A Novel Fabrication Method of Optical Transportation Media Using a Vacuum Transportation Technique

Hiroyuki Mochizuki, Toshiko Mizokuro, Noritaka Yamamoto, Nobutaka Tanigaki, and Takashi Hiraga

Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Midorigaoka 1-8-31 Ikeda, Osaka 563-8577

Keywords: refractive index, optical transport media, vacuum technique, vapor transport

1. Introduction
Expanding optical fiber network systems to a communication infrastructure,[1] polymeric optical devices have attracted much attention and interest due to high processability.[2-5] Reactive ion etching[6,7] and interfacial-gel polymerization[8] have been developed to define a polymeric optical waveguide and a graded-index polymer optical fiber (POF), respectively. However, these methods require time, highly-skilled techniques and some complicated processes. In recent, the fabrication processes of POF, waveguide, and the related components are presumed to be easier.[9,10]

We have added our energy to development of a novel method of organic thin film preparation termed “vapor transportation methods”. [11-13] This method enables us to add functions such as colors, surface energy, and electrostatic property to polymers with retaining initial shapes, further, characteristics of the polymers could be controlled. In this method, first, a dye is sublimated in a vacuum ampoule. Second, gas molecules of the dye diffuse in the vacuum ampoule under thermal equilibrium state. Final, the molecules of the dye dispersed into a polymer. By this method, we could prepare a polymer film, in which functional organic molecules are densely dispersed.

In this study, we prepare an organic optical transportation media by the vapor transportation method as a novel process and show here characteristics of the media. This process possesses preferable properties for fabrication of an optical media such as 1) dispersion of a pure dopant into a polymer like a sublimation purification; 2) molecular dispersion without deformation of initial shape. Preparation of an optical media is molecular dispersion of a low-molecular weight compound with a lower refractive index into a polymer plate, so that, the dispersed region plays a role as a cladding and a center of the plate, a non-doped region, is a core.

2. Method
The schematic presentation for preparations of samples in this method is displayed in Fig. 1(a). A test piece, which was made from poly(methyl methacrylate) (PMMA; Mitsubishi Rayon; Mw, few million) and approximately 5 x 5 x 40 mm³ in size, was loaded in a φ15 mm glass tube with a sufficient amount of the organofluorine compounds (about few ml). Some organofluorine compounds (Tokyo Chemical Industry Co., LTD.; see Fig. 1(b)) were chosen as models for evaluations of the present method and were employed without further purification. The pumped pressure in the tube was steeply decreased by using a turbo molecular-pump (V70; Varian Vacuum Products) as shown in Fig. 1(a). In pumping, these organofluorine compounds were cooled down by liquid N₂ in order to decrease vapor pressure of the compounds because these melting points are below room temperature. After an ultimate pressure of around 10⁻⁶ Pa was reached, the glass tube was sealed by melting to form an ampoule. The ampoule was set in a constant temperature, and then cooled down slowly over several hours. During the ampoule in an oven at a constant temperature, the vaporized organofluorine compounds filled the ampoule because the
treatment temperature is above each boiling point of the organofluorine compound under a base pressure of about $10^{-6}$ Pa.

![Diagram](image)

Fig. 1. a) Schematic representation of vacuum apparatus used for making the glass ampoule; LN: liquid nitrogen, OF: organofluorine compound, S: sealing after pumping, V: vacuum pump, V.T.: vacuum transportation. b) Chemical structures of the compounds used in this study.

3. Results

It is evident, as shown in Fig. 2, that an optical media with a transparent double-layered structure was formed by the method in this study. This demonstrates that the dispersion of ethyl heptasterobutylate (EH; b.p. 96 °C; n₂₀, 1.302) with a lower refractive index produces this structure, and the refractive index of the core, which was non-doped, is clearly different from that of the cladding.

As characteristics of the optical media prepared by this method need to be clarified, thickness of the cladding, namely, dispersion depths of the organofluorine compound were measured. Measurements of dispersion depths of the organofluorine compounds into the PMMA plates were performed with a phase contrast microscope equipped a micrometer scale in a stage. A detailed mechanism of dispersion of the organofluorine compound into PMMA is under investigation. Observation of cross-sectional surface with the phase contrast microscope gave a result that homogeneous pattern was in the doped layer. Further, an interface between the doped layer and the non-doped layer was clearly observed, so that, it is assumed that the doped layer does not show a graded-index but a homogeneous refractive index. Dispersion depths of EH into the PMMA plate by thermal treatments are exhibited in Fig. 3. As shown in Fig. 3, the thickness of the doped layer in the PMMA plate increased with temperature. It is well known that a saturated vapor pressure increases with temperature. As temperature increasing, more gas molecules of EH exist in the ampoule and contact the surface of the PMMA plate, thus, molecules of EH are considered to permeate more deeply into the PMMA plate. As an initial PMMA plate showed a glass transition temperature (Tg) at 120 °C, EH could disperse into PMMA even below Tg, as demonstrated in Fig. 3.

Next, optical characteristics of the media were...
evaluated. We confirmed that a beam incident of an edge of the core of the prepared optical media emerged from the other edge (see Fig. 4). When the prepared media in this study was rotated around the center of the edge, light propagated

\[
\begin{align*}
\text{Depth (mm)} & : 0.7 \quad 0.6 \quad 0.5 \quad 0.4 \quad 0.3 \quad 0.2 \quad 0.1 \\
\text{Temperature (°C)} & : 100 \quad 110 \quad 120 \quad 130 \quad 140 \quad 150 \quad 160
\end{align*}
\]

Fig. 3. Temperature dependence of the dispersion depth of EH into PMMA after 24 h.

\[
\sin(m/2-\beta) = x/1.491 \\
sina/sin\beta = 1.491
\]

Fig. 4. Schematic representation for measurements of the indices of the claddings.

From a rotation center as repeated reflections on an interface between the doped layer and the core, suggesting that doped PMMA functioned as a cladding. A refractive index of the cladding was calculated by Snell’s law as shown in Fig. 4, namely, evaluated from the refractive index of the core (1.491) and a critical angle \( \beta \). \( \beta \) was determined by rotating the sample, where \( \alpha \) is a rotation angle. When the angle was above \( \beta \), light did not propagated in the media. According to results of evaluation for refractive indices of the cladding as a function of temperature, the refractive indices of the claddings prepared by dispersions with EH and 2-propyl trifluoroethanate (PT; b.p. 73 °C/749mmHg ; \( n_\infty \) 1.319) lowered with increasing temperature. As described above, the saturated vapor pressures of EH and PT increase with temperature, meaning that more molecules of EH and PT permeate into the surface of the PMMA plate. It is clarified that the concentrations of EH and PT in the doped layer increase with temperature, namely, the refractive indices decrease. On the other hand, it was found that the refractive indices did not vary with treatment time, as shown in Fig. 5. Fig. 5 shows time dependence of the refractive indices of the cladding at 150 °C. While the refractive indices increased with temperature as mentioned above, they remained unchanged with treatment time. This results mean that the saturated vapor pressures of EH and PT do not vary with treatment time. In recent, by heat drawing of the waveguide at ~190 °C, a fiber could be obtained.

\[
\begin{align*}
\text{Refractive index} & : 1.46 \quad 1.47 \\
\text{Time (h)} & : 10 \quad 15 \quad 20 \quad 25
\end{align*}
\]

Fig. 5. Time dependence of the refractive indices of the cladding formed by the dispersion of each organofluorine compound. Open square, PT; closed circle, EH.

4. Conclusions

In conclusion, an optical transportation media was fabricated by a novel method using the vacuum transportation technique termed “vapor transportation method”, giving a cladding by dispersion of organofluorine compounds with a lower refractive index into a PMMA plate. The thickness and the refractive index of the cladding were controllable by treatment temperature and time. In recent, materials with a low optical loss and a controllable refractive index are required for
optical waveguides in such devices as optoelectronic integrated circuits. Thus, it is assumed that this technique enables us to prepare the integrated circuits on a polymeric board as well as the waveguide.

References