SUPPORTING INFORMATION

Radical-triggered Cross-Linking for Molecular Layer Deposition of Thermally Stable SiAlCOH Hybrid Thin Films

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EXPERIMENTAL SECTION

The MLD process was performed in a custom made hot-wall type reactor. Ultra-high purity nitrogen was used as a carrier gas. The deposition was performed under a constant nitrogen flow of 50 standard cubic centimeters per minute (sccm) and a reactor pressure of ~1 Torr. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V₄D₄), trimethylaluminum (TMA) and di-tert-butyl peroxide (TBPO) were purchased from Sigma-Aldrich and had purity of 98, 97, and 98 %, respectively. TMA and TBPO were kept at room temperature during deposition and 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V₄D₄) was heated to 70 °C to provide sufficient vapor pressure. During the deposition, 6, 2, and 2 second doses of V₄D₄, TBPO, and TMA were producing partial pressures of 0.30, 0.40, and 0.25 Torr, respectively. The MLD experiments were carried out at 150 to 200 °C reactor temperatures, with MLD cycle timing for the two step process of 6/22/2/22/2/2 where 6, 2, and 2s are V₄D₄, TBPO and TMA dose times, respectively, and 22s is the purge time.

TEM characterization was carried out with a Cs-corrected microscope FEI Titan 60-300 (Thermo Fisher, USA). To study the morphology of the deposited film on zirconia nanoparticles, the microscope was operated in a monochromatic mode at an accelerating voltage of 80 kV.

In-situ QCM measurements were performed using RC-cut, 6 MHz resonant frequency, polished, gold-plated, quartz crystal sensor (Phillip Tech.). The QCM crystal was mounted in a bakeable sensor housing (Inficon) and sealed using high-temperature epoxy (Epoxy Technology, U.S.A.). The QCM mass resolution was ~0.3 ng/cm². The quartz crystal of the QCM was pre-coated with an ALD-grown, 60-80 Å thick Al₂O₃ film prior to any new measurements, to generate identical conditions for all processes.

The thicknesses and densities of samples were extracted from XRR measurements with a PANalytical X’Pert Pro diffractometer with Cu Kα radiation. Single-side polished P-type silicon (100) wafers were used as substrates for the XRR measurements. The error bars obtained for MLD film growth on silicon wafers represent variations between three samples processed in the same experiment at different reactor positions.

ATR-FTIR measurements were carried out in a PerkinElmer Frontier spectrometer. In order to increase the signal to noise ratio, pressed nanopowder of ZrO₂ (Sigma Aldrich, particle size <100 nm) was used as substrate for the ATR-FTIR measurements. All spectra were recorded in the range from 600 to 4000 cm⁻¹ with 20 scans at 4 cm⁻¹ resolution.

The chemical composition and bonding in the MLD films deposited onto a Si (100) substrate were examined by XPS using a SPECS instrument, equipped with a hemispherical electron analyzer and a monochromatized source of Al Kα x-rays. The calibration of the energy scale in all XPS spectra was done by placing the binding energy of the characteristic C 1s peak at 284.5 eV. The XPS spectra were deconvoluted into several sets of mixed Gaussian-Lorentzian functions with Shirley background subtraction.
A CARBOLITE GEROL laboratory high-temperature furnace was used for sample annealing. The ramp rate was 10 °C per minute.

1. QCM studies of the self-limiting surface chemistry of the V₄D₄, TBPO and TMA reactions, performed at 200°C. The error bars obtained for each point represent the data spread from 35 data points (ABC reaction cycles) for different experiments. The timing sequence used for the V₄D₄ saturation experiment was X/22/2/2/22 (V₄D₄ pulse/ N₂ purge/ TBPO pulse/ N₂ purge/ TMA pulse/ N₂ purge) in seconds, where X stands for a variable dosing time. In this experiment, the MGPC saturated at 18 ng/cm² at 6 and 10s dosing times of V₄D₄. The timing sequence for the TBPO saturation experiments was 6/22/X/22/2/22. After 2 seconds dosing of TBPO, the MGPC saturated at 18 ng/cm². The timing sequence for the TMA saturation experiments was 6/22/2/22/X/22. After 2 seconds dosing of TMA, the MGPC saturated at 18 ng/cm². Consequently, all surface reactions were found to be self-limiting. Purging times above 22 seconds did not alter the mass gain after V₄D₄, TBPO, and TMA pulses. Consequently, the timing sequence of 6/22/2/22/2/22 was used for all further experiments to fulfill a self-saturated condition for the studied MLD processes.

![Figure 1S](image)

**Figure 1S.** QCM mass gain per cycle vs. V4D4, TBPO or TMA dosing time at 200°C.

2. QCM mass gain versus time for an MLD process using V₄D₄, TBPO and TMA: growth over 15 reaction cycles at 150 °C. No mass gain was observed upon TBPO dosing at 150 °C MLD process temperature.
3. XRR data and fits for $V_4D_4$/TMA and $V_4D_4$/TBPO/TMA films on Si/SiO$_2$.

**Figure 2S.** (a) QCM mass gain versus time for an MLD process using $V_4D_4$, TBPO, and TMA: growth over 15 reaction cycles at 150 °C. (b) Expanded view of a QCM signal during two MLD cycles.

**Figure 3S.** (a) XRR plot of 130 cycles $V_4D_4$/TMA film deposited at 200 °C. XRR data fit gives a density of 2.2 g/cm$^3$ and a root mean square roughness of 5.5 Å.

(b) XRR plot of 140 cycles $V_4D_4$/TBPO/TMA film deposited at 200 °C. XRR data fit gives a density of 2.5 g/cm$^3$ and a root mean square roughness of 5.4 Å.