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Initiated chemical vapor deposited nanoadhesive for bonding National Ignition Facility's targets

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Abstract

Currently, the target fabrication scientists in National Ignition Facility Directorate at Lawrence Livermore National Laboratory (LLNL) is studying the propagation force resulted from laser impulses impacting a target. To best study this, they would like the adhesive used to glue the target substrates to be as thin as possible. The main objective of this research project is to create adhesive glue bonds for NIF's targets that are ≤ 1 μm thick. Polyglycidylmethacrylate (PGMA) thin films were coated on various substrates using initiated chemical vapor deposition (iCVD). Film quality studies using white light interferometry reveal that the iCVD PGMA films were smooth. The coated substrates were bonded at 150 °C under vacuum, with low inflow of Nitrogen. Success in bonding most of NIF's mock targets at thicknesses ≤ 1 μm indicates that our process is feasible in bonding the real targets. Key parameters that are required for successful bonding were concluded from the bonding results. They include inert bonding atmosphere, sufficient contact between the PGMA films, and smooth substrates. Average bond strength of 0.60 MPa was obtained from mechanical shearing tests. The bonding failure mode of the sheared interfaces was observed to be cohesive. Future work on this project will include reattempt to bond silica aerogel to iCVD PGMA coated substrates, stabilize carbon nanotube forests with iCVD PGMA coating, and kinetics study of PGMA thermal crosslinking.

Introduction

Currently, the target fabrication scientists in National Ignition Facility (NIF) Directorate at Lawrence Livermore National Laboratory (LLNL) are studying the propagation force resulted from laser impulses impacting a target. To conduct this study, the NIF physicists require targets that contain two dissimilar materials bonded together. Furthermore, they would like the adhesive between the two substrates to be as thin and uniform as possible. The thinnest bond line they have produced thus far is approximately 2 μm. The main objective of this research project is to create adhesive glue bonds for NIF's targets that are ≤ 1 μm thick. In order to do so, we aim to deposit polymer thin films on substrates then subsequently bond them to prepare a nanoadhesive.

Polymer thin films have a wide range of uses in both the industry and the research community. They are used for surface coating, surface modification, species adhesion or adsorption, species sensing, separation, lithographic imaging, photonics, and microfabrication. Two prominent methodologies of polymer thin film deposition are spin-on deposition and chemical vapor deposition (CVD). Spin coating uses a liquid phase as the mass transfer media, while CVD uses a gas phase to transport volatile molecules to the surface serving as substrate. There is a fundamental resemblance between the two methodologies − the way that the final material is created. In both cases, molecules of chemical compounds serving as precursors are delivered to the substrate surface and chemically modified to obtain the desired film. One notable difference − the use of solvents − translates to many differences between the applicability and the characteristics of the two processes.[1]

One difference in characteristics of the two methodologies is how the polymerization of the precursor monomer occurs. In CVD, polymerization occurs in situ on the substrate and involves no solvents. The process is usually achieved via thermal conversion of precursor molecules and/or their reactions with molecules of other volatile precursors, or reactive gases such as oxygen or hydrogen. In contrast spin-on deposition involves solvents; the polymers for use are pre-made and must be soluble. To obtain a polymer film, the spin coating process uses a series of processing stages in solution and solid state. They include preparation of polymer solution using an appropriate solvent (sol), evaporation of the solvent (drying), gelation (gel), and thermal treatment (sintering).

As a result, this difference gives CVD methodology an important advantage over spin coating method in applicability – substrate insensitivity. Since polymerization occurs in situ on the substrate in the CVD processes, virtually any kind of substrate and substrate geometry can be used for deposition. In comparison, spin-on deposition is limited to more conventional substrates and substrate geometries. It is also easier to control the film thickness in CVD than in spin coating. These advantages are the reasons that we chose to use CVD method over spin-on deposition for our work. Among the various CVD methods, we chose to use initiated chemical vapor deposition (iCVD) because successful bonding of substrates coated using iCVD have been reported in literature.[2]

As mentioned earlier, we are interested in investigating the adhesive properties of iCVD polymers and evaluating the feasibility of using iCVD thin films for bonding NIF's targets. To that end, ≤500 nm thick iCVD polyglycidylmethacrylate (PGMA) films were coated on various substrates and the substrates were used to bond. PGMA was chosen due to the presence of reactive pendant epoxy groups that can undergo a ring-opening reaction allowing thermal crosslinking. We used a bonding condition similar to the one described in Bergkvist et. al with some modifications.[3] It employs a "symmetric" polymer interface where iCVD PGMA films were deposited on each respective substrate. Through multiple bonding experiments, we were able draw conclusion of the key parameters required for successful bonding. Additionally, mechanical testing of the bonded Si wafers was done to evaluate the bond strength of thermally crosslinked PGMA polymer. Failure mode of the mechanically sheared PGMA film interfaces were examined under a microscope.

Materials and Methods

Materials: GMA monomer (Sigma-Aldrich, ≥97%) and tert–butyl peroxide (TBPO) initiator (SAFC Hitech, ≥99%) were used in the iCVD process. Ethylenediamine (EDA), used for reaction with epoxy groups, was purchased from Sigma-Aldrich (99.9%). All chemicals were used as received.

iCVD of PGMA : All polymer depositions were performed using a iLab initiated chemical vapor deposition reactor (GVD Corporation). All the substrates used were summarized in Table 1. A series of resistively heated wires (Nichrome) maintained at 240 ± 10 °C (22V, 1.3A) were used to crack the radical initiator. For fast deposition (40 nm/ min), the substrates were maintained at 30 °C with the aid of a backside-cooled sample stage. For slow deposition (15 nm/ min), the substrates were maintained at 35 °C. Typically we perform fast depositions on substrate No. 1 through 4, and slow depositions on substrate No. 5 through 10 (see Table 1). Slow deposition condition was used when films ≤ 100 nm thick were desired. The chamber pressure was maintained at 200 mTorr during the deposition, where TBPO flow rate was fixed at 5 sccm. The GMA flow rate was controlled by temperature and manual valve. The monomer jar was heated to 60 °C, while the monomer line to 70 °C. The manual valve was opened completely. The GMA flow rate is estimated to range from 10 to 35 sccm during the depositions. The sample thickness was monitored in situ by a Helium Neon Gas Laser (JDSU). Exact sample thickness was measured using a spectroscopic ellipsometer (J.A. Woollam Co. Inc, ESM-300). Film quality was assessed using white light interferometry (Veeco Instruments Inc). Polymerization and functionality of GMA was confirmed through Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific, Nicolet iS10). Spectra were collected over a range of 800–4000 cm^{-1} and averaged over 64 scans at 4 cm^{-1} resolution.

Bonding of iCVD PGMA Coated Substrates: iCVD PGMA coated substrates were bonded at 150 °C under vacuum, with low inflow of N_2. The various sources of bond pressure are listed in Table 3(a). The bonding time was fixed at 30 min for all samples.

Mechanical testing of bonded Si wafers: Testing assemblies were prepared by gluing bonded Si wafers or KBr substrates to Al substrates using Stycast 2850FT/Cat 23LV (Loctite). The testing assemblies were set aside to cure for eighteen hours before testing. 100g weight standards were placed on top of the assembly to ensure stability. Mechanical shearing test of the bonded Si wafers were performed using Instron Universal Testing Machine (Model 4201). The samples were tested at a speed of 0.5 mm/ min. The amount of load and extension were acquired by a LXI Data Acquisition/ Switch Unit (Agilent 34972A). Failed PGMA film interfaces were examined under a microscope (Ergolux AMC) to observe the bond failure mode.

Results and Discussion

Confirmation of iCVD polymerization and epoxy retention in PGMA film

Figure 1 shows the FTIR spectrum of glycidylmethacrylate (GMA) monomer, iCVD PGMA film, and ethylenediamine treated iCVD PGMA film. Polymerization of GMA during iCVD was confirmed through disappearance of the peak at 1635 cm^{-1}, which is characteristic of C=C vinyl stretching and unique to the monomer spectra (Figure 1 a,b).[4] Retention of functional epoxy groups in iCVD PGMA films was confirmed by the nucleophilic addition of ethylenediamine (EDA) to the pendant epoxy group through a ring opening reaction. The EDA-PGMA reaction was carried out at room temperature in a homemade desiccator. The PGMA film was exposed to EDA vapor for 14 hours. The sample was then heated at 60 ^{o}C for 96 hours to vaporize physically-adsorbed EDA on the film surface. In Figure 1c, EDA-PGMA sample has shown the disappearance of the epoxy group-symmetric stretching vibration peaks at around 909 cm^{-1} compared with the original PGMA (Figure 1b), while new peaks appeared at 3315 and 1585 cm^{-1} corresponding to the –NH and $–NH_2$ stretching vibration, respectively.[5] These results indicate that the epoxy groups retained their functionality under our iCVD process conditions. With functionality retained, the epoxides should crosslink and bond the coated substrates upon annealing.

iCVD PGMA film smoothness

Film quality was assessed using white light interferometry. Table 2 reports root mean square (Rq) roughness values in three different areas. The low Rq values indicate that the iCVD PGMA film on Si is smooth. They also indicate that iCVD PGMA does indeed coat conformally to substrate, as reported in literature.[6]

Bonding of iCVD-PGMA coated substrates

The results of bonding various iCVD-PGMA coated substrates are detailed in Table 3(a). Sets No. 1 and 2 were used as preliminary tests to see if bonding conventional substrates is possible. Sets No. 3 through 8 were designed to test the results of bonding NIF's mock targets. Set No. 9 was used as a control sample for set No. 8. Sets No. 10 and 11 were designed to prepare samples for bond strength measurements. Images of some of these sets are shown in Table 3(b). It is worth noting that the bonds we produced were at least 2x thinner than current state of the art and that the thinnest one was 70 nm.

From these bonding tests, we learned that three key parameters are required to get successful bonding of the iCVD-PGMA films.

1) Bonding of the symmetric iCVD PGMA interfaces must be done in an inert atmosphere. Bonding iCVD PGMA coated substrates in air was unsuccessful. This is most likely due to the side reaction of epoxide reacting with oxygen. Interestingly enough, bonding in air of substrates coated with iCVD PGMA to substrates coated with iCVD PGMA that has been amino-modified with EDA was reported to be successful.[7]
2) There must be sufficient contact between the PGMA films. In Bergkvist et. al,[2] this was achieved by thermocompressive bonding of the coated wafers using an automated wafer bonder. In our setup, this was achieved by pressure exerted from binder clips, weight standards, or hot press.
3) The substrate must be smooth, in both the microscopic and macroscopic length scale. Since the iCVD-PGMA film coats conformally,[6] the film smoothness will mostly depend on the smoothness of the substrate.

Unsuccessful bonding of the coated Al substrates (Table 3a, set No. 10) and that of the coated glass slides (Table 3a, set No. 11) are most likely attributed to the third parameter. In the case of aerogel bonding to iCVD-PGMA coated Si wafer (Table 3a, set No. 8), the failure is most likely attributed to the second and third parameter. It is also possible that the low density of aerogel (250 mg/ mL) provides insufficient amount of material needed for successful bonding per unit area. These key parameters demonstrated the limitations of using symmetric iCVD PGMA thin films as nanoadhesive quite well. The first and second parameter show that the nanoadhesive is not as robust as many other glues in its curing process. The third shows limitation in the substrate geometry. Although the iCVD process is substrate insensitive, in terms of both material and geometry, the subsequent curing process is substrate geometry sensitive.

Bond strength of the PGMA nanoadhesive

One of the objectives in this work was to investigate the feasibility of using iCVD polymers as thin film adhesives for bonding NIF's targets. To do so, we performed mechanical testing on the bonded Si wafers. Table 4 shows the bond strength of the PGMA nanoadhesive. An average bond strength of 0.60 MPa was obtained. The highest bond strength obtained was 0.79 MPa. The variation in bond strength is most likely due to the handling of samples. As a benchmark reference, Stycast 2850FT/Cat 23LV is the adhesive currently being used in target fabrication, and it has bond strength of 25-35 MPa, which is approximately 50-70 times the bond strength of our nanoadhesive. However, a trade-off between bond strength and thickness is expected.

It is important to understand what the extreme bond strength values mean. The highest bond strength value is representative of the highest amount of stress the nanoadhesive is able to handle when prepared in optimal conditions, and the lowest bond strength value is representative of the lowest amount of stress the nanoadhesive is able to handle if successful curing does occur. To put these bond strength values in another perspective, the amount of weight that the nanoadhesives, with two different areas, are able to support is calculated. It is also worth noting that the bond strength of the nanoadhesive does not seem to correlate with thickness in the nm to μm length scale. One possible explanation for this would be that the entire adhesive is only as strong as the weakest crosslinked interface, which was where it failed, and that a thicker film in this length scale does not help lower the shearing stress applied to that interface.

Failure Mode

Figure 2 shows images of the failed assembly and microscope images of the mechanically sheared PGMA film interfaces. Although some patterns did appear on the film interfaces, all parts of both substrates were still covered with PGMA film. This indicates that the bonding failure mode is cohesive, meaning a failure in the bulk layer of the adhesive. An adhesive failure would occur at the interface between the adhesive and the adherend.

Conclusions

In this work, we demonstrate successful bonding of various substrates at 150 °C using iCVD PGMA thin films as adhesives. From white light interferometry, the iCVD PGMA films were identified to be smooth. Success in bonding most of NIF's mock targets at thicknesses ≤1 μm indicates that our process is feasible in bonding the real targets. Key parameters that are required for successful bonding were concluded from the bonding results. They include inert bonding atmosphere, sufficient contact between the PGMA films, and smooth substrates. Average bond strength of the thermally crosslinked PGMA was 0.60 MPa. The bonding failure mode was observed to be cohesive.

Several more experiments appeal to our interests for future investigations. First, we would like to successfully bond silica aerogel to iCVD PGMA coated substrates. As shown by the control sample (Set No. 9, Table 3a), successful bonding of this set of substrates is theoretically possible. Second, there is an interest in iCVD of PGMA on carbon nanotube forests. We would like to use the iCVD PGMA to stabilize the carbon nanotube forests during solvent infiltration. Finally, we will study the kinetics of PGMA thermal crosslinking, as this parameter was not explored in Bergkvist et. al.[2]

Acknowledgment

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Tables and Figures

Substrate No.	Substrate Type	Dimensions
1	Si wafer with native oxide film	10mm x 10mm x 1mm, 20mm x 20mm x 1mm
2	KBr	25mm x 12mm x 2mm
3	Glass Slide	25mm x 75mm x 1mm
4	Al Coupon	25mm x 45mm x 2mm
5	V foil	20mm x 40mm x 500um
6	Pb foil	20mm x 40mm x 500um
7	Ta foil	1mm x 5um
8	LiF foil	1mm x 1mm x 5um
9	LiF foil with 750 nm Ti anti-reflective coating	1mm x 1mm x 5um
10	Silica aerogel	10mm x 10mm x 10mm

Table 1. Substrates used for iCVD.

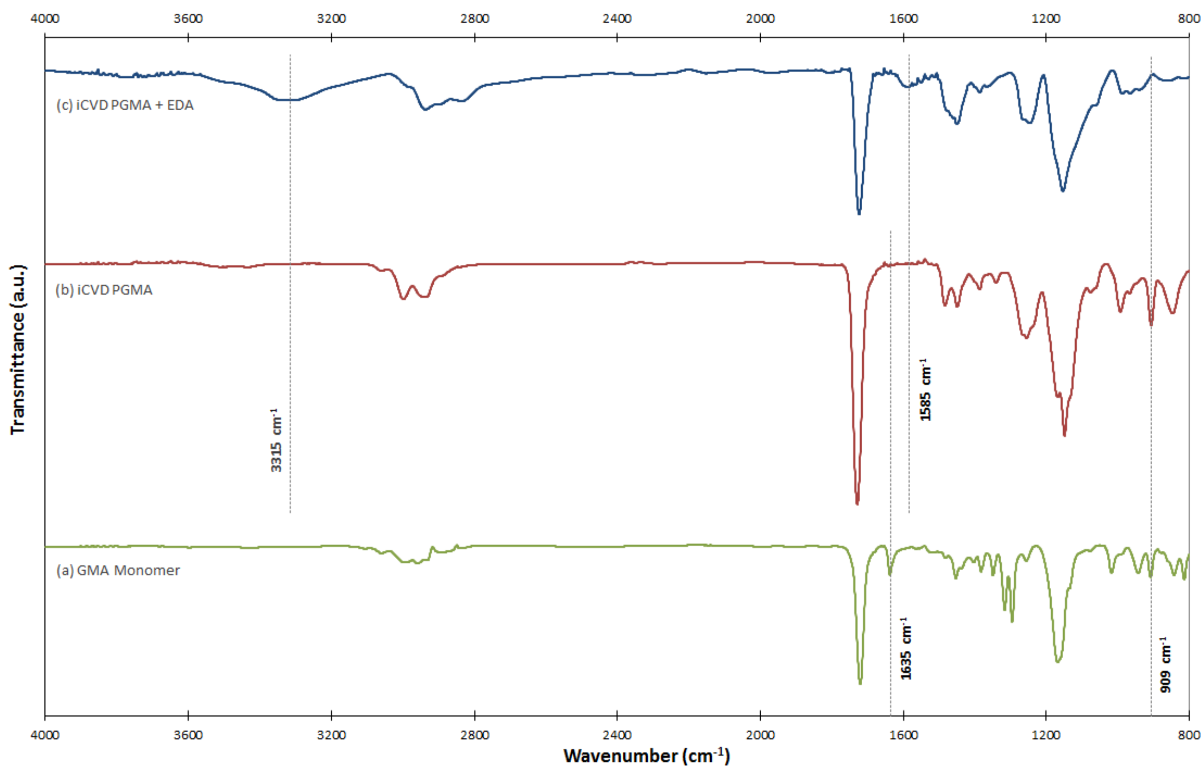


Figure 1. FTIR spectra of a) GMA monomer, b) iCVD PGMA film, and c) iCVD PGMA treated with ethylenediamine. Dotted lines indicate peaks of interest with epoxy ring deformation at 909 cm^{-1}, vinyl C=C stretching at 1635 cm^{-1}, –NH_2 stretching at 1585 cm^{-1}, and –NH stretching at 3315 cm^{-1}.

(a)	Rq values (nm)
Area 1	0.78
Area 2	0.62
Area 3	0.67

(b)	Rq values (nm)
Area 1	1.23
Area 2	1.45
Area 3	1.55

Table 2(a). the root mean square (Rq) roughness values of PGMA film on Si. Viewing area dimension is 0.13 mm x 0.094 mm.
Table 2(b). the root mean square (Rq) roughness values of PGMA film on Si. Viewing area dimension is 0.63 mm x 0.47 mm.

Set No.	Substrate 1	Substrate 2	Source of Bond Pressure	Result of Attempted Bonding	Bond Line
1	Si wafer	Si wafer	Binder clips	Success	1000 nm, 100 nm, 70 nm
2	KBr substrate	KBr substrate	Binder clips	Success	1000 nm
3	Ta foil	Pb foil	Thermocompression	Success	1000 nm
4	V foil	Pb foil	Thermocompression	Success	1000 nm
5	Ta foil	Ta foil	Binder clips	Success	1000 nm
6	LiF	Ta foil	Binder clips	Success	1000 nm
7	LiF with 750 nm Ti anti-reflective coating	Ta foil	Binder clips	Success	1000 nm
8	Si wafer	*Silica aerogel	100 g weight standard	Failure	N/A
9	Si wafer	*Si wafer	Binder clips	Success	500 nm
10	Al substrates	Al substrates	Binder clips	Failure	N/A
11	Glass slides	Glass slides	Binder clips	Failure	N/A

Table 3 (a). Results of bonding various iCVD-PGMA coated substrates. Substrates with asterisk were not coated with PGMA.

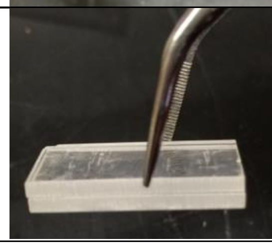
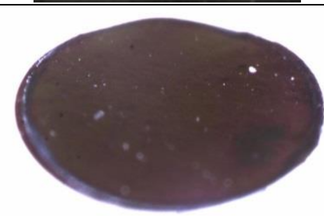
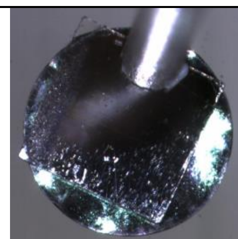
Set No.	Substrate 1	Substrate 2	Picture of bonded assembly
1	Si wafer	Si wafer	
2	KBr substrate	KBr substrate	
5	Ta foil	Ta foil	
6	LiF	Ta foil	
7	LiF with 750 nm Ti anti-reflective coating	Ta foil	

Table 3 (b). Images of some of the successfully bonded assemblies.

Bonded Substrates	Bond Line	Bond Strength (MPa)	Weight a 2x2 cm Nanoadhesive Able to Suppport (kg)	Weight a 2x2 mm Nanoadhesive Able to Suppport (g)
KBr	1000 nm	0.48	19	190
Si	1000 nm	0.71	29	290
Si	1000 nm	0.45	18	180
Si	116 nm	0.79	32	320
Si	70 nm	0.57	23	230

Table 4. Bond strength of the PGMA nanoadhesive in megapascal (MPa) and weight able to support.

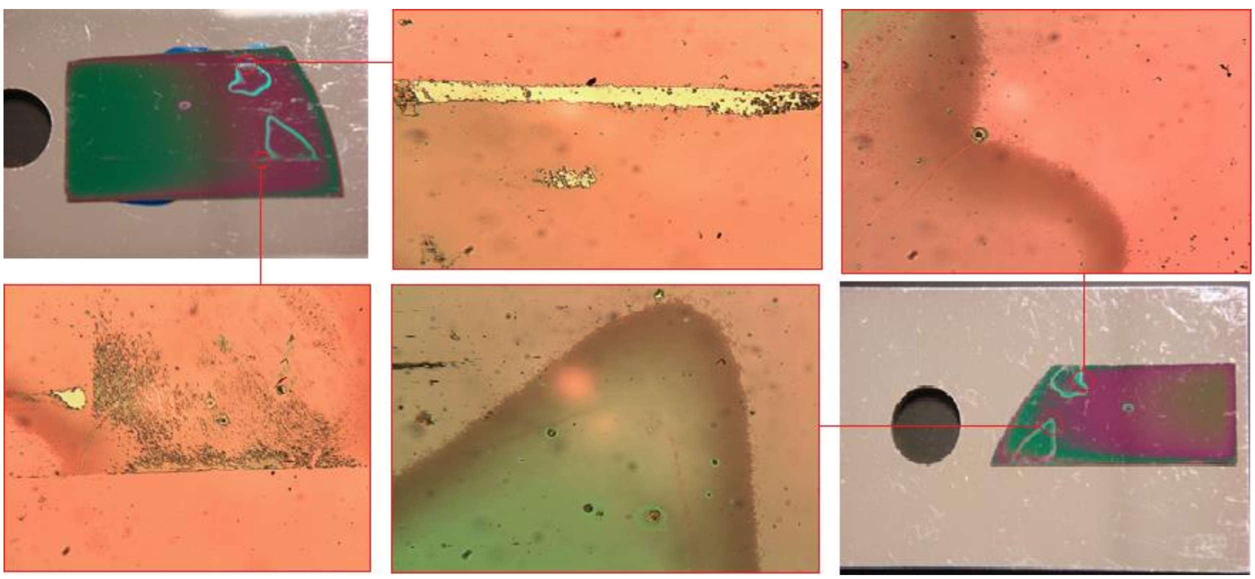


Figure 2. Images of the failed assembly and microscope images of the mechanically sheared PGMA film interfaces.

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