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Review Paper

Materials and process optimization in the reliable fabrication of polymer photonic devices

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The development of organic polymers with high optical quality and high performance has led to a maturing of the polymer based photonic device field. There are two important approaches to develop reliable photonic devices. The first approach is the materials and process optimization, and the other is the reliability assurance during the fabrication and operation period. They are the well-known potential showstopper to the growth of polymer photonic devices. These critical issues needed to be addressed in order to bring commercialization of these devices closer. In this review, the issues are investigated in fabricating reliable waveguide devices, whereas the results are very useful for other applications, too.

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1. Introduction

Planar Lightwave Circuit (PLC) devices have numerous advantages as regards their use in optical fiber communication systems. PLC technology is a combination of large-scale integrated circuit (LSI) patterning technology and optical fiber technology, where the PLC devices can well match with single-mode optical fibers from the viewpoint of optical characteristics. They offer compactness and ruggedness and also provide excellent controllability, compatibility, high reliability, and mass productivity. In fact, this allows for different components to be integrated on same substrate and hence enhancing chip level reliability. PLC-technology also provides the potential for low-voltage and low-power electrical tunability of the devices by using either thermo-optic or electro-optic effects. Other devices such as bulk-optic or fiber technologies have many shortcomings. They need a lot of other expensive components, such as polarization controllers, optical isolators, couplers, or half-wave plates etc., in order to build up the whole device. In addition, these devices are usually not compact and not rugged to use in practice. In fact, it is very difficult for them to be integrated to chip level scale of density. On the other hand, PLC-based optical devices can overcome the above-mentioned shortcomings [1].

Most PLC devices including lasers, modulators, switches, power splitters, directional couplers and filters are in the form of optical waveguide [2]. Waveguide technology shares a number of advantages for optical interconnection. They provide well-controlled and accurately directed connections for optical transmission. They do not require impedance matching, as required in high speed electrical interconnections, and thus support extremely large bandwidths for optical interconnect. It can also provide additional functions to enhance the coupling efficiency or to incorporate component redundancy [3-4]. The fabrication process of optical waveguide mainly includes the deposition of multi layered thin film structure. These multi layered structure supports electromagnetic waves, which are guided in the core region as wave propagates along the propagation direction. These waves are stable and their energy generally stays mostly within the core region [5].

However, the main challenges facing in the development of reliable waveguide based optical devices are material and process optimization. They are the addressing issues for better PLC functionalities and performances of the device. In general, waveguide based devices can easily suffer from polarization issue. This problem may possibly be circumvented through the proper selection of optical waveguide geometry and materials [6]. In summary, the study developed in this review paper is related to the optimization of materials and process parameters in the reliable fabrication of such waveguide devices.

2. Material issues

Several inorganic materials capable of multiple functions (such as modulation, switching/attenuation, wavelength conversion, and amplification) are under intensive investigation, including lithium niobate ($LiNbO_3$), silica (SiO_2), silicon on insulator (SOI) and III-V compound semiconductors. Such materials exhibit polarization-dependent loss for many active and passive devices. Sharp and polarized absorption and emission lines result in an amplification bandwidth too narrow to be useful for multiple wavelength systems such as wavelength division multiplexers and bit-parallel multi-wavelength interconnects. Such characteristics limit their use for optical gain circuits in specific fiber systems unless polarization converters are used. These materials are strictly substrate selective due to the lattice matching required for single-crystal thin-film growth. Finally, the fabrication costs associated with these materials are very high, which seriously jeopardizes the commercialization of the end products [7].

As an alternative, polymers offer many advantages over the aforementioned materials for the fabrication of PLC devices [8-9].

1. Polymers are usually in an amorphous state that can provide a wider bandwidth of amplification if an appropriate gain mechanism is identified.
2. Polymer offers large thermo-optic (TO) coefficient ($\sim 10^{-4}$) in compared with other conventional inorganic materials such as silica ($\sim 10^{-5}$), allowing a more efficient way to drive a polymer device using TO effect.
3. The microstructure can be easily engineered to provide desired optical parameters such as bandwidth of transparency, high electro-optic (EO) coefficient values, and temperature stability for specific applications.
4. Unlike any of the inorganic materials that cannot be transferred to other substrates, the polymeric passive and active devices proposed herein can be easily integrated on any surface of interest.

Therefore the study has been mainly focused on the polymer based waveguide devices fabrication. Among different kind of polymer used in this application, epoxy is the best suited due to: [10]

1. Low cost compared to other acrylic and polyimide based polymer.
2. High thermal stability: the resins have a high glass transition temperature ($T_g \sim 200^oC$) and is therefore expected to have good thermal stability.
3. Precise controllability of refractive index: by mixing several epoxy resins together, it can precisely control the refractive index in the region of 1.48 - 1.60 with a 0.001 order accuracy.
4. Photo-curable property: the resin can be easily patterned with a conventional mask process using a UV light source.
5. Acceptable optical loss: this issue can be minimized when epoxy is used as cladding layer.

The epoxy used in this study, is a commercial UV curable adhesive. It is clear, slightly amber in appearance and 100% reactive liquid that can be cured readily by exposing of UV light. The viscosity of this adhesive is less than 1000 cps at 25^oC. It consists mainly of (i) epoxy resin and (ii) a hardener. The term 'epoxy' refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms that are already bonded in some way. The simplest epoxy is a three-member ring structure known by the term 'alpha-epoxy' or '1,2-epoxy'. The hardener, often an amine, is used to cure the epoxy by an 'addition reaction'. During the curing, the epoxy resin reacts with amine and forms a complex three-dimensional molecular structure. The cured adhesive is also optically clear.

3. Processing issues and performance

Recent advances in the development of organic molecules and polymeric epoxy adhesive with high optical quality and performance have led to a maturing of the PLC device field and bring commercialization closer. However, the physical, optical and mechanical properties of epoxy adhesive are very critical to the success of the reliable fabrication and mainly depend on the processing. They are all interrelated and it is not possible to look at one property alone to determine suitability. A balance of these properties is obviously needed for reliable fabrication of PLC devices. Only a clearer fundamental understanding of the deposition, fabrication and degradation mechanisms can allow manufacturers to develop high reliable, low cost and better performance polymer photonic devices [2]. The performance of polymeric epoxy adhesive based PLC devices mainly depends on the following issues.

3.1 Thin film deposition

Fig. 1 shows the overview of one of the photolithography processes for the fabrication of inverted rib polymer optical waveguide using benzocyclobutane (BCB) as core and epoxy as cladding material. Polymeric thin film is the fundamental building block of polymer based optical devices. One of the simplest and most common techniques of applying thin polymers films onto wafers is the spin coating. The process solely involves the dispensing of an excessive amount of fluid onto a stationary or slowly spinning substrate and then spinning at high speed. Therefore, it is also very interesting to study and understand the behavior of complex mixed solutions under the conditions of rapid fluid flow and convectively-driven evaporation that occur during spin coating [11].

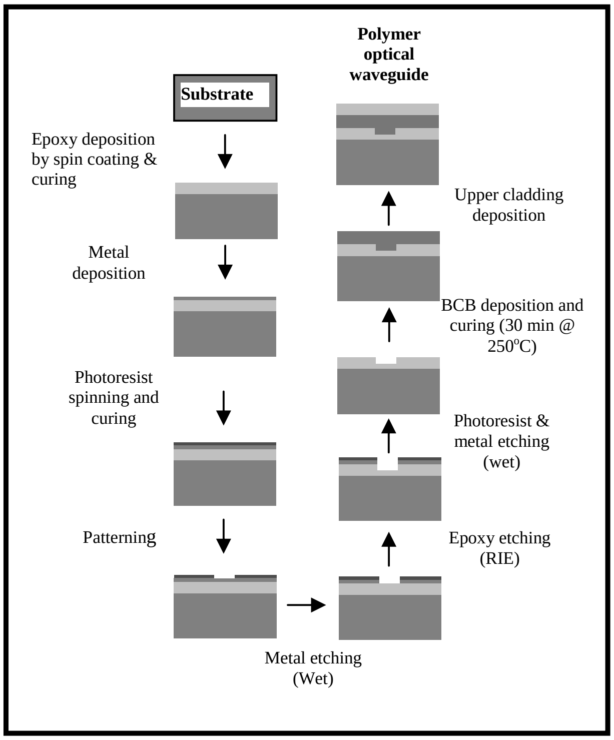


Fig. 1. Overview of photolithography process for the fabrication of polymer optical waveguide.

3.2 Curing condition

The curing of epoxy adhesive is of a great importance in applications. It is a process of its conversion from a liquid to a solid state, accompanied by a physical or chemical modification in the polymeric adhesive. Changing a liquid state into a solid state is accomplished by physical and chemical modification in the polymer. Therefore, curing is believed to be critical to develop the ultimate mechanical and optical performance of polymer devices. A minimum degree of curing is needed to provide a certain level of that performance. An under-cured adhesive is not optimized to acquire those performances, especially in regards to environmental resistance and dimensional properties. However, over cured adhesives also become brittle resulting in greater stress on the adhesive bond and interfaces [12-14].

3.3 Stability

In this application, after the deposition of initial adhesive layer, additional heating and chemical etching is required for the fabrication of subsequent step of photonic devices. Therefore the polymeric adhesive material should have sufficient thermal and chemical stability to withstand typical fabrication processing and operation condition with good performances [15]. The knowledge of stability, degradation and mode of decomposition under the influence of heat and chemical solution is very important in the process optimization. The threshold gives an indication of the ultimate processing condition that can be used during the subsequent fabrication and operation process. Correct understanding of potential degradation mechanisms can greatly aid the appropriate selection of material and process parameter in the fabrication and extend the outdoor longevity of the product [16-17].

3.4 Mechanical strength

The curing condition and stability of the polymeric adhesive film also should have influences in the adhesion strength of the coated film to the substrate. High adhesion strength is a critical parameter of multi layer interconnections that are fragile to shocks encountered during fabrication, handling and lifetime. For example, Fig. 2(a) shows the typical SEM picture of the interfacial failure (large delamination) of a channel waveguide. Fig. 2(b) also shows the typical failure of spin coated thin adhesive film where it is peeling out the from the silicon substrate. Concerning this technology, surface finish or surface roughness are other important parameters that control the state of the adhesion. The interfacial strength also depends on the environmental and processing condition of subsequent fabrication and operation process [18]. Thermo-mechanical failures are also caused by stresses and strains generated within an optical device due to the mismatch in the coefficient of thermal expansion (CTE) among different materials during thermal loading from the environment or internal heating in service operation [19].

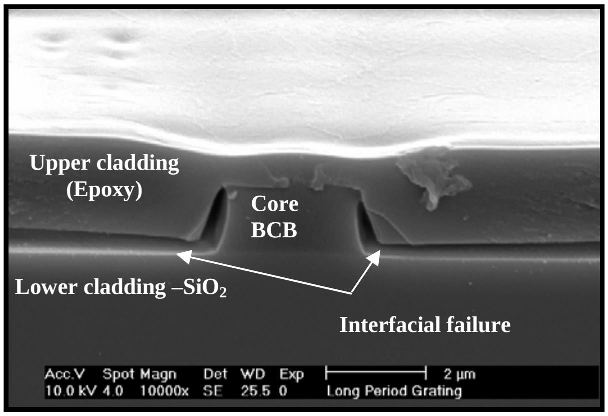


Fig. 2(a). Typical SEM picture of the interfacial failure (larger delamination) in a channel waveguide.

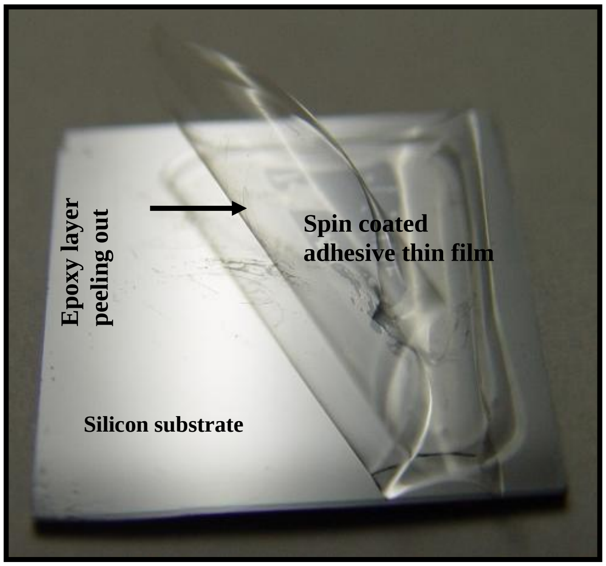


Fig. 2(b). Typical interfacial failure of a spin coated thin polymer film from the silicon substrate.

3.5 Surface condition of adherence

Continuous effort is paying to improve the interfacial adhesion in polymeric adhesive based PLC devices. Interfacial strength is fundamentally related to surface attachment, the properties and conditions of the adherend surface are of paramount importance. The silicon wafer is commonly using as substrate for the fabrication of photonic devices. The main advantages of silicon wafer is easy to cut in pieces as the samples need to be sectioned to the area of interest or for easier handling and therefore no need to polish the end faces of the devices. However, the previous study shows that the adhesion of polymeric adhesive to the silicon surface is comparatively low [20]. The oxidized silica containing (thin layer of silica on silicon) silicon wafer can be use as substrate and becoming very attractive due to its matching refractive index with optical polymer. Thermal oxidation of silicon is easily achieved by heating the substrate to temperatures typically in the range of 900-1200 ^{o}C. Another potential alternative is to use a thin metal layer on silicon wafer to improve the adhesion of polymeric adhesive to the substrate. The thin metal layer can be deposited rapidly on silicon wafer by typical deposition process such as sputtering, thermal or E-beam evaporation. Thus, a careful treatment and modification of the surfaces before the adhesive deposition is essential for realizing a strong interfacial strength [21].

4. Research studies

For a better understanding of the mechanisms underlying these problems, the following studies are being conducted in order to develop and improve the performance of polymeric adhesive material in this application.

4.1 Effect of spin coating on the curing rate of epoxy adhesive

Spin coating is a simple process for rapidly depositing thin solid polymeric adhesive films onto relatively flat substrates. The deposition process involves the dispensing of fluid onto a stationary or slowly spinning substrate. An excessive amount of fluid is used to prevent coating discontinuities caused by the fluid front drying prior to reaching the wafer edge. Evaporation occurs during spinning of the relatively volatile species in any solution. The curing behavior of spin coated polymeric adhesive film is influenced by the evaporation of any reactive component. An investigation was carried out on a silicon substrate to study the effects of spin coating on the curing behavior of the epoxy adhesive. The curing rate for both spin and without spin coated epoxy adhesive was measured by fourier transform infrared spectroscopy (FTIR) [13].

4.2 Thermal and chemical stability of spin coated epoxy adhesive

The curing state initially affects the stability of the materials. Therefore, thermo-gravimetric analyzer (TGA) was used to explore the thermal stability of both spin coated and without spin coated epoxy adhesive. When the polymeric adhesive was chemically and physically changed, the TGA showed significant reduction in weight at that effective temperature. Chemical resistance was measured by the changes in refractive index and microscopic observation before and after immersion in metal-etchant chemical solution. A better understanding of the effects of the spinning on the thermal and chemical stability is important in making high-quality polymer thin film [22].

4.3 Interfacial adhesion of spin coated polymer film

Both the curing state and stability determines the interfacial adhesion of the multilayer structure. Therefore an investigation was carried out to study the interfacial adhesion of spin coated epoxy adhesive on a silicon substrate. The interfacial adhesion of the epoxy layer was determined by using a Dage D2400 shear tester. Shear button was made of adhesive of 10 μm height with 100 μm by 100 μm patterned on silicon wafer substrate using photolithography process. Fig. 3 shows the schematic of shear button fabrication process. Figure 4(a) and 4(b) show the prepared shear button and schematic instrumental arrangement respectively for measuring the shear strength. The test was carried out with 100 μm shear tips at a shear speed of 100μm/s, so that uniform shear force applied to the whole edge. Shear lift off height was 2 μm. Three samples were tested per given condition. The interfacial adhesion was measured with and without heat exposure of polymer film and on different plasma treated silicon surface. A better understanding of the interfacial adhesion of spin coated polymer is important in making reliable thin film [20].

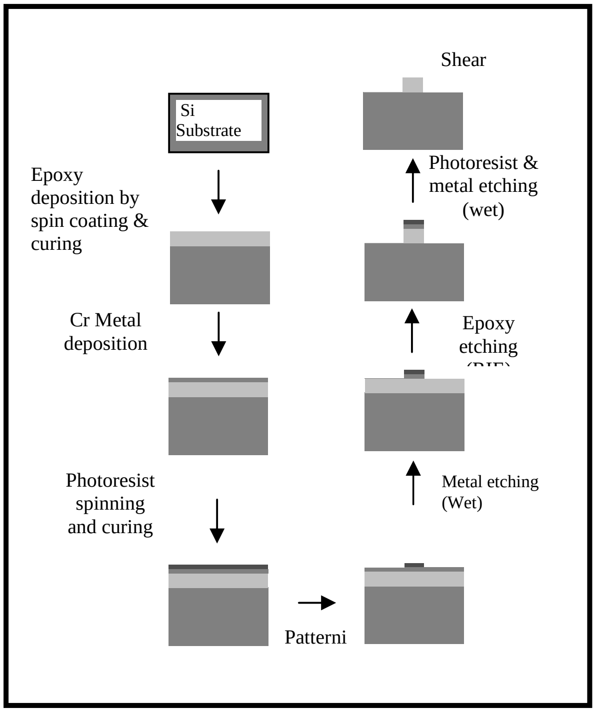


Fig. 3. Shear button fabrication process for shear test.

4.4 Effect of surface structure on the interfacial adhesion of polymer film

Three different types of substrate structure (as received silicon wafer, oxidized silica on silicon wafer & thin metal layer on silicon wafer) were used to verify the interfacial adhesion using a Dage D2400 shear tester. Shear button of adhesive was made of (10 μm height with 100 μm by 100 μm patterned) on the substrates using photolithography process. For each type of substrate, four categories of sample were prepared to measure the interfacial adhesion. Firstly, the shear button was prepared just after curing the adhesive to see the effect of different substrate structure. Secondly, the spin coated adhesive film was put on a hot plate at 275^{o}C for one hour in a N_2 chamber (considering the curing of subsequent core layer of benzocyclobutene -BCB) before making the shear button to observe the effect of heat treatment. Lastly, another two different sets of prepared shear button fabricated on the above two methods were put in humidity chamber (75^{0}C /95% RH /168 hours) to observe the effect of damp heat test. A better understanding of the interfacial adhesion among those substrates is very important for manufacturers to optimize the materials and fabrication process of highly reliable polymer PLC devices [21].

5. Results and discussion

Optical adhesive has gained much attention, and significant technological progress has been made recently for future PLC devices in order to meet the requirement of high-speed, large-capacity transmission of information and low cost. However, it is believed that polymeric adhesive will not be a complete drop-in replacement for other conventional material and technique, at least in the very near future. There have been several major obstacles to overcome, including compositional and processing induced lower curing rate, limited thermal and chemical stability, weakened mechanical strength, interfacial delamination, surface structure and environmental condition, which have been studied in this research.

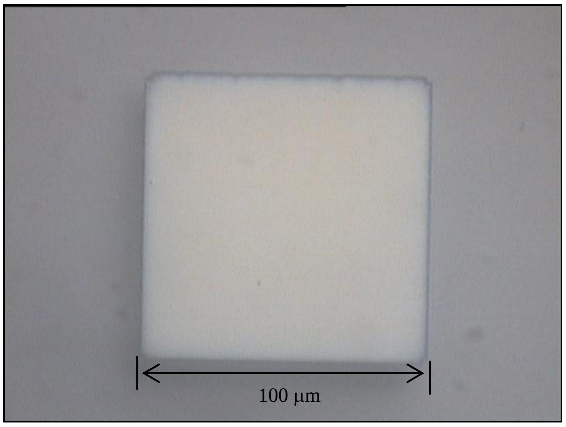


Fig. 4(a) Prepared shear button for measuring the adhesion strength.

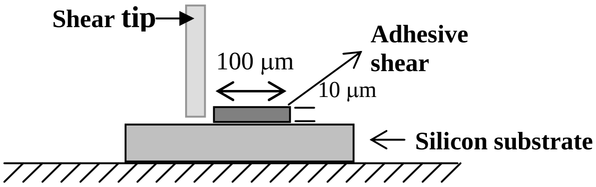


Fig. 4(b) Schematic instrumental arrangement for measuring the adhesion strength.

5.1 Curing degree of spin coated polymeric film

Thin polymer adhesive films can be deposited by a variety of techniques with different complexity and applicability. The choice of deposition technique depends upon the physicochemical properties of the material, the film quality requirements and the substrate being coated. The final properties of these films also depend on their morphologies that are largely affected by the polymer chain orientation and the state of aggregates. One of the simplest and most common techniques of applying thin films onto wafers is spin coating.

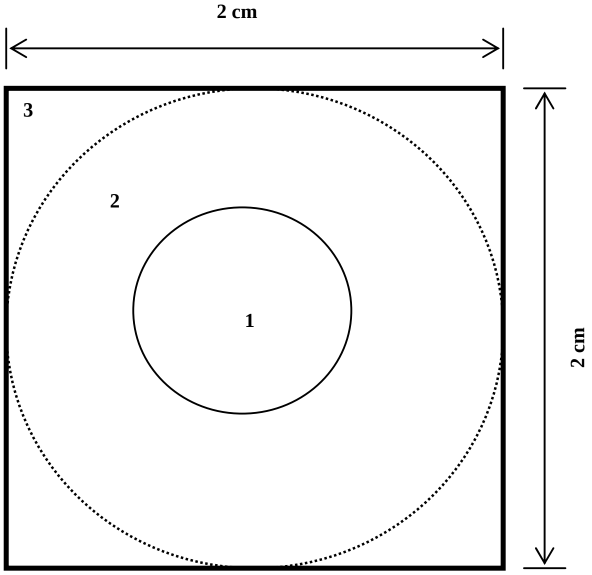


Fig. 5. The three measurement locations used for spin-coated adhesive film in the study.

Degree of curing of spin-coated polymer film (over 3 locations of deposited sample indicated in Figure 5) was measured using the same FTIR method. Fig. 6 shows the effect of spin coating on the curing rate of epoxy adhesive at different location for different UV exposure time. The Figure shows that the curing rate decreases abruptly for spin-coated adhesive film compared to adhesive that was not spin coated. Degree of curing also varies at different locations of the spin-coated substrate. At the center of the substrate it is higher than the other locations. The slower reaction rate is mainly due to changing the material properties during spinning. The spin coating involves transient fluid flow and mass transfer in a medium that experiences drastic changes in properties. Both fluid viscosity and solvent-solute diffusivity can change by several orders of magnitude from the initial stages [23].

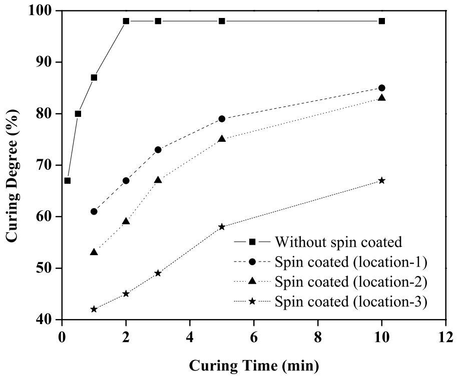


Fig. 6. Effect of spin coating on the curing behavior of epoxy adhesive at different locations of the substrate for different UV exposure time (min).

5.1.1 Factors affecting the curing rate of spin coated polymer film

The spin-coated liquid usually contains a volatile solvent that evaporates during spinning, leaving behind a thin solid film. The solvent during spin coating is the most influential for obtaining good spin-coated films. Its evaporation has a tremendous influence on the control of the final film thickness after mass transfer and spreading of the solvent [24]. The evaporation rates are influenced by such factors as the temperature of the fluid, ambient temperature, heat conductivity, molecular association, molecular weight, vapor pressure, surface tension, humidity, latent heat of evaporation and vapor density. The high degree of uniformity in the evaporation rates leads to a similar uniformity in the final polymer film [25].

Solvent evaporation couples liquid-phase diffusive transport of solvent toward the interface to gas-phase convective mass transport of solvent away from the interface. The solvent vapor is carried away in a stream of air that is drawn down axially toward the surface and driven radially across it by a centrifugal pumping action created by the spinning substrate [24]. Solvent is continually evaporating from the film, altering the material properties (e.g., viscosity, diffusivity, vapor pressure, surface tension) and eventually producing a film of finite thickness. As a result, the reaction rate of spin coated adhesive decreased due to:

1. <u>Solvent evaporation</u>: Due to the evaporation during spinning, the viscosity of the adhesive increased. Increased viscosity reduces the mobility of the polymer molecules and slows the reaction rate. The number of solvent molecules also decreased and the free volume increased [26]. Due to the lack of solvent molecules, the reaction rate and the total amount of reacted species reduced, hence, the lower the curing degree of spin coated adhesive film.

2. <u>Composition gradient</u>: Evaporation also establishes a composition gradient at the surface as volatile species leave and less volatile components are left behind [27]. The top surface becomes the high volatile species-rich layer and the bottom is that of low volatile species. Constituents need to further inter-diffuse for chemical cross-linking reaction during the UV exposure. This takes additional time that decreases the curing reaction rate substantially compared to the adhesive that haven't been subjected to the spinning process.

The curing degree of spin-coated adhesive is lower than that of without spinning, even after long time (10 min) UV exposure. At the center of the substrate, the rate of evaporation is low due to the low angular momentum of the fluid. On the other hand, higher evaporation rates are caused by the combination of both radial and axial flow at the edge of the substrate. Therefore, the evaporation, as well as the composition gradient varies from the center to the edge of the substrate. They are lower at the center and higher at the edge. The cross-linking reaction rate is higher in the center (location-1) rather than other locations of the substrate. Due to the variation in curing degree and surface tension, the topography also varies at different locations of the spin coated adhesive film. Fig. 7 shows the surface topography at the corner of the spin coated adhesive film after curing for 10 min. The figure clearly shows how the topography differs from center to the corner due to the spinning process of the adhesive.

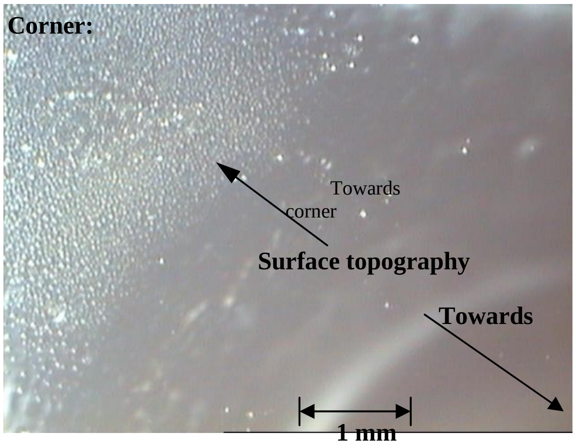


Fig. 7. Surface topography, near the corner of the spin coated adhesive film after curing for 10 min.

Before curing, the fluid properties dictate a constant angle at the solid-liquid- gas interface. The result is a thick edge bead confined at the wafer's edge. Another reason for such a film pattern is the increased friction with air at the periphery, resulting in an increased evaporation rate that causes a dry skin to form at the edge and impedes fluid flow. As a result, the fluid in the center of the substrate still being driven out by centrifugal forces begins to flow over the dry film and dries, resulting in buildup the edge bead [28]. The thickness and the viscosity of the edge bead is very high compared to other locations, so the degree of curing at location 3 of spin coated adhesive film is very low [29]. As the free volume shrinks during the curing of spin coated adhesive film, the film size is reduced and a few millimeters of the substrate becomes unoccupied by the adhesive.

5.1.2 Recommendations

The uneven curing induces the internal stresses, shrinkage and interfacial delaminations in the devices. This type of adhesive should not use in spin coating purpose for the fabrication of polymeric thin film of optical devices. Therefore, when designing coating solutions solvents should be selected with relatively lower vapor pressures to reduce the solvent evaporation also the composition gradient during spinning and no variation of curing speed observed after spin coating. This is one of the major criteria of selecting spin coating solution for the fabrication of thin film for PLC devices.

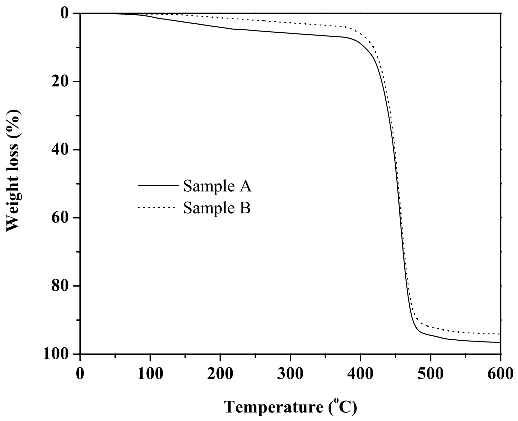


Fig. 8. Thermo-gravimetric results of the epoxy adhesive that was not spin coated.

5.2 Stability of spin coated polymeric film

The previous studies have found that the curing reaction rate of spin coated epoxy adhesive is much slower than that of without spinning. The reaction rate at the center of the substrate is also higher than other locations. The slower reaction rate is mainly due to changing the material properties during spinning [13]. The changes in material properties during the spinning as well as the curing degree or cross-linking density of the cured material greatly influence the stability of the adhesive.

5.2.1 Thermal stability

Thermo-gravimetric analyzer (TGA) was used to explore the thermal stability of spin coated epoxy adhesive. Fig. 8 shows a typical TG diagram (weight loss during the temperature rise) of cured epoxy adhesive (sample A and B) that was not spin coated. The weight loss profile for those two samples is almost similar through out the weight loss process and differs only at initial degradation temperature. Lower initial degradation temperature was observed for sample A (70 °C) than sample B (100°C). Because sample A was not post cured by heat after UV curing and therefore sample B is more stable than sample A. Sample A may contain absorbed moisture in the adhesives existed in a state of free or loosely bound water, which started to evaporate at low temperature. It also indicates that only the UV light energy is not sufficient for optimum curing of UV curable epoxy adhesive and needs post thermal exposure for moisture evaporation. The major concern involving the presence of moisture at elevated temperatures is hydrolytic degradation. Hydrolysis is a chemical change, which occur when moisture is present above or near the glass transition temperature (T_g) of the polymer. Hydrolytic degradation causes random chain scissions to occur, which causes a reduction in molecular weight and in turn, a reduction in mechanical integrity of cured adhesive. During the post thermal exposure, cross-linking density also increases [30]. The anhydride group and hydroxyl group of the resin reacts to form ester cross-links. These ester networks are more thermo-stable than other types of linkage [31].

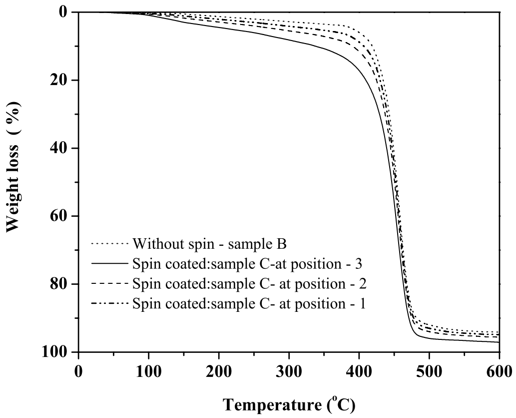


Fig. 9. Effect of spin coating on the thermal stability of epoxy adhesive.

Thermal stability of spin-coated adhesive film (sample C, over 3 locations of Fig. 5) was also measured using the same TGA method. Figure 9 shows the corresponding TG curve of sample C at three different locations with the TG curve of the sample B. A comparison of the stability change due to the spin-induced degradation of epoxy adhesive determined here with other previously found characteristic temperature is shown in Table 1. The result shows that the thermal stability decreased for spin-coated adhesive film compared to adhesive that was not spin coated.

Table 1. A comparison of the thermal stability change due to the degradation of epoxy adhesive.

Sample		Characteristic temperature (^oC)		
		Initial degradation	Degradation	Decomposition
Sample A		70	408	448
Sample B		100	416	450
Sample C	Position-1	90	407	445
	Position-2	70	385	438
	Position-3	55	338	432

Thermal stability also varies at different locations of the spin-coated substrate. At the center of the substrate it is higher than the other locations. The lower thermal stability is mainly due to changing in material properties to various degrees at various location of the spin coated epoxy adhesive during the spinning process. The spin-coated liquid usually contains volatile component that evaporates during spinning and leaving behind a thin solid film. Solvent evaporation from the film alters the material properties (e.g., viscosity, diffusivity, vapor pressure, surface tension). The high degree of uniformity in the evaporation rates leads to a similar uniformity in the final polymer film properties [26].

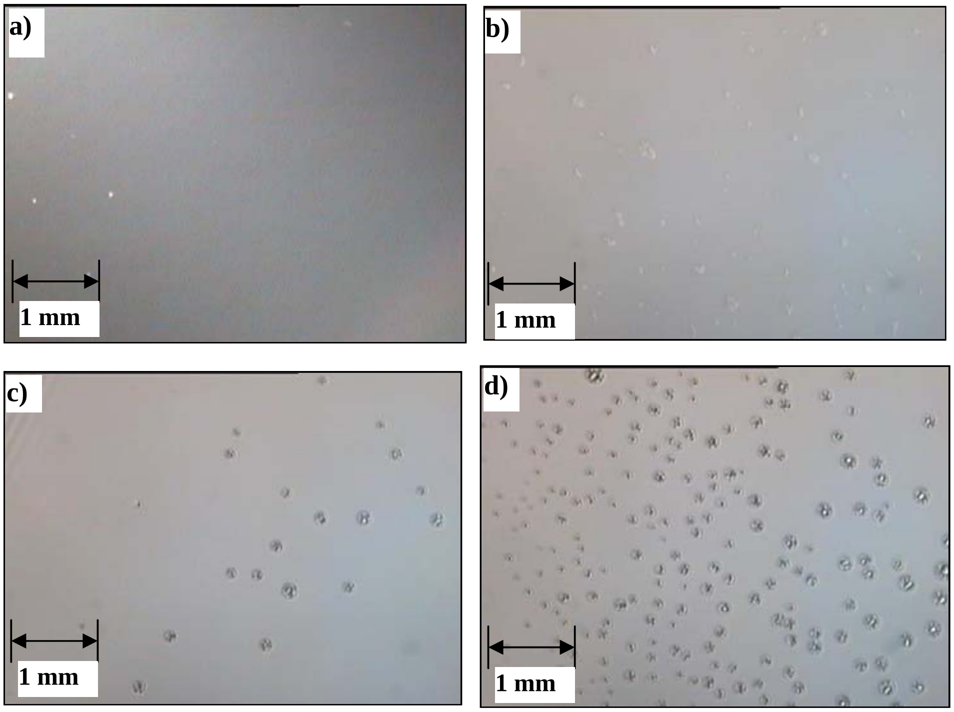
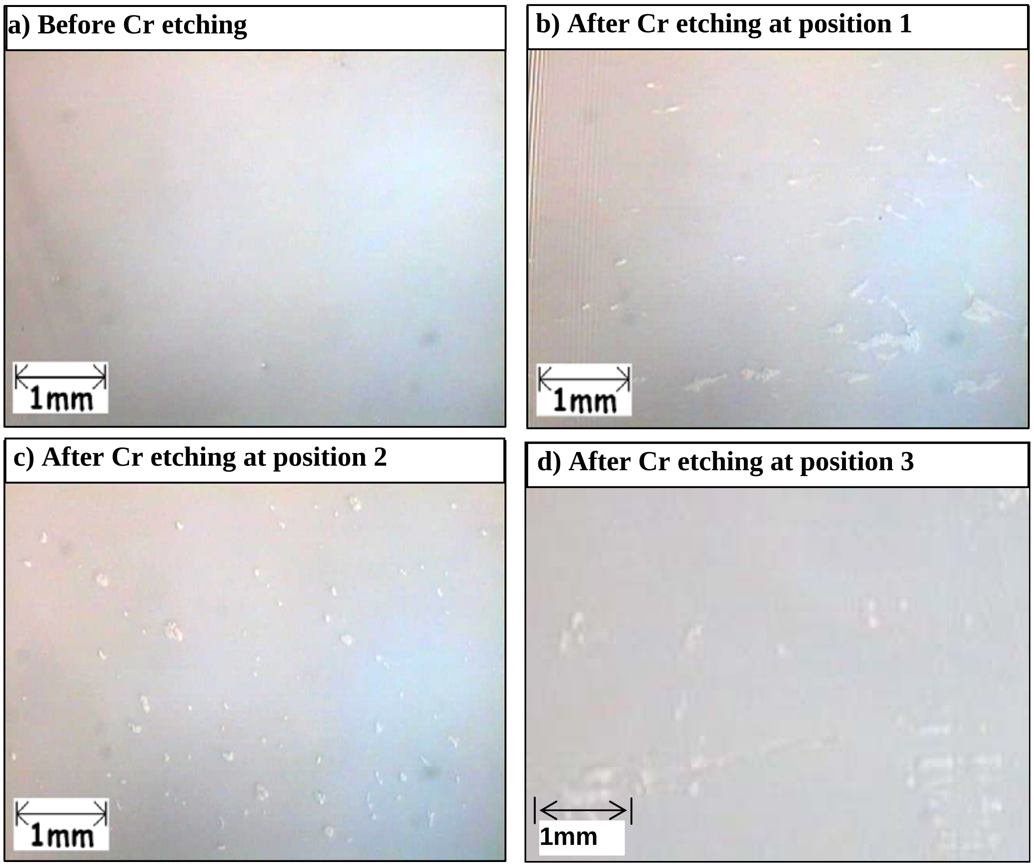


Fig. 10. Optical micrograph of the cured epoxy after the immersion in Nickel (Ni) metal etchant (a) without spin (b) spin coated position-1 (c) spin coated position-2 (d) spin coated position-3.

5.2.2 Chemical stability

Chemical stability is the material's ability to withstand change from chemical contact. This issue involving the corrosive fluid exposure should be evaluated to ensure chemically stable polymeric thin film for optical waveguide. The immersion test shows that the spin coated epoxy surfaces were also deteriorated to various degrees at various location of the coated epoxy adhesive. Fig. 10(a) shows the optical micrograph of sample B after the immersion in nickel etchant. It is very clear that the without spin sample surface is chemically stable in that solution and almost no change in surface morphology. However for the spin coated sample (sample C), it shows some different results. Fig. 10(b)-(d) display the optical micrographs of different locations on the spin coated cured adhesive after the immersion in solution. The chemical attack leads to porosity in polymer interface, which results in excessive increasing of optical loss. However it was more stable in chromium etchant than that of nickel.

Fig. 11 shows the optical micrograph of sample C after the immersion in chromium etchant. The spinning also affects the refractive index of the cured adhesive. Fig. 12 shows the refractive index of spin coated adhesive (sample C) before and after immersion in chemical solution. Before immersion higher refractive index was found at the corner and after immersion the higher drop also indicates the lower stability at that portion. Moreover the change of refractive index in chromium etchant is lower than that in the nickel.


a) Before Cr etching

b) After Cr etching at position 1

c) After Cr etching at position 2

d) After Cr etching at position 3

Fig. 11. Optical micrograph of the cured epoxy after the immersion in Chromium (Cr) metal etchant (a) before immersion (b) spin coated position-1 (c) spin coated position-2 (d) spin coated position-3.

5.2.3 Factors affecting the stability of spin coated polymer film

Earlier studies have found that the curing reaction rate of spin coated epoxy adhesive is much slower than that of without spinning. The reaction rate at the center (location-1) is also higher than other location of the substrate. The slower reaction rate is mainly due to changing the material properties during spinning [13]. It clearly indicates the spin-induced degradation of spin coated epoxy adhesive during the spinning. Compared with without spin, the thermal and chemical stability of spin coated adhesive decreased mainly due to-

1. Mechanical degradation during spinning: Under the influence of spinning forces, intermolecular interactions between certain molecules at certain sites of polymer are disrupted. Spin induced main chain rupture might also initiate the de-polymerization of linear polymers [32]. This type of chain scission plays a significant role on the thermal and chemical stability of polymeric material [33]. During the heating or chemical etching, less energy is needed to fragmentize the polymer, hence there is a lower stability in spin coated polymeric film.

2. Changes in the ratio of resin and hardener: Epoxy resin is higher volatile than the hardener (amine). Therefore, the evaporated amount of epoxy resin is larger than that of amine during the spinning. As a result, the correct mix ratio of amine and epoxy, to ensure the complete reaction of that reactive component is disrupted. Since the amine molecules 'co-react' with the epoxy molecules in a fixed ratio, unreacted amine remains within the matrix after the cure reaction, this alters and affects the final properties of the adhesive.

3. Void Formation: Due to the variation in spinning force, surface tension and the topography also varies at different locations of the spin coated adhesive film. Fig. 7 shows a micrograph of the surface topography at the corner of the spin coated adhesive. The figure clearly shows how the topography differs from center to the corner due to the spinning process of the adhesive. As shown there are a large number of voids at the corner and almost no voids at the center side of the substrate. The void formed during the spinning and curing of epoxy adhesive released from the coated adhesive layer at the heating or etching step and induced the excessive weight loss or porosity.

4. Cross-linking density: Lower curing degree, higher mechanical degradation and more void formation decreasing the cross-link density. Decreasing cross-link density, that is, increasing the distance between reactive sites usually has the effect of reducing thermal and chemical resistance by decreasing the compressive and tensile modulus as well as the impact. Less thermal or chemical energy is required to degrade a given mass into its volatile products [34].

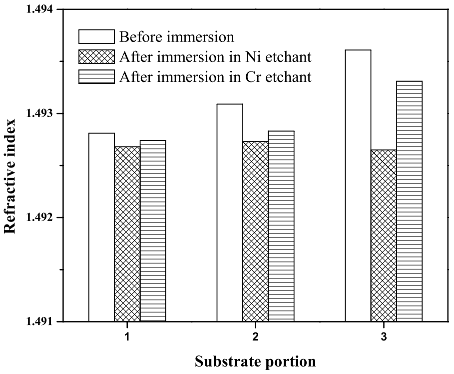


Fig. 12. Refractive index of spin coated cured adhesive (sample C) before and after immersion in metal (Ni & Cr) etchant chemical solution.

At the periphery of the substrate, the polymer experienced highest spinning force, more void and low cross-link density. Therefore the lowest thermal and chemical stability observed at the periphery of spin coated adhesive due to rapid fluid flow and convectively-driven evaporation that occur during spin coating. On the other hand, at the center of the substrate, highest stability observed due to lowest stress, no void and higher cross-linking density.

5.2.4 Recommendations

To overcome the problems, it is proposed to use lower spin speed during the spin coating. Also the reactive components of the spin coating solutions are preferred those are less volatile, having higher intermolecular forces and allow a greater part of the thinning behavior to occur without significant degradation of materials during the spinning process. The adhesive was also found physically and chemically more stable in chromium etchant solution than that of nickel etchant. Therefore chromium is also proposed to be used as hard mask in photolithography process during the fabrication of PLC devices.

5.3 Interfacial adhesion of spin coated polymeric film

Earlier studies have found that the curing reaction rate of spin coated epoxy adhesive is much slower than that of without spinning. The reaction rate at the center (location-1) is also higher than other location of the substrate. The slower reaction rate is mainly due to changing the material properties during spinning [13]. In another study, lower thermal and chemical stability for spin coated adhesive were also found due to rapid fluid flow and convectively-driven evaporation that occur during spin coating. It was also lower at the periphery of the spin coated polymer substrate due to the highest experienced spinning force, more void and low cross-link density. On the other hand, at the center of the substrate, higher stability was observed due to lowest stress, no void and higher cross-linking density. It clearly indicates the spin-induced degradation of spin coated adhesive during the spinning [22].

5.3.1 Different adhesion strength at different location

Properties of adhesive completely depend on the degree of cross-linking of the curing reaction. During the curing, the polymer chains locked together and their movement became consequently somewhat restricted. Cross-linked polymer chains are also chemically bound together to give a three-dimensional "chicken wire" molecular structure or chemical network. The higher the curing degree, the stronger the chemical bonding and the better adhesion strength at the adhesive interface. In this work, shear strength was measured for studying the interfacial adhesion of the spin coated epoxy layer on Silicon substrate. The result shows that the adhesion strength is higher at the center and lower at the boundary of the substrate. Fig. 13 shows the average shear strength at three different positions for without and with heat exposure of deposited & cured adhesive layer. Different adhesion strength was found at different portions of the same sample. As the curing degree and stability of adhesive is higher at the center and lower at the border side, consequently, the adhesion strength is also higher at the center and lower at the border side of the spin-coated adhesive.

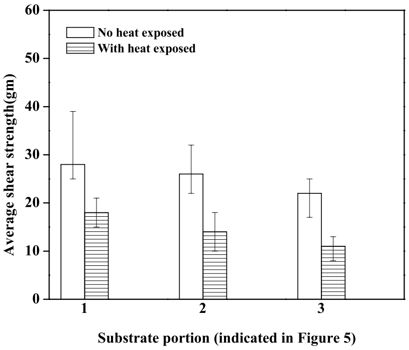


Fig. 13. Results regarding the shear button test at three different positions for without and with heat exposure.

5.3.2 Interfacial adhesion after heat exposure

After heat exposure, it decreases substantially from all locations of the substrate. The heat exposure was performed at a higher temperature (250^{o}C) which is over 130^{o}C of T_g (120^{o}C) of adhesive material. The epoxy adhesive exhibits a lower coefficient of thermal expansion (CTE) of 64 ppm/^{o}C below T_g and a higher CTE of 143 ppm/^{o}C above T_g. The difference between the CTE of epoxy adhesive and silicon is also very high (4 ppm/^{o}C for silicon while over 143 ppm/^{o}C for adhesive at higher temperature). Therefore, the adhesion strength of heat exposed sample substantially decreased due to-

1. Above T_g, the amorphous or semi-crystalline polymer is transformed to the rubbery viscous state and drops the mechanical integrity of the adhesive.
2. When the temperature rises in the solid, it expands and this thermal expansion is directly proportional to the coefficient of thermal expansion (CTE) of the material, its length and the temperature change. In this bi-material "sandwich" structure, the layers are rigidly connected to each other. Therefore when they attempted to expand in accordance with their CTE, each layer imposed a force along the interface to expand in an identical manner, and caused stresses to appear. The generation of these stresses may be understood from the sketch presented in Figure 14. The generated stresses at the interface decreased the adhesion strength.
3. Fig. 14 also shows that all the stresses ultimately concentrated at the border side. Therefore, the highest stresses experienced at the border side and lowest at the center. Due to the highest developed stresses at the interfaces of border side, the loss of mechanical strength is also higher at that portion. As a result, the higher drop of interfacial adhesion was observed at that position.

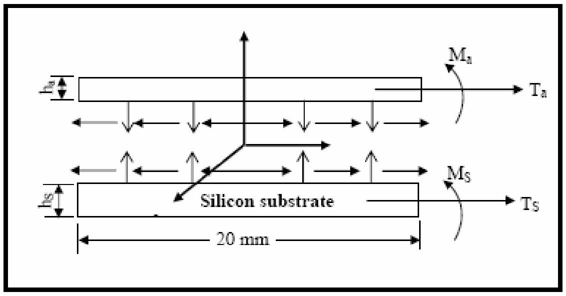


Fig. 14. Free- body diagram of bi-material structure.

Therefore, the adhesive should not be exposed at above the glass transition temperature during the subsequent fabrication process or operating life. In other words, the adhesive material with glass transition temperature, lower than the curing temperature of waveguide core material, should not use as lower cladding of optical waveguide. Otherwise, the adhesive has to be processed at or above its T_g, thus weakened its adhesive strength.

5.3.3 Interfacial adhesion on plasma treated substrates

Considering the mechanical interlocking theory of adhesion, the substrate was plasma treated to increase the surface roughness and adhesion strength. Figure 15 shows the 3-D AFM image of untreated and plasma treated substrate surfaces for different plasma conditions. Table 2 shows the surface roughness data for these different pre-treatment conditions.

Table 2. Surface roughness of silicon substrate for different surface condition.

Surface Condition	Rp-v (Å)	Rms Roughness (Å)	Average Roughness (Å	Mean Ht. (Å)
1	331	20.2	15.2	106
2	223	12.1	8.1	92.9
3	637	52.2	31.6	131
4	0.161 μm	126	97.3	398

It is very well known that the plasma etching increased the surface roughness. However in this study, it was found that surface roughness decreased after etching in highly reactive process gas, SF_6 (100%), but again increased with the addition of more oxygen to the feed gas mixture ($SF_6 + O_2$). The following is the discussion of the mechanism of the plasma etching of the silicon substrate in order to increase the surface roughness using SF_6 or mixture of ($SF_6 + O_2$). Etching in SF_6 (100%) causes the gas phase to consist of F and SF_x ($1 \le x \le 5$) formed by electron impact dissociation. Their interaction with the silicon surface causes the formation of non-volatile thin fluorosilane SiF_x layer ($1 \le x \le 4$) with a thickness of 1 to 3 nm. Therefore, after SF_6 etching, the thin fluorosilane (SiF_x) layer covered the silicon surface and decreased the roughness of the silicon substrate. However, if O_2 is added to the feed gas, besides F and SF_x, sulphur oxyfluorides (SO_2F_2, SOF_2, SOF_4) were also produced in the discharge. The formation of oxyfluorides is due to the reactions of oxygen with SF_x radicals. The oxyfluorides are powerful etching agents. Thus they inhibit the formation of fluorosilane on top of the substrate and increase the surface roughness by etching. Therefore more O_2 added to the feed gas results in higher the surface roughness [35].

It is also well known that increased surface roughness by plasma etching improve the adhesion. However in this study the adhesion strength after plasma treatment becomes lower than that of without plasma treatment. Figure 16 shows the average shear strength at different position, without and with plasma surface treatment. With such deterioration in the adhesion strength, it is necessary to investigate the mechanism behind. The mechanisms for adhesion include physical adsorption (Van der Waals force), chemical bonding (Covalent, ionic or hydrogen bonds), diffusion (inter-diffusion of polymer chains), and mechanical interlocking of irregular surface. With regards to adhesion mechanisms in the absence of surface treatment, the mechanical interlocking has little role because the substrate surface was found to be very smooth (R_a = 20.2 Å). The role of inter-diffusion of polymer chains or other strong bond such as covalent or ionic bonding is not considered here, as there was no surface deformation and smearing in the fracture surfaces. Therefore, only the Van der Waals force and hydrogen bonds are considered to be responsible for the adhesive bonding in the untreated condition. Although after plasma etching, surface roughness increased but the adhesion strength decreased. The probable reason may be -

1. The roughness of substrates is generally a contributing factor only if the coating penetrates completely into all the irregularities of the surface and wet surface. Failure to completely penetrate can lead the less coating-to-interface contact than the corresponding geometric area and will leave voids between the coating and substrate. The increased roughness can lead to decreased adhesion, since trapped air bubbles in these voids allow an accumulation of moisture.
2. During the plasma etching, the surface structure may changes chemically, which suppress the mechanical interlocking effect and reduced the adhesion strength [20].

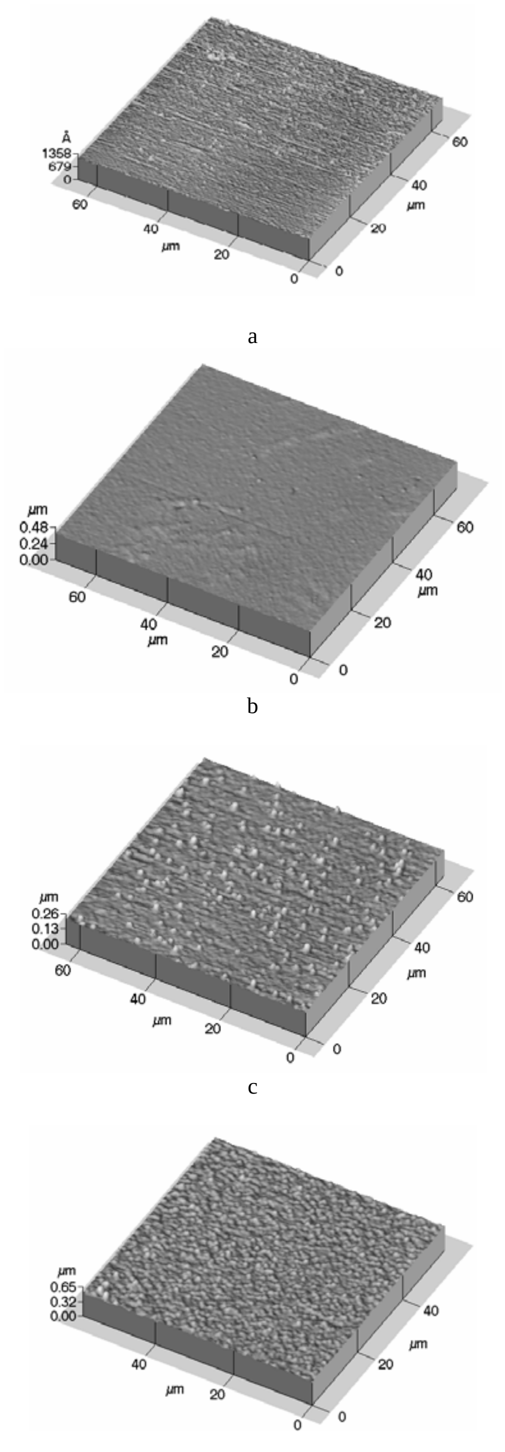


Fig. 15. The 3-D AFM image of untreated and plasma treated substrate surface for different plasma conditions (a) Without plasma treatment (b) Plasma treatment condition -100% SF_6 (c) Plasma treatment condition - 90 %-SF_6 + 10%-O_2 and (d) Plasma treatment condition – 80 %-SF_6 + 20%-O_2.

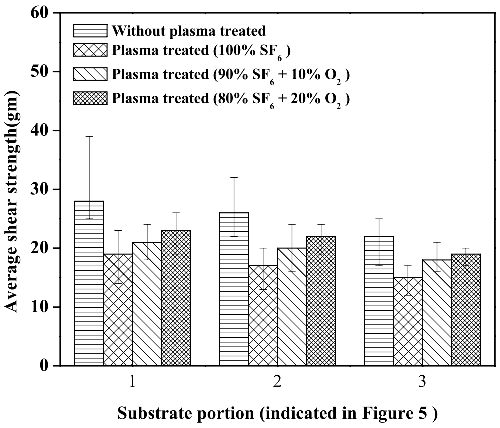


Fig. 16. The average shear strength at different positions for without and with plasma surface treatment.

5.3.4 Recommendations

It is proposed that adhesives that exhibit different adhesion strengths at different parts of the substrate not be used. The developed internal stresses in the devices may damage the functionality of these systems. An adhesive material with T_g lower than the curing temperature of the waveguide core material should also not be used as the lower cladding of an optical waveguide. An adhesive material with higher T_g is also proposed. Silicon substrates that were plasma-treated to improve adhesion were found to be inefficient in increasing the adhesion strength. Lower adhesion strength was unexpectedly observed after plasma treatment, even for higher surface roughness. Changes caused by plasma etching of the silicon wafer surface are yet not clearly understood.

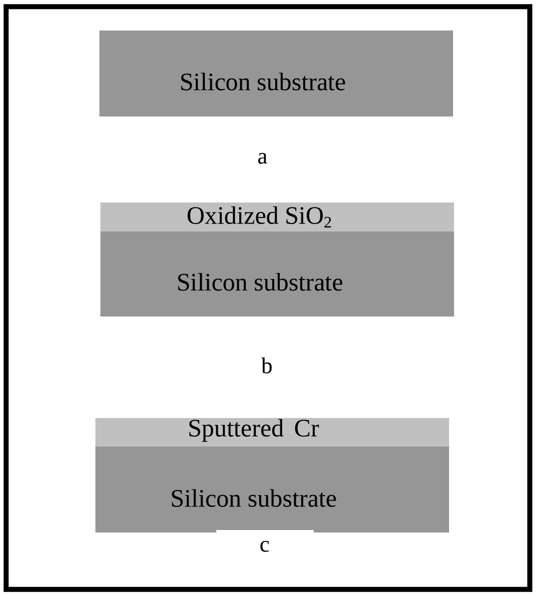


Fig. 17. Schematic of the X-section of different type of substrate used in this experiment (a) As received silicon wafer, (b) Oxidized SiO_2 on silicon wafer and (c) Sputtered Chromium on silicon wafer.

5.4 Interfacial adhesion on different substrate

In this work, three different types of substrate structure (as shown in Figure 17) were used to verify the interfacial adhesion. For each type of substrate, four categories of sample were prepared according to Figure 18. Another epoxy adhesive of higher T_g (150^oC) is used in the experiment. Interfacial adhesion was measured to examine the effect of surface structure on the interfacial adhesion of adhesive film to the substrate for the different process condition. Different adhesion strength was found for different type of sample and process conditions. Even for the same substrate and process condition, different interfacial adhesion was found at different portion of the substrate like as our previous study [20]. However, the differences within the same substrate are not so larger like the previous study and therefore the distribution is not showing again in this study. Here, the results are presenting the averages (solid bar) and the full distribution of the data values (36 samples per each bar) of the interfacial adhesion for each corresponding substrate structure with respect to a specific process condition. Fig. 19 shows the comparison of shear strength for three different types of substrate structure with different type process condition. The results are summarizes below:

1. Among the surfaces evaluated the thin sputtered Cr containing surface has the highest strength, followed by oxidized SiO_2 surfaces. Lower adhesion strength was observed for as received silicon wafers.
2. The adhesion strength slightly decreased in silicon and silica surface but increased in Cr surface due to applying the heat treatment on the spin coated thin adhesive layer before fabrication of shear button.
3. However, the interfacial adhesion decreased substantially due to exposing on the damp heat condition (75^0C /95% RH /168 hours) after shear button preparation in all substrates. However, the degradation is much high in silicon substrate than the silica and Cr containing substrate.

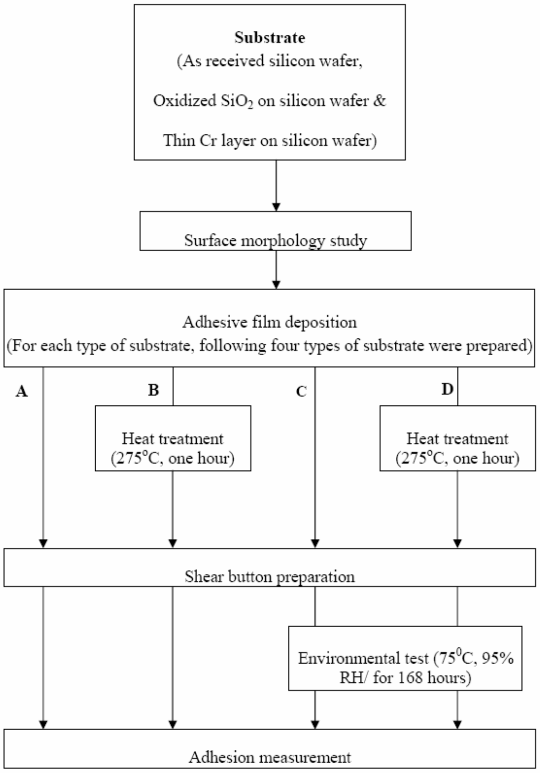


Fig. 18. An overview of the experimental procedure to study the effect of substrate structure.

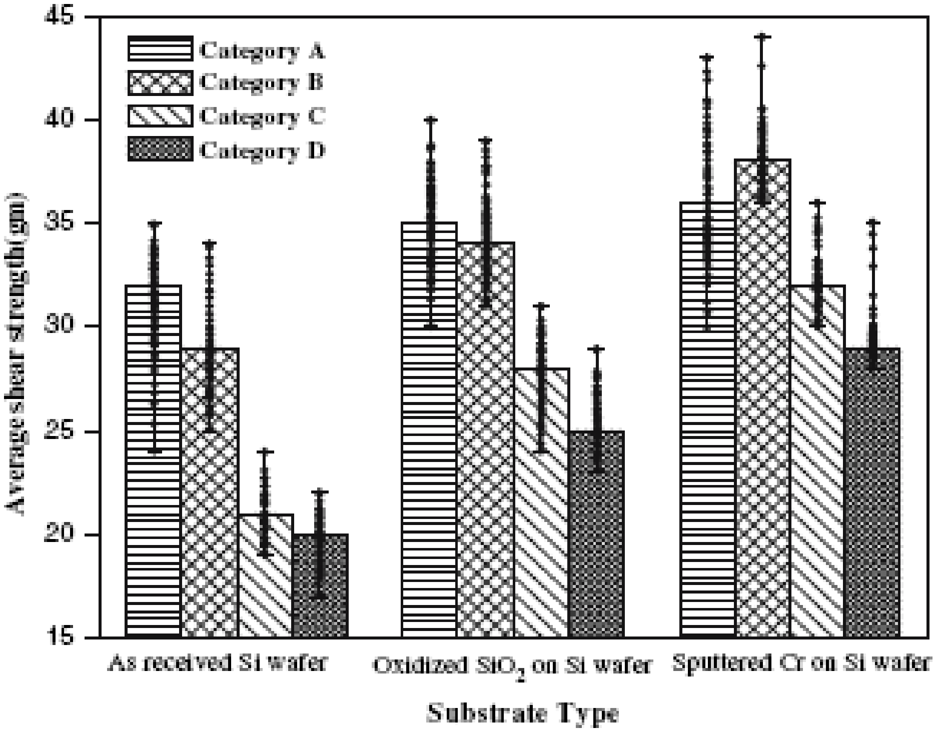
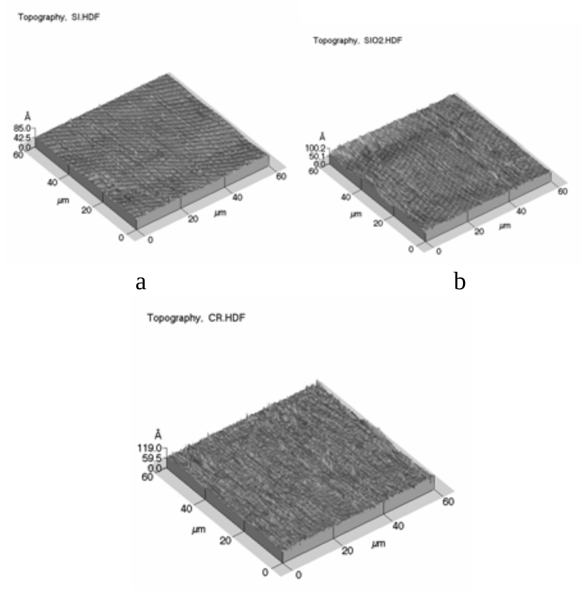


Fig. 19. Comparison of interfacial adhesion for different surface structure and processing.



a b

c

Fig. 20. The 3-D AFM image of substrate surface for different surface structure (a) As received silicon wafer, (b) Oxidized SiO$_2$ on silicon wafer and (c) Sputtered Chromium on silicon wafer.

To understand the variations in the adhesion strength on different substrates, it is very necessary to investigate the morphology study of the substrate surfaces. In these experiments, the morphological study was carried out under Atomic Force Microscope (AFM). Among the morphology, one of the known variables affecting the adhesion is surface roughness, because of its effect on wetting at the bonding surfaces and mechanical interlocking. Therefore it was measured to quantify the surface morphology. The 3-D AFM images of three substrate surfaces were also exposed in Fig. 20.

5.4.1 Interfacial adhesion on Silicon surface

With regards to mechanisms of adhesion, the mechanical interlocking has little role for adhesion of the silicon substrate because the substrate surface was found to be very smooth (average surface roughness, R_a = 1.81˚A). The role of inter-diffusion of polymer chains or other strong bond such as covalent or ionic bonding is not considered here, as the silicon surface is very inactive to the polymeric adhesive and there was no deformation or smearing on the fracture surfaces. Only weak bonds such as Van der Waals force or hydrogen bonds is considered to be responsible for the bonding in the as received silicon wafer [20].

5.4.2 Interfacial adhesion on Silica surface

The average surface roughness (R_a = 3.32 ˚A) is higher then the silicon surface and therefore the role of mechanical interlocking for adhesion also higher. Beside this, covalent bonds are formed during the polymerization. Since functionalities such as hydroxyl groups are generated during the epoxy curing reaction [36]. The hydroxyl produces polymeric chains of–$Si(OH)_2$-O-$Si(OH)_2$-OH groups with the silica surface which can link up in many different ways to form a three dimensional network and increases the adhesion strength [37].

5.4.3 Interfacial adhesion on Cr surface

Among the surfaces evaluated the thin sputtered Cr containing surface has the highest average surface roughness (R_a = 4.71 ˚A) and therefore contributed for higher adhesion strength. Also for polymer-metal interfaces, other major adhesion mechanisms such as diffusion (or inter-diffusion), Lifshitz-Van der Waals interaction, molecular interaction (acid-base interaction) and chemical adhesion (covalent bond) should have contribution for higher adhesion strength [38].

5.4.4 Effect of heat treatment on the interfacial adhesion

The heat exposure was performed at a higher temperature (275^{o}C). Above T_g, the amorphous or semi-crystalline polymer is transformed to the rubbery viscous state and drops the mechanical integrity of the adhesive. Therefore, the adhesion strength of heat exposed sample normally decreased. In this study, for the case of silicon and silica surfaces it is also found that the interfacial adhesion decreased due to the heat treatment of the spin coated adhesive film. But the decreased adhesion strength due to the heat exposure on silicon surface is not higher as our previous study. Because in this study, the adhesive used has higher T_g. Also we have used lower spin speed according to the recommendation of previous study to reduce the spin-induced degradation. Therefore, it is confirmed that adhesive with higher glass transition temperature and lower spin speed is very appropriate to reduce the degradation of the polymer photonic devices.

However, for the sputtered Cr surfaces, the adhesion increased after the heat treatment. The possible reason is that chemicals bonds are formed at the interface, usually as a result of a charge transfer from the metal to the polymer. The metals (Ti, Cr, Zr, Al) can strongly bond to oxidized (due to heat treatment at 275^{o}C) polymer surfaces, when the hydrophilic groups on the polymer surface make contact with the metal layer, electrons are transferred from the metal to hydrophilic groups, resulting in the formation of a charge transfer complex, which enhances the adhesion between metal and polymer [38].

$$\overset{\curvearrowright}{M + O{=}C<} \longrightarrow M\text{--}O \rightleftharpoons C<$$

Formation of M-O-C complex (M=Cr, Ti etc.)

$$2Cr + (O)\text{-polymer} \rightarrow Cr_2O_3 + \text{organic fragments}$$

Formation of Cr(III) oxide by a redox reaction between Cr and oxygen-containing functional group of the polymers increased the adhesion strength. Also there is a higher possibility of typical inter-diffusion between the metal polymer interfaces in increasing the adhesion strength [11, 15].

5.4.5 Effect of damp heat condition on the interfacial adhesion

The epoxy-based adhesive absorbs moisture and experiences hygroscopic swelling, hence degrading adhesion strength and elasticity in humid environments. Any uncured adhesive can severely attack by the moisture during the reliability test. Such hydrolytic attack breaks the ester linkages (`R–(C=O)–OR') of polymer chain and creates two new end groups, a hydroxyl and a carbonyl. Hydrolyzation of adhesive would appear to weaken its mechanical strength and adhesion with the substrate. The reduced adhesive strength also induced the delamination on that interface [39]. However, the reduction in adhesion strength is very larger in silicon surfaces followed by oxidized SiO_2 surfaces. Smaller reduction in adhesion strength was observed for Cr surface during the temperature humidity test. Because, the formation of chemical bond in metal-adhesive interface by charge transfer is stronger than both the covalent bond in silica-adhesive interfaces and other weak bonds such as Van der Waals force or hydrogen bonds in silicon-adhesive interfaces. Therefore, the Cr containing interface is more reliable in that humid environment compare to other two interfaces.

5.4.6 Recommendations

It is proposed to use a thin metal layer (such as Cr) on the silicon wafer to increase the adhesion and reliability of polymer photonic devices. The oxidized silica on silicon wafer is an alternative choice at the expense of reducing adhesion performance. Moreover, using silica layer has the advantage over Cr layer that one fabrication step can be reduced since the silica layer itself can effectively act as the lower cladding of the devices.

6. Conclusions

Polymeric adhesives have gained much attention, and significant technological progress has been made recently for future planner lightwave circuit (PLC) devices in order to meet the requirement of high-speed and large-capacity transmission of information at low cost. Thus the manufacturing infrastructure for polymer based PLC devices is fully deployed and capable of meeting the demands of current optical modules. This study was aimed at obtaining a better understanding of the materials and process optimization in fabricating polymer based PLC devices. Within each area, major research findings and recommendations are given. Insights gained from this study are very useful for adhesive manufacturers to formulate better polymer with favorable performance for this application. In contrast, the industry is still learning about polymer material and the process technologies have yet to be fully developed. It is believed that only after the polymer materials and the processes have been broadly learned, incorporated and the manufacturing infrastructure is built, would polymeric adhesive be widely used and eventually replaces other conventional materials and techniques. Therefore, there is still a long way to go in term of polymer advancement; the corresponding process development and infrastructure built before polymeric adhesive become the vital part of the PLC device. However, from the polymer evolution history and the current explosive technological breakthroughs, it is certain that polymer will be more widely utilized and will play an important role in the photonic industry.

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