Near-Field Optical Drilling of Sub-λ Pits in Thin Polymer Films

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ABSTRACT: Under UV illumination, polymer films can undergo chain scission, and contract. Using this effect, tightly-focused laser light is shown to develop runaway near-field concentration that drills sub-100 nm pits through a thin film. This sub-wavelength photolithography can be controlled in real time by monitoring laser scatter from the evolving holes, allowing systematic control of the void diameter. Our model shows how interference between the substrate and film together with near-field focusing by the evolving crevice directs this formation, and predicts minimum pit sizes in films of 100 nm thickness on gold substrates. The smallest features so far are 60 nm diameter pits using 447 nm light focused onto polystyrene through a ×100 objective (NA=0.8). Such arrays of pits can be easily used as masks for fabricating more complex nanostructures, such as plasmonic nanostructures and bio-microfluidic devices. This demonstration shows the potential for harnessing near-field feedback in optical direct-writing for nanofabrication.

Nanolithography technologies play a significant role in the fabrication of nanodevices for integrated electronic circuits, optics, and biochips. Traditional lithography techniques such as photolithography, soft lithography, beam pen lithography, and imprint lithography need expensive mask/master preparation, which have to be replaced every time the pattern is changed. Electron-beam lithography, although achieving high resolutions (<10 nm) for arbitrary patterns, is very expensive and operates in vacuum. Optical direct-write techniques (either single photon or two-photon) use dedicated photoresists however their resolution is still diffraction limited in most cases, even with advanced surface transfer techniques. While this limitation can be scaled by using extreme-ultraviolet wavelengths, this again requires vacuum processing. Photothermal effects can yield holes in polymer films but only larger than 100 nm. Recent developments of stimulated emission depletion microscopy in combination with two-photon lithography have yielded feature sizes of 120 nm or even smaller, but
specialized photoresists, photo-initiators, and photo-inhibitors are required together with an additional inhibition laser beam, adding cost and complexity.

Here, spontaneous near-field light concentration is found to produce sub-100 nm pits in polystyrene (PS) films. The intense optical field concentrated in the developing crevice accelerates the photo-degradation of the polymer film coated on gold. The size of the pits can be tuned below the diffraction limit, controllably from 60 nm to 1 μm by monitoring light scattering from the pits. This strongly contrasts with other near-field lithography techniques such as contact imaging, which use the near-field to transfer an already sub-wavelength pattern (produced by EUV or electron beam fabrication) into deeper layers. Although scanning near-field optical lithography can write sub-diffraction patterns, it suffers from slow scan speeds due to the need to move a mechanical near-field probe across the sample maintaining sub-wavelength proximity.

The optical drilling process starts with 100 nm PS films which are spin-coated onto Au substrates (Fig.1). A laser with wavelength of 447 nm is focused down onto the surface of the film through a ×100 dark field objective with NA=0.8 (Fig.1b inset, see supporting information (SI) Scheme S1 for details). The white-light scattering peak gradually increases and red-shifts as the irradiation proceeds, which indicates the growth of a pit (Fig.1a). The increasing scattering intensity extracted at 560 nm (red line Fig.1b) shows the evolving increase in pit size, allowing us to monitor the growth in real time. We define the effective diameter of the pits using the full-wave-half-maximum (FWHM) of the depth profile. The rapid degradation process via free radicals causes the pit to widen and deepen into a hole of size >200 nm in less than a second (SI-Fig.S1). More sensitive feedback is provided by the scattered laser light (blue line Fig.1b) which shows a sharp increase at the beginning of pit formation. This allows irradiation to be terminated within 100 ms of the pit initiating. We use a threshold scattering rate, $S_{th}$, to shut off the laser, with $S$ measured as the rate of increase in laser scattering (Fig.1b). Irradiating an array (pitch 1 μm) in PS films using $S_{th}=2$ forms pits of 65±5 nm in FWHM (Fig.1c, e), far below the diffraction limit (175 nm) of the laser (447nm, NA=0.8). Evaporating a 30 nm Au layer on top of this shrinks the size of the pits to 45±5nm (Fig.1d). The AFM profiles show pit depths of 45±5 nm with good consistency (Fig.1e), but this does not reflect the full depth due to the probe width. By controlling $S_{th}$, pits with different size and depth are obtained (Fig.1f), showing how the pit grows with light dosage. Initially a shallow depression with diameter matching the focused laser beam forms, followed by rapid deepening and narrowing into a cone shape (Fig.1f, SI-Fig.S2). Further growth gives wider and deeper holes. Clearly, some new mechanism beyond geometric optics has to be involved in the sharp narrowing of the pit size, because diffraction places absolute limits on the focal spot size.
This polymer photo-degradation process cannot be due to photothermal effects as estimates of the local temperature increase caused by irradiating the metallic film are less than 10°C for the powers applied (4-10 mW/μm²).21 Moreover, such optical drilling does not work on PMMA films unless much higher powers (>12 mW/μm²) are applied for longer irradiation times (30 s), and even then the pits produced are much shallower (SI-Fig.S3). This evidence of chemical selectivity suggests that the degradation of PS is likely to be a photochemical process,22,23 in which free radicals break vinyl bonds and benzyl rings in the presence of oxygen at the surface.24 Although PS has strongest absorbance around 240 nm in the UV, it quickly develops induced absorbance at wavelengths up to 490 nm after initial chain scission, which makes photo-degradation with a 447 nm CW laser possible.25 One possibility is that this initial trigger
occurs via two-photon absorption or multi-photon ablation,\textsuperscript{26} which have been shown to occur in polymers even from CW lasers.\textsuperscript{26, 27} Further evidence suggesting subsequent photochemical changes is that irradiated regions of PS film close to the substrate cannot be dissolved in toluene, leaving arrays of thin polymer pads (35 nm in height) on the gold (SI-Fig. S4). Cross-linking must occur near the substrate surface where no oxygen is present.

![AFM profiles of pits in PS formed under different conditions.](image)

**Fig.2.** AFM profiles of pits in PS formed under different conditions. (a-c) Dependence on PS film thickness (on Au at $S_{th}=2$), (a) 70 nm, (b) 100 nm, (c) 140nm. (d-f) Substrate dependence of pits formed at $S_{th}=3$ on (d) Ag, (e) Al, (f) Si, PS film thickness is 100 nm. Insets are corresponding AFM images.

To explore how focused illumination and photochemical degradation can result in sub-100 nm pits, we vary the PS film thickness $t$ (Fig. 2a-c) and substrate material (Fig. 2d-f). We find that as the film gets thicker, irradiation for the same $S_{th}$ results in shallower pits, with sharpest pits for film thicknesses of $t=100$ nm. The scattering kinetics of these films presents different spectral features mainly due to interference of the scattered light for different film thickness (SI-Fig. S5). However, they all show a similar depth profile, with the pits developing from a 400 nm-wide surface depression, quickly narrowing down with depth (sharpest for $t=100$ nm). The substrate also influences pit formation significantly (Fig. 2d,e), with Ag and Al most similar, though less reproducible than Au. Pits formed on Si substrates are much shallower and wider (Fig. 2f), while no pits can be formed on glass substrates. Scattering kinetics reveals that pits form first on Ag, then Al, Au, and finally Si, under the same irradiation power (SI-Fig.S6).

These results suggest that thin film optics plays a crucial role in the drilling kinetics of the PS. The near-field distributions from 3D finite difference time domain (FDTD) simulations show that light is more confined within the crevices for PS thicknesses of 100 nm (Fig.3a-c). This is due to two effects. The first is the constructive interference of light above the reflective substrate
which locates a standing wave maximum below the top of the PS only for $t=100$ nm. The
second effect is the concentration of light in the developing crevice, due to constructive
interference from reflections off each side. For $t=100$ nm, when a dip forms in the PS surface,
the bottom of the dip experiences a higher intensity and thus faster photochemical
degradation. This narrows and deepens the pit, further increasing the intensity at the bottom
and its etching rate. As a result, near-field drilling will only occur where the intensity increases
as the pit deepens (Fig.3d, red point), matching the experimental results (Fig.2b).

Fig.3. FDTD simulations of near field distributions. (a-c) PS films of different thickness on Au. (d) Intensity
of 447 nm light above planar PS/Au films, with dashed lines showing the three film thicknesses. (e-h)
Substrate dependence of 100 nm PS films on different substrates, (e) Au, (f) Al, (g) Si, (h) SiO$_2$. Light
distributions are normalized, while artificial pit is imposed initially.

The dependence on substrate material can also be understood from this model. While Al and
Si are highly reflective at 447 nm producing standing waves more than 60 nm above the metal
surface (Fig.3f,g), Au has interband transitions at this wavelength and its standing wave is phase
shifted closer (Fig.3e). This means that the evolving pit above Al or Si rapidly reaches a depth
where the light decreases with further etching, thus blunting the runaway process resulting in
wider and shallower pits. For Au substrates the increasing pit etching rate persists nearly down
to the substrate, while for glass substrates (Fig. 3h) there is no reflection to give standing waves
and the laser intensity is below the photochemical threshold. Although the field profile above a
Ag substrate is similar to the Au substrate (Fig. S7), its relative poor reproducibility in creating
nanoholes may arise from surface oxidation, which changes the actual field distribution. The
sub-100nm pits are thus formed due to near field concentration feedback effects caused by
interference in three dimensions.
Fig. 4. Fabrication of Au nanoparticle arrays. (a) Fabrication scheme. (b-e) SEM images of (b) hole array (used as mask), and Au NPoM arrays from (c) top view, (d) tilted 45° view, (e) magnified view. Inset is oblate spheroidal Au NPoM. (f) Scattering spectra of fabricated structures from (a): 1. optical drilled holes, 2. with Au evaporated on top, and 3. after lift-off. Insets show corresponding dark field optical images. (g) Simulation of scattering from nanostructures at process stages as in (f).

From this understanding and controllability of the optical near-field drilling process, we can make arrays of holes with sizes ranging from 60 nm to 1 μm and use them as deposition or etch masks for the fabrication of more complicated plasmonic nanostructures, such as arrays of holes in Au films (SI-Fig. S8) or Au nanoparticle-on-mirror (NPoM) arrays (Fig. 4). For strong plasmonic coupling and easy characterization, we fabricate 215±15 nm holes (Fig. 4b) and then evaporate 40 nm Au on top, followed by lift-off in toluene (Fig. 4a). The resulting Au pattern shows good reproducibility and uniformity of the particles, with diameter 225±10 nm (Fig. 4c,d). The magnified view shows their oblate spheroidal shape arising from the shape of the holes (Fig. 4e). Characterization by AFM shows that the Au nanoparticle is 70 nm high, suggesting there is a 30 nm polymer pad underneath the 40 nm Au, which matches previous results (SI-Fig. S4). The scattering spectra from these arrays (Fig. 4f) directly track the change of
nanostructures from PS holes to Au NPoMs, and agree well with simulations (Fig. 4g). The spectra are sensitive to all the nano-structure dimensions (details will be discussed elsewhere), and serve to show how plasmonic coupled structures can be easily produced by this simple near-field direct-write photolithography.

Fig.5. Au NPoMs of increasing size. (a-e) SEM images of Au NPoMs of different sizes. Insets are dark field images. (f) Change of Au NPoM sizes with scattering threshold value. (g) Experimental and (h) simulation of scattering spectra of Au NPoMs with different sizes. (i) Shift of coupled plasmon resonances (dipolar mode) with increasing size of the Au NPoM. The longest-wavelength dipolar mode (cyan curve) shifts out of the detection range, and its value is therefore estimated.

As the size of the pits can be controlled through $S_{th}$, which stops laser irradiation before larger holes evolve (Fig.1f), a series of Au NPoMs with increasing size can be produced (Fig.5a-f). The scattering spectra show a gradual red shift of the coupled modes for larger sizes (Fig. 5h), which matches simulation results very well (Fig. 5i). When the diameter of the Au NP exceeds 400 nm, its shape changes from spheroid to disk (Fig. 5e), which changes the scattering spectra completely and no longer follows the trend of redshifts (blue lines in Fig. 5g,h). This shows the flexibility of the nanofabrication possible using this technique, with a wide variety of pit/hole and particle shapes and spacings. Note that attempts to drill nano-pits in close proximity are
complicated by additional near-field scattering from the existing pit, though it is possible with larger holes (SI-Fig.S9). Using alternative (such as elliptical) shaped focal spots should also modify the pit circularity. The mechanism introduced here may also be implicated in the recent demonstration of two-photon lithography of resists which produces microexplosions at >10mW 532nm power CW irradiation.\textsuperscript{27} Full understanding of the interaction of light with polymer films including local bond breaking and cross-linking is crucial for advanced direct-write lithographies but involves near-field interactions.

In conclusion, we have developed a near-field-enhanced photolithography based on the photochemistry of thin polymer films. The synergistic effects of 100 nm thick PS films and Au substrates produces constructive interference in the crevice, thereby generating strongly localized optical fields which constrain photo-degradation of PS to regions far smaller than the diffraction limit of light. This contrasts traditional far field two-/multi-photon lithography as the latter hardly gives features smaller than 200 nm\textsuperscript{28-33} unless STED inspired technique is applied.\textsuperscript{16, 17} Real-time spectroscopic monitoring of the pit drilling process enables smallest pit sizes currently of 60 nm. This can be further improved using lasers of shorter wavelength and objectives with higher NA, but should be possible to extend to a wide range of polymeric films and substrates. This technique brings new opportunities for sub-100nm structuring based on near-field direct-write lithography (NF-DWL) at low cost. This near-field enhanced multi-photon mechanism also differs from plasmon enhanced multi-photon process,\textsuperscript{34-36} which is based on constructive interference of the beams from scattering at the crevices at the top surface of PS film and reflection of Au mirror. This high resolution DWL can place nanostructures accurately, and enables rapid prototyping of advanced electronics and photonics devices.

**ASSOCIATED CONTENT**

**Supporting Information.** Experimental details, SEM images of irradiation time series, irradiation of PMMA films, fabrication of PS pad arrays, thickness and substrates dependence on the scattering kinetics, fabrication of Au hole arrays, SEM images of holes with different separations, and FDTD simulation model setup and result for Ag substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**

TD conceived the idea and performed the experiments. JM built the setup and wrote the codes for irradiation control. RC did the FDTD simulations. TD and JJB analyzed the data, built the
model and wrote the manuscript. All authors have given approval to the final version of the manuscript.

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