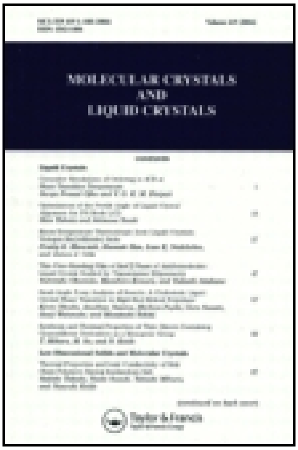

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DEVELOPMENT OF POLYSILOXANE ELECTRON BEAM RESIST FOR OPTICAL ELEMENTS

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DEVELOPMENT OF POLYSILOXANE ELECTRON BEAM RESIST FOR OPTICAL ELEMENTS

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Electron beam lithography is a highly flexible method that can be used to fabricate diffractive optical elements. However, the long exposure time required is the most serious point that needs addressing, and this is derived from the lack of sensitivity of the electron beam resist. We have investigated the physical properties of polydimethylsiloxane and poly(dimethylsiloxane-co-methylvinylsiloxane) for electron beam lithography. The results show that these polysiloxanes exhibit much higher sensitivities than the conventional substances, of 1.5 and 0.9 $\mu C/cm^2$*, respectively, and that they have a* γ *value of 1.3. Using these polysiloxanes, we succeeded in fabricating a four-level phase computer-generated hologram.*

1. INTRODUCTION

Electron beam lithography (EBL) is widely used in optics because it is a highly flexible method that enables the fabrication of innovative patterns that can potentially give high resolution results. Furthermore, continuous profiles can be realized by EBL [1]. For example, EBL allows diffractive optical elements (DOEs) for novel optics to be formed by a single process. A single process for making a DOE is very important, because optical aberrations can be minimized without any misalignment of the patterns [2].

The major problem with the EBL process is the long writing time required, which is derived from the lack of the sensitivity in conventional

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carbon-based electron beam resists (CEBRs). As in optical lithography, there are two types of electron beam resist (EBR): positive tone (polyacrylate-based resists) and negative tone (Novolac-based chemically amplified resists). For both positive and negative resists, EBRs are also divided into two further types: digital or analogue. Electron beam (EB)-exposed regions show perfect changes that are independent of the dosage for digital resists, whereas in the case of analogue resists, exposed regions change with dosage. Because of the shape of optics fabricated by EBL, analogue resists are the desired format. To develop novel resists and to fabricate DOEs by EBL, therefore, we examined the properties of polysiloxanes for EB applications as an alternative to CEBR to show that they can provided high sensitivities and an adequate γ (contrast) value. Also, we succeeded in fabricating a computer-generated hologram (CGH) by writing the relief structure (corresponding to the target Fourier plane) in these polysiloxanes. CGHs are DOEs that use diffraction to manipulate light [3].

2. EXPERIMENTAL

2.1. Synthesis of Polysiloxanes

Using a literature method, we prepared polydimethylsiloxane (PDMS, Fig. 1(a)) and poly(dimethylsiloxane-co-methylvinylsiloxane) (PMVS, Fig. 1(b) [4]. PMVS was prepared by mixing hexamethylcyclotrisiloxane and 1,3,5-Trimethyl-1,3,5-trivinyl-cyclotrisiloxane monomers in a molar ratio of 98:2. The molecular weights of both the PDMS and PMVS were determined to be

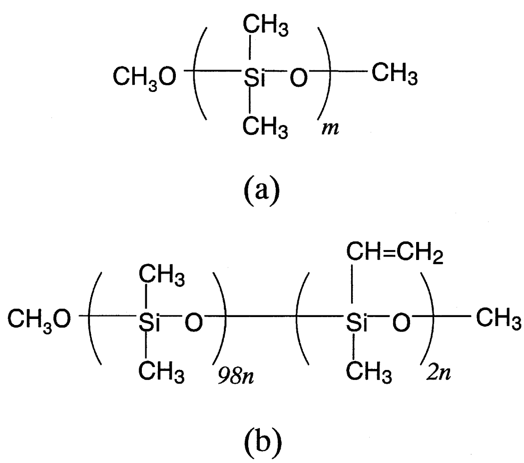

FIGURE 1 Fabrication process for optical elements by EBL.

400,000 (Mw/Mn = 80) by gel-permeation chromatography, using polystyrene as the standard. We did not attempt to carry out elemental analysis of these polysiloxanes, as this is generally unreliable owing to the high ceramic yields. All the organic solvents used in this study were of electronics grade, and were not subject to any further purification.

2.2. Evaluation

Polysiloxane films were obtained by spin coating onto a Si wafer (2000 rpm) from a toluene solution (3.5 wt%). The resulting film thickness was about 0.6 μm. These films were then heated to 170°C for 2 min on a hot plate. EB exposure was performed using a JEOL JBX-5000SI EB machine with an accelerating voltage of 50 kV and a current of 50 pA. The films were developed in an 8:2 tetrahydrofuran(THF)–acetonitrile (CH_3CN) solution.

2.3. Characterization of the Surface Topology

The film thickness of the polysiloxane films was determined using a ZYGO Inc., New-View 5020 profilometer.

2.4. Fabrication of the CGH

2.4.1. Synthesis of a Four-level Phase CGH

The target pattern of the synthesized four-level phase CGH was computed using an iterative Fourier transform algorithm [3]. The CGH pattern consisted of 512×512 pixels in the Fourier plane, with each pixel being $10\times10\,\mu m^2$.

2.4.2. Fabrication of the CGH

The fabrication of the CGH was accomplished using the following procedure (see Figure 2). A 1-μm PMVS film was obtained by spin coating onto a glass substrate that had an ITO surface film. This film was then heated to 170°C for 2 min on a hot plate. The CGH data were first transformed into EBL data using a computer program. Then, the programmed CGH data were written onto this film using EBL under an accelerating voltage of 50 kV and a current of 150 pA. To obtain a four-level phase, the dosage was modulated at 2.50, 1.07, 0.59, and 0 $\mu C/cm^2$ for each pixel to minimize the proximity effect [5]. The films were developed in an 8:2 THF–CH_3CN mixture for 1 min. The time of the EBL process for such a pattern lasted for ~30 min.

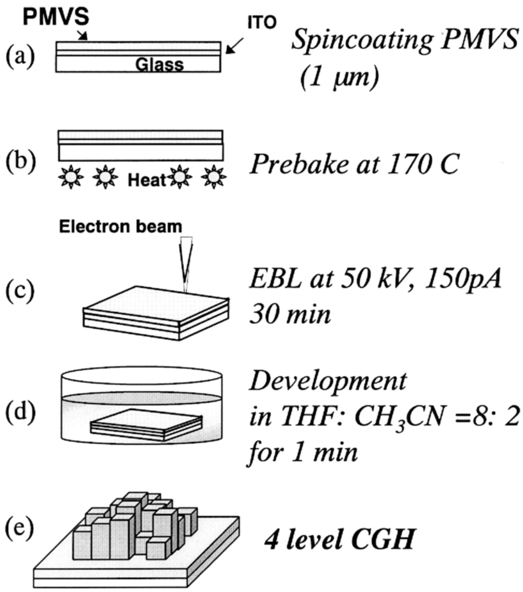

FIGURE 2 Structures of: (a) PDMS, and (b) PMVS.

3. RESULTS AND DISCUSSION

3.1. Resist Performance of the PDMS and PMVS

Figure 3 shows the EB sensitivity curves of PDMS and PMVS. From Figure 3, we found that the film depended on the dosage (i.e., the amount of developed region remaining after development increased with dosage), so both polysiloxanes were negative tone. We considered that the EB would generate a cross-linked three-dimensional network, which would be insoluble in the polysiloxanes. In this resist system, the dosage needed for half of the remaining saturated film thickness and the tangent at this dose were adopted as the sensitivity and γ value, respectively. From Figure 3, the sensitivity and γ value were 1.5 $\mu C/cm^2$ and 1.2 for PDMS, whereas those of PMVS were 0.9 $\mu C/cm^2$ and 1.3, respectively. These sensitivity values are *ca.* 100 times more than that of poly(methylmethacrylate) (the conventional CEBR). Also, the γ values obtained are adequate for fabricating optical elements. In general, we cannot fabricate optical elements easily for high γ values, as it is hard to control the remainder of the film by modulating the dosage after development (at *ca.* $\gamma = 3$ and above, the tangent at the dosage for half of the remaining saturated film thickness becomes too large). In contrast, we cannot fabricate optical elements easily when the

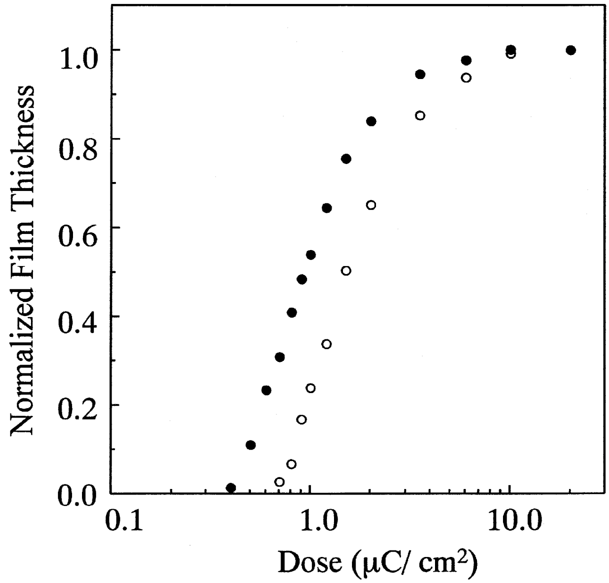

FIGURE 3 Sensitivity curves of PDMS (○) and PMVS (•).

γ value is too low (at *ca.* $\gamma = 1$ and below, the tangent at the dosage for half of the remaining saturated film thickness is too small). Accordingly, a γ value of 1–3 was required to fabricate the DOEs, and the obtained γ value of the polysiloxanes ($\gamma = 1.3$) was suitable for the fabrication of optical elements with an analogue tone.

3.2. Fabrication of the CGH

A CGH is a DOE that uses diffraction to manipulate light. CGHs have the ability to generate arbitrary patterns at the Fourier plane [3]. Using PMVS, we fabricated a four-level phase CGH on a glass substrate having an ITO film. The target pattern, the synthesized four-level phase CGH computed by the iterative Fourier transform algorithm, and the diffraction output of the synthesized CGH are shown in Figure 4. The CGH pattern consisted of 512×512 pixels in the Fourier plane (the example shown is our logo, TRI). To obtain four levels, we fabricated the relief structure to have four heights in the PMVS. In practice, from the data in (Figure 3), we performed EB writing at dosages of 2.50, 1.07, 0.59, and 0 $\mu C/cm^2$ for each pixel. These dosages were calculated to correct the proximity effect (to solve the shape-to-shape interactions) [5]. Because of the high sensitivity of PMVS, the EBL process for such a pattern was finished in ~30 min, whereas the EBL

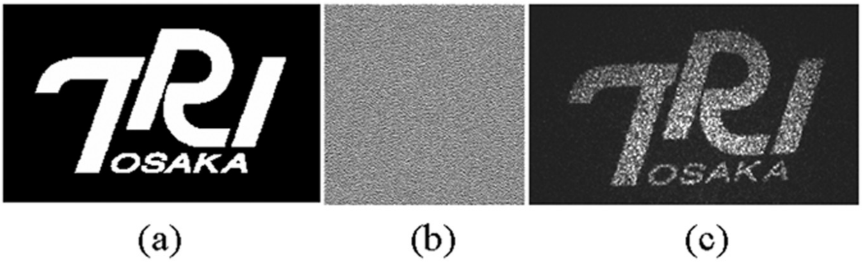

FIGURE 4 (a) The target pattern, (b) synthesized four-level phase-only CGH pattern, and (c) a reconstructed image captured by CCD camera when the fabricated CGH was illuminated with a He-Ne laser.

process would last ∼1 day if a CEBR was used. When the fabricated CGH was illuminated with a He-Ne laser, the reconstructed pattern shown in Figure 4 (c) was obtained. The phase modulations within the pixels of the CGH pattern are displayed by the brightness of a bitmap image, as shown in Figure 4 (b). Higher phase modulations correspond to brighter pixels. Comparing the target pattern in Figure 4 (a) with the reconstructed output of Figure 4 (c) reveals that a four-level phase CGH can reconstruct our target pattern. A CGH was also fabricated using PDMS.

CONCLUSIONS

PDMS and PMVS exhibited high sensitivities of 1.5 and 0.9 μC/cm^2, and had a γ value of 1.3, which was adequate for the fabrication of optical elements by EBL. Using these polysiloxanes, we succeeded in fabricating a four-level phase CGH on a glass substrate having an ITO film. As a result of their high sensitivity and adequate γ values, these polysiloxanes allow for the fast and easy fabrication of optical elements using EBL.

REFERENCES

[1] Kley, E. B. & Tunnermann, A., Optical surfaces fabricated by the use of e-beam lithography and their applications. Proceedings of 8th microoptics conference 2001, The Japan Society of Applied Physics: 296–299.

[2] Shiono, T., Hamamoto, T., & Takahara, K., High-efficiency blazed diffractive optical elements for violet wavelength fabricated by electron-beam lithography. Proceedings of 8th microoptics conference 2001, The Japan Society of Applied Physics: 300–303.

[3] Yu, W., Takahara, K., Konishi, T., Yotsuya, T., & Ichioka, Y. (2000). Fabrication of multilevel phase computer-generated hologram elements based on effective medium theory. *Appl. Opt.*, *39*, 3531–3536.

[4] Japan Chemical Society: Shin Jikken Kagaku Koza 29, Kobunshizairyo. Tokyo: Maruzen: 1993; 205–212.
[5] Kratschmer, E. (1981). Verification of a proximity effect correction program in electron beam lithography. *J. Vac. Sci. Technol.*, *19*, 1264–1268.