Design Rules for Polyimide Solvent Bonding

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This paper describes a method for bonding polyimide layers to previously patterned polyimide layers and the results of a factorial study on bond quality (the amount of voids present at the void interface). The polyimide-to-polyimide bonding process has been demonstrated for forming *microfluidic channels*. First, a photosensitive polyimide precursor layer on the first substrate is patterned with the desired geometry and vent channels, but not cured. Next, a thin layer of solvent with dissolved precursor is used to coat a soft-baked layer of Pyralin® PD PI-2723, a polyimide precursor, on a second substrate. The two halves are placed in contact and cured. Tests on a dozen samples show that several factors are statistically significant for void-free bonds. These factors include soft-bake duration, vent channel spacing, quantity of polyimide precursor in the solvent layer, and spin-coat speed for solvent application. The bonding method has been used to make 50- to 1000-μm-wide, 3- to 30-μm-deep channels for chemical analysis and heat transfer devices.

1. Introduction

We introduce a method of solvent bonding polyimide to polyimide that is simple and versatile. Polyimide has been used in a variety of microdevices.[1,2] Relative to other polymers, it has excellent material properties, such as good chemical resistance and high mechanical strength.[3] Of particular interest in this work is the use of polyimide as a structural material in microfluidic devices and systems. The solvent bonding technique described, which uses precursor dissolved in the solvent, has been used to fabricate rigid

microchannels in an integrated fluidic nuclear magnetic resonance (NMR) system,[4] Fig. 1(a), and flexible fluid channels,[5] Fig. 1(b). The fluidic NMR device has relatively large channels, 1 mm wide and 30 μm deep, which consist of three polyimide layers: a 2.4-μm-thick base layer, a 30-μm-thick patterned intermediate layer, and another thin top layer. The flexible channels also have polyimide on all four sides. However, the solvent bonding technique seals a layer of Kapton® (DuPont High Performance Films, Circleville, OH), a cured, commercial polyimide, instead of a spin-coated layer, to the channel walls. Neither of these microchannel devices exhibited any leaking after several months of use. These

(a)

(b)
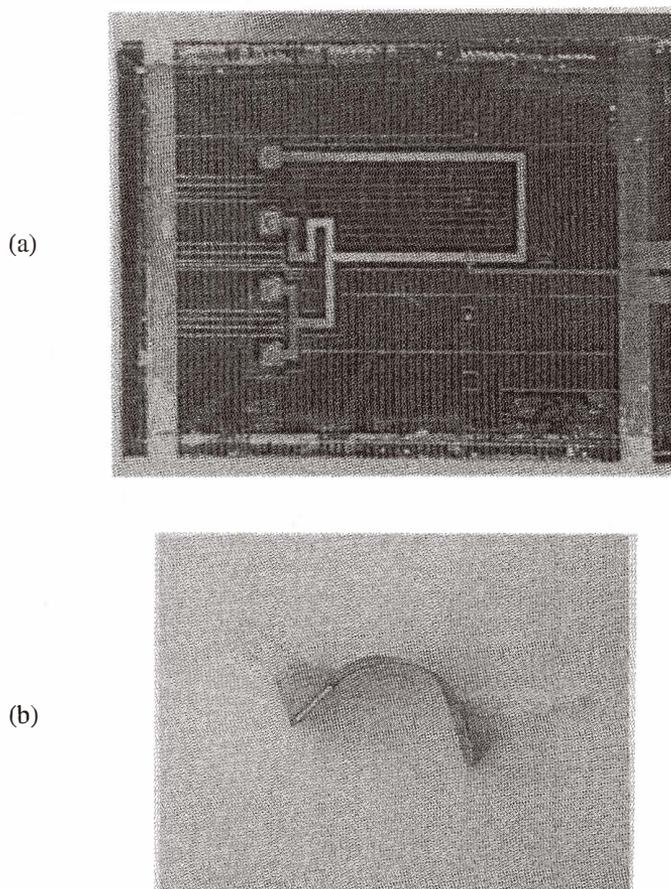
Fig. 1. Two microfluidic devices fabricated by polyimide-to-polyimide solvent bonding. The fluidic NMR device (a) contains a 1-mm-wide, 30-μm-deep channel and numerous 100-μm-wide vents typically spaced 1 mm apart. The flexible device (b) contains a 500-μm-wide, 30-μm-deep channel, with a Kapton® cover layer.

two devices demonstrate the utility of the bonding process.

Several researchers have tested the adhesion of spin-coated layers of polyimide to each other. Brown *et al.*[6] spin-coated one layer of pyromellitic dianhydride/oxydianiline (PMDA-ODA) on a previously cured layer and found that self-adhesion strength increased with interdiffusion (diffusion of the two layers into each other) distance, and interdiffusion distance increased with lower cure temperatures of the first layer. Saenger *et al.*[7] emphasized the importance of a swelling agent, such as n-methyl-2-pyrrolidone (NMP) to enhance interdiffusion. Frazier[8] patterned open channels in a photosensitive polyimide layer, spin-coated a second wafer with a polyimide material, and then bonded the two polyimide layers together by placing them in contact with each other inside a vacuum oven. Without the open channels, vapors were trapped and voids were prevalent. This method relied upon the residual solvent in the uncured polyimide films to enable interdiffusion at the bond interface. Void formation and bond repeatability were problems, while bond strength was observed to be stronger than the polyimide/substrate (SiO_2) bond. As an extension of Frazier's work, we have developed and statistically studied a method for bonding photosensitive polyimide Pyralin® PD PI-2723 (DuPont Electronics, Wilmington, DE) to a previously patterned layer. The PI-2700 series Pyralins are precursors of BTDA/ODA/MPD (benzophenonetetracarboxylic dianhydride/oxydianiline/*m*-phenylene diamine) polyimides. This work addresses the problems of void formation and process repeatability. As mentioned above, the technique has been used to fabricate microfluidic devices using different polyimides and geometric configurations.

2.   Bonding Technique

The described technique is analogous to welding plastics such as acrylonitrile butadiene styrene (ABS), polyvinylchloride (PVC), polystyrene, and polycarbonate[9] whereby some of the plastic is dissolved in the solvent, and after the solvent dissipates, the joint is practically the same as the adherends themselves. While Frazier's method[8] relied upon residual solvent, in the method presented here most of the solvent is soft-baked out, and a small, controlled quantity of solvent solution containing polyimide precursor is added at the interface. The presence of dissolved precursor molecules at the interface may provide improved bonding by acting as a conformal polymer layer allowing more intimate and complete contact between the two surfaces to be bonded.

The bonding process begins by soft-baking and patterning the first layer of PI-2700 series polyimide precursor with the desired geometry and additional vents. Next, a layer of polyimide precursor is spin-coated on a second substrate and soft-baked. Next, the solvent solution: T-9039 (80% NMP and 20% 1-methoxy-2-propanol, DuPont Electronics) with about 3% by weight dissolved polyimide precursor solids (10% by volume of PI-2723), is spin-coated on the nonpatterned layer. Immediately the two layers are placed in contact, pressed together, and then cured with weights on top (0.1 N/cm²) to complete the bonding process.

3.   Evaluation

While bond strength is an important issue, in some applications bond quality and the effect of the bonding process on the substrate material are equally important. For example, small leaks or voids in microfluidic systems may degrade their performance and surface inhomogeneities and voids at the bond interface may reduce the sensitivity of chemical analysis instruments. In these tests we define bond quality as the amount of voids present at the bond interface. We performed exploratory studies which indicated that several parameters are important for void-free bonds including soft-bake duration, vent channel spacing, amount of polyimide precursor in the solvent layer, and speed of solvent application. Voids formed throughout most of the interface if the vent channels were more than several mm apart or were not incorporated at all. We then statistically evaluated the importance of these parameters by running a nested, full factorial test (of all possible combinations of the chosen parameter values).

Twelve test samples were fabricated, one each for each combination of two durations of the soft-bake, three concentrations of polyimide precursors in the solvent, and two spin-coat rotation speeds. Each test sample (typical sample shown in Fig. 2) had multiple regions of the six combinations of two vent channel widths, 100 and 200 μm, and three wall widths of 1, 2, and 4 mm separating the vent channels. The channels extended to the edge of the substrate so ambient air could travel through the channels, even after bonding. The samples were fabricated on two consecutive days, in a class 100 clean room, with an ambient temperature of 22°C and relative humidities of 48 and 49%. Corning™ glass cover slips, 22×30 mm × no. 1 thickness (0.15 mm) (Corning, Inc., Corning, NY) served as the substrates for both the bottom PI-2721 (3.8 μm) and top PI-2723 (1.9 μm) layers. To
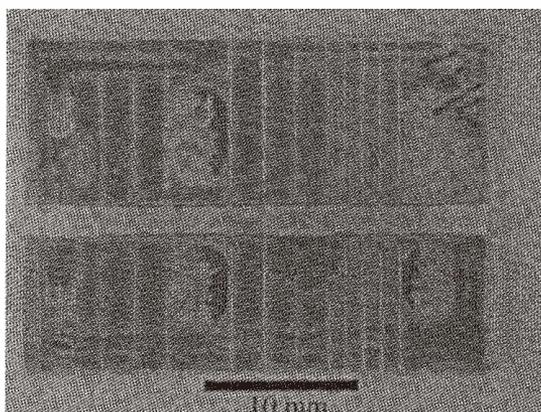
Fig. 2.   This test sample contains 100- and 200-μm-wide channels, spaced 1, 2, and 4 mm apart. Large oblong voids formed above the 4 mm walls. The extrawide vent channel up the middle separates the duplicate left and right sides.

ensure repeatable pressure for contact between the two layers, a 13.6 N steel weight resting on a 25 mm diameter acrylic cylinder, rolled across the entire sample, applying a mean pressure of 4–5 MPa.[10] Figure 3 shows the fabrication procedure, including the weight, which rolled left and right to apply pressure on the polyimide joint. Because we were most interested in bond quality (as defined above), the strengths of the polyimide-to-polyimide bonds were not quantitatively measured. Test samples were evaluated with an optical microscope with a graduated X-Y reticle. The percentage of voids, by area, at the bond interface equals the percentage of a reticle cross hair that passes through voids. The void percentages were separately tallied at two locations in each wall: midway and quarter-way between channel edges. An analysis of variance (ANOVA) (Minitab release 10.5, Minitab, Inc., State College, PA) identified the salient parameters.

a) Pattern polyimide on
a glass coverslip.

b) Coat a coverslip with
polyimide and solvent
solution.

Steel weight

Acrylic
bar

Steel weight

c) Press together.

d) Cure in a furnace with a
weight on the sample.

▨ Polyimide precursor
▨ Glass coverslip
■ Solvent solution

e) Completed sample.
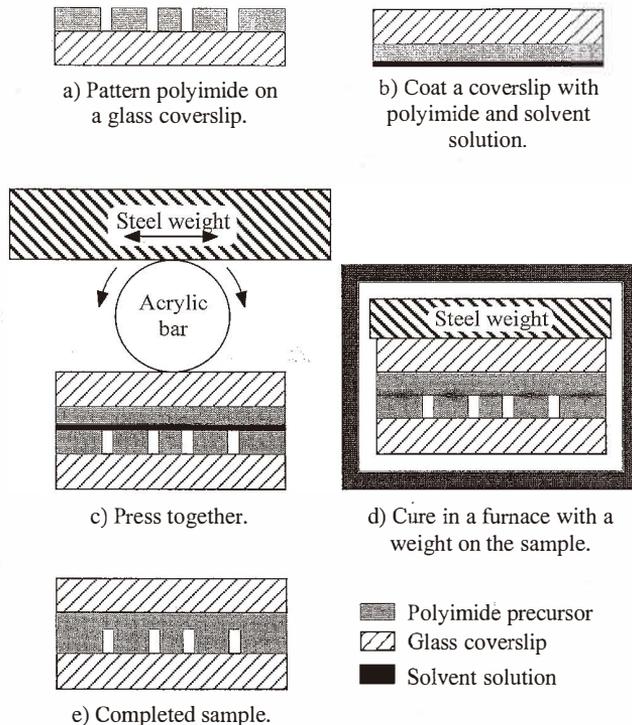
Fig. 3. To fabricate the test samples, (a) first the polyimide precursor was patterned with channels on a substrate. (b) A second substrate was also coated, but not patterned, and then coated with solvent solution. (c) This second layer was pressed onto the first, patterned layer and (d) placed in a furnace where the two layers diffused into each other, and some solvent escaped from the interface. (e) A cross section of the completed sample.

4.   Results and Discussion

Two types of defects are present, oblong voids at the interface due to bonding defects, and spherical microbubbles in the bulk material due to degassing of the bulk polyimide. The best bonds exhibited 0 to 0.1% voids, by area, at the interface. They occurred with the longer soft-bake (same duration as for the standard application), the faster solvent spin-coat speed of 8000 r/min, and wall widths of 1 mm for all solvent solutions and channel widths, and with 2 mm walls when the solvent solution contained 9 or 20% by volume PI-2723. See Table 1 and Figs. 4 and 5. Longer soft-bakes limit the amount of solvent remaining in the bulk layer. Likewise, faster solvent spin-coat speeds limit the amount of solvent solution applied at the interface. Some solvent is required for the bonding to occur, but too much solvent leads to voids. Solvent solution with dissolved polyimide precursor works better than solvent alone.

The percentage of voids that existed above the centerline of each wall and above a line one-quarter of the way across the wall did not differ significantly (paired $t = 1.20$, $p = 0.24$)*. Walls 1 or 2 mm wide between vents were sufficiently narrow, but large voids formed above 4-mm-wide walls. Above thicker walls, there is a greater likelihood that

Table 1
Full factorial test and analysis of variance. Best values are in bold.

Fabrication parameters:	Low value	Mid value	High value	F ratio	p
Soft-bake duration: PI-2721 @ 60 & 105°C & PI-2723 @ 75° C	1 & 1 min 1 min		**3 & 3 min** **4 min**	21.44	< 0.0005
Concentration of PI-2723 in T-9039	0%	**9% (1:10)**	20% (1:4)	20.36	< 0.0005
Spin coat speed for solvent mixture	4000 r/min		**8000 r/min**	91.22	< 0.0005
Geometric parameters:	Low Value	Mid value	High value	F ratio	p
Wall width	**1 mm**	2 mm	4 mm	19.84	<0.0005
Channel width	**100 μm**		**200 μm**	1.14	0.294

Higher F ratios and $p < 0.05$ denote statistical significance.[11] Because the substrate-to-substrate error term could not be estimated independently, the within-substrate error term was used instead for assessing statistical significance.

*Two paired variables differ significantly if |t| is greater than about 2 (depending on the sample size), which indicates that the probability (p) of a false positive is less than 0.05.[11]
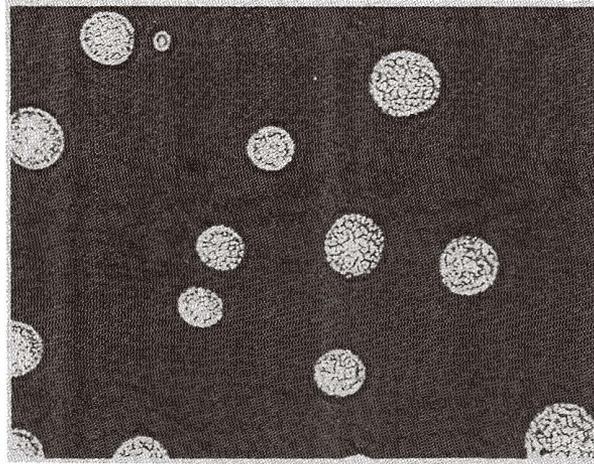
Fig. 4. This photograph shows 10% voids by area at the interface (20 – 70 μm diameter each) and microbubbles (typically 2 μm diameter) entrapped in the bulk polyimide. The minor stress cracks in this sample are also visible.
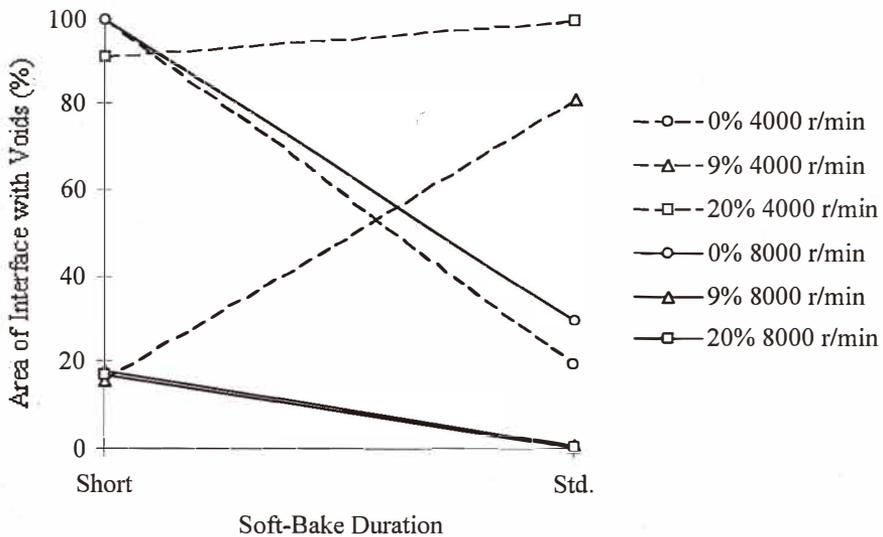
Fig. 5. This graph shows a trend toward fewer voids with longer soft-bakes and higher spin coat speeds. Nine or 20% by volume of PI-2723 precursor dissolved in the solvent also reduces the percentage of voids at the interface. Each plotted point is the mean of the data for 1 and 2 mm walls and 100 and 200 μm vent channels.

solvent solution will be trapped at the interface when the top is pressed on. The pattern of the voids is not due to diffusion since the voids were evenly distributed at the interface. We suspect that the voids form as the additional solvent at the interface escapes and the polyimide precursor layers shrink. Results were similar for 100- and 200-μm-wide vent channels, i.e., the narrower vent channels used in these tests allowed sufficient ventilation.

Other work in our laboratory with standard 2×3 inch glass microscope slides confirms that high-quality bonds depend upon the flatness and stiffness of the substrates. If both substrates are thick, say 1 mm or more, good contact across most of the interface requires the substrates to be very flat, on the order of the compliance of the soft-baked layers. However, if one substrate can conform, e.g., a 150-μm-thick cover slip, then good contact can occur throughout the interface. In addition, surface tension forces tend to encourage wicking, i.e., pulling the solvent into gaps, thereby encouraging more complete contact of the two polyimide layers. The solvent swells the polyimide layers, which also encourages contact between the layers.

Upon prying apart the test samples, the self-adhesion of polyimide proved to be stronger than the polyimide-to-glass bonds. Previous tests also showed the bonds to be stronger than polyimide-to-silicon bonds. The polyimide-to-polyimide bond strengths were not quantified, but they were relatively strong. Because both polyimide layers are only soft-baked before the solvent is applied, the interdiffusion distance and bond strength are maximized.[6] Bonds with greater percentages of interfacial contact, such as those with only 0.1% voids, are presumed to be stronger than bonds with voids covering significant portions of the interface. In addition, because the top and bottom layers are composed of the same material and thoroughly interdiffused at the interface, the stability of the bond should be a function of the curing (temperature and duration) of the polyimide. The interface is not visible after curing, nor is it more susceptible to chemical attack than the top and bottom layers.

Spherical bubbles up to several μm in diameter formed in the bulk polyimide. (Recall that irregularly shaped voids were at the interface.) More microbubbles formed in the polyimide layers at distances further from the vent channels ($p < 0.05$) independent of the wall thickness ($p > 0.05$). Observation of the set of samples used to study microbubbles showed that microbubbles were more prevalent further from the vent channels. Microbubbles are trapped in the coating if the coating temperature increases so rapidly such that crosslinked photoreactive groups volatilize more quickly than they can diffuse to the surface[12] or to vent channels. As expected, fewer bubbles occurred where byproducts of curing could more easily diffuse to the vent channels. No microbubbles are present in "open-faced" samples in which bubbles could diffuse to the surface.

The vent channels should be open to the ambient environment. While statistical evaluation did not assess this, the preliminary tests clearly showed that trapped solvent resulted in large voids at the interface. Also, care should be taken that solvent does not remain in the vent channels. The solvent could cause degradation during future processing or leave a corrosive residue. While it is possible that the vent channels may be initiation sites of delamination, there was no evidence of this.

5.   Conclusion

Vent spacing, soft-bake duration, spin-coat speed during solvent application, and concentration of polyimide precursors dissolved in the solvent affect bond quality ($p<0.05$). Closely spaced vents allow the solvent to leave more easily, while long soft-bakes, and high spin speeds limit the amount of solvent at the interface. One of the interface layers should contain vents no more than 1 or 2 mm apart. The spin-coated layer of solvent solution should contain some dissolved polyimide precursor and should be spin-coated at a high rotation speed for a minimal quantity, uniformly distributed at the interface. Microfluidic channels made by solvent bonding Kapton® to photosensitive PI-2723 demonstrate the versatility of this technique.

Future work should develop better methods of applying pressure and ensuring contact between the two polyimide layers. Bonding patterned layers to patterned layers, using other polyimide bonding agents with different polymer structures, and stressing and aging (long term stability) effects on bond quality should also be studied. More testing is required to optimize the bonding parameters, especially if other polyimides are used.

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