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Thin Teflon-like Films for MEMS: Film Properties and Reliability Studies

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1. ABSTRACT

This work presents film properties and initial reliability studies for thin Teflon-like films applied to a unique test vechicle, the Sandia-designed and fabricated microengine. Results on microengines coated with the film show a factor of three improvement in their lifetime and an order of magnitude reduction in the coefficient of friction when compared to uncoated samples. Coefficients Of Friction (COF) of 0.07 for the Teflon-like film and 1.0 for uncoated samples are extracted from models which match the measured behavior of working microengines. These films, deposited from a plasma source, exhibit the ability to penetrate into very narrow, deep channels common to many MEMS devices. For as-deposited film, both the refractive index at 1.4 and the contact angle with water at 108° show the film to be very similar to bulk Teflon PTFE. Film stability as a function of temperature has been examined using Fourier Transform Infrared (FTIR) spectroscopy. The film structure as observed by the fluorine-carbon (F-C) peak is stable up to 200 C, but starts decomposing above 250 C. Film composition has been examined using X-ray photoelectron spectroscopy (XPS) and is quite different for directly exposed surfaces compared with deep, narrow channels where the deposition process is diffusion limited.

Keywords: Micromachining, Adhesion, Stiction, Teflon, Microstructures, Fluorocarbon, Polysilicon, MEMS.

2. INTRODUCTION

The reliability of MicroElectroMechanical Systems (MEMS) is a critical performance issue regarding the incorporation of these devices into safety and severe service applications. Recently, much effort has been put into silicon surface passivation or coatings (e.g. SAMS, surface passivation, fluorocarbon, etc.) to minimize both initial startup and in-use adhesion that often cause devices to fail. Adhesion or "stiction" is a prevalent failure mechanism for surface micromachined devices.[1] These adhesion forces generate friction, static and dynamic, that contributes to wear, seizure, and consumes a significant portion of the motive torque.[2,3] Several methods are being employed in an effort to eliminate stiction during and after the sacrificial release.[4-7] If the surface of the microstructure remains hydrophilic, capillary condensation of water can occur in narrow contact gaps, even in reduced humidity environments. The condensation generates capillary pressure that can pull surfaces into contact causing adhesion or stiction in devices that were initially free. If the contact angle, θ_c, of the droplet on the surface is $< 90°$, then the capillary pressure is attractive and the surfaces are pulled into contact. If on the other hand $\theta_c > 90°$, the capillary pressure is repulsive and no surface contact occurs.[4] To alter θ_c, it is necessary to modify the surface by depositing a material with a different surface energy. To make the surface hydrophobic, $\theta_c > 90°$, low surface energy coatings are required.

There are several approaches for modifying the surface energy of a microdevice. One technique involves the use of ordered monolayer-thick films referred to as self-assembled monolayers, SAM's.[7] Since these films are only a monolayer thick, they are of limited usefulness for applications where surfaces come into repeated contact or continuous sliding contact. For thicker films, plasma polymerized fluorocarbons, which resemble pTFE (Teflon), have many good qualities (e.g. very hydrophobic ($\theta_c \approx 109°$), smooth, and durable).[4] Plasma deposited films have the added flexibility of controllable film thickness when compared to the self-assembled monolayer (SAM) approach.[7]

A discharge of fluorocarbon gas in a plasma reactor generates ions, excited molecules, and radicals. Depending upon the feed gases, substrates exposed to the plasma can be etched or have a polymeric film deposited on them. For this application, the later effect is desired. Polymerized tetrafluoroethylene {pTFE, $(CF_2)_x$} can be grown provided the fluorine-to-carbon ratio of the feed gas is $F/C \approx 2$. If the substrate is placed directly on the cathode or anode of the plasma reactor, ionized species will be accelerated from the plasma to the substrate and will impinge on the substrate normal to the surface.

Ion impingement coupled with the short diffusion length of the plasma will cause the fluorocarbon film to deposit anisotropically with the majority of the deposit being line of sight to the plasma. To make the film growth more conformal and likely to penetrate beneath microstructures, the substrate needs to be in a shielded, field-free zone adjacent to the plasma.[4] Several researchers[4-6] have studied fluorocarbon films deposited in field free zones within plasmas. These studies have shown improved film quality and conformality.

This work utilizes a reactor easily configured for remote (field–free) or RIE operation and a feed gas (CHF_3) that is readily available. Deposition rates, nonuniformities, film conformality, breakdown voltages and hydrophobicity as measured by contact angles are presented. Thermal stability of the films has been examined with FTIR and film structure with XPS. Device lifetime and friction measurements have been obtained from fully-functional microengines.[5]

3. EXPERIMENTAL

3.1 Experimental Apparatus

A Lam Research 384T etch system is used to deposit the teflon-like films. This reactor is a triode design whereby either the lower electrode, upper electrode, or both can be powered. The etcher is configured for 150mm (6 in.) silicon wafers. A single 13.56 MHz power supply with a matching network directs power to the electrodes. A grounded diffuser plate separates the upper and lower electrodes. The diffuser plate is filled with an array of holes that allow gas transport between the upper and lower plasma regions. When the lower electrode is powered, the system operates as a conventional reactive ion etcher. Directing the RF power solely to the lower electrode is referred to as the RIE mode. In the direct mode, the wafer is not shielded from the plasma and is subjected to a significant ion flux in addition to neutral species. When the upper electrode is powered, the plasma is confined to the region between the upper electrode and ground grid, referred to as "remote plasma" mode. In the remote mode, the substrate or wafer is shielded from ion bombardment, but free radicals and neutral species can be readily transported to the wafer surface. The wafer is placed on the lower electrode or cathode and clamped in place with a quartz ring. Constant temperature is maintained with helium cooling on the backside of the wafer. For these experiments, trifluoromethane (CHF_3) is used as a monomer source. Though CHF_3 has a $F/C = 3$, which is higher than the recommended value of 2, it is still easy to deposit plasma-polymerized coatings. The presence of hydrogen modifies the F/C ratio by recombining with much of the fluorine to produce HF. In this way the F/C ratio is held close to 2.

Film thickness and index of refraction are measured with a Rudolph Focus Model FE-III, which is a single wavelength HeNe laser (λ=6328 Å), multiple-angle of incidence, microspot (12 μm x 24 μm) ellipsometer.

For measurement of contact angles aVideo Contact Angle (VCA) 2000 Contact Angle Measurement System, by AST Inc., is used. The VCA 2000 provides a means to accurately measure the contact angle of a liquid on a horizontal surface by use of a video magnification system. This magnified image, which is viewed on a computer screen, provides an image of the water droplet on the surface. The contact angle of this droplet can then be measured on-screen.

For the measurement of thermal breakdown characteristics a Perkin Elmer System 2000 Fourier Transform Infrared Spectroscopy (FTIR) unit is used to analyze F-C bond degradation as the film is subjected to elevated temperatures.

X-Ray Photoelectron Spectroscopy (XPS) spectra are obtained digitally using a PHI 3057 XPS system with a spherical capacitor analyzer and a multichannel detector. Spectra are acquired in fixed analyzer transmission mode, using an Al anode (1486.6 eV) at 400 W and a pass energy of 46.95 eV for high resolution spectra and 93.90 eV for survey spectra. Elemental compositions, in atomic percent, are obtained by using published sensitivity factors, assuming a homogeneous distribution of composition with depth.

3.2 Deposition rates and Nonuniformities

Early efforts focused on using the remote mode to duplicate the efforts of other researchers. Recent efforts have focused on the RIE mode for deposition, since the film nonuniformity is reduced and there is little difference in the film conformality. Statistical experiment designs were used to explore the parameter space and quickly locate a desirable operating region. Details of the deposition process have been presented previously.[8] Optimization for minimizing film nonuniformities showed the predominant variables to be power, pressure, and the electrode to which the power was supplied. The optimal settings to obtain a uniform film were 300 watts (lower electrode), 600 mTorr, a CHF_3 flow rate of 200 sccm, and an electrode temperature of 18 C. The deposition rate and nonuniformity (defined as range/(2*mean)) under these conditions are 2700Å/min and 8%, respectively. If the outer 20 mm of the wafer radius is excluded, the nonuniformity improves to 2 %. The optimal film thickness is 400Å, which is achieved with a 9 second deposition time.

3.3 Sandia Microengine

The Sandia microengine[9] is the MEMS structure used for time-to-failure and friction studies. The microengine, shown in figures 1 and 2, consists of two electrostatic comb drives positioned at right angles to each other and linked to a 50 µm-diameter gear. The thin Teflon-like film is deposited on a released and dried microengine wafer sample. The friction measurements are obtained from operating microengines and time-to-failure measurements are obtained when the engine seizes. The microengine is created through a process that utilizes four-levels of polysilicon with silicon dioxide sacrificial layers.

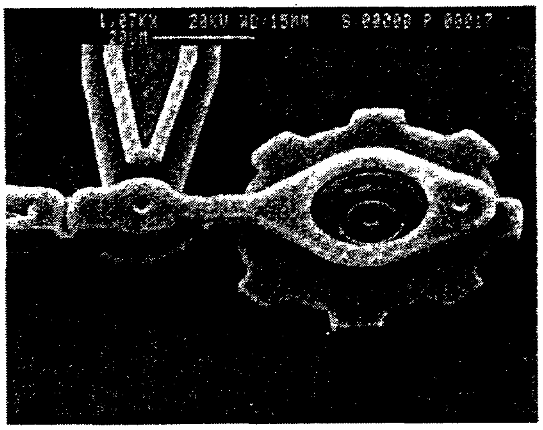

Figure 1. Electrostatic Comb-driven Microgear [10]

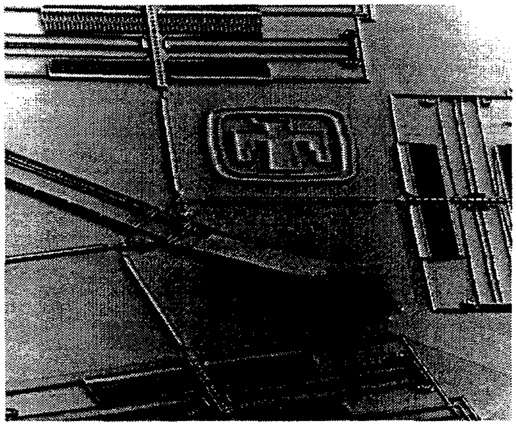

Figure 2: Sandia Microengine positioning a mirror

4. RESULTS AND DISCUSSION

4.1 Contact Angles, Index of Refraction, and Breakdown Voltage

Several film properties of the teflon-like films are consistent and repeatable over a wide range of deposition conditions. Measurement of the contact angle with water for the film showed the average contact angle to be 107.8 with a range of 102° to 112°. Figures 3 and 4 illustrate the difference in contact angles for SiO_2 and the teflon-like films. The refractive index is 1.4 with a standard deviation of 0.01. The refractive index and contact angle indicate the film is very similar to bulk Teflon pTFE, Table 1, and of comparable quality to those reported elsewhere.[4-6] Breakdown voltages (V_{bd}) for a 150 Å thick film) are between 3 and 4 volts, which translates to an electric field breakdown (E_{bd}) of 2 to 3 MV/cm or 20 to 30×10^7 V/m. These values are relatively low when compared to that of SiO_2 which is on the order of 110 to 120×10^7 V/m, but significantly higher than the value reported in table 1. This higher breakdown voltage of these films compared with thin bulk Teflon films may be due to fewer defects.

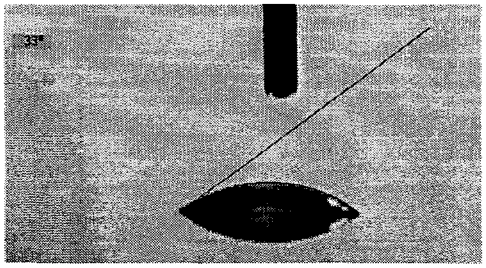

Figure 3. Contact Angle of Water on SiO_2

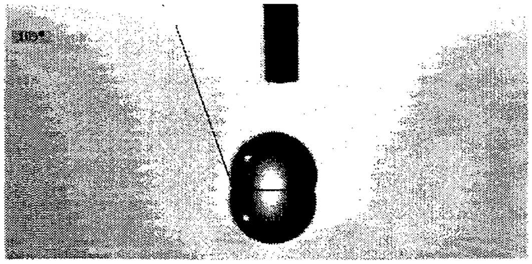

Figure 4. Contact Angle on Polymer Film

Electrical

Volume resistivity: 10^{16} Ohm m

Surface resistance: 10^{16} Ohm

Bulk breakdown voltage: $\approx 4 \times 10^{7}$ V/m

Thin-film breakdown voltage: $>> 4 \times 10^{7}$ V/m

Dielectric constant: 2.1 (50 Hz - 10 GHz)

Dissipation factor: 0.0003 (50 Hz - 10 GHz)

Chemical

Stable and inert (-190° up to +250° C)

Oxidative stable

Mechanical

Young's modulus: 4×10^{8} N/m^2

Bending strength: 18×10^{6} N/m^2

Tensile strength: 25×10^{6} N/m^2

Fracture strain: 300 - 500%

Optical

Refractive index: 1.4

Optical transmission: >95%

Thermal

Stable, unflammable, and shape memory

Minimum temperature: - 190° C

Maximum temperature: 225° C

Melting point: 327° C

Decomposition temperature: ≈ 400° C

Melt viscosity: 10^{10} Pa sec

Thermal conduction: 0.24 W/mK

Thermal capacity: 1.05 J/gK

Expansion coefficient: 8×10^{-5} 1/K

Physical

Critical surface tension: 18×10^{-3} N/m

Contact angle with water: 108°

Friction coefficient with respect to steel: 0.04

Specific gravity: 2.20 g/cm^3

Non-permeable for fluids (except He)

Table 1. Properties of Teflon® (PTFE) from Literature Data [11-13]

It was discovered that these Teflon-like films are readily removed with oxygen plasmas, and could be patterned using a suitable masking material. After stripping the Teflon-like film, the contact angle measures 45°, which is comparable to those prior to exposure.

4.2 Film Conformality

Film thickness falls off rapidly in the undercuts beneath polysilicon overhangs, as seen in Figure 5. The nonconformal nature of the film deposition is common to both the remote and RIE deposition modes. Work by Man[4] showed that it is possible to deposit films that have top-to-bottom aspect ratio of 3. In that study, depositions were performed in a Faraday cage and required deposition times on the order of one hour. Efforts to duplicate the Faraday cage approach by operating the triode etcher in remote mode, were unsuccessful. To confirm the presence of the teflon-like film beneath overhangs, large microgears with a diameter of 1600 μm are used. The microgear is first released and supercritically dried with CO_2 to create the narrow diffusion channel. This provides for a maximum lateral diffusion of 800 μm with diffusion gap thickness between the gear and the substrate of approximately 2 μm. Our teflon-like films have the ability to penetrate the narrow diffusion channel. To confirm the presence of polymer beneath the microgears, the gear is removed using adhesive tape following a deposition. The contact angle is then measured with water in the area that is directly beneath where the gear was located. Contact angle measurements of 108° indicate the surfaces are hydrophobic confirming the presence of polymer. For comparison purposes, the contact angle underneath structures on uncoated wafers was 33° (hydrophilic). From the contact angle study, it is apparent that the film is depositing deeply into the undercut regions, however the film thickness is indeterminant.

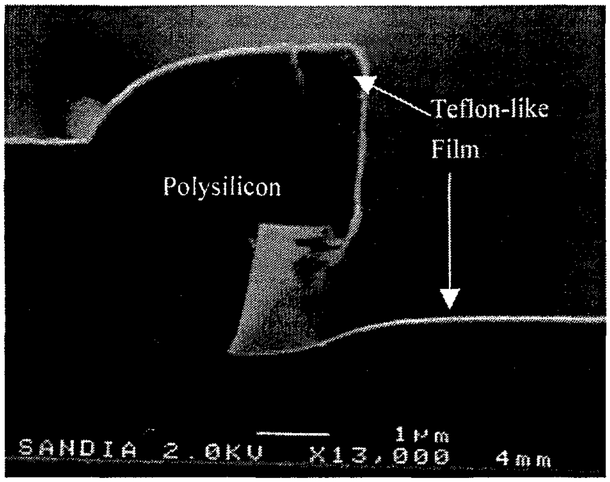

Figure 5: Teflon-like Film deposition into a narrow channel.

To determine the limits of how far the diffusion-limited film can penetrate into a narrow channel, quarter-wafer samples coated with a thermal oxide are turned upside-down on top of an underlying wafer with etched support structures to provide a diffusion gap of approximately 3 μm. Following the deposition, the wafer sample is turned back over and the contact angle measured from the outside edge towards the middle of the sample. Thirty-one separate contact angle measurements were obtained. Our measurements indicate that the film diffuses approximately 4 mm before the contact angle values fall below 90°. This diffusion distance is also confirmed through XPS as discussed in Section 4.4. The maximum contact angle is 112° with values decreasing further into the channel.

4.3 Thermal Film Breakdown

Microstructures are subjected to a multitude of thermally stressing environments, particularly the packaging operation, that have the potential to cause film breakdown and subsequent loss of the hydrophobic and lubrication properties for the teflon-like films.

We performed two sets of experiments to study the effects of the film composition as a function of temperature for the RIE mode films. The fluorine content of the film is monitored using FTIR by observing the F-C bond peak, at approximately 1230 cm^{-1}, as a function of temperature. To provide a baseline an FTIR background spectrum of a bare silicon wafer is taken. An FTIR spectrum is taken of the Teflon-like film before being subjected to elevated temperatures. The wafer is then held at the specified temperature for 20 to 25 minutes before each spectra is taken to allow any compositional changes to stabilize. The initial starting thickness of the film is 5670Å measured with the Rudolph ellipsometer. The large film thickness is chosen to ensure a reliable FTIR spectrum is obtained.

In the first set of experiments the wafer was subjected to temperatures of 100, 200, 300, and 400 C in air to replicate the conditions likely to be encountered in packaging operations. There was little change in the F-C bond peak at 200 C, but a dramatic change in peak height is observed between 200 and 300 C, as shown in Figure 6. After heating to 400 C, the contact angle with water decreases from 105° to an average value of 98°.

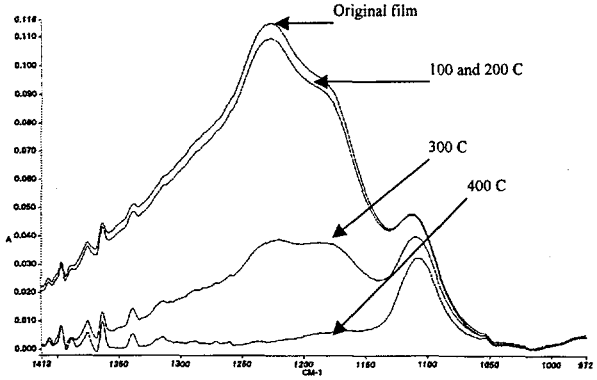

Figure 6. FTIR Spectrum Initial Thermal Test

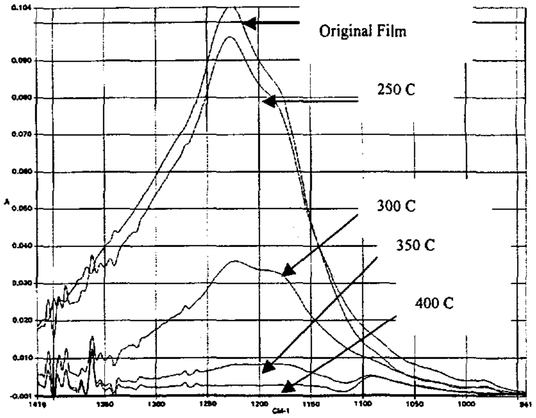

Figure 7. FTIR Spectrum for Detailed Thermal Test

In the second set of experiments the wafer was subjected to temperatures of 250° C, 300° C, 350° C, and 400° C to more closely examine film changes over the range of temperature. As seen in Figure 7, the major film changes occur between 250°C and 300° C. The final film thickness was determined to be approximately 100-150 Å with the original film thickness being 5650 Å. After exposure to 400 C, the index of refraction increased to 1.75. Previous work[14] has shown that Teflon does not decompose by releasing fluorine. The strength of F-C bond is very large and thermodynamically stable. Rather, Teflon is thought to decompose in small C_xF_y fragments that combine to form C_2F_4 or CF_4. As the film decomposes, the F to C ratio stays relatively constant with a loss in film thickness. Since the absorbance at a given wavelength is proportional to the film thickness, the height the F-C peak is proportional to the film thickness. As the film thickness declines so does the peak height. After exposure at 400 C, the peak height has been significantly reduced indicating little film remains. The average contact angle also decreases to 88°.

It should be noted that these tests were performed in open air and atmospheric pressure to represent a worst-case scenario. Film loss might be less less pronounced if the heating were performed in vacuum or with an inert gas purge.

4.4 XPS Surface Analysis

The Teflon-like films were analyzed for elemental composition and surface chemistry by XPS. Analysis was performed on two wafers that had the direct plasma exposure film and two samples with the diffusion limited film. The direct plasma exposure samples had an average film thickness of 440 Å. For the two diffusion-limited film samples, we were not able to obtain a film thickness. It is believed these films are monolayer or perhaps several monolayers in thickness.

A normalized survey spectrum from near the center of the wafer is shown in Figure 8. The spectra are quite similar for both wafers, showing a film containing primarily C and F, with small amounts of O and trace amounts of Na, Si, Ca, Cr, Zn and I. Elemental compositions are listed in the Table 2. The Zn probably occurs as a contaminant in the vacuum system, and is not thought to originally be present on the coated wafer samples. The small Si is probably an artifact of the minimal film thickness. All other detected elements are believed to be present in the deposited films but those other than F and C are most likely from handling or deposition cross-contamination.

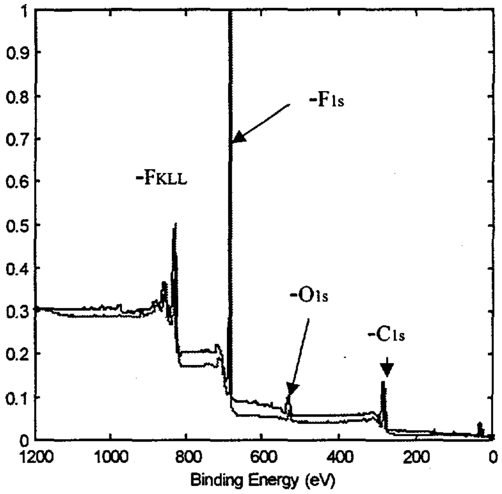

Figure 8. Full XPS Spectrum for RIE mode deposition

RIE mode Teflon-like film	C	O	F	Na	Si	Ca	Cr	Zn	I
1	43.0	2.2	54.3	0	0.2	0.0	0.0	0.1	0.1
2	46.4	5.2	47.3	0.1	0.5	0.1	0.3	0.1	0.1

Table 2. XPS Elemental Compositions (%) for Direct Plasma Exposure Teflon-like films.

To provide more detail as to the bonding structure for the Teflon-like films, normalized high resolution spectra for the C1s region are shown for the RIE mode and diffusion-limited films in figures 9 and 10. The spectrum for the RIE mode film shows the primary peaks corresponding to -CF_3, -CF_2-, -CF-, and $(C\text{-}CF)_x$, respectively, with the highest population in the $(C\text{-}CF)_x$ peak. For the diffusion-limited film, the spectrum shows peaks corresponding, from left to right, to -CF_3, -CF_2-, -CF-, $(C\text{-}CF)_x$, and C-H, with the highest population in the -CF_2- peak. The diffusion-limited sample shows a shift to higher order F-bonding species, relative to the direct-plasma exposure samples. Given that the diffusion-limited films are deposited great distances from the channel entrance, it appears that whatever species are responsible have low sticking coefficients and surface reaction probabilities.

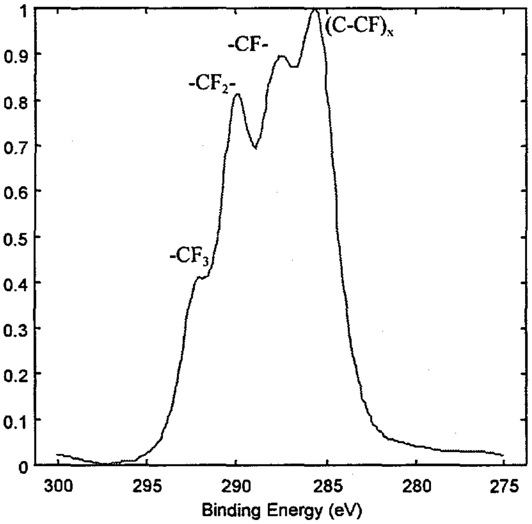

Figure 9. High Resolution C1s Spectrum forDirect-Plasma Exposure or RIE mode Film

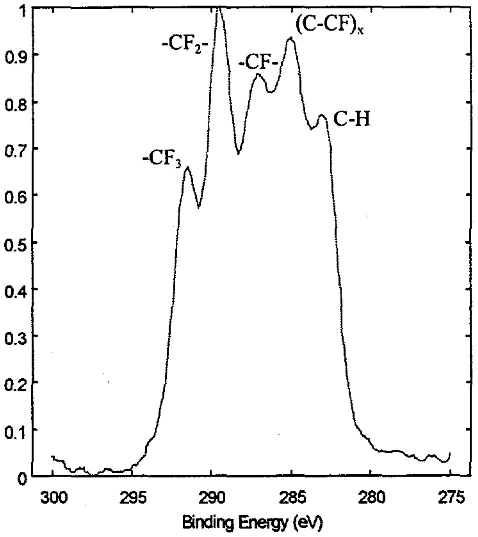

Figure 10. High Resolution C1s Spectrum for Diffusion-limited film

XPS can be used to determine how far into a channel the teflon-like films can be deposited. We acquired XPS spectra every 1.270mm starting at the entrance to the channel. Review of the spectra shows there to be a steady loss of intensity in all of the CF_x species peaks, while intensity steadily gains in the C-H/C-C peak region. Since there is no significant change in the "fingerprint" of the CF_x species peaks as a function of location, it is apparent that the concentration of CF_x species simply decreases the deeper the species have to travel into the diffusion channel.

Shown in figure 11 is a plot of F, C, Si, and O as a function of distance from the entrance to the diffusion channel. The figure shows that F is lost fairly smoothly as the distance from the edge is increased, with a slight overall decrease in concentration of total C species. In addition, it is observed that both the Si and O concentrations increase with distance from the edge of the wafer, consistent with a decrease in total coating coverage as the distance from the channel entrance increases. We estimate from figure 11 that some teflon-like film is still present approximately 5 to 6 mm's into the channel. This distance is consistent with the distance obtained from contact angle measurements, which indicated that the film is still present 4 mm into the channel

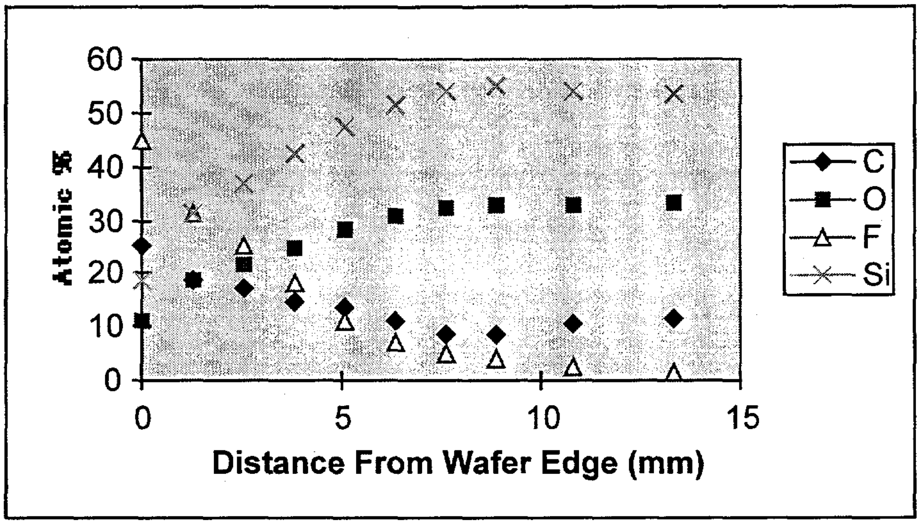

Figure 11. Fluorocarbon Diffusion Distance into Diffusion-limited channel

4.6 Friction and Time to Failure Measurements

Although plasma-deposited fluorocarbon films have been shown to reduce or eliminate post-release stiction and are durable under repeated contact of coated surfaces[4], their impact on friction under continual sliding contact is not known. Sliding friction is of significant interest in the case of the Sandia microengine and geared micromechanisms where the rotating elements are supported by journal-type bearings. We have begun a series of experiments to investigate the effect of the fluorocarbon films on the coefficient of friction (COF) and wear lifetime in such mechanisms. The approach is based on the analysis of friction in the microengine by Miller et al.[15]. The method involves the acquisition of gear position versus time data under the influence of specified drive signal to the microengine. By matching the data to the model, which includes the effect of friction, a coefficient of friction is extracted.

An initial observation is that film thicknesses greater than approximately 1000Å provide enough material in the bearing areas to interfere with normal device operation. Therefore, film depositions in the range of 100 to 500Å are analyzed. Figure 12 is an example of the data taken on a microengine coated with 200Å of fluorocarbon film and operated for 30 minutes at 15,000 revolutions per minute. Following the method of Miller et al[14] the first 90° of rotation, where the model is most accurate, is used to extract a coefficient of friction of 0.07. This coefficient of friction corresponds well with that typically observed for bulk Teflon on Teflon (COF = 0.04) [16]. The overall effect of the fluorocarbon film is improvement in the behavior of the microengine relative to an engine which has no coatings of any type, i.e. polysilicon-to-polysilicon contact (COF =0.7-1.0). For engines with a SAM coating of octadecyltrichlorosilane, ODTS, the COF of 0.08 is nearly identical to that of the fluorocarbon film.

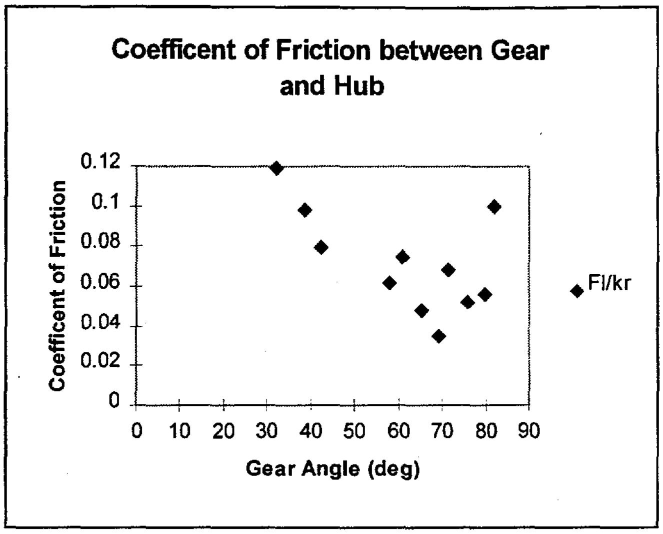

Figure 12: Coefficient of Friction versus Angle

In an effort to determine the potential lifetime of the microengine, we deposited the teflon-like film on three wafer samples containing the Sandia microengine. A fourth wafer sample was left uncoated and used as a control. The film was deposited at the optimized parameters of 300 watts power to the lower electrode, 200 sccm CHF_3 and 600 mTorr pressure. Deposition time was 9 seconds, which results in an estimated film thickness of 400 Å to the plasma-exposed regions.

Failure of the microgear used for the test was determined by measurement of free rotation of the gear with an applied square-wave voltage of 25-35 volts. The microengines are driven at 30,000 revolutions per minute (RPM), with a drive signal preferentially chosen to result in rapid failure of the gear mechanism. Optimized signals used for normal conditions would result in a longer operational lifetime. When the gear would no longer freely rotate, it was considered to have met it's failure limit. Results of the tests are provided in Table 4. Application of the teflon-like film results in a marked improvement in lifetime, with the mean time to failure increasing by a factor of 3.1.

Sample	Time To Failure (minutes)	Total Revolutions
Control 1, Uncoated Sample	7	210,000
Control 2, Uncoated Sample	11	330,000
Control 3, Uncoated Sample	14	420,000
Mean and (Standard Deviation)	**10.7 (3.5)**	**320,000 (105,360)**
Teflon-like Film 1	31	930,000
Teflon-like Film 2	30	900,000
Teflon-like Film 3	39	1,170,000
Mean and (Standard Deviation)	**33.3 (4.9)**	**1,000,000 (147,990)**

Table 4. Microgear Time to Failure Summary

5. CONCLUSIONS

Teflon-like films can be readily deposited on microstructures using a Lam 384T oxide etch system utilizing CHF_3 as the polymer precursor. Lifetimes of microengines with the film are a factor of 3 greater and the COF is reduced by an order of magnitude when compared to samples with no friction reducing coating. The COF for these films at 0.07 is nearly identical with SAM coatings and are only slightly higher than bulk Teflon. The breakdown voltage of the teflon-like film is a factor of 5 greater than that of thin bulk Teflon. Film properties, such as contact angle with water of 105° to 110°, an index of refraction of 1.4, are constant over a wide range of processing conditions. The films are very hydrophobic and have the ability to penetrate into narrow openings beneath microstructures. Conformality is similar whether the film is deposited using the remote or RIE plasma modes. Film properties are comparable with those of bulk Teflon.

The plasma conditions to obtain a uniform film at 400 Å are 300 watts, 600 mTorr, a CHF_3 flow rate of 200 sccm, a electrode temperature of 19 C, and power being supplied to the lower electrode (RIE mode) for 9 seconds. Film deposition is predominately line-of-site, but our studies prove that the film is deposited into narrow openings. The diffusion-limited film is very thin and exhibits monolayer coverage with properties similar to those deposited line-of-site.

XPS and FTIR analysis of the films shows chemical structure similar to that of bulk Teflon® and to films presented in the literature for plasma deposited films using CHF_3. These analyses also showed the film to be susceptible to degradation when subjected to temperatures, in atmosphere, above 250 C. XPS analysis showed line-of-site depositions to be dominated by $(C\text{-}CF)_x$ bonds followed by, in order of decreasing concentration, -CF-, $-CF_2-$, and $-CF_3$. Films deposited through diffusion, and therefore not line-of-site to the plasma, where dominated by $-CF_2-$ followed by $(C\text{-}CF)_x$, -CF-, $-CF_3$, and a minor amount of C-H bonds.

6. ACKNOWLEDGEMENTS

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