Supplementary material

Incomplete elimination of precursor ligands during atomic layer deposition of zinc-oxide, tin-oxide, and zinc-tin-oxide

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Figure S1. (a) Gas-phase FTIR spectra recorded during the TDMASn half reaction of SnO₂ ALD at 150 °C. The similarity of the C-H peaks for > 1 s TDMASn dosing confirms that the 5 s dosing step used in this study is sufficient for saturated ALD growth. (b) Gas-phase FTIR spectra recorded during the H₂O half reaction of SnO₂ ALD at 150 °C. Saturation of the H₂O half-reaction can be deduced from the presence of unreacted H₂O in gas-phase, and the similarity of the C-H peaks for 7 s and 10 s H₂O dosing. For the experiments corresponding to Fig. 1 and 2, the leak valve in the H₂O delivery line was opened further to increase the H₂O exposure. The H₂O dose was therefore much higher than what is required to reach saturation of the H₂O half-reaction.
**Figure S2.** Surface FTIR spectra recorded during the TDMASn half reaction of SnO₂ ALD at 150 °C corresponding to the data of Fig. 5.

**Figure S3.** (a) Surface FTIR spectra recorded during the DEZ half reaction of ZnO ALD at 150 °C corresponding to the data of Fig. 6. (b) Infrared absorbance at 2000 cm⁻¹ as a measure for DEZ precursor decomposition. An increase of the background absorbance has been related in a previous study to decomposition of the DEZ precursor.¹ The graph shows a constant background infrared absorbance at 2000 cm⁻¹ for these low DEZ exposures. This indicates that there is no significant contribution of decomposition reactions in the data presented in this article.
Figure S4. Surface FTIR spectra recorded during the TDMASn and H₂O half reactions of SnO₂ ALD (a) at 100 °C, and (b) at 150 °C. These cycles were performed after cleaning the surface using a 300 s H₂O dose at 300 °C. In (a), both spectra are referenced to the spectrum recorded before the half-reaction. The spectrum representing the H₂O pulse shows a small positive OH peak at 3740 cm⁻¹, and in addition there is a broad peak from 3670 to ~3300 cm⁻¹. This reveals that a mixture of free and H-bonded OH groups are generated during the H₂O pulse. The H-bonded OH stretches are broad and difficult to distinguish from the baseline of the spectrum, which makes it hard to accurately quantify the hydroxyl groups by integrating the OH-related peaks. However, by comparing the sum of the free and H-bonded OH signals in the spectrum of the H₂O pulse to the negative OH signal in the spectrum of the TDMASn pulse it appears that the amount of OH is almost completely regenerated. In (b) the spectrum of the TDMASn half-reaction is referenced to a spectrum taken before this half-reaction (and after the H₂O pre-treatment), while all the spectra of the H₂O half-reaction are referenced to the spectrum of the TDMASn half-reaction. This graph illustrates that both the free and H-bonded OH peaks increase as a function of H₂O dosing.
Figure S5. Surface FTIR spectra recorded during three consecutive ALD cycles representing SnO$_2$ after one cycle of ZnO ALD. The experiments were performed after cleaning the surface using a 300 s H$_2$O dose at 300 °C. The spectra in (a) were recorded after the H$_2$O pulses and are referenced to a background spectrum recorded before the ZnO ALD cycle. Each spectrum in (b) is referenced to the spectrum of the previous half-reaction. (c) Integrated absorbance of C-H stretching peaks for the spectra shown in (a) as a function of cycle number. Each individual data point is scaled to the integrated absorbance of the saturated precursor signal from the preceding half-reaction. These cycles were performed after the cycles corresponding to Figs. 5-9 when the underlying layer was relatively thick, which gives a lower signal to noise. These graphs suggest that the amount of persisting ligands decreases when SnO$_2$ is carried out after ZnO ALD.
References