Hot on the trail of ultrathin films of patternable polyethylene

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Low-density polyethylene (LDPE) is a ubiquitous plastic with a wide range of physical properties that depend on molecular weight and intramolecular branching, among other characteristics. In the solid phase, LDPE and other semicrystalline thermoplastics tend to self-assemble into spherulites, which are irregular microscale domains with striations radiating from central nucleation sites. For this reason, forming ultrathin films of LDPE that are sufficiently uniform for nanoscale patterning is an open challenge.[1, 2, 3] Meeting this challenge would create new opportunities for nanofabrication, with diverse applications ranging from forming nanoplastic standards[4] for studying environmental pollution to hosting quantum emitters in polymeric matrices for making photonic devices.[5]

Accepting this challenge, we introduce a systematic study of hot spin coating of LDPE on silicon substrates. A previous study of hot spin coating of other plastics[2] informs preliminary tests of our process. Optical microscopy and profilometry allow inspection of test films, which manifest spherulites (Figure 1a-c) and show variation of film thickness (Figure 1d). Ellipsometry provides an estimate of mean film thickness of a few hundred nanometers, trading lateral resolution for temporal throughput to facilitate screening. We hypothesize that spin temperature and spin speed are only two of many factors that are important to control film thickness and uniformity. Accordingly, we design a two-level fractional factorial screening experiment to study the effects of six factors of the hot spin coating process (Table 1). The screening experiment consists of eight combinations of factors, two of which will serve as replicates, for a total of ten trials.

Beyond this initial study of film structure, we begin to pattern LDPE films, building on our previous demonstration of the nanoplastic array in phenolic resin at EIPBN 2022.[3] We deposit hydrogen silsesquioxane (HSQ) resist on an ultrathin film of LDPE, pattern the resist by electron-beam lithography, and etch the LDPE with an oxygen plasma to form an array of LDPE nanopillars (Figure 1d-f). Atomic force micrographs show both nanopillars and defects due to spherulite boundaries, which require further study. Nonetheless, our study promises new capability for nanofabrication of an important plastic material and is extensible to other plastic materials to study plastic pollution and make plastic devices.

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[1] E. Lock, *et al.*, *Internal Report*, *Defense Technical Information Center* (2008).
[2] O. Mellbring, *et al.*, *Macromolecules* (2001).
[3] A. C. Wirtz, *et al.*, *Chemical Physics Letters* (2006).
[4] A. C. Madison, *et al.*, *EIPBN* (2022).
[5] D. Rattenbacher, *et al.*, *arXiv* (2023).

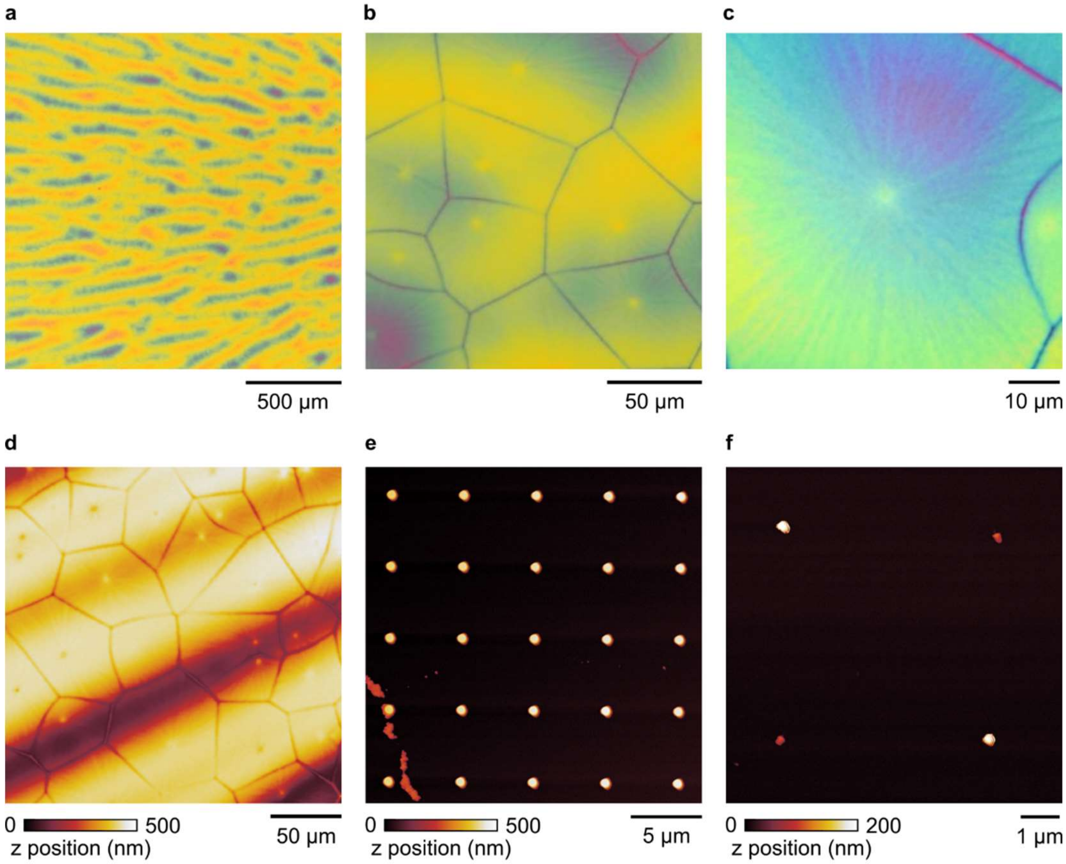

Figure 1. Ultrathin films and nanopillar arrays of LDPE. (**a**-**c**) Optical micrographs showing an LDPE film resulting from preliminary test parameters (Table 1). Undulating thickness is apparent in (a) and (b) as structural colors, with yellow regions indicating ridges and blue regions indicating valleys of the LDPE film. Spherulite microstructures are apparent as (b) domains with irregular boundaries containing (c) a nucleation center and radial striations. (**d**) Interferometric optical micrograph showing thickness undulation and spherulites. (**e-f**) Atomic force micrographs showing arrays of LDPE nanopillars with nominal diameters of (e) 500 nm and (f) 100 nm, a nominal pitch of 5 µm, and fabrication defects due to film nonuniformity.

Table 1. A two-level fractional factorial screening experiment. (Gray) Preliminary test parameters and (white) screening parameters to study the hot spin-coating process.

Solvent	Melt flow rate[a] (g/10 min)	Mass fraction (%)	Spin temperature (°C)	Spin speed (RPM)	Annealing time[b] (min)
Decalin	25	2	80 to 120	3000	–
TCB[c]	5.1	1	160	3000	5
TCB	25	1	120	3000	60
Decalin	5.1	2	120	3000	60
Decalin	25	1	160	5000	60
TCB	25	2	120	5000	5
Decalin	5.1	1	120	5000	5
Decalin	25	2	160	3000	5
TCB	5.1	2	160	5000	60

[a] Different melt flow rates correspond to different LDPE materials with different molecular weights and branching structures.
[b] The annealing temperature for each process is 100 °C.
[c] We abbreviate 1,2,4-trichlorobenzene as TCB.

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