Characterisation and process optimisation of photosensitive acrylates for photonics applications

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Abstract

In this paper, we present our recent progress on the characterisation and process optimisation of photoresist-like fluorinated acrylate and Cyclomer acrylate copolymers. Different acrylate formulations from cyclized acrylic copolymers (Cyclomer) have been exploited and compared with fluorinated acrylate, ORMOCER from available sources. Refractive indices of the Cyclomer acrylate at transverse electric (TE) mode is 1.56 while refractive index of fluorinated acrylate at TE is 1.52 at room temperature. Both acrylates show negative thermooptic (TO) effect with temperature. The thermooptic coefficient, \( \frac{dn}{dT} \) of the polymers are as high as the order of 10\(^{-4}\), which is comparable to those of available optical polymers. Higher values of \( \frac{dn}{dT} \) are shown by the Cyclomer acrylate compared to that of the fluorinated acrylate. Thermal stability determination were measured using Thermal Gravimetric Analysis and decomposition were evaluated at 5 and 10% decomposition. It was found that Cyclomer is more stable than ORMOCER. From glass transition and specific heat capacity values obtained using Differential Scanning Calorimeter, fluorinated acrylate has more specific heat capacity than Cyclomer. Characterisation of pre baked and UV cured polymer samples had been analysed using FTIR. The time and intensity of UV curing were optimised to obtain waveguide channel of width between 40 and 10\( \mu \text{m} \) for Cyclomer. For fluorinated acrylate, only the UV curing time parameter had been optimised. The development techniques of these acrylates are also different; the Cyclomer used the aqueous based developers while fluorinated acrylate used hydrocarbon solvent. Microstructural channel waveguide had also been analysed via scanning electron microscope (SEM), which shows the channel waveguide structures.

Keywords: Photosensitive acrylates; Polymer characterization; UV curing

1. Introduction

Polymer materials have become increasingly attractive for use in optical waveguide devices in recent literature [1–4], and the use of this material is expected to lead to reduced cost and improved price-performance ratio. Switches, variable optical attenuators (VOAs), and tunable filter-based products have been introduced, and components such as modulators, lasers, and amplifiers are under development [4].

Several material systems are being pursued as integrated optics platforms [4]. State-of-the-art optical polymers are particularly attractive in integrated optics because of their low cost fabrication method, potential of easy fabrication, low temperature, good processability and mass production for large size substrate [5].

Fabrication of waveguides require multisteps technique to obtain waveguide with specified properties in order to withstand temperature and environmental conditions incurred during processing and handling. Traditionally they require multi-step processes involving photolithography, etching and annealing [6]. Thus photosensitive monomers are employed which use the same technique as photoresist. Acrylates had been used before for UV lithography but as photoresist materials [7,8]; however new direct UV-patterning of waveguide can be made using the same technique hence the use of photosensitive
materials. The direct UV-patterning provides low cost fabrication because of reduced number of processing steps in comparison with dry etching methods in combination with high reproducibility of the optical components. The combination of the UV- and thermal curing leads to highly environmental stable materials with low stress and good adhesion to silicon substrates [9]. Waveguide fabricated using photosensitive materials include epoxy and acrylate moiety, thermoset urethanes, fluorinated acrylate and polyimides [10,11]. The refractive indices of the polymer can be controlled by changing parameters such as components used, composition ratios, postbaking, development and UV curing time. These parameters are important for optimisation of the polymeric materials suitable to construct waveguide structures in passive devices for optical communication.

2. Materials and methods

2.1. Cyclomer acrylate

Photosensitive cyclized acrylic copolymers are obtained from UCB Chemicals Malaysia Sdn Bhd. Fig. 1(a) shows the structures of the Cyclomer polymer. Cyclomer is an acrylic copolymer resin having acrylic and carboxyl groups on the side chains. Since Cyclomer has acrylic groups that readily cause curing, it is applicable to various coating resins, coatings, adhesives, and resins for various resists. It has carboxyl groups that allow it to be dissolved in water, making it adaptable to water-based coatings, and resistant to development under alkaline conditions. Cyclomer has a basic structure composed of acrylic copolymers, which permits the free design and property control of resins.

The Cyclomer acrylates are dissolved in its solvent with photoinitiator Irgacure 500(5%) and coinitiator, thioxanthone (3%) from Ciba Geigy. The fabrication process involved coating the silicon substrate with the Cyclomer using spin coater. No adhesion promoter is required. After spin coating, the polymer is prebaked for 5 min at 90 °C using hotplate. The polymer is then exposed using ultra violet (UV) light at 365 nm wavelength. In this exposure step, the photomask and the wafer did not have separation gap (contact printing). After the UV exposure step, the waveguide is developed by immersing in sodium carbonate(1%) solution and postbaked for one hour.

Fig. 1. (a) Structure of Cyclomer acrylate polymer. It is an acrylic copolymer resin having acrylic and carboxyl groups on the side chains. Since it has acrylic groups that readily cause curing, it is applicable to various coating resins, coatings, adhesives, and resins for various resists. It has carboxyl groups that allow it to be dissolved in water, making it adaptable to water-based coatings, and resistant to development under alkaline conditions. Cyclomer has a basic structure composed of acrylic copolymers, which permits the free design and property control of resins.

Fig. 2. Flowchart of optical waveguide fabrication via direct UV-patterning technique. The basis of UV patterning technique is similar as UV lithography for negative resist fabrication in microfabrication technique. The process involve lower cladding coating, (prebake and UV curing), core coating (prebake and UV curing), development and postbake.
2.2. Fluorinated acrylate, ORMOCER

The ORMOCER is obtained from Micro Resist Technology. Fig. 1(b) shows the structures of the ORMOCER. It consists of 3-methacryloxypropyltrimethoxysilane (MEMO-NT) and diphenyldiolsilane (DPD). It has an index of refraction of 1.521 at 1550 nm measured at room temperature. The fabrication step is also the same with Cyclomer acrylate except that in term of exposure, proximity printing is applied. In this exposure step, the photomask and the wafer are separated by a small gap. After the UV exposure step, the waveguide is developed in methyl isobutyl ketone (MIBK) solution.

The curing characteristics can be visualised from infrared spectroscopy and absorption bands of the relevant monomers are analysed. The intensity and curing time with spin parameters for thickness required is then optimised to obtain channel waveguide through direct photopatterning for Cyclomer acrylate and only curing time for ORMOCER.

Fig. 2 shows fabrication steps of polymeric waveguide using photosensitive polymer as waveguide material via direct UV-patterning technique which include wet etching and development.

Structural investigation to determine cure characteristics at various UV exposure time were done using PERKIN ELMER FTIR Spectrum ONE spectroscopy. Thermal characterization were done using PERKIN ELMER DSC-7 and TGA-6 while optical characterization were measured using SAIRON SPA- 4000 prism coupler.

3. Results and discussions

From FTIR studies as illustrated in Figs. 3 and 4, the Cyclomer had optimised UV cured at 3 min with UV intensity of 10 mWcm\(^{-2}\) whereas the fluorinated polymer cured at 1 min with intensity of 16 mWcm\(^{-2}\). Epoxy group showed opening of ring immediately after polymerization; hydroxyl group were formed. The C=O at 1600 cm\(^{-1}\) from the acrylate monomer had reduced absorbance and diminish at full curing stage. The highly absorbing peak from C-O at between 1250 and 1050 cm\(^{-1}\) were maintained with progress of curing. Material showed high transmittance as polymerisation nears to completion.

Fig. 5 shows the variation of refractive index of fluorinated polymer at TE and TM mode versus temperature. The temperature range is 25 \(^\circ\)C to 80 \(^\circ\)C restricted by the ability of prism coupler with temperature-controlled system. The figure illustrates linear reduction of the refractive index with the temperature. The \(dn/dT\) coefficient of fluorinated polymer is approximately \(-0.4 \times 10^{-4}/^\circ\)C for TE polarization and \(-0.3 \times 10^{-4}/^\circ\)C for TM polarization measured at 1550 nm.

Fig. 6 shows the variation of refractive index of Cyclomer acrylate polymer at TE and TM mode versus temperature. The figure also illustrates linear reduction of the refractive index with the temperature. The \(dn/dT\) coefficient of Cyclomer polymer is approximately \(-7 \times 10^{-4}/^\circ\)C for TE polarisation and \(-10 \times 10^{-4}/^\circ\)C for TM polarisation.

![Fig. 3. FTIR spectrum of UV curing for ORMOCER. Absorption of ORMOCER was found to be changed at O-H stretch, C=O stretch and epoxy C-O-C stretch.](image-url)
polarisation. The increasing of temperature causes the expanding of the film hence, reducing the optical density and varies the refractive index of the material. Large TO coefficient of Cyclomer acrylate makes it possible to realise TO switch with small electrical power [12].

Thermal stability is an important issue for optical components. Thermal stability of the waveguide material was studied by techniques such as differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

For stability determination, normally 5 and 10% material decomposition are measured. For ORMOCER, 5 and 10% decomposition occured at 400 °C and 430 °C respectively. In comparison, Cyclomer have 5 and 10% decomposition at 400 °C and 480 °C respectively. Figs. 7 and 8 showed this from their TGA (Thermal Gravimetric Analysis) curve. Hence, it is found that Cyclomer is more stable than ORMOCER. DTG (Differential Thermal Gravimetric) curve showed maximum decomposition for ORMOCER and Cyclomer occurred at 574 °C and 578 °C, respectively. It is found that Cyclomer is more stable than ORMOCER.

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Referred to Table 1, glass transition temperature (Tg) of Cyclomer and ORMOCER was found to be 149.9 °C and
136.3 respectively. Hence, Cyclomer is more brittle and can withstand higher temperature operation and fabrication. Glass transition temperature ($T_g$) of Cyclomer and ORMOCER was found to be 149.9 °C and 136.3 °C respectively. Hence, Cyclomer is more brittle and can withstand higher temperature operation and fabrication. Physical property shifts at glass temperature of resins can cause optical losses and severe stress built up in optical components leading to premature device failures. The resin was measured after second heating as cured acrylates are necessary for $T_g$ determination. Specific heat capacity for Cyclomer is much lower than ORMOCER; these values are important as specific values will affect the amount of heat transfer from the polymer to substrate and components in optical devices. Cyclomer will heat and cool faster than ORMOCER per degree rise in temperature; it has greater effect with temperature variation (Figs. 9 and 10).

![Fig. 7. Thermal gravimetric analysis (TGA) and Differential Thermal Gravimetric (DTG) curve of ORMOCER.](image)

Fig. 7. Thermal gravimetric analysis (TGA) and Differential Thermal Gravimetric (DTG) curve of ORMOCER. Thermal analysis measurement done at a rate of 50 °C/min produced TGA curve which showed partial decomposition of ORMOCER below 500 °C with maximum rate of decomposition at 560–580 °C and total enthalpy change of 80%. 20% residue remaining (which is not decomposed) up to 1000 °C is attributed to ORMOCER Si content up to 1000 °C.

![Fig. 8. Thermal gravimetric analysis (TGA) and Differential Thermal Gravimetric (DTG) curve of UV-cured CYCLOMER.](image)

Fig. 8. Thermal gravimetric analysis (TGA) and Differential Thermal Gravimetric (DTG) curve of UV-cured CYCLOMER. Thermal analysis measurement done at a rate of 50 °C/min produced TGA curve which showed partial decomposition of CYCLOMER below 500 °C with maximum rate of decomposition at 530–580 °C and total enthalpy change of 100%. All the acrylic content had been burnt out at 1000 °C.

| Material Characteristics | ORMOCER | Cyclomer |
|--------------------------|---------|----------|
| $T_g$ (°C)               | 136.3   | 149.9    |
| $C_p$ (J/g °C)           | $1.6 \times 10^{-1}$ | $5.406 \times 10^{-3}$ |
with temperature; there is small difference when measured at TE and TM modes. Fluorinated polymer has lower CTE probably due to fluoro group which prevent volume expansion of polymeric chain (Figs. 12 and 13).

The refractive index of the Cyclomer acrylate is higher than the fluoro acrylate; these are expected as the fluoro C-F bond has lower absorption at near IR frequencies. These are due to the polarisability and vibrational molecular effect of the bond which affects the light absorption and refraction.

A serious problem in polymer acrylate at near IR and IR regions is the large attenuation due to high harmonic vibration loss by C-H vibration. A reasonable solution that satisfies both easy polymerisation and low attenuation in the near IR region is the use of partially fluorinated polymer acrylate monomers instead of perfluorinated polymers and acrylate monomer. Cross-linkable fluorinated polymers has an excellent stability even at high temperature and a low absorption for the wavelength around 1.55 μm. The fluorinated polymer

![Graph showing DSC trace of Cyclomer after undergoing UV-curing](image1)

**Fig. 9.** DSC trace of Cyclomer after undergoing UV-curing at a scan rate of 20 °C per min., with glass transition temperature, \( T_g \) at 149.89 °C and \( c_p \) of 0.005405 J/g °C.

![Graph showing DSC trace of Omcocer after undergoing UV-curing](image2)

**Fig. 10.** DSC trace of Omcocer after undergoing UV-curing at a scan rate of 20 °C per min., with glass transition temperature, \( T_g \) at 136 °C and \( c_p \) of 0.151 J/g °C.
waveguide usually has the propagation loss of about 0.5 dB/cm \([13]\). It is thought that with the fluoro group, absorption losses can be greatly reduced hence applicability of the material as waveguide for long distance communication are highly preferred.

4. Conclusions

The application of photosensitive materials in photonic integrated optics as waveguide is highly recommended. Various steps involved in fabricating waveguide channels can be greatly reduced; this will reduce fabrication time and costs. Controlled refractive index can be easily tailored by composition of the materials and parameters during the fabrication steps. The Cyclomer and fluoro acrylates can be potential materials for waveguide as their refractive index is 1.52–1.53 and 1.52 respectively. If cladding and core need to be chosen, composition of both Cyclomer and fluoro acrylate can be varied for suitability as cladding or for its core. From measurement, both acrylate shows a negative TO effect with temperature and \(dn/dT\) of polymers are as high as the order of \(10^{-4}\), which are comparable to those of optical polymers. Higher value of \(dn/dT\) was shown by Cyclomer acrylate compared to the fluorinated type.
This shows the potential of Cyclomer acrylate to be used as possible material for fabricating thermo optical switch.

Fabrication parameter such as UV curing time for both acrylates can be optimized by infra red spectroscopy; cure time is higher for Cyclomer than fluoro acrylate. Optimisation of UV time and intensity other than developer mixtures are necessary prerequisite for constructing waveguide channels for photonic applications.

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