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Supporting Information

Achieving Area-Selective Atomic Layer Deposition with Fluorinated Self-Assembled Monolayer

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EXPERIMENTAL SECTION

Materials

Decylphosphonic acid (C10PA) (98%) was obtained from Alfa Aesor. 1H,1H,2H,2H-perfluorodecylphosphonic acid (FC10PA) (96%) was obtained from Tokyo Chemical Industry Co., Ltd. Isopropyl alcohol (IPA) (99.5%), *t*-Butanol (99%), and acetone were purchased from Echo Chemical. Hydrogen fluoride (HF) (49%) was obtained from Union Chemicals. Trimethylaluminum was obtained from Sigma-Aldrich. Blanket PVD Co (thickness ~200 nm) and bare Si wafers were purchased from Advanced Materials Technology.

Fabrication of SAM Substrates

C10PA and F10PA solutions in *t*-butanol with a concentration of 1mM were first prepared. Blanket Co and Co/SiO_2 patterned wafers were then pretreated sequentially by diluted HF (10 s), EtOH (5 min), and acetone (5 min) and dried under nitrogen flow to remove native oxide and organic contaminations. After the cleaning processes, the wafers were transferred to glass petri dishes for the SAM process. The wafers were immersed in the SAM solutions for 48 h at 60 ^{o}C. The wafers were then removed from the SAM solutions and rinsed with IPA for 1 min to remove unreacted SAM molecules, followed by drying with nitrogen flow. From the post rinse experiments, the minimum post rinse time should exceed 2 s to remove the unreacted SAM molecule. As shown in Figure S4, the XPS and contact angle results all suggest that the minimum post rinse time should exceed 2 s to obtain a single layer of SAMs; therefore, 1 min should be enough to remove the unreacted SAM molecule in this work.

Fabrication of Al_2O_3 Films Using ALD Process

The SAM-treated and untreated wafers were placed in the ALD chamber simultaneously, where Al_2O_3 films were deposited by repeated ALD process. First, the substrate surfaces were saturated with trimethylaluminum at 130 ^oC, followed by N_2 purge. Subsequently, the substrate surfaces were hydrolyzed using deionized water to generate the Al_2O_3 layers. The cycle was repeated to deposit the films with desired thicknesses. For each cycle, the thicknesses of the Al_2O_3 films on the Si blanket and Co blanket wafers were 1.7 and 2.0 Å, respectively.

Structure Analysis and Characterization

The wettability of the SAMs-treated surfaces was determined using Drop Shape Analyzer (KRÜSS DSA100E). Approximately 2 μL of distilled water and hexadecane were dropped on the wafers to measure the contact angles. The surface free energy (SFE) was calculated by the Fowkes model and OWRK model (Owens-Wendt-Rabel & Kaelble) using the contact angles of water and hexadecane on the substrates. The chemical compositions of the samples were analyzed using XPS (Thermo Scientific™ Nexsa™ X-Ray Photoelectron Spectrometer System) by survey and high-resolution modes. The instrument was operated at 14 W and 15 kV with an X-ray beam size of 400 μm^2. The planar and cross-sectional views of the samples were investigated by TEM (Thermo Scientific™ Talos™ F200X) at an accelerating voltage of 200 kV. The compositional mapping and line scanning of the samples were performed by EDS (Thermo Scientific™ Super-X detector).

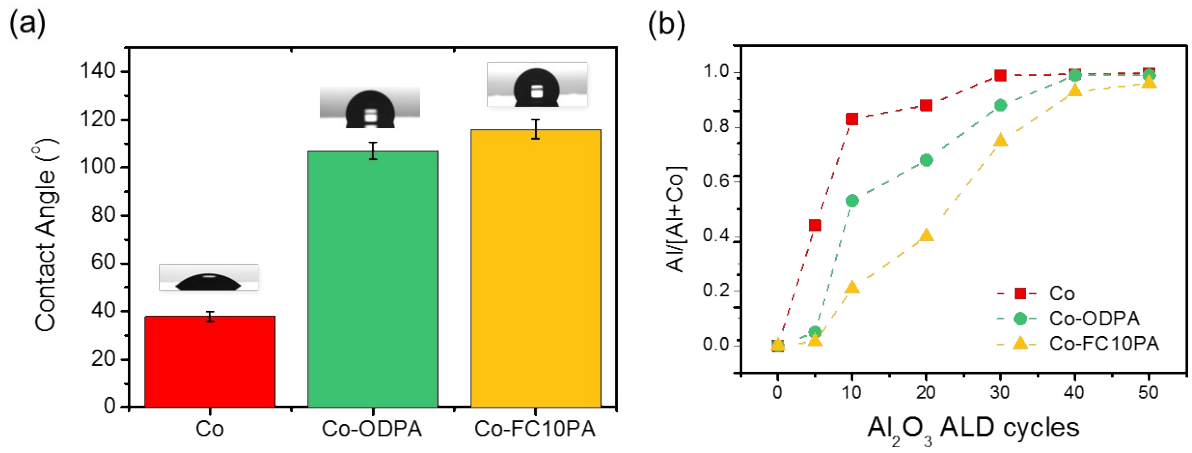

Figure S1. (a) Contact angles measurements of water on the surfaces of untreated, ODPA-modified, and FC10PA-modified Co substrates. (b) XPS composition analysis on the surfaces of Co, Co-ODPA, and Co-FC10PA after different cycles of Al_2O_3 ALD.

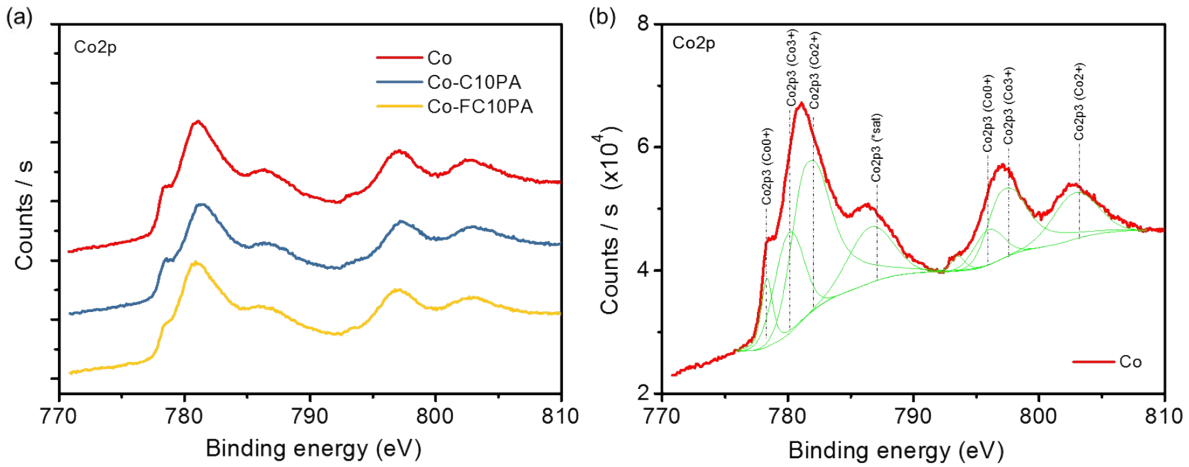

Figure S2. (a) HR-XPS scans of Co2p on a pristine Co wafer and Co wafers treated by C10PA and FC10PA. (b) HR-XPS scans of Co2p on a pristine Co wafer with best fitting and component peaks.

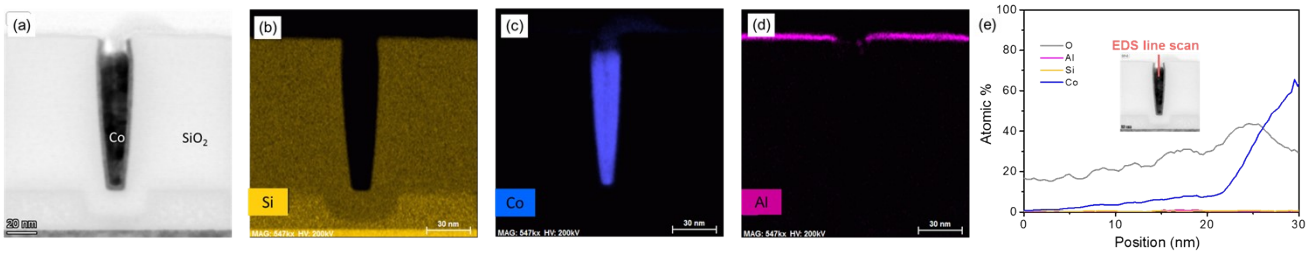

Figure S3. FC10PA-treated Co/SiO_2 patterned substrate consisting of 20 nm wide Co-filled SiO_2 trenches after 10 cycles of Al_2O_3 ALD: (a) bright-field cross-sectional TEM image, (b-d) EDS composition mapping analysis of Si, Co, and Al elements (yellow, blue, and pink colors), and (e) cross-sectional TEM line scans. The TEM line scan direction is marked by the red line.

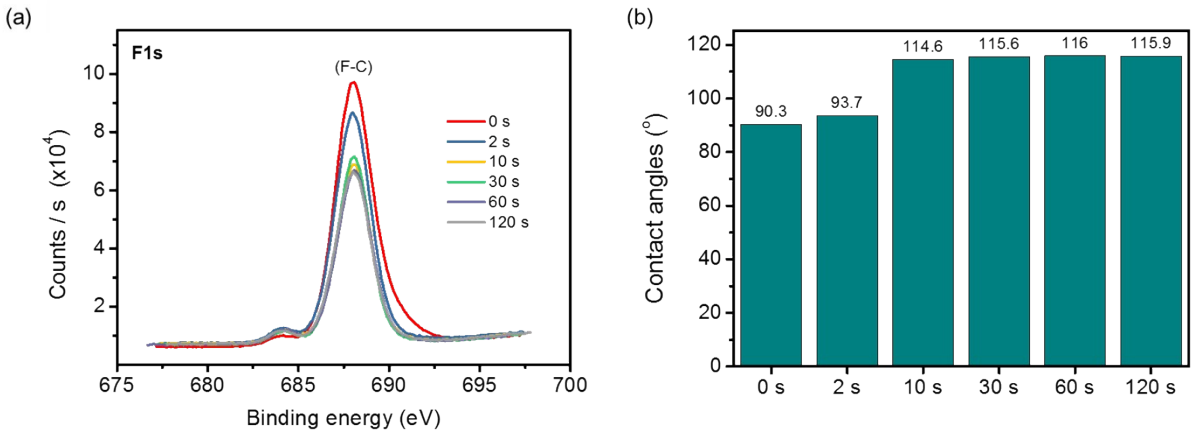

Figure S4. (a) HR-XPS scans of F1s on the FC10PA-treated Co substrate by the rinse time of 0, 2, 10, 30, 60, and 120 s. (b) The plot of water contact angles on the FC10PA-treated Co substrate by the rinse time of 0, 2, 10, 30, 60, and 120 s.

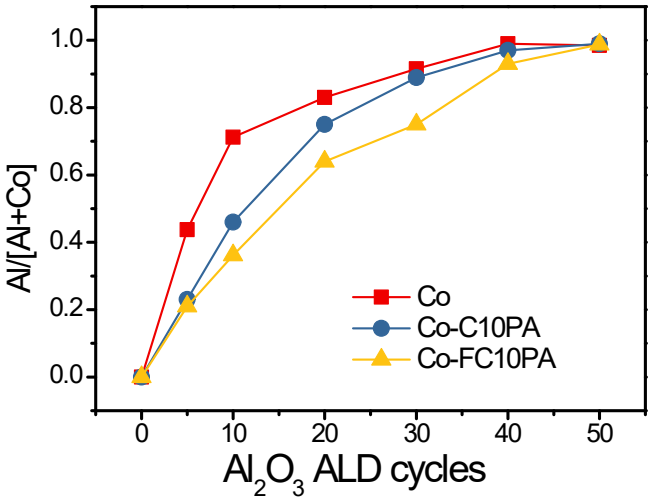

Figure S5. XPS composition analysis on the surfaces of Co, Co-C10PA, and Co-FC10PA after different cycles of Al_2O_3 ALD using O_3 as co-reactant.