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Polycarbonates as temporary adhesives

Nathan Fritz, Huy Dao, Sue Ann Bidstrup Allen, Paul A. Kohl *

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 303320-0100, United States

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ABSTRACT

In this study, a series of polycarbonates were examined as temporary adhesives for wafer-to-wafer bonding. Temporary adhesives require adequate adhesion strength, solvent resistance, and thermal stability during processing of the mated wafers. Polycarbonates were shown to have thermal and chemical stability over a range of values, as well the ability to thermally release the substrates over a range of temperatures. The polycarbonates had adequate adhesion strength for wafer processes, such as polishing. Little or no mechanical force is required to release the wafers after thermal decomposition of the polycarbonate.

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1. Introduction

Thin and ultrathin silicon substrates are of interest for a variety of devices and fabrication approaches. Thin silicon substrates, which can be used in technologies such as 3-D stacking, are flexible, have high thermal conductivity for heat dissipation, and exhibit low electrical resistance. However fabricating devices on thin substrates, or thinning a fabricated wafer generally requires a rigid carrier substrate for handling to prevent damage to the device wafer. The rigid carrier substrate prevents fracture, warping, and folding of the device wafer. Temporary adhesives have become increasingly important for integrated circuit, solar cells, MEMS, and packaging applications due to their low cost, adaptability, and ease of processing [1,2]. Adhesive materials used for the wafer-to-wafer bonding need to be easily deposited and require adequate adhesive strength during use [3].

The chemical and thermal stability of the polymer is important so that it is able to withstand typical fabrication processing steps, such as wet/dry etching or material deposition. While some current adhesive materials meet these requirements, many of them require undesirable high temperature and/or mechanical force to release the substrates [4]. Also, after substrate release, the substrates may have to undergo aggressive or costly clean-up processes to remove residues.

Polycarbonates are currently being studied as sacrificial placeholders in microelectronic build-up processes. They may provide a unique alternative to current polymer adhesives [5–7]. Polycarbonates thermally decompose into small, volatile compounds with little to no residue. Also, they can be uniformly applied to the substrates by spin-coating or other means at a variety of thicknesses. The polymer formulations may also be chosen for particular chemical or thermal resistance so as to maintain film quality during processing. The processed wafer can be thermally released in a standard furnace at the decomposition temperature of the selected polycarbonate. In this project, a number of polycarbonate formulations were characterized and studied as temporary adhesives.

2. Experimental and material selection

Four polycarbonates were chosen for testing as temporary adhesives: polyethylene carbonate (PEC), polypropylene carbonate (PPC), polycyclohexene carbonate (PCC) and a copolymer of polypropylene carbonate and polycyclohexene carbonate (PPC/PCC). The chemical structures of the polycarbonates are shown in Fig. 1. PPC was obtained from Novomer Inc. and the other polycarbonates were obtained from Empower Materials Inc. The polymer PEC had a molecular weight of 170 kg/mol and a polydispersity index (PDI) of 3.5. Several samples of PPC with different molecular weights were tested, ranging between 150 kg/mol and 260 kg/mol with a PDI value between 2 and 3. Both PEC and PPC polymers were dissolved in gamma butyrolactone (GBL) forming a 20 wt% solution for spin casting. An iodonium photo acid generator (PAG) was sometimes added to the formulations to adjust decomposition temperature. The PAG loading was 3 wt% based on the polymer mass. Photo or thermal activation of the PAG results in the creation of a strong acid, which can catalyze decomposition of the polycarbonate.

The decomposition products of PCC and PPC/PCC were investigated using gas chromatography–mass spectrometry. Previous studies have examined the decomposition products of polycarbonates [5]. The monomer ratio in the PPC/PCC copolymer ratio was determined by an H NMR. The materials were dissolved in a

* Corresponding author. Tel.: +1 404 894 2893; fax: +1 404 894 2866.
E-mail address: kohl@gatech.edu (P.A. Kohl).

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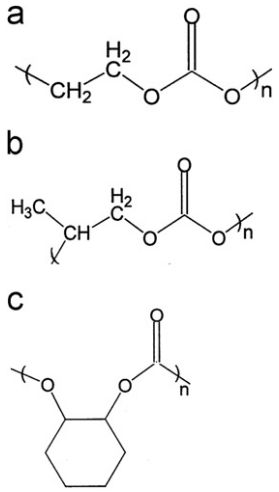

Fig. 1. Structure of polycarbonates. (a) Polyethylene carbonate, PEC. (b) Polypropylene carbonate, PPC. (c) Polycyclohexene carbonate, PCC.

number of solvents to determine the best casting solvent. PCC was mixed with anisole to form a 12 wt% solution. The PPC/PCC copolymer was dissolved in an anisole/N-methylpyrrolidone (NMP) cosolvent to form a 11 wt% solution. The decomposition temperature and mass of residue after decomposition were investigated using dynamic thermal gravimetric analysis (TGA) employing a ramp rate of 1 °C/min in a nitrogen atmosphere.

The substrate-to-substrate bonding test was carried out using spin coating onto silicon wafers or glass slides. The polymer was soft baked after coating to remove the solvent. The wafers were then bonded using a heated, hydraulic press. The bonding parameters, soft bake time and temperature, film thickness, pressure, and temperature were optimized for each material. The adhesive strength of the polymers was tested using an ASM D429 Rubber—90° peel test. The tests were conducted by bonding untreated aluminum foil to silicon wafers at various film thicknesses, bonding temperature, and bonding pressure. The aluminum foil was bonded to silicon wafers using the same hot-press method. The samples were then diced into strips and separated using an Instron, model 5842. The aluminum foil was pulled 90° perpendicular to the wafer surface. Additional bonding tests consisted of monitoring adhesion during the polishing two bonded wafers. The wafers were polished on rotating polishing table at 350 rpm. Wafers were inspected for damage and undercut of the adhesive during the processes. Wafers were released by heating in a nitrogen purged tube furnace for 1 h where the polycarbonate decomposed.

3. Results and discussion

In this study polycarbonates were examined for use as temporary wafer-to-wafer adhesives. Four polymers were characterized and tested, including PPC, PEC, PCC, and PPC/PCC copolymer. PEC decomposed at the lowest temperature of the four. PCC and PPC/PCC copolymer were tested for higher temperature applications.

Although PEC and PPC have been used in previous air cavity studies, PCC and PPC/PCC copolymer have not been investigated as extensively; therefore, additional characterization was carried out in this work. The molecular weight of the polymers was determined through gel permeation chromatography. PCC material had an average molecular weight of 350,000 g/mol and polydispersity index of 5.5. The PPC/PCC copolymer had an average molecular weight of 300,000 g/mol and polydispersity index of 7. The large polydispersity index, PDI, is important to note because it indicates a large distribution of molecular masses. PPC and PEC have a low PDI and show a very tight control in molecular weights. The high PDI for PCC and PPC/PCC suggests that the materials may have a greater variation in decomposition temperature as well as possible affect on the residue. Differential scanning calorimetry (DSC) was used to determine the glass transition, T_g, of the materials. The PCC and PPC/PCC had glass transition values of 107 °C and 115 °C, respectively. This is higher than PEC and PPC, which are 25 °C and 40 °C, respectively [8]. An increase in the T_g helps stabilize the material from low temperature reflow or softening.

The PPC-to-PCC ratio in PPC/PCC was invested using H NMR. The reference spectra for PPC and PCC were used for peak assignments [9–11]. PPC has the following chemical shift values, δ (ppm) from the H NMR $CDCl_3$, as follows: 1.34 (3H, CH_3), 4.17 (2H, CH_2) and 5.00(H, CH) [9]. PCC has the following chemical shift values, δ (ppm): 1.00–2.30 (2H, CH_2) and 4.6 (H, CH) [10,11]. The same peaks were identified in the present spectra. The PPC-to-PCC monomer ratio was determined by comparing the area of the 5.00 (H, CH) peak to the 4.6 (H, CH) peak, accounting for the number of hydrogens present in each case. The ratio was determined to be 1:2.78 PPC-to-PCC.

PEC and PPC decompose into small molecular weight, volatile products upon thermal decomposition, such as acetone and carbon dioxide [12]. The thermal decomposition of PCC was analyzed via mass spectrometry. Above 250 °C, the primary volatile products consisted of cyclohexane and carbon dioxide. When the decomposition temperature increased beyond 320 °C, higher molecular weight products were formed. The higher molecular weight could be formed through ether linkage between the other materials or contaminants in the pure polymer. The decomposition of the PPC/PCC copolymer resulted in the formation of similar products as identified with PCC, including acetone and other low molecular weight products from the PPC.

TGA analysis was performed on each polymer to determine their decomposition temperature. The TGA temperature was ramped at a constant 1 °C/min, and the results are shown in Fig. 2. PEC decomposed (50% weight loss) at 165 °C, and PPC decomposed at 210 °C. The PPC/PCC copolymer and PCC showed similar decomposition profiles with 50% weight loss at 275 °C. This shows that the PCC component of the PPC/PCC copolymer dominates its thermal behavior. Since each polymer decomposes at a unique temperature, the material system can be selected in order to decompose at the desired temperature for the intended

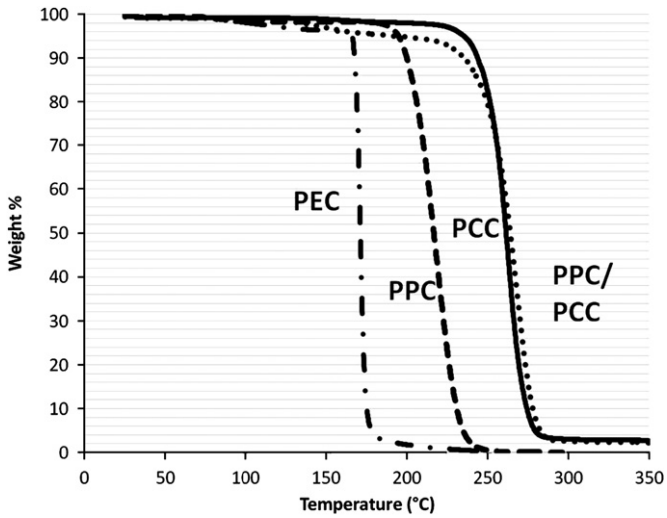

Fig. 2. Dynamic thermal gravimetric analysis of polycarbonates ramped at 1 °C/min. PCC is solid line.

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process. The TGA results were also used to evaluate the residual residue after decomposition. PPC and PEC showed no measurable residue after decomposition in the TGA. The PPC/PCC and PCC had ca. 2–5 wt% residue remaining thermal cycling. This residue material was soluble in NMP and was found to decompose at temperatures higher than 320 °C.

Additives, such as a PAG, can be added to PPC to lower decomposition temperature. The thermally or ultraviolet activated PAG can catalyze thermal decomposition of the polycarbonate [13]. Fig. 3 shows a dynamic TGA spectrum of pure PPC and a sample with 3 wt% PAG loaded PPC. The PAG itself thermally decomposes and creates an acid which decreases the decomposition temperature of the PPC. When exposed to ultraviolet radiation, the acid is generated at a lower temperature than the thermal case, catalyzing the PPC decomposition at temperatures as low as 100 °C. When PAG was added to the PCC, the polymer thermally decomposed at 180 °C. This shows that for a PAG-loaded sample, polymer decomposition is controlled by the thermal or UV activation of the PAG.

The solubility of the polycarbonates was investigated in order to find the best solvent. Swelling, as a result of solvent uptake, may cause the polymer film to release from the wafer surface causing undercutting and damage to the device wafer. Polycarbonate films were exposed to a number of solvents for a 48 h period. Table 1 shows the results of the solvent exposure after extended soaking. The PEC and PPC experienced significant solvent uptake in many of the solvents used in microelectronic processing. PCC and PPC/PCC were insoluble to a number of solvents making these polycarbonates desirable as an adhesive because they would not be affected by use of those solvents in other processes.

The most appropriate solvent for spin-casting was also considered. The casting solvent should completely dissolve the material and have a low evaporation rate so as to produce a uniform film. Anisole was chosen as the best casting for PCC. It has a relative mass evaporation rate of 0.322, with respect to an n-butyl-acetate standard with a value of one. Although solvents like methylene chloride, with a high evaporation rate value of 27.5, provide excellent solubility for the polymer, they evaporate too rapidly to produce a smooth spin coated film. GBL was chosen as the most effective solvent for PPC and PEC. GBL has a relative evaporation rate of 0.03. It was found that a 90/10 vol% solvent mixture of anisole/NMP was the optimum system for PPC/PCC.

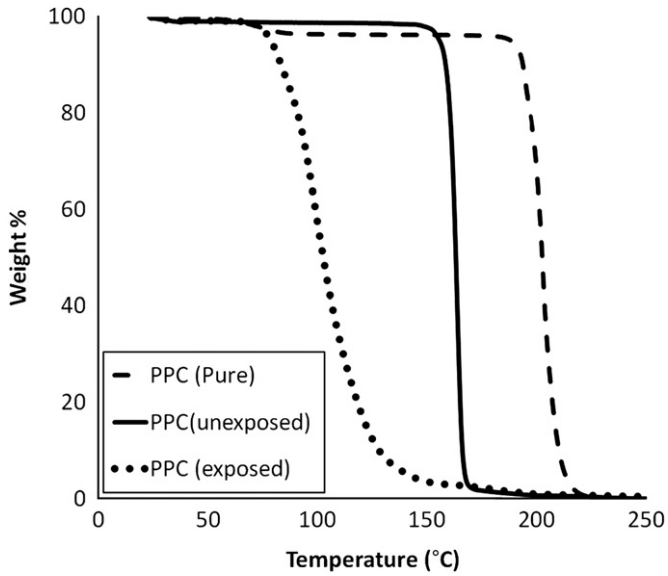

Fig. 3. Dynamic thermal gravimetric analysis showing the effects of PAG on decomposition temperature.

Table 1
Solubility chart for polycarbonates. D = Dissolved, S = Swelled, I = Inert, and N = Not tested.

	Polycarbonates			
Solvent	**PEC**	**PPC**	**PCC**	**PPC/PCC**
Mesitylene	I	I	D	I
Isopropanol	I	I	I	I
Acetone	D	D	I	I
NMP	D	D	S	D
Anisole	D	D	D	D
PGMEA	D	D	I	S
GBL	D	D	I	S
Cyclohexane	S	S	S	D
Propylene carbonate	D	D	I	I
Methylene chloride	D	D	D	D
Toluene	I	I	D	D
PGME	N	N	I	I
Diglyme	N	N	I	S
Benzotrifluoride	N	N	I	S
Ethyl acetate	S	S	I	I
Xylenes	I	I	I	I

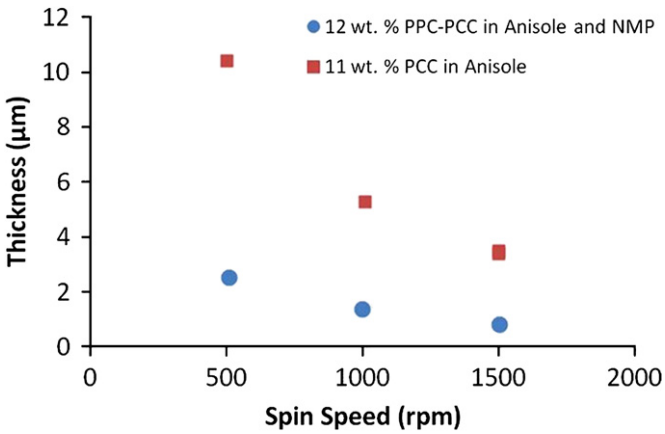

Fig. 4. Spin speed curves for PCC and PPC/PCC formulations.

When anisole alone was used, excessive surface roughness was obtained. The peak-to-valley surface roughness was about 2 µm. NMP increased the solubility of PPC/PCC in the solution. The roughness of the film cast from the solvent mixture was less than 0.05 µm, similar to the other polycarbonates.

Once the appropriate casting solvent was chosen, a spin speed curve was created by coating the film at different spin speeds, as shown in Fig. 4. The polycarbonate films were uniform with smooth surfaces after soft-baking. The wafers had a visibly even-coat on the wafer except for the edge bead which covered the outermost 4 mm of the wafer.

The bonding conditions for each polycarbonate was optimized. After coating, the samples were soft-baked to remove all the solvent. The soft bake time was varied based on thickness and casting solvents. Excess residue solvent prevented adequate substrate adhesion when bonding. The polymers dissolved in GBL required 6–8 min soft bake at 100 °C. The polymers dissolved in anisole had a faster evaporation rate and were soft baked for 1–3 min at 100 °C. The soft bake time was slightly extended for thicker films. The wafers with polycarbonate coating were bonded to aluminum foil by hot-pressing for 8 min. The bonding conditions were set to 135 °C and 225 kPa. The samples were then diced into strips and clamped in an Instron, where the aluminum was pulled 90° perpendicular to the wafer surface.

The average load to debond the aluminum strip was recorded for 10–20 samples for each material. Fig. 5 shows the load for a

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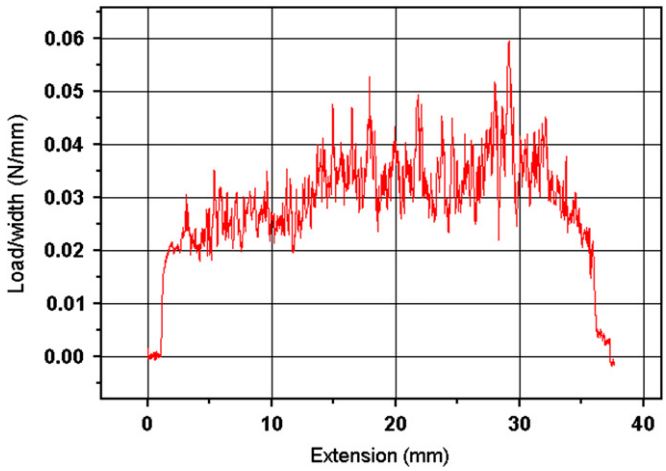

Fig. 5. Result of a single PPC 90° peel test.

Table 2
Average adhesive strengths for bonded polycarbonates and tapes.

Material	Adhesion strength (N/mm)
PEC	0.01 ± 0.005
PPC	0.03 ± 0.02
PCC	0.05 ± 0.02
PPC/PCC	0.05 ± 0.01
Furukawa tape #1	0.05 ± 0.02 (unexposed)
Furukawa tape #2	0.15 ± 0.03 (unexposed)
Scotch tape	0.09 ± 0.02

typical peel test for a PPC film showing an average peel strength of 0.03 N/mm. Table 2 shows the average value for each material along with the standard deviation.

For each of the bonding conditions, the aluminum foil debonded from the polycarbonate rather than the polycarbonate debonding from the wafer. This means that the bond strength to the wafer was greater than the measured value reported in Table 2. The polycarbonate bonding strength was compared to the adhesive tape and Furukawa UV tape. The Furukawa tape is a thermally bonded double-sided tape. When exposed to UV light, the adhesive decomposes allowing for a low force release. The tapes provided slightly higher values due to their embedded polymer backbone requiring a higher pull-force to initiate release. All polycarbonates demonstrated adhesion values within an order of magnitude compared to the tapes. This is due to the fact that there is no chemical interaction between the polycarbonates and the wafer surface. The adhesion is due to the low surface energy film when in a large area surface.

The film thickness, bonding temperature, and bonding pressure were optimized using the 90° peel test as a guide. Films with thicknesses between 1 and 15 μm thick were tested for each polymer. It was found that the film thickness played no role in the adhesion strength. This is most likely due the fact that the adhesion is a surface property. This allows the use of thin film adhesives between the substrate and the handle wafer. Bonding temperatures between 80 °C and 180 °C were tested. Fig. 6 shows the thermal optimization of PPC as an example. The best adhesion was found to be above the reflow temperature of all the polycarbonates. The films were reflowed to help uniformly bond the polymer across the entire wafer surface. Although no upper temperature limit for bonding was determined, there was no advantage found at higher temperatures.

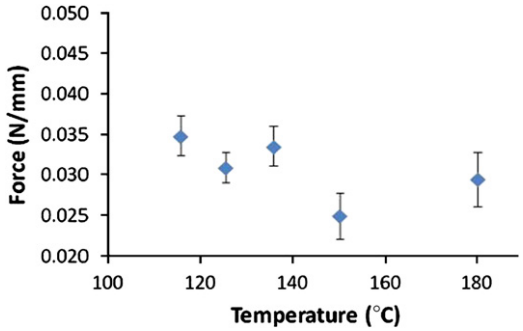

Fig. 6. Peel test results from optimization of bonding temperature for PPC adhesive.

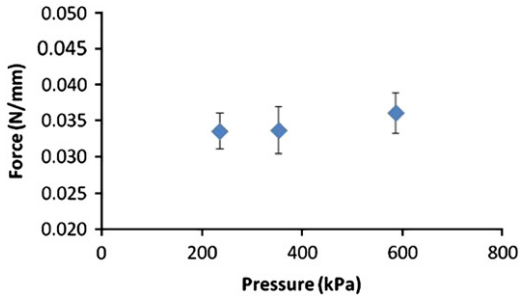

Fig. 7. Peel test results from optimization of bonding pressure for PPC adhesive.

Bonding pressure between 100 kPa and 600 kPa were tested. Fig. 7 shows the debonding force as a function of bonding pressure for PPC. The wafers did not adequately bond at pressures below 200 kPa. Above 200 kPa, the bond strength was adequate and only a weak function of bonding pressure.

Each polycarbonate tested and showed a similar debonding strength as PPC, Fig. 7. Thus, an optimum bonding condition was found for polycarbonate adhesive, which includes 3–5 μm polycarbonate thickness, bonding at 135 °C and 225 kPa pressure for 8 min. These conditions were used to bond wafers followed by chemical mechanical polishing. A set of 100 mm diameter wafers were bonded with each of the polycarbonates. The wafers showed excellent adhesion and were not separated during mechanical polishing at 350 rpm during the removal of 300 μm of silicon. No wafer debonding was observed during polishing. The adhesive at the edge of the samples was optically investigated. No erosion of the polycarbonate adhesive was observed, except for PEC which showed several micrometers of undercut during the polishing process.

A thermal debonding process was used to the release of the wafers after processing. Debonding was performed in a nitrogen-purged tube furnace. Samples were examined for residue, damage, and adhesion regions. The PPC and PEC bonded samples were heated to 220 °C for 2 h to debond the wafers. The debonded wafers were released without applying an external mechanical force. Inspection of the wafers showed no visible residue on the surface or mechanical damage. The PCC and PPC/PCC copolymer bonded wafers were debonded at 280 °C for 2 h. These wafers did not release freely and required a slight force to separate. Once separated, the wafers showed a thin residue film dispersed over much of each surface. The mass of the residue was approximately 2–5% of the original adhesive used. This corresponds to the TGA and mass spectrometry results presented above and is due to high molecular weight material remaining after thermal decomposition. The residue was easily removed with an NMP rinse and soft polish. A corresponding set of wafer/Al foil adhesive samples were

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Table 3
Average adhesive strengths in wafer debonding for polycarbonate residues and UV exposed tapes.

Material	Adhesion strength (N/mm)
PEC	0
PPC	0
PCC	0.0035 ± 0.02
PPC/PCC	0.0035 ± 0.02
Furukawa tape #1	0.024 ± 0.001 (exposed)
Furukawa tape #2	0.004 ± 0.0005 (exposed)

decomposed and peeled to determine the adhesive strength of the PCC and the PPC/PCC residues. The residue tests were comparable to the exposed Furukawa tapes. Table 3 shows the result of the 90° peel test. The PCC and PPC/PCC samples show a factor of ten decrease in adhesion strength after the thermal debonding process. The adhesion tests were within an order of magnitude of the peel strength of the exposed tapes. The quantity of residue is most likely due to impurities in the original polycarbonate samples, which can be improved with higher purity starting materials.

4. Conclusion

Polycarbonates were explored as a temporary adhesive in wafer–wafer bonding. Polycarbonates were formulated for debonding at temperatures between 160 °C and 270 °C. Polycarbonates were formulated for spin-coating and optimal bonding conditions. Bonded wafers using the polycarbonates showed adequate adhesion for wafer thinning. Low temperature polycarbonates, PEC and PPC, showed modest resistance to chemical and thermal processing and were free from residue after wafer debonding. High temperature polycarbonates demonstrated excellent chemical resistance, but did not spontaneously release upon polymer decomposition due to remaining residue.

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