

Supporting Information

Increased Chemical Stability of Vapor Phase Infiltrated AlO_x -Poly(methyl methacrylate) Hybrid Materials

Emily K. McGuinness¹, Collen Z. Leng¹, and Mark D. Losego*

*Corresponding author. Email: losego@gatech.edu

¹These authors contributed equally to this work

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

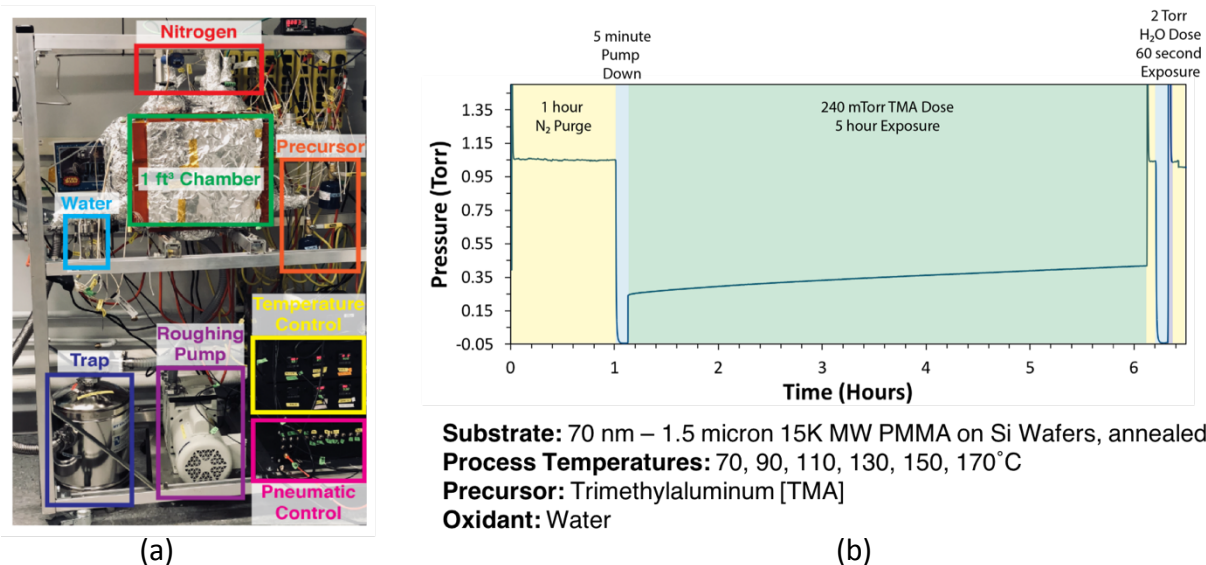


Figure S1. Overview of the vapor phase infiltration process for creating hybrid AlO_x -PMMA materials. (a) Custom-designed vapor phase infiltration chamber utilized for several experiments in this work. (b) General overview of the vapor phase infiltration process (timing of individual steps varied with substrates being infiltrated, as outlined in the body of the paper). In a general VPI process, the chamber is first purged with an inert gas to remove excess solvent or water from the polymer. The chamber is then pumped to rough vacuum. Once rough vacuum is reached, the chamber is isolated to a static environment. A metalorganic or metal halide vapor phase precursor is then introduced and the substrate is exposed for a variable duration of time. Varying exposure time results in precursor sorption, diffusion, and entrapment to differing

extents (often seen as depth of infiltration). Chamber is then purged with inert gas to remove precursor from the chamber. The purge time can be varied to remove more or less dissolved, but non-interacting precursor from the polymer bulk prior to co-reaction. The chamber is then pumped to rough vacuum and once more isolated. An oxidant (commonly water) is then introduced as a co-reactant into the static environment. The hybrid can be exposed to this environment for a variable amount of time. Ultimately, the chamber is purged once more with inert prior to removal of infiltrated materials. (c) In this study, substrates consisting of 70 nm – 1.5 micron thick PMMA films on silicon wafers prepared via spin coating were used for the bulk of the experiments. The films were annealed prior to infiltration at process temperatures varying from 70-170°C. The metalorganic precursor used for this study was trimethylaluminum and the oxidant used as co-reactant was DI water.

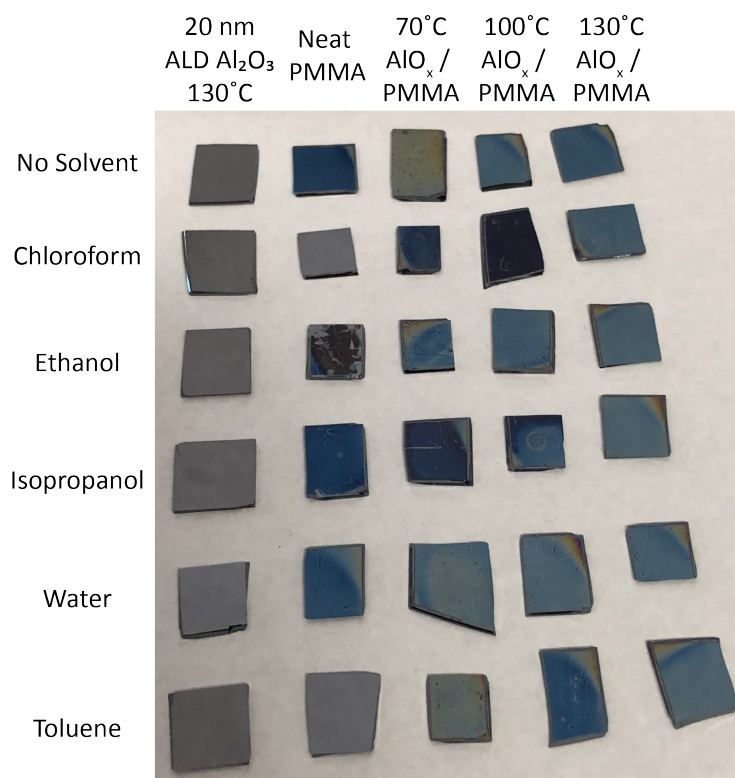


Figure S2. Visual inspection of films after storage in varying solvents for seven days reveals strong stability at high infiltration temperatures and partial dissolution at low infiltration temperatures. 20 nm ALD aluminum oxide films show no visual change in different solvent systems, as expected for transparent films. After spin-coating, the PMMA films appeared blue in color as a result of interference effects from the film thickness on a reflective substrate. PMMA films stored in chloroform and toluene dissolve completely. PMMA films stored in ethanol and isopropanol show slight visual changes. 70°C AlO_x-PMMA films turn a yellow color due to thickness increase on infiltration. When stored in chloroform, ethanol, isopropanol, and water, slight changes in thickness result in differences in film color, reflecting thickness changes measured with ellipsometry. For 100°C AlO_x-PMMA, films show visual changes only in chloroform and isopropanol, while 130°C AlO_x-PMMA films do not show any visual changes after 7 days in any solvents tested here.

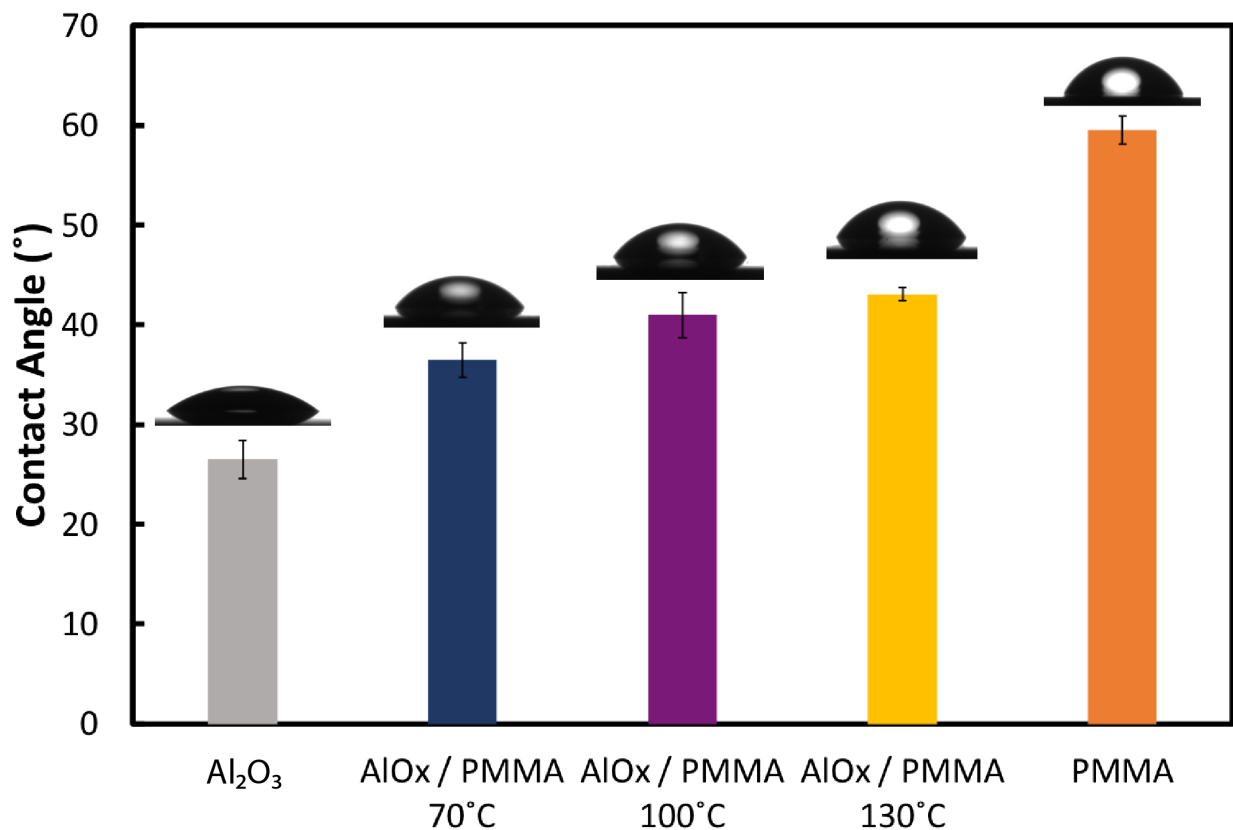


Figure S3. The interaction between water and AlO_x -PMMA hybrid materials varies with infiltration temperature, possibly contributing to changes in solvent stability. 20 nm ALD prepared Al_2O_3 films show the lowest contact angle (most hydrophilic) while PMMA shows the highest contact angle (most hydrophobic). Infiltrated films exhibit properties between these two contact angles that vary with infiltration temperature. Error bars are the standard deviation of five measurements.

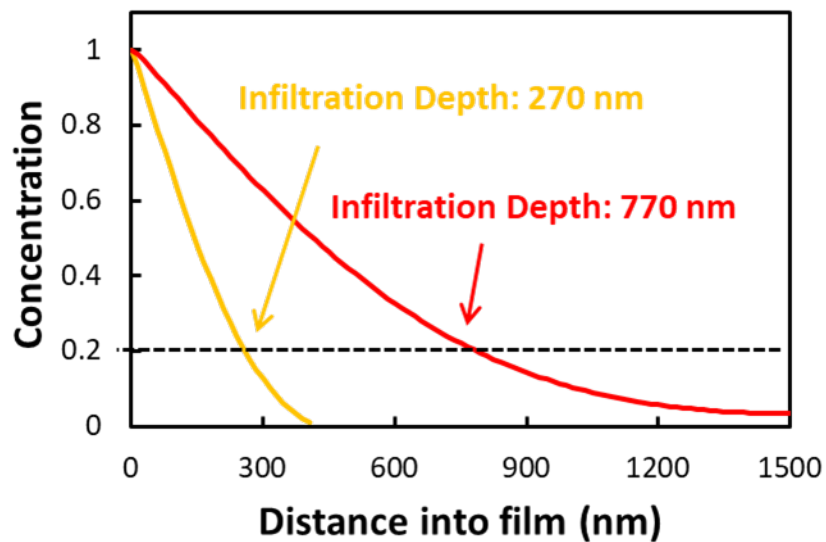


Figure S4: Infiltration depth into the film as defined by concentration levels of the precursor.

Infiltration depth is defined as the depth where the concentration of the precursor is 20% of the maximum precursor concentration found at the surface of the film (**Fig. S1**). The yellow line represents an infiltration depth of 270 nm since the line crosses 20% of maximum concentration at 270 nm. The red line represents an infiltration depth of 770 nm since the line cross 20% of maximum concentration at 770 nm.

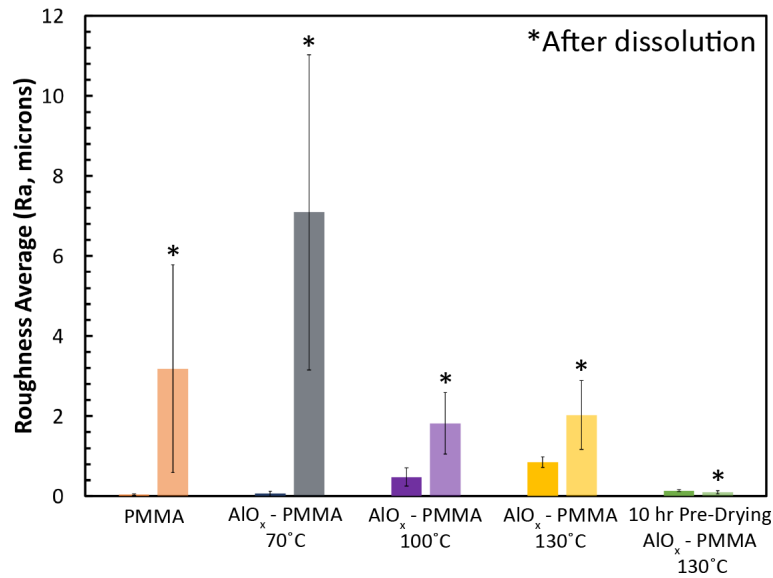


Figure S5: Surface roughness values as calculated from stylus profilometry of neat and infiltrated bulk acrylic coupons before and after dissolution. Without a sufficient pre-drying step, all three infiltration temperatures result in an increase in surface roughness. After exposure to toluene at 60°C for 30 minutes, the surface roughness drastically increases for all coupons. When sufficient pre-drying is used, the surface roughness does not increase drastically post-infiltration and no significant change is observed following dissolution.