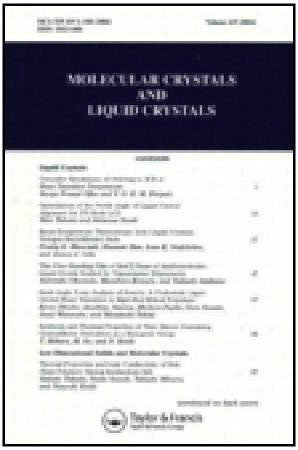

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Fabrication of Channel Waveguide and Submicron $\chi^{(2)}$ Grating by Direct Electron-beam Writing Method in Azo-dye-substituted Polymer

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Fabrication of Channel Waveguide and Submicron $\chi^{(2)}$ Grating by Direct Electron-beam Writing Method in Azo-dye-substituted Polymer

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The study of poled azo-dye-substituted polymers using direct electron-beam exposure technique is demonstrated. The mechanism of absorption spectrum change and decay of nonlinearity of polymer films via direct EB irradiation are investigated. Channel waveguide and submicron $\chi^{(2)}$ grating are successfully fabricated.

Keywords: direct electron-beam writing; azo-dye-substituted polymer; second-order nonlinearity; $\chi^{(2)}$ grating;

INTRODUCTION

Organic nonlinear optical (NLO) materials have attracted much interest because of their large second-order nonlinearity, high speed response, possibility of various molecular designs and potential application for electro-optic (EO) devices[1]. Recently, the technique to create a waveguide-type device for application such as an EO modulation[2] or frequency conversion[3] in poled polymer film has gained attention. Especially $\chi^{(2)}$ grating structure is an important and attractive component in order to realize the quasi-phase-matching (QPM), EO tunable Bragg grating, and nonlinear coupling. Several methods have been demonstrated to create the periodic modulation of $\chi^{(2)}$

grating in polymer films: periodic poling[3], UV-photobleaching[4] and direct laser beam writing[5]. On the other hand, the direct electron beam (EB) writing technique[6] has advantage over other techniques. Recently, our group has proposed the fabrication of the NLO channel waveguides and $\chi^{(2)}$ gratings on the order of 100μm with thin guest-host polymer films[6],[7] by direct EB irradiation technique. As far as we know, there have been very few reports of high resolution $\chi^{(2)}$ pattern using poled polymer films. In this paper, we report our studies of the EB exposure properties and absorption spectrum change of a side-chain type polymer with larger second-order nonlinearity than previous guest-host polymers. Moreover, optical waveguide and submicron $\chi^{(2)}$ diffraction grating via direct EB writing are fabricated.

EXPERIMENTAL

The polymer we investigated is a kind of azo-dye-substituted polymer named 3RDCVXY [1]. First, the polymer films were obtained by spin coating of 3RDCVXY solution on clean microscope slides. The thickness of 3RDCVXY films could be controlled from 0.5μm to several micrometer. Since the solvent remaining in films had a strong influence on stability of the films, which were put on a hot-plate at 140°C for 60min. Next, the corona-poling process was carried out at 130°C by applying a DC electrical field of 10kV for 10min. The poled films were cooled down, maintaining the electric field, to room temperature, and the electrical field was removed. Then, a conductive EB resist was spin-coated onto polymer films in order to eliminate the charging effect during EB exposing. Finally, the samples were introduced into an EB lithography system with accelerating voltage of 25kV. The beam current was kept at 0.1nA for an EB spot diameter of 30nm.

RESULTS AND DISCUSSION

1. Characteristics of 3RDCVXY by EB Exposure

PMMA is the main chain of 3RDCVXY, which has been well studied as a positive resist for EB lithography[8], thus the commercially available developer and conventional technique could be used in the process of 3RDCVXY. First, we studied sensitivity characteristics of 3RDCVXY films processed by EB irradiation. After exposing, the films with 2.65 μm thickness were wet-developed by the mixture of isoamyl acetate and ethyl acetate for 1.0, 1.5 and 2.0min, respectively, then rinsed by dipping into deionized water for 2.0min. The depth after development depending on exposure dose is shown in Fig. 1.

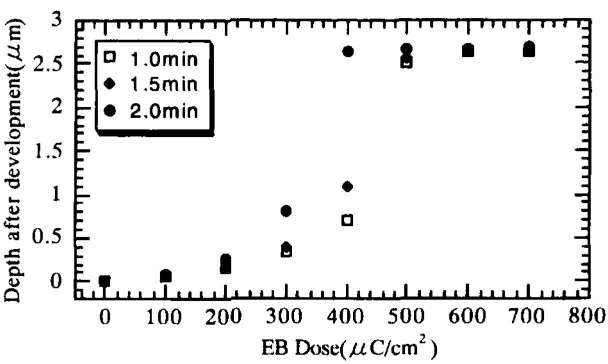

FIGURE 1 EB sensitivity of 3RDCVXY at different development time.

As it is readily shown the depolymerization behavior is nonlinear with respect to the exposure dose. The penetration depth is 2.65 μm at 500 μC/cm^2, which is the same as the thickness of film. This means the complete depolymerization was obtained through the film.

2. Absorption Spectrum and SH Intensity Measurement

Next, we studied the absorption spectra of 3RDCVXY film using a spectrometer; the absorption spectra measured at different conditions are shown in Fig.2. After applying electrical field onto the polymer at temperature higher than T_g, chromophores orientate to the direction parallel to the direction of electrical field, resulting in the decrease of peak absorption. In Fig.2, the absorption peak in line 2 (after poling) becomes lower than that in line 1 (before poling). Then that in line 3 (irradiated with 30 μC/cm^2) is higher than that in line 2, and that in line 4 (irradiated with 250μC/cm^2) is less than that in line 2. Moreover, there shows no charge-transfer (CT) band in line 5 (irradiated with 800μC/cm^2).

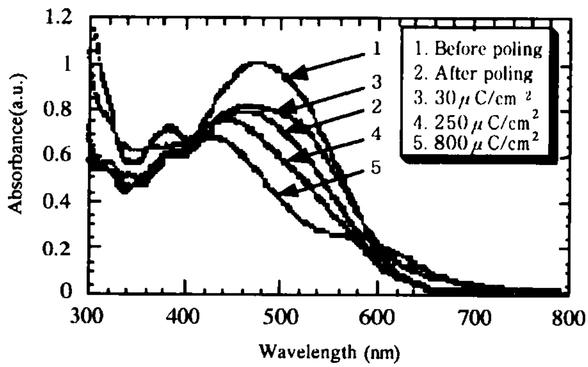

FIGURE 2 Absorption spectrum measured at different EB dose.

3. Fabrication of Channel Waveguide and Submicron $\chi^{(2)}$ Grating

Then, second-harmonic (SH) intensity of the poled polymer films was measured with the Maker-fringe technique using a Q-switched Nd:YAG laser (1064nm). The polarization of both input fundamental wave and output SH wave was set as p wave. At exposure dose 200μC/cm^2 condition, only 20% SH intensity remained. And we could not observed any SHG signal at 600μC/cm^2, which means the second-order nonlinearity of the poled polymer is completely erased. According to the results, suggesting mechanism of the erasure of second-order nonlinearity by EB exposure in the poled polymer is: (1) The instantaneous high temperature results and the depolymerization of the main chain resulting from the EB irradiation induces the NLO chromophores to orient back to their natural isotropy under high-sensitivity conditions. (2) NLO chromophores are destroyed by the long-time EB exposure.

These results enabled us to fabricate the channel waveguide and the $\chi^{(2)}$ grating. Variety of waveguides designed with CAD system were fabricated. Fig. 3 shows the microscopic photograph of actually fabricated bending-type channel waveguide (single-mode). Moreover, we tried to fabricate the submicron $\chi^{(2)}$ grating in poled 3RDCVXY films with the film thickness of

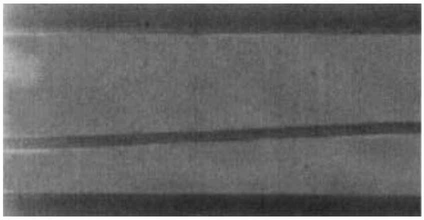

FIGURE 3 Photograph of bending-type channel waveguide.

0.8μm. EB dose was set at 300μC/cm^2, development time was 1.5 min. Fig.4(a) shows the atomic force microscopic (AFM) photograph of a $\chi^{(2)}$ grating. The grating was obtained with the period of 0.61μm and the depth of 150~200nm for the designed period of 0.60μm.

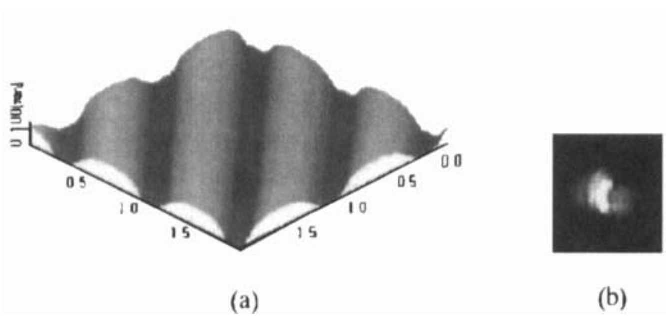

FIGURE 4 (a) AFM photograph of submicron $\chi^{(2)}$ grating.
(b) Photograph of SHG signal spot.

The SHG was observed as shown in Fig. 4(b) from the grating area by inserting the fundamental wave, and the transmitted SH power was about 40% in comparison with that generated from the poled area without EB irradiation, suggesting that there still remains the second-order nonlinearity in the grating area. These results indicate that the $\chi^{(2)}$ grating with sub-micron period in 3RDCVXY polymer thin film was successfully realized.

CONCLUSION

The linear and nonlinear characteristics of a poled azo-dye substituted polymer film processed by direct EB irradiation and the possible application to fabricate waveguide-type optical devices were investigated. Second-order nonlinearity of poled film could be erased by direct EB exposure The mechanism of absorption spectrum change and the decay of second-order nonlinearity in the poled azo-dye-substituted polymer films via EB exposure was suggested. Channel waveguide and submicron $\chi^{(2)}$ grating were successfully fabricated. In addition, further research is necessary to obtain the optimum condition for high resolution $\chi^{(2)}$ pattern with high aspect ratio. We believe that this simple, effective direct EB writing can be applied to the fabrication of polymer-based optical waveguide devices.

Acknowledgments

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References:

[1.] Y. Shuto, S. Tomaru, M. Hikita, M. Amano, IEEE J. Quantum Electron., **31**, 1451 (1995).
[2.] J .Thackara, G. F. Lipsconrb, M. A. Stiller, A. J. Ticknor, and R. Lytel, Appl. Phys. Lett., **52**, 1031 (1988).
[3.] G. Khanarian, R. A. Norwood, D. Haas, B. Feuer, and D. Karim, Appl. Phys. Lett., **57**, 977 (1990).
[4.] G. Rikken, C. Seppen and S. Nijhuis, Appl. Phys. Lett., **58**, 435 (1991).
[5.] X. Ni, M. Nakanishi, O. Sugihara, and N. Okamoto, Opt. Rev., **5**, 9 (1998).
[6.] H. Nakayama, O. Sugihara, and N. Okamoto, Opt. Lett., **22**, 1541 (1997).
[7.] H. Nakayama, O. Sugihara, and N.Okamoto, Appl. Phys. Lett., **71**, 1924 (1997).
[8.] M. Rooks, H. Roussell, and L. Johnson, Appl. Opt., **29**, 3880(1990).