Support Material for

Controlled dopant distribution and higher doping efficiencies by surface-functionalized atomic layer deposition

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Mass spectrometry (MS) measurements

MS data was taken using a Stanford Research Systems SRS-300 RGA placed downstream of the reactor (Ref. 12). Mass fragments m/z=31 and 32, attributed to CH_2OH^+ and its corresponding isotopic shift, were followed as a function of time. Figure S1 shows data taken during multiple EtOH/H_2O and EtOH/D_2O exposures in an Al_2O_3-coated reactor at 200°C using 1 Torr of ultrahigh purity N_2 as a carrier gas. Upon dosing with H_2O, an increase of m/z=31 was observed. When D_2O was substituted as the co-reactant, a significant increase in m/z=32 was observed during the D_2O pulse. These observations are consistent with the displacement of functional groups (either ethoxides or acetates) by H_2O to produce CH_2OH^+ fragments, and by D_2O to produce CH_2OD^+ fragments.

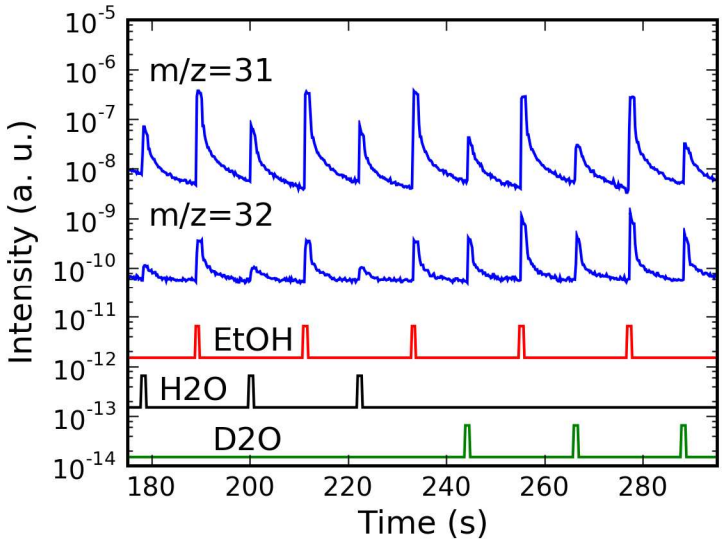

Figure S1: Time dependence of the intensities of m/z=31and 32 during the sequential dosing of EtOH/H_2O and EtOH/D_2O on an Al_2O_3 surface as measured by MS.

Thickness uniformity measurements

A series of Si(100) substrates were evenly spaced in the axial direction of flow along the ~40 cm deposition zone of the ALD reactor. The substrates were coated using 200 cycles of surface functionalized ALD with the sequence iPrOH/TMA/H_2O at 200 □C. The coating thicknesses for these samples were measured by spectroscopic ellipsometry (SE) and are shown in Fig. S2. The coating thicknesses were highly uniform along the reactor (+/- 0.5%) with an average value of 125 Å.

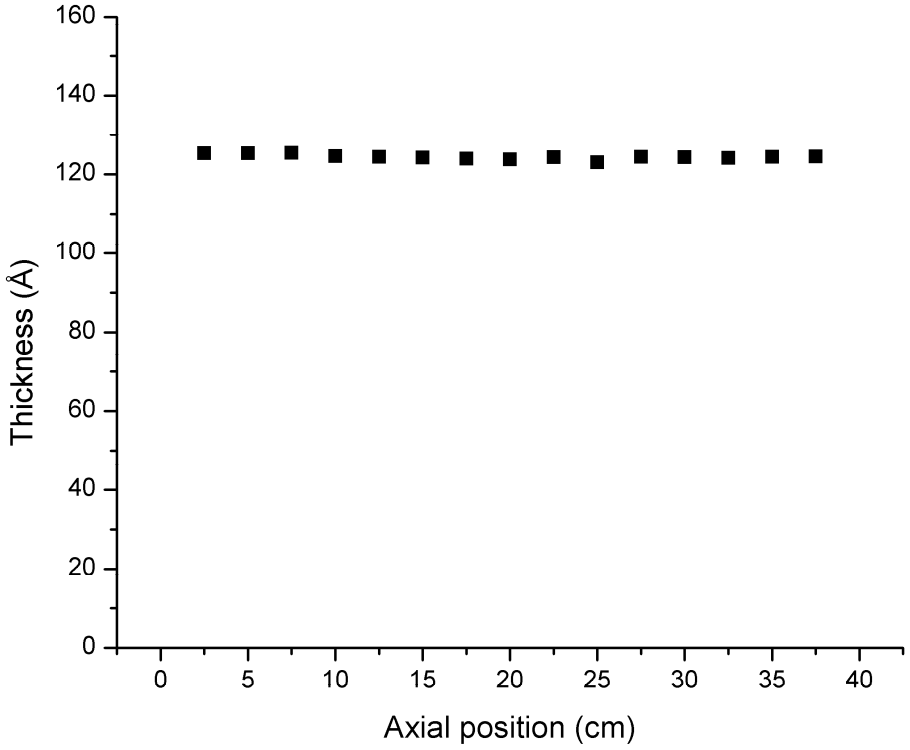

Figure S2: Thickness of Al_2O_3 films prepared by surface functionalized ALD on Si(100) versus position along axial direction of flow in the ALD reactor as determined by SE.

Quartz crystal microbalance (QCM) measurements

QCM measurements during repeated EtOH/H_2O exposures on an ALD Al_2O_3 surface show that the mass gain during the first EtOH exposure was higher than in subsequent exposures (Fig. S3). This difference is consistent with the adsorption of some EtOH on bridging O or OH sites without releasing H_2O. During the subsequent EtOH exposures, EtOH reacts only with OH sites releasing H_2O so that the net mass change is smaller.

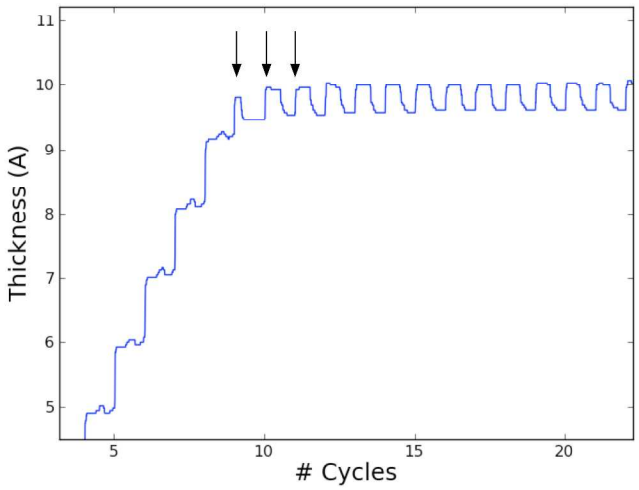

Figure S3: Mass gain during repeated EtOH/H_2O exposures on an Al_2O_3 surface as measured by QCM. EtOH exposures are indicated by arrows in the figure.

Elemental analysis of ALD Al_2O_3 and ZnO films

X-ray photoelectron spectroscopy (XPS) depth-profiling measurements of the C, O, Al, and Si concentrations were performed on Al_2O_3 films deposited on Si(100) substrates prepared both using conventional ALD and surface functionalized ALD using EtOH. Figure S4 shows that the C signals are below the XPS detection limit of ~0.2 at% for both samples demonstrating that surface functionalization does not introduce C impurities into the Al_2O_3. Similar XPS measurements performed for the C, O, Zn, and Si concentrations on ALD ZnO films prepared with and without EtOH surface functionalization. These measurements showed no C impurities in the ZnO films. These results demonstrate that the functionalization species deposited by EtOH are completely removed by the H_2O coreactant.

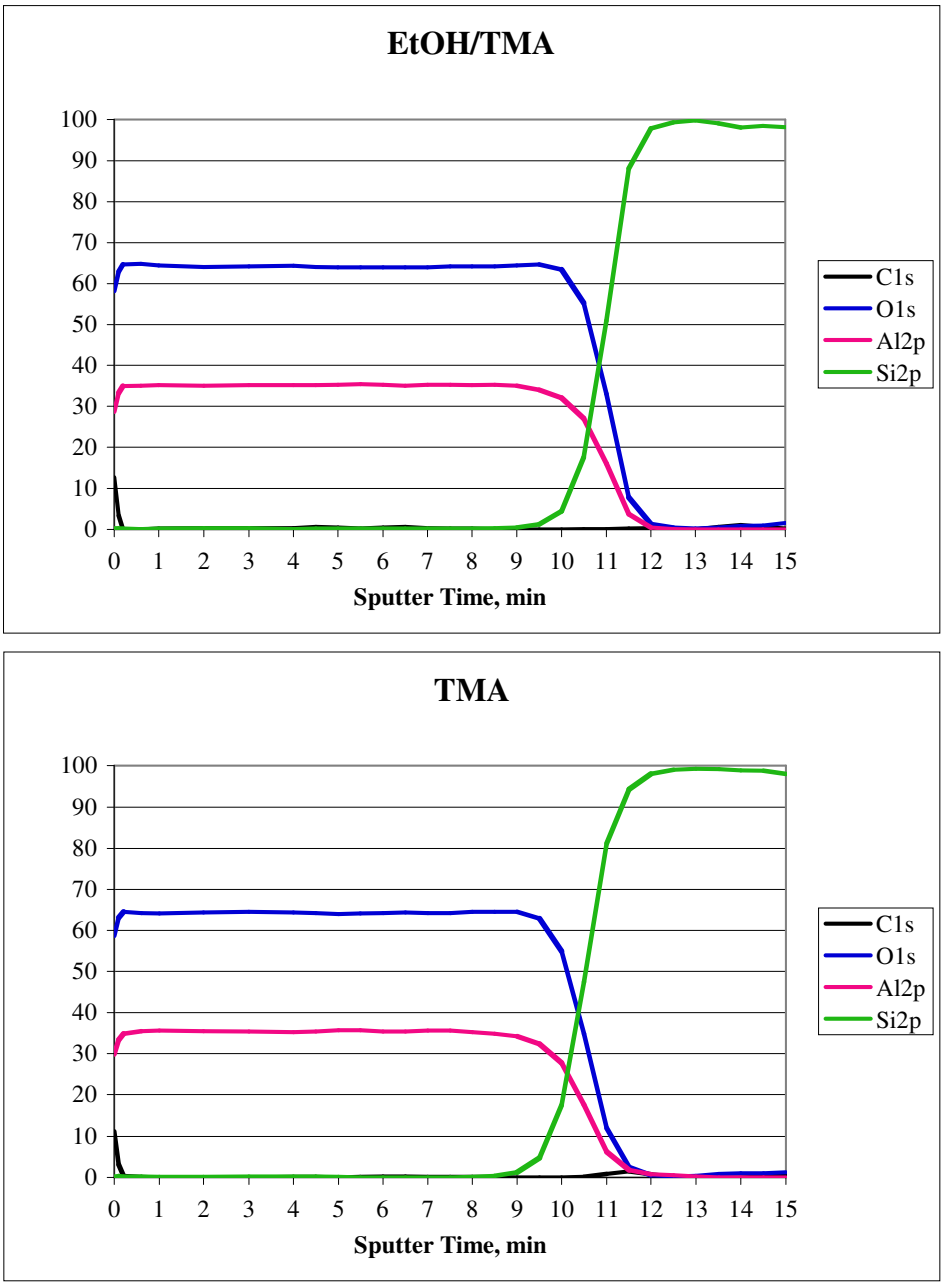

Figure S4: XPS depth profile measurements for the C, O, Al, and Si concentrations in Al_2O_3 prepared using surface-functionalized ALD with EtOH (top) and conventional ALD (bottom)

Spectroscopic ellipsometry of ALD Al_2O_3 films

We carried out ex-situ spectroscopic ellipsometry (SE) measurements of Al_2O_3 films prepared using both conventional and by surface functionalized ALD with EtOH using a J. A. Woollam Co. Alpha-SE ellipsometer over the wavelength range 375-900 nm.

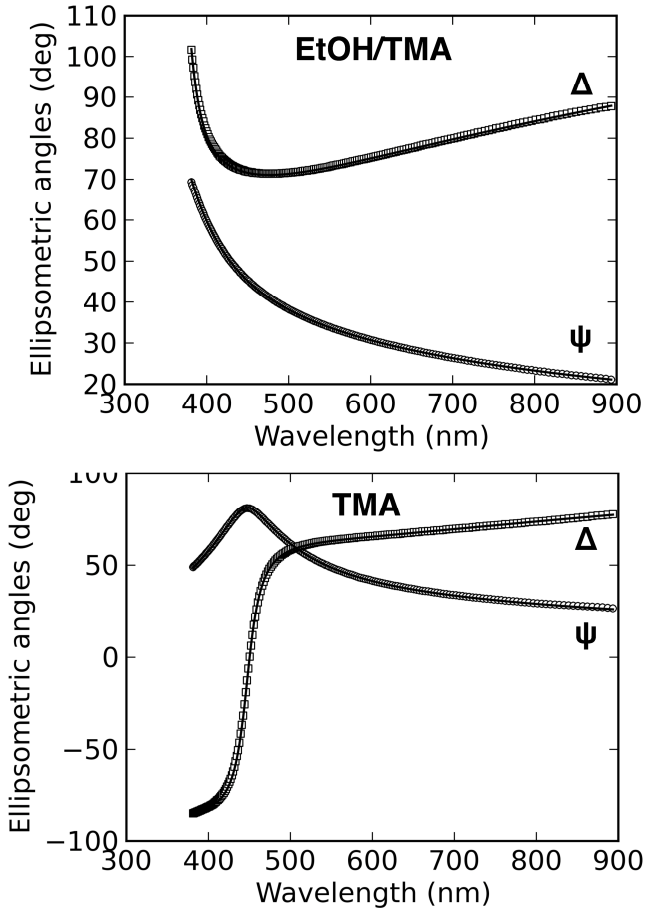

Figure S5: Spectroscopic ellipsometry data of ALD films grown both using conventional (bottom) and surface-functionalized (top) ALD. Solid lines show the results of fitting the data using identical fitting parameters for the refractive index of both films

The raw SE data (Ψ and Δ) for the films prepared using surface functionalized ALD and conventional ALD are shown as the open circles in the top and bottom panes of Fig. S5, respectively. These data were fit using a Cauchy model for the Al_2O_3 refractive index:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

and the best fits were obtained for both samples using the same fitting parameters: A=1.649, B=0.0012 μm^2 and C=0.00074 μm^4. The solid lines in Fig. S4 show the results for these fits where only the film thicknesses are different, and this difference accounts for the different shapes of the curves for the two samples. The identical refractive index for the two films demonstrates that surface functionalization does not contaminate the Al_2O_3 films.