New Results on Plasma Activated Bonding of Imprinted Polymer Features for Bio MEMS Applications

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Abstract. Nanoimprint Lithography is a well-acknowledged low cost, high resolution, large area 3D patterning process for polymers. It includes the most promising methods: high pressure hot embossing (HE) and UV-Nanoimprint Lithography (UV-NIL). Curing of the imprinted structures is either done by cooling down below the glass transition temperature of the thermoplastic polymer in case of HE or by subsequent UV-light exposure and cross-linking in case of UV-NIL. Both techniques allow rapid prototyping for high volume production of fully patterned substrates for a wide range of materials. The advantages of using polymer substrates over common Micro-Electro-Mechanical Systems (MEMS) processing materials like glass, silicon or quartz are: bio-compatible surfaces, easy manufacturability, low cost for high volume production, suitable for use in micro- and nano-fabrication, low conductivity, wide range of optical properties just to name a few. We will present experimental results on HE processes with PMMA as well as UV-NIL imprints in selected UV-curable resists.

In the second part of the work we will describe the bonding techniques for packaging of the micro or nano structures. Packaging of the imprinted features is a key technology for a wide variety of field of applications: μ-TAS, biochemistry, micro-mixers, micro-reactors, electrophoresis cells, life science, micro-optical and nano-optical applications (switches) nano-fluidics, data storage, etc. for features down to sub-100 nm range. Most bonding techniques for polymer use adhesives as intermediate layers. We will demonstrate a promising technique for dense and very strong bonds using plasma activation of polymers and glass. This bonding technology allows for bonding at low temperatures well below the glass transition temperature of the polymers, which will ensure that the structures are not deformed.

Keywords: Nanoimprint, hot embossing, plasma activated bonding, polymer packaging, Bio MEMS
1. Introduction
Aging populations, global health risks and biochemical disease defense have increased the need for inexpensive, disposable analysis systems for fluids and gases. Because many of the diagnostic methods are spectral, a transparent package is required. Plastics offer the least expensive options for these applications. Although most of the molecules requiring analysis are large compared to state-of-the-art IC transistor sizes these devices still require critical dimensions on the order of one micron.

Several methods are available for the fabrication of the channels and other structures in polymer materials. The most obvious method is stamping, otherwise called, Hot Embossing (HE). Alternative methods include UV-nanoimprint lithography, UV-NIL.

Once the patterns and channels are fabricated the devices must be packaged into usable systems. Initial methods were fairly brute force and involve heating the samples near the glass transition temperature of the polymer so that the interface became fused. The drawback to fusing the interface is that material flow is not restricted and small features become distorted and the functionality is lost. Therefore a low temperature process for making the channel devices and packaging the devices is needed.

2. Definition Processes
The prerequisites for imprinting techniques are the ability to replicate high aspect ratio patterns, good structure height vs. residual thickness (underlying thickness at bottom of a channel), accurate and easy separation of stamp and substrate, accurate replication of features across the whole substrate area, and short cycle times. This requires dedicated equipment, reliable and robust stamps, and low temperature processing of structured substrates.

3. Hot Embossing Technique
The HE method uses structured silicon or metal stamps to imprint thermoplastic polymers at elevated temperatures. The stamps are accurately patterned by conventional silicon etching methods or in the case of metal stamps by etching, micromachining, or LIGA processing.

The polymer is driven into the cavities of the stamp by applying high contact forces and heating above the glass transition temperature of the polymer to assure sufficient material flow to conform to all surfaces of the stamp. During cool down below or close to Tg, the stamp can be separated and the negative structure remains in the polymer with all features frozen in dimension.

Different feature sizes from 70nm to 100µm have been imprinted by HE into thermoplastic polymer layers on 200mm carriers (figure 1) [2]. The key parameters for HE are cycle time, imprint uniformity, temperature uniformity, repeatability from wafer to wafer, reproducibility, contour accuracy, fast heating and cooling at minimized stress and minimum feature sizes vs. highest aspect ratio.

![Figure 1: SEM picture of 300 nm channels imprinted on an EVG520HE](Courtesy of CNRS-LTM and CEA-LETI)
4. UV-NanoImprint Lithography
UV-NIL uses UV curable resists imprinted with transparent stamps (PDMS or glass) and cured by light in the near-UV range. Common UV curable resists are acrylate monomers and photo initiators. The applied force needed to press the stamp into the substrate is significantly less that the forces used in HE. During the UV exposure process cross-linking in the resist forms the hard polymer features. The process is performed at room temperature, which minimizes stress in the imprinted layer and the substrates and therefore has the potential for accurate overlay alignment. Structures in the sub-100nm range on wafer sizes up to 150mm have been replicated on an EVG620NIL. Figure 2, shows recent features replicated using this technique.

5. Packaging Technique
The main goal of assembly and packaging operations is either to attach the two halves of a device together (generally used in bulk micromachined sensors) or to provide a protective cover (common for surface machined parts). Nano/micro structured polymer devices can be heterogeneously (polymer to glass or Si) or homogeneously (polymer to polymer) bonded. The method chosen to attach the components is based on various physical and mechanical considerations. The two most important are the temperature range that is compatible with the device and the surface topography and flatness. Because of the low Young’s modulus of these materials the topographical requirements for direct bonding methods are relaxed and plasma activation can be used to further reduce the annealing temperatures and minimize thermal distortion of the features and degradation of alignment accuracy.

In wafer bonding applications the creation and development of chemical bonds between two surfaces creates a permanent interface seal. This is accomplished by providing reactive species that will not only participate in the chemical reactions ongoing at the bond interface, but also catalyze the reaction or speed up the kinetics of the bond development (bond strength). To improve the physical and chemical reactions, EVG introduced low temperature plasma activation [3]. This is accomplished by exposing the one or both of the surfaces to be bonded to a room temperature, low power plasma for approximately 30 seconds. The RF frequency in the EVG®810LT plasma activation chamber is supplied to the chamber via top and bottom electrodes. The plasma conditions are optimized for cleaning and surface activation. The main parameters for this step are: process gas, gas pressure, treatment time, plasma frequency, coupled power and the chamber design.

The interactions of the plasma and the polymer are versatile and very complex. Reactions of the plasma gas occur on the surface of the polymer: (de-) polymerization, cross-linking, oxidation, functionalization or micro-etching and surface roughening. Depth effects inside the polymer (several 5-10μm depths) are caused by the emitted UV radiation and are responsible for photo-oxidative degradation, formation of radicals or dehydration. Different reactions can be obtained by using reactive gases like water and nitrogen, reducing gases like hydrogen, hydrogen-argon and inert gases like argon.
After activation the samples are loaded into a wafer bonding system, like the EVG®501. By applying a modest and uniform contact pressure at low temperatures permanent bonds are formed. The final structures are hermetically sealed cavities free from destruction or distortion of small features (figure 3).

Figure 3: Plasma activated PMMA bonds with alternating channels from 3-50µm before and after destructive separation of the bond (cracks in the top layer)

To study the bond strength, blank polymer sheets of PMMA and COC were used. These sheets were pre-treated under different plasma conditions in an EVG®810. The selected plasma gases were oxidizing (oxygen, nitrogen), reducing (hydrogen/helium) or inert (argon) in nature. The results demonstrated, that the oxidizing gases had the biggest impact on the surface activation. Hydrogen gas gave almost no improvement in bond strength for the tested polymers, PMMA and COC (Zeonex). The argon plasma even reduced the bond strength – probably an effect of micro-etching. Oxygen gave the highest bond strength of >100J/m². The activation with nitrogen plasma was around 50% of the one achieved by oxygen. Activation with O₂ and subsequent N₂ treatment destroyed the beneficial effect of O₂ plasma treatment. Subsequent cleaning with liquid IPA or DI water destroyed the activation, as well. PMMA and COC showed similar behaviour in terms of plasma gas source. The plasma pressure has more impact on the studied COC materials, Zeonex, compared to PMMA, where no correlation between the plasma pressure and the bond strength was measured (demonstrated in [4]). Figure 4 illustrates the activation results on COC. For comparison the strengths achieved in Si-SiO₂ has a maximum value of 2.5 J/m².

The influence of the bond parameters (contact force, bonding temperature, heating and cooling ramp) was studied in an EVG®520 wafer bond chamber. The bonding process ran through 5 process steps: 1) heat up top and bottom side heater simultaneously from room temperature to 50°C or 80°C within 5 minutes, 2) hold temperature and apply contact force of either 2000N or 5000N, 3) hold force and temperature for 10min, 4) cool down for 10min (40-50°C) and 5) release contact force. In order to avoid any thermal stress, the samples were cooled down to room temperature at ambient atmosphere for another 30 minutes.
For increased contact force uniformity the samples were loaded on a rubber coated metal chuck with a surface roughness of below 800nm. This coating distributes the force quasi-hydrostatically across the full wafer. At a contact force of above \(~3000-4000\text{N}\), this coating looses its function. This was reflected in the bond uniformity. With standard rigid metal chucks, the polymers couldn’t be bonded at all. Compared to 5000N, a two times higher bond strength was obtained at 2000N.

The evaluation of the impact of annealing temperature on the bond strength showed the expected result of direct correlation in the temperature range between 30-50°C. Temperatures above 50°C didn’t improve the bond strength significantly (see figure 5).

The results were quantified by fracture surface analysis and surface energy (\(\gamma\)), measurements using the method by Maszara [5] on bonded bulk materials. In this test a razor blade of thickness \(h\), is inserted at the interface of the two polymer sheets. The ensuing crack length \(L\), is measured from the blade edge to the edge on the remaining bonded area. Using additional constants such as the material thickness \(t\) and Young’s modulus \(E\) of the polymer, the surface energy can be calculated as shown in figure 6. The Young’s modulus values for the polymers are: Topas (COC) 2.6-3.2GPa, Zeonex (COP) 2.2-2.5GPa and PMMA 2.5-3.0Gpa. The optical and SEM pictures in figure 7 shows the fracture surface after destructive separation of the bonded samples. The reference samples, bonded without plasma activation and with the same annealing process, immediately separate after the applied force was removed.
Figure 6: Surface energy calculation method; bond strength formula for similar materials [6]

Figure 7: OM and SEM picture of fracture surface of debonded PMMA to PMMA samples.

Additional tests have been performed with bonded channels and destructive test results are shown in figure 3. The interfacial bonds are developed at 70°C are exceeding the bulk fracture limits of the material as evidenced by the textured fracture surfaces

Conclusion
Several techniques for structuring polymers in the nanometer range have been developed for future production of devices in the two most promising fields of nanosciences, information technology and bio technology. Nanoimprint lithography (NIL), a technique just developed the last decade, is the most promising technique to accomplish the requirements for these fields. Packaging of the polymer channels is the logical next step and must preserve the delicate structures. High strength bonding techniques have now been demonstrated for low temperature at processing of PMMA-PMMA and COC-COC polymers.

Oxygen produces the most reactive radicals on the surfaces and produces the best activation (final bond strength) for the materials studied (PMMA and COC). Other reactive gases like water and nitrogen, reducing gases like hydrogen and inert gases like argon were also tested. The development of bond strength with annealing is very rapid and occurs significantly below the glass transition temperatures for the polymers tested. COC bonds have been realized as low at 50°C.

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