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Exploration of thermolithography for micro- and nanomanufacturing

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Lithography is a critical enabling technology for manufacturing micro- and nanoscale devices and structures. The present work explores alternative lithography techniques that pattern photoresist layers through selective thermochemical cross-linking. Microfabricated thin-film heaters are used as precisely defined heat sources to determine the thermal transport properties of photoresist layers and study the kinetics of cross-linking reactions. The present work identifies heating temperature, heating duration, and UV exposure dose as independent control parameters in thermolithography and demonstrates its potential for three-dimensional micro- and nanomanufacturing. © 2006 American Institute of Physics. [DOI: [10.1063/1.2187948](https://doi.org/10.1063/1.2187948)]

The ability to create precisely defined and densely populated micro- and nanoscale features is essential for manufacturing a wide variety of novel devices and structures. For example, photonic crystals consist of arrays of micro- or nanoscale features and provide unique ability to control propagation and other behavior of electromagnetic waves.¹ In patterned magnetic data storage media, lithographically defined data bits help delay the onset of the superparamagnetic limit.² Nanostructured surfaces with extreme wetting characteristics³ are also promising for microfluidic and protective coating applications.

Various alternative lithography techniques, such as softlithography,^{4,5} have been proposed to enable low-cost high-throughput manufacturing of these micro- and nanoscale structures and devices. In fact, nanoimprint lithography⁶ has received much attention as a potential next generation lithography technique by the semiconductor industry. Each original template necessary for nanoimprint lithography, however, must still be made using other expensive or slow nanolithography techniques, such as deep UV and e-beam lithography. This has impeded widespread adoption of nanoimprint lithography.

We are exploring a broad class of alternative lithography techniques, termed thermolithography, which utilize controlled and localized heating to enable economic fabrication of precisely defined micro- and nanoscale patterns. Localized heating can be induced, for example, by focusing a laser beam on the surface of a transparent substrate with a high index of refraction. This approach is appealing since sophisticated control hardware and algorithms are already being developed to position a focused laser beam with submicrometer precision on compact disks and other data storage media.

Thermolithography techniques may also offer other intriguing possibilities. Since heat conduction in highly disordered media is expected to be a diffusive phenomenon even at nanoscales, it may not suffer from backscattering or near field effects that complicate pattern transfer in e-beam or near-field lithography. Heat diffusion is also a slow process compared with the propagation of electromagnetic waves or

energetic material beams. For example, in one nanosecond, light travels approximately 0.3 m across common solid or liquid media. The corresponding heat diffusion length in disordered polymers is much shorter, only ~ 10 nm. This attribute potentially offers an intriguing leverage in developing novel three-dimensional or on-demand micro- and nanofabrication schemes.

In this letter, we present our recent progress in developing one type of thermolithography scheme that exploits a thermochemical cross-linking of photoresist layers through so-called image reversal. We measure the thermal conductivity of photoresist layers and study the kinetics of cross-linking reactions using microfabricated thin-film heaters as localized heat sources. The present work provides important quantitative data to help guide further development of thermolithography.

Image reversal⁷ refers to photothermochemical processes that reverse the tone of a photoresist layer. In common positive photoresists, UV exposure generates special chemical compounds that make the exposed region soluble in a developer solution. When subjected to appropriate post exposure bake (PEB), however, certain types of photoactivated compounds may instead catalyze cross-linking reactions. Because the cross-linked region is insoluble in a developer solution and insensitive to further UV exposure, the tone of the photoresist becomes effectively reversed from positive to negative.

In the present thermolithography scheme, an image reversal photoresist layer is first flood exposed to UV illumination. Select areas of the resist layer are then heated above a threshold temperature to locally induce cross-linking. The unheated area is then removed by immersing the sample in a developer solution. A similar process was demonstrated previously using a focused laser beam⁸ or the tip of a specially designed AFM⁹ as a localized heat source. These heat sources, however, are not well suited for a detailed quantitative study. The previous studies, for example, could not measure temperature rise in the photoresist layers nor did they report any systematic data on the kinetics of cross-linking reactions.

We determine the thermal conductivity and heat capacity of commercially available image reversal photoresist, AZ 5214E (Clariant Corp.), using the electrical resistance thermometry method.¹⁰ Details of the measurements will be re-

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FIG. 1. Predicted and measured temperature rise in a microheater subjected to sinusoidal currents of different frequencies. The heater is formed on a 1.9- μm -thick AZ 5214E photoresist layer. The frequency dependence of the in-phase and out-of-phase component is analogous to that of the electrical impedance of a resistor-capacitor circuit. The symbols correspond to the data and the lines correspond to the simulation results obtained using a thermal conductivity of 0.19 W/m K and three different values of heat capacity, 1.4, 1.6, 1.8 MJ/m³ K, for the photoresist layer.

ported elsewhere.¹¹ Briefly, photoresist layers of different thicknesses are spin coated on silicon substrates, exposed to UV illumination, and subjected to post-exposure bake to produce fully cross-linked samples. An aluminum film is subsequently deposited and patterned into four-point probe structures, which serve as both electrical resistance heaters and thermometers. By analyzing the temperature rise in these heaters using numerical solutions to the heat conduction equation, as illustrated in Fig. 1, we can extract the thermal transport properties of the layers. For the numerical simulation results shown in Fig. 1, the bottom surface of the substrate is maintained at room temperature and heat loss from the top surface of the sample is assumed to be negligible.

The thermal conductivity and heat capacity obtained for AZ5214E are comparable to those of PMMA. Measurements performed at temperatures up to 125 °C do not reveal any significant temperature dependence. The present thermal conductivity is much larger than the *effective* thermal conductivity reported previously¹² for another commercially available photoresist (Shipley SPR-700) based on a similar novolac resin. We believe that the discrepancy is due to the significant thermal boundary resistance between the metal heater and photoresist layer of the previous study, which was not corrected for.

Our recent work used freestanding membranes to measure the in-plane thermal conductivity of nominally identical photoresist layers before and after UV exposure as well as before and after post-exposure bake.¹¹ The polymer thermal conductivity was found to change by only ~5%. This rather small change may be explained by the fact that the mean free

FIG. 2. Schematic illustration of the process flow used to study the image reversal based thermolithography scheme.

path of dominant heat carriers in highly disordered polymers is so small that additional covalent bonds formed through cross-linking reactions do not lead to significant increase in heat conduction. We assume that the thermal conductivity of the photoresist layers remains constant during thermolithography processes.

Next, we investigate the effects of post-exposure bake temperature and duration on cross-linking reactions using the process flow schematically illustrated in Fig. 2. A micropatterned metal stripe serves once again as both a heater and thermometer. A thick (~1 μm) amorphous SiO_x underlayer, whose thermal conductivity is two orders of magnitude smaller than that of the silicon substrate, helps reduce the amplitude of heating currents required and the effective heater thermal time constant. The heater thermal time constant is determined primarily by heat diffusion time across the SiO_x layer, which is estimated to be of the order of 1 μs .¹⁰ This allows us to study the kinetics of cross-linking reactions on time scales inaccessible to conventional macro-scale calorimeters.

An approximately 1.5- μm -thick photoresist layer is spin coated and subsequently flood exposed to UV illumination to globally generate photoactivated compounds. Each heater is then subjected to a current pulse of a different magnitude and duration. The samples are immersed in a developer solution (AZ Developer, Clariant Co.) to remove regions that are not cross linked.

Figures 3(a)–3(c) are the cross-sectional scanning electron micrograph (SEM) images of photoresist patterns obtained using heaters of widths approximately 1.4 μm and average heater temperatures of 100, 120, and 140 °C, respectively. The heating duration is fixed at 120 s, which is much longer than heat diffusion time across both the silicon dioxide and photoresist layers.

Overlaid on each SEM image are the isotherms predicted from the steady-state heat conduction equation using the experimentally determined thermal conductivity. We can determine the threshold PEB temperature for a given heating duration and heater temperature by identifying an isotherm that matches the corresponding resist profile. Figure 4 shows the threshold temperature we obtain using various average heater

FIG. 3. Cross-sectional SEM images of the photoresist patterns obtained using thermolithography. A high dose of UV exposure (1000 mJ/cm²) is used for (a)–(c) and a lower dose for (d). The average heater temperatures are (a) 100, (b) 120, and (c), (d) 140 °C, respectively.

FIG. 4. Experimentally determined threshold PEB temperature of the AZ 5214E photoresist as a function of heating duration.

temperatures, ranging from 100 to 180 °C, and various heater widths, ranging from 0.6 to 6 μm . The threshold temperature decreases rapidly with heating duration, but, within experimental uncertainties, it does not vary with the heater temperature or width. This observation suggests that one can tailor resist profiles using heating temperature and duration as two independent control variables.

The present data provide some guidance in estimating a potential throughput of the image reversal based thermolithography scheme. A photoresist layer typically serves as an etch mask and must subsequently be removed from the substrate without leaving behind residues. Thermal reflow or degradation caused by excessive temperature rise may therefore be problematic. The upper limit will depend on details of subsequent processes, but we recognize that photoresist hard bake temperatures do not usually exceed 200 °C. The corresponding minimum heating duration is estimated to be approximately 20 ms. Further studies may explore the use of different photoacids or thermally activated acid generators to reduce this value.

We can also tailor photoresist profiles by controlling the duration and shape of heating pulses. Figure 5(a) shows the AFM image of a semicircular photoresist pattern obtained using a heating pulse of duration 100 ms. The width of the pattern is approximately half that of the underlying heater

FIG. 5. AFM images of (a) the resist pattern produced using thermolithography and (b) the two-level silicone nanofluidic channel fabricated using the pattern in (a) as a template.

stripe. The occurrence of the peak temperature rise at the center of the heater stripe and the concave shape of the isotherms are believed to be responsible for the observed resist profile. Figure 5(b) shows the atomic force microscopy (AFM) image of an inverted T-shape silicone fluidic channel fabricated using the pattern shown in Fig. 5(a) as a template.

In the experiments discussed so far, a very high dose (1000 mJ/cm^2) of UV exposure is used so that a sufficient amount of photoactivated compounds is generated across the entire photoresist thickness. The concentration of these compounds, however, generally varies due to finite UV absorption. Such concentration gradients lead to corresponding variations in the threshold PEB temperature. As an extreme case, Fig. 4 includes the threshold temperature obtained from samples that are processed in an identical manner except that the UV exposure step is omitted. The threshold temperature is significantly increased, which is consistent with previous differential scanning calorimetry data.¹³

We can exploit this concentration dependence to further control resist profiles in thermolithography. One approach is to use a low dose of UV exposure such that the concentration of photoactivated compounds near the bottom is not sufficient to fully catalyze cross-linking reactions. An example is the T gate of nearly vertical walls shown in Fig. 3(d). One may also employ multiple layers of resists with different concentrations of photoacid generators to create more complex three-dimensional patterns.

In summary, we experimentally show that localized heating can be used to pattern polymer films in a deterministic manner using heating temperature, heating duration, and UV exposure dose as independent control variables. The thermal transport property and kinetics data as well as experimental approaches presented in the present work will facilitate systematic evaluation and development of thermolithography schemes.

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