High Resolution Pattern Recording on Photosensitive Urethane-Urea Copolymer Film Surface by Laser Irradiation through Photo-mask

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1. Introduction
Optical nano-fabrication on organic films is attractive in the field of optical data storage, micro machining, photolithography, etc.\textsuperscript{[1]} Since near-field techniques overcome the diffraction limit of light by the contribution of evanescent wave, it is possible to fabricate nanometric structures or to store a bit-datum in a nanometric region. Many research groups have demonstrated the patterning of surfaces at resolutions below the diffraction either evanescent near-field optical lithography\textsuperscript{[2]} or an embedded-amplitude mask\textsuperscript{[3]}. Highly sensitive materials are required for optical near-field lithography, just as they are for optical near-field recording. In this study, we used an azobenzene-containing urethane-urea copolymer film\textsuperscript{[4]} for the high resolution recording media. A photo mask with a few hundred-nanometer was fabricated, and the pattern was directly transcribed on the surface of the urethane-urea copolymer film by visible laser recording.

2. Experiments and Results

\textit{Characteristics of urethane-urea copolymer as photosensitive material}

A material whose surface topography is modulated by the intensity distribution of light was required. In this research, a kind of azobenzene-containing urethane-urea copolymer was selected as recording material of the optical intensity distribution. The glass transition temperature (Tg) is 141 °C. The copolymer films were spin-coated onto clear microscopic glass slides. The absorption spectrum of the film was measured using a spectrometer, and found an absorption peak at 480 nm. We have fabricated holographic gratings on the films by irradiating Ar\textsuperscript{+} laser beam (488 nm) directly using simple interferometric setup in order to investigate the surface modulation of films. Figure 1 shows the depth of surface relief grating (SRG) as a function of laser illumination time, where grating period is 0.8 µm and light intensity is as high as 9.31 W/cm\textsuperscript{2}. Then, the heat treatment was carried out. The fabricated SRGs keep undulation profile although they were place into an oven heating at 150 °C, which is higher than the Tg of copolymer. Therefore, the copolymer has both good thermal stability and high resolution for nano-pattern recording.

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acetate and ethyl acetate. Then, the substrate was etched into Cr etching solution and the nano-patterned photo mask was fabricated. Figure 2 shows the topographic image of fabricated photo-mask with pit size of 580 nm measured with Atomic Force Microscopic (AFM). We have also fabricated a mask with smaller pit size of 400 nm.

**Replication of master pattern**

We placed the photo mask onto the urethane-urea copolymer film. The Ar⁺ laser at 488 nm was used as light source to illuminate the surface of urethane-urea film through photo mask. The illumination condition is as follows: light intensity was 255 mW/cm² and the exposure time was 180 sec. The intensity distribution of light passed through the photo-mask modulated the topography of the films. After illumination, the mask was moved and the surface profile of the copolymer films was measured by AFM. The topographic images of replication of master pattern measured by AFM were show in Fig. 3(a) and (b), while the polarization of incident light perpendicular and parallel to the plane of copolymer film, respectively.

**4. Conclusions**

High-resolution pattern from a photo-mask was successfully transcribed on the surface of azobenzene-containing urethane-urea copolymer films using optical recording by visible light illumination. By using a photo-mask with nanometer patterning, higher density recording by optical near field is possible. The nanofabrication technique is useful for optical data storage, and nanolithography.

Fig. 2 Topographic image of fabricated photo-mask measured by AFM.

Fig. 3 Topographic images of replication pattern measured by AFM on the surface of urethane-urea film as polarization of incident light perpendicular (a) and parallel to (b) the plane of copolymer film.

**References**