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Title: Fabrication of Polymer-Based Micro Devices: Formulation and Study of the Past

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Abstract: We investigate in the present work the fabrication of polymer-based micro-fluidic and micro-mechanical devices using sacrificial, resistive/conductive pastes, through a screen-printing process. An organic sacrificial paste is first screen-printed onto a substrate, building the future empty space (channels, cavities...) where it lies. Then, a resistive paste based on thermosetting polymer resin and graphite is deposited onto the previous layer. Finally, the sacrificial paste is removed at 150°C by sublimation through the composite, thus yielding the desired pattern. For such applications, the key is naturally the formulation of the pastes. In a previous work, we already proposed a potential formulation for the organic sacrificial paste, based on polyols [1]. In the present paper, we will focus on the formulation of the cover paste, which must be adapted rheologically for the screen-printing process, but also chemically due to strong potential interactions between the sacrificial layer and the over-layer. Finally, micro-devices such as simple fluidic channels and suspended structures were produced and shown to be operational, demonstrating the high potential of our process.

Fabrication of Polymer-Based Micro Devices: Formulation and Study of the Paste

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COVER LETTER

30.9.2010

Dear Editor,

Please find attached the files for the paper entitled “Fabrication of Polymer-Based Micro Devices: Formulation and Study of the Paste” authored by Nathalie Serra, Thomas Maeder, Olivier Gentsch and Peter Ryser, which is an extension of the extended abstract presented at Eurosensors XXIV as contribution #3185.

This work covers the formulation of organic materials enabling facile fabrication of micromechanical and microfluidic structures by thick-film screen-printing operations, which of course could be further extended to other printing processes such as inkjetting. The main challenge is to find a suitable organic sacrificial material that has sufficient structural and mechanical integrity to allow further screen-printing operations, is chemically compatible with the overlying structural layers, yet is afterwards easily removed, even from closed structures. Preferably, removal is achieved by a direct solid-to-gas process such as decomposition / depolymerisation or sublimation, and the polyol-based materials used here are quite promising in this regard. Preliminary work on cantilevers is shown to demonstrate the potential of this technique.

Please let me know in case you find anything missing during the review of the paper.

Best regards

Thomas Maeder

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Abstract

We investigate in the present work the fabrication of polymer-based micro-fluidic and micro-mechanical devices using sacrificial, resistive/conductive pastes, through a screen-printing process. An organic sacrificial paste is first screen-printed onto a substrate, building the future empty space (channels, cavities...) where it lies. Then, a resistive paste based on thermosetting polymer resin and graphite is deposited onto the previous layer. Finally, the sacrificial paste is removed at 150°C by sublimation through the composite, thus yielding the desired pattern. For such applications, the key is naturally the formulation of the pastes. In a previous work, we already proposed a potential formulation for the organic sacrificial paste, based on polyols [1]. In the present paper, we will focus on the formulation of the cover paste, which must be adapted rheologically for the screen-printing process, but also chemically due to strong potential interactions between the sacrificial layer and the over-layer. Finally, micro-devices such as simple fluidic channels and suspended structures were produced and shown to be operational, demonstrating the high potential of our process.

Keywords: organic sacrificial layers; silicone resins; screen-printing; thick films

1. Introduction

In the micro-electromechanical systems (MEMS) field, sacrificial layers are widely used for fabrication of free-standing structures by surface or volume micromachining. However, many applications, due to size or cost reasons, do not require clean-room processes, and/or are just as well or better fabricated using other substrates than silicon. For instance, the thick-film and low-temperature co-fired ceramic (LTCC) technologies, principally based on glass/ceramic materials, are commonly used for sensors, and have recently seen considerable developments in structuration techniques [2-3] for fabrication of elements such as cantilevers, bridges, membranes and fluidic structures.

Nowadays, a move towards polymers is observed as their properties such as low cost, transparency and good biocompatibility make them particularly suitable for disposable biomedical applications. Micro-structures based on organic sacrificial layers, such as the combination of SU-8 (over-layer) and polypropylene carbonate (sacrificial material) have already been reported in the literature [4]. However the polypropylene carbonate decomposes around 300°C which remain too high for most polymer applications. Therefore we introduced [1] materials with significantly lower sacrificial layer removal temperatures, thereby considerably extending the application field of this process. Moreover, the materials employed are also chosen for their sublimation ability. This particular property has the advantage to allow closed structures such as micro-channels, cavities and membranes as the compounds sublimate cleanly through the over-layer, without collapse due to surface tension, and do not require any etching process. Two different organic sacrificial pastes, both of them based on mixes of non-polymeric polyol-type organic materials (so-called plastic crystals) were tested. Polyols are widely used in industry for paints and coatings formulation, due to the viscosity and fast drying properties they give to the final paste. Some polyols have also attracted considerable attention due to their solid-solid order-disorder phase transitions, which make them interesting for thermal energy storage [5]. Finally, these materials have the advantage to be non-toxic.

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In a previous work, we had characterized epoxy-graphite resistive pastes for micro-heater manufacturing [6]. The point here is to analyze to what extent what we developed can be adapted to this other application. Particular care must therefore be given to the formulation of the over-layer. Various epoxy resins and silicones as thermosetting polymers were used in this study. A key factor in screen-printing process is the rheology of the paste (ca. honey-like consistency). In order to tune this property, the use of additives and/or solvents can be envisaged. We already tested different solvents that are well-suited for epoxies [6]. Here, this study was also extended to silicone, with the purpose of finding suitable solvents, i.e. having good solvency towards silicone resins, yet without chemical reactions.

2. Experimental

Fabrication of the micro-fluidic and micro mechanical devices is performed by screen-printing: the sacrificial material is first screen-printed onto a substrate (here alumina) and dried around 80°C. Then a second layer is over-printed and dried at 100°C. Finally, the structures are placed at typically 150°C and sublimation of the organic paste occurs, leaving clean structures with the desired pattern (see Fig. 1).

FIGURE 1

Formulation of the sacrificial layers was developed previously [1,7]. Two kinds were tested, both based on trimethylolethane (TME). Two mixes are prepared with resp. 2,5-dimethyl-2,5 hexanediol (DMHD) and neopentyl glycol (NPG). The materials are then partly dispersed and dissolved with solvents. Cyclohexanol was chosen for its high viscosity, completed with water in order to obtain a good screen-printable paste. Table 1 sums up the different characteristics of these compounds.

Regarding its physical properties, TME is the main sacrificial material, i.e. the ultimately sublimating compound. It will be in suspension in the solution. However, TME alone essentially yields a powdery substance unsuitable for overprinting. Therefore, NPG and DMHD are added as “waxy binders” in the mixture, but presumably do not work the same way. NPG and TME have a high chemical compatibility – they in fact form a continuous solid solution series [8-9], NPG promoting a waxy consistency suitable for screen-printing by stabilising the high-temperature “plastic” phase. The system is however further complexified by the particular role of cyclohexanol; it was recently demonstrated that cyclohexanol also forms a complete solid solution with NPG [10], and therefore is not “just” a solvent and most likely forms a ternary solid solution with NPG and TME, which to our knowledge has not yet been investigated. Due to its different molecular structure, DMHD is not expected to form extensive solid solution with the cyclohexanol/ TME “plastic crystal” compounds. The detailed interactions in both systems (DMHD or NPG additive) will be the object of further studies.

TABLE 1

Formulation of a structural over-layer that is both compatible with the sacrificial layers and screen-printable is here the key for successful fabrication of our structures. As explained before, the organic sacrificial pastes we use are based on mixes of polyols partly dispersed and dissolved in cyclohexanol [1]. These were found to be well compatible (i.e. not significantly interact) with silicones and ethylcellulose, but not with epoxies, which are reactive to the polyol –OH group, resulting in the destruction of the structure. In this paper, we focus on the formulation of silicone resin, filled with graphite to impart electrical conductivity and improve mechanical stability. Regular silicone resin (see Table 1) was used as a matrix and graphite (KS4, ellipsoidal shape with 95% of the particles having a large axis smaller than 4 µm, Timcal, Switzerland) as a filler. As high graphite loadings tend to yield an excessive paste viscosity, the introduction of suitable high-boiling solvents, whose properties are given in Table 2, was studied to allow convenient tuning of the paste rheology.

TABLE 2

Solvents must be carefully chosen: they should be miscible with the resin, yet remain inert without chemical reaction. Miscibility can be easily predicted using the Hansen solubility parameter theory [11-12]. One would notice

that our list includes also polar solvents (octanol and tetraglyme), which are not *a priori* suitable solvents for silicones. However, our sacrificial material having polar groups, it might be interesting to have also a certain percentage of a polar solvent in the over-layer to promote wetting and adhesion between the layers. Therefore, knowing the behavior of these solvents with silicones would be of great use. In order to prove their efficiency and validate their use for paste formulation, mass loss tests were performed for 10% and 20% in volume of graphite. A second “qualitative” test consisting in rheological measurements was done at 10% vol. of graphite in order to classify the “solvative” nature of the materials. Finally, fabricated structures were tested and compared.

3. Results

3.1. Study of solvents

A first series of mass loss experiments was performed in order to determine whether solvents evaporate completely during the curing process (see Fig.2a). A mass loss profile was made for 10% and 20% vol. graphite by measuring the composite mass after 30, 60 and 120 min at 150°C. Only the profile for 10% is shown here, as no significant difference between both loadings was observed. A/B0 samples correspond to the reference measurement, i.e. without solvent. Whatever the solvent or the graphite loading, essentially all the mass loss occurs in the first thirty minutes, which is noticeably faster than with epoxies [6] and agrees with the higher permeability of silicones. The somewhat slower removal of tetraglyme stems from its very high boiling point. Finally, the small mass loss seen in the reference sample probably corresponds to water.

A second series of experiments consisted in rheological measurements. The dynamic viscosity was measured with a rotative viscosimeter, Rheomat RM180 from Mettler. No measurement was possible for the reference sample, the viscosity being too high for our device. Fig. 2b reports the data for the four solvents.

FIGURE 2

First, we can see that the pastes present a typical shape of a thixotropic / shear thinning behaviour, which is satisfactory for screen-printing [13]. We can see that theoretical suppositions are confirmed, i.e. dodecane and limonene have a higher solvative power compared to the other two. Octanol and tetraglyme first form a gel but nevertheless may be incorporated into the resin under shear, yielding a strong thixotropic behaviour. This can be explained by their rather low polarity. Likewise, the long alkane chain of octanol is expected to facilitate its observed easier incorporation into the resin than tetraglyme. Octanol is therefore expected to be particularly useful as a wetting agent for silicone (affinity with alkane chain) on polyol (hydroxyl head) layers. In practice, an acceptable combination of wetting and solution stability must be found, which may be done by combining octanol with dodecane or limonene.

3.2. Applications

3.2.1. Fabrication of micro-channels

Micro-channels using silicone as over-layer were fabricated, with the aim of studying the influence of a polar solvent on the good functionality of the structures. Silicone/graphite pastes were prepared using first only dodecane as solvent, than mixes of dodecane:octanol (2:1 and 1:1). Test structures were dipped in water in order to check for leaks, air (≈ 6 bar) was blown through the channel, and the maximum flow was determined in each case. The results (Table 3) show that without octanol, the structures tend to tear away from the substrate. On the other hand, an equal mix of dodecane and octanol gives the best results in terms of reproducible channel geometry. However, a too large amount of octanol (not tested in this study) may lead to an unstable solution, another possible problem being dissolution of the sacrificial layer by octanol during the curing of the silicone resin.

TABLE 3**3.2.2. Fabrication of position/force-sensing cantilevers**

Fabrication of cantilevers was also investigated using this process. The elastomeric silicone resin alone being too soft for cantilever structures, a carbon-filled ethylcellulose-silicone bilayer structure was used, the idea being to combine the thermal stability of the cross-linked silicone resin during sublimation of the sacrificial layer with the rigidity of ethylcellulose at room temperature. The distance between the cantilever and the base was sensed capacitively. The top electrode was the cantilever itself (both ethylcellulose and silicone filled with 15%vol KS4 graphite), and the bottom electrode consisted of an Ag thick-film paste, previously screen-printed and fired onto the alumina substrate (see Fig 3.a).

Preliminary tests are presented here. Capacitance of the cantilevers was measured through an Analog Devices AD7746/7745 integrated circuit that allows differential capacitance measurements between -4 and +4 pF, with a resolution of ± 4 fF [14]. Different balsa loadings were then applied on the cantilever, changing the distance between the electrodes (see Fig 3.b). It is therefore possible to calculate the capacitance with the following equation:

$$C = \varepsilon_0 \cdot \varepsilon_r \cdot A / z \quad (1)$$

where C is the capacitance, ε_0 the electric constant, ε_r the relative permittivity, A the electrodes area and z the distance between the electrodes.

FIGURE 3

Cantilevers with a length of 10, 8 and 6 mm and a width of 1, 2 and 3 mm were fabricated. The theoretical capacitance without any loading was calculated using equation (1) and is reported in table 4. However, due to the difference of thermal expansion coefficient between the two over-layers, leading to a stress during the cooling, some cantilevers were initially highly bent. Therefore, the two electrodes are no longer parallel and the area changes in each case, following the cantilever bending. This is the reason why the theoretical capacitance is so different from the experimental one. Indeed, the combined effects of different possible sources of error (area not equal, inhomogeneity of the charge along the cantilever leading to changes in the electrical field...), yield large errors in the calculations.

TABLE 4

The force response was then determined for each cantilever by loading them with small balsa wood weights. The fabricated devices were able to measure small forces (0...1 mN). The following graphs present the results for each length (Fig 4).

FIGURE 4

These graphs highlight the fact that the capacitance increases with an increasing width, i.e. an increasing area of the electrode. This can be easily understood by equation (1). In most of the case, we can see that the evolution of the curves is not linear but quadratic with an increase of the applied force at the end of the cantilever. Once again, this is due to the bending of the cantilever. The parallel plate model capacitor is therefore no longer applicable as two phenomena occur: change of the distance between the electrodes and change of the electrode area. The over-layer must therefore be improved in order to have a better resolution.

4. Conclusion

Screen-printable silicone/graphite structural over-layers compatible with an organic polyol sacrificial paste were successfully formulated. A study of solvents showed that dodecane and limonene have a high dilutive power on silicone resins, allowing therefore the tuning of paste rheology and extending the achievable range of filler loadings. We also demonstrated that adding a solvent with a polar group (i.e. octanol) to the formulation improved wetting

and adhesion between the over-layer and the sacrificial material, thereby allowing reliable and convenient fabrication of printed micro-fluidic devices.

Our process also allowed us to fabricate polymer cantilevers. The results shown here are just preliminary, but they are promising for measurements of small forces.

Acknowledgements

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Biographies

Nathalie Serra graduated in September 2007 (master degree in chemistry) at the “École Nationale Supérieure de Chimie de Lille” which is part of the French “Grandes Ecoles” network, and is pursuing a PhD in resistive nanocomposites at the EPFL.

Thomas Maeder graduated at the Ecole Polytechnique Fédérale de Lausanne (EPFL) in materials science, and continued with a PhD in piezoelectric thin films, then a post-doc at IBM Rüschlikon in single-crystal conductive oxides. He now heads the thick-film technology group at the EPFL, where current areas of interest are thick-film and LTCC technology for advanced sensor, packaging, biomedical and harsh-environment applications.

Olivier Gentsch is currently carrying out his master thesis. He will receive a Master degree in Microtechnology from the Ecole Polytechnique Fédérale de Lausanne (EPFL) in 2011.

Peter Ryser received a Master degree in Physics (University Neuchâtel 1979), a PhD in applied Physics (University Geneva 1985) and a Masters Degree in Corporate Management (Lucerne 1993). His professional background includes several R&D activities. From 1990-1998 he was the head of research at Siemens Building Technologies. Since 1999 Peter Ryser is Professor at the Swiss Federal Institute of Technology EPFL in Lausanne and act as a director for the micro engineering section.

5. Figure captions

Fig.1: (a) Process of structures using sacrificial pastes; (b) Cross-section of a micro-channel after sublimation of the sacrificial paste.

Fig 2. Relative composite mass vs. solvent in silicone with 10% vol KS4 (a); Viscosity measurements for the different solvents (b).

Fig 3. Schema of the cantilever (a); Set-up of the capacitance measurement (b).

Fig 4. Capacitance measurements for cantilevers with a length of 10 mm (a), 8 mm (b) and 6 mm (c).

6. Table captions

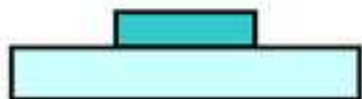
Table 1. Properties of the compounds used in this work . T_m = melting point; T_b = boiling point.

Table 2. Properties of tested solvents. T_b = boiling point; M = molar mass; d = density.

Table 3: Influence of solvent formulation on the maximum air flow.

Table 4. Comparison of the theoretical and experimental capacitance.

Figure 1
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1) Screen-printing of the sacrificial paste

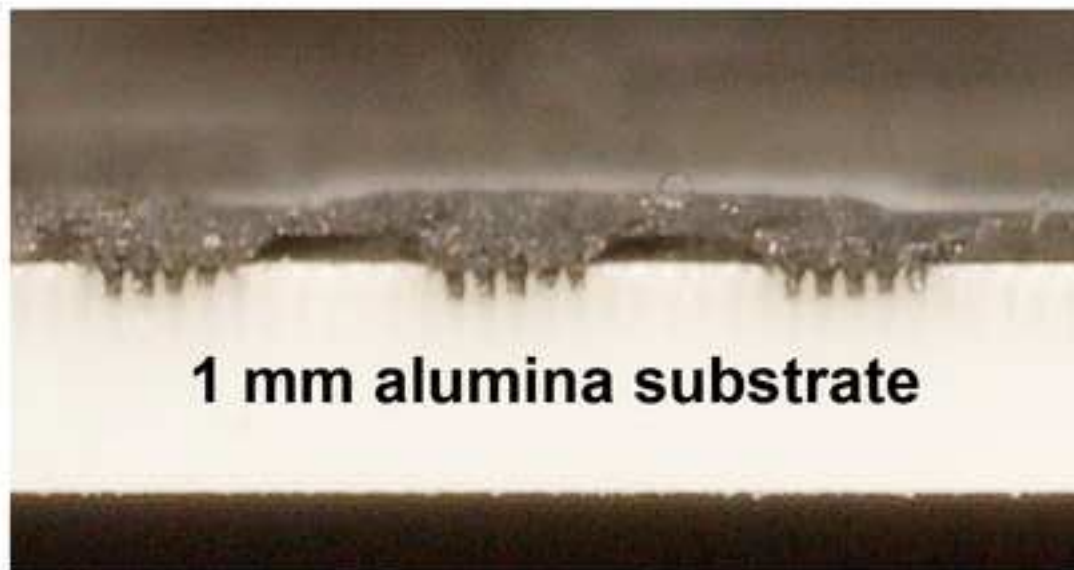


2) Over-printing with silicone resin



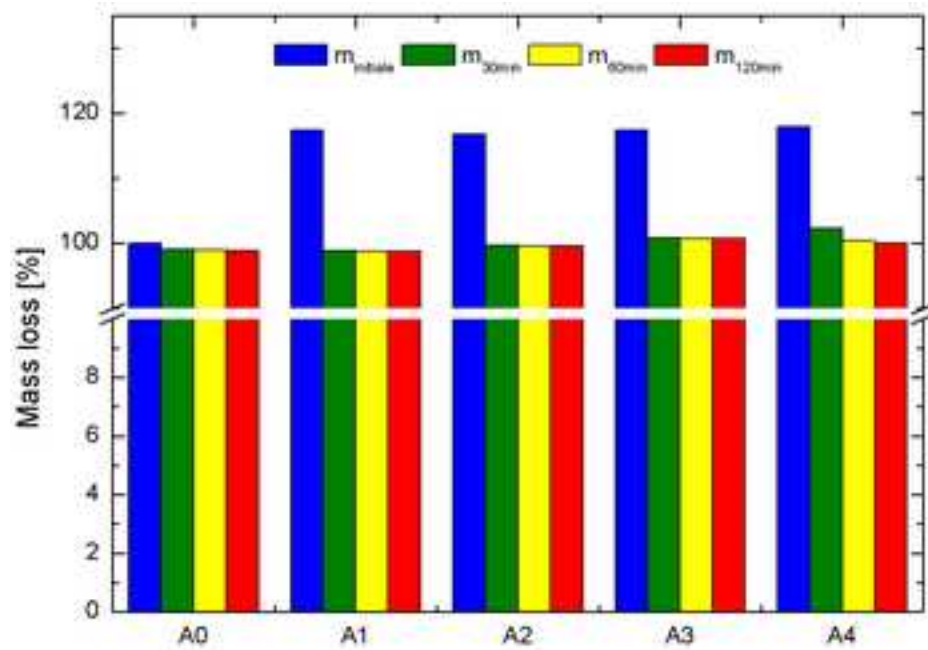
3) Sublimation of sacrificial layer at 150°C

(a)

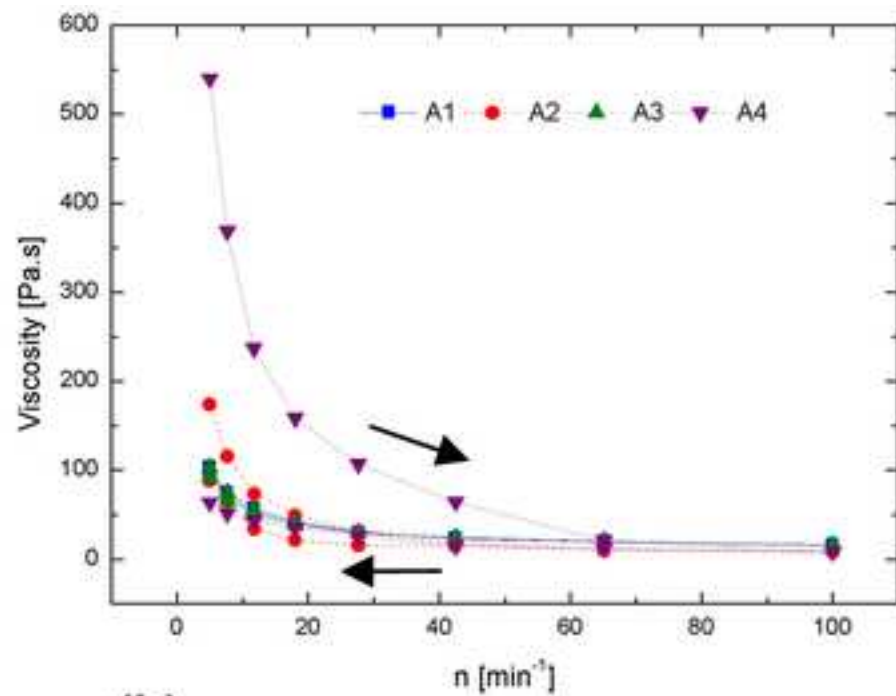


(b)

Figure 2
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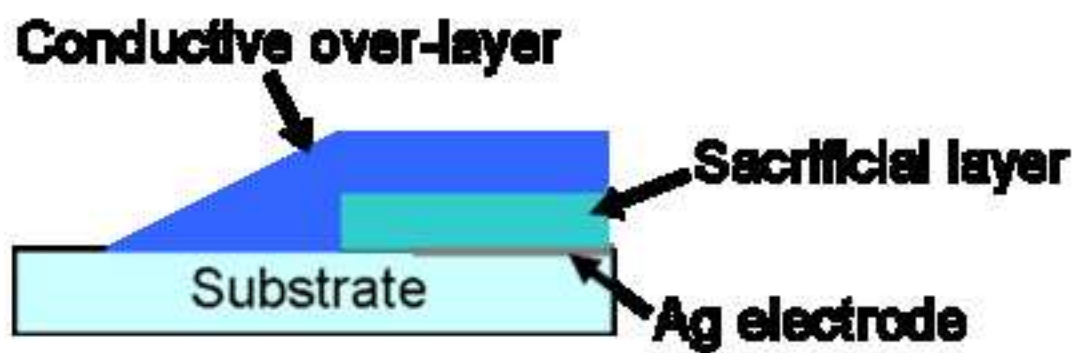


(a)

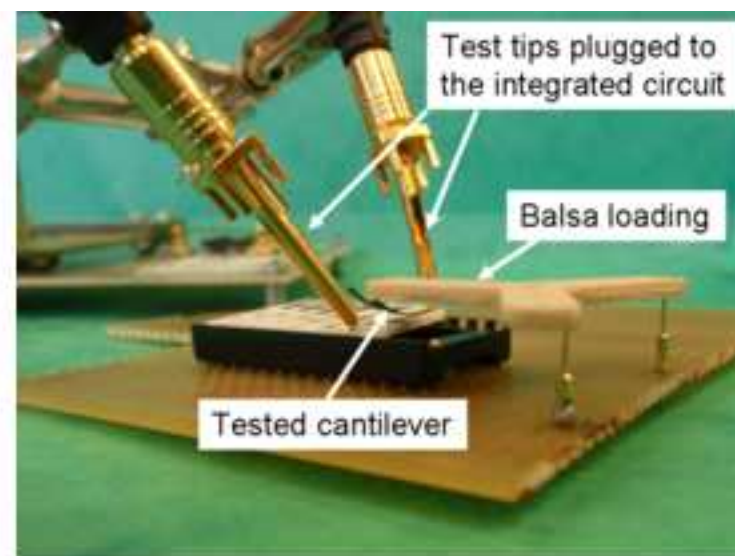


(b)

Figure 3
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(a)



(b)

Figure 4
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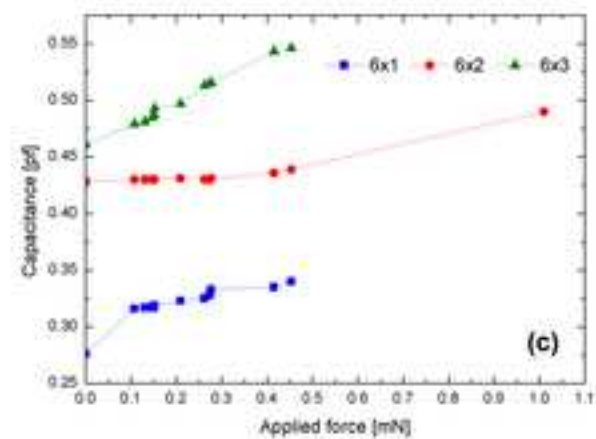
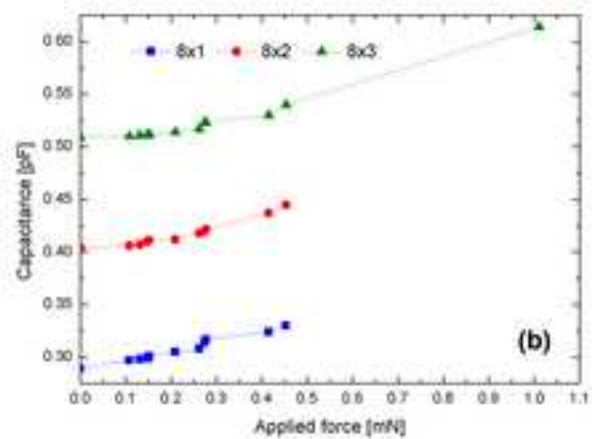
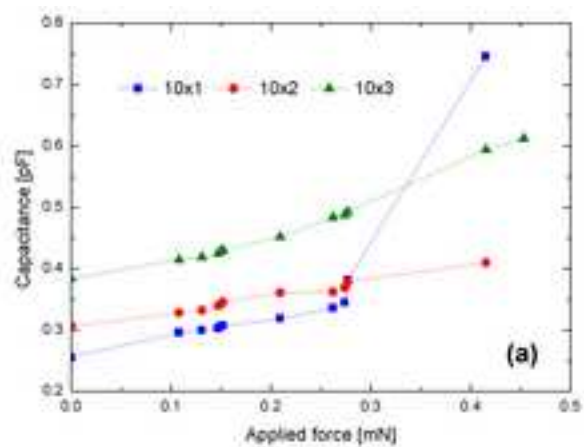


Table 1. Properties of the compounds used in this work . T_m = melting point; T_b = boiling point.

Name	CAS-n°	Source	T_m (°C)	T_b (°C)	Code
Trimethylolethane	77-85-0	Sigma-Aldrich	200	293	TME
Neopentyl glycol	126-30-7	Sigma-Aldrich	130	207	NPG
2,5-dimethyl-2,5-hexanediol	110-03-2	Sigma-Aldrich	86	214	DMHD
Cyclohexanol	108-93-0	Sigma-Aldrich	24	160	CH
2-component silicone resin Q5-8401		Dow Corning			silicone
Ethylcellulose, 46cps grade, 48% ethoxyl content	9004-57-3	Sigma-Aldrich	170		EC-46-48

Table 2. Properties of tested solvents. T_b = boiling point; M = molar mass; d = density.

Name	CAS-n°	T_b (°C)	M (g/mol)	d (kg/m ³)	Symbol
Dodecane	112-40-3	215	170.33	750	A/B1
Octanol	123-96-6	196	130.23	827	A/B2
(R)-(+)-limonene	5989-27-5	175	136.24	840	A/B3
Tetraglyme	143-24-8	275	222.28	1009	A/B4

Table 3: Influence of solvent formulation on the maximum air flow

Dodecane:octanol ratio	Max. Flow [lN/min]
1:0	(unreliable)
2:1	1.7
1:1	2.8

Table 4. Comparison of the theoretical C_{th} and experimental C_{exp} capacitance.

Cantilever	C_{th} (pF)	C_{exp} (pF)	Ratio
10x1	0.0210	0.256	13
10x2	0.0397	0.307	8
10x3	0.0418	0.384	9
8x1	0.0165	0.289	17
8x2	0.0509	0.404	8
8x3	0.0770	0.509	7
6x1	0.0176	0.276	15
6x2	0.0516	0.429	8
6x3	0.0738	0.461	6