Novel PDMS(silicone)-in-PDMS(silicone): Low Cost Flexible Electronics without Metallization

Joshua .C. Agar, Katy J. Lin, Rongwei Zhang, Jessica Durden, Kyoung-Sik Moon and C.P. Wong
Georgia Institute of Technology
Department of Materials Science and Engineering
771 Ferst Drive
Atlanta, GA 30332
cp.wong@mse.gatech.edu

Abstract

Future electronics will undoubtedly require natural integration at the system, device and package level in the form of a functional, flexible package. Functional, flexible electronics expand the functionality of devices allowing morphological-electronic response for ergonomic and natural interfaces between the device and its surroundings. Recent technological successes have been able to fabricate functional, flexible electronics, however have all failed to develop a package capable of meeting the stringent cost, reliability and performance required of consumer electronics.

We demonstrate the application of electrically conductive adhesive technology to produce low cost, flexible electronics without metallization. We have shown the capability of fabrication of highly conductive Poly(dimethlysiloxane) (PDMS) (ρ~$7x10^{-4}$ Ω•cm) by incorporation of 80 wt% bimodal distribution of micron sized silver flakes. PDMS is both the ideal substrate and composite matrix material due to its unique properties; PDMS is optically transparent, viscoelastic, chemically and thermally stable, highly flexible, hydrophobic and can easily be molded with high resolution and aspect ratio. These unique properties of PDMS allow for high resolution molds to be prepared from photolithographically defined substrates. Screen printing of electrically conductive PDMS into these molds with micro-sized features creates a low cost, flexible electronic package. We have coined this package PDMS-in-PDMS.

We show that PDMS ECA can be prepared by curing a novel formulation of PDMS at curing temperatures of 150 °C for 15 minutes. Upon curing, the ECA undergoes a transition from insulating to conductive. TMA results have shown that this transition is due to ECA shrinkage >20%. Furthermore, we show simultaneous conductivity and tensile strain measurements to show the electrical properties of PDMS ECA are unaffected by tensile strains of >40%. We show the feasibility of this technology to create low cost, flexible devices without the need for metallization.

Introduction

The future of electronics will not be constrained to the simplicity of planarity. The electronics of the future will be designed on flexible substrates enabling functionality impossible within the confines of a ridged planar surface. This transformation from the simplicity of planarity to complex curved and flexible surfaces will require eloquent materials and design of component, integration and interconnection at the system, device and package level. Current electronic design and interconnection technologies have been unable to meet the stringent cost, reliability and performance required for application in a flexible, functional package. New electronics fabrication and interconnection technologies must be developed for flexible electronics which focuses on simplicity of design and functionality. Focusing on simplicity will enable the design, fabrication and implementation of functional, flexible electronics capable of natural integration with non-planar environments and applications.

Polymeric materials are ideal material candidates to be used in future flexible electronics. Polymeric materials, due to their highly controllable chemistry, can be engineered to have a wide variety of mechanical and electronic properties enabling their intricate design. Polydimethylsiloxane(PDMS) is an ideal material to serve as a substrate for flexible electronics. PDMS is a viscoelastic material with highly tunable mechanical properties. PDMS is also hydrophobic and will not swell in the presence of moisture. However, metallization on PDMS is a difficult process generally involving surface pretreatment, pre-straining and E-beam deposition processes [1]. The process patterned of metallization in PDMS is complex and cost prohibitive for low cost flexible electronics. PDMS metallization prepared using pre-strained methods have highly anisotropic properties which limit their functionality. Furthermore, metallization of definable patterns will require secondary steps for interconnection increasing cost and complexity of device fabrication.

We show a simple alternative solution to metallization involving a printable and stretchable electrically conductive adhesive (ECA). ECAs are conductive composites composed of metallic fillers within a polymeric matrix. We demonstrate a simple method to fabricate functional, flexible electronics on PDMS substrates using a novel PDMS ECA. We coin this technology PDMS-in-PDMS electronics.

Experimental Methods

The experiments conducted were divided into three sub-categories: 1. Fabrication and characterization of highly conductive flexible PDMS ECA. 2. Effect of tensile strain on conductivity. 3. Patterning and device level integration.

Fabrication and characterization of highly conductive flexible PDMS ECA

ECA was fabricated using polydimethylsiloxane (Dow Chemical) with a bimodal distribution of silver flakes (Ferro Corporation). Silver flakes were added to two part PDMS mixture in an 80:20 by weight ratio. Silver flakes were dispersed in PDMS using a mixture of manual stirring and ultrasonication. Two strips of Kapton tape (Dupont) were applied onto pre-cleaned glass slides. ECA was printed onto glass slides. Following thermal cure at temperatures in the range of 120-180°C for 15 minutes, the bulk resistance was measured using a Keithley 2000 (Keithley Instruments Inc.) multimeter; using the four wire method. The width and length of the specimen was measured using a digital caliper (VWR). The thickness of the sample was measured by Heidenhain (thickness measuring equipment, ND 281B, Germany). The bulk resistivity was calculated using equation 1 where l, w and t are the length, width and thickness respectively:

$$\rho = \frac{t \times w}{l} \times R \tag{1}$$

Characterization of the shrinkage during cure was measured isothermally at 150 °C using a thermal mechanical analyzer Model Q400 (TA Instruments).

Effect of tensile strain on conductivity

Two pieces of 2 mil kapton tape (Dupont) was placed within a metallic pan. A two part mixture of PDMS (Dow Chemical) was poured into the metallic pan ~0.75 cm thick. The PDMS was degassed using sonication until no air bubbles were visually apparent. PDMS was cured at 70 °C for 1 hour. Following cure PDMS molds were removed from the metallic pans. Tensile specimens were cut using a razor blade from the PDMS mold using a custom designed dogbone shaped tensile template. UV-Ozone treatment (UVO) (Samco International) for 7 minutes was used to clean the surface and alter the surface properties. Contact angle measurements were measured using Model 190 CA Goniometer (Ramé-Hart Instrument Co.). Immediately following UVO treatment ECA prepared as described was screen printed into the inlayed impression of the tape. Copper foil (Sigma Aldrich) was placed on the ECA at the far ends of the tensile mold. The tensile mold was cured at 150 °C for 15 minutes. Following cure, simultaneous tensile and electrical measurements were measured. Specimen dimensions were measured with a digital caliper (VWR). The tensile testing was conducted with a Instron 5548 microtester (Instron Corp.) at an extension rate of 2 mm/min. Electrical resistances were recorded simultaneously at 2 second intervals using a Keithley 2000(Keithley Instruments Inc.) multimeter connected through testpoints software.

Compressive DMA model 2980 (TA instruments) of mold following initial cure was conducted isothermally at 150 °C for 15 minutes and following cure at room temperature.

Patterning and device level integration

Negative Photoresist NR9-8000 (Futurrex) was spin coated on 4 inch silicon wafer (University Wafer) using a Karl Suss RC8 spin coater (Karl Suss) at 750 rpm. Soft bake was conducted at 70 °C for 3 minutes followed by 150 °C for 2 minutes. Lithography was completed using a custom designed transparency mask on a Karl Suss MA-6 Mask Aligner (Karl Suss) exposure time 180 seconds. Post bake was conducted at 70 °C for 2 minutes. Pattern was developed using RD6 developer (Futurrex) for 5 minutes. The developed wafer was imaged using an optical microscope (Leica Microsystems). Degassed PDMS was poured over the pattern mold and cured at 70 °C for 1 hour. The PDMS mold was removed from the silicon wafer revealing the patterned PDMS substrate.

Results and Discussion

Fabrication and characterization of highly conductive flexible PDMS ECA

PDMS ECA prepared as described was shown to undergo a transition from insulating to highly conductive following a high temperature (>150 °C) curing process. Thermal mechanical analysis showed that the PDMS ECA dimensions shrank 20% following the curing process (Figure 1). This high shrinkage at elevated curing temperature is the cause of the transition from insulating to conductive in PDMS ECA.

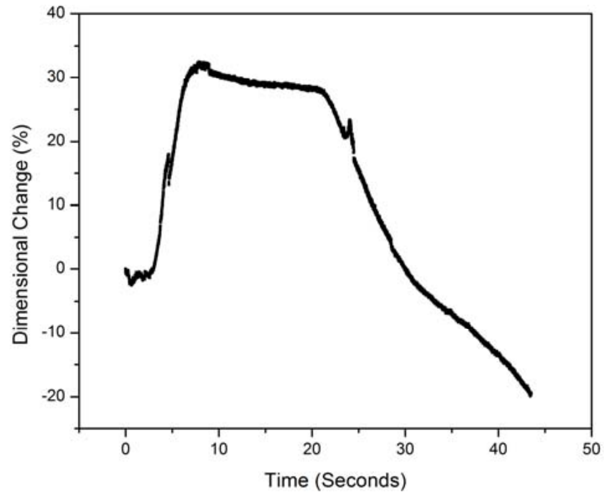

Figure 1. TMA showing dimensional changes during the curing process.

It was found experimentally that PDMS-ECA conductivity increased as a function of curing temperature until conductivity reached ~7×10^{-4} Ω•cm (Figure 2). The conductivity expressed in our novel PDMS ECA is comparable to standard epoxy based ECA [2].

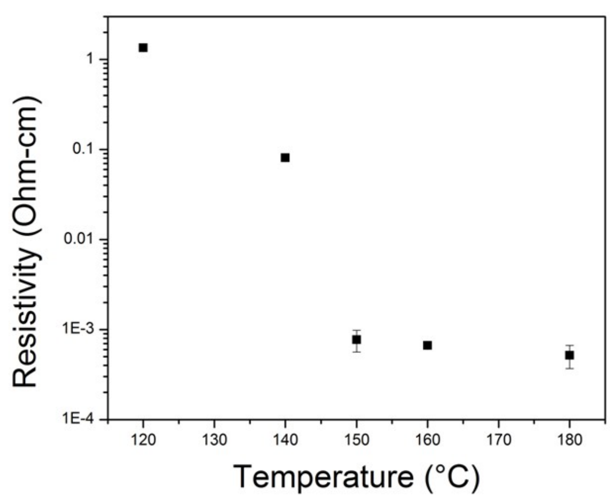

Figure 2. Bulk resistivity of PDMS ECA as a function of curing temperature

Effect of tensile strain on conductivity

Commercially available ECAs have shown the capability to function under flexural and compressive strains. However, when applied to stretchable surfaces they fail under tensile strain >5%. Use of highly elastic matrix materials with high poissons ratio enables electrical contact between fillers to be maintained during tensile strain. PDMS which can be formulated to have nearly ideal poissons (υ~0.5) is an ideal matrix material for use as flexible ECA [3]. Good compatibility and adhesion between the ECA and the substrate is essential for reliability. PDMS ECA inlayed in a predefined PDMS mold had excellent adhesion and compatibility. Preparation of a PDMS substrate material that could withstand ECA curing at 150 °C for 15 minutes required the development of a novel PDMS formulation. Commercial PDMS all exhibited undesirable changes in their mechanical properties during the ECA curing. Compressive DMA showed that the storage modulus of commercial PDMS changed from 90 MPa to 300 MPa during the ECA curing process. Tensile testing of PDMS-in-PDMS molds made with commercially available materials failed at tensile strains of 5-10%. DMA confirmed that the custom designed PDMS formulation used as a mold for PDMS-in-PDMS ECA has a much lower storage modulus of 0.2-0.8 MPa and exhibited minimal change during the ECA curing process (Figure 3). Furthermore, the mold was able to withstand tensile strains (>80%) without failure.

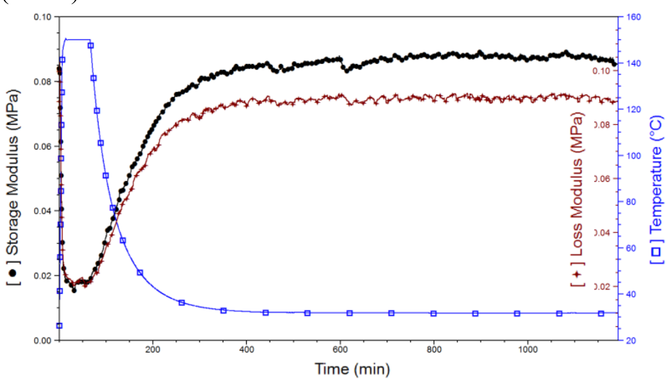

Figure 3. DMA of PDMS mold formulation during ECA curing process

Due to the chemical compatibility between the PDMS substrate material and the PDMS ECA surface treatment was used to facilitate the printing process. UVO treatment of the PDMS mold substrate creates a temporary transformation of the surface from hydrophobic to hydrophilic. This transformation is believed to be the result of a “silica” like layer that forms as PDMS oxidizes on the surface [4]. This silica like layer will undergo hydrophobic recovery over the course of a couple of hours, enabling PDMS ECA to adhere well to the surface of the PDMS substrate [1]. Contact angle measurements of the UVO treated PDMS (85.7°) and the untreated PDMS (116.1°) are shown in Figure 4A and Figure 4B respectively.

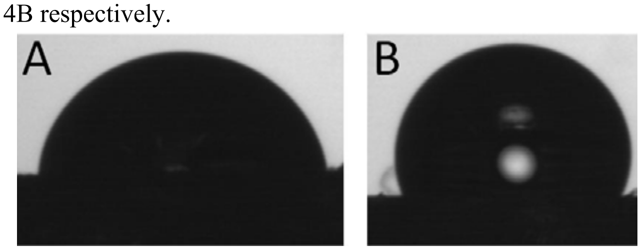

Figure 4. Contact angle measurements of A. UVO treated PDMS and B. Untreated PDMS

Tensile specimens were prepared as described. Images of the tensile specimen are shown after initial cure (Figure 5A), following ECA cure (Figure 5B) and during tensile-conductivity experiment (Figure 5C and D). A plot of electrical conductivity as a function of percent elongation is shown in Figure 6. It is evident that there was no significant change in resistivity at elongations up to 40%. There was no noticeable change in resistivity for repeated tensile strains. The PDMS-in-PDMS also performed well under compressive and flexural strains. Proper characterization of the ECA could not be conducted, as failure tended to occur at the surface mounted metallic foil-ECA interface.

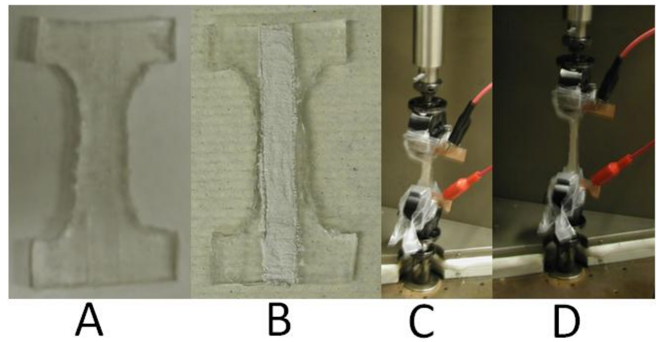

Figure 5 Images of A. tensile mold, B. tensile mold embedded with ECA, C. unextended tensile specimen, and D. extended tensile specimen.

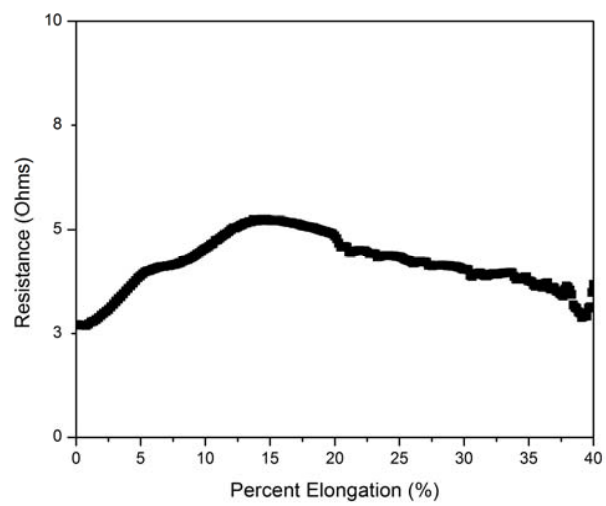

Figure 6. Resistance as a function of elongation

Patterning and Device Level Fabrication

Functional electronics require the ability to fabricate complex structures with fine feature size in a simple way. PDMS represents the ideal material for use as a flexible substrate. PDMS has been the leading material candidate for microfluidics and soft lithography processes because of its ability to be defined into complex structures with sub-micron scale resolution [3]. PDMS, because of its very low glass transition temperature in the uncross-linked state is a viscous liquid, allowing high resolution inverse structures to be prepared from a master mold via a pour and cure process. This technique is the ideal process necessary to fabricate low cost circuitry in PDMS for subsequential PDMS ECA screen

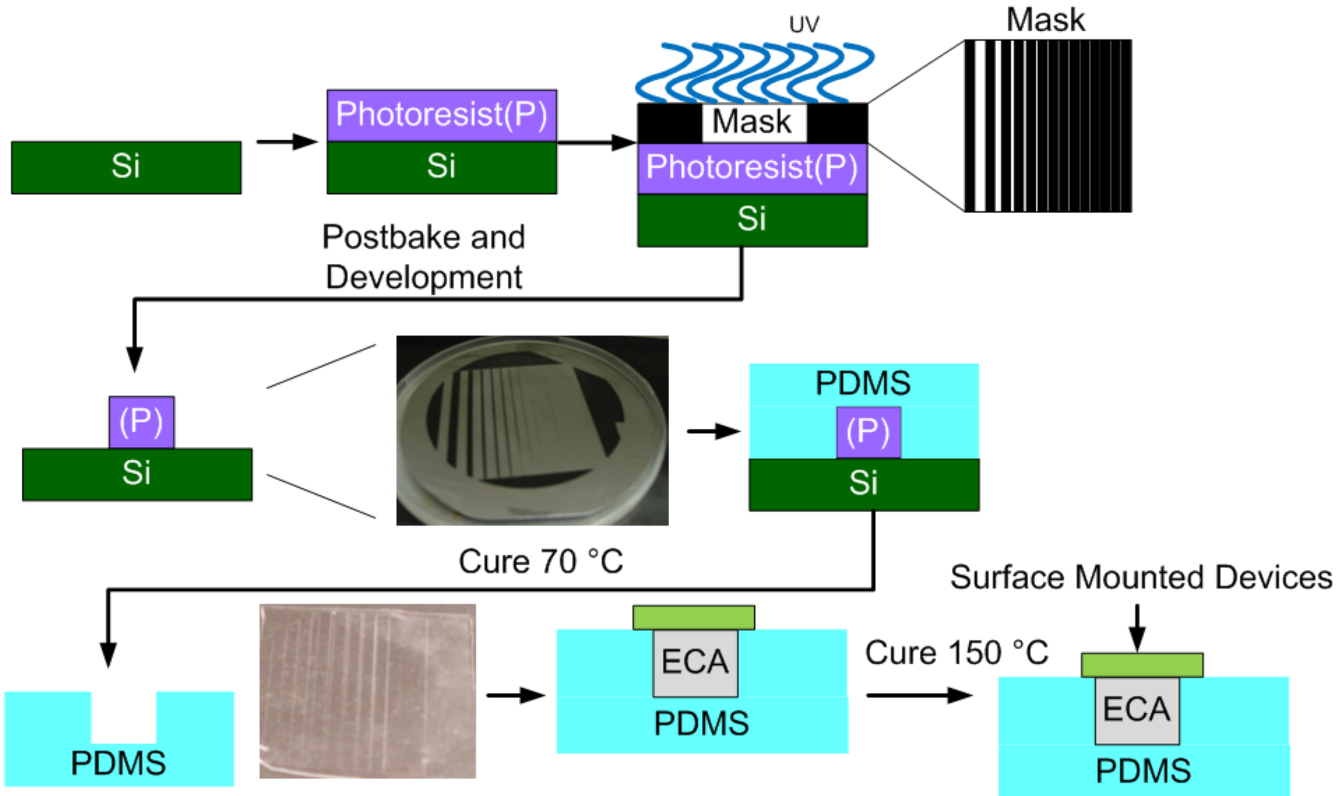

Figure 7. Schematic drawing showing fabrication process of PDMS-in-PDMS electronics.

printing before connection of discrete micron sized surface mounted devices. Fabrication of PDMS-in-PDMS devices will consist of initial mold fabrication via conventional lithography processes. Master mold structures can be fabricated from SiO_2, Si_3N_4, metals, photoresist or wax [3]. Master mold can be used to produce >50 molds, dramatically reducing the cost of fabrication [3]. Following fabrication of a master mold, inverse structures of PDMS can be formed by pouring PDMS on top of the master molds surface and crosslinking the PDMS. We defined our master molds using photoresist as described. Upon fabrication of the PDMS mold, PDMS ECA can be screen printed into the defined structures. Subsequent surface mounting of micron sized discrete electrical components and curing will enable the formation of super low cost flexible, stretchable electronics. The procedure to fabricate these devices is described in Figure 7. An image of the lithographic features and the resulting features in PDMS substrate can be seen in Figure 8.

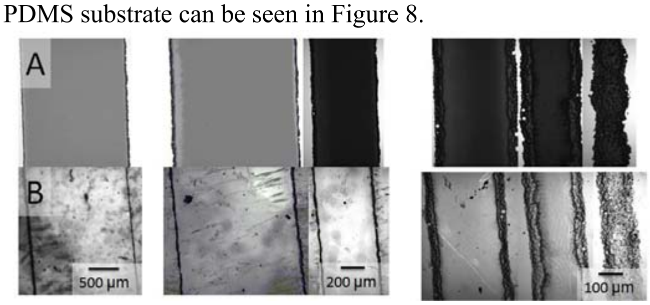

Figure 8. Images of traces of A. Photoresist B. PDMS

Outlook and Perspective

A new flexible stretchable platform for electronics has many currently unimaginable applications. The ability to design electronics on non-planar adaptable platforms enables the natural integration of electronics with the world in which we live. The ability to alter conformation and structure mechanically while maintaining function will enable enhanced device versatility and function. Electrical systems on mechanically flexible curved surfaces have unique advantages for optical systems. Optics based on curved, mechanically flexible platform eliminates the need for expensive optics. Optical advantages of curved optics include uniform focus, wider field of view, more homogeneous imaging and reduced geometric distortions [5]. All of these optical advantages are accomplished while maintaining an improved form factor. Recently, Ko et al. have shown the capability of developing a flexible hemispherical charged coupled device camera (CCD) with compressible metallic interconnects [5]. Application of a novel flexible electrically conductive adhesive to curved devices may eliminate the need for complex fabrication of metallic interconnects and transfer printing processes. The emphasis on simplicity of the fabrication in PDMS-in-PDMS electronics will reduce cost and increase availability.

However, before PDMS-in-PDMS electronics can be applied in useful and functional devices further materials development is needed. Creating flexible electronics on curved surfaces of PDMS generally requires processing in planar form. More research must be done on how to design printed PDMS substrates capable of planarization during fabrication. Furthermore, the PDMS ECA fabricated was a high viscosity paste. Improvements must be made on the rheological properties of the ECA to enable increased resolution during the screen printing process. Alterations to the rheological properties will likely come in the form of volatile plasticizers and nanosized conductive fillers. Current designs for PDMS-in-PDMS are confined to single level device integration. If PDMS-in-PDMS based electronics are going to be designed on the system level, multi-level integration will be required. Eloquent processing and design are needed to fabricate PDMS-in-PDMS with multi-level integration. Finally, the PDMS ECA, although having adhesive properties, has weak adhesion strength compared to the epoxy based ECA. Modification of the polymeric properties to improve adhesion is mandatory for fabrication of reliable devices.

The development of PDMS-in-PDMS is a new platform with promising future for development. This technology will enable the simple design, prototyping and fabrication of ultra-low cost flexible electronics for future consumer electronics.

Conclusions

We show a novel method to fabricate highly flexible electronics which we term PDMS-in-PDMS electronics. A novel PDMS based ECA was designed with rapid cure (15 minutes) and low resistivity (~$7x10^{-4}$ Ω•cm). Simultaneous tensile and electrical measurements showed that tensile strains of up to 40% had minimal effects on bulk conductivity. Printing of PDMS ECA patterns was accomplished by creating a master mold via photolithography and using it as a mold for formation of an imprinted PDMS substrate. Furthermore, we showed the UV-ozone treatment was capable of altering the surface properties of the PDMS substrate enabling high resolution screen printing of ECA into predefined PDMS molds. Finally, we showed the feasibility of producing low cost, flexible stretchable electronics on a curved platform using a novel PDMS-in-PDMS technology.

Acknowledgments

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References

1. Béfahy, S., et al., *Stretchable Gold Tracks on Flat Polydimethylsiloxane (PDMS) Rubber Substrate.* Journal of Adhesion, 2008. **84**(3): p. 231-239.
2. Li, Y. and C.P. Wong, *Recent advances of conductive adhesives as a lead-free alternative in electronic packaging: materials, processing, reliability and applications.* Materials Science & Engineering, R: Reports, 2006. **R51**(1-3): p. 1-35.
3. Xia, Y. and G.M. Whitesides, *SOFT LITHOGRAPHY.* Annual Review of Materials Science, 1998. **28**(1): p. 153.
4. Befahy, S., et al., *Thickness and Elastic Modulus of Plasma Treated PDMS Silica-like Surface Layer.* Langmuir, 2010. **26**(5): p. 3372-3375.
5. Ko, H.C., et al., *A hemispherical electronic eye camera based on compressible silicon optoelectronics.* Nature, 2008. **454**(7205): p. 748-753.