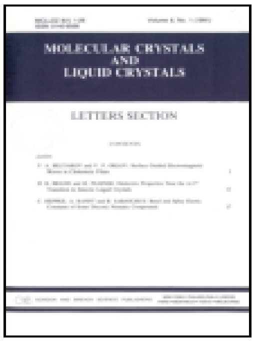

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Fabrication of moth-eye structure on photoresist film by laser control of reaction time constant

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ABSTRACT
We have proposed the fabrication of high-contrast-moth-eye structure using continuous wave (CW) laser. Nonlinear-optical reaction time constant of the photoresist can be controlled by manipulating the exposure intensity and scanning speed of the laser. As a result, shortening the time constant in the intense beam area and lengthening that in the weak beam area compared with the scanning speed, we can limit the exposed area.

KEYWORDS
CW laser; moth-eye; photoresist; nonlinear optics; reaction time constant

Introduction

The major method of high-contrast-moth-eye structure fabrication on photoresist film employs photolithography with electron beam (EB) lithography. The fabrication method with EB can be providing extremely high accuracy. However, the method, which needs vacuum chambers, is not suitable for manufacturing large mold at a low cost. Therefore, we propose CW laser on direct drawing methods by a third-order nonlinear optical effect. We fabricated a high-contrast-moth-eye structure on a positive type photoresist film. In general, the CW laser drawing tends to become a heat mood process, which decreases accuracy of fabrication. However, we focused on the nonlinear optical dynamics of the photoresist with triplet transition. Therefore, our method can fabricate fine structures in a photon mode process by controlling the reaction time constant of the photoresist.

Experimental and theorical backgrounds

Figure 1 shows an energy diagram of photoresists which absorb incident photons. ϕ_{1B} and ϕ_{2B} are quantum yields for stimulated transition between ground state (S_0) and excited state (S_1). The energy diagram defines the following rate equations for the photochemical reaction.

$$\frac{dN_1}{dt} = \sigma_2\phi_{2B}\frac{I_0}{h\omega}N_2 + \phi_{2A}N_2 - \sigma_1\phi_{1B}\frac{I_0}{h\omega}N_1 \quad (1)$$

$$\frac{dN_2}{dt} = \sigma_1\phi_{1B}\frac{I_0}{h\omega}N_1 - \sigma_2\phi_{2B}\frac{I_0}{h\omega}N_2 - \phi_{2A}N_2 - QN_2 \quad (2)$$

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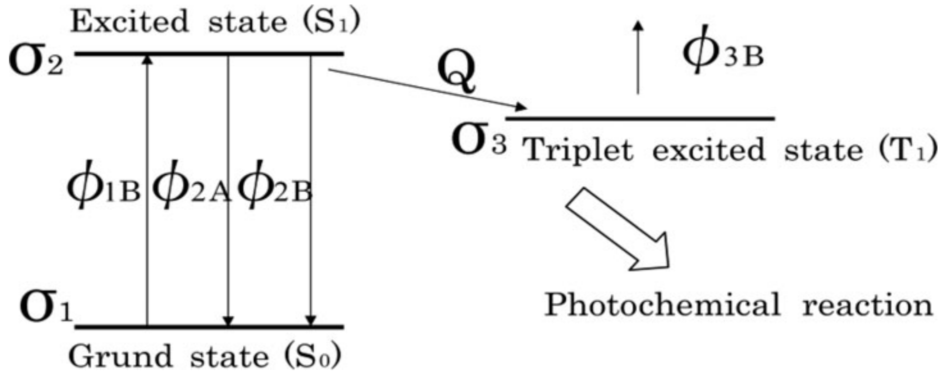

Figure 1. An energy diagram of photoresist.

$$\frac{dN_3}{dt} = QN_2 - \sigma_3\phi_{3B}\frac{I_0}{h\omega}N_3 \tag{3}$$

ϕ_{3B} is a quantum yield for stimulated transition for triplet excited state (T_1) to some upper states. ϕ_{2A} is a quantum yield for spontaneous transition from S_1 to S_0. Q is a triplet yield for S_1 to T_1. σ_1 and σ_3 are absorption cross-sections for S_0 and T_1, which may be defined as an absorption coefficient per unit inversion per unit volume. σ_2 is a stimulated emission cross-section for S_1. I_0 is a beam intensity. We assume that the transition from S_1 to T_1 is very fast, and the lifetime in T_1 is relatively long. In this case, reaction time constant τ is estimated

$$\tau = \left(\frac{\sigma_1\phi_{1B}}{\sigma_3\phi_{3B}}Q + \sigma_2\phi_{2B}\frac{I_0}{h\omega} + \phi_{2A} + Q\right)^{-1} \tag{4}$$

Under these conditions of general exposure using incoherent light sources, τ is approximately constant. This is because the second term including I_0 is smaller than other terms. However, if a laser is used as an exposure light source, I_0 becomes very large. In contrast, if the wavelength of the laser is sufficiently shifted from the resonance center of an absorption spectrum, σ_1 and ϕ_{2B} become very small. For that reason, we use positive type photoresist OiR-907-17, Fujifilm Arch product. OiR-907-17, which employs Novolak technology in g-line, is well known in the semiconductor exposure technology. The absorbance at a wavelength of 532 nm is sufficiently low (0.09). In this case, the transient photochemical reaction depends on the second term including I_0. Then the reaction time constant depends on beam intensity I_0.

We exposed the photoresist film with a 4.7-μm thickness to a focused SHG-YAG laser beam. Figure 2 shows a sensitometric curve of photoresist employed. The figure indicates that a dose dependence of residual film thickness measured over a 1.02–33.6 W/cm^2 beam intensity range. Also, we observed the change in the reaction time constant with the exposure beam intensity (see Fig. 3). By changing the beam scanning speed and the beam intensity, we estimated the time constant of photoresist from the details of the formed line pattern. The above two experiments determined the peek exposure beam intensity of 105 kW/cm^2. The exposure dose, which is expected to modulate the reaction time constant nonlinearly, is set at the center of the curve shown in Fig. 2. Then, shortening the time constant in the intense beam area and lengthening that in the weak beam area compared with the scanning speed, we can spatially limit the exposed area (see Fig. 3).

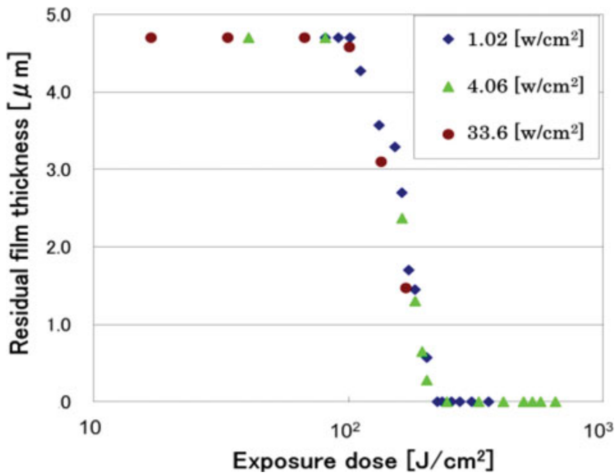

Figure 2. Profile of residual film thickness.

Experiment

The laser beam is focused through an objective lens (NA = 0.9), and the focal plane has 721 nm in diameter and 906 nm in focal depth. The peek exposure beam intensity and scanning speed are set to be 105 kW/cm^2 and 500 μm/s, respectively. The exposure beam at the scanning speed selected takes time approximately 1.4 ms to pass through the airy disk size. A moth-eye structure was fabricated on the photoresist film by sweeping the exposure beam toward x-axis and y-axis repeatedly (Fig. 4). From the details of the fabrications, the spatial resolution is up to 70 nm.

Results and discussion

Figure 5 (a) and (b) show photographs without and with moth-eye structures on the film. The reflection of the moth-eye film was greatly reduced. Figure 5 (c) is a part of Figure 5 (b) magnified. The moth-eye structures have hundreds of rows protrusions measuring peak-to-peak 1.7 μm and depth 2 μm. Despite the photoresist's surface being multi-exposed during

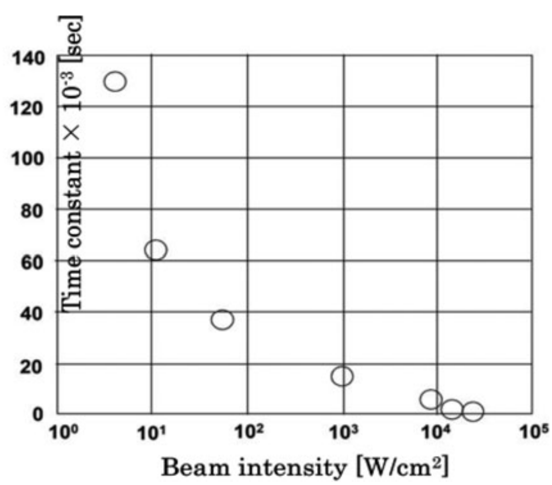

Figure 3. Profile of time constant curve curve on exposure dose of OiR 907-17 on beam intensity.

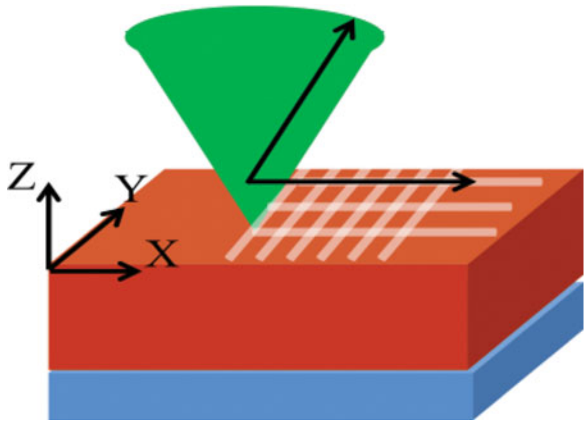

Figure 4. A schematic image of fabricating moth-eye structure.

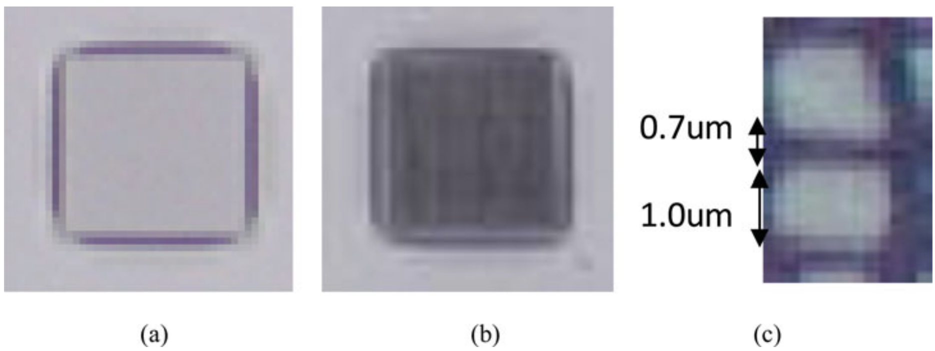

Figure 5. A photograph without and with moth-eye structures on the film.

the line drawing, we can expose the only center of the Gaussian beam. As a result, the moth-eye structures were fabricated on the photoresist by controlling reaction time constant of the photoresist.

Conclusion

We have fabricated moth-eye structures by manipulating photoresist's time constant nonlinearly. The reflection of the moth-eye film was greatly reduced. From this study, the antireflection film has been made easily.

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