Cryogenic two-photon laser photolithography with SU-8

Kwan H. Lee, Alex M. Green, Robert A. Taylor, David N. Sharp, and Andrew J. Turberfield
Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom
Frederic S. F. Brossard and David A. Williams
Hitachi Cambridge Laboratory, Hitachi Europe Ltd., Madingley Road, Cambridge CB3 0HE, United Kingdom
G. Andrew D. Briggs
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom

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We have shown that photolithography can be used to create alignment markers on a semiconductor substrate at cryogenic temperatures. The epoxy resist SU-8 can be exposed effectively by two-photon absorption at a temperature of 4 K. By this means a spectroscopy apparatus can be used to find the positions of randomly distributed structures at low temperatures, such as InGaAs/GaAs quantum dots, and mark their positions. We present a systematic study of the optical exposure parameters for cryogenic two-photon laser photolithography with SU-8. © 2006 American Institute of Physics.

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In this letter we demonstrate photolithography at cryogenic temperatures. We have used two-photon absorption (TPA) of 100 fs pulses from an 800 nm Ti:sapphire laser to expose SU-8, a negative photoresist widely used in the microelectromechanical systems community. This technical advance opens up new applications, especially in nanophotonics, because it allows one to label the positions of interesting optical features that are only identifiable at cryogenic temperatures. This work was motivated by the desire to find and label single InGaAs/GaAs quantum dots (QDs) for the purposes of quantum information processing experiments.

We discuss the suitability of this photoresist for low-temperature applications and present a survey of optical exposure parameters that give good results.

TPA laser photolithography relies on nonlinear absorption by a photoinitiator of high-peak-power laser pulses at a wavelength that is too long to expose the resist by single-photon absorption. The quadratic intensity dependence of TPA enhances the resolution of the process. TPA laser photolithography has been used to make intricate three-dimensional structures ranging from micromachines to photonic crystals. The MicroChem Nano SU-8 2025 resist used in this study consists of EPON® SU-8 resin, a solvent (cyclopentanone) which is removed by heating prior to exposure, and triaryl-sulphonium hexafluoroantimonate photoacid generator (PAG). Photoexcitation of the PAG causes it to decompose, liberating H+ and other side products in a process that does not require thermal activation. At temperatures below the glass transition of the resist the spatial distribution of photogenerated acid is stable and reflects the spatial distribution of the optical exposure. The exposed regions are rendered insoluble by an acid-catalyzed polymerization chain reaction, which is initiated upon heating the photoresist above the glass transition temperature (which is typically well above room temperature). The possibility of separating photoexcitation, which can occur at low temperature, and polymerization, which can be delayed and initiated at a higher temperature without loss of resolution, makes SU-8 an attractive candidate for low-temperature exposure. Furthermore, room-temperature TPA laser photolithography with SU-8 has been studied in detail.

The samples consisted of 1 μm thick MicroChem Nano SU-8 2025 photoresist (diluted one part Nano SU-8 2025 is to two parts cyclopentanone) spin coated over a 60 nm tungsten film on a GaAs substrate. After application of the SU-8 the sample was baked at 95 °C for 2 min. Low-temperature TPA photolithography was carried out using the apparatus shown in Fig. 1; the sample was mounted in a continuous-
flow liquid helium microscope cryostat (Janis ST-500). Optical excitation for TPA photolithography was provided by an 80 MHz, 800 nm mode-locked Ti:sapphire laser with \( \sim 100 \) fs pulses (Spectra Physics Mai-Tai), with pulse energies in the range of 0.12–1.2 nJ/pulse (average power 10–100 mW). The laser pulses were focused by a 0.5 numerical aperture (NA), 100\( \times \) objective lens (Mitutoyo), which was mounted on a piezoelectric XYZ stage with 100 \( \mu m \) travel along each axis and 1 nm resolution (PI P-611.S). It is straightforward to extend the apparatus in Fig. 1 to allow the use of microphotoluminescence to locate and then label the position of interesting optical features. Spectroscopy can be performed using much lower laser powers (\( \sim 5 \) \( \mu W \)) that do not cause significant TPA exposure of the SU-8 overlayer.

Test patterns were defined by scanning the focal spot of the laser (Airy disk diameter \( \sim 2 \) \( \mu m \)) along the tungsten/SU-8 interface with the sample at a temperature of 4 K. The exposed samples were then warmed to room temperature over a period of \( \sim 2 \) h, baked at 95 \( ^{\circ}C \) for 5 min, developed in propylene glycol methyl ether acetate (PGMEA), rinsed with isopropanol, and blown dry. Figure 2(a) shows an alignment structure fabricated in SU-8 by TPA laser photolithography at 4 K. Figure 2(b) shows the same pattern transferred into the tungsten film by \( \text{CF}_4: \text{O}_2 \) reactive ion etching (RIE), followed by \( \text{O}_2 \) plasma ashing to remove the SU-8. Despite the order-of-magnitude difference between the thermal expansion coefficients SU-8, tungsten and GaAs, the adhesion of the SU-8 layer was generally good. During thermal cycling the small amount of cracking that occurred did not cause problems for the subsequent processing steps. In Fig. 2(a), a crack can be seen running diagonally through the feature; it was faintly transferred to the tungsten after RIE, with no loss of feature quality, as can be seen in Fig. 2(b).

Figure 3(a) shows an electron micrograph of a line written by scanning the laser spot, followed by RIE only. This shows that the fabricated features posses well defined edges and good uniformity, which is essential for usage as alignment markers. Here the width of the tungsten line was measured to be \( \sim 800 \) nm, consistent with the high resolution expected of TPA laser lithography. We have employed this technique to demonstrate registration of the QDs. Overall, the registration process consisted of four steps: (1) Preparation of a metal layer with a grid of clear apertures on the sample; (2) microphotoluminescence spectroscopy to locate a QD within an aperture; (3) laser exposure of a resist layer to define alignment markers in the surrounding metal; (4) fabrication of the alignment markers. Figure 3(b) shows the spectrum from a QD at 4 K, taken before the lithography (step 2) and after the alignment marker fabrication (step 4). We demonstrate that the same QD has been reacquired using the fabricated alignment markers, except for a small redshift (\( \sim 1 \) nm) in the spectrum following the RIE. This has been observed throughout the sample and was likely caused by a Stark shift, due to the electric fields set up by the creation of surface states from the RIE process.

The test structures used to characterize optical exposure parameters for TPA photopolymerization of SU-8 consisted of \( 5 \times 5 \) \( \mu m \) squares formed by a continuous zigzag scan of...
the laser spot along 11 parallel 5 μm lines linked by ten 0.5 μm lines. The incident laser power $P$ and writing speed $v$ were varied, and the resulting structures were examined by optical microscopy and classified into five categories: damaged if more than 2/3 of the structure experienced laser induced damage (LID); partially damaged if between 2/3 and 1/3 of the structure experienced LID; acceptable if less than 1/3 of the structure experienced LID and less than 1/3 was missing; partial polymerization if between 1/3 and 2/3 of the feature was missing; no polymerization if more than 2/3 of the feature was missing. Figure 4 shows the laser power plotted against the write speed used for each of the 37 exposed structures; the category of each test structure is indicated by the use of different symbols. On Fig. 4, it was possible to position two straight lines, one at the boundary between acceptable test structures and damaged ones, and the other line at the boundary between acceptable test structures and the underexposed ones. These boundaries can be identified as the LID and photopolymerization thresholds, respectively. The shaded area between the two lines shows the region of parameter space over which cryogenic two-photon laser photolithography produces acceptable results. In Fig. 4, a point approximately at the center of the shaded region ($P=24$ mW, $v=2$ μm/s) corresponds to a time-averaged dose of 2.88 MJ/cm$^2$, which is also averaged over the area of the test structure. The laser powers and writing speeds are comparable to those used by Teh et al.$^{11}$ at room temperature so there is clearly a broad process window in which TPA photolithography can be used successfully.

In summary, we have demonstrated TPA laser photolithography at cryogenic temperatures with SU-8, a chemically amplified negative resist. SU-8 can be exposed at 4 K as photoinduced polymerization is delayed until the resist is heated above the glass transition temperature. There is a broad process window for successful exposure, with exposure parameters comparable to those used at room temperature. Cryogenic photolithography opens up new applications, particularly in nanophotonics, because it allows the generation of alignment marks to locate structures identified by low-temperature spectroscopy.

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9. We have experimented with Novolak positive photoresists Shipley S1818 and S1805 and have been unable to expose them successfully at low temperatures (4 or 100 K) using single-photon or two-photon excitation. These photoresists require the presence of water, usually adsorbed from the laboratory air. Other positive photoresists that work on the principle of photoinduced polymer chain scission may be suitable for low-temperature lithography. See W. M. Moreau, Semiconductor Lithography: Principles, Practices, and Materials (Plenum, New York, 1988).