysics Simulation



Figure S2: Cross-section view of the scheme of the AP-SALD injection head used in this work.  $W_{out}$ ,  $W_{exh}$ ,  $W_{edge}$ ,  $d_{spacing}$ ,  $h_{ch}$  and  $h_{gap}$  denote the dimensions for gas outlets, gas exhaust channels, distance from the last gas inlet to the edge of the head, space between gas channels, height of each gas channel and the head/ substrate gap. The flows for metal precursors, oxidizer, purging nitrogen and exhaust channels are represented in green, red, blue, and blank arrows, respectively.

Symbols	Description	Value (unit)
$h_{gap}$	Distance between the injection head and the substrate	150 µm
W <sub>out</sub>	Width of the precursors, oxidizer, and nitrogen outlets	0.5 mm
W <sub>exh</sub>	Width of the exhaust channel	1.5 mm
$h_{ch}$	Height of the precursors and nitrogen outlets	6 mm
$d_{spacing}$	Distance between gas channels	1.0 mm
W <sub>edge</sub>	Distance from the last nitrogen inlets to the edges	4 mm
$[Sn(acac)_2]$	Concentration of $Sn(acac)_2$ at the top of the $Sn(acac)_2$ outlets	$0.1 \text{ mol/m}^3$
[H <sub>2</sub> O]	Concentration of H <sub>2</sub> O at the top of the H <sub>2</sub> O outlets	$0.1 \text{ mol/m}^3$
<i>M</i> <sub><i>H</i><sub>2</sub><i>O</i></sub>	Molar Mass of H <sub>2</sub> O	18 g/mol
$M_{Sn(acac)_2}$	Molar Mass of Sn(acac) <sub>2</sub>	316.7 g/mol
$f_{H_2O}^{outlet}$	Flow rate of H <sub>2</sub> O containing gas at each H <sub>2</sub> O outlet	200 sccm
$f_{\mathit{Sn}(\mathit{acac})_2}^{\mathit{outlet}}$	Flow rate of Sn(acac) <sub>2</sub> containing gas at each Sn(acac) <sub>2</sub> outlet	250 sccm
$f_{N_2}^{outlet}$	Flow rate of N <sub>2</sub> purging gas at each outlet	200 sccm

Table S3: Parameters used for the 2D COMSOL Multiphysics simulation



Figure S3: a) concentration profiles of precursors (the middle channel) and two channels of co-reactant in the AP-SALD injector, obtained with Comsol Multiphysics simulation in the case of an immobile substrate. The color bar schematically represents values precursor concentration, where the hotter color corresponds to higher values. The top image illustrates the initial stage (0.1 s) of the gas injection, and the bottom one represents the stationary condition, showing the spatial separation of exposures of precursor and co-reaction to the substrate surface.

The gas manifold injection head for atmospheric pressure spatial atomic layer deposition (AP-SALD) of amorphous SnO<sub>2</sub> thin films was fabricated by metal 3D printing technique. The head was studied with COMSOL Multiphysics Simulation to validate its suitability for use in AP-SALD technology. We have combined three modules in COMSOL: heat transfer, laminar flow, and transport of diluted species (precursors and water vapor in a nitrogen atmosphere) to model the head. In practice, the SALD process involves oxidizing gases (water vapor, ozone, or oxygen plasma), tin precursor vapor, by-product gas. But these are largely diluted in a carrier gas, i.e., nitrogen. Despite the complexity of the phenomenon, for the sake of simplicity, we assume that the physical properties of the different gas mixtures (viscosity, density, specific heat, thermal conductivity) are similar to nitrogen, which is the most abundant species. A schematic representation of the AP-SALD injection head and the details of parameters used for the 2D COMSOL Multiphysics simulation are shown in Figure S2 and Table S3, respectively. Figure S3 shows the spatial separation of precursor exposures from the gas injector to the substrate surface. This indicates the possibility of depositing functional materials in ALD condition with proper design of AP-SALD injection head.

#### 4. Effect of deposition pressure

Following the kinetic theory of gases, the mean free path of an ALD precursor can be approximately calculated as follows:

$$\lambda_{mfp} = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

Where  $\lambda_{mfp}$ , *R*, *T*, *d*, *Na* and *P* refer to the mean free path, gas constant, temperature, effective diameter of precursor molecule, Avogadro's number and working pressure.

The gas impingement flux is given by:

$$\Phi = \frac{N_A P}{2\sqrt{2\pi MRT}} \quad (molecules.m^{-2}.s^{-1})$$

Where *M* denotes the molar mass of precursor molecules.



Figure S4: a) mean free path (nm) and b) gas impingement flux (molecules/ $m^2/s$ ) as a function of precursor size and molar mass, respectively. Different deposition pressure ranges from  $10^{-3}$  mbar to atmospheric pressure are presented.

Figure S4a shows the mean free path as a function of precursor molecule size at various pressures, ranging from 0.001 mbar to atmospheric pressure (1 bar). As can be seen, the mean free path can increase up to 5 orders of magnitude when the deposition pressure decreases from 1 bar in the case of AP-SALD to about  $10^{-2}$  mbar as in the case of conventional ALD. The trend is reversed for the gas impingement flux (Figure S4b). Indeed, the atmospheric pressure presents a very high impingement flux (~  $10^{26}$  molecules/m<sup>2</sup>/s). It should be noted that the precursor molecules represent only a small amount of  $10^{26}$  molecules/m<sup>2</sup>/s, but at high atmospheric pressure, the adsorption rate is significantly increased, leading to a faster surface coverage by precursor molecules.<sup>5,6</sup> As a result, the high growth per cycle in the case of atmospheric ALD is in some cases observed. Remarkably, the variation of gas impingement flux versus the considering precursors (P1 to P6) is not very significant. Indeed the precursor size would mainly affect the growth rate via the steric hindrances rather than the impingement flux. We note that the possibility of having SCVD growth can also result in a higher GPC that expected based on ALD data. Again, it is important to verify that the growth is actually in ALD mode when using SALD in order to properly evaluate the GPC obtained.

# 5. Hydrophobic surface after bis[bis(trimethylsilyl)amino] tin(II) exposure

Figure S5 illustrates a silicon substrate exposed to the bis[bis(trimethylsilyl)amino] tin(II) for 1 min at the atmospheric pressure. The exposed area (in the middle) appears hydrophobic due to the - Si(CH<sub>3</sub>)<sub>3</sub> groups. This hinders the ALD growth of SnO<sub>2</sub> even though the higher oxidizing agents such as H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> were used.



Figure S5: Hydrophobic area in the middle observed after bis[bis(trimethylsilyl)amino] tin(II) exposured for 1 min at the atmospheric pressure.



#### 6. XRD and UV-Vis measurements

Figure S6: XRD patterns of as-deposited and annealed SnO<sub>2</sub> samples, a) samples deposited on glass, b) samples deposited on a silicon substrate. In both cases, the films were grown at 200 °C, and the film thickness is about 200 nm. All annealing processes were performed under vacuum.

Figure S6 shows XRD diffractograms of as-deposited and annealed SnO<sub>2</sub> samples deposited on glass (left) and silicon wafer (right). On glass substrate, the as-deposited film appears amorphous, even with annealing at 300 °C under vacuum. On silicon substrate, the film is slightly crystallized with the preferential growth orientation (101). This interesting observation could originate from the surface states of silicon substrate compared to borosilicate glass substrate. Further studies are required to fully understand the effect of substrate nature on the crystallinity of the deposited SnO<sub>2</sub> films. In general, the crystallinity improves when the annealing temperature increases. For samples annealed at 400 and 500 °C, XRD patterns show characteristic peaks (110), (101), (200), (211), and (220) of crystalline SnO<sub>2</sub>.

The optical transmittance curves of as-deposited and annealed  $SnO_2$  films at different temperatures under vacuum are presented in Figure S7. The annealing at high temperatures (400 and 500 °C) appears to improve optical transparency of the samples, which can be attributed to a better crystallinity.



Figure S7: Optical transmittance of as-deposited and annealed SnO<sub>2</sub> films at different temperatures and under vacuum conditions.



Figure S8: Total transmittance (a) and reflectance: The inset graph shows the optical bandgap estimated using Tauc plot approach. (b) of SnO<sub>2</sub> deposited at 200 °C with various thicknesses.

## 7. XPS spectra

Here below are XPS spectra of SnO<sub>x</sub> films deposited at different temperatures:



The XPS spectra of Sn3d region for pristine and annealed samples is shown below:



#### References

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