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Photosensitive terpolymer for all-wet-etching process: Material characterization and device fabrication

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A photosensitive terpolymeric composition suitable for practical waveguide devices is provided. The terpolymer was produced from pentafluorostyrene, perfluoro-n-octyl acrylate, and glycidyl methacrylate. We present a fabrication process where the device structure utilizes the same class of material for the core and cladding layers and it was fabricated without a plasma etching process. Based on this developed material and process, a 16-channel arrayed waveguide grating with good performance has been realized. During temperature cycling, a slight thickness hysteresis and refractive index hysteresis was observed above the glass transition temperature and is ascribed to the fact that the terpolymer material may not completely recover its elasticity in the heating/cooling cycle.

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1. Introduction

Polymers are no longer simply inexpensive disposable materials, they have emerged as a promising class of materials for various high technology applications. The promise of inexpensive electronics has fuelled widespread interest in the field of organic devices. Although organic devices will not replace existing silicon technology, they will offer interesting alternatives in a number of niche applications. Envisioned applications range from flexible or bendable electronic systems to integrated devices with different functionalities such as energy generation [1], light emission [2], polymer transistors [3], and optical communication [4]. Polymeric waveguide devices have been actively studied with an attraction of economical merit based on its simple fabrication process, and are entering into industrial markets as commercial products such as variable optical attenuators [5,6] and coarse wavelength division multiplexing [7].

The fiber optic applications require that the materials and their waveguide devices meet many specifications such as low optical insertion loss in the useful wavelength region of 1300–1610 nm, low birefringence and high reliability. This is challenging and requires a unique material and device approach to meet all the requirements. For these purposes, we designed and synthesized a photosensitive fluorinated polymer, shown in Fig. 1. The fluorinated polymer was produced from pentafluorostyrene, perfluoro-n-octyl acrylate, and glycidyl methacrylate (terpolymer). The polymeric optical properties are systematically studied, such as glass transition temperature, heat stability, and thermo-optics properties. Based on the developed material, a 16-channel arrayed waveguide grating (AWG) multiplexer with excellent performance has been realized. The average insertion loss is about 5 dB and the best channel shows an insertion loss of 4.7 dB. The adjacent crosstalk is more than 28 dB, and a polarization dependence loss (PDL) of ~0.2 dB. The device structure utilizes the same class of material for the core and cladding layers and it was fabricated without plasma etching process.

2. Material and characterization

The chemical structure of the terpolymer and the reaction scheme are shown in Fig. 1. Pentafluorostyrene (PFS) and glycidyl methacrylate (GMA) were purchased from Aldrich. 1H,1H-perfluoro-n-octyl acrylate (PFOA) was purchased from Fluorochem Limited. The reagents were each injected individually into a purification column containing an inhibitor remover (HQ/MEHQ, Aldrich). The synthesis of the polymer was carried out by solution radical polymerization using benzoyl peroxide (BPO) as initiator (0.1 mol%). BPO was recrystallized from methanol.

The PFS (67.936 g, 0.35 mol), PFOA (45.412 g, 0.1 mol), GMA (7.108 g, 0.05 mol), and BPO (6.060 g, 0.025 mol) were mixed in n-propyl acetate (400 ml) in a three-necked flask and stirred under a nitrogen flow for 20 min before heating. The resulting solution was heated at 70 °C for 16 h and cooled to room temperature. The precipitated white polymer was washed three times with 300 ml of methanol. The final product was dried for 4 h using vacuum filtration and air-dried for about 12 h. The photoinitiator used for lithography was (RH-2074, Rhodia, Inc) in the presence of photosensitizer (CTX, Aldrich Ltd). Solutions were prepared by dissolving the photoinitiator (5 wt.%) and terpolymer into cyclohexanone.
(47% wt/wt). The solution was filtered with a 0.2 µm filter before spin casting. The refractive index of the composite was measured to follow a linear function of the PFS concentration. The refractive index at 633 nm for the terpolymer varies between 1.4758 and 1.4939, as PFS content varies from 88 to 45 mol%. Before index measurement, the terpolymer films were cured according to the fabrication process described in the fabrication section.

In this work, all the measurements were carried out in the laboratory atmosphere and FilmTek™ 2000-Thin Film Measurement System was used to measure the index of refraction and thickness of planar waveguide films. With its hot plate option, it can characterize the index of refraction and thermal expansion of a film as a function of temperature. The temperature dependence of refractive index of the terpolymer thin-film waveguides is plotted in Fig. 2. The refractive index of the film decreases with increasing temperature (i.e., dn/dT < 0), indicating a volumetric expansion of the film and a consequent lowering of its density. This conclusion is consistent with the results seen when the thickness of film increases with increasing temperature (see Fig. 2). The discontinuity in the temperature curves indicated a phase transition occurrence within the film structure. The temperature at which the refractive index discontinuity occurs is well known as the glass transition temperature (Tg) [8], it is of the order of 100 °C. The change in refractive index depending on temperature was linear in the various temperature ranges where no phase transition occurred, and whose slope could give the thermo-optic coefficients (dn/dT). In the temperature range between 25 and 100 °C the thermo-optic coefficient of the terpolymer films is of the order of $-0.97 \times 10^{-4}$ °C$^{-1}$. And in the temperature range between 100 and 200 °C the thermo-optic coefficient is of the order of $-3.06 \times 10^{-4}$ °C$^{-1}$.

During the temperature cycling a slight hysteresis structure in the refractive index and film thickness appears. From Fig. 2, we can see that the hysteresis is more pronounced in the temperature range above Tg. The change in refractive index in this temperature range is largely a result of the change in volume, and the volume is in turn affected by the deformation during heating or cooling process. The terpolymer material may not completely recover its elasticity in the heating/cooling cycle and thus results in the hysteresis structure [9].

Fig. 1. Chemical structure and polymerization of the terpolymer.
The coefficient of thermal volume expansion has a value that may be directly obtained from the inverse of the Lorentz–Lorenz relation [8]. In the temperature range between 25 and 100 °C the thermal volume expansion of the terpolymer film is of the order of $1.48 \times 10^{-4}$ °C$^{-1}$. And in the temperature range between 100 and 200 °C the thermal volume expansion is of the order of $6.21 \times 10^{-4}$ °C$^{-1}$. The results of the Thermogravimetry Analysis shows that the temperature at which a 5% weight loss occurred for terpolymer was 390 °C, suggesting that the polymer exhibits a higher thermal stability.

3. Device design and fabrication

The organic materials are divided into photosensitive and non-photosensitive which differs in fabrication technologies to realize the optical components. Most of the fabricated components using photosensitive materials and wet etching process are limited to simple structures such as channel waveguides, $1 \times 2$ splitters [10]. In this work, we fabricated an AWG made without a plasma etching process. Based on this polymer material, first we carry out the structural design of the AWG, the schematic waveguide layout of our designed 16-channel AWG device is presented in Fig. 3. The multiplexer consists of input/output waveguides, two focusing slab waveguides, and arrayed waveguides with a constant path length difference between neighboring waveguides. The input light is launched into the first slab waveguide and then excites the arrayed waveguides. After traveling through the arrayed waveguides, the light beam interferes constructively at one focal point in the second slab. The location of the focal point depends on the signal wavelength. Since the focusing position differs with wavelength, lightwaves with different wavelengths in the input waveguide are output in specific output waveguides determined by their wavelengths. Because of these characteristics, AWGs are widely used as wavelength multi/demultiplexers. We used commercial software BeamPROP (Rsoft Design Group, Inc.) to design the 16-channel AWGs with channel spacing 0.8 nm and central wavelength 1547 nm. The computation core of the software is based on the finite difference beam propagation method. The AWG has a diffraction order of 55, free spectral range of 28 nm, grating waveguide number of 71, and waveguide path difference of 57 mm. The calculated transmission spectrum is plotted in Fig. 4a. The total insertion loss of the submitted design includes fiber coupling loss, propagation loss, and the bending loss.

To produce good quality devices, the fabrication process is a critical factor and needs to be monitored carefully. The fabrication of our cross-linking polymer single mode waveguides is based on conventional contact-printing photolithography and all-wet-etching process. The fabrication process was as follows: a low refractive index ($n = 1.478$) solution of the terpolymer was spun onto the silicon substrate to give a 10 µm thick cladding layer. After being baked at 60 °C for 1 min on a hot plate, the film was UV-exposed under an Hg–Xe lamp and postbaked at 140 °C for 60 min. The core of the waveguide was a higher refractive index (1.490) of terpolymer spin-coated on top of the bottom cladding to form a 6 µm thick film. The layer was dried at 60 °C for 1 min and patterned through a negative photomask. After post-exposure baking took place for 1 min at 125 °C (25 °C above the polymer glass transition temperature), the film was developed in spray mode using acetone solvent. The pattern was dried in air to remove residual swelling.

![Fig. 3. Schematic configuration of the arrayed waveguide grating.](image)

![Fig. 4. Calculated (a) and measured (b) optical response of 16-channel AWG.](image)

![Fig. 5. SEM micrograph of the star coupler of the AWG after wet etching.](image)
and height of the waveguide were 6 and 5.9 µm, respectively. Finally, the
top cladding solution (identical to the bottom cladding solution) was
spin-coated, dried at 60 °C for 1 min, UV-exposed, and postbaked at
140 °C for 3 h. The device was diced and side-polished in order to form
the input/output facets for coupling the light. Fig. 5 shows a scanning
lectron microscopy (SEM) micrograph of the star coupler at the taper
region of the AWG after wet etching.

Fig. 6 shows the setup for measuring the spectral transmission
characteristics of the AWG. Light from a tunable laser source is passed
through a polarization controller and launched into the inputs of the
AWG. The use of a polarization controller allows simultaneous mea-
surement of the polarization dependent loss of the device. At the out-
pit of the AWG, the light is focused and collected by an optical spectrum
alyzer. The spectral response of the AWG is obtained by measuring
the optical power, while sweeping the wavelength of the tunable laser
source. Fig. 4b shows the spectral response of the fabricated 16-channel
AWG device. Reference waveguides running alongside the AWG show
a loss of ~2.9 dB, which include fiber coupling loss, bending loss and
propagation loss. The measured propagation loss of the terpolymer
channel waveguides amounted to less than 0.5 dB/cm at 1550 nm and
0.2 dB/cm at 1310 nm. The measured data in Fig. 4b shows adjacent
crosstalk levels of about 28 dB with an average insertion loss of 5 dB,
the best channel shows an insertion loss of 4.7 dB. The polarization shift
at center wavelength is less than 0.16 nm, and the 3-dB bandwidth is
about 0.5 nm. It is noted that the output power uniformity over the
16 channels is 1 dB. Thus, we have developed a 16-channel AWG with
satisfactory characteristics using all-wet-etching process. A reasonable
polarization dependence loss for communication application is less than
0.5 dB; our device shows a PDL of 0.20 dB. The low PDL and the good
performance of the device are mainly due to the design to use the same
class of material for the core and cladding layers, what enabled low-stress
loading during the waveguide fabrication process. We see a wavelength
shift between the measured and calculated spectrum, this shift can be
cause by the change in the index of refraction. For the simulation, we
used the refractive index measured in a slab waveguide film; however,
during the fabrication process we believe that a slight change in refractive
index may occur. The measured adjacent channel crosstalk was 28 dB.
This value is relatively low comparing with the designed value (35 dB)
and is likely due to phase errors that are probably related to the geo-
metric deviations of ridge waveguide shape created during the fabrication
process. These waveguide geometric deviations could be caused by lower
cladding layer roughness or lithography variations. The phase errors in
the arrayed waveguides contribute also to the sidelobes in the measured
transmission spectrum.

In order to evaluate the fabrication method used in this work, we
compared the fabricated device with other AWGs developed by other
fabrication techniques. The results are summarized in Table 1. It can
be noted that except this work and the work reported by Choi et al.
[16], all other fabrication techniques are based on UV lithography
followed by Reactive Ion Etching (RIE). This method involves many
processing steps, and can lead to long fabrication time and costly pro-
cess. Photolithography followed by wet etching (this work) is a low
cost and simple method for the fabrication of polymer waveguides,
but it does require the polymeric materials to be UV sensitive. The
data presented in Table 1 (Loss, crosstalk, uniformity, PDL) are the
most representative parameters for comparing different AWGs. From
Table 1, we can see that we have developed a 16-channel AWG with
good characteristics using all-wet-etching process. In the case of the
5-channel AWG fabricated by the embossing technique, we did not
find any data related to the fabricated device.

A particularly difficult challenge for material development has been
to find the combination of good optical properties and good thermal,
environmental and mechanical stability. The low Tg and the appear-
ance of thermal hysteresis in refractive index and film thickness affect
the thermal stability of the device. Presently, our efforts are focused
on optimizing the monomers ratio to impart stability and to retain
desirable properties. We found that increasing the proportion of GMA
provides a greater degree of crosslinking and increases the Tg and de-
composition temperature but also increases optical loss. However, it
becomes a tradeoff between the thermal stability and optical properties.
The hysteresis of optical materials can arise for several reasons. In sol-
gel silica thin films, it has been attributed to the unrelaxed strain during
the heating and cooling cycle [9]. Anisotropically expanding materials
undergo extensive microcracking during cooling due to thermal strain
[17], crystallization, and phase transition [18]. It is possible to remove
or reduce the hysteresis in the film by optimizing the backing process
and using a substrate having the same thermal expansion coefficient as
the polymer.

4. Conclusion

In summary, we illustrated a photosensitive cross-linkable terpoly-
mer, with fluorinated groups, for optical waveguide applications. They
exhibit small light absorption at the optical communication wave-
lengths. The design to use the same class of material for the core and
cladding layers enabled low-stress loading during the waveguide fab-
rication process and a good adhesion between the layers. High per-
formance 16-channel AWG has been demonstrated using all-wet-
etching process. Again, we note that the all wet-etch processing used
to make this AWG will allow inexpensive devices fabrication. The high
thermo-optic coefficient of this material also makes it useful for thermo-
optic switches and variable optical attenuators.

**Table 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>Patterning process</th>
<th>AWG</th>
<th>Average loss</th>
<th>Adjacent crosstalk</th>
<th>Uniformity</th>
<th>PDL</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terpolymer</td>
<td>UV lithography/wet-etching</td>
<td>1 × 16, 100 GHz</td>
<td>5 dB</td>
<td>28 dB</td>
<td>1 dB</td>
<td>0.2 dB</td>
<td>This work</td>
</tr>
<tr>
<td>Perfluoropolymer</td>
<td>UV lithography/RIE</td>
<td>1 × 16, 100 GHz</td>
<td>2.8 dB</td>
<td>30 dB</td>
<td>NA</td>
<td>NA</td>
<td>[11]</td>
</tr>
<tr>
<td>PFPE</td>
<td>UV lithography/RIE</td>
<td>1 × 16, 100 GHz</td>
<td>18 dB</td>
<td>15 dB</td>
<td>3 dB</td>
<td>3 dB</td>
<td>[12]</td>
</tr>
<tr>
<td>PFS-co-GMA</td>
<td>UV lithography/RIE</td>
<td>1 × 5, 200 GHz</td>
<td>6 dB</td>
<td>20 dB</td>
<td>NA</td>
<td>NA</td>
<td>[13]</td>
</tr>
<tr>
<td>BPE</td>
<td>UV lithography/RIE</td>
<td>1 × 33, 100 GHz</td>
<td>11 dB</td>
<td>20 dB</td>
<td>NA</td>
<td>NA</td>
<td>[14]</td>
</tr>
<tr>
<td>BCB</td>
<td>Embossing</td>
<td>1 × 5, 100 GHz</td>
<td>7 dB</td>
<td>27 dB</td>
<td>2.8 dB</td>
<td>1.2 dB</td>
<td>[15]</td>
</tr>
</tbody>
</table>

Note: The table contains the average loss, adjacent crosstalk, uniformity, and PDL for various materials used in thin film applications.
References