

Electronic Supplementary Information

Electrically Charged Selectivity of Poly-*para*-xylylene Deposition

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Experimental Section

Materials

Conducting glasses with fluorine-doped SnO₂ (FTO; NSG America Inc., USA) were commercially obtained and cleaned with deionized water and isopropyl alcohol before use. Metal substrates were fabricated from a 4-inch silicon wafer with a 3500-Å insulating layer of silicon nitride followed by a 1000-Å metal layer. The metals of Ti, Cu, Ag, Au, and Zn were prepared using a thermal evaporator (Kao Duen Technology Co., Taiwan). All metal pellets were purchased from Goldeninent Inc. (Taiwan). The patterned Al samples were fabricated with a thermal evaporator (Kao Duen Technology Co., Taiwan) on glass substrates. Photomasks with selected corresponding patterns were designed using AutoCad and were printed on a high-resolution emulsion transparency (TKK, Taiwan) with a spatial resolution of 10,000 dpi. Photomasks were used during the photolithography process to generate the Al patterns.

*CVD polymerization to deposit poly-*para*-xylylenes*

The syntheses of the substituted-[2,2]paracyclophanes were conducted by following previously reported data for 4-formyl [2,2]paracyclophane,[1] 4-trifluoroacetyl [2,2]-paracyclophane,[2] and 4-aminomethyl [2,2]paracyclophane.[3] A CVD polymerization process was performed using a self-designed CVD that comprises a sublimation zone, pyrolysis zone, and deposition chamber. The starting material of the substituted-[2,2]paracyclophanes was first sublimated in a vacuum in the sublimation zone at a temperature of approximately 90-125 °C, depending on the substituted-[2,2]paracyclophane that was used. The sublimated species were then transferred in a stream of argon carrier gas (30 sccm) to the pyrolysis zone, in which the temperature was adjusted to 670-750 °C, also depending on the starting materials selected. Following pyrolysis, the resulting quinodimethanes (diradical monomers) were transferred to the deposition chamber, where polymerization occurred on a rotating holder maintained at 20 °C to ensure the uniform deposition of the polymer and the wall temperature was adjusted to 100 °C to prevent any residual deposition on the chamber walls. A pressure of 75 mTorr was maintained during the entire CVD polymerization process. Depending on the specific study of interest, deposition rates were controlled at 0.3 Å/s - 20 Å/s, as monitored by an in situ quartz crystal microbalance (QCM) system. Electrically charged substrates were prepared by providing DC currents to the substrates using a GPS 3030D power supply (Good Will Instrument, Taiwan). Silver wires were used for the connection between the substrate and the power supply, and an electroconductive paste Dotite XA-3499 (Fujikura Kasei, Japan) was used to secure the junctions.

Surface characterizations

Infrared reflection absorption spectroscopy (IRRAS) spectra were recorded using a 100 FT-IR spectrometer (PerkinElmer, USA) equipped with an advanced grazing angle specular reflectance

accessory (AGA, PIKE Technologies, USA) and a liquid nitrogen-cooled MCT detector. The samples were mounted in a nitrogen-purged chamber, and the recorded spectra were corrected for any residual baseline drift. The elemental analysis was confirmed by energy dispersive X-ray spectroscopy (EDS), which was performed on a scanning electron microscope (Nova™ NanoSEM 230, FEI, USA). The EDS was operated at a primary energy of 5 keV with a pressure of 5×10^{-6} Torr in the specimen chamber. The film thickness analysis was recorded using a stylus-based surface profiler (Dektak 6M, Veeco, USA).

Immobilization

The immobilization of the Alexa Fluor® 568-conjugated hydrazide (Thermo Fisher Scientific Inc., USA) was conducted using a 5 mM concentration on the patterned PPX-aldehyde samples for 1 hr. A washing procedure was performed after the reaction using phosphate-buffered saline (PBS, pH = 7.4; containing Tween 20, Sigma-Aldrich, USA) three times and PBS (pH=7.4, Sigma-Aldrich, USA) one time and, finally, rinsing with deionized water. The resulting samples were then examined by fluorescence microscopy (TE-2000U, Nikon, Japan).

Sticking Coefficient

The calculation of the value of S for the deposition of poly-*para*-xylylenes was performed following the reported model and equations.[4] This model is based on the fact that the maximum deposition rate (R_d) for any CVD process can be given by:

$$R_d = \frac{SPN_a V_m (6 \times 10^{11})}{(2\pi m_r RT_0)^{0.5}},$$

where the quantity $\frac{PN_aV_m(6 \times 10^{11})}{(2\pi m_r RT_0)^{0.5}}$ is the flux of the reactant to the substrate surface in collisions per square metre per second, P is the pressure in pascals, N_a is Avogadro's number, m_r is the molecular mass in kilograms per mole, R is the Rydberg gas constant, T_0 is the temperature of the reactant gas in kelvin, and V_m is the volume of one molecule in cubic meters.

Thus, the expression for S is

$$S = \frac{R_d \times (2\pi m_r RT_0)^{0.5}}{PN_aV_m(6 \times 10^{11})}$$

The value of S was calculated for polydichloro-*para*-xylylene (PPX-C) on three surfaces that represented three different cases: (i) a silicon (Si) surface represented an uncharged, non-inhibitory surface; (ii) an iron (Fe) surface was used as an inhibitory surface (it was previously reported to be the best inhibitor) and (iii) a charged aluminium (Al) surface with an applied charge density of 0.05 C/cm² was used to represent charged inhibition. Deposition parameters including temperature = 300 K, system pressure = 15 Pa and deposition rate = 2000 Å/min for Si, 300 Å/min for Fe and 30 Å/min for charged Al were used for the calculation to obtain values of $S = 1.29 \times 10^{-4}$ for Si, $S = 1.94 \times 10^{-5}$ for Fe and $S = 1.94 \times 10^{-6}$ for charged Al.

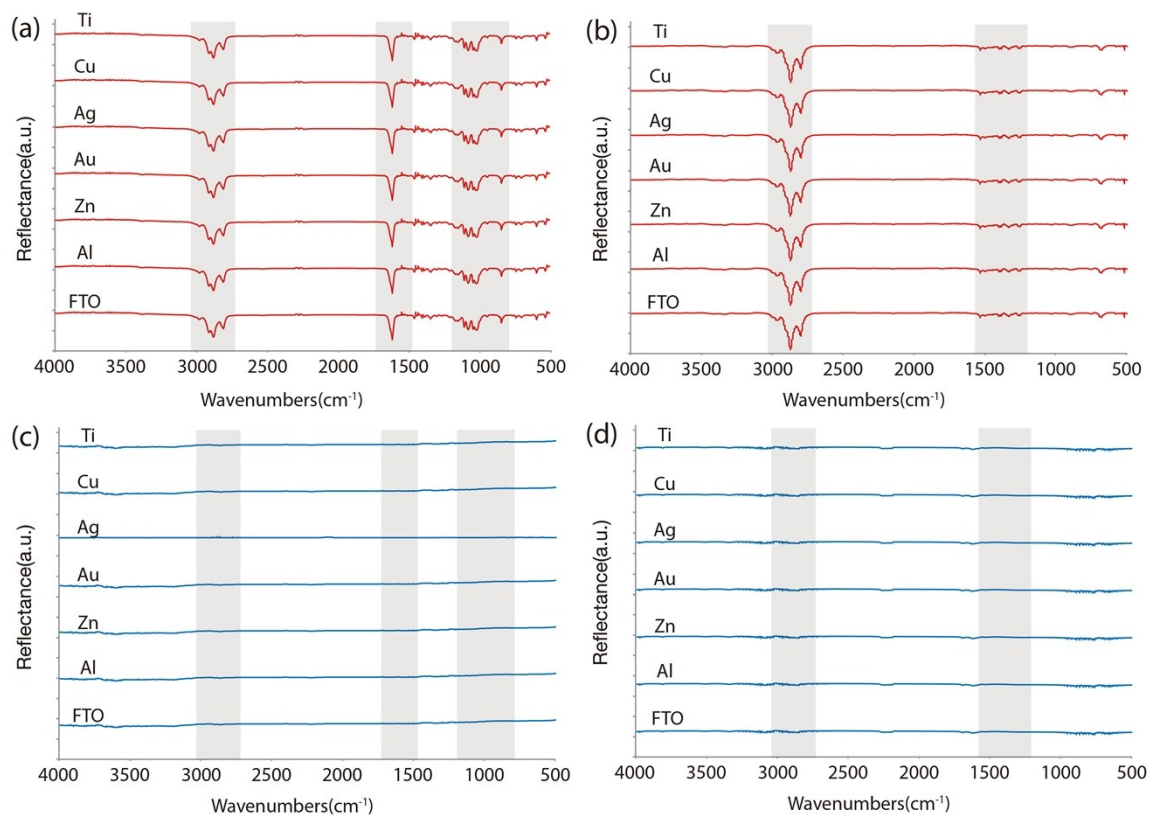


Figure S1. IRRAS characterizations of selectively deposited PPX-TFA or PPX-amine on different conducting substrates (Ti, Cu, Ag, Au, Zn, Al, and FTO) with deposition rate of 30 Å/s. The deposition of (a) PPX-TFA and (b) PPX-amine showed no inhibition on the surfaces before applying charges to the substrates. By contrast, the deposition of these two polymers of (c) PPX-TFA and (d) PPX-amine were inhibited on all surfaces after applying charges to the substrates. Film thickness of approximately 150 nm PPX-TFA or PPX-amine was measured for non-inhibitory surfaces.

References

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