Benzocyclobutene (BCB 4022-35) Polymer Thin Films by Spin Coating Method

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Abstract—**Benzocyclobutene (BCB 4022-35) polymer thin films were fabricated by spin coating technique in this work. Final thicknesses and refractive indices of BCB films for various coating speeds and curing times were characterized by prism coupling system (Metricon-2010) and profilometer (Dektak-3030ST). Final thicknesses of BCB thin films were changed from 2.60 to 5.22 μm. Refractive indices of BCB thin film at 632.8 nm and 1553 nm was 1.5845 and 1.5606 respectively. In addition, extent of curing for BCB thin films was determined by FT-IR spectrometer. As a result of this study, the basic features of BCB thin films were high accuracy determined. The BCB thin films that fabricated high quality are a suitable material for optical applications. This knowledge allows the fabrication of optical waveguides.**

Index Terms—**Benzocyclobutene (BCB 4022-35), refractive index, spin coating method, thin film**

I. INTRODUCTION

The rapid, radical and qualified changes in electronic communication industry pay a critical role in investigation of the properties of polymer. Understanding properties of polymer films has been necessary for the successful using of soft materials in technological applications. Polymers play a critical role in the advancement of microelectronics industry. Polymers are expected to play an important role in the realization of integrated optical devices for applications in the fields of optical communications, optical data processing, electro-optic and thermo optic switching devices, directional couplers, nonlinear optics etc. Extensive interest has been shown in the development and application of polymers for various optically active and passive waveguide devices because of potential of these materials for low cost and high performance commercial products. Classes of polymers used in integrated optics include acrylates, polyimides, polycarbonates, and olefin (e.g., cyclobutene). Benzocyclobutene (BCB), a product of Dow™ [1] is a photodefinable polymer. Due to excellent planarization, low dielectric constant, low moisture uptake, low optical loss, high chemical resistance and high glass transition temperature, BCB is then often used for optical waveguides in recent years [2].

It is well known that benzocyclobutene (BCB) has been widely used for flat panel display, interlayer dielectrics and microelectronics packing applications. Recently, it is also used for making waveguides [3], [4], [5], [6] because BCB has a high glass-transition temperature of over 350 oC and high optical transparency over the wide wavelength range from ultraviolet to infrared [7]. Moreover, BCB on silicon substrate is compatible with the standard processing techniques of integrated circuits [8].

Polymer optoelectronic devices can be fabricated either by thermal evaporation (for small molecules), spin coating technique or dip coating (for polymers). Spin coating method is a well-known technique by which one can produce a very thin and uniform film of viscous liquid by the action of centrifugal force over spinning disk. This technique is widely used in the microelectronics industry to manufacture microelectronic devices, optical mirrors, magnetic disk for data storage, etc. Benzocyclobutene polymers are derived from monomers of the generic form 1 [9]. The polymerization of such molecules is based on thermal rearrangement of cyclobutyl functionality to give the highly reactive intermediate o-quinodimethane which can polymerize with similar molecules or react with a variety of other unsaturated functional groups. The polymerization is a purely thermal process. No catalysts are required and no volatiles. A new class of organic dielectrics, benzocyclobutene has a siloxy containing BCB derivative include low dielectric constant (2.7), low loss (0.008 at 1 MHz), low water absorption (0.25% after 24 h water boil and high degree of planarization (>90% from one layer coverage) [9].

Production of uniform thin films is of paramount importance in microelectronic fabrication. Deposition by spin coating is the primary process fort thin film formation of polymeric materials used in the electronic industry. However, the molecular understanding of process of thin film formation has relatively little attention. The process of spin coating deposition involves consideration of various factors which include the hydrodynamics, rheology of polymer solutions, solvent mass transfer, surface and interfacial phenomena heat transfer and interplay of these processes. A number of semi-empirical models have been proposed to rationalize experiment data with theory [10]. Spin coating involves

flooding the substrate with a polymer solution and then rapidly rotating the substrate at a constant speed between 1000 and 10000 revolutions per minute until the film is dry.

We fabricated Benzocyclobutene (BCB 4022-35) polymer from DowTM [1] thin films by spin coating technique and the final thicknesses and refractive indices of the polymer films for various coating speeds and curing times were characterized by Prism Coupling System (Metricon-2010) and profilometer (Dektak-3030ST).

II. EXPERIMENTAL DETAILS

Fabrication of thin films were carried out with Benzocyclobutene (BCB 4022-35) obtained from of DowTM [1]. For convenience, a silicon wafer [100] is used as the substrate. Silicon wafer to be coated with Benzocyclobutene (BCB 4022-35) resin should be free of all organic impurities and other contaminations prior to coating. A clean surface is important to ensure good adhesion. In order to maintain good adhesion with substrate layer, AP3000 adhesion promoter which is an organosilane coupling agent in an organic solvent was spin coated on the Si wafer, after a conventional semiconductor cleaning. AP3000 comes premixed and does not require further mixing or dilution. The wafer was then spun dry at 5000 rpm for 50 second. BCB (4022-35) were spun onto silicon wafer at 2500 rpm for 30 s directly after adhesion promoter application and spin dry. After the polymer was spun coated, the film was heated on a hotplate for a specific time and temperature to drive out the residual solvent. The time and temperature depend on the film thickness such as to prevent film wrinkle. The polymer was polymerized by thermal cure. Thermal curing was performed at 250 ₒC and 300 ₒC for 1h in nitrogen flowing furnace. Extent of cure of thin films is important for properly processing the materials and ensuring their optimal performance. The extent of curing for BCB thin films was determined by FT-IR spectrometry. The thickness was measured by profilometer (Dektak-3030ST) using average of five measurements. Table I. shows the final thickness of BCB layer for various coating speeds and 250 ₒC curing time. The refractive index of cured BCB film was then measured prism coupling method.

TABLE I. FINAL THICKNESS OF BCB (4022-35) THIN FILM FOR VARIOUS COATING SPEEDS

BCB (4022-35)	
Spin speed (rpm)	Final thickness (m) (After curing at 250 C)
1500	5.22
2000	4.38
2500	3.82
3000	3.45
3500	3.12
4000	2.96
5000	2.60

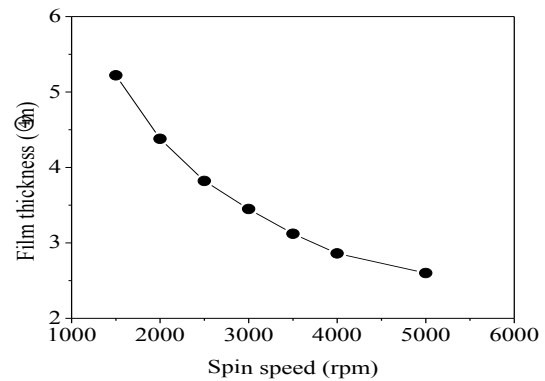Relation between BCB (4022-35) polymer film thickness and coating speed is shown in Fig. 1.

Figure 1. Relation between BCB (4022-35) polymer film thickness and coating speed.

III. CHARACTERIZATION

Polymer characterization using prism coupling technique provides useful ideas on its abilities in optoelectronic applications. The refractive index of cured BCB film was then measured using a Metricon[TM] thin film prism coupler. The basic operation for a prism coupler is to let the incident light interacts with prism/air gap/film/substrate, and the external detector intensity is recorded. The mode positions determined by the local minima of the detected intensity are then used calculate the refractive index and thickness of the measured film. The linear polarized monochromatic light [transverse electric (TE) and transverse magnetic (TM)] is incident onto one side face of prism. As the table rotates, the reflected intensity is recorded on the opposite side of prism by detector as a function of angle. If the measured film is optically weakly absorbing, the observed intensity of the reflected light dramatically decreases and then increases again it certain discrete angles to form an intensity minimum that is called the mode of the film. From the angles, at which local intensity minima are observed, the refractive index and thickness of the measured film sample can be obtained by solving the waveguide mode equation [11]. Measurements were taken in the transverse electric (TE) in order to obtain the in-plane refractive indices of the cured films. Table 2 shows the refractive indices of BCB films for TE polarization.

TABLE II. REFRACTIVE INDICES OF BCB FILMS FOR TE POLARIZATION

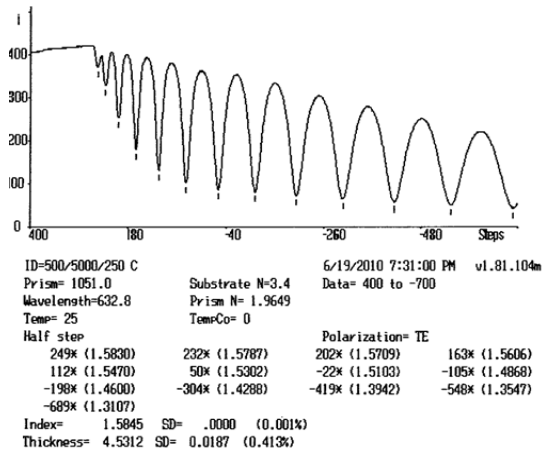| 4022-35			
Wavelength (nm)	Cure temperature (➡C)	Spin speed (rpm)	Refractive index
632.8	250	5000	1.5845
1553.0	250	5000	1.5606
632.8	300	2500	1.5680
1553.0	300	2500	1.5471

Figure 2.   Modes of BCB polymer film which spun 500 and 5000 rpm and then baked 250 oC at 633 nm.

Fig. 2 shows the modes of BCB polymer film which spun 500 and 5000 rpm and then baked 250 C. Because the film is thick at 632.8 nm it shows many modes ad for each pair of modes we can calculate a thickness and a refractive index. In this case, where there are 13 modes we use mode pairs 1-2, 1-3, 1-4, …1-13, where mode 1 is the first (leftmost) mode. The index value displayed (1.5845) is the average of the 12 index measurements. The measured thickness at 632.8 nm was 4.5312 microns.

Fig. 3 shows the modes of BCB polymer film which spun 500 rpm and 5000 rpm and then baked 250 C at 1553 nm measurement.
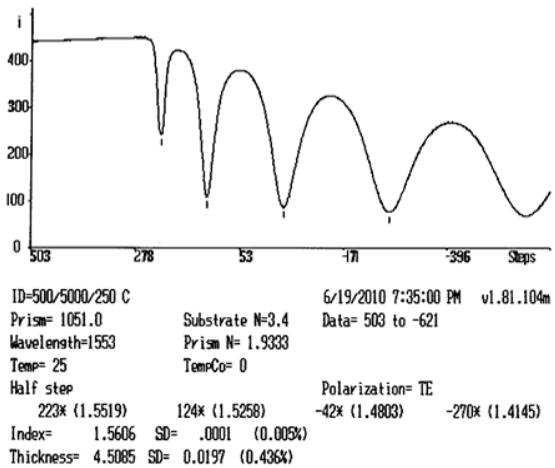

Figure 3.   Modes of BCB polymer film which spun 500 and 5000 rpm and then baked 250 C at 1553 nm.

Only 4-5 modes are seen because the film looks much thinner to the long wavelength light and so films support fewer modes at long wavelengths. Index, as expected is less at 1553.0 nm and thickness is the same to within 0.5%.

Fig. 4 and Fig. 5 show the modes of BCB polymer film sample spun at 500 rpm and 2500 rpm and then baked 300 C at 632.8 nm and 1553.0 nm respectively. This sample is thicker and because it is so thick the first mode (on the left side of the curve) is not clearly resolved and the computer can only accurately find the second mode

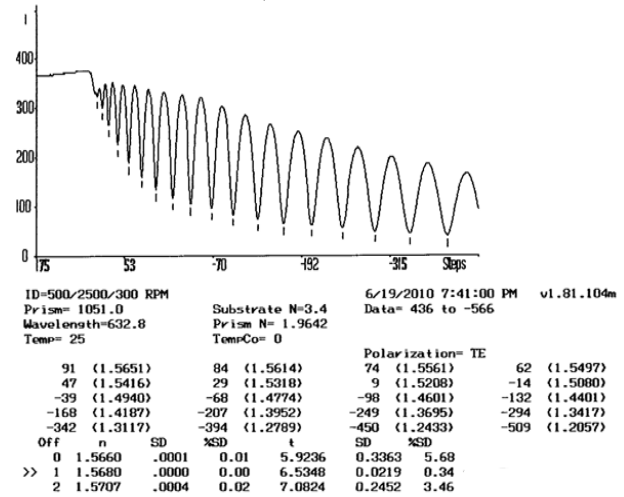(the computer marks modes it has found by placing small vertical line underneath).

Figure 4.   Modes of BCB polymer film which spun 500 and 5000 rpm and then baked 300 C at 633 nm.
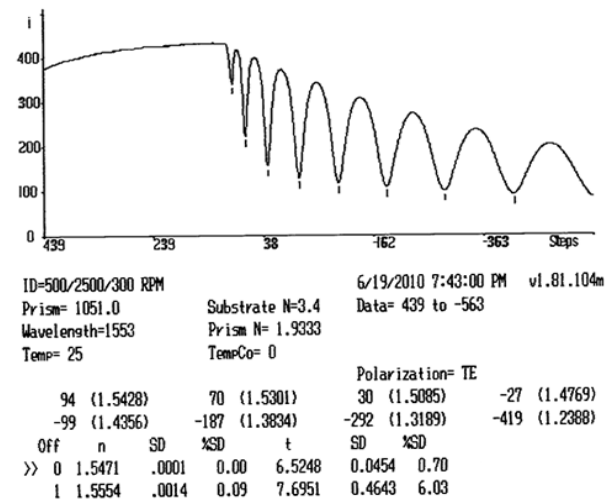

Figure 5.   Modes of BCB polymer film which spun 500 and 5000 rpm and then baked 300 C at 1553 nm.

So for this sample, because of its thickness we have one missing mode at the start of pattern. The numbering of modes is important because equations which calculate thickness and index need to know the correct numbering of modes. If the first mode cannot be resolved and the second mode is assumed to be the first mode, when we calculate all the multiple solutions for thickness and index from all the mode pairs, the standard deviation will be much higher than normal because the multiple estimates for thickness and index are not the same.

Extent of cure of polymer thin films is important properly processing the materials and ensuring their optical performance. Infrared spectroscopy can be used as a non destructive in situ probe of both the cure level of thin films for either free-standing films or films coated on any type of substrate. FT-IR analysis has been shown to be an effective analytical tool in following the reaction progress of BCB. FT-IR was used to examine the changes

in chemical structure of BCB during the bonding test. Unlike other polymer materials, the chemical structure of BCB affecting bonding (cure reaction) was clearly distinguishable. Such a distinctive cure reaction of BCB helped determine the bonding mechanism of BCB. Typical changes in the infrared spectrum observed during curing are shown in Fig 6. Fig. 7 shows FT-IR spectra of BCB after curing.
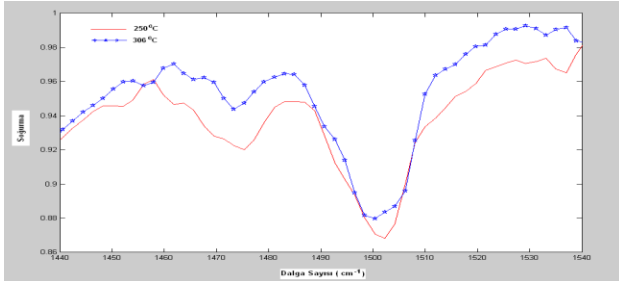

Figure 6.   Typical changes in the infrared spectrum of BCB (4022-35) thin film on silicon wafer
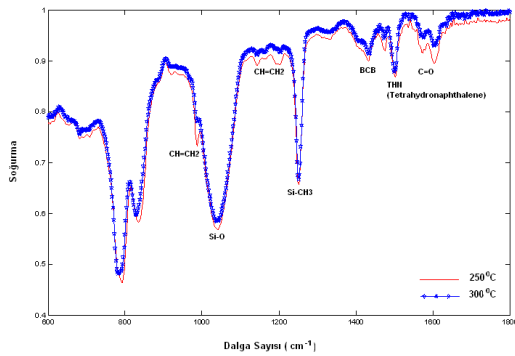

Figure 7.   FT-IR transmission spectra of Benzocyclobutene (BCB 4022-35) polymer thin film on silicon wafer

TABLE III.   PEAK POSITION AND ASSIGNMENTS OF BCB

BCB (4022-35)	
Peak Position (cm^{-1})	Peak assignments
985	Vinly moiety
1050	Si-O stretch
1194	Vinly rocking
1254	Si-CH$_3$ rocking
1472	BCB stretch
1498	Tetrahydronaphthalene (THN)
1710	Carbonyl

Table III presented the peak positions all components that affect the cure reaction of BCB. 1500 cm-1 band increases with cure, while the 1475 cm-1 band decreases. The thermal curing of BCB polymer is a two step process. The first step is a thermally activated opening of

benzocyclobutene ring to form an o-quinodimethane intermediate. The o-quinodimethane reacts with residual alkene groups in the polymer via Diels-Alder reaction, forming a tri substituted tetrahydonaphthalene. The extent of curing is monitored by following either the growth of a band at 1500 cm-1 in the infrared spectrum, associated with a vibration of tetrahydonaphthalene polymerization product, or alternatively by decrease in absorbance of the 1475 cm-1 band associated with motion of four membered cylobutene reactant group. As the cure progresses, the 1500 cm-1 band grows in intensity, while the 1475 cm-1 band disappears. The degree of cure in the polymer is a function of the temperature and the time at that temperature. The standard recommended thermal cure process is a 1hr cure art 250 C [12], [13].

The atomic force microscopy (AFM) is a unique microscope based on a mechanical method. We used AFM to observe the morphology and determine the surface roughness of thin BCB films.

Surface roughness is reported as the average absolute deviation about the mean film height (Ra), which is in proportion to the root mean square (RMS) value for a Gaussian distribution of roughness [14], [15], [16]. For roughness calculations, the raw images were flattened prior to analysis. The equation for average roughness (Ra) of the prepared film surface is express by (1) [17].

$$Ra = \frac{1}{S_o} \iint |Z(X,Y) - Z_o| dXdY$$

(1)

Where Z(X, Y) is the elevation for a given point; Z_0 is the average of the elevation within the given area; and S_0 is the projected area of the given area.

The results are given Fig. 8-9 which gives a surface roughness in root mean square (RMS) of 0.272-0.331 nm, which indicates good coating quality. It is observed that the surface roughness of BCB polymer cured at 300 C has good coating quality than the surface roughness of BCB polymer cured at 250 C.
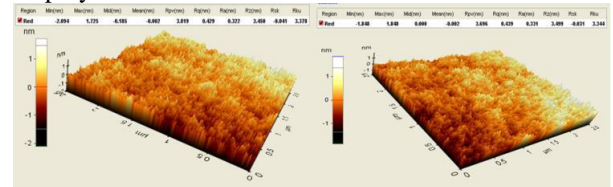

Figure 8.   Atomic force microscope (AFM) images of BCB polymer films which were spun at 5000 rpm and cured 250C surface roughnesses
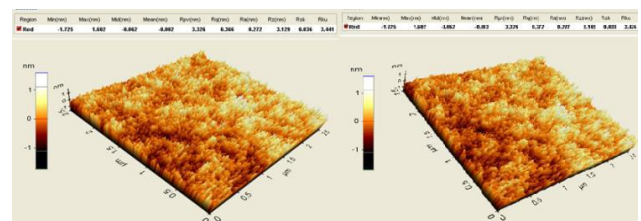

Figure 9.   Atomic force microscope (AFM) images of BCB polymer films which were spun at5000 rpm and cured 300 ➡C surface roughnesses

IV. RESULT AND DISCUSSION

Thin films based on organic BCB 4024-35 polymer have been fabricated using silicon [100] as a wafer. In order to view the uniformity of polymer coating, the atomic force microscope (AFM) is used. The results are given Fig. 8-9 which gives a surface roughness in root mean square (RMS) of 0.272-0.331 nm, which indicates good coating quality. It is observed that the surface roughness of BCB polymer cured at 300_{o}C has good coating quality than the surface roughness of BCB polymer cured at 250_{o}C. The characterization of BCB polymer provides useful ideas on its abilities in optoelectronic applications. FT-IR showed no serious changes in the cured BCB bond. The BCB thin films that fabricated high quality are a suitable material for optical applications. This knowledge allows the fabrication of optical waveguides.

ACKNOWLEDGMENT

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