Microfabrication

Water-Soluble Sacrificial Layers for Surface Micromachining

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This manuscript describes the use of water-soluble polymers for use as sacrificial layers in surface micromachining. Water-soluble polymers have two attractive characteristics for this application: 1) They can be deposited conveniently by spin-coating, and the solvent removed at a low temperature (95–150°C), and 2) the resulting layer can be dissolved in water; no corrosive reagents or organic solvents are required. This technique is therefore compatible with a number of fragile materials, such as organic polymers, metal oxides and metals—materials that might be damaged during typical surface micromachining processes. The carboxylic acid groups of one polymer-poly(acrylic acid) (PAA)-can be transformed by reversible ion-exchange from water-soluble (Na⁺ counterion) to water-insoluble (Ca²⁺ counterion) forms. The use of PAA and dextran polymers as sacrificial materials is a useful technique for the fabrication of microstructures: Examples include metallic structures formed by the electrodeposition of nickel, and freestanding, polymeric structures formed by photolithography.

Keywords:

- microelectromechanical systems
- polymers
- sacrificial layers
- spin coating
- surface micromachining

1. Introduction

The sacrificial layers currently used for surface micromachining are almost exclusively inorganic materials, the most commonly used being silica (SiO₂). Aqueous hydrofluoric acid (HF) selectively etches SiO₂ in the presence of silicon and silicon nitride. This acid also etches phosphosilicate glass (PSG) faster than thermally grown SiO₂, and can under-etch PSG over dimensions up to 2000 μ m, with only minor damage to the silicon or silicon nitride microstructures. HF also etches many other materials, including metal oxides and organic polymers. Although some non-sili-

cate-based materials (e.g., titanium and aluminum) can be used as sacrificial layers with a HF etch, [2] the poor selectivity of this etch limits its usefulness with fragile materials, and its toxicity makes it inconvenient or hazardous for inexperienced users. HF-free etching solutions for aluminum are available, based on mixtures of acids and oxidants (i.e., concentrated phosphoric and nitric acids, hydrogen peroxide, and acetic acid), [2] but are also incompatible with some fragile materials. Porous silicon is also used for the fabrication of microsystems, and is coupled with a final dissolution in alkaline environment (KOH). [3]

Organic polymers—poly(imide), PMMA, and photoresist—have also been used as sacrificial layers for surface micromachining. The removal of poly(imide) films by reactive ion etching (RIE) is compatible with most inorganic materials, but RIE has little selectivity in etching most organic materials. [4] Sacrificial layers of photoresist are removed by dissolution in acetone, or by thermal degradation. [5,6] These removal steps are incompatible with many other organic polymers. Photoresists that are used as sacrificial layers are also

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limited by their thermal sensitivity, that is, the photoresist film becomes insoluble in acetone after extended exposure to high temperatures. Sacrificial layers of photoresist are, therefore, restricted to under-etching inorganic materials, and to processes having a minimal exposure to high temperatures. Polycarbonate,^[7-9] polystyrene,^[10] and polynorbornene[11] have been reported as sacrificial materials for very specific applications, such as the preparation of sealed nanochannels.[11] Poly(dimethylsiloxane), poly(methyl methacrylate), and epoxy-based polymers, removed by etching or thermal decomposition, have been used as sacrificial templates for the fabrication of metallic heat-exchangers.[12]

Table 1. Selection of water-soluble polymers for sacrificial layers.

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Polymer	Film uniformity ^[a]	Film solubility in water ^[b]	Film solubility in water after photolithography ^[c]	Roughness (RMS in nm) ^[d]	
Poly(acrylic acid)	good	good	good	0.28	
Dextran	good	good	good	0.27	
Poly(methacrylic acid)	good	good	good ^[e]	-	
Poly(acrylamide)	good	good	irreproducible	_	
Poly(ethylene imine)	good	only in acidic or alkaline media	-	_	
Poly(vinyl alcohol)	good	insoluble	_	_	
Poly(ethylene oxide),	good	good, but also soluble in	_	_	
2 kDa		organic solvents			
Poly(ethylene oxide),	Not uniform	_	_	_	
100 kDa					
Chitosan	Not uniform	_	_	_	
Sucrose (table sugar)	Not uniform	_	_	_	

[a] The films were prepared by spin-coating (3000 rpm, 15 s) from a 5% (w/v) polymer solution in water, except for the polymers with a poor solubility in water, including poly(ethylene oxide) (100 kDa; 1% w/v), poly(methacrylic acid) (1.7% w/v), and poly(vinyl alcohol) (2.5% w/v). The films were then dried by placing the substrates on a hot plate at 150°C for 2 min. "Good" is a subjective finding of fewer than two inhomogeneities detectable by optical microscopy (bright-field mode) on a 3-inch wafer. [b] "Good" indicates that dissolution of the film in water required less than 1 s. [c] "Good" means that disks of SU8-2010 photoresist could be lifted-off in water (refer to text for further details). [d] Root mean square (RMS) roughness of the film as measured by AFM. Before preparation of the films, we measured a RMS roughness of 0.21 nm on silicon substrates. [e] The poor solubility of the polymer in water limits the range of film thicknesses that can be prepared, in comparison to dextran and PAA (see text for details).

This paper describes the application of water-soluble polymers as sacrificial layers in surface micromachining. Although the water-soluble poly(vinyl alcohol) has already been reported for the replication of microstructures, [13] we found that PAA and dextran had the most useful combination of properties in the context of sacrificial layers. The most important properties of the sacrificial layers were the homogeneity of the films after spin-coating, and their solubility in water. For films of PAA, we have demonstrated the reversible modification of its solubility in water, by ion exchange of Na⁺ with Ca²⁺. This technology is useful for micromachining on silicon wafers, and expands multilevel fabrication to a range of materials that previously were excluded because of their sensitivity to HF, plasma oxidation, or other harsh chemicals. We describe methods to prepare metallic microstructures by electrodeposition on poly(ethylene terephtalate) (PET) disks coated with indium-tin oxide (ITO), and to fabricate free-standing structures in epoxybased polymers prepared on plastic substrates and silicon wafers.

2. Results and Discussion

2.1. Selection of the Polymers

We initially surveyed water-soluble polymers that are available in bulk quantities (see Table 1). Films of many organic polymers can be prepared on flat substrates by spin-coating, followed by baking to remove the remaining solvent. We prepared films from aqueous solutions of the polymers listed in Table 1, and tested the solubility of the baked films in water. From this selection of ten polymers, only

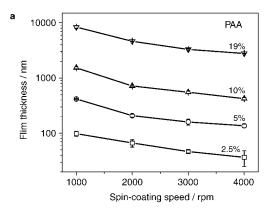
PAA, dextran, and poly(methacrylic acid) (PMA) fulfilled our initial requirements for a water-soluble sacrificial layer: 1) Homogeneous films after spin-coating, 2) water-soluble films before and after photolithography, and 3) insoluble films in organic solvents before and after photolithography. Because of the poor solubility of PMA in water, we were unable to prepare aqueous solutions of this polymer with a concentration larger than 1.7 % (w/v). This limitation makes it impractical to prepare thick films (>500 nm) by spin-coating. We concluded that PAA and dextran are the most promising organic polymers, among those we surveyed, for use as water-soluble sacrificial layers.

2.2. Characterization of the Sacrificial Layers

The final thickness of the film depends on the viscosity of the polymer solution (that is, on the concentration and the molecular weight of the polymer) and on the speed of spin-coating. We prepared films from aqueous solutions of 2.5 to 19% (w/v) PAA and 2.5 to 20% (w/v) dextran, by spin-coating these solutions onto planar substrates at velocities from 1000 to 4000 rpm. Figure 1 shows the film thickness of the PAA and dextran films measured by profilometry. The thickness can be adjusted between \approx 40 nm and 9 µm for PAA, and between \approx 40 nm and 1.1 µm for dextran. We also measured the viscosity for the solutions most frequently used in our study. The viscosities for aqueous solutions of 50 kDa PAA were 1.49×10^{-2} Pas at 5% and 3.67×10^{-1} Pas at 19%, and for solutions of 66 kDa dextran were 2.94×10^{-3} Pas at 5% and 2.85×10^{-2} Pas at 20%.

Dextran and PAA films are insoluble in most organic solvents. We investigated the stability of these polymer films

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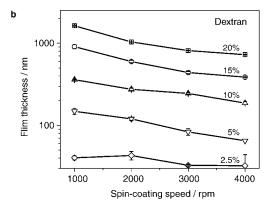


Figure 1. Film thickness as a function of spin-coating velocity and polymer concentration: a) PAA films using 19 % to 2.5 % (w/v) aqueous solution of PAA (50 kDa); b) dextran films using 20 % to 2.5 % (w/v) aqueous solutions of dextran (66 kDa). Error bars indicate the standard deviation with n=3.

upon exposure to a selection of organic solvents. More specifically, we were interested in the stability of these films upon immersion in acetone and isopropyl alcohol, because of the widespread use of these solvents in surface micromachining. We were also interested in their stability upon immersion in y-butyrolactone, 1-methoxy-2-propanol-acetate (PGMEA) and 1-methyl-2-pyrrolidinone (NMP), which are three key solvents (the solvent for the prepolymer resin, the developer, and the solvent for lift-off, respectively) for bisphenol-A-formaldehyde epoxy-based photoresists (e.g., SU8 from MicroChem, Inc.). We also investigated the stability of the film in acetonitrile, dimethylformamide, hexanes, ethanol, and dimethylsulfoxide, because of their importance as solvents for further chemical modification of the film. The PAA films were insoluble in all of these solvents. The thickness of these films did not change by more than 20% after immersion in the appropriate solvent for one hour. The dextran films were damaged (i.e., millimeter-scale holes appeared in the film) upon exposure to ethanol and completely dissolved in dimethylsulfoxide. Films of dextran were, however, stable in the other solvents (that is acetone, isopropyl alcohol, γ-butyrolactone, PGMEA, NMP, acetonitrile, and hexanes).

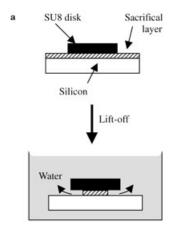
We characterized the dissolution of the sacrificial layer in water by lifting off arrays of disks fabricated from SU8-2010 photoresist. The disks were patterned directly on the sacrificial layer in a single step of photolithography (Figure 2a). We tested the lift-off of disks with diameters ranging from 20 to 1200 µm. The data for dextran and PAA show that the disks prepared on PAA lifted-off twice as rapidly as those on dextran (Figure 2b). We also compared the etching rate of PAA and dextran to other types of materials used as sacrificial layers (see Table 2). The etch rate of a sacrificial layer can depend on the geometry of the item to be released.^[14] The data presented in Table 2 do not take into account a dependence on geometry, and should only be used as guidelines. These data suggest that water-soluble sacrificial layers dissolve in water up to four orders of magnitude more rapidly than currently used materials in their respective etchant (e.g., SiO₂ in 1% HF). The selectivity of water for PAA and dextran relative to other materials is also much better than that of traditional etchants, such as HF towards silicon nitride. [15] We used the etch selectivity of these polymers to lift-off microfabricated features prepared on plastic disks or ITO-coated substrates (Figure 2c). The rapid dissolution of the sacrificial layers in water is also useful for the release of microstructured films that cover distances up to the size of a wafer. For instance, we prepared centimeter-scale structures of SU8 on PAA films as a mask for shadow evaporation of metal films (see Supporting Information; Figure S1). We also lifted-off 4 cm² solid sheets of polymerized SU8 from dextran after soaking the substrate for $\approx 12 \text{ h}$ in water.

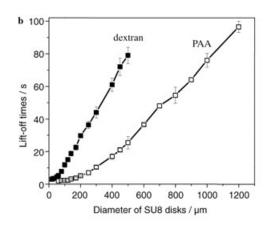
2.3. Modifying the Solubility of PAA by Ion Exchange

The ease of dissolution of the water-soluble films is an advantage for: 1) Quick release of features by lift-off, and 2) applications involving materials that are incompatible with currently used etchants. It is, however, a limitation for micromachining processes that require exposure to aqueous solutions prior to lift-off. We overcame this limitation by using a chemical treatment specific to PAA to modify the water-solubility of the film. The side chains of the PAA polymer contain (Na⁺)-carboxylate groups. The Na⁺ ions can be exchanged for calcium ions; this process cross-links the PAA chains, and produces a water-insoluble PAA-Ca²⁺ polymer. [16] We observed the same behavior with other bivalent ions, such as Cu2+ in the form of an aqueous solution of CuCl₂ and CuSO₄, but trivalent ions such as Cr³⁺ failed to turn the PAA film water-insoluble. We created water-insoluble films of PAA by soaking the films in a 1 m aqueous CaCl₂ solution for 1 min. We found that PAA-Ca²⁺ films were stable for at least 1 h in water, and could be rendered water-soluble again by immersion in a solution of NaCl ([NaCl] = 10 mm - 1 m). The excess of sodium ions in solution displaces the calcium ions in the PAA-Ca²⁺ film, and dissolves the calcium-exchanged PAA film within 1 s for solutions of > 10 mm NaCl.

Preventing the dissolution of PAA films by soaking the substrate in a solution of CaCl₂ was successful for films with thicknesses of less than 700 nm. We found that films thicker than 700 nm became insoluble, but lost their adhesion to the substrate. To improve the adhesion of the PAA films on sili-







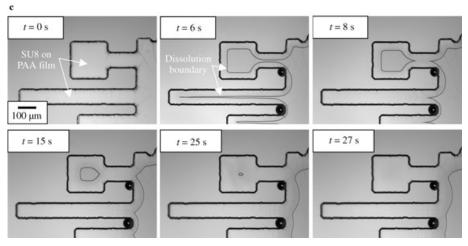


Figure 2. Characterization of lift-off: a) Schematic illustration for the etching of the sacrificial layer under a disk of SU8. b) The time required to lift-off 10-µm-thick disks made of SU8, by dissolution of sacrificial layers of PAA and dextran in water. Error bars indicate deviation from the mean (n=3). c) Time-lapse pictures of the dissolution a sacrificial layer of dextran. The dissolution of the sacrificial layer ($\approx 1 \mu m$ thick), is rapid and compatible with a wide range of substrates. The pictures show the release, in 27 s, of a 200 × 200 µm² square cantilever prepared in epoxy photoresist (SU8-2010), from a sheet of PET coated with an ITO film.

con wafers, we used an adhesion layer prepared with an acidic solution of PAA (pH \approx 2.5). We spin-coated a 5% (w/v) acidic solution of PAA and baked the resulting film at 150°C on a hot plate for 15 min. We found that these films of acidic PAA become water-insoluble only after prolonged

Table 2. Etching rates of commonly used sacrificial layers, PAA and dextran.

Material	Etchant	Rate [$\mu m min^{-1}$]	Reference		
PAA, 50 kDa	water	750			
Dextran, 66 kDa	water	380			
SiO ₂ (thermal)	HF 1 %	0.06	[19]		
PSG (15wt% P) ^[a]	HF 1 %	2.4	[19]		
SiO ₂ (thermal)	conc. HF (24 M)	1.3	[19]		
PSG (8wt % P) ^[a]	conc. HF (24 M)	25	[20]		
Poly(imide) ^[b]	oxygen plasma	4	[4]		
Positive photoresist ^[c]	acetone	1	[5]		

[a] PSG = phosphosilicate glass. [b] Thermally cured PI2610 epoxy resin from HD Microsystems (Parlin, NJ). [c] Resin based on novolak-diazquinone, such as AZ1518, AZ4400, and AZ4620 from Clariant (Charlotte, NC).

baking on Si or quartz substrates (but not on glass and metalcoated surfaces). These observations suggest that the PAA chains form a covalent bond with the SiO₂ surface (Si wafers have a native layer of SiO2 at their surface). We think that above ≈ 100 °C, the formation of esters is favored by condensation of the carboxylic groups of PAA with the silanols of the silicon through the loss of water by evaporation: (R-COOH $R'\text{-}SiOH \! \leftrightarrow \!$ $R-COO-Si-R' + H_2O$).

The resulting PAA film is no longer soluble in water. This thin, baked film of PAA improved the adhesion of a second PAA film (deposited from a solution of neutral pH), to permit treatment of the second PAA film with a CaCl₂ solution. In our experiments, we could prevent the aqueous dissolution of PAA films with thicknesses up to 9 µm using this twostep procedure.

The films of PAA-Ca2+ are completely insoluble in water, but have only a limited stability (e.g., immersion for $\approx 5 \text{ min}$) in an aqueous solution of salts, such as 100 μm NaCl, HCl (pH 4), or NaOH (pH 9). The addition of CaCl2 to the aqueous solutions of other salts improves the stability of the PAA-Ca2+ films by several orders of magnitude. For example, the PAA-Ca2+ films remained in-

soluble for several hours in a 500 mm NaCl solution containing an equimolar quantity of Ca2+ ions. More generally, we found that the presence of 0.1 equivalents of Ca²⁺ in solution relative to the sum of all the monovalent cations was sufficient to maintain the insolubility of the PAA-Ca²⁺

> films. This approach did not, however, prove successful in very alkaline solutions, because the calcium ions precipitate in the form of Ca(OH)2, and could not be maintained at a sufficiently high concentration to maintain the ionic cross-linking of PAA. As a result, alkaline developers with pH values of 12-13 (such as the 351 developer used for Shipley positive photoresists) are currently not compatible with the PAA films.



2.4. Ionic Cross-Linking of PAA for the Electrodeposition of Nickel

To illustrate the usefulness of the ionic cross-linking of PAA, we fabricated metallic features by the electrodeposition of nickel through a structured film of PAA (Figure 3a). In this approach, we patterned the PAA by selectively dissolving the PAA through the openings of a photostructured film of SU8, and then removed the SU8 mask by immersion in NMP. Removal of polymerized SU8 is difficult and typically requires the application of a release layer, but we found that SU8 could be removed from the PAA-based films much more rapidly (i.e., in less than one hour) than from the surface of silicon wafers. It is, therefore, more convenient to pattern the PAA-based films using an SU8 mask than to use SU8 directly on the substrate.

We prepared the PAA features by etching the exposed regions of the PAA layer through the openings in an SU8 mask. The edges of the resulting PAA features were, howev-

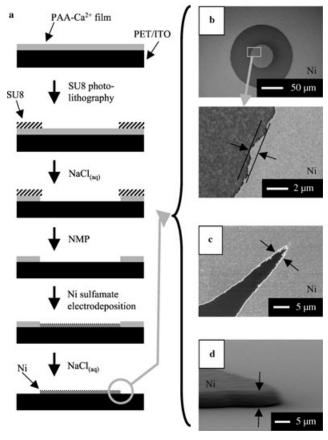


Figure 3. Electrodeposition of nickel: a) Schematic illustration of the microfabrication of nickel features by electrodeposition through a film of patterned PAA–Ca²⁺. The substrates of ITO-coated poly(ethylene terephtalate) (PET) conducted the electric current required for the deposition of metal into the openings of the patterned film of PAA–Ca²⁺. b–d) SEM images of electrodeposited nickel on ITO-coated PET. The edge resolution (b) and the lateral resolution (c) of the nickel features was determined by the transparency mask used for the photolithography. The regions of nickel appear bright in the SEM images. d) The PAA–Ca²⁺ film was stable in the commercial solution of nickel sulfamate for extended periods of time (> 3 h at 40 °C) during the electroformation of thick nickel features.

er, poorly defined (see Supporting Information, Figure S2). The edges of the PAA-Ca2+ features, however, closely matched those of the SU8 mask when the PAA film was cross-linked before spin-coating the SU8. We etched the exposed film of PAA-Ca²⁺ with 1 M NaCl, containing a detergent (0.05% Tween) to ensure that the aqueous solution could wet the surface of the SU8. The saline solution could then penetrate through the openings with small diameters (i.e., $<50 \,\mu m$) in the SU8 to reach the exposed film of PAA-Ca²⁺. On an ITO-coated PET substrate with a structured layer of PAA-Ca2+, we electroplated nickel by dipping the substrate into nickel sulfamate, with currents of 1 or 20 mA cm⁻². Figure 3b and 3c indicate that the edge roughness and lateral resolution achieved for the nickel features was similar to that of the transparency photomasks we used to pattern the initial layer of SU8 (i.e., with a resolution of about 8 µm).^[17] Nickel ions are bivalent—like the Ca²⁺ cations—and they cannot dissolve the PAA-Ca²⁺ features. The PAA-Ca2+ layer was stable for at least 3 h at 40°C in a solution of nickel sulfamate, which is commercially available in the form of a "ready-to-use" solution for applications in electronics. This stability of the PAA-Ca²⁺ features allowed us to prepare thick features of nickel (i.e., 5 μm thick in Figure 3 d).

2.5. Free-Standing Structures

Free-standing micrometer-scale structures can be fabricated using films of PAA and dextran as sacrificial layers. Because the conditions used for etching were mild, this method is compatible with a wide variety of materials, such as the three materials we chose for microfabrication, namely, PET, SU8, and aluminum. Using the approach illustrated in Figure 4a, we successfully fabricated free-standing structures in SU8, including bridges that spanned distances >500 µm on PET substrates (Figure 4b). We observed, however, one limitation in using flexible, polymeric materials as substrates for microfabrication. The stress produced in the substrate while baking thick sacrificial layers (i.e., 10 µm of PAA) deformed the flexible substrate (e.g., PET sheets). To reduce the deformation of the substrate, we applied a force at the edges of the substrate during baking $(\approx 50 \text{ g metallic weights placed along the perimeter of the})$ substrate). After partial dissolution of the sacrificial layer, the process yielded flat substrates that we cut into chips of about 1 cm² for observation by scanning electron microscopy (SEM). We observed no deformations of the substrate when using submicrometer-thick sacrificial layers. To avoid the collapse of the features upon evaporation of the water used for the release, we rinsed the substrates immediately with isopropanol (to quench the etch process), and then with hexanes (to lower the surface tension upon release of the features). We observed that drying the free-standing SU8 features from hexanes prevents collapse of the structures.[18]

For applications requiring the preparation of electrically conductive features, we evaporated a film of aluminum on the SU8 microstructures before lift-off (Figure 5a). This



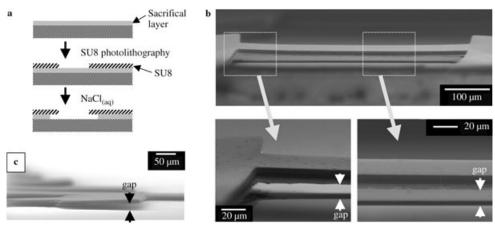


Figure 4. Polymeric free-standing structures: a) Schematic illustration of the fabrication of free-standing polymeric structures using a water-soluble sacrificial layer. The sacrificial layer is etched in water until the small features become free-standing (\approx 40 s), while larger structures remain bound to the substrate by the underlying, intact sacrificial layer. b) SEM images of the 80- μ m-wide bridges of SU8 fabricated on a sheet of PET using PAA sacrificial layers (PAA solution at 19% w/v). Because all the materials used in (b) are insulating organic polymers, we evaporated a 10 nm film of gold on the sample to allow SEM observation. c) SEM image of a cantilever of SU8 prepared on a Si wafer using a dextran film (dextran solution at 20% w/v). The shape of the SU8 cantilever is identical to that shown in Figure 2 c.

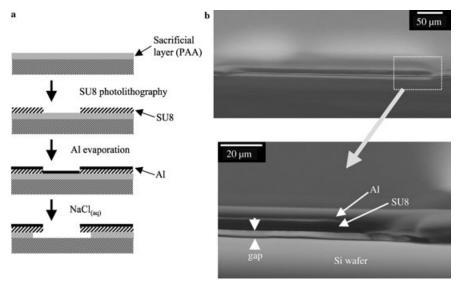


Figure 5. Electrically conductive free-standing features: a) Schematic illustration of the microfabrication (based on the technique described in Figure 4). To produce electrically conductive features, a 50 nm aluminum film was evaporated on the SU8 before the lift-off (see text for further details). b) The SEM pictures show the side view of electrically conductive bridges prepared on a Si wafer using a PAA (19% w/v) sacrificial layer.

process is especially appropriate for the use of PAA sacrificial layers because the aluminum film adheres poorly to the PAA, but adheres strongly to the SU8 features. In contact with water, the aluminum on PAA formed flakes that rapidly detached from the surface, uncovering the underlying PAA film. Upon immersing the substrate in a sonication bath, we found that all the aluminum on PAA could be removed in less than 5 s with no damage to the metal-coated SU8 features. Leaving the substrates in water, we continued to etch the sacrificial layer of PAA until the free-standing structures were released from the substrate in $\approx 40 \, \text{s}$ (Figure 5b). In contrast, evaporated aluminum showed good ad-

hesion on dextran, and lifting-off the aluminum films in water was slower than what was required to release the metal-coated features of SU8.

3. Conclusions

We have demonstrated the use of water-soluble polymers-PAA and dextran-as sacrificial layers with applications to surface micromachining. The preparation of these sacrificial layers is rapid and simple, and their dissolution is carried out in mild environments, such as in water or in an aqueous NaCl solution. These sacrificial layers offer an alternative to HF-based chemistry for surface micromachining applications, and enable the use of organic polymers, easily oxidized metals, ITO, and other metal oxides. We have presented methods that may be especially useful for the fabrication of MEMS directly on the surface of CMOS chips, which are typically encapsulated in either SiO2 and/or aluminum. It also avoids the use of toxic etchants, such as HF, which present serious health hazards. We found three major advantages to the use of PAA over dextran: 1) The range of possible film thicknesses is greater with PAA than with dextran, 2) the solubility of PAA films can be chemically

controlled by the addition of Ca²⁺ or Cu²⁺ ions, and 3) the preparation of electrically conductive features is possible because metallic films adhere weakly to PAA.

4. Experimental Section

Reagents and materials: PAA (50 kDa) and poly(methacrylic acid) were purchased from Polysciences (Warrington, PA). Dextran (66 kDa), chitosan, poly(ethylene oxide) (2 kDa), poly(vinyl

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alcohol), and poly(ethylene imine) were obtained from Sigma-Aldrich (St. Louis, MO). PAA (2 kDa), poly(ethylene oxide) (100 kDa), and poly(acrylamide) were bought from Sp² (Scientific Polymer Products Inc., Ontario, NY). SU8-2010 photoresist was purchased from Microchem (Newton, MA). ITO-coated PET substrates (200 μ m thick, R_s < 10 Ω) were obtained from Delta Technologies (Stillwater, MN) and uncoated PET substrates $(\approx 100 \, \mu m \, \text{thick})$ were bought from Policrom (Bensalem, PA). The profilometry measurements were obtained with an Alpha-Step 200 from Tencor (San Jose, CA). The source of nickel for electrodeposition was an "S" nickel sulfamate ready-to-use (RTU) solution purchased from Technic Inc. (Providence, RI). The $\,$ applied current for electrodeposition was controlled with a current generator Pentiostat/Galvanostat Model 273 from Princeton Applied Research (Oak Ridge, TN). The photomasks for photolithography were obtained from CAD/Arts (Poway, CA).

Sacrificial layer preparation: The PAA purchased as a 25% (w/v) solution in water was neutralized with a saturated solution of NaOH until reaching a pH of 7.5 with a pH indicator band test, and then diluted to the appropriate concentration. The dextran solution was prepared by mixing the appropriate amounts of dextran and water in a vial; complete dissolution of dextran was obtained by placing the vial in a bath of hot water (90-95 °C). The silicon wafers were immersed in a 5% aqueous solution of HCl for 5 min, rinsed with deionized water, and dried with a stream of nitrogen gas. The surface of the polymeric substrates (e.g., PET) was rendered hydrophilic by a brief exposure to oxygen plasma (30 s, 18 W). Both of these treatments improved the wettability of the aqueous solutions of PAA and dextran on the substrates. The solutions of water-soluble polymer were filtered (0.45 µm or 5 µm pore size for solutions of polymer with less or more than 5% (w/v), respectively) and dispensed onto the substrate until about 90% of the surface was covered with the solution. The sacrificial layer was then prepared by spin-coating the substrate at 1000-4000 rpm for 15 s, and baking the film on a hot plate (at 150°C for silicon, or 95°C for polymeric substrates) for 2 min.

Film-thickness measurements: We dissolved the sacrificial layer from over about half of the surface of the substrate with a stream of water (from a water bottle), and dried the substrate with a stream of nitrogen gas. The thickness of the film was then determined by averaging profilometry measurements at three different locations on each substrate.

Microfabrication: We prepared the photoresist structures according to the manufacturer's instructions. For the characterization of the etching speed of PAA and dextran, for the experiments with Ni electrodeposition, and for the shadow-mask evaporation of metals, we used sacrificial layers prepared from solutions of polymer of 5% (w/v) and spin-coated at 3000 rpm. The sacrificial layers for the free-standing structures were prepared from solutions of 19% PAA and 20% dextran (w/v) and spin-coated at 1000 rpm. The characterization of the etching of the sacrificial layer was carried out with deionized water. For all other experiments we added Tween 20, at a concentration of 0.05%, to improve the wettability of the water (or NaCl solution) on the SU8 features. The nickel was electrodeposited at constant current, between 1 and 20 mAcm⁻². The free-standing features were released by immersion in water for 40 s.

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