Supporting Information

Multi-metal coordination polymers grown through hybrid molecular layer deposition

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Experimental

Chemicals. Trimethyl aluminum (TMA, %%), diethyl zinc (DEZ, %%), and anhydrous ethylene glycol (EG, %%) were purchased from Sigma Aldrich. Tetrakis(dimethylamino)hafnium (TDMAHf, %%) was purchased from Strem Chemicals. All chemicals were stored in the glove box when not in use and used as received. N-type single-sided polished silicon wafers were purchased from WRS materials and cut into approximately 1x1 cm squares prior to cleaning. Silicon wafers were cleaned by sonication in acetone, isopropanol, and deionized water for five minutes each and were stored in deionized water. Immediately prior to the deposition, the Si wafers were dried over N₂ gas and cleaned for at least 5 minutes with UV/O₃.

Hybrid MLD reactor. A custom built, hot-walled tube reactor was used throughout this work. The reactor was heated by external heating tapes controlled by a variable transformer. The base pressure of the reactor was below 500 mtorr which was measured by a K. J. Lesker convection gauge. Precursors were introduced into the chamber through solenoid valves which were controlled by LabVIEW.

Hybrid MLD deposition. The reactor was held at 110 \pm 5 °C for all depositions. The transfer lines and bubblers containing TDMAHf and EG were heated to between 50-55 °C and 55-60 °C, respectively. The TMA and DEZ bubblers were left unheated. Each cycle consisted of the following steps: (1) a precursor pulse time in which the precursor valve was opened to the reaction chamber with nitrogen flowing and vacuum pumping; (2) a soak time where the valves for the precursor, N₂, and pump were all closed, yet precursor vapor remained in the chamber; and (3) a purging time with nitrogen flow with the vacuum pump open to remove excess precursor and reaction byproducts. The times of the pulse – soak – purge for DEZ, TMA, and TDMAHf half cycles were 1 s – 2 s – 60 s, and for EG these times were 3 s – 2 s – 300 s. All depositions were carried out for a total of 80 cycles as described in the main manuscript.

Materials Characterization

X-ray photoelectron (XPS) spectroscopy was performed using a PHI VersaProbe III spectrometer with a monochromatic AI K α X-ray source. Measurements were taken using a 200 μ m X-ray spot size. Low-resolution survey spectra averaged over 3 scans were collected for element identification at energy steps of 0.8 eV/step, a dwell time of 20 ms/step and a 224 eV pass energy. High-resolution scans were averaged over 2-10 cycles, at energy steps of 0.1 eV/step, dwell times of 20-50 ms/step and a 55 eV pass energy. The Zn 2p_{3/2} peak was used as an internal reference for energy calibration and was set to 1022 eV.

Fourier transform infrared (FTIR) spectroscopy of the hybrid MLD films was performed on a Nicolet iS50 FT-IR from ThermoFisher Scientific fitted with the VariGATRTM grazing angle accessory from Harrick Scientific Products. An MCT detector cooled with liquid N₂ was used for data collection. The scan range encompassed 700 – 4000 cm⁻¹ to adequately capture all regions of interest. For each sample, 264

scans were collected at an incidence angle of 65° (relative to the surface normal) with resolution of 8 cm⁻¹. A background scan with no substrate present was performed prior to collecting the spectra.



Figure S1. Characterization of Zn-Al hybrid films at varying Zn cycle ratios. a) Normalized highresolution XPS spectra of the Zn 2p and Al2p regions. b) FTIR spectra of Zn-Al films.



Figure S2. Survey XPS scans of the Zn-Hf hybrid films grown at varying Zn cycle ratios.



Figure S3. FTIR spectra of the [Zn-Hf]-EG films grown at different cycle ratios. The vertical black lines represent peaks from the Si-O stretches of a UV-O₃ treated Si wafer for reference.



Figure S4. Variation in the FTIR spectra of two "as-deposited" zincone films. Both spectra were collected within 10 minutes of removal from the ALD reactor and exposure to ambient.



Figure S5. FTIR spectra of a hafnicone film exposed to ambient conditions over 24 hours.



Figure S6. Fitted high-resolution XPS spectra of a 1Zn-1Hf hybrid film as-deposited and after 3 days of exposure to ambient. The full-width half-max of the peaks were locked to the main peak in each spectrum.