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Liquid crystal polymer composite films for reconfigurable photomasking applications

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We show proof of concept of a real-time reconfigurable photomask fabricated from holographically formed polymer-dispersed liquid crystal (H-PDLC) reflection gratings on etched indium tin oxide patterned electrodes. H-PDLC films were formed using a thiolene based polymer to have a reflection wavelength that modulates 440 nm, the peak sensitivity wavelength of Shipley 1800 series positive photoresist. A working prototype of this adaptable photomask device is shown by comparing patterns formed using the H-PDLC mask and similar patterns formed using a static contact photomask showing that H-PDLC films have the ability to modulate 440 nm light and control the exposure dose of photoresist. © 2007 American Institute of Physics. [DOI: 10.1063/1.2794735]

Holographically formed polymer-dispersed liquid crystal (H-PDLC) films are a class of composite materials that have the ability to modulate a predetermined wavelength of incident light by selective reflection. This film, or reflection grating, is formed from a homogeneous mixture of monomer, initiator, and liquid crystal uniformly spaced in an electrically conductive glass cell that has been exposed to an optical interference pattern created by two counterpropagating UV laser beams. During exposure, the monomer polymerizes in the bright fringes while the liquid crystal forms 50–100 nm droplets and diffuses to the dark areas. Index mismatch between the randomly aligned liquid crystal droplet layers and the polymer layers results in reflection of the Bragg wavelength, which is determined by the angle of the interfering beams. Application of sufficient bias across a conductive layer of indium tin oxide (ITO) coated on the glass cell aligns the liquid crystal droplets and reduces the Bragg reflection. Removal of the applied field results in the liquid crystal droplets returning to their original state.\(^1\) H-PDLC has been used for applications in wavelength demultiplexing and optical spectroscopy, as well as improving display technology through fabrication of conformal and reflective displays.\(^2-5\)

Bulk liquid crystal materials have previously been proposed in adaptable photomasking applications by Peng \textit{et al.} who suggested using a liquid crystal display as a light valve to control the resist curing UV light in the lithographic process.\(^6\) Additionally, Jeon \textit{et al.} have used polymer-dispersed liquid crystal (PDLC) films as reconfigurable photomasks. PDLC films differ from H-PDLC films in that they have voltage controlled scattering and transparent states rather than voltage controlled reflection and transmission states. Using PDLC films for reconfigurable lithography allows different levels of isotropy in the resist etch depending on the amount of scattering from the film. In the complete scattering state, the etch is shallow with rounded undercut walls while in a transparent state the resulting etch exhibits near vertical walls.\(^7\)

In this paper, we discuss an application in which H-PDLC reflection gratings are used as a real-time reconfigurable photomask to replace traditional contact photomasks in the lithographic process. The H-PDLC Bragg reflection is precisely tuned to reflect the peak sensitivity wavelength of Shipley 1800 series positive photoresist. Since the H-PDLC can modulate a 10 nm (full width at half maximum) FWHM portion of incident light, a spectral filter is introduced to remove extraneous light produced by the UV exposure source. The resulting device can selectively modulate a 10 nm FWHM spectrum centered at 440 nm, as shown in Fig. 1. Figure 1 also illustrates the method used to select the printed pattern or adapt the photomask. The ITO coating on the glass in which the H-PDLC is formed is etched to electrically isolate different regions. Application of voltage to different regions yields different patterns in the photomask.

H-PDLC films were formed using a thiolene based syrup consisting of 65% Norland optical adhesive 65 (Norland Optical Products, Inc.), 30% BL038 liquid crystal (EM Industries), and 5% Darocure 4265 UV initiator (Aldrich, Inc.). The ordinary refractive index of BL038 is \(n_o=1.527\), and its birefringence is \(\Delta n=0.272\). The index of cured NOA65 polymer is \(n=1.524\). Index matching of BL038 and cured NOA65 in the biased state is within 0.2%. The laser used to form the gratings was a Coherent 308C Ar+ ion tuned to 351 nm. The intensity used was approximately 80 mW/cm\(^2\). The method of fabricating the gratings was the prism method, developed by Natarajan \textit{et al.},\(^8\) which uses total internal reflection inside a prism as the source of the optical illumination.

![FIG. 1. Schematic of H-PDLC photomask device in the lithography process. Broadband UV exposure is filtered by 10 nm FWHM spectral filter. H-PDLC reflects filtered exposure except region with voltage applied.](image-url)
H-PDLC films were formed on ITO coated Corning 1737 glass prefabricated with electrically isolated rows. ITO rows were etched 5 mm wide with 264.6 μm isolation gaps. These structures were fabricated using a photolithography pattern transfer technique with positive resist and a HCl etch.

To use the H-PDLC film formed on etched ITO glass as a reconfigurable photomask, the mask was placed in contact with a resist coated substrate. A filter was placed above the H-PDLC mask device. Bias was applied to regions intended to be transparent. Regions with no bias acted as light valves for the 440 nm light reaching the mask, attenuating it below the threshold for curing. Exposure dose measured in transparent “on” regions was 120 mJ/cm², attenuated dose in the reflecting “off” regions was measured to be 93 mJ/cm². Resist used was Shipley 1813 positive photoresist spin coated to a thickness of 1.4 μm. Postexposure samples were developed in Microposit 351 for 2 min.

Theoretical resolution of a photolithographic technique is determined by the diffraction limit of the optical system projecting the mask image on the resist substrate. Resolution is calculated using the equation

\[ R = \sqrt{\frac{\lambda}{s + \frac{z}{2}}} \],

where \( z \) is the resist thickness, \( s \) is the distance between the mask and resist surface, and \( \lambda \) is the exposure wavelength. Resist thickness in this experiment was 1.4 μm, exposure wavelength was 440 nm, and the thickness of the glass between the H-PDLC film and resist substrate was 1 mm. Theoretical resolution of this lithographic system is therefore calculated to be 21 μm. To show proof of concept that H-PDLC can sufficiently modulate resist curing UV light, structures with intentionally large feature size were fabricated. The smallest reproducible feature fabricated was a 264.5 μm line. This feature was fabricated using both the H-PDLC photomask device and a static mask under similar exposure and development conditions for comparison.

Figure 2 is an example of the line shape of the smallest reproducible structure using a H-PDLC mask superimposed with a similar sized feature fabricated with a static mask. These data were collected using a Zygo NewView 6200 white light interferometer profiler. The ideal linewidth of this structure is 264.5 μm, the mean linewidth (measured at the base of the microstructure) of several samples fabricated using the static mask was 320.7 μm, while the mean linewidth of the same structure fabricated under the same exposure and development conditions using the H-PDLC photomask device was 321.4 μm. As summarized in Table I, it can be seen that the linewidth profiles between structures fabricated using the H-PDLC mask and the static mask are on average within a percent of one another. The calculated standard deviation between samples shows that the static mask produces a more repeatable linewidth than the H-PDLC mask.

Structure edge slope in positive resist is governed by several factors. It can be seen in Fig. 2 that both resist structures have different amounts of overcut in their profile though linewidth measured from the base is approximately the same. The expression for edge slope or \( \frac{dz}{dx} \) can be separated into the product of a derivative term entirely dependent on resist and developer properties, \( \frac{dz}{dx} \), and a derivative term entirely dependent on the exposure wavelength, intensity, and imaging system, \( \frac{dD}{dx} \). In these derivative terms, \( z \) is defined as the feature height, \( x \) is defined as the lateral distance across the substrate, and \( D \) is the exposure dose. \( \frac{dz}{dx} \) is referred to as the developer elution term, and it defines the final structure profile as a function of resist and developer properties. \( \frac{dD}{dx} \) is known as the intensity profile term which characterizes the final structure’s dependence on the exposure optical properties. Rewriting the developer elution term as the quotient of resist contrast and resist sensitivity, and simplifying the expression

\[ \frac{dz}{dx} = \frac{1}{D_p \left( \log \frac{D_p}{D_p^0} \right) \lambda} \] (2)

it can be seen that this term is a function of \( D_p \) and \( D_p^0 \). \( D_p^0 \) is a threshold term defining the minimum exposure dose required to develop a resist while \( D_p \) is defined as the dose required to fully develop a layer of resist. These terms are dependent on resist thickness and absorbance, which are properties of the positive resist used for the lithography process. This term is independent of imaging system and should stay constant between sample structures fabricated using the static and the H-PDLC mask.

Examining the intensity profile term, the derivative can be written as

\[ \frac{dD}{dx} = \frac{2NA}{\lambda \left[ 1 - k \left( \frac{\delta NA^2}{\lambda} \right) \right]^2} \] (3)

where \( \lambda \) is the wavelength of the exposure, \( \delta \) is the depth of focus of the exposure optical system, NA is the numerical aperture of the imaging optics, and \( k \) is a constant quantifying the coherence of the exposure light. It is clear that this term is defined only by the exposure wavelength and optical properties of the photomask.

**TABLE I.** Characterization data of microstructure samples.

<table>
<thead>
<tr>
<th></th>
<th>Static mask</th>
<th>H-PDLC mask</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge slope (μm/mm)</td>
<td>25.2</td>
<td>19.0</td>
</tr>
<tr>
<td>Mean linewidth (μm)</td>
<td>320.7</td>
<td>321.4</td>
</tr>
<tr>
<td>STD linewidth (μm)</td>
<td>37.2</td>
<td>53.4</td>
</tr>
<tr>
<td>Linewidth error (%)</td>
<td>21.2</td>
<td>21.5</td>
</tr>
</tbody>
</table>

*Compared with ideal linewidth of 264.5 μm.
imaging system, and is independent of resist properties.  

In order to quantify the discrepancy in edge slope between the structures made using the different mask systems, it is necessary to examine the intensity profile term. This term is highly dependent on the exposure wavelength, but that variable was held constant in comparisons between the two masking systems. Depth of focus is a term that itself is related to numerical aperture of the imaging system, the variable that was not controlled in the comparison experiments. Numerical aperture of the imaging system used to pattern resist structures is dependent on the angle of the light spreading out from the mask reaching the resist. Diffraction from the mask edges accounts for an increase in numerical aperture for both the static and the H-PDLC mask. In addition to edge diffraction, transmission through H-PDLC in its biased state creates an amount of forward scattered light. There is, on average, a 24.6% difference in edge slope between samples fabricated using the two masking methods; it is expected that there is approximately that much discrepancy in the numerical aperture of the two imaging systems. Scattering angle accounts for the increased numerical aperture of this imaging system.

In order to ensure that the H-PDLC photomask device was attenuating the UV exposure light below the threshold for curing resist, profilometry was performed to determine the quality of the developed resist and glass areas. Resist samples for this comparison were fabricated using the H-PDLC mask in both the biased and unbiased states to show that the grating can fully modulate the exposure dose to cure or protect from curing the resist substrate. To fabricate the sample shown in Fig. 3(a), the H-PDLC mask is unbiased, therefore, preventing UV exposure. The resulting bulk region formed under the grating shows some indentation and dimpling, but these defects are comparable to a typical region of developed resist formed with the static mask shown in Fig. 3(b). No grating line defects are apparent or other evidence that it was cured under a film grating. The inverse sample was subsequently formed by biasing the H-PDLC mask into its transparent state. The exposure penetrates the mask curing the resist. The resist is developed leaving little resist residue, as shown in Fig. 3(c), compared to the sampled formed with the static mask [Fig. 3(d)] which indicates that a small amount of resist residue is left on the glass substrate.

Finally, an example of a structure patterned using a H-PDLC mask is shown in Fig. 4. Two samples were fabricated, first with the H-PDLC mask in an unbiased reflective state resulting in a flat developed resist area. The second sample was fabricated with the H-PDLC mask in a transmissive state. Regions of conducting ITO switch the mask and allow resist exposure [Fig. 4(b)].

We have shown proof of concept of an adaptable and computer controllable photomask using H-PDLC reflection gratings as a method for selecting UV exposure regions. This device produces repeatable microstructures whose line shapes deviate from features fabricated using a static mask as a function of the amount of scattered light transmitting though the mask. Scattered light transmitted through the film in its transmissive state accounts for less than 25% discrepancy in edge slope due to an increase in exposure numerical aperture. Additionally, we have shown that a H-PDLC mask can selectively transmit a sufficient quantity of UV light to fully cure positive photoresist or sufficiently attenuate UV exposure to prevent resist curing depending on bias state. Resist profilometry detects defects comparable to that of resist cured using a static mask.

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