Origin of Electrokinetic Variability in Microfluidic Devices Cast on SU-8 Epoxy

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Abstract—**Microchannels of silicone elastomer that had been cast on master molds made of SU-8 epoxy exhibit unexpected electrokinetic behavior. The speed of fluid flow induced by applied electric field indicated that the surface potential of the silicone was much more negative than that of "native" silicone. Several sets of experiments indicated that the surface potential had been made more negative by transfer of a negatively charged species from the SU-8 during molding. Analytical work indicates this to be an antimony species, such as $[SbF_6]^-$, which is present in SU-8 as a photo-initiator of polymerization.**

I. Introduction

The technique of soft lithography is in widespread use for production of microfluidic devices: it consists of casting a solidifying polymer on a pre-formed master mold. The product molding is peeled away and bonded to a further plate or molding to form one or more closed channels. Using polydimethyl siloxane (PDMS) elastomer as the polymer, faithful reproduction of feature sizes down to much less than one micron is achievable. A popular way to fabricate the master mold is to selectively polymerize the epoxy resin "SU-8" [1,2], typically using near-UV light to cross-link and lithographically structure it. The production of a simple rectangular microchannel in PDMS from an SU-8 master mold is shown in Fig. 1. Many - sometimes hundreds of - channels can be made from a single SU-8 master.

The flow resistance of such microchannels is very high, yet analytically useful speeds of flow can be induced electrically *via* the double-layer-driven phenomenon of electro-osmosis [3,4]. However, many authors have found this flow rate to be inconsistent [5-11]. For this procedure to be reproducible it is important that the electrical charge on the walls of the channel is both stable and consistent between production samples, and not influenced by the master mold used. We have found that such an influence is in fact difficult to avoid when SU-8 is used as the master.
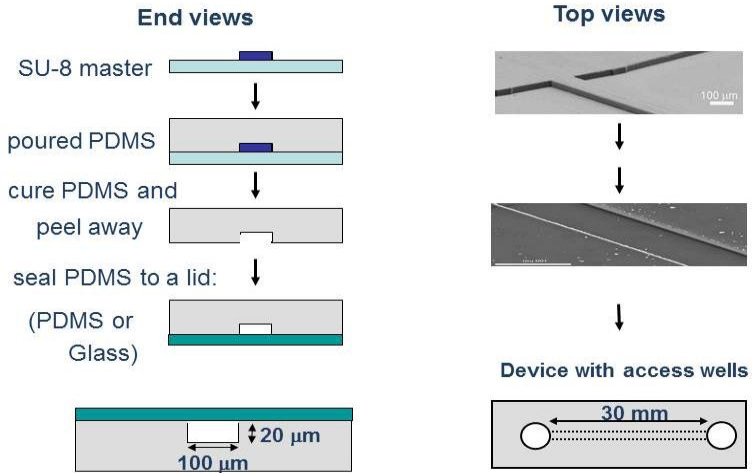
Fig. 1. Sequence of operations producing a channel in PDMS from a ridge-shaped master made of SU-8. This master is produced by photo-cross-linkage: in our work, this is achieved by laser-writing at 375 nm into a thin SU-8 oligomer film formed by spin-coating onto a polymethylmethacrylate (PMMA) wafer.

II. ELECTRO-OSMOSIS

The directed motion of fluids through porous insulating materials under the influence of electric fields has been a recognized phenomenon for more than two hundred years [12]. The recognition of the origins of this motion in the electric double layer [13], and its exploitation for driving fluids through analytical capillaries [3,4], are more recent. Fig. 2 gives a diagrammatic explanation of capillary electro-osmosis.
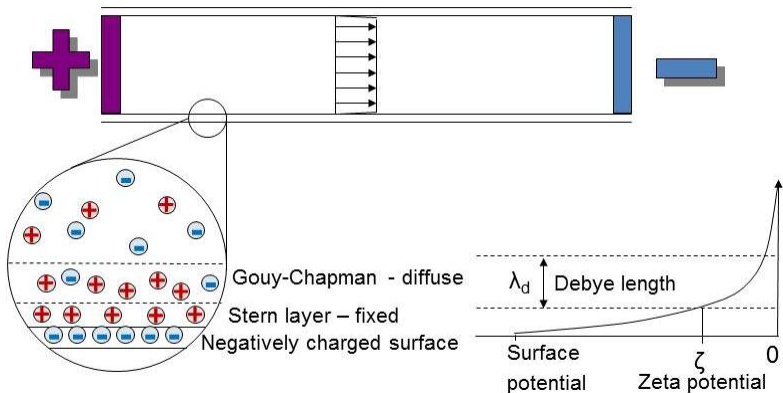

Fig. 2. Electric-field-induced motion of liquid in a capillary having fixed charges present on the surfaces. This movement due to electro-osmosis is driven by the motion of net charge in the diffuse double layer, which exists as a response to a surface charge. The mobile, diffuse part of the double layer starts at the plane of shear, where the potential is defined as the zeta-potential. From this point, the potential and *excess* ion concentrations fall exponentially with distance: one Debye length (about 2nm in our work) into the liquid, the *excess* charge density has fallen by 63% (or to 5% in three Debye lengths). Hence a flowing plug of liquid, 20-50 microns in width, is driven by a 6nm-thin layer of excess charge close to the walls.

The electro-osmotic flow velocity (EOF) can be observed experimentally, and then used to derive the zeta potential ζ (explained in Fig. 2) by use of the Helmholtz-Smoluchowski equation [13]:

$$EOF = - E\, \varepsilon_r \varepsilon_0 \zeta / \eta \tag{1}$$

where E is the applied electric field strength, ε_r and ε_0 are the relative and vacuum permittivities, and η is the dynamic viscosity. The zeta-potential is usually taken to be an approximation to the surface potential, and therefore a proxy for the surface charge density. The relationship is linear only up to about 25 mV for univalent ions (less for multiply charged ones) [14].

In a microfluidic channel, the EOF can be measured by the "current-monitoring method" [15,16] in which a plug of different conductivity liquid is moved electro-osmotically down the channel: the transit time is observed from the resulting ramp in current (Fig. 3).
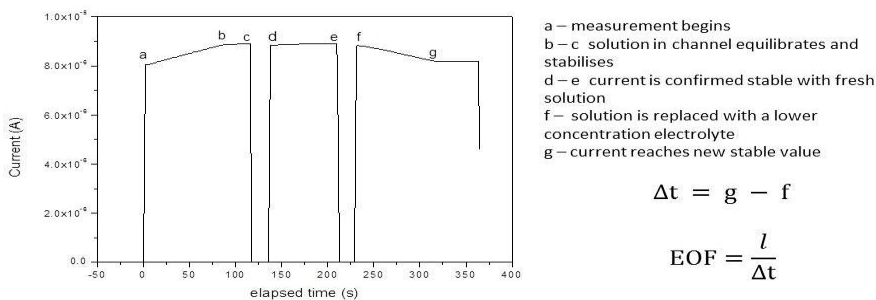

a – measurement begins
b – c solution in channel equilibrates and stabilises
d – e current is confirmed stable with fresh solution
f – solution is replaced with a lower concentration electrolyte
g – current reaches new stable value

$$\Delta t = g - f$$

$$EOF = \frac{l}{\Delta t}$$

Fig. 3. Typical current-monitoring trace for the micro-channels (length l = 30 mm) used in this work. The 20mM phosphate buffer solution used for equilibration (times **a** to **e**, seconds) is replaced (time **f**) at the anodic end of the channel with a 18mM buffer, the voltage re-applied and the progress of the concentration front followed from the current decrease (from almost 90µA to 80µA) at constant applied field (500V across 30mm).
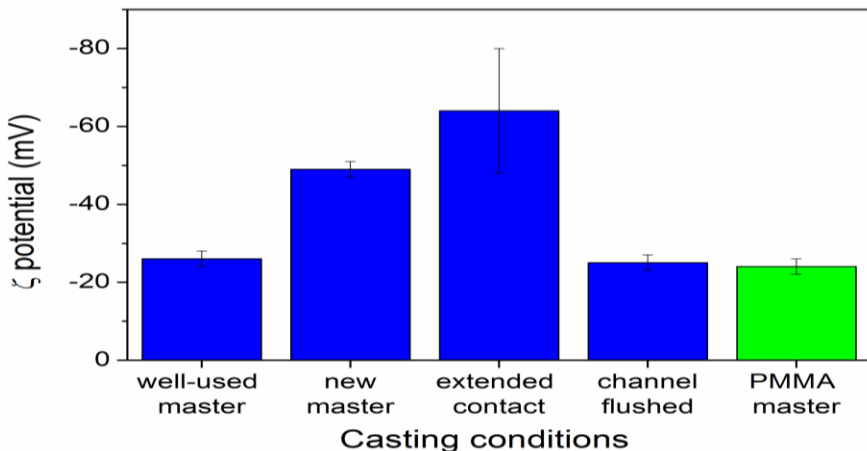
III. RESULTS

Fig. 4. The zeta-potentials observed for channels cast from a variety of masters: all masters were SU-8 except for one, made in a mechanical process lacking photo-initiator, was made of PMMA (polymethyl methacrylate).

We found that the EOF and derived zeta-potentials were highly dependent on how many castings had been made from a given master (Fig. 4). A master that had been used tens of times resulted in a channel with a zeta-potential of about -26 mV, which was also found for channels molded on a specially-fabricated methacrylate master, and indeed this potential is also reported for unmodified PDMS. However, previously unused masters, and/or longer contact times, gave rise to channels with much more negative zeta-potentials. Extended flushing of the channel was observed to reduce the effect.

These results suggested that there was a surface contaminant on the PDMS channel that was derived from freshly fabricated SU-8. This was confirmed as follows:

a) Rutherford backscattering [17] of 2.5 MeV $^4He^+$ ions, accelerated using a Van de Graaff voltage source [18], showed that antimony, a component of SU-8, to be progressively removed from the surface layer of the masters during repeated use (Fig 5);

b) Synchrotron X-ray fluorescence (XRF) confirmed [19] the presence of antimony on PDMS samples that had been in contact with SU-8 (not shown).

Rutherford backscattering spectrometry profile of antimony concentration.

A well-used master has significantly less Sb at the surface.
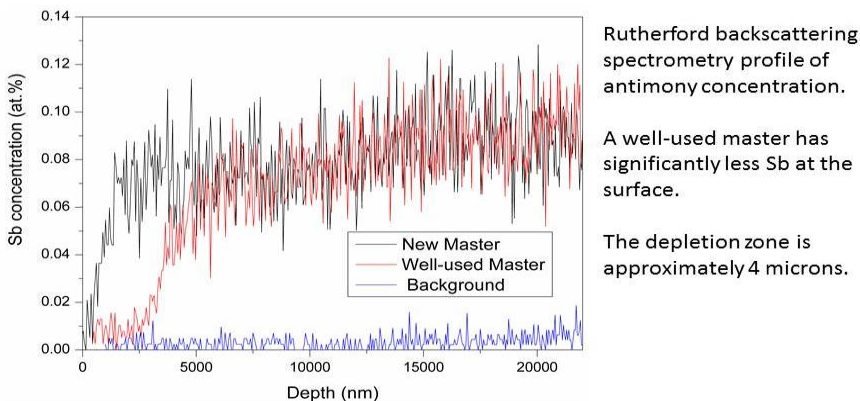
The depletion zone is approximately 4 microns.

Fig. 5. Energy-spectrum analysis of back-scattered accelerated protons was used to determine the concentration profile of antimony in the surface of SU-8 masters. The level of 0.09 atom percent seen in the bulk was severely depleted in the top 4 microns after repeated casting runs with PDMS. On-line version in color.

IV. DISCUSSION

Literature on the chemistry of SU-8, and also data sheets from the supplier [1,2,20], point to the existence of the stable anion $[SbF_6]^-$ in SU-8. The ion acts as a transfer agent - in fact then a "super-acid" - for a proton derived by UV-photolysis of an "onium" salt [21,22]: usually containing a triaryl sulfonium cation. The resulting cationic ring opening polymerisation drives a chain of epoxide ring-openings that induces cross-linking of the originally octo-functional SU-8 molecules.

Our data indicate that small amounts of anion are transferred to the PDMS surface on casting on SU-8, and that this anion contains antimony. Due to the stability of $[SbF_6]^-$, it is reasonable to conclude that it is this anion that is transferred. The XRF measurements indicate an antimony concentration of approximately 100 ppb in the PDMS after casting. It may be asked if this is sufficient to cause the observed changes in zeta potential: to answer this we shall next consider the surface potential and derive the required surface charge density.

The zeta potential (defined as the potential at the hydrodynamic shear plane, Fig. 2) is at or very close to the beginning of the diffuse part of the double-layer system [13], rather than at the surface. However, at low salt concentrations, the zeta potential is expected to be a close approximation to the surface potential, at least in the absence of specific binding or ion condensation. Microelectrophoresis of charged lipid droplets indicates that this is the case at ionic strengths < 0.1 M [23], which is the case in this work.

We expect only electrostatic interactions between the ions in our buffer system and the PDMS surface, so the relationship between surface charge and surface potential can be calculated by Gouy-Chapman theory [14] which predicts the following relationship between surface charge density σ and surface potential ψ when immersed in a 1:1 electrolyte solution of ionic strength C:

$$\sigma/(8N\varepsilon_r\varepsilon_0 kTC)^{1/2} = sinh\ (e\psi/2kT) \tag{2}$$

where N is the Avogadro number, k is the Boltzmann constant, T is the absolute temperature, and e is the electronic charge. If σ is expressed in electronic charges per nm^2 and C=0.03M (appropriate for our buffer), and T=298K, then inserting accepted values for the other quantities yields:

$$\sigma = 0.1268\ sinh\ (\psi/51.38) \tag{3}$$

Eqn (3) predicts that in an aqueous buffer of ionic strength 0.03M, the observed surface potential change from −25mV to −64mV requires an increase of density of charge at the surface from 0.06 electronic charges per nm^2 to 0.20 charges per nm^2.

In the XRF measurements, a 3 mm-thick effective sample depth was exposed to the synchrotron beam. Hence the mean concentration of 100 ppb found by that method translates to 4.4 Sb-containing ions per nm^2 of surface. Therefore the 100 ppb estimate of antimony found in the PDMS moldings is more than sufficient to give rise to the observed change in zeta potential.

V. CONCLUSION

We have shown that the unpredictability of electro-osmotic flow observed in PDMS castings is derived from a similar unpredictability in the amount of residual antimony-containing cation (probably $[SbF_6]^-$) available from the SU-8 master. This contamination, transferred during casting, intensifies the level of negative surface charges on the microchannel surface. The uncontrolled nature of this interaction leads to variability in EOF. We have summarized the process in a cartoon (Fig. 6).
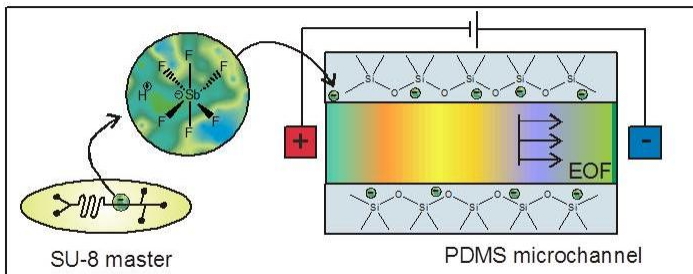

Fig. 6. The transfer of $[SbF_6]^-$ that we conclude causes variability in the EOF of PDMS channels cast on SU-8.

VI. ACKNOWLEDGEMENTS

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