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High aspect ratio polymer microstructures and cantilevers for bioMEMS using low energy ion beam and photolithography

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Abstract

In this paper, the high etching selectivity of different fluoropolymers and for the fabrication of high aspect ratio polymer (HARP) microstructures is reported. Free standing polymer cantilevers for the development of transparent fluoropolymer-based microfluidic devices are presented. Fluoropolymers, such as Teflon®-based polymers, are hydrophobic and inert to most solvents and chemicals. The low surface energy of fluoropolymers makes the fabrication of microstructures from these substrates most difficult when using conventional silicon microfabrication steps. Low energy ion beam methods are used to improve the wetting characteristics of photoresists on a family of fluoropolymers including polytetrafluoroethylene (PTFE), Tefzel®, fluoroethylenepropylene (FEP), and Teflon® AF. Satisfactory pattern transfer capability down to submicron dimensions is achieved through low energy ion beam technology. The optimum selectivity of etch rates between fluoropolymers and photoresists is determined through variations of incident beam angles for multilayer integration. HARP microstructures and cantilever arrays of fluoropolymers are achieved by controlling surface profile with the high etching selectivity between different polymers and an oblique angle of incident beam. These polymer cantilevers have direct applications as biochemically functionalized tips for an atomic force microscope or as near field probes within integrated microfluidic systems.

Keywords: High aspect ratio polymer microstructures; Biomedical microelectromechanical systems (BioMEMS); Ion beam; Photolithography

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1. Introduction

While silicon micromachining remains the method of choice due to diverse applications in microelectromechanical system (MEMS) technology, it is limited primarily to single-crystal and polycrystalline silicon systems [1–3]. Most recently, there is an increasing trend toward the utilization of polymer materials in the biomedicine and microelectronics fields [4–6]. Among the many different classes of polymers, it is the fluoropolymers which provide the most unique material characteristics [7–11].

Fluoropolymers commonly known as Teflon®-based polymers are inert to most solvents and chemicals, hence micromachining of these polymers offers great potential for use in biomedical microdevices or micropumps containing corrosive fluids and gases. The integration of fiber optics and microchannels on a fluoropolymer substrate or a thin film of fluoropolymer on other substrates can be utilized to build a microchamber for biotechnology applications [12]. These microstructures on polymer substrates can also provide us with more sophisticated biomaterials research tools, drug delivery systems and devices for tissue engineering studies [13]. Moreover, if one uses a specialized polymer such as Teflon® AF, which is an amorphous copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, one can develop novel microdevices with specialized characteristics including excellent optical transmission properties, low dielectric constant, thermal stability, and better creep resistance than standard polytetrafluoroethylene (PTFE) polymers. Thus, a polymer such as Teflon® AF can be an excellent material for the integration of micro-optoelectrical and mechanical systems (MOEMS).

Although Teflon®-based polymers have the advantage of chemical inertness, this property can become an obstacle to the processing steps during fabrication of microstructures on

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the fluoropolymers. Further, owing to the poor adhesion characteristics of Teflon®-based polymers, the conventional silicon integrated circuit fabrication technology cannot be directly applied to fabricate micromachined structures.

Previous research on micromachining of fluoropolymers has been limited by the adhesion properties of fluoropolymers. Garner et al. [14] made PTFE tubes with a shadow mask technique using a nickel mesh. This work resulted in the fabrication of PTFE microtubules; however, their method was not practical for integrated MEMS as their resolution was limited by their shadow mask. Recently, Berenschot et al. [15] used a shadow, intermediate titanium, or nitride masks to etch PTFE. However, these researchers avoided wetting the photoresist on the PTFE because the roughening surface adhesion process of the photoresist interfered with their polishing techniques.

The work presented here is distinct from previous studies in that we focus on improving the wetting of photoresists on fluoropolymers with minimum surface modification (10–40 nm). The importance of this emphasis is that single step photolithographic processing is more efficient than both the shadow or intermediate masking methods. Further, this methodology provides a clean surface for integrated MEMS development in comparison to multiple steps of intermediate metal masks since no subsequent step is needed to remove the intermediate layers of the metal or nitride mask.

Simple modification of the fluoropolymer surface is one of the most crucial steps in producing high quality or precision fluoropolymer microdevices. In this paper, the fabrication of HARP microstructures and cantilever arrays of fluoropolymers for MEMS applications is presented.

2. Experimental

The ion beam etching system employed in this work was an 11 cm diameter Kaufman ion source from Ion Tech. Using the IBE system, four fluoropolymers were modified and characterized in this study. Three different Teflon®-based polymers were used as the substrates for this work and include PTFE, Tefzel®, and FEP (Dupont, Wilmington, DE). In addition a thin film of Teflon® AF on oxidized silicon wafers was examined. All samples were placed on the sample holder, which was cooled by circulating water during the etching process. The sample distance from the ion source was approximately 60 cm and the sample holder was 30 cm in diameter. The system was pumped by a cryopump backed by a rotary pump. The base pressure of the system was on the order of 3×10^{-7} Torr. The gas used in this work was research grade Ar gas with a purity of 99.99% and it was introduced into the chamber via electronic mass flow controllers. For this system, the gas flow rate was 4.00 sccm and the operating pressure 1.0×10^{-4} Torr.

For the surface modifications, the parameters of the beam voltage, current density, and incident angle were 250 eV, 0.25 mA/cm^2, and 10°, respectively. The minimum duration of Ar^+ ion beam treatment was optimized for different fluoropolymers by spin-coating the photoresist. Surface topography was evaluated with a Digital Instruments Nanoscope III atomic force microscope (AFM) in order to characterize the ion beam treated fluoropolymer substrates and films. The AFM used a two section photodetector to monitor the laser and was operated in a tapping mode with feedback to maintain a constant force between the cantilever and the sample. All the scans were made in air at room temperature. The voltage applied to an x-piezo as a function of x and y position was recorded to define a three-dimensional representation of the surface morphology.

After successful adhesion of the photoresist to fluoropolymers for satisfactory pattern transfer capabilities in the submicron range, the substrates were etched using IBE to fabricate the desired microchannels. The lithographic process was performed using Shipley 1818® or AZ 4000® series photoresist and developed using conventional integrated circuit fabrication techniques. The fluorocarbon polymer samples were spin-coated with photoresist at 4000 rpm and subsequently baked on a hot plate at 90°C for 60 s. The energy density of UV exposure, development time, postbaking temperature and time were 80 mJ/cm^2, 30 s, 120°C for 60 s, respectively. The fluoropolymers were etched by Ar^+ ions at an energy of 500 eV and a current density of 0.5 mA/cm^2 with a cooling system on the sample holding area.

To characterize the incident angle dependence of etching rates, four different fluoropolymers were studied: PTFE, Tefzel®, FEP, and Teflon® AF. Each of these materials was prepared into 10 individual test pieces in order to study the effect of 10 different etching angles. For the Teflon® AF sample preparation, first the thin film was spin-coated on an oxidized silicon wafer and then cured at 200°C for 1 h prior to surface modification. After the surface modification had been applied to the samples, they were then patterned with Shipley 1818® or AZ 4000® series photoresist as described above. Substrates were then etched in the IBE system with the stage rotation at 2 rpm. and at a particular stage tilt angle in order to make a uniform etching. The angle of incidence was different for each sample in the set, beginning with an angle of 0° (normal incidence) and increasing to 80° in 10° increments (the tenth angle being 45°). Each set of samples was etched in the same manner. After the etch cycle the samples were put through a chemical process with acetone to remove the photoresist strips left on the film surface. The Dektak 3030 (Sloan Technology) profilometer was used to measure the change in the film thickness resulting from the etching of the unprotected strip. Four of these measurements were taken across each wafer to get an average loss of film thickness. The characterization of surface morphology on micromachined fluoropolymers was performed using scanning electron microscopy (SEM) and AFM in order to observe the unique etching profiles of each fluoropolymer. Other effects such as chemical structure change and physical damage are currently being investigated. The experimental

Table 1
Experimental parameters examined in this study

Parameter	Surface modification	Ion beam etching
Voltage	250–500 eV	500–750 eV
Current density	0.25 mA/cm^2	0.5–0.75 mA/cm^2
Pressure	1.0×10^{-4} Torr	1.0×10^{-4} Torr
Flow rate	4.0 sccm	4.0 sccm
Ar percentage	100%	100%

parameters examined in this study are summarized in Table 1.

3. Results

3.1. Wetting photoresists on fluoropolymers

Fig. 1 shows an AFM image of the surface morphology of Teflon® AF (a) before and (b) after ion beam treatment of 60 s. These micrographs demonstrate the effect of low energy Ar$^+$ ion beam treatment on the adhesion between the photoresist and fluoropolymer. The root mean square roughness of the ion beam treated surface is approximately 40 nm and this condition is more than sufficient to produce better adhesion for the photoresist. Each Teflon® surface has a unique root mean square roughness for the same ion beam treatment condition and has to be optimized individually due to the structural difference in the fluoropolymers. In order to wet the photoresists (Shipley 1818® or AZ 4000® series) on fluoropolymers with minimum surface modification, the roughness of each fluoropolymer was measured using AFM. The root mean square of PTFE, FEP, Tefzel®, and Teflon® AF for optimum adhesion of the photoresist is found to be on the order of 15, 18, 17, and 22 nm, respectively. These values can be further reduced by proper design of the polymer for photoresist. However, these values provide acceptable roughness for microfluidic devices that have microchannels with dimensions in the greater than 10 µm range.

3.2. High etching selectivity for HARP microstructures

Fig. 2 shows the results for the dependence of etching rates on the incident beam angles for the four different fluoropolymer materials. This graph shows the high selectivity of the etching rates of fluoropolymers and photoresists. The maximum etching rates are achieved at a beam incident angle of 10° in PTFE, FEP, and Tefzel® cases while the AZ 4210® photoresist case is obtained at 60°. The graph also provides the optimum angle needed to etch two different materials at the same etching rate. For example, the etching rates of PTFE, Teflon® AF, and AZ photoresist are almost identical at an incident angle of 60°. This value can be used for the planarization processing step when these materials are used for the integration of microdevices. Fig. 3 shows submicron HARP microstructures on FEP.

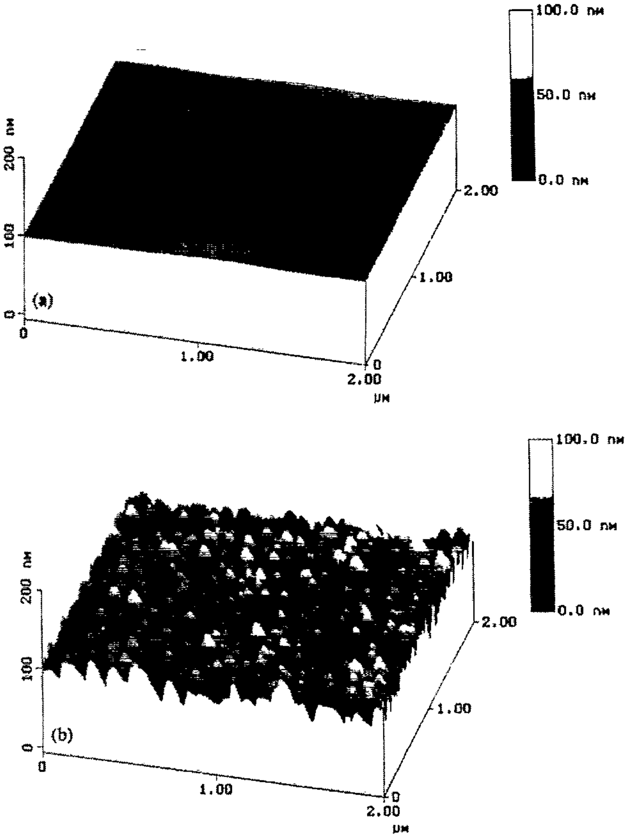

Fig. 1. AFM surface of Teflon® AF (a) before and (b) after low-energy ion beam treatment: 250 eV Ar$^+$ ion beam with a current density of 0.25 mA/cm^2 for 60 s.

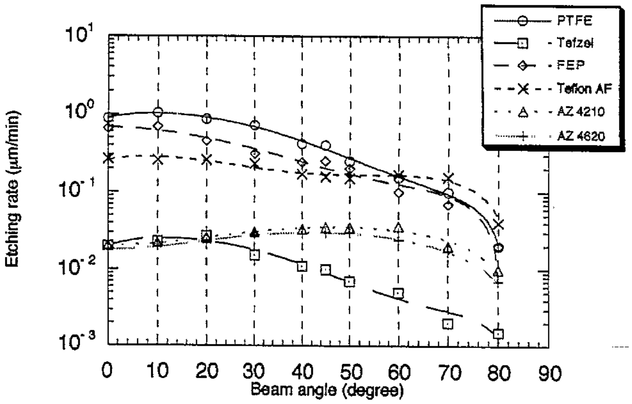

Fig. 2. Ion beam etching rates vs. incident beam angles in four different Teflon®-based polymer samples by using 500 eV Ar$^+$ ion beam (the current density: 0.5 mA/cm^2).

Scanning electron microscopy (SEM) of the different fluoropolymer samples reveals unique surface characteristics and etching profiles. These results provide insight into the structural conditions and unique behavior of each fluoropolymer. The etched surface of each sample is quite different. The Teflon® AF has the smoothest surface morphology amongst the four different fluoropolymers. The etching depth can be increased to obtain a higher aspect ratio by choosing the appropriate Teflon®-based polymer and photoresist mask.

Fig. 3. A SEM photograph of HARP submicron microstructures: 0.7 µm width and 19 µm height.

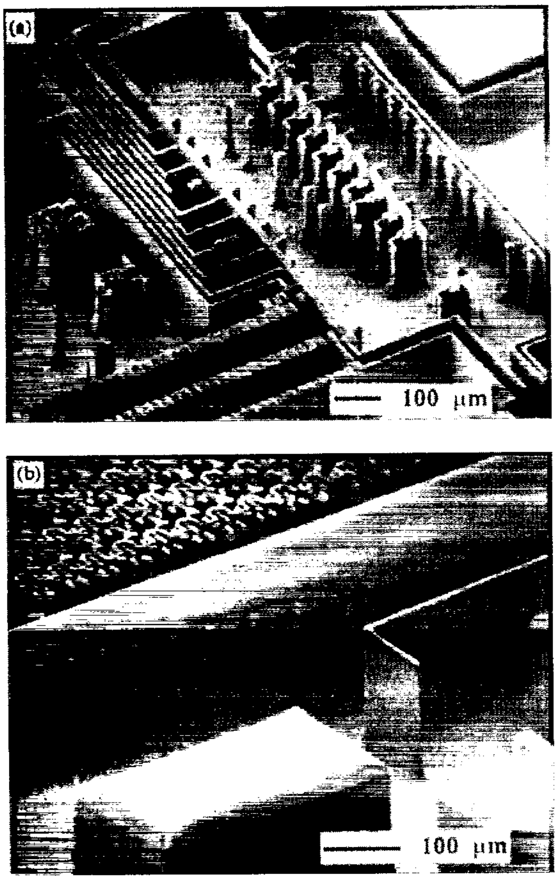

Fig. 4. (a) A SEM photograph of HARP microchannels with etched depth of 170 µm and a minimum width of 6 µm on Teflon® FEP. (b) A SEM photograph of high density arrays of HARP microstructures on transparent Teflon® FEP.

As an example of HARP microstructure, more than 170 µm of the etching depth with a minimum width of 5.5 µm on transparent FEP is fabricated as shown in Fig. 4(a) and (b). Currently the aspect ratio of height vs. width is about 27, but it is possible to obtain higher aspect ratios from Teflon® substrates with UV hardening photoresists.

3.3. 3-D microfabrication of polymer cantilever arrays

Fig. 5(a) shows a SEM photograph of the microfabricated polymer cantilever arrays on fluoroethylenepropylene (FEP). Advantages of these microprobe arrays are their capability to be integrated within microfluidic devices and their ability to be modified for biochemically functionalized tips of an atomic force microscope or near field probes. Also, unique cantilever arrays of polymer are created by 3-D microstereophotolithography. These 3-D microstructures are created with an oblique angle of incident beam (45°) subsequent to HARP etching on fluoroethylenepropylene (FEP) as shown in Fig. 5(b). These 3-dimensional microfabricated polymer structures can be applied to biomedical prostheses.

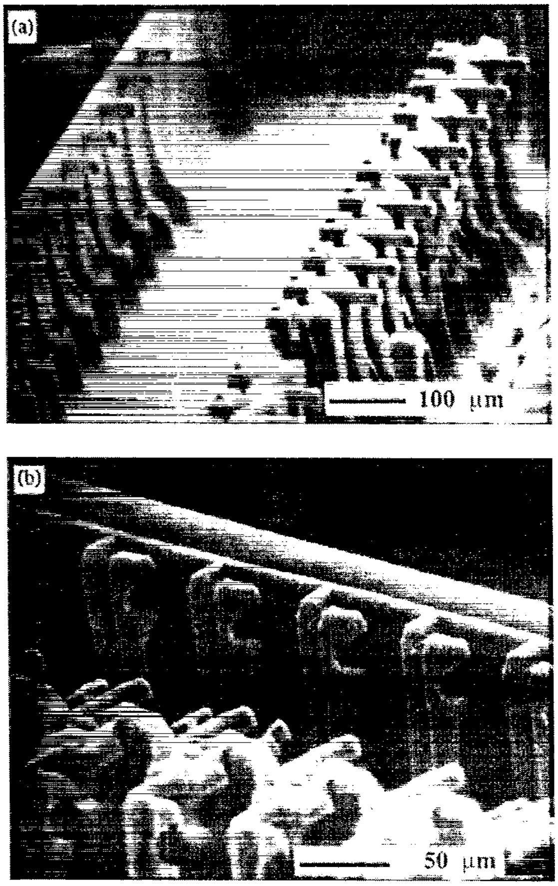

Fig. 5. (a) A SEM photograph of 3-D fabrication on Teflon® FEP: cantilever array within microfluidic devices. (b) A SEM photograph of 3-D microstructure etching with an incident beam of 45° within microfluidic devices.

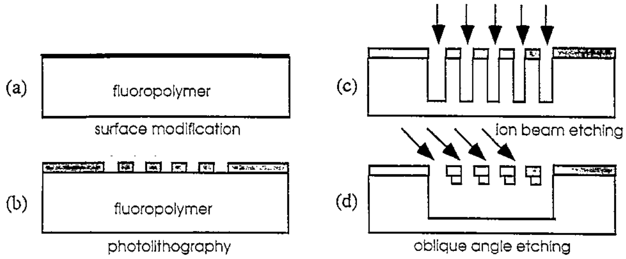

Fig. 6. Schematic of the fabrication procedure of the polymer cantilevers.

Fig. 6 shows the schematic diagram of fabrication steps of free standing cantilevers using FEP and photoresist only. The process consists of only one mask on FEP with two etching steps without using a sacrificial layer.

Microstereolithography is a new microfabrication process that allows one to build small size 3-dimensional polymer structures which are complex in shape. Instead of layer-by-layer light-induced polymerization of a liquid resin which has the spatial resolution of few hundred microns, this surface microstereolithography allows one to integrate with other microelectronics monolithically with a spatial resolution on the order of a few microns.

4. Discussion

Wetting mechanisms of photoresists on fluoropolymers by low energy ion beam surface modification can be controlled through the surface formation of unsaturated surface functionality and the generation of dangling bonds achieved by sputtering. Effective enhancement for the minimum roughness for acceptable adhesion of photoresist might be achieved by the mechanical interlocking and increased contact areas of the fluoropolymer's surface morphology. A more detailed study of surface chemistry is required to confirm the existence of C–O bonding on the modified surface area and its role in the interface of fluoropolymers and photoresists.

In order to fabricate submicron fluoropolymer microstructures precise control of etching rates and minimum structural evolution of the surface are required. Since fluoropolymers are inert to most chemicals, wet etching is not a preferred method for processing. Rather, dry etching techniques of reactive ion etching (RIE), chemically-assisted ion beam etching (CAIBE), or IBE are the practical techniques employed for Teflon®-based polymers. RIE and IBE differ in that the former is a chemical process, and the latter is a physical process. To achieve good uniformity with the RIE process, care must be taken to ensure that residues from photoresist are minimized. Surface film formation of new polymers as a byproduct of the etching reaction is also a concern. The buildup of byproducts causes nonuniform etching and therefore must be minimized. Since IBE uses a physical process it is less affected by a thin film surface because these residue byproducts have a finite ion etch rate and are removed rapidly [16]. One disadvantage of IBE is that it is not possible to obtain the chemical selectivity in etch rate between two materials, which can be achieved with wet etching or RIE.

However, to its benefit, different incident angles of the ion beam in IBE can improve the selectivity in the etch rates of different fluoropolymer substrates and films as shown in Fig. 2. At the incident angle of 10°, the selectivity of PTFE and FEP with respect to the photoresist (AZ 4610®) are 48 and 32, respectively. In order to fabricate HARP microstructures with a photoresist mask, this high selectivity is a beneficial factor. Dependence on the angle of incidence of ion beam on the sputtering yield is well known due to the momentum transfer mechanism of ion beam etching. This effect is well documented and has been studied using inert gas ions [17,18] and theoretically by Sigmund [19].

In terms of relative etching rates of fluoropolymers, PTFE exhibits the highest etching rate followed by FEP. Tefzel® shows the lowest etching rate, probably due to its enhanced polarity and accompanying interpolymer chain attraction associated with its copolymer structure (polyethylene and polyfluoroethylene). Teflon® AF thin film also exhibits a low etching rate (the second lowest of the four fluoropolymers) but it provides the smoothest surface morphology among the fluoropolymers studied here.

The relative selectivity of PTFE and FEP over the Tefzel® and Teflon® AF provide a useful advantage for the development of multilayered polymer MEMS. Further, ion beam etching is not limited to polymers but is also effective on other thin film materials including metals, insulators, and photoresists. For these reasons, IBE is an ideal method for use in the microfabrication steps of fluoropolymers including different metal layers for integrated Teflon® microdevices.

Another advantage of IBE is oblique angle etching for the microfabrication of polymer cantilevers without a special sacrificial layer (Fig. 5(a)). Selective lateral etching of polymer microstructures is achieved by controlling the profile with an oblique angle of incident ion beam. These new processing techniques enable the production of polymer cantilevers. For biomedical applications, these polymer microtips can be biochemically functionalized and used for near field chemo-optical probes within integrated microfluidic devices. Moreover, these polymer structures offer tremendous potential for diagnostics tools as they allow rapid, sensitive and economical detection of molecular interactions.

5. Conclusions

In summary, high selectivity etching of fluoropolymers including PTFE, FEP, Tefzel®, and Teflon® AF with and without photoresist masks have been investigated using low-energy ion beam techniques. Successful surface modifications were demonstrated for the adhesion of photoresists on the fluoropolymers. After patterning photoresist down to submicron scale geometry these substrates were etched using an IBE system to fabricate the HARP microstructures. The etching rates for all four materials depended strongly on the incident angles of ion beam. The maximum etching selectivity of fluoropolymers relative to AZ 4000® series were found at different angles of incident beam. The etch rates of PTFE, FEP, and Teflon® AF are 48, 32, and 12 times greater than AZ® photoresists, respectively. Unique fluoropolymer microstructures of cantilevers were developed by controlling profiles through an incident angle of beam.

The results of this work have broad applications in the MEMS community. These polymer cantilevers can be used for biochemically functionalized tips for an atomic microscope or near field probes within integrated microfluidic devices. Further polymer transducers will allow rapid sensing of molecular interactions. The technology presented here offers tremendous potential in both basic biomedical sciences and applied MEMS research.

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Biographies

Stanley Berger is a Professor of Engineering Science at the University of California at Berkeley, where he has been since receiving his Ph.D. in Applied Mathematics at Brown University and doing a post-doc at Princeton University. His research interests over the years have included blast waves, hypersonic flow, wake flows, MHD, viscous and boundary layer flows, low Reynolds number flows, and biofluiddynamics. He is the author of Laminar Wakes, published by Elsevier, and one of the editors of *Introduction to Bioengineering*, recently published by Oxford Univ. Press. He was an Associate Editor of the *Journal of Biomechanical Engineering*, and currently is an Associate Editor of the *Journal of Applied Mechanics*, the *International Journal of Engineering Science*, and *Applied Mechanics Reviews*. He is a Fellow of the American Physical Society, the American Institute of Aeronautics and Astronautics, the American Society of Mechanical Engineers, and the American Association for the Advancement of Science. He is currently serving as Chair of the Applied Mechanics Division of the ASME.

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Lisa Pruitt is an Assistant Professor of Mechanical Engineering and the Joint Bioengineering Graduate Group at the University of California at Berkeley, where she has been since receiving her Ph.D. in Engineering at Brown University. Her research interests include fatigue, fracture, tribology, and structural characterization of advanced polymers and biomaterials. At U.C. Berkeley she heads the Medical Polymer Group which focuses on the processing, sterilization, surface treatments and mechanical characterization of polymers used in orthopedic, cardiovascular, and reconstructive surgical applications. She is an NSF Career award recipient and and ONR Young Investigator. She is currently the author of more than thirty papers published in the area of engineering polymers. She is a member of the American Society of Mechanical Engineers, Materials Research Society, Society of Plastics Engineers, and the Society for Biomaterials.

Luke PyungSe Lee received the B.A. in Biophysics and he is currently working toward the Ph.D. at the University of California, Berkeley. During 1986–1990 he worked on integrated optoelectronics and superconducting electronic devices at TRW, Redondo Beach, CA. He first participated in the development of high power surface-emitting GaAs laser diodes using micromachined mirrors and a holographic photolithography technique. At the superconducting group he developed high-quality, submicron geometry of niobium Josephson junctions and planarization technologies for the fabrication of integrated niobium digital circuits and low-T_c SQUIDs. After joining Conductus in 1990, he was extensively involved with the development of low-noise high-T_c SQUID sensors for biomedical applications. His current research interest is in the development of new microfluidic integrated biosensors and its flexible manufacturing technology at UC Berkeley. He has authored or co-authored over 30 technical papers and presentations.