

Thermally stable multi-mode polymer optical waveguide fabricated by single-step photo-patterning of fluorinated polyimide/epoxy hybrids

Yuichi Urano*^a, Ningjuan Chen^a, Kaichiro Nakano^b, Katsumi Maeda^b, and Shinji Ando^a

^aDepartment of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152-8552, JAPAN ^bNano Electronics Research Laboratories, NEC Corporation, Nakahara, Kawasaki, Kanagawa, 211-8666, JAPAN

ABSTRACT

Novel polyimide (PI)/epoxy hybrid material for single-step photo-patterning of optical waveguides was prepared by blending of a semi-aromatic fluorinated poly(amic acid silylester) (PASE), a cycloaliphatic epoxy compound, and a photo-acid generator. A large refractive index change (δn , > 0.01), which is sufficient for multi-mode optical waveguides, was obtained between the polymer films prepared with and without UV irradiation. The refractive index change was generated by cationic reaction between the silylated carbonyl ester groups of PASE and epoxy rings, which was initiated by UV irradiation and promoted by successive thermal curing. The difference in molecular structures, which results in the refractive index changes, were characterized by FT-IR measurements, and it was clarified that the films with and without UV irradiation showed PASE and PI structures, respectively. These films exhibited high thermal stability higher than 230°C, which are desirable for waveguide fabrication for optical inter-connects and lightwave circuits. Using this hybrid material, channel-type optical waveguides were successfully fabricated by the single-step photo-patterning procedure without development by aqueous or organic solvents, which is more facile and economical for waveguide mass-fabrication.

Keywords: Polymer optical waveguide, Fluorinated polyimide, Photo-induced refractive index change, Photo patterning

1. INTRODUCTION

Polymer optical waveguides have attracted much attention in the fields of integrated optics and optical inter-connects, because of their economic efficiency, good processability and flexibility [1]. However, conventional polymer optical waveguides do not have high thermal stability and demonstrate high propagation losses at the optical communication wavelengths (1.3 and 1.55 μm) in the near-infrared region. The higher optical losses are owing to the stronger vibrational absorptions due to plural kinds of carbon-hydrogen (C-H) bonds compared Si-O(H) bonds in amorphous silica (SiO_2). In order to reduce the losses, substitution of fluorine or deuterium for hydrogens in polymers have been reported for poly(methyl methacrylate) and epoxy resins [2–4]. Moreover, optical waveguides using fluorinated polyimide [5], benzocyclobutene [6] or poly(arylene ether sulfide) [7] have been investigated to improve not only propagation losses, but also thermal stability. Among these polymers, polyimides (PIs) have been widely used in microelectronics and optoelectronics industries because of their outstanding characteristics such as thermal stability, mechanical strength, resistance to organic solvents, and good processability [8]. Furthermore, several types of fluorinated and perfluorinated PI have been 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 photolithographic procedures, consisting of many processes including photo-resist patterning, development using aqueous or organic solvents, and etching [9–15].

In recent years, there have been demands for ‘single-step photo-patterning procedures’ for direct fabrication of channel-type (buried-type) waveguides without using photolithographic procedures (i.e. photo-resist patterning and dry- or wet-etching processes). Single-step photo-patterning is advantageous in process efficiency, low manufacturing cost and environmental friendliness [16]. Hence, many types of polymer materials, in which photo-chemical reactions can induce changes in refractive indices between exposed and unexposed areas, have been reported [16–21]. For example, polymer films doped with photochromic dyes can induce a large change in refractive index of ~ 0.01 [19–20], but the removal of remained reactants is a serious problem for fabricating highly transparent films. Further, cycloaliphatic-type epoxy

compounds such as 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate [22] exhibit faster response to UV curing in the presence of photo-acid generator compared with epi- and bis-epoxy resins. Their good transparency and high thermal deformation temperatures enable applications for electric-insulating varnishes and transparent sealants for optoelectronics (e.g., for light-emitting diodes). However, cycloaliphatic epoxy compounds do not provide tough and flexible films [22,23], which restrict their applications to optical thin films.

In this study, a novel organic hybrid system consisting of polyimide (PI), epoxy compound, and photo-acid generator (PAG) is reported to achieve facile formation of thermally stable polymer optical waveguides. This system can induce sufficient changes in refractive index by the UV-initiated cationic reaction between precursor of PI and epoxy compound. The PI precursor was a fluorinated semi-aromatic poly(amic acid) (6FDA-DCHM), and it was mixed with an aliphatic epoxy (CEL2021) and a photo-acid generator (PAG). By using thermogravimetric (TG) and spectroscopic (FT-IR) analyses, the photochemically-induced changes in the refractive indices and the birefringences are investigated, and the generation mechanism of the refractive index differences between the exposed and unexposed areas is clarified at the molecular level. Furthermore, a channel-type optical waveguide consisting of a central core, lower- and upper-claddings are fabricated by the single-step photo-patterning method.

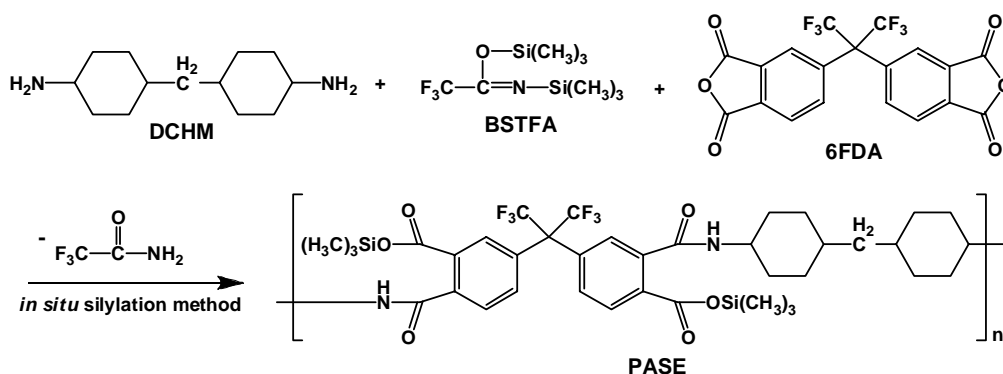
2. EXPERIMENTAL

2.1 Materials.

Bis(4-diaminocyclohexyl)-methane (DCHM) purchased from Tokyo Kasei Co. Ltd., was purified according to the literature [24]. 4,4'-(1,1,1,3,3,3-hexafluoro-2-propylidene) diphthalic anhydride (6FDA), kindly supplied by AZ materials Co. Ltd. was sublimated at 300°C under reduced pressure. Photo-acid generator (PAG) of hexafluoroantimonate salt was kindly supplied by Midori Kagaku Co. Ltd., 3,4-epoxy-cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CEL2021), purchased from Daicel Chemical Industries, Ltd., was used without further purification. *N,N*-dimethylacetamide (DMAc, Aldrich, anhydrous grade), *N,O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, silylation agent, Aldrich), were used without further purification.

2.2 Preparation of poly(amic acid silylester) (PASE).

Poly(amic acid silylester) (PASE) of 6FDA/DCHM was prepared by the *in-situ* silylation method [25] as shown in **Scheme 1**: In a nitrogen-purged glove box, DCHM (0.5015g, 2.38 mmol) was dissolved in 10 g of DMAc, and then BSTFA (0.6444g, 2.5 mmol) was added with stirring at 0–5°C. The solution was stirred at 0–5°C for 30 min, and 6FDA (1.0592g, 2.38 mmol) was slowly added to the solution. after the solution was kept at 0–5°C for 3 h, a transparent, colorless, and viscous PASE solution was obtained. Note that, the carbonyl esters in the side chains of PASE are protected by trimethylsilyl groups (–COOSi(CH₃)₃).



Scheme 1. Synthesis of poly(amic acid silyl ester) (PASE) by *in situ* silylation method.

2.3 Formulation of PASE/epoxy hybrid solutions.

In a nitrogen-purged glove box, 3,4-epoxy-cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CEL2021, 0.1575g, equivalent molar to PASE) was added into PASE solution (3.0 g) together with PAG (5% of epoxy in weight). The solution was stirred for 10 min with a deforming mixer (Thinky Corp., ARE-250) to obtain a homogeneous photosensitive mixture solution of PASE/epoxy hybrid.

2.4 Preparation of polymer hybrid films and UV irradiation.

To form thin films, the PASE/epoxy solution thus obtained was spin-coated onto 4-inch silicon substrates. 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/cmPP². UV exposure was conducted with SUSS MicroTech Mask Aligners MJB4 equipped a high-pressure mercury lamp. Wavelength filters were not used for irradiation. Then, the PASE/epoxy films were cured in a vacuum oven by heating stepwise at 120°C for 20 min, 150°C for 1 h, and 200°C for 1 h under nitrogen flow.

2.5 Measurements.

The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the thicknesses of PASE/epoxy films were measured with a prism-coupler (Metricon, PC-2000) at the wavelength of 1320 nm. The experimental errors for the refractive index and thickness are less than 0.0003 and 0.2 μ m, respectively. The average refractive index (n_{av}) and birefringence (Δn) were calculated as $n_{av}^2 = (2n_{TE}^2 + n_{TM}^2)/3$ and $\Delta n = n_{TE} - n_{TM}$, respectively. The Fourier transformed infrared (FT-IR) absorption spectra were measured with a JASCO FT-IR-4200 attached with an IR microscope (IRT-3000). The thermo-mechanical analysis (TMA) of films was conducted with a Shinku-riko TM-7000 under nitrogen. The thermo-gravimetric analysis (TGA) was conducted with a Shimadzu DTG-60 under nitrogen flow (20 ml/min).

3. RESULTS AND DISCUSSION

3.1 Photochemically-induced change in refractive index

Figure 1 shows the observed changes in n_{av} for PASE/epoxy films, at each curing process, namely 1) pre-bake (PB) at 70°C for 20 min, 2) post-exposure bake (PEB) at 120°C for 20 min, 3) thermal curing at 150°C for 1 h (Cure-1), and 4) successive thermal curing at 200°C for 1 h (Cure-2). By comparing the n_{av} values of the films with and without UV-irradiation, no significant difference for n_{av} was observed until the Cure-1 process. However, it is evident that the film cured at 200°C shows a significant change in refractive index larger than 0.01, in which the unexposed film exhibit higher refractive index (1.5197) than exposed film (1.5090). This refractive index difference corresponds to a 0.72 % of n_{av} , which is sufficient to confine optical signals into a core of multi-mode waveguide. In addition, the Δn values observed for the films with and without UV-irradiation are 0.005 and 0.002, respectively, which are sufficiently small for optical inter-connects applications.

Figure 2 shows the FT-IR spectra of PASE/epoxy films with and without UV-irradiation followed by curing at 150°C and 200°C. For the film cured at 150°C (Cure-1), almost no differences are observed between the UV exposed and unexposed areas as expected from their refractive indices. The signal assignments of the characteristic peaks are indicated in **Figure 2**. The films of Cure-1 show absorption peaks attributable to poly(amic acid silylester) at 1650 cmPP⁻¹ and 1530 cm⁻¹, which are assigned to the stretching at the amide linkages [amide-I band] and the vibration in the amide linkage [amide-II band] [26], respectively. In contrast, significant differences are observed between the IR spectra for the UV exposed and unexposed areas of the films cured at 200°C (Cure-2). The UV exposed area shows the same spectral shape as those cured at 150°C, which indicates that the PASE structure was kept and not thermally imidized. Whereas, the film cured at 200°C without UV-irradiation display peaks at 1770 cm⁻¹ and 1370 cm⁻¹, which are readily assignable to the stretching of carbonyl bonds in imide rings [imide-I band] and the vibration of C-N bond in imide rings [imide-II band], respectively [26]. These facts clearly indicate that the PASE component in the UV unexposed area was fully converted to polyimide structures through the Cure-2 process.

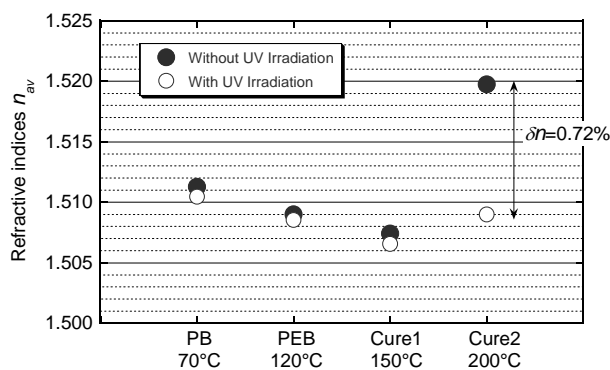


Figure 1. Average refractive indices of PASE/epoxy hybrid films measured at each curing process, i.e. pre-bake (PB) at 70°C for 20 min, post-exposure bake (PEB) at 120°C for 20 min, Cure-1 at 150°C for 1 h and Cure-2 at 200°C for 1 h. The films were prepared with (○) and without (●) UV-irradiation after pre-bake at 70°C.

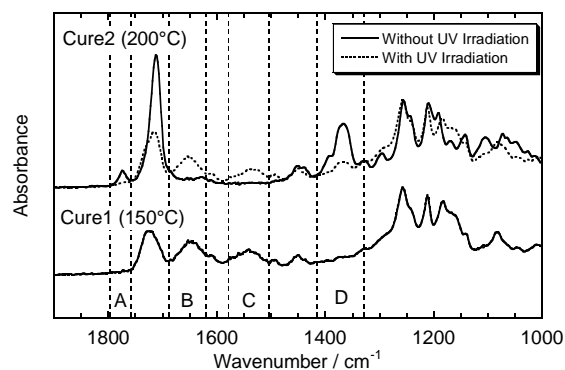
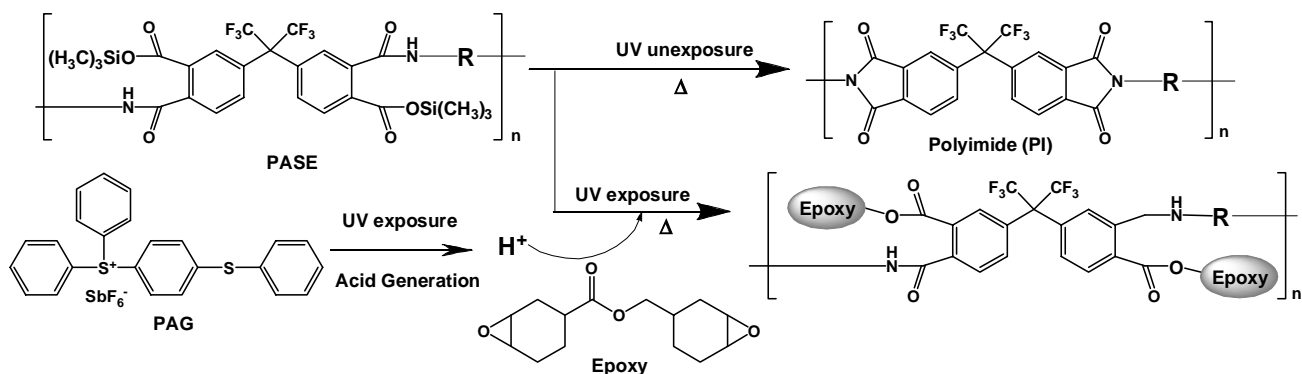


Figure 2. FT-IR spectra of PASE/epoxy films with (dotted line) and without (solid line) UV-irradiation cured at 150°C and 200°C. IR band A: imide stretching (imide I); B: amide stretching (amide I); C: vibration of amide linkage (amide II); D: vibration of imide linkage (imide II)

The difference in the reaction mechanisms in the PASE/epoxy films with and without UV irradiation can be inferred as follows. Under UV-irradiated films, PAG molecules absorb UV radiation at the wavelengths shorter than 365nm, then promptly liberate strong acid (H⁺), which promotes coupling reactions between epoxy ring of CEL2021 and silylated carbonyl ester groups of PASE. Accordingly, the side chains of PASE, that are silylated carbonyl ester linkages, are replaced and bonded with epoxy compounds through ether linkages. 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 for 1h. In contrast, for the films without UV-irradiation, the thermal imidization of PASE was efficiently promoted and completed after curing at 200°C because the silylated carbonyl ester groups in PASE are not resistant to imidization. The reaction mechanisms occurring during curing for the films with and without UV-irradiation are shown in **Scheme 2**. Due to the higher molecular polarizability of imide groups, the formation of typical polyimide structure in the UV unexposed area gives a higher refractive index than the UV exposed area.



Scheme 2. The reaction mechanisms with and without UV irradiation. In the UV-unexposed area, the thermal imidization of PASE was completed after curing at 200°C. On the other hand, the carbonyl ester linkages, which formed by the reaction between epoxy and PASE, effectively inhibited the thermal imidization in the UV exposure area.

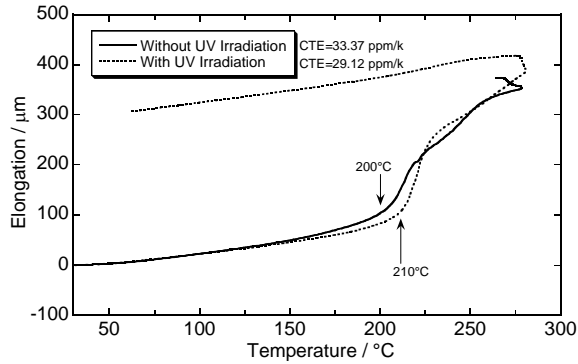


Figure 3. The TMA curves of PASE/epoxy films with (dotted line) and without (solid line) UV-irradiation.

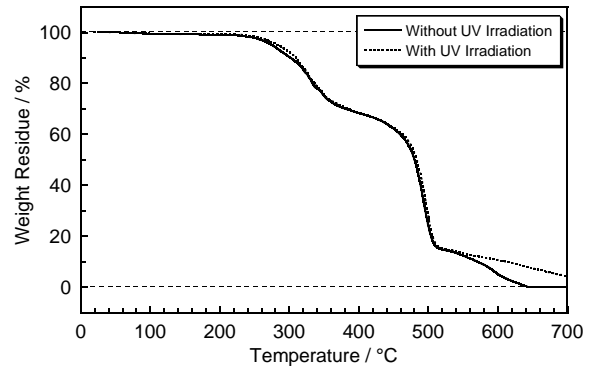


Figure 4. The TGA curves of PASE/epoxy films with (dotted line) and without (solid line) UV-irradiation.

The TMA and TGA curves of the films prepared by curing at 200°C (Cure-2) with and without UV-irradiation are shown in **Figure 3** and **4**, respectively. These films show high glass transition temperatures higher than 200°C and thermal decomposition temperatures (5% weight-loss) above 230°C. Although these temperatures are slightly lower than the working temperatures of commercial lead-free solders, these materials can withstand solder-reflow processes for several minutes.

3.2 Preparation of poly(amic acid) (PAA) and epoxy hybrid solutions for cladding.

As stated above, the novel PASE/epoxy hybrid system demonstrates a refractive index change larger than 0.01 by UV-irradiation. This system is promising for efficient fabrication of thermally stable optical waveguides by the single-step photo-patterning procedure. Although this hybrid material can be used for the lower- and upper-cladding layers with lower refractive indices in channel-type waveguides, homogeneous UV-irradiation to the whole area is required to reduce the refractive indices. To avoid such additional processes another hybrid material was proposed.

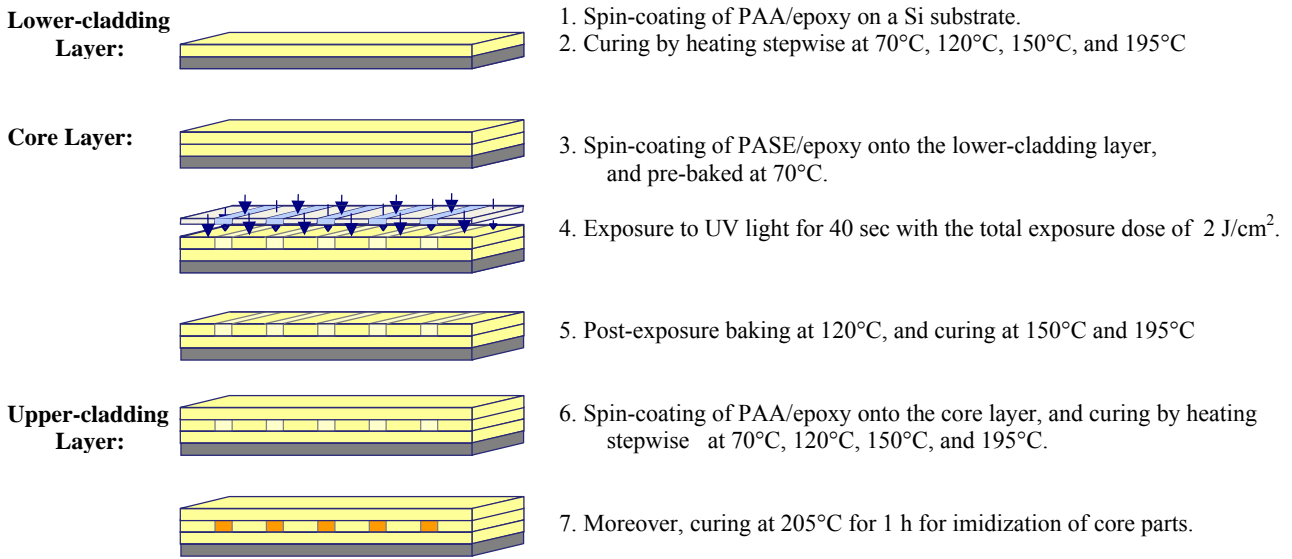
Poly(amic acid) (PAA), which is synthesized from equimolar amount of dianhydride and diamine without BSTFA, has side chains of carboxylic groups (–COOH). The carboxylic groups in PAA act as acids and can spontaneously react with epoxy compounds without strong acids generated by PAG. A PAA/epoxy hybrid solution was prepared as follows: In a nitrogen-purged glove box, CEL2021 (0.1575g, equimolar to PAA) was added into a PAA solution (3.0 g) and stirred at 0–5°C for 3 days to complete the intermolecular coupling reactions between PAA and epoxy. When the PAA/epoxy hybrid solution was used for film formation followed by thermal curing at 200°C (Cure-2), imidization reaction of PAA was effectively inhibited despite the omission of UV-irradiation process. In addition, the refractive index of this hybrid material is as low as that of the UV exposed area in PASE/epoxy film. This result clearly indicates that the PAA/epoxy system can be readily used for the lower- and upper-cladding layers in channel-type waveguides.

3.3 Fabrication of polymer optical waveguide by single-step photo-patterning procedure.

The fabrication processes for multi-mode optical waveguides using PASE/epoxy hybrid and PAA/epoxy hybrid systems were shown in **Scheme 3**. A PAA/epoxy solution was spin-coated on a Si substrate and cured by heating stepwise at 70°C for 20 min, 120°C for 20 min, 150°C for 1 h, and 195°C for 1 h under nitrogen flow to obtain the lower-cladding layer. And then, a PASE/epoxy solution dissolving PAG was spin-coated onto the lower-cladding layer and pre-baked (PB) at 70°C for 20 min. The UV-irradiation process was conducted with a mask aligner by the direct contact method. The exposure time was 40 sec, and the total exposure dose was 2.0 J/cm². The hybrid film was post-exposure baked (PEB) at 120°C for 20 min after UV irradiation. During the UV irradiation and PEB processes, intermolecular coupling reactions between PASE and epoxy compounds are promoted in the UV-exposed area. The film was further cured at 150°C for 1 h and 195°C for 1 h under nitrogen flow to obtain a core layer. At this stage, no thermal imidization was occurred both in the UV-exposed and unexposed areas due to the relatively lower curing temperature (195°C). As we

mentioned above, significant imidization occurs in the UV unexposed area only when a PASE/epoxy hybrid film is thermally cured above 200°C, while no imidization occur in the UV exposed area. It was found that solvent-induced cracking might occur in the UV unexposed area of the core layer. This is because a certain degree of micro phase separation may be generated between polyimide and epoxy domains due to the absence of intermolecular cross-linking. Accordingly, the curing at 195°C, which is not sufficient temperature for thermal imidization of the UV unexposed area, can effectively prevent the solvent-induced film cracking.

To form the upper-cladding layer, a PAA/epoxy solution was spin-coated onto the core layer and cured by heating stepwise at 70°C for 20 min, 120°C for 20 min, 150°C for 1 h, 195°C for 1 h and 205°C for 1 h under nitrogen flow. During the final heating at 205°C for 1 h, a significant difference in the refractive index between the UV exposed area and UV unexposed areas in the core layer should be generated. The photographs of a top-view and a cross-sectional view of the waveguide fabricated by the above process are shown in **Figure 5**. The cores of waveguides are clearly confirmed between the upper- and lower-cladding layers. The optical waveguide film peeled from Si substrate exhibits high transparency and good flexibility. **Figure 6** shows the transmission FT-IR spectra of the channel-type waveguide consisting of the three layers, in which the incident IR beam penetrates the whole layers. Although a part including a UV exposed area in the core layer is partially imidized, it is obvious that unimidized PASE and PAA structures with low refractive indices are dominant. In contrast, the FT-IR spectrum of a parts including UV unexposed area in the core layer clearly show imidized PI structures with higher refractive index are dominant, though several peaks assignable to PAA structure in the cladding layers are weakly observed. These facts demonstrate that the novel PAA/PI/epoxy hybrid systems proposed in this study is promising for facile fabrication of thermally stable channel-type multi-mode waveguides by the single-step photo-patterning procedure.



Scheme 3. The fabrication procedure of optical waveguide by the single-step photo-patterning method of PAA/epoxy and PASE/epoxy system.

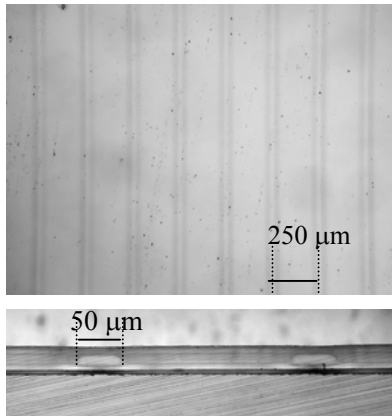


Figure 5. The top-view and cross-sectional view of the optical waveguides. The pitch of waveguide channels is 250 μm . The size of the cores is 15 x 50 μm .

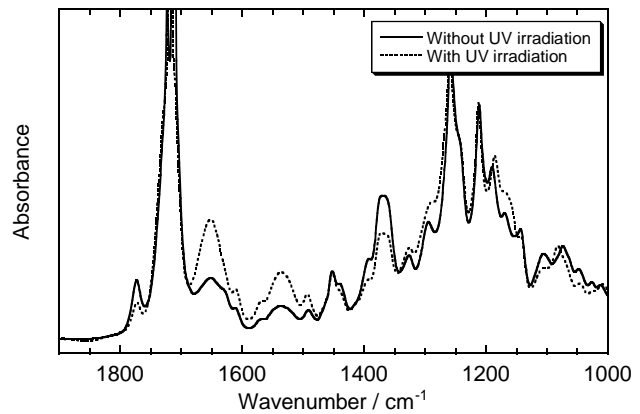


Figure 6. The microscopic transmission IR spectra of the 3-layered optical waveguides fabricated by single-step photo-patterning with (dotted line) and without (solid line) UV irradiation. The characteristic peaks for PAA (1530 and 1650 cm^{-1}) are significantly decreased without UV-irradiation

4. CONCLUSIONS

Novel Polyimide (PI)/epoxy hybrid material was prepared by blending a semi-aromatic fluorinated poly(amic acid silylester) (PASE), a cycloaliphatic epoxy compound, and a photo-acid generator (PAG). The hybrid solution was spin-coated onto silicon substrates and pre-baked at 70°C for 20 min followed by UV-irradiation with the total exposure dose of 2.0 J/cm² to decrease the refractive indices. Then, the films with and without UV irradiation were cured by heating stepwise at 120°C for 20 min, 150°C for 1 h, and 200°C for 1 h under nitrogen flow. The films prepared with and without UV-irradiation showed a large refractive index contrast ($>0.01 \approx 0.72\%$). The mechanisms of these refractive index changes were inferred as follows. Under UV exposed films, PAG molecules absorb UV radiation, and then liberate strong acid, which promotes coupling reactions between silylated carbonyl ester groups of PASE and epoxy rings. The carbonyl ester linkages thus formed effectively inhibit the thermal imidization of PASE even by curing at 200°C for 1 h. On the other hand, for the UV unexposed films, the imidization of PASE was efficiently promoted and completed by curing at 200°C for 1 h because the silylated carbonyl ester groups in PASE are not resistant to imidization. The corresponding changes in the molecular structures were confirmed by FT-IR microscope measurements, and it was clarified that the films with and without UV irradiation kept unimidized PASE and imidized PI structures after the final curing, respectively. These films showed glass transition temperatures above 200°C and thermal decomposition temperature (5% weight-loss) above 230°C. Three-layered channel-type optical waveguides were fabricated by single-step photo-patterning procedure, and the core shapes of waveguides were clearly confirmed due to the refractive index difference between the upper- and lower-cladding layers.

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