New Photosensitive Polyimide Materials and Their Application to Low-loss Optical Waveguides

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A negative-working photosensitive polyimide-precursor (PSPI-precursor) for optical waveguide based on a poly(amic acid) (PAA) and 1,4-dihydropyridine derivatives (DHP)s has been developed. The PAA was prepared by ring-opening polyaddition of aromatic fluorinated tetracarboxylic dianhydrides and diamines. The PSPI-precursor was capable to resolve a 2-μm width pattern when a 10-μm-thick film was used. Fabrication of optical waveguides by a simple patterning process using the PSPI is also described. PSPI is directly patterned by UV exposure and wet chemical development, avoiding use of photore sist. By using the standard cut back method, optical propagation losses were found to be as low as 0.4 dB/cm at 1.55 μm.

Keywords: photosensitive polyimide, waveguide, development, core, clad, optical loss 1,4-dihydropyridine, negative type

1. Introduction

Polymer optical waveguides have attracted considerable attention for use in economical and practical optoelectronic devices and as interconnections in optical communication systems, because the fabrication of these waveguides by spin casting is easier than that of inorganic material waveguides. Organic polymers such as poly (methyl methacrylate) (PMMA), poly (styrene) and poly (carbonate) have excellent optical transparency in the visible wavelength, and optical waveguides using these polymers have been studied [1,2]. However, these polymers do not have sufficient thermal stability. On the other hand, polyimides (PIs) are widely used in microelectronic devices due to their excellent properties such as thermal and chemical stabilities and low dielectric constants, and they have been taken for the candidate materials of waveguide [3-5]. Kobayashi et al. fabricated thermo-optic switches and arrayed-waveguide grating (AWG) using fluorinated PIs [6,7]. These PIs waveguides have been fabricated using conventional photolithography and reactive ion etching (RIE) techniques. However, RIE process requires complex multilevel resist schemes and expensive equipment. To overcome these process limitations, Shibata et al. reported a new replication process with antisticking layer for volume production of a PI waveguide [8]. This process is unique and gives low loss optical waveguides, instead of RIE process, but additional processes to deposit and remove the antisticking layer are needed.

On the other hand, PSPIs are widely used as dielectrics in multichip module fabrication because they offer a combination of good electrical and mechanical properties and low-cost processing relative to non-photosensitive polyimides [9]. Recently, we have reported the PSPI-precursor for high speed multilayer printed wiring boards (PWB) s and found that the higher propagation velocity of signals was achieved using PSPIs as an insulating materials having lower dielectric constants than that of conventional PSPIs [10].

These findings prompted us to employ the new approach to the development of a new PSPI-precursor for optical waveguide. In this paper, we introduce a new PSPI-precursor for optical waveguide and a simple process for the fabrication of low loss waveguide.
2. Experimental

2.1. Materials
Monomers and solvents were obtained commercially and used as received. 1,4-Dihydropyridine derivatives (DHPs) were synthesized according to the reported procedure [11].

2.2. Poly (amic acid) (PAA) and photosensitive polyimide (PSPI)-precursor synthesis

Equimolar amount of fluorinated tetracarboxylic dianhydrides and diamines were dissolved in N,N-dimethylacetamide (DMAc). The mixture was stirred at room temperature for 20 h, and then heated at 50 °C - 70 °C for several hours. In the resulting viscous solution, DHPs were dissolved and used as a PSPI-precursor solution.

2.3. Lithographic evaluation

Typical procedure is as follows; the PSPI-precursor solution was spin-coated on silicon wafer. It was prebaked at 90 °C for 15 min, and then exposed to a 250W filtered super high-pressure mercury lamp using mask aligner (Mikasa MA-60F). Imagewise exposure was carried out in a contact mode. The exposed film was baked at 180 °C for 10 min. The film was developed with 5 % tetramethylammonium hydroxide (TMAH) aqueous solution containing ethanol at 40 °C.

2.4. Measurements

The film thickness was measured by surface texture measuring instrument with Dektak 3030 system (Veeco Instrument Inc.). The pattern was observed by scanning electron microscopy (SEM) (Hitachi S-570). FT-IR was measured by Thermo Nicolet, Magna 760 system. Thermal analyses were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10 °C/min for TG and a Seiko SSS 5000 DSC220 at a heating rate of 10 °C/min for differential scanning calorimeter (DSC) under nitrogen. Refractive index was measured by prism coupling method. Waveguides were cut with a Disco No.522 dicing machine and the optical loss measurement was performed by cut back method.

3. Results and discussion

3.1. Formulation of PSPI-precursor

The polyimide materials for the waveguide application must have highly transparency to the telecommunication band. We selected fluorinated monomers, which have effective to reduce the absorption in near infrared region. Poly (amic acid)(PAA) as a matrix polymer was prepared in N,N-dimethylacetamide (DMAc) from aromatic fluorinated tetracarboxylic dianhydrides and diamines (eq. 1). 1,4-Dihydropyridine derivatives (DHP) are well known as photosensitive compounds and are converted to the corresponding pyridine derivatives after UV exposure and have been utilized for photosensitive polyimide (PSPI) precursors in combination with various PAA [12]. Thus, the PSPI system based on the PAA and DHPs was formulated.

3.2. Lithographic evaluation

Dissolution behavior to the developer of the PSPI-precursor was evaluated as shown in Fig. 1. DHPs is converted to corresponding pyridine derivatives after exposure to UV light. The imidization of the PAA in the exposed area easily occurs compared to that of the unexposed area, because the photo-generated pyridine derivatives work as a base catalyst for imidization. Thus, the PSPI-precursor film comprising the PAA and DHPs was exposed to UV light, and the PEB was performed at 180 °C for 10 min. The results

Figure 1. Patterning process of PSPI-precursor based on PAA and DHP
are shown in Fig. 2. The dissolution rate was calculated from remaining film thickness after development with 5% tetramethylammonium hydroxide (TMAH)/ethanol solution at 40 °C. Increasing with exposure dose, a dissolution rate in exposed area is decreased. It was found that the dissolution rate of the exposed area was approximately ten times slower than that of the unexposed area. Therefore, the sensitivity curve for 8 µm-thick PSPI precursor film shown in Fig. 3 indicates that sensitivity ($D^{0.5}$) was 6 mJ/cm². These excellent sensitivity is considered to be introducing fluorinated structure which has higher transparency to UV region compared to conventional monomers.

3.3. Properties of PSPI film

After development the PSPI precursor film was converted to the PI by thermal treatment at 380 °C for 2h in vacuo. Fundamental properties of the PSPI film are listed in Table 1. PSPI film formed on silicon wafer has a refractive index of 1.520 for TE and 1.510 for TM at 1.55 µm. The PSPI film has high thermal stability. Glass transition temperature (Tg) and coefficient of thermal expansion (CTE) are 330 °C and 40 ppm, respectively. These excellent film properties would be expected to use for optoelectronic devices, which need soldering process.

To make low loss optical waveguide, it is very important to know the absorbance of PSPI film. So, we evaluated the absorbance spectrum in the infrared region using FT-IR with a white light source. Fig. 4 shows the absorbance of PSPI film. It was found that the PSPI film poses colorless low absorption at the optical communication wavelength of 1.3 or 1.55 µm.

3.3. Propagation properties of PSPI waveguide

In order to evaluate propagation properties of PSPI waveguide, we fabricated waveguide pattern using PSPI precursor. After preliminary optimization studies [13] involving selection of under and over-cladding materials, difference of refractive index between core and cladding, we prepared buried channel waveguides. Fig. 5 shows a schematic diagram of the fabrication process.

Under-cladding layer of 10 µm thick was formed on 1 mm thick of quartz glass substrate by spin coating and curing. Then, the PSPI vanish was spin-coated on the under-cladding layer. After prebake at 90 °C for 15 min, the film was exposed to UV light through a photo mask. After development, core pattern was cured at 380 °C for 2 h in vacuo. Final thickness of core was almost 7 µm. Fig. 6 shows a scanning electron

![Figure 4. Absorbance of PSPI film](image-url)
4. Conclusion

A photosensitive polyimide (PSPI)-precursor for optical waveguide based on a PAA and DHPs has been developed. The PSPI have provided negative type image and possessed excellent sensitivity to UV light. The PSPI system was capable to resolve a 2-µm width pattern with smooth surface when a 10 µm-thick film was used. Furthermore, the fabricated waveguide using the PSPI as a core material indicated low propagation loss of 0.4dB/cm at 1.55 µm. This simplification of the fabrication process is very attractive in manufacturing optoelectronic devices.

References