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LIMIT is a new approach for creating highly space selective patterns of molecules in thin polymer films. Photochromic implants of <800 nm dimensions are now possible using interference modulated implantation. In this way implanted diffraction gratings have been made which operate as photo-switching optical devices. Here we report the implantation of four different classes of organic photochromic molecule.

Keywords: Photochromic; laser implantation; holographic grating

INTRODUCTION.

LIMIT occurs as a result of a laser induced photothermal increase in molecular diffusion at a surface or cavity doped with organic molecules, sometimes polymer dispersed, (the "source"). This leads to

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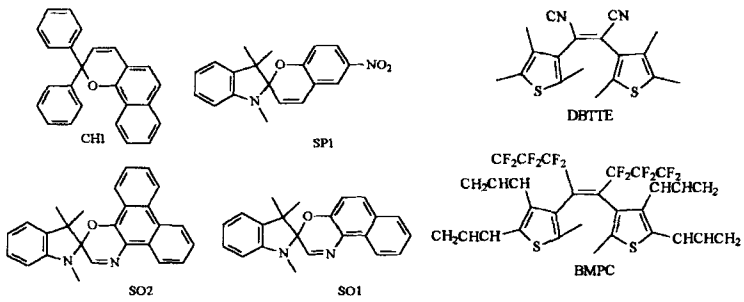
ejection of dopant molecules from the source across a space gap (approximately 1 μm) between the source and the target. Dopant molecules become dispersed into the target polymer film by laser induced activated diffusion. **LIMIT** has a photo activation threshold, so if there is low or no fluence there is no implantation.

LIMIT is effective for preparing space selective patterning of organic molecules in polymer films[1-5] and biological material.[6] **LIMIT** works by creating patterned areas and not by destructive material removal as in the cases of etching or lithography. Hence it has been possible to create patterns from organic molecules that are fluorescent[1-4] or photochromic.[5,7] These molecular functions survive the pattern creation process. We first reported **LIMIT** applied to photochromic molecules in 1998[5] and here we summarise that work and the advances that have been made since that time. The compounds in **Scheme 1** have all been successfully implanted.



SCHEME 1.

EXPERIMENTAL.

Solutions of PEMA and PBMA polymer and of dopants **SO1, SO2, CH1, SP1, DBTTE** and **BMPC** in chlorobenzene were spin coated onto optical quality quartz discs to make polymer "target" and dopant "source" films. The target and source films were placed in tight contact ready for implantation. The apparatus used for grating writing has been previously described.[5,7] The third harmonic from a Coherent Infinity^{tm} 40-100 Nd-YAG laser was split with a beam splitter. These beams were recombined at the target-film/source-film interface to form an interference modulated light source of alternating high and low laser fluence with a period Λ, given in **equation 1,**[5,7] for which θ is the beam recombination angle and λ the wavelength of the implantation beams.

$$\Lambda = \lambda / [2 \sin (\theta / 2)] \quad (1)$$

$$\Delta\eta \alpha (\pi \Delta n \, d / \lambda)^2 + (\Delta\alpha \, d / 4)^2 \quad (2)$$

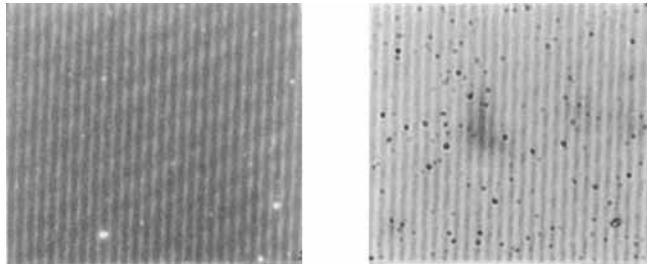


FIGURE 1. CH1 grating, left fluorescence image, right optical image.

Photochromic molecules only implant if there is high fluence creating a photochromic grating of period Λ at the target. 3-5 pulses, of fluence 0.2 $mJ{\cdot}mm^{-2}$ were needed to write gratings. After the grating was implanted into the target the films were separated. Grating re-activation was possible with a single beam 355 nm 10 Hz pulse train of fluence of between 0.1-0.2 $mJ.mm^{-2}$ per pulse. Grating photoswitching performance was then observed using a photodetector to measure the intensity of a single 633 nm spot from a He-Ne laser beam diffracted by the grating.

RESULTS AND DISCUSSION.

For grating implantation one form of the photochromic must absorb at 355 nm. For grating switching the probe absorbance (633nm) must photochromically modulate within the grating lines. **Equation (2)** is for 1st order diffraction by a grating.[5] Δn is the refractive index change, $\Delta\alpha$ the absorbance change at 633nm (λ), d is the optical pathlength and $\Delta\eta$ is the diffracted spot intensity change.

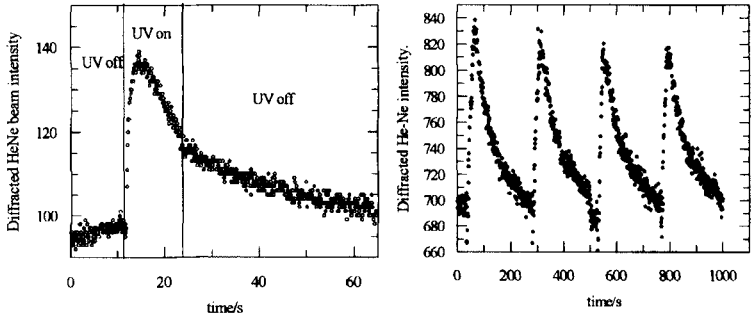


FIGURE 2. SP1 grating switch in PBMA (L) and **SO2** in PEMA (R).

Of **DBTTE** and **BMPC**, best results were obtained for **DBTTE** implants into PBMA. The fluorescence of **DBTTE** open form modulated following the photochromic response. **DBTTE** and **BMPC** gratings were only 2.5% switchable due to a small $\Delta\alpha$ at 633 nm upon photoswitching.

Fluorescence of the **CH1** merocyanine form in grating lines is seen in **Figure 1** (Λ =2.8 μm). The **CH1** photochromic response time is slow. **SO1** and **SP1** grating photostationary states were unstable due to decomposition. **Figure 2** shows switching of an **SP2** grating in PBMA. **PC2** gratings were stable to switching. Photographs of a **PC2** grating with and without UV excitation are shown in **Figure 3**. The blue colour of the UV activated form demonstrates the photochromism of the grating lines. The grating spacing period, Λ, was 1.6 μm. The individual implanted grating lines had a width dimensions of < 800 nm. The **PC2** implanted grating's diffraction efficiency in PEMA was 23% switchable above the baseline when UV re-excited. This is clearly seen in **Figure 2**.

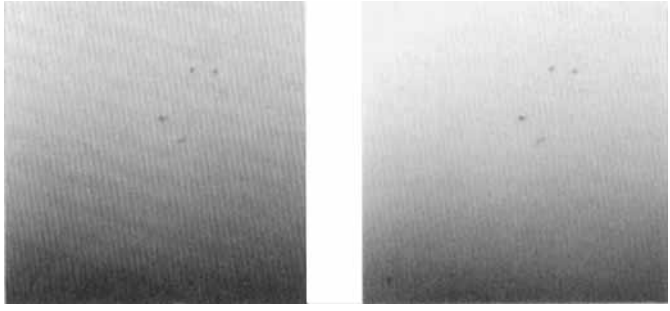


FIGURE 3. SO2 grating, photoactivated (L) and deactivated (R).

CONCLUSION.

LIMIT is generally applicable to patterning of organic photochromics into thin polymer films. The photochromic response remains after implantation. Photochromic features of hundreds of nanometers in size are possible. Durable switchable holographic gratings have been made using interferometric methods. Many holographic micro and nano scale features can now be envisaged with the added feature of molecular functionality.

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