A Spirothiopyran based photoresist for large area sub-diffraction nanopatterning

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Optical interference lithography is an attractive technique to cheaply and rapidly pattern three dimensional features in polymer photoresists[1]. However, both resolution and feature size obtained are limited by the diffraction limit[2]. In the past few years, Stimulated Emission Depletion Microscopy (STED) inspired lithography schemes using reversibly saturable switching systems have shown the ability to direct-write features well below the diffraction limit using light[3–5]. However, the high laser intensity required for saturation limits their use to point by point writing. The Menon group[6] has pioneered the use of photochromic molecules for sub-diffraction patterning, utilizing the difference in solubility and transmission between two diarylethene photo-isomers[7,8]. However, the high extinction coefficients of these molecules restrict these patterning strategies to 2D.

Here, we propose combining the reversibly saturable photoisomerization of Spirothiopyran with the Michael addition ‘click’ chemistry to formulate a low intensity threshold photoresist suitable for sub-diffraction resolutions over large areas. Proton NMR studies confirm an exponential decrease in the ‘writing’ reaction yield with low depletion intensity required for saturation. Photokinetic simulations demonstrate the potential to fabricate patterns with feature sizes less than 50 nm over a range spanning hundreds of microns using a simple 2W 532 nm laser. Furthermore, spatial control of crosslinking is demonstrated using a Spirothiopyran-PEG Methacrylate copolymer. Absorption within the photoresist can be mitigated by controlling the concentration of the photoswitch covalently attached to the polymer comprising the photoresist. These experiments demonstrate the viability of a Spirothiopyran based photoresist to become a prime candidate for large area 3D direct writing with sub-diffraction resolutions.

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