Preparation of Optical Waveguide by Dispersal of Compound with a Higher Refractive Index

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The waveguide was fabricated by dispersal of a compound with a higher refractive index into poly(methyl methacrylate). Preparation of the waveguide was performed by the vacuum process. The doped region showing the higher refractive index acted as a core and non-doped matrix PMMA surrounding the core acted as a cladding layer. The refractive index of core was controlled by the treatment temperature. As the waveguide prepared in the present study possessed a large core size, it was favorable for the short-range optical network.

Keywords: vapor, refractive index, organosilicon compounds, optical transportation medium

1. Introduction

Multimode waveguides comprised of a large core structure on cladding is necessary for access of network optical communication devices or optical interconnection technologies. Among the waveguides, polymeric waveguides (POWs) have attracted much interest because of cost effectiveness compared with conventional silica-glass optical waveguides. There have been various reports of fabrication processes for POWs, such as a photolithography, a reactive ion etching method,[1-3] a UV-direct patterning,[4] a photobleaching,[5] an electron-beam direct writing,[6] a hot embossing,[7] and a molding[7, 8].

Among these processes, the fabrication technique employing the mold has a potential for POWs with large core at a size of more than 100 μm. In the mold process, so far masters are fabricated by the LIGA (A German acronym for three step processes of a lithography, an electroforming and a molding) or the SIGA (A German acronym for a silicon micro-machining, an electroforming and a molding) process.[8] As the masters require a number of expensive processes, these are, therefore, very expensive. The fabrication processes of waveguides and related components are anticipated to be easier and be more inexpensive.

We have developed a novel method of organic thin-film preparation termed the “vapor transportation method.”[9-15] This method enables us to add functions such as color, surface energy, and electrostatic properties to polymers while retaining initial shapes. Furthermore, the characteristics of the polymers can also be controlled. In this method, a dye is first sublimated in a vacuum ampoule. Then, vaporized molecules of the dye diffuse in the vacuum ampoule under thermal equilibrium. Finally, molecules of the dye are dispersed into the polymer. This method enables us to prepare a polymer film, in which functional organic molecules are densely dispersed, and the dispersion depth and quantity of the dopant are tunable by varying the treatment temperature and time. In addition, it is possible to selectively disperse a dopant into polymers.

It is important to be able to control the refractive index of a polymer, which is a key technique for the fabrication of optical components using the polymers.[16-18] Waveguides, lenses, gratings, and holograms can be prepared by the refractive index modulation. The present process has advantages for fabrication of an optical medium in points described follows: 1) dispersal of
a pure dopant into a polymer similar to sublimation purification, 2) molecular dispersal without deformation of the initial shape, and 3) do not require expensive equipments because of a simple process.

In our previous works, preparation of the waveguide involved the molecular dispersion of a low-molecular weight compound with a low refractive index into a polymer rod, and the dispersed region functioned as a cladding layer and the center of the rod (the non-doped region) was the core.[10,15] Furthermore, the dispersal behavior was evaluated in these works, resulting in the information that the concentration of the dopant was uniform throughout doped region. This meant that the prepared waveguide showed a step index.[15]

Reported here is the formation of the waveguide core by the vapor transportation method as further developments of the waveguide preparation, i.e., the waveguide fabrication was carried out by the molecular dispersion of a low-molecular-weight compound with a high refractive index into a polymer plate.

2. Method

Poly(methyl methacrylate) (PMMA: Mitsubishi Rayon; Mw, 5 ~ 6 million) was used as a matrix polymer showing a refractive index (n_d) of 1.491 and phenyl benzoate (PB: obtained from TCI co., LTD.) was employed as a dopant whose n_d was 1.58. Fig. 1 shows the chemical structures of the compounds used in the present study, and Fig. 2 shows the schematic representation for sample preparation. The PMMA plate measuring approximately 1 x 1 x 40 mm³ was covered by a mask; the opening between masks was several hundred micrometers. The PMMA plate with the

![Chemical structures of the compounds used in the present study.](image)

mask was treated by the vapor transportation method as follows (see Fig. 2b). The plate with mask was placed in a φ15 mm glass tube with a sufficient amount of PB. PB was used without further purification. The pumped pressure in the tube decreased using a turbo molecular pump. After a final pressure of around 10^-6 Pa was reached, the glass tube was sealed by melting to form an ampoule. While the ampoule was set at a constant temperature in an oven, the vaporized PB filled the ampoule. The masked PMMA plate was exposed to the PB vapor in the ampoule. The vapor came into contact with the polymer surface through the opening of the mask and dispersed gradually into PMMA. BP dispersed into the linear region of the plate through the linear
opening, followed by putting another PMMA plate on the doped one under vacuum heating (see last sentence in Figure 2a).

3. Results and discussion

A cross section of the resulting sample is shown in Fig. 3. As shown in Figure 3, an optical medium with a transparent double-layered structure was prepared in the present study. The dispersal of BP with a high refractive index produced this structure, and the refractive index of the core formed by doping was clearly different from that of the cladding layer. As dispersion by the present method was isotropic, even if the PB vapor made contact with the PMMA in the restricted surface, the dispersal area would have become larger than the limited area. The width of doped region was larger than that of the mask gap causing the formation of the elliptic core. Observation of a cross-sectional surface under the phase contrast microscopy revealed a homogeneous pattern throughout the doped layer. Furthermore, the interface between the doped layer and the non-doped layer was apparent, and it was assumed that the doped layer did not show a graded index but a homogeneous refractive index. The vapor transportation method was characterized by homogeneous concentration of the dopant in the doped region. In our works, the uniform concentrations of each dopant in organofluorine compound/PMMA,[15]cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)-ethane (CMTE)/ polycarbonate, CMTE/ PMMA, and CMTE/polystyrene (PS)[9] were observed.

The time dependencies of dispersion depths (mean the core radius) of PB were evaluated at various treatment temperatures, as shown in Fig. 4. The radius of core is indicated upside of Fig. 4. The radius of the core was measured by the observation with a phase contrast microscope equipped the micro scale. The phase constant microscopy enables us to recognize difference in the refractive index of the mixture even though colorless sample. As shown in Fig. 4, the dispersion depths of PB increased simply with increasing treatment time. It took 10 h for the formation of a region of 400 µm doped with PB at 140 °C, while doped region progressed to no more than 100 µm at 90 °C. The increase in dispersion depth of PB became larger in the order
of the treatment temperature; 90 °C < 110 °C < 120 °C < 140 °C. Behavior shown in Figure 4 appeared commonly in our previous work reported.[9,10,14] The organic photochromic dye, CMTE, was dispersed in various polymers, such as PMMA, PC, and PS. The curves showing CMTE dispersal into these polymers are similar to the curve in the present study.[9] The slope of the curve at 140 °C was much larger than that of the curves at other treatment temperatures. PMMA used in the present study showed glass transition temperature (Tg) of 120 °C. At treatment temperature of 140 °C above Tg, the core radius increased dramatically with treatment time.

Fig. 5 shows radiuses of the core as a function of treatment radius. The core radius increased with treatment temperature in every treatment time as shown in Fig. 5. The curve of 12 h treatment time was similar to the profiles of curves in other treatment times; the profiles of three curves showed an exponential growth as temperature increased. Slopes of the lines changed above Tg in every treatment time, i.e., the slope above Tg was larger than that below Tg. Our previous works reported the dispersion depths as a function of temperature in a variety of experiments.[9,12-14] In the CMTE dispersal into PMMA or PS, dispersion depths increased as temperature approached Tg, but dropped above Tg.[9] On the other hand, dispersion depth of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)4H-pyran (DCM) in photo-polymer also increased slowly as temperature came near to Tg and increased steeply above Tg.[14] Dispersion behavior in the present method and its mechanism have been under investigation but not yet clear.

We measured PB concentration against treatment temperature. PB concentration was measured by increase in weight after complete dispersion of PB in the PMMA plate. No aggregation of PB was observed even at 35 wt% in the PMMA (at 140 °C). The PB concentration increased linearly as temperature rose. As the saturated vapor pressure rises with temperature, more PB molecules vaporized come in contact with PMMA surface and permeate into the surface of the PMMA plate.

We confirmed a beam incident on the edge of the doped layer (g ~1000 μm) of the prepared sample emerged from the other edge. When the medium prepared in the present study was rotated around the center of the edge, light propagated from the center of rotation as repeated reflections on the interface between the doped layer and the cladding (non-doped region), reconfirming that the doped layer functioned as a core, i.e., the medium acted as a waveguide.

Fig. 6 shows the refractive indices of PMMA plate doped with PB. The refractive indices were reflected on the PB concentrations. The refractive indices were measured with the refractometer (ATAGO) for the PMMA plate coped completely with PB. As another method (see Fig. 7), the refractive index of the doped layer (core) was calculated by Snell’s law as shown in Equations (1) and (2); evaluated from the refractive index of the cladding (as was the non-doped region, corresponding to a PMMA refractive index of 1.491) and the critical angle, β. The measurement wavelength was 589 nm due to parallel light of d ray in Na. The angle, β, was determined by rotating the sample, where α is the rotation angle:

$$\sin \alpha/\sin \beta = n_{\text{core}}/n_{\text{air}}$$  
$$\sin (\pi/2-\beta) = 1.491/n_{\text{core}}$$

Fig. 6. Temperature dependence of the refractive index of the core.
There was no appreciable difference between use of the refractometer and calculation by Snell’s law. The refractive index of doped region increased simply with temperature. The refractive indices showed 1.510 and 1.521 at 110 °C and 140 °C, respectively. As non-doped PMMA showed 1.491, rise in the refractive index was 0.03.

We also measured the refractive indices of the core against treatment time at various treatment temperatures. The refractive indices of cores by doping with PB remained unchanged without reference to the treatment time. As the saturated vapor pressure of PB varies with temperature but do not change with the treatment time, the refractive index of the core did not change with the treatment time. No change of refractive index was observed even above Tg at 140 °C. These results indicate that the refractive index of the cladding is controlled by only the treatment temperature.

The relationship to total loss and waveguide length in the same input power was measured in order to estimate the propagation loss of the waveguide in the present study. The resulting loss was 0.44 dB/cm.

4. Conclusion

In conclusion, optical transportation media were fabricated by a novel method using the vacuum transportation technique termed the “vapor transportation method,” producing a core by dispersion of PB with a high refractive index into a PMMA plate. The radius and the refractive index of the core were controllable by treatment temperature and time. Recently, materials with a low optical loss and a controllable refractive index are required for optical waveguides in such devices as optoelectronic integrated circuits.[19] Thus, it is assumed that this technique enables us to prepare the integrated circuits on a polymeric board as well as waveguides.

References

