Electrophoretic Deposition of the Piezoelectric Polymer P(VDF-TrFE)

Jonathan D. Foster and Richard M. White
Berkeley Sensor & Actuator Center
University of California, Berkeley
497 Cory Hall, Berkeley, CA 94720-1770

We describe a new technique for depositing piezoelectric polymer films. This technique, called electrophoretic deposition (EPD), has been used to electrodeposit films of poly(vinylidene fluoride – trifluoroethylene) copolymer, or P(VDF-TrFE). EPD can be used to deposit thick films (e.g. 30 μm) and thin films (≤ 1 μm) of P(VDF-TrFE) in a conformal manner.

Spin coating, the typical technique used to deposit P(VDF-TrFE), is not capable of depositing conformally over severe variations in topography (such as the high-aspect-ratio features often found in MEMS). At UC Berkeley we are developing high-aspect-ratio microactuators that utilize sidewall piezoelectric films [1], and we have developed electrophoretic deposition as a means to deposit P(VDF-TrFE) on those sidewalls.

Electrophoretic deposition (EPD) is an electrodeposition technique in which films are formed by charged particles migrating under the effect of high electric fields (see Fig. 1). These charged particles may be generated in one of two ways: the "suspension approach", where polymer particles are dispersed in a nonsolvent, or the "solution approach", where polymer is dissolved in a solvent. P(VDF-TrFE) films have been deposited using both approaches, as shown in Figs. 2 & 4.

The suspension approach to EPD is primarily used for forming thick P(VDF-TrFE) films. The suspension is formed by ultrasonically dispersing 0.2 μm diameter P(VDF-TrFE) particles in isopropanol. During electrodeposition these particles form a porous film that can be subsequently densified by annealing at 150-200°C. Electrodeposition for 20 minutes at 80 V produced the porous 100 μm thick film shown in Fig. 2. Attempts to anneal films of 20-100 μm thickness produced cracks that extended through the entire thickness of the film (or pinholes when cracks were not evident). Repeated cycles of electrophoretic deposition and annealing were conducted to produce dense, thick P(VDF-TrFE) films without pinholes or cracks. Fig. 3 shows a ferroelectric hysteresis loop taken from a 25 μm thick film formed by 5 deposition/anneal cycles. This hysteresis loop indicates that the film is piezoelectric as well as pinhole free (no breakdown occurred with a 1 mm diameter top electrode at voltages up to 535 V, the limit of the power supply). A drawback of using repeated deposition/anneal cycles is that surface roughness of the film tends to be high.

The solution approach to EPD is used for forming thin P(VDF-TrFE) films. This approach deposits P(VDF-TrFE) polymer strands from an acetone solution, after which the film is annealed. Fig. 4 shows a ~0.5 μm thick film electrophoretically deposited for 2.5 minutes at 170 $\mu A/cm^2$ constant current density (130-190 V) over a silicon substrate with fins etched by a DRIE plasma. Note the fairly good conformality and sidewall coverage. Solution deposited films are more conformal than suspension deposited films, due to their higher unannealed density and consequently higher resistivity.

The conformal nature of P(VDF-TrFE) electrophoretic deposition makes it suitable for depositing films for high-aspect-ratio piezoelectric microsystems. Additionally, EPD is more versatile than spin coating because it can produce thick and/or porous films. The P(VDF-TrFE) EPD technique we have described is the first example of piezoelectric polymer electrodeposition in the literature.

[1] Microactuator geometry described in abstract to Hilton Head 2002 (Transducers Research Foundation).

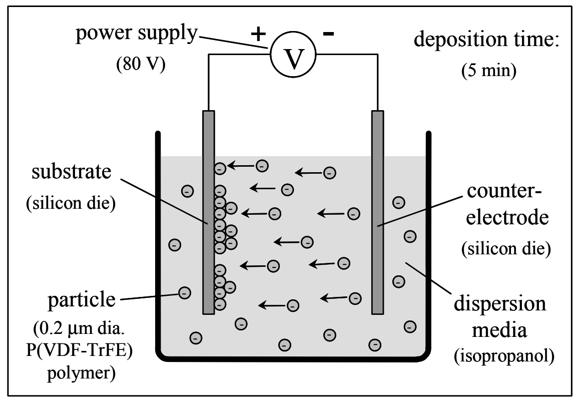

Fig. 1: *Schematic of electrophoretic deposition setup. (Typical values shown in parentheses, suspension approach.) Solution approach differs in that "particles" are solvated polymer strands.*

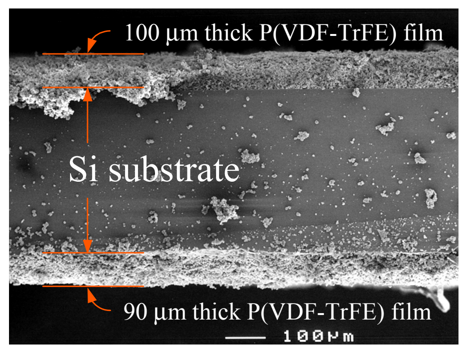

Fig. 2: *Cross-sectional SEM of thick, porous (unannealed) P(VDF-TrFE) films formed by electrophoretic deposition (suspension approach). Deposition occurred on substrate frontside (100 μm thick) and backside (90 μm) simultaneously.*

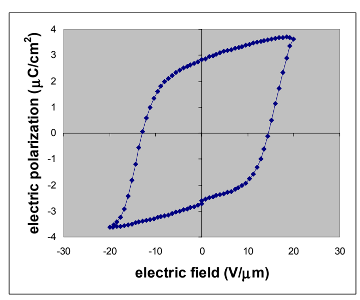

Fig. 3: *Hysteresis loop showing ferroelectric response of 25 μm thick P(VDF-TrFE) film with aluminum electrodes on silicon substrate. The measured remanent polarization of 2.8 $\mu C/cm^2$ was limited by the 535 V maximum voltage of the power supply.*

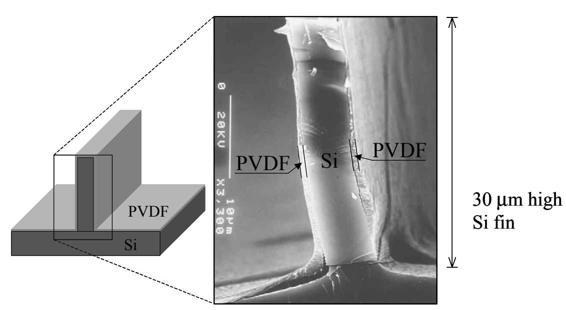

Fig. 4: *SEM with schematic showing thin P(VDF-TrFE) film (~0.5 μm thick) electrophoretically deposited (solution approach) over a high-aspect-ratio silicon fin.*