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Molecular Layer Deposition of Hybrid Siloxane Thin Films By Ring Opening of Cyclic Trisiloxane (V_3D_3) and Azasilane

Kristina Ashurbekova,*[a] Karina Ashurbekova,[c] Iva Saric,[b] Evgenii Modin,[c] Mladen Petravić,[b] Ilmutdin Abdulagatov,[a] Aziz Abdulagatov,[a] Mato Knez*[b,c,d]

1. *In-situ* QCM measurements of growth rate versus deposition temperature

The temperature dependance of the MLD process was studied with an in-situ QCM in a temperature range between 150 and 225 °C. QCM data of growth rate versus deposition temperature for the poly(Azasilane-V3D3) film growth are shown in figure S1. The highest GPC of 14 ng/cm2 per cycle was observed at 200 °C. The GPC at 150 °C was lower and amounted to 8 ng/cm2 per cycle. Figure S1 shows no “temperature window” where the GPC is constant, which is very typical for MLD processes and also many ALD processes.

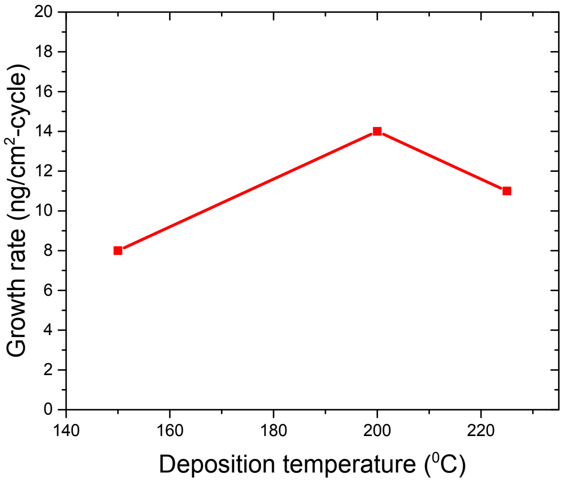

Figure S1 QCM measurements of growth rate versus deposition temperature for poly(Azasilane-V3D3) growth in a steady state regime.

2. Film nucleation and growth

The nucleation period of the MLD process was studied with *in-situ* QCM measurements at 150 °C. The QCM measurements of mass gain (MG) versus time for the poly(Azasilane-V_3D_3) growth during the first 10 reaction cycles is shown in Figure S2. The MG after the first Azasilane dose is 16 ng/cm^2, the MG after the first V_3D_3 dose is 6 ng/cm^2, which gives a total GPC of 22 ng/cm^2. The GPC settles to a constant value of 8 ng/cm^2 within 9 reaction cycles, showing a linear growth in a steady regime. This nucleation behavior, with the GPC being higher in the beginning of the growth than during the steady regime, confirms a substrate-enhanced growth type, which is typical for MLD processes. Substrate-enhanced growth can occur, when the number of reactive sites on the substrate is higher than on the MLD-grown material. This can be explained, considering that the quartz crystal of the QCM was pre-coated with ALD-grown Al_2O_3 that has among the highest concentrations of surficial reactive hydroxyl groups.

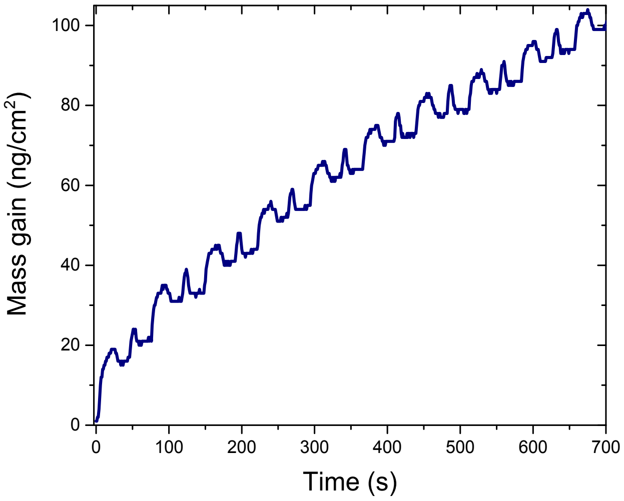

Figure S2 QCM measurements of the mass gain versus time during the nucleation period of the poly(Azasilane-V3D3) growth; the first 10 reaction cycles deposited at 150 °C.

The total range of the QCM measurements of mass gain versus time for poly(Azasilane-V_3D_3) growth during 45 reaction cycles at 150 °C is shown in Figure S3.

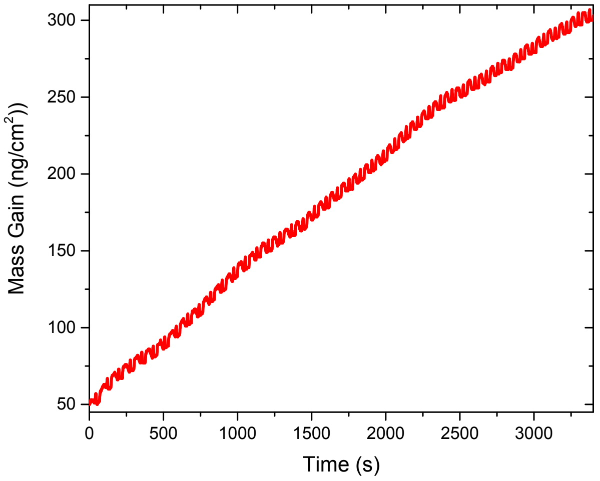

Figure S3 QCM measurements of mass gain versus time for poly(Azasilane-V_3D_3) growth during 45 reaction cycles at 150 °C.

3. Saturation curves

The self-limiting behavior of the surface reactions was studied at 150°C. The QCM results, showing the mass gain per cycle versus Azasilane and V_3D_3 dosing time, are shown in Figure S4 (a) and 4 (b), respectively. The timing sequence used for the Azasilane dosing in Figure S4 (a) was (X, 30, 5, 30). A 5 s dose of Azasilane yields an 8 ng/cm^2 mass gain per cycle, demonstrating saturative behavior. The timing sequence in Figure S4 (b) was (5, 30, X, 30). A 3 s pulse time of V_3D_3 produces saturative behavior that yields an 8 ng/cm^2 mass gain per cycle.

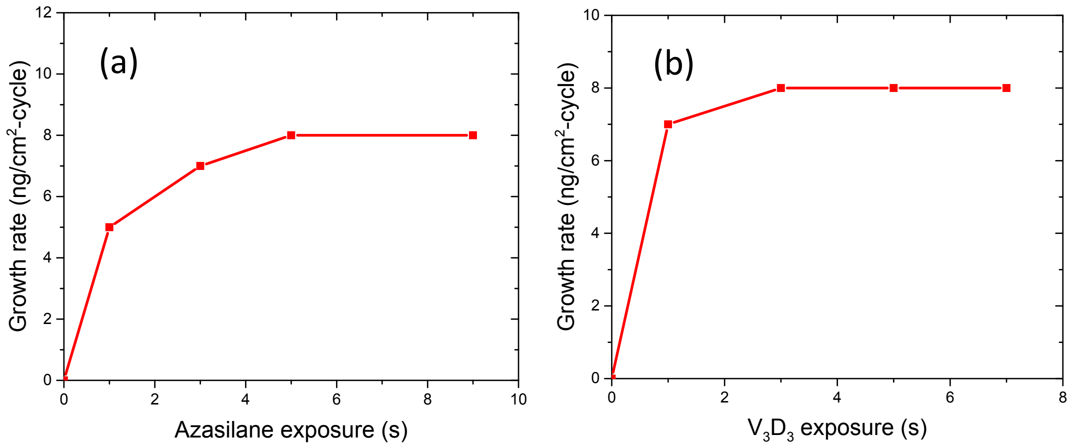

Figure S4 QCM measurements of growth rate versus reactant dose time for poly(Azasilane-V_3D_3) growth in a steady state regime at 150 °C. (a) Growth rate versus Azasilane dose time using a timing sequence of (X, 30, 5, 30). (b) Growth rate versus V_3D_3 dose time using a timing sequence of (5, 30, X, 30).

4. Major assignments of the ATR-FTIR spectra (figure 2 (a) and (b)) are summarized in the Table 1.

Wavenumber (cm^{-1})	**Chemical bond/ Vibration mode**	**Reference**
805	Si-C stretching, CH_3 rocking	(1-4)
842	Si-C stretching, CH_3 rocking	(1-4)
960	Si–N asymmetric stretching vibration	(5)
1067	Long chain Si-O-Si asymmetric stretching vibration	(1-4)
1220	C-N stretching	(6)
1258	Si-CH_3 symmetric bending in $O_2Si(CH_3)_2$ (D group)	(1-4)
1409	=CH_2 bending in vinyl groups	(1, 4)
1460	CH_2 asymmetric bending	(1, 3, 4)
1600	C=C stretching in vinyl groups	(1, 4)
1650	NH bending	(6)
2857	CH_2 symmetric stretching	(1-4)
2902	CH_3 symmetric stretching	(1-4)
2927	CH_2 asymmetric stretch	(1-4)
2960	CH_3 asymmetric stretching	(1-4)

Table 1 ATR-FTIR peak assignments for the MLD-grown V_3D_3/azasilane thin film.

5. Experimental

The MLD process was performed in a custom made hot-wall type reactor. Ultra high purity nitrogen was used as a carrier gas. Deposition was performed under a constant nitrogen flow of 40 standard cubic centimetres per minute (sccm) at a reactor pressure of 1 Torr. N-methyl-aza-2,2,4-trimethylsilacyclopentane (azasilane) and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3D_3) were supplied by Fluorochem and had purity of 97 and 95% respectively. N-methyl-aza-2,2,4-trimethylsilacyclopentane was kept at room temperature during deposition and V_3D_3 was heated to 45 °C to provide a sufficient vapor pressure. During deposition, five second doses of azasilane and V_3D_3 were producing of partial pressures of 0.35 Torr and 0.22 Torr of the respective precursors. The MLD experiments were carried out at reactor temperatures ranging from 150 to 225 °C, with sequences of 5/5/30/5/5/30 seconds of azasilane dose/azasilane soak/purge/V_3D_3 dose/V_3D_3 soak/purge in each cycle.

High resolution transmission electron microscopy (HRTEM) characterization was carried out with an Cs-corrected microscope FEI Titan (Thermofisher, U.S.A.). In order to study the morphology of the deposited layer, the microscope was operated in monochromated mode at 80 kV. This allowed to visualize atomic chains of the deposited hybrid film on the surface of zirconia nanoparticles.

In-situ QCM measurements were performed using RC-cut, 6 MHz resonant frequency, polished, gold-plated, quartz crystal sensor (Phillip Technologies, U.S.A.). The QCM crystal was mounted in a bakeable sensor housing (Inficon, U.S.A.) and sealed using high temperature epoxy (Epoxy Technology, U.S.A.). The QCM mass resolution is 0.3 ng/cm^2. The quartz crystal of the QCM was pre-coated with the ALD grown 6-8 nm Al_2O_3 film prior any new measurements to regenerate the same surface.

The thicknesses and densities of the samples were extracted from X-ray Reflectivity (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.

Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) measurements were carried out with a PerkinElmer Frontier spectrometer. In order to increase the signal to noise ratio, pressed nanopowder of ZrO_2 (Sigma Aldrich, <100 nm) was used as substrate for ATR-FTIR measurements. All spectra were recorded in the range from 600 to 4000 cm^{-1} with 4 cm^{-1} resolution.

The chemical composition and bonding of MLD films to the ZnO substrate was examined by x-ray photoelectron spectroscopy (XPS) using a SPECS instrument equipped with a hemispherical electron analyzer and a monochromatized source of Al Kα x-rays. The calibration of energy scale in all XPS spectra was done by placing the binding energy of characteristic C 1s peak at 284.5 eV. The XPS spectra were deconvoluted into several sets of mixed Gaussian-Lorentzian (G-L) functions with Shirley background subtraction. Pressed ZnO nanopowder (Sigma Aldrich, <100 nm particle size) used as substrate for the XPS analyses.

Notes and references

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