Ellipsometric Porosimetry

The layers were modeled using a Cauchy function. The alucone layers were analyzed in the spectral range 246-1000 nm. The probe molecule multilayer uptake was fitted by adding a Cauchy layer on top of the layer with fixed refractive index of the adsorptive, and with its thickness being the only fitting parameter. More details on the modeling can be found in ref. [1] and [2].

The adsorptive volume is generally reported as a function of the ratio between the partial pressure (P_l) and the vapor pressure (P_{sat}) of the probe molecule, resulting in classical adsorption/desorption isotherms, generally categorized according to the IUPAC classification.[1,3–5] A type I isotherm is associated with porous materials with a narrow distribution of pore size with a diameter below 2 nm (nano-porous or microporous materials), and a type II isotherm is associated with non-porous materials. Mesoporous materials are instead characterized by a type IV isotherm, in which a hysteresis arises in the desorption step, due to the condensation of the adsorbate in the pores.

The home-built porosimeter consisted of a vacuum chamber, equipped with a spectroscopic ellipsometer, Ar is used as carrier gas, and a source of toluene ($d = 0.6$ nm) and ethanol ($d = 0.42$ nm) are used as adsorptives. The SE measurements were carried out at an angle of 70°. After loading the samples, the chamber was evacuated in order to remove the adsorbed water due to the layer exposure to ambient. The refractive index value of the layers was followed in time until a constant value is reached, taken as the starting point for the adsorption measurements (*i.e.*, n_0). Then, the adsorptive and Ar are injected into the chamber, and the ratio is adjusted by equilibrium steps in order to scan the entire P_l/P_{sat} range, from 0 to 0.86-0.93. The whole range of P_l/P_{sat} from 0 to 1 was not investigated. Approaching the saturation value

(P/P_{sat} of 1), the contribution to the V_{ads}/V_{film} is solely attributed to multilayer formation, and was, therefore, discarded from the plots.
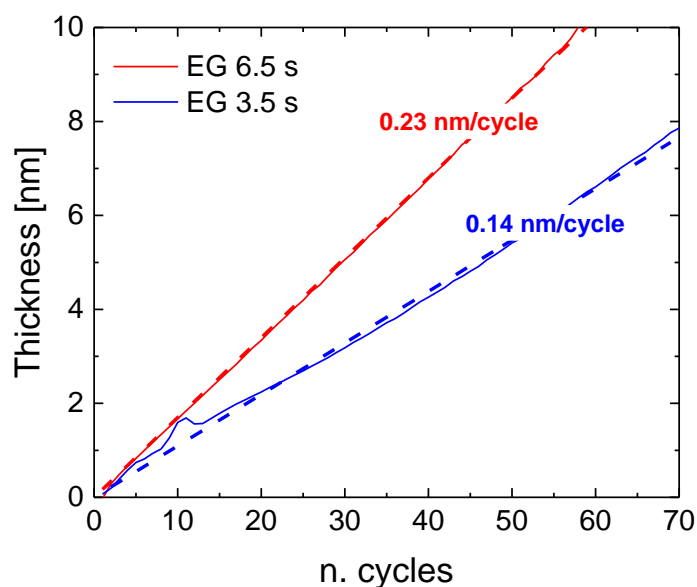
S1. *In-situ* SE measurements for the t-MLD layers deposited choosing 3.5 s and 6.5 s of EG exposure.

References

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