Binary amplitude holograms made from dyed photoresist

Quandou Wang, Ulf Griesmann,* and John H. Burnett

National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

**Corresponding author: ulf.griesmann@nist.gov*

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A method for fabricating binary amplitude holograms from a dyed photoresist is described. It is of particular interest for holograms that are used as null optics in the form metrology of aspheric surfaces and wavefronts. A pigment that strongly absorbs light near 633 nm was dissolved in a positive photoresist and the dyed resist was spun onto silica glass substrates. Stable resist layers were obtained that were essentially opaque at 633 nm with little effect on the transmittance of the resist in the UV. A Fresnel zone plate was fabricated from the dyed resist layer using contact lithography, and its performance was demonstrated at 633 nm. © 2011 Optical Society of America

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Binary holograms have become indispensable auxiliary optics in the interferometric form metrology of aspheric surfaces since they were first described by Brown and Lohmann [1] and Lohmann and Paris [2] because they can generate a wide range of reference wavefronts [3,4]. Because of the advances in photolithography and electron beam lithography, binary holograms can now be used to generate wavefronts with very low uncertainty [5–9]. They are used for the interferometric testing of aspheric precision surfaces [10,11] and are employed in a diverse range of applications [12].

Amplitude holograms are commonly fabricated by patterning an opaque chromium layer on a transparent glass substrate using photolithography processes. It has long been recognized that the light-sensitive photoresist, which is needed for most types of photolithography, is itself an attractive media for the recording of holograms. Photoresist has been used to create binary phase holograms [13], or transmission holograms and gratings with sinusoidal surface relief [14–16].

Dyes were first added to photoresists to increase their absorbance in the UV [17,18]. This attenuates interference effects during patterning of photoresists on highly reflective substrates, which have a detrimental effect on the line edge roughness. Dyed photoresists have also found uses as optical filter materials that can be patterned with photolithography [19].

Here we describe a method for fabricating binary amplitude holograms with a design wavelength of 633 nm from a dyed photoresist and demonstrate it by fabricating a Fresnel zone plate.

A triarylmethine dye [20] (Epolight 5262 , Epolin Inc. [21]) was dissolved in a conventional UV-sensitive positive photoresist (Shipley S1813, Rohm and Haas Inc. [22]). The dye was selected because its peak absorbance is near 633 nm, the absorption band is relatively narrow, and it is soluble in several organic solvents. Relative absorbances, normalized to one, of the photoresist in the exposed (bleached) and the unexposed state and the absorbance of the dye dissolved in acetone are shown in Fig. 1 (the absorbance data for photoresist and dye are published in the data sheets for both products [21,22]). Figure 1 shows that the absorption spectra of dye and photoresist lie in separate wavelength regions. This suggests that the optical properties and performance of the photoresist at the lithographic exposure wavelength are only weakly affected by the addition of the dye even when the resist is made strongly absorbant near 633 nm by adding a considerable quantity of dye.

At first, we determined the dye concentration in the photoresist required to obtain resist layers that are sufficiently opaque at 633 nm. Dye quantities of 96, 144, and 192 mg were dissolved in 10 mL undiluted photoresist. The dye was fully dissolved at all concentrations and the solutions were stable. The photoresists with the three different dye concentrations were spin-coated onto fused silica substrates with 25 mm diameter and 6 mm thickness at an angular velocity of 100π rad/s (3000 rpm) for 45 s. Prior to resist coating, the substrates were baked and vapor coated with hexamethydisilazane to improve resist adhesion. The thickness of the resist layer was measured by removing the resist in a small area and measuring the resulting resist edge height with a profilometer. For the resists with the three different dye concentrations, the thicknesses were 1.75, 1.79, and 1.84 μm, with an uncertainty (1σ) of 0.011 μm. Clearly, the resist thickness increases with dye concentration, which indicates an increase in resist viscosity due to the added dye.

The spectral absorbance $A(\lambda) = -\ln(I(\lambda)/I_0(\lambda))$, where λ is the wavelength and I and I_0 are the intensities transmitted by the resist-coated and identical uncoated

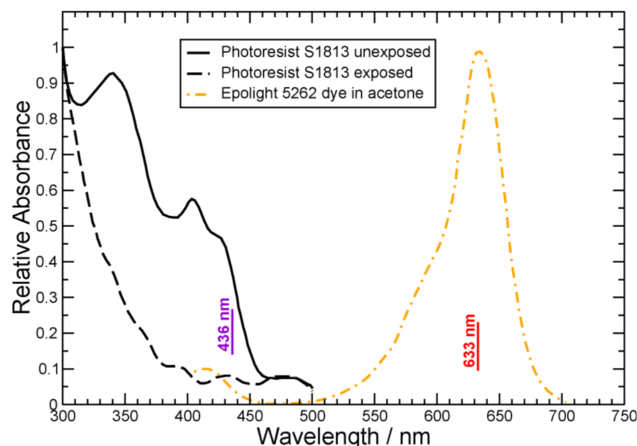

Fig. 1. (Color online) Relative absorbances of Epolight 5262 dye dissolved in acetone (dash-dotted curve), of unexposed S1813 photoresist (solid curve), and of exposed S1813 photoresist (dashed curve).

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substrate, were measured using a grating spectrophotometer between 375 and 750 nm for resist layers with dye concentrations 9.6, 14.4, and 19.2 g/l in the liquid resist. Figure 2 shows the absorbance curves that were obtained for the three dyed resists and the absorbance of the undyed resist. The measurements were repeated three or four times. The worst case repeatability (1σ) of the measurements was 0.025, or 2.5%. The oscillations in the absorbance curves, which are especially noticable in the curve for the undyed resist, are due to interference in the thin resist layer. All absorbance curves of the dyed resist show pronounced absorption in the red portion of the spectrum with a peak very close to 633 nm. For the highest concentration of 19.2 g/l, the light intensity is attenuated by a factor of $\exp(-4.6) \approx 1/100$.

The optical properties of the dyed resist at the lithographic exposure wavelength, e.g., at 436 nm, or "g-line" in lithography jargon, determine its performance as a resist for photolithography. Figure 2 shows the absorbance of resists that were neither exposed with UV light nor developed. The short wavelength portions of the curves in Fig. 2 show the absorbances at an unknown degree of exposure due to the absorbance measurements and the handling of the samples in room light. Since it is necessary to know how much the dye contributes to the absorption of the resist in the UV, resist-coated substrates were exposed with UV light at 436 nm (g-line) for 12 s with an intensity of about $27\ \mathrm{mW/cm^2}$. The resulting exposure dose of $324\ \mathrm{mJ/cm^2}$ was about twice the minimum dose required to fully expose (bleach) the resist. After exposure, the resist material has the absorbance shown by the dashed curve in Fig. 1. Any additional absorbance of the dyed photoresist is due to the added dye. This is clearly seen in Fig. 3, which shows that adding the dye to the photoresist increases its absorbance by about 0.2 at 436 nm when compared to the undyed resist.

The optical properties of unexposed, developed resist determine the properties of a hologram made from the dyed resist, because the resist has positive tone and exposed resist dissolves in the developer. Figure 4 shows the absorbances of unexposed and developed resist without dye and with dye at a concentration of 14.4 g/l.

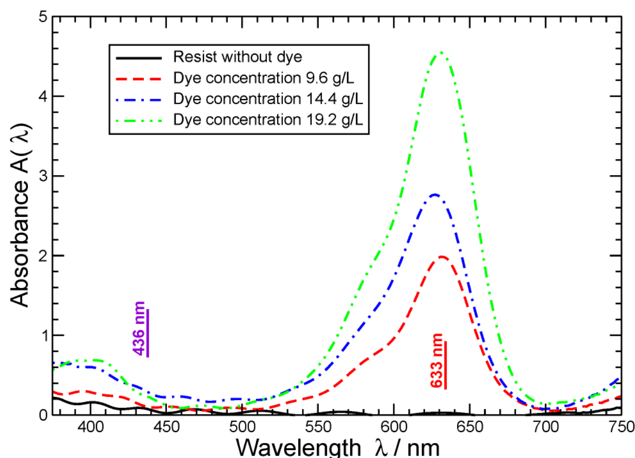

Fig. 2. (Color online) Absorbance of 1.8 μm thick photoresist layers containing different concentrations of dye. The uncertainty (1σ) of the absorbances is 0.025, or 2.5%.

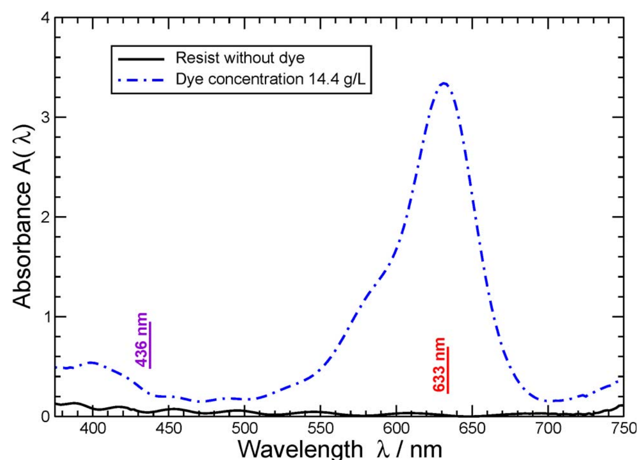

Fig. 3. (Color online) Absorbance of fully exposed, undeveloped photoresist with and without dye.

Resists were developed in a puddle for 70 s at 20 °C. The undyed resist becomes absorbant in the near UV after developing. The dye further increases the absorbance of the resist. However, in the red part of the spectrum, the absorbance of the resist is unaffected by the development process. The dyed photoresists were stable for at least several months. No change in the visual appearance of resist coatings or their absorbance was noticeable.

Fabricating smaller features generally requires thinner photoresist layers. The dye concentration must then be raised proportionally to maintain the absorbance of the resist. We found that increasing the dye concentration to about 38 g/l (380 mg dye dissolved in 10 ml resist) resulted in dye precipitation during spin coating and resist layers that could not be patterned with lithography. This suggests that it is not possible to obtain dyed resist layers with an absorbance of 4.6 and a thickness less than about 1 μm using this combination of resist and dye.

A Fresnel zone plate was fabricated using the dyed resist to demonstrate the performance of a binary amplitude hologram made from dyed resist with a standard photolithography process. Several substrates were coated with an approximately 1.8 μm thick layer of dyed photoresist at a concentration of 14.4 g/l in the liquid resist. A mask aligner was used to transfer a zone plate pattern with a focal length of 100 mm from a photomask

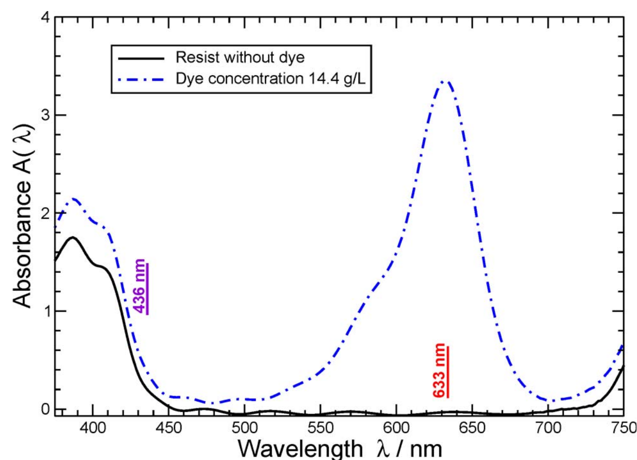

Fig. 4. (Color online) Absorbance of unexposed, developed photoresist with and without dye.

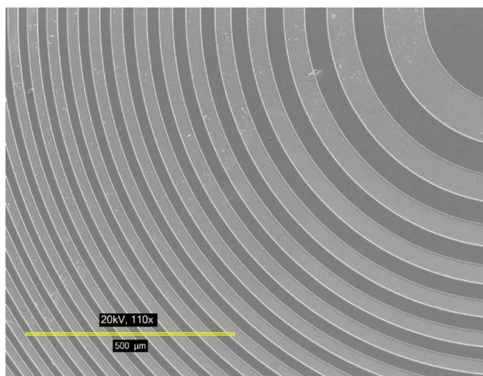

Fig. 5. (Color online) Scanning electron microscope image of a Fresnel zone plate made from dyed photoresist. The scale bar represents a distance of 500 μm.

to a resist-coated substrate with 25 mm diameter and 6 mm thickness. One of the zone plates was coated with gold and investigated with a scanning electron microscope. Figure 5 shows the central area of the zone plate. The dark rings in Fig. 5 are photoresist, in the light areas the resist is removed. The side walls of the resist areas are not vertical, because the dye increases the absorption of the resist at the exposure wavelength (see Fig. 1). This results in a vertical exposure dose gradient in the resist layer. The angle included between sidewalls and the vertical is about 20°. One of the zone plates was set up in a collimated beam of laser light with a wavelength of 633 nm. A screen was placed at the primary focal plane of the zone plate at a distance of 100 mm from the zone plate as shown in Fig. 6. The inset in Fig. 6 is a photograph of the back side of the screen.

In conclusion, we have demonstrated how modifying the optical properties of a photoresist can lead to a new process for fabricating diffractive optics with new properties. In this particular case, binary amplitude holograms were fabricated using a standard lithographic process from photoresist containing a suitably chosen absorbing dye. An obvious advantage is that a dyed photoresist simplifies the fabrication process because metal deposition and etching are both eliminated. Holograms that are intended for form metrology of precision surfaces, an important application of amplitude holograms, may benefit because fewer process steps improve pattern fidelity. Beyond amplitude holograms, controlling the absorption of the resist layer enables a new way of adjusting the diffraction efficiency of a hologram. It can be varied between ≈10% in the case of complete absorption and ≈40% when no dye is present and the hologram is a pure phase hologram. While holograms made from photoresist are more fragile than those made from a metal layer, they can be made more durable by heat treating, which results in hardening of the resist as a result of cross-linking of polymer chains in the resist.

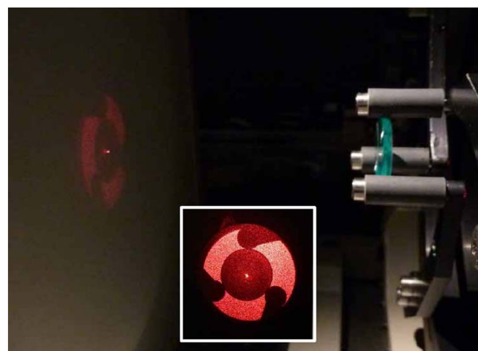

Fig. 6. (Color online) Focusing of a collimated laser beam with wavelength of 633 nm by a Fresnel zone plate with 100 mm primary focal length made from dyed photoresist.

The full description of the procedures used in this Letter requires the identification of certain commercial products and their suppliers. The inclusion of such information does not indicate that these products or suppliers are endorsed by National Institute of Standards and Technology (NIST) or are recommended by NIST or that they are necessarily the best materials or suppliers for the purposes described.

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