Fluorinated Polyimide/Epoxy Hybrid Material for Fabrication of Optical Waveguide by Single-step Photo-patterning

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Introduction: Optical waveguides using fluorinated polyimide (PI), benzocyclobutene and poly(arylene ether sulfide) have been investigated to improve not only propagation losses, but also thermal stability and long-term durability. Among these polymers, PIs have been widely used in micro- and opto-electronics industries because of their thermal stability, mechanical strength, chemical resistance, and good processability. Furthermore, fluorinated and perfluorinated PIs have been widely developed as optical waveguide materials due to their low water sorption and high transparency in the visible and near-IR regions. The polymer optical waveguides have been fabricated by the conventional photo-lithographic procedures, consisting of multi-step processes of photo-resist patterning, development using aqueous or organic solvents, and dry- or wet-etching. There have been demands for ‘Single-step photo-patterning’ procedures for direct fabrication of channel-type waveguides without using photolithographic procedures (i.e. photo-resist patterning, developing and dry-etching). Single-step photo-patterning is highly advantageous in process efficiency, manufacturing cost, and environmental friendliness.

Experimental: DMAc solution of poly(amic acid) (PAA) of 6FDA/DCHM was prepared by mixing equimolar amounts of the source materials. The corresponding poly(amic acid silylester) (PASE) was prepared by the in-situ silylation method using BSTFA as a reagent. An equimolar amount of epoxy compound (CEL-2021, Daicel Chem. Ltd.) was then added to PASE and PAA solution, and a photoacid generator (PAG, Midori Chem.) was added to PASE/epoxy solution (5 wt% of epoxy). A homogeneous solution was obtained by stirring for 10 min with a deforming mixer (Thinky, ARE-250), and it was spin-coated onto 4-inch Si wafer. The PASE/epoxy films were pre-baked at 70°C for 20 min, and then exposed to UV-irradiation for 40 sec with the total exposure dose of 2.0 J/cm². UV exposure was conducted with SUSS Microtech mask aligners (MJ4) equipped a high-pressure mercury lamp. Then, the films were thermally cured stepwise at 120°C for 20 min, 150°C for 1 h, and 200°C for 1 h under nitrogen. The in-plane ($n_{TE}$) and out-of-plane ($n_{TM}$) refractive indices of the films were measured with a prism-coupler (Metricon, PC-2000) at 1324 nm. The average refractive index ($n_{av}$) was calculated as $n_{av} = (2n_{TE}^2 + n_{TM}^2)/3$. The FT-IR absorption spectra were measured with JASCO FTIR-4200 attached with IR microscope (IRT-3000). Thermo-mechanical (TMA) and thermo-gravimetric analysis (TGA) were conducted with Shinku-riko TM-7000 and Shimadzu DTG-60, respectively. The heating rate was 10°C/min.

Results and Discussion: The reaction mechanisms occurring in the PASE/epoxy films with and without UV exposure is shown in Scheme 1. In the UV-exposed areas, PAG molecules that absorb UV radiation ($\lambda < 365$ nm) promptly liberate strong acid (H⁺), which promotes the coupling reactions between epoxy ring and silylated carbonyl ester groups of PASE. The carbonyl ester linkages thus formed by the cationic coupling effectively inhibit the thermal imidization ($i.e.$ imide-ring formation) of PASE even by curing at 200°C. In contrast, in the UV-unexposed area, thermal imidization of PASE was efficiently promoted and completed after curing at 200°C. Due to the higher molecular polarizability of imide groups, the formation of typical polyimide structure in the unex-

Scheme 1 Reaction mechanisms with and without UV irradiation in PASE/epoxy hybrid system. In the UV-exposed area, ester linkages are inter-molecularly formed between epoxy and PASE side groups catalyzed by photo-generated acids, and they effectively inhibit thermal imidization. In the unexposed area, thermal imidization is completed by curing at 200°C.
posed area gives a higher refractive index than the exposed area. On the other hand, when a PAA/epoxy hybrid solution is used for the film formation followed by curing at 200°C, imidization reaction of PAA was effectively inhibited even in the UV-exposed area because the carboxylic groups in PAA, which act as catalyst, spontaneously react with epoxy compounds without photo-acid by PAG. As a result, the refractive index of PAA/epoxy is as low as that of the UV-exposed area in PASE/epoxy film, which can be readily used for the low refractive cladding layers.

Fig. 1(a) shows the FT-IR spectra of PASE/epoxy films with and without UV-irradiation followed by curing at 150°C (Cure 1) and 200°C (Cure 2). The films after Cure 1 show the peaks attributable to PASE at 1650 cm\(^{-1}\) (amide I, \(B\)) and 1530 cm\(^{-1}\) (amide II, \(C\)), and no differences are observed between the exposed and unexposed areas. In contrast, significant differences are observed between the areas in the films after Cure 2. The unexposed area displays characteristic peaks at 1770 cm\(^{-1}\) (imide I, \(A\)) and 1370 cm\(^{-1}\) (imide II, \(D\)). These facts confirm the reaction mechanisms designed by the authors. Fig. 1(b) shows the UV-Vis absorption spectra of the films with and without UV-irradiation after Cure 2. Despite the difference in chemical structures, no significant changes are observed. Fig. 2 shows the UV-irradiation time dependence on the refractive indices (\(n_{av}\)) of the films after Cure 2. A large difference in \(n_{av}\) (\(\delta n\)) of 0.73 % was generated after 20 sec, but the maximum \(\delta n\) was obtained after 120 sec. The fabrication processes for channel-type multimode optical waveguides by combining PASE/epoxy (core layer) and PAA/epoxy (cladding layers) hybrid system are shown in Scheme 2.