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NOTE

Probe-Based Nanolithography: Self-Amplified Depolymerization Media for Dry Lithography

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Patterning of resists at the submicrometer scale and the corresponding transfer of patterns onto various underlying substrates is a widespread, versatile method for device production and became the driving technology for micro- and nanofabrication. However, optical lithography is approaching its scaling limits and potential successors are few.[1] One of them, nanoimprint lithography,[2] requires to-scale fabrication of masters and hence does not solve the fundamental lithographic problem. Currently the foremost technology at hand to produce such masters is high-resolution electron beam lithography.

Scanning probe technologies are intrinsically capable of addressing real space with atomic resolution and have been used to fabricate nanoscale structures and devices with exceptional quality.[3] Current approaches are designed for specific systems, for example, the use of local anodic oxidation to define barriers for a 2D electron gas in GaAs systems.[4] A more universal patterning of resists for lithography-style pattern transfer has been demonstrated with high resolution, however, approaches based on electron currents or mechanical removal of material require conductive substrates or involve high mechanical loads on the tip resulting in tip lifetime challenges, respectively.[5] Demonstrations of heated probes on decomposable polymers have been hindered by debris and pile-up.[6] To overcome these problems we synthesize a metastable material tailored for heat-assisted patterning by probes that enables high resolution and large area patterning with considerable throughput and low mechanical stress to the probe.

Our preferred strategy is to use a polymer medium that fully volatilizes on heating.[7] This enables a solvent-free, that is, dry patterning approach without the need to expose the substrate and the resist to solvents, thus avoiding swelling induced distortions and cross-contamination of the sample. Here we present a polymeric material that has a low ceiling temperature where one degradation event is amplified via an unzipping of the entire chain. A similar dry-develop strategy was demonstrated in the early days of microlithography by Wilson, Ito, and Frechet and showed that polyaldehydes are such a class of low ceiling temperature materials with a tunable degradation temperature that represent one of the early examples of chemical amplification in lithography.[8] Despite many reports on the polymerization of aliphatic aldehydes, only few have focused on aromatic aldehydes, for example, benzylaldehydes, since these monomers show limited reactivity toward nucleophiles.[9] Enhance polymerization control was expected since aliphatic dialdehydes polymerize spontaneously.[9b,c] Moreover, phthalaldehyde was expected to polymerize better than benzaldehyde due to the resonance interaction between the two adjacent formyl groups regardless possible steric and direct field effects.[9d] The polymerization of phthalaldehyde monomer has been accomplished using γ-ray irradiation,[10] anionic,[11] cationic,[10,12] and coordinative polymerization processes.[13,14] It should be pointed out that none of these synthetic techniques provides predictable molecular weight, narrow polydispersities, or end-group fidelity. Our efforts have focused on an organocatalytic approach to the polymerization of phthalaldehyde using dimeric 1-*tert*-butyl-2,2,4,4,4-pentakis-(dimethylamino)-2Λ^5,4Λ^5-catenadi(phosphazene) (P$_2$-*t*-Bu) phosphazene base as an anionic catalyst in the presence of an alcohol initiator (Scheme 1).[15]

Scheme 1. Anionic Cyclopolymerization of Phthalaldehyde

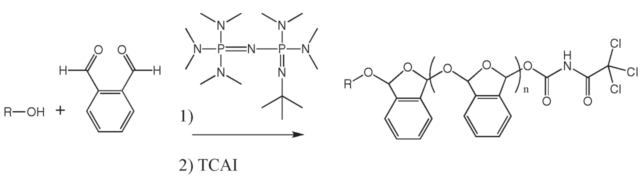

Table 1. Molecular Characterizations of Polyphthalaldehydes Obtained after 1 h in THF at −78°C Using Alcohol (I) as Initiator and P$_2$-*t*-Bu (P$_2$) as Catalyst

entry	$[M]_0/[I]_0/[P_2]_0$	$[M]_0$ (mol/L)	conv (%)[b]	Mn[c] (g/mol)	PDI[c]
1	200/1/1	0.7	73	10180	1.83
2	200/1/1	0.15	64	12070	1.67
3	200/1/0.05	0.7	90	36080	1.14
4	400/1/0.05	0.7	92	44400	1.12
5[a]	600/1/0.05	0.7	93	153640	1.25

[a] Initiator = 1-pyrenebutanol. [b] Determined by ^{1}H NMR spectroscopy. [c] Molecular weight and polydispersity index determined by gel permeation chromatography.

The polymerization of phthalaldehyde was carried out in THF (−78 °C) for 1 h using benzyl alcohol or 1-pyrene butanol as initiator for two different monomer concentrations and different monomer-to-initiator-to-catalyst-ratios (Table 1). Polymerizations were quenched with trichloroacetyl isocyanate (TCAI), known to react rapidly and quantitatively with hydroxyl chain ends preventing depolymerization as the reaction returns to room temperature.

Clearly, lower catalyst and solution concentrations provide narrowly dispersed products, high conversions, and predictable molecular weights. A comparison between the polyphthalaldehyde measured molecular weights (M_nGPC) and those calculated

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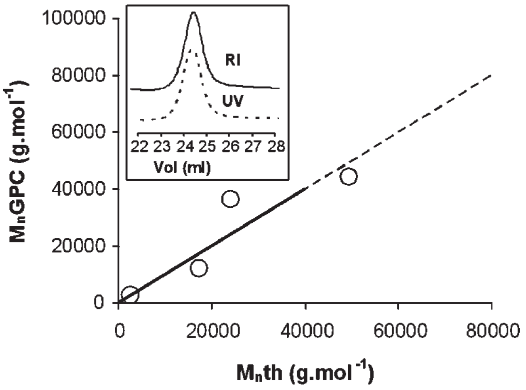

Figure 1. Graph showing the relationship of the molecular weight calculated theoretically (M_nth) and by GPC (M_nGPC in reference to polystyrene calibration). Dashed line serves as reference (slope = 1). Inset: GPC traces from UV and refractive index detectors showing homogeneous distribution of pyrenebutanol initiator.

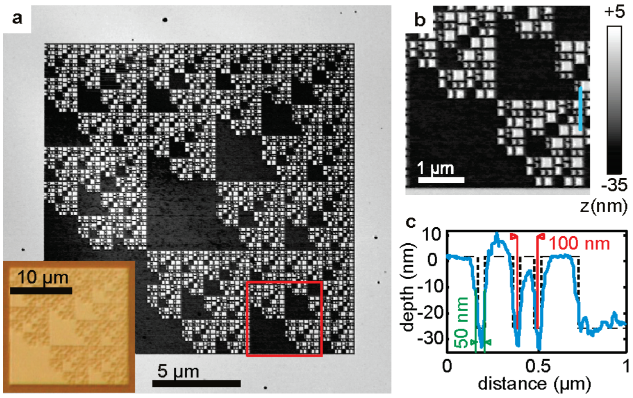

Figure 2. Large area patterning application. (a) AFM image of a patterned 18 × 18 μm area. Inset bottom left: optical image; (b) close-up view of the area marked with a red box in panel a; (c) actual line profile (blue line) taken along blue cross section line in panel b. Black dashed line represents idealized programmed line profile.

(M_nth = 134.13 × ($[M]_0/[I]_0$ × Conv (%)) (Figure 1) shows a linear fit to molecular weights up to 45 000 g·mol^{-1}, consistent with a living polymerization, Figure 1.

The GPC chromatograms show a Gaussian distribution of molecular weights for each sample with PDI varying from 1.12 to 1.25, for the optimized conditions. The crude product of the 1-pyrenebutanol-initiated polymerization (Table 1, entry 5) shows the pyrene is homogeneously distributed throughout the sample (UV detector) and overlays with the data from the refractive index detector (Figure 1, inset). These data indicate a quantitative initiation of polymerization from the initiating alcohol allowing predictable molecular weights from the monomer-to-alcohol ratio and end-group fidelity (also see Supporting Information). The preferred formation of the *cis*-microstructure (~60 mol %) (Figure 2S in Supporting Information) indicates an anionic polymerization process,[13] supporting previous reports that P_2-*t*-Bu activates the initiating alcohol as the polymer forming reaction. The decomposition temperature onset is ~150 °C and independent of molecular weight.

To demonstrate the properties of the material as a lithographic medium, a 50 nm thin film of the polymer was spun-cast on a silicon substrate and patterned using heated probes. The probes are electrostatically actuated and heated with an integrated heater in immediate contact to the tip.[16] In the provided example, a "pixel" was written by simultaneously applying a force and a heat pulse to the cantilever for 20 μs. Because of the short interaction time the temperature of the tip needs to exceed the ceiling temperature of the polymer considerably. In our case we used 700 °C tip-heater temperature, corresponding to elevating the polymer temperature[17] to 300−400 °C.

A fractal pattern[18] has been chosen to demonstrate uniform and high fidelity patterning over a large area. Figure 2a shows a topographic image and an optical micrograph (inset) of the patterned 18 × 18 μm^2 area using a pixel size of 20 nm. The time between pixels was 60 μs, resulting in a total patterning time of ~3 min. Figures 2b and 2c demonstrate the feature quality on a zoomed area of Figure 2a (red square) through which a cross-section has been drawn as shown in Figure 2c. A digital outline of the programmed input used to create the patterned surface is shown as black dashed line for comparison. The lowest pitch between written lines in the image is 100 nm. The width of the trenches between the raised features is approximately 50 nm, corresponding well to the programmed trench width of two pixels. No degradation in feature quality or patterning depth was observed over the patterned area.

Clearly a large volume of resist material has been removed from the surface and no pile-up or redeposition of material can be detected. The low applied force of 20 ± 10 nN is sufficient to make conformal contact with the polymer surface and to penetrate into the material. The patterning depth of about 25 nm amounts to half the film thickness and is controlled by the applied force. Patterning is uniform, akin to a well-controlled and reproducible single patterning event. The clean removal of material at low applied forces indicates an effective triggering of the unzipping process of the polymer due to the contact with the hot tip. The resulting monomer constituents are effectively removed from the substrate, that is, sufficiently heated by the tip to be evaporated.

In conclusion, we have demonstrated a low temperature, organocatalytic method to create polyphthalaldehydes of predictable molecular weights and narrow polydispersities that show themselves to be ideal candidates as a lithographic medium. Lithographic patterning is demonstrated in a debris-free polymer decomposition reaction triggered by the proximity of a heated probe. The process has been exploited to pattern large areas of a polymeric film with high throughput and resolution, demonstrating a first step to a low-cost, tabletop, and nanoscale patterning method.

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Supporting Information Available: Experimental procedures and extra analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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