**Limits of Electrochemical Processes at Si Electrodes used at High Field for Aqueous Microfluidic MEMS Applications**

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The use of polycrystalline silicon as an electrode is often a requirement in microfluidic surface micromachined (SMM) devices due to fabrication constraints. Silicon, complete with its passive surface oxide, is a potentially acceptable electrode material for a variety of microfluidic MEMS applications as demonstrated in the direct electrostatic ejection of picoliter fluid drops (1). In such a device, an electrostatic force is used to drive a movable piston mounted on springs toward an aperture plate (see Figure 1) by applying a high field (20 to 30 V· $\mu m^{-1}$) across a micron sized aqueous fluid filled gap. The use of high field with a Si electrode creates a risk of dielectric breakdown in the fluid, electrochemical processes like electrolysis, and anodization of the Si electrode. All three of these processes result in field attenuation and therefore impact the performance and longevity of this type of device. These processes can be monitored using a piston attached with rigid springs (force constant > 12.5 kN· $m^{-1}$) and measuring the current produced as a function of applied field and the minimum field necessary for piston motion. In this paper, we describe the limits of these three system level processes and suggest approaches for extending device performance.

The hydrated passive oxide on silicon formed after sacrificial oxide etching and piston release is sufficiently insulating to prevent dielectric breakdown in $H_2O$-filled, micron-sized inter-electrode gaps. Figure 2 shows the cell current density as a function of applied field measured at 1 μs in a 2 μm $H_2O$-filled gap. These steady state current density values are the result of electrolysis of $H_2O$, as evidenced by gas bubble production at current densities in excess of 250 A· $cm^{-2}$. A field of 55 V· $\mu m^{-1}$ along with current densities of 950 A· $cm^{-2}$ can be supported with no indication of either piston motion or dielectric breakdown in the fluid. For devices where piston motion does occur, we find that the piston eventually contacts the aperture electrode producing limiting current controlled by the oxide rather than fluid breakdown. The small gap sizes of these devices may also contribute to this observed breakdown inhibition (2,3). We learn that the use of short pulses leaves the passive oxide intact and inhibits fluid breakdown.

Electrolysis is the primary limit to achieving maximum electrostatic field across the fluid layer. This limit is demonstrated with the addition of 5 wt. % ethylene glycol and 5 wt. % diethylene glycol, common additives in dye-based printing fluids, which reduces the current density at a given field by a factor of 5 to 50 (Fig. 2). This reduction in electrolysis efficiency is correlated with a reduction in the field necessary for first detectable movement of the piston. Repetitive, sequential current measurement in diol and diol-free solutions show that this effect of current reduction is largely irreversible and occurs with exposure of a piston to the diol solution at both open circuit and under an applied field. The use of either select additives or oxide pretreatment is a potential strategy for maximizing the field across the fluid layer.

Anodization is observed with repetitive polarization of the Si piston. We find that both the measured current density decreases and the minimum applied field for piston movement increases after the first 10 to 30 pulses. The anodization efficiency with the diol additives is significantly lower than without. This slower anodization along with the irreversible reduction in electrolysis current indicate that modification of the passive oxide bulk and/or surface is an additional potential strategy for maximizing the field across the fluid layer. The observed delay in anodization appears to be related to $OH^-$ accumulation in the oxide and suggests bi-polar biasing of the Si electrode might be effective in slowing oxide growth.

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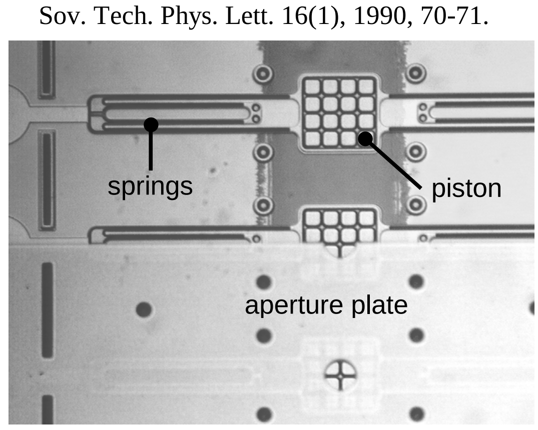


Figure 1: View of drop ejector with the upper half of the aperture plate removed

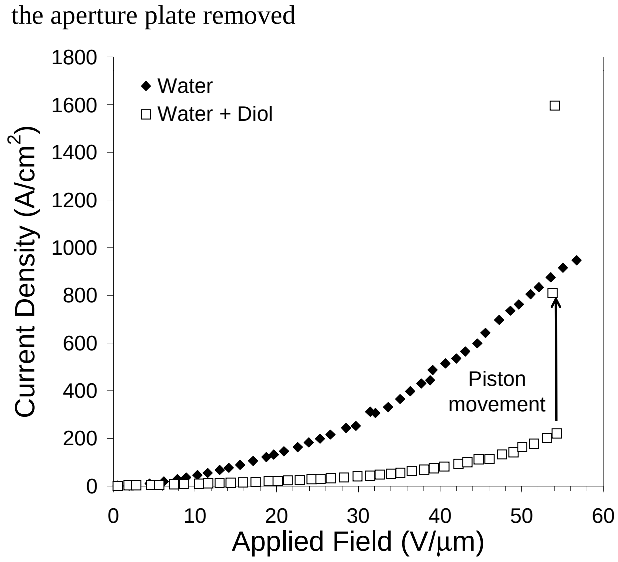


Figure 2: Current density measured at 1 μs for a 2 μm fluid filled gap - arrow indicates minimum field where piston movement was detected.