Super-resolution Interference Lithography using Spirothiopyran molecular switches

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Rapid, high throughput patterning in bulk polymeric systems with nanoscale resolution in three dimensions has long remained a coveted target for materials scientists. Optical interference lithography has been an attractive technique to cheaply and rapidly pattern three dimensional features in polymer photoresists despite both the resolution and feature size being limited by diffraction[1]. In the past few years, Stimulated Emission Depletion Microscopy (STED) inspired lithography schemes have shown the ability to direct-write features well below the diffraction limit using visible light[2-4]. However, the high light thresholds required for effective photoinhibition renders them unsuitable to be used for interference lithography and limits their use to point by point writing.

Recently, we have shown that combining the reversibly saturable photoisomerization of spirothiopyran with the thiol-Michael addition chemistry can be used to formulate a super-resolution writing system with the desired low light thresholds for parallel patterning[5]. To study super-resolution patterning using spirothiopyran writing chemistry, a 1D prototype system was designed using self-assembled monolayers on glass substrates. After optimizing the kinetics of photoisomerization of covalently bound spirothiopyran by tuning its microenvironment, we experimentally demonstrate large area nanopatterning with sub-diffraction resolution and molecular thickness using a 2-color interference lithography setup. The lateral feature size of the written patterns is shown to be tunable by controlling the relative intensity of the initiation and inhibition wavelengths, with feature sizes below $\lambda/7$ obtained using a 1.5 W laser. The resultant nanopatterns formed are characterized using super-resolution microscopy. The reversible switching of spirothiopyran allows for multiple phase-shifted exposures to achieve sub-diffraction resolution. These experiments demonstrate the versatility of spirothiopyran based writing systems for rapid high throughput nanopatterning. Efforts are currently underway in our laboratory to adapt the spirothiopyran writing chemistry for 3D nanopatterning in bulk polymeric gels.

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