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Citation: Applied Physics Letters **81**, 3663 (2002); doi: 10.1063/1.1519329
View online: http://dx.doi.org/10.1063/1.1519329
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/81/19?ver=pdfcov
Published by the AIP Publishing

Near-field two-photon nanolithography using an apertureless optical probe

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(Received 23 July 2002; accepted 13 September 2002)

Near-field two-photon optical lithography is demonstrated by using ~120 fs laser pulses at 790 nm in an apertureless near-field optical microscope, which produces lithographic features with ~70 nm resolution. The technique takes advantage of the field enhancement at the extremity of a metallic probe to induce nanoscale two-photon absorption and polymerization in a commercial photoresist, SU-8. Even without optimization of the resist or laser pulses, the spatial resolution of this technique is as high as λ/10, nearly a factor of 2 better than techniques based on far field two-photon lithography. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1519329]

There has been great recent excitement over the development of techniques for exceeding the diffraction limit in high-resolution optical imaging and photolithographic nanometer-scale device fabrication. In particular, there have been two different approaches to improve optical resolution below the limits dictated by diffraction. The first approach takes advantage of the nanoscale aperture of a near-field scanning optical microscope (NSOM) probe,[1–3] while the second approach is based on the nonlinear absorption of light by a chromophore exposed to an intense electromagnetic field.[4,5]

The NSOM approach to improved spatial resolution takes advantage of the small, nanometer-sized aperture formed by a metal-coated optical fiber tip from which light can be either directed to or collected from the sample. Unfortunately, due to the propagation cutoff of the waveguide mode in fibers with such restricted apertures, only a very small fraction of the light can be transmitted through the tip,[1] making it difficult to use such probes in lithographic applications. Apertureless near-field scanning optical microscopy (ANSOM) has overcome this problem by using sharp metallic tips instead of fiber apertures to achieve nanometer-scale resolution. In ANSOM, light polarized along the sharp axis of a metallic tip induces a high concentration of surface plasmons that results in strong enhancement of the electromagnetic field in the local vicinity of the tip (typically over a few tens of nanometers).[6] This localized enhancement in the light field has been widely applied in near-field imaging,[7,8] single molecule excitation,[9,10] and most recently, in one-photon near-field optical lithography,[11,12] where a metal-coated atomic force microscope (AFM) tip was used to enhance the local electromagnetic field to pattern a photoresist.

The multi-photon absorption approach to improved optical spatial resolution, in contrast, does not require an external element (such as an AFM tip) to provide local enhancement of the electromagnetic field, but instead relies on the nonlinear optical properties of a material. When high-intensity light shines on a material, the probability for two-photon absorption is proportional to the square of the field intensity, and thus is greatest at the center of a Gaussian laser spot. By carefully choosing the laser pulse energy and duration so that only this central region is above the intensity threshold for two-photon absorption, a material can absorb two photons of light over a much smaller spatial region than could be achieved using one-photon absorption. Two-photon absorption-based photolithography experiments utilizing this idea recently have achieved ~120 nm spatial resolution using femtosecond laser pulses with a 780 nm central wavelength.[4,13]

While each of the two approaches, ANSOM and two-photon absorption, can achieve subdiffraction-limited spatial resolution, the combination of these two techniques can provide even higher spatial resolution, as demonstrated recently in near-field fluorescence and second harmonic microscopy experiments.[7,9] In spite of this potential for outstanding spatial resolution, however, there have been no reports on using the marriage of these two techniques to further improve the resolution of photolithography. Thus, in this letter, the combination of apertureless near-field enhancement and nonlinear absorption techniques is applied in photolithography to achieving a spatial resolution as high as λ/10, nearly a factor of 2 better than the resolution achieved in previous far-field two-photon lithography experiments.[13] In our experiments, we make use of a metallic ANSOM tip and femtosecond laser pulses to demonstrate lithographic patterning with ~70 nm spatial resolution in a commercial negative photoresist, SU-8. Since none of the experimental parameters—the nature of the tip, the choice of resist, and the wavelength of the laser pulses—have been optimized for this application, we expect that even greater spatial resolution should be possible using this two-photon apertureless near-field lithographic technique.

A schematic diagram of the experimental setup for two-photon apertureless near-field lithography is shown in Fig. 1. The experiments were carried out on the platform of a com-

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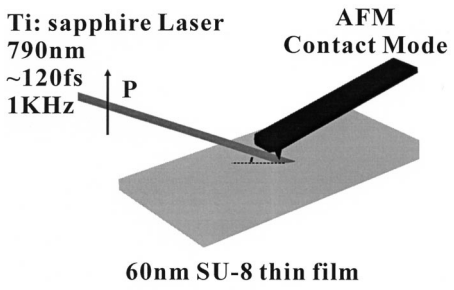

FIG. 1. Schematic diagram of the experimental setup for two-photon apertureless near-field photolithography.

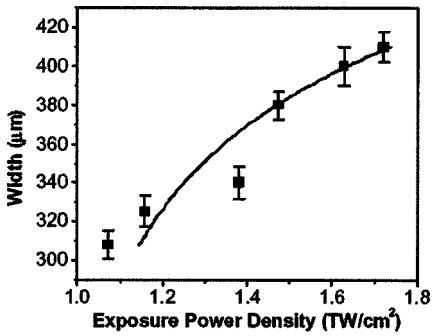

FIG. 2. Size of the developed features written by far-field two-photon exposure of SU-8 as a function of laser irradiation intensity. The minimal features in far-field exposure were obtained at 1.07 TW/cm^2 (dosage of 350 μJ/pulse), while no pattern can be observed in the developed resist at intensities below 0.92 TW/cm^2 or lower in the absence of the metal-coated AFM tip. The solid curve is a logarithmic fit,[15] which determines the far-field exposure threshold to be 0.96 TW/cm^2.

mercial AFM (PScanII, Pacific Scan) operating in contact mode, using a sharp conical silicon tip with either a Pt/Ir (NCHPt, Molecular Imaging) or Au coating. The SU-8 photoresist precursor (Nano SU-8 5, Microlithography Chemical) was first diluted with γ-butyrolactone by a factor of 1:2.5 and then spin coated onto pre-cleaned glass substrates to obtain 60-nm-thick photoresist films, as measured by AFM. Laser pulses with *p* polarization were incident on the films at a glancing angle, illuminating both the metallic tip and the substrate while the tip was scanned across the surface (Fig. 1). To obtain the high intensity levels required for two-photon absorption in SU-8 films, a Ti:sapphire laser (Spectra Physics) that produces 1 mJ, ~120 fs duration pulses at 790 nm and a 1 kHz repetition rate was used. The laser pulses were telescoped to ~1 mm-diameter at the sample, and the pulse energy was controlled in the range from zero to 800 μJ/pulse by means of a variable neutral density filter. After scanning the tip across the sample, the films were baked first at 65 °C and then at 95 °C for 1 min, respectively. The films were then developed, and the resulting structures were characterized by atomic force microscopy (Dimension 3100, Digital Instruments).

As discussed in previous two-photon absorption work,[14] the SU-8 photoinitiator does not absorb the 790 nm fundamental wavelength from the laser; thus any absorption of the femtosecond pulses must occur from a two- or higher-order photon process. A precise determination of the order of the multi-photon absorption process is difficult due to the low photodamage threshold of SU-8, which is only a factor of ~2.5 higher than the polymerization threshold for 790 nm pulses.[14] Thus, while we refer to the absorption in this letter as two photon, it is certainly possible that a higher-order process could be involved for photoinitiation.

To determine the two-photon polymerization threshold of SU-8, we performed a series of exposure experiments without the AFM tip. Figure 2 shows the diameter of the features written (after the resist is developed) as a function of the laser power density (intensity) assuming a Gaussian beam profile. We note that the size of the features written was determined by a combination of the size of the (unfocused) laser beam and the two-photon absorption threshold of SU-8, and thus these are not the smallest possible two-photon features that could be written. As expected, Fig. 2 shows that the size of the features increases with increasing laser intensity. In the experiments, the minimal features in far-field exposure were obtained at 1.07 TW/cm^2 (dosage of 350 μJ/pulse), while no pattern can be observed in the developed resist at intensities below 0.92 TW/cm^2, which is in good agreement with a theoretical logarithmic fit to the data,[15] as shown as the solid curve in Fig. 2.

Once the metal-coated AFM tip is brought into contact with the sample, however, we were able to observe two-photon polymerization of SU-8 at intensities as low as 0.15 TW/cm^2, indicating that the ANSOM tip provides a factor of ~7 field enhancement for enabling two-photon polymerization. Control experiments using a silicon nitride tip failed to produce observable structures even at intensities as high as 1.0 TW/cm^2, suggesting that the field enhancement from the metal coating was responsible for the decreased far-field polymerization threshold. In addition, we verified that the size of the field-enhanced features produced when the metal-coated tip was in contact with the sample did not depend on the size of the laser spot, but instead was related to the characteristic size of the ANSOM probe. We also were able to raster the ANSOM tip across the sample at scanning speeds ranging from 10 to 200 μm/s with no apparent effect on the decreased polymerization intensity threshold.

Figure 3(a) shows an AFM image of a 20 μm$\times$20 μm area of a developed SU-8 film following ~0.9 TW/cm^2 laser exposure while the ANSOM probe was rastered across the sample at 160 μm/s. The diagonal lines, which each have a ~250 nm width, correspond to single passes of the ANSOM tip separated laterally by 600 nm. Figure 3(b) shows a magnified area (2.5 μm$\times$5.5 μm) from a similar experiment in which the laser intensity was lowered to ~0.45 TW/cm^2, while Fig. 3(c) shows the corresponding height profile along the dark vertical line in Fig. 3(b). A Gaussian fit to 30 of the line structure profiles measured from Fig. 3(a) yields an averaged full width at half modulation (FWHM) of 72 nm $\pm$10 nm. Taking the tip convolution of AFM profiling into account, the actual feature width is even smaller than 70 nm. Since the polymerization is accomplished with the 790 nm fundamental wavelength of a Ti:sapphire laser, it is clear that the combination of ANSOM and two-photon absorption improves the spatial resolution as high as $\lambda/10$, about a 50% improvement from the previous record in far-field two-photon lithography.

While our two-photon apertureless near-field lithographic technique provides a significant improvement in spatial resolution, we believe that there is considerable room for

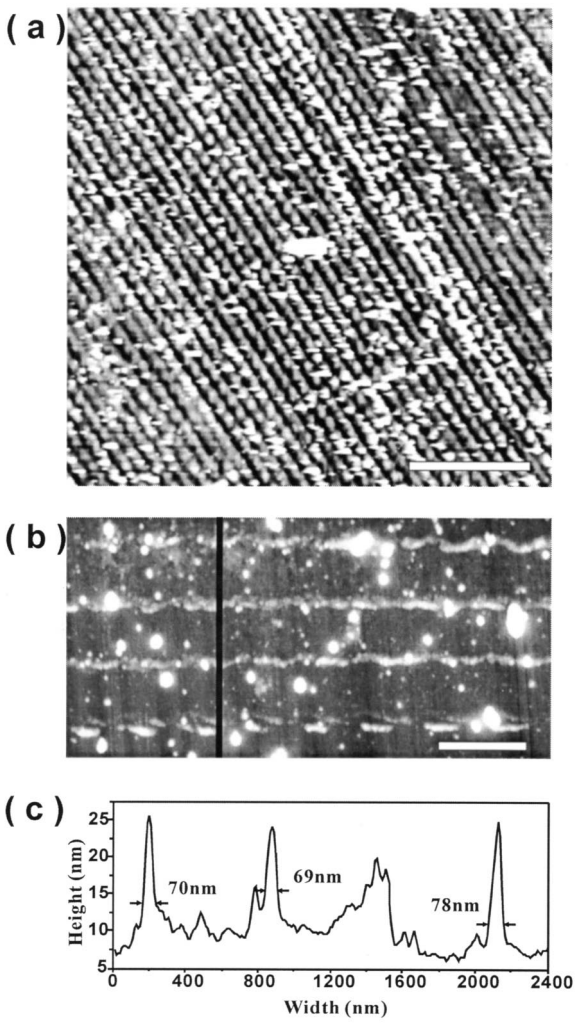

FIG. 3. AFM images of two-photon produced line structures in SU-8 exposed using the field enhancement of the ANSOM tip with far-field intensities of (a) 0.9 TW/cm^2 and (b) 0.45 TW/cm^2. Panel (c) shows a cross-sectional view (height profile) along the dark vertical line in (b), suggesting that two-photon apertureless near-field lithography can produce $\sim$72 nm $\pm$10 nm features using 790 nm light. The scale bars in (a) and (b) are 5 and 1 μm, respectively.

further optimization. For example, sharpening the metallic tip could help to further localize the enhanced portion of the electromagnetic field. The use of shorter incident wavelengths that are in direct two-photon resonance with the photoinitiator also should improve the sensitivity of the process by significantly lowering the polymerization threshold.[14] Furthermore, while it is gratifying that this technique can be used with an off-the-shelf commercial resist, it is well known that tailoring the photoinitiator can significantly lower the nonlinear polymerization threshold.[16] Finally, it should be possible to spread the full power of an amplified femtosecond laser over a large area, allowing simultaneous exposure with multiple ANSOM tips, similar to the parallel multi-AFM tip recently used in data storage applications[17,18] to allow for the parallel production of nanometer-scale devices. Overall, by utilizing a combination of apertureless near-field microscopy and two-photon absorption; we have demonstrated a direct-writing photolithographic technique capable of about 70 nm resolution.

X.Z. acknowledges the support from the Department of Defense Multi-disciplinary University Research Initiative (MURI) under Grant No. N00014-01-1-0803, the Office of Naval Research (ONR) Young Investigator Award under Grant No. N00014-02-1-0224, and the National Science Foundation (NSF) CAREER Award under Grant No. DMI-0196395. B.J.S. is a Cottrell Scholar of Research Corporation, an Alfred P. Sloan Foundation Research Fellow, and a Camille Dreyfus Teacher-Scholar.

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