On-Demand Laser-Induced Polymerization of Evaporated C_{60} Thin Films

Direct-Write Micropatterning and Thickness-Dependent Kinetics

PI: Dr. Humberto R. Gutiérrez

James Watt, Yasinthara Wadumethsri, Humberto R. Gutiérrez · Department of Physics, University of South Florida

Gutiérrez Lab, University of South Florida

Abstract

Evaporated C_{60} is used in device layers only a few nanometers thick, yet its photochemistry in this ultrathin regime is largely uncharacterized. We present a resist-free workflow for **on-demand, laser-induced polymerization** of evaporated C_{60} films on Si/SiO_2. Films of **2, 3, 5 and 10 nm** were grown under QCM control, verified by AFM, and shown to be **Raman-pristine**. A focused **532 nm** beam drives the [2+2] cycloaddition signature, the $A_g(2)$ redshift from **1469 to 1460 cm⁻¹**, writing polymerized **spots, lines and rectangles** verified by Raman maps. The $A_g(2)$ intensity decays as a **single exponential**, and the relative timescale τ(d)/τ(2 nm) **falls monotonically to 0.50 at 10 nm**, making film thickness a kinetic control variable in the ultrathin limit.

Introduction

Solid C_{60} is a molecular crystal of fullerene cages held together only by van der Waals forces. Under light, 6:6 double bonds on neighboring cages join through a **[2+2] cycloaddition**, forming covalent **poly-C_{60}**[1,2].

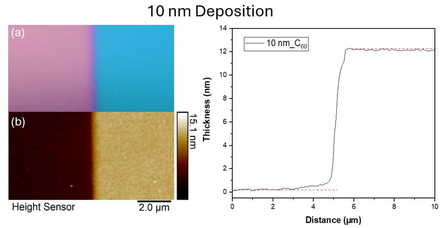
The clearest Raman fingerprint is the **$A_g(2)$ pentagonal-pinch mode** shifting from **~1469 to ~1460 cm⁻¹**, which can be mapped directly.

Few-nm evaporated C_{60} is used as the electron-transport layer in perovskite solar cells[3], yet ultrathin growth, direct-write polymerization and thickness-resolved kinetics had not been combined.

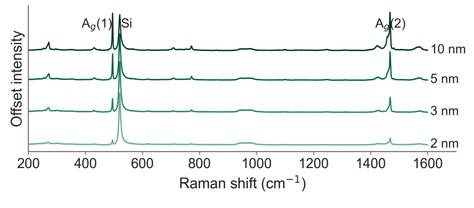
Methods

- **Growth:** thermal evaporation at 5.5 Å/s under closed-loop QCM control onto Si/SiO_2; a contact mask leaves a step edge for AFM thickness checks.
- **Raman:** HORIBA LabRAM HR Evolution, 532 nm, 1800 gr/mm, ×50 LWD objective (~6 µm spot), 3×10^{-4} W/µm².
- **Writing:** spots (120 mW, 40 s), lines (overlapping spots), rectangles (DuoScan raster).
- **Kinetics:** 10 s spectra over 600 s of irradiation; $A_g(2)$ intensity fit to $I(t) = A_0 e^{-t/\tau} + i_0$.

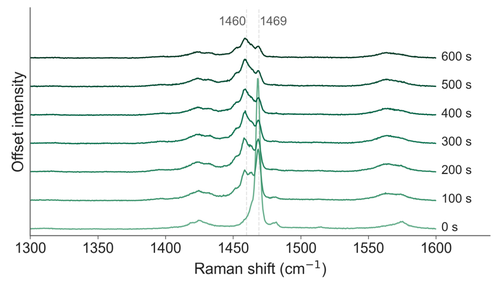
Films & Local Polymerization



10 nm film: (a) optical and (b) AFM across the mask edge. Measured plateaus are 3 / 4 / 6 / 12 nm for nominal 2 / 3 / 5 / 10 nm.



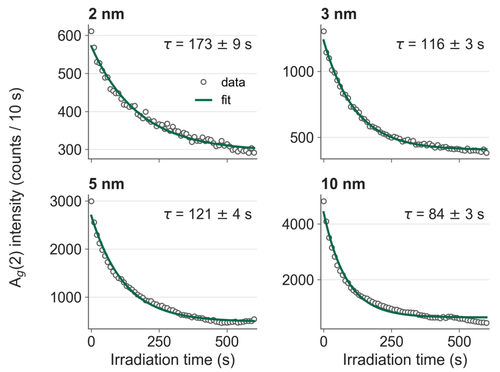
As-deposited films are Raman-pristine: all C_{60} modes, no 1460 cm⁻¹ component. The 520 cm⁻¹ line is the Si substrate.



Continuous 532 nm irradiation of the 10 nm film: $A_g(2)$ moves from 1469 to 1460 cm⁻¹ and a ~1425 cm⁻¹ satellite grows in. Four cosmic-ray pixels removed.

Polymerized fingerprint: the 1460 cm⁻¹ $A_g(2)$ line, a ~1425 cm⁻¹ satellite, and an **$H_g(8)$-region shift from ~1575 to ~1566 cm⁻¹**. $H_g(8)$ changes are known[4]; to our knowledge this is the first time-resolved view in few-nm films.

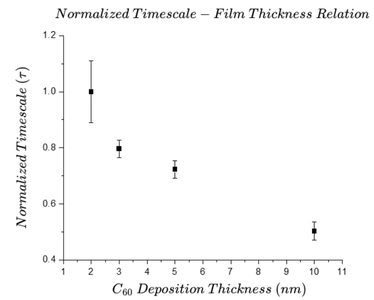
Thickness-Dependent Kinetics



Representative $A_g(2)$ decays with single-exponential fits; no second timescale appears at any thickness.

τ(10 nm) / τ(2 nm) ≈ 0.50

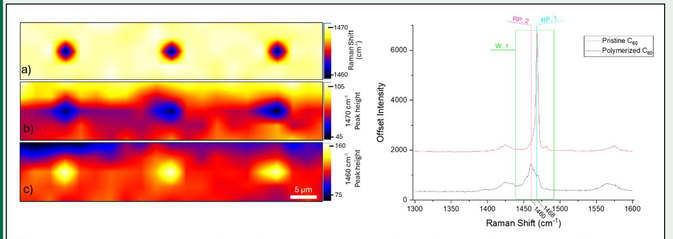
thicker films polymerize twice as fast



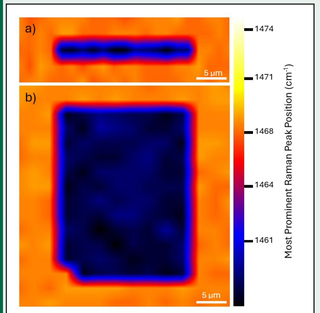
Median τ(d)/τ(2 nm) over three measurement epochs: 1.00 / 0.79 / 0.72 / 0.50. Absolute τ drifts with lab temperature; the ratio does not.

Why does τ shrink? Every film is far thinner than the optical penetration depth, so τ should not depend on thickness. Something **slows the reaction near the substrate**: Si as a heat/exciton sink, the optical standing wave of the stack, or substrate-templated disorder.

Direct-Write Patterning



Three polymerized dots (10 nm film): (a) peak position, (b) 1470 and (c) 1460 cm⁻¹ intensity. Right: pristine vs. polymerized spectra with the analysis window W.1.



(a) Line, (b) rectangle.

Spots match the ~6 µm laser spot.

Lines: overlapping spots write a ~20 µm line.

Areas: rastering writes a ~25 × 30 µm rectangle.

Patterns sit within ±2 cm⁻¹ of 1460; the film around them stays at ~1470 cm⁻¹.

Conclusion

- Evaporated 2–10 nm films are **AFM-uniform and Raman-pristine**.
- A focused 532 nm beam **writes poly-C_{60} on demand** as spots, lines and areas; feature size is set by the laser spot.
- Polymerization is **single-exponential**, and **thickness is a kinetic variable**: τ(10 nm)/τ(2 nm) ≈ 0.50.
- **Next:** transparent substrates, varied SiO_2 thickness and N_2 purge to separate substrate, optical and oxygen effects.

Thanks & References

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1. Rao et al., *Science* 259, 955 (1993)
2. Eklund et al., *Thin Solid Films* 257, 185 (1995)
3. Said et al., *Nat. Commun.* 15 (2024)
4. Burger, Winter & Kuzmany, *Z. Phys. B* 101, 227 (1996)