Chapter 4
Chapter 4: PTFE as an masking material: Results and Discussion

In Chapter 3 the results on use of PMMA as masking material are given. The other material selected for the present work is polytetrafluoro ethylene (PTFE). PTFE is deposited by sputtering. Structural characterization of the film is carried out by FTIR and XPS. Further the physical characterization of the films is done by contact angle and thickness measurements. This is very important as the adhesion of the film and the substrate is a very important criterion for masking. The interfacial tension and work of adhesion is calculated from the contact angle data for calculating the adhesion between the PTFE film and silicon substrate. Its performance as masking material is tested and results are given and discussed in this chapter.

Polytetrafluoro ethylene (PTFE) is a very unique polymeric material because of the various distinguished properties such as high electrical resistivity, chemical and thermal stability, high hydrophobicity, low surface tension, potential biocompatibility and so on. PTFE has large number of applications in bulk as well as thin film form. Very recently the thin films of PTFE are being tested as masking material in MEMS technology. Large number of research papers are available on these topic. Following article is on literature survey limited of PTFE thin films obtained by various techniques.

4.1 LITERATURE SURVEY

PTFE thin films have been deposited by various techniques such as plasma polymerization, RF, DC and magnetron sputtering, laser ablation etc. Some researchers have also carried out surface modification of PTFE to increase wettability, hence, adhesion

4.1.1 Deposition of PTFE by various deposition techniques

He JL et al. employed ion beam sputtering technique to prepare thin films of PTFE. The sputtering energies of 100, 1000 and 1500 eV were used. The IR spectra show a strong absorption band in the region of 1000-1400 cm\(^{-1}\) which is characteristics
of CF stretching vibrations. For Ion Beam Sputtering Deposition (IBSD), absorption around 1200 cm\(^{-1}\) is strong. Peaks at 1220 and 1150 cm\(^{-1}\) are attributed to CF asymmetric and symmetric stretching vibrations in CF\(_2\) groups. Therefore author reports that thin films prepared by IBSD may be structurally quite similar to PTFE target material. XPS of these films show peaks at 294, 292, 289.5, 287.4, and 284.6 eV due to CF\(_3\), CF\(_2\), CF, G CF and C-CH bonds respectively. No signal due to C=O or C-OH could be observed for any films. The carbon to fluorine (C/F) ratio of 0.8 and 0.6 are obtained from the analysis of the films deposited using 700 and 1200 eV bombardment respectively. This confirmed that ion beam bombardment at higher energy caused a higher degree of defluorination and molecule damage.

Smasuz T \etal\(^2\) prepared PTFE films from pressed powder pellets via pulsed laser deposition using ArF excimer laser. The films were deposited at different temperatures and then annealed at 500°C for 30 min. They found that the thickness does not depend upon substrate temperature. Further the annealed films were found to be pin hole free. FTIR spectra show peaks at 1207 and 1151 cm\(^{-1}\) for GF\(_2\) asymmetrical and symmetrical stretching, 640 and 626 cm\(^{-1}\) for CF\(_3\) wagging modes; as well as the PTFE bending and rocking modes at 553 and 507 cm\(^{-1}\). XPS intensities corresponding to CF and GF\(_3\) groups were negligible compared to CF\(_2\). The F/C ratio was near to N\(_2\). Authors measured the adherence of the films to the substrate by tensile strength technique. Strength values up to 2.1 MPa were obtained. These properties are of great significance for the purpose of protecting coating.

Womack M \etal\(^3\) have deposited PTFE thin films using femto-second pulsed laser ablation. A Ti-sapphire femto-second pulsed laser was used to deposit thin films of PTFE on <100> oriented single crystal silicon substrate. SEM, AFM, XRD, XPS and FTIR were used to characterize the structure, composition and properties of PTFE films. SEM showed a continuous, strongly adherent, pin hole free and stoichiometric film. The film color was white suggesting absence of fluorine deficiency. Films were also smooth due to impact of high kinetic energy species emitted from the target and high substrate temperature. Thickness of the film was in the range of 700-900 nm. The deposition rate was averaged to 20 nm/min. XPS indicated identical composition of PTFE target and deposited film. The surface of the film is composed of F and C atoms. The F/C ratio for the bulk and the thin film were calculated to be 1.1 and 1.2 respectively. The F/C ratio is the measure of stoichiometry. FTIR spectrum indicated peaks at 1250 cm\(^{-1}\) (CF\(_3\) stretch), 1195 and 1145 cm\(^{-1}\) (CF\(_2\) asymmetric and symmetric stretching) which confirms that the
deposited film is exclusively PTFE. The absence of CF$_2$ deformation band at 620-640 cm$^{-1}$ suggests the possibility of cross linking or alternatively well oriented film with main chains perpendicular to the substrate surface. A femto-second laser is also a superior processing tool for micromachining and thin film deposition of PTFE. Direct write technique using femto-second laser, can be used to fabricate fraction of mm size motor machined into bulk PTFE.

4.1.2 Surface modification of PTFE by various techniques

Kim SR et al  have carried out Chemical etching, plasma and ion beam treatments to modify the surface of PTFE. The chemical etching showed substantial defluorination and the adhesion strength was fairly high. The argon plasma treatments introduced very large amounts of oxygen into the surface, and the surface was very smooth with a crater like structure. XPS showed an F/C value of 1.4 for the 30 min argon plasma treated sample which is quite low compared to the 1.97 F/C ratio of untreated PTFE. Chemical etching lowered the contact angle to 50°, while argon plasma treatment lower the contact angle to 30°. It is reported that the reason for low contact angle values might be defluorination of PTFE film surfaces. This also can be seen from the low F/C ratio of 1.4 for argon treated films. The SEM photograph of the argon ion treated PTFE at 1 x 10$^9$ ion dose show morphological change after treatment. The treated sample shows a widely spaced spire-like surface.

Wilson DJ et al  treated PTFE in low power plasma using a series of feed gases viz. oxygen, argon, nitrogen and hydrogen and sputtering the resulting surface modifications were evaluated by X-ray photo electron spectroscopy (XPS), SIMS, contact angle measurement and AFM. The treatment was carried out in a half wave helical resonator at a resonant frequency of 13.56 MHz. Gas flow was set to 85 sccm. The operating pressure was in the range of 8.59*10$^{-5}$ mbar. The irradiation time was one min. For untreated PTFE, the B.E. at 291.8 eV is attributed to CF$_2$ and the 285.0eV is attributed to C-H moieties. The difference of B.E. in these two peaks is 6.8 eV which is in close comparison to 6.5 eV given by D Briggs. The F1S spectra showed the peak at 689 eV. The F/C ratio was calculated to be 1.98. The treated PTFE showed peaks at 293.5, 291.8, 289, 286.5 and 285 eV corresponding to CF$_3$, CF$_2$, CCF, O=C=O, C=O, C=O and GH moieties respectively. The F1s spectra showed the peaks at 689, 687.7 and 686 eV attributed to CF$_3$, C-CF$_2$ and C-CF groups respectively. This shows an increase of symmetry after Ar treatment.
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An increase in wettability was observed for Ar treatment films. The contact angle of 85° and 28° compared to 104° and 75° for untreated films was observed. This change may be attributed to constant formation of polar groups at the surface. In order to correlate surface chemistry with wettability in a simplified manner, authors have imagined a surface to be comprised of two regions with distinct chemistry, one being relatively less wettable and the other more wettable by a working fluid of interest. The surface concentrations of these two regions are designated $X_l$ and $X_r$ for the less and more wettable fractions, respectively, with $X_l = X_r = 1$. Thus, for example, when the working fluid is PBS, the idealized surface of virgin PTFE is smooth and chemically homogeneous with $X_l = 1$, and plasma treatments can induce finite concentrations of $X_r$, depending on the number and nature of polar groups introduced to the surface in addition to some roughness. The authors have reported $X_l$ and $X_r$ values for PTFE surfaces on the basis of deconvolution of peak areas in C1s spectra of XPS measurements. The wettability of idealized virgin material is regarded as arising from a smooth surface saturated with CF$_2$ groups. Plasma modification may introduce groups that are either more polar than C-OH and C-N, or more apolar, than CF$_3$ and HCF$_3$. The former groups are thought to arise by modifications of side groups in the initial material, and the latter at chain terminae either present initially or introduced by chain scission. For Q plasma treated sample, only a small fraction of polar side groups is introduced, combined with additional light etching. By contrast Ar, N$_2$ and NH$_3$ plasma treatments progressively introduce concentration of $X_r$ larger than for O$_2$ treatment, but the level of etching is similar. The chemical changes induced were side-group modification; Q treatment

The extent of plasma etching, which occurs by ablation of chain segments on the outer layers of materials, was investigated using atomic force microscopy (AFM). The observations by the authors imply that all low power plasma treatments caused light etching of the sample surfaces, producing characteristic relief of PTFE surfaces, and the macroscopic topography of the original surfaces was maintained. According to authors, etching occurred by virtue of chain scission of G-C bonds in the polymer backbone and subsequent release of -[CF$_2$]- fragments. The increase in surface rugosity was found to be on the submicron scale, leading to enhancements of surface are by $\sim 5 - 11$ % for all treated surfaces.

Hua X et al. have treated PTFE films by non equilibrium microwave plasma of a mixture of water vapor and argon at lower pressure. The power used for the
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Modification was 400 W for 120 s. The properties of the PTFE surfaces were evaluated by the means of contact angle measurements, adhesion strength measurements, ATR-IR and XPS. H₂O/Ar plasma treatment led to significant decrease of the water contact angles from 110 to 23.6 ° under optimal conditions, which resulted from the substantial surface defluorination and the introduction of an unusual amount of oxygen and polar functionalities as revealed from XPS and FTIR. The adhesion strength increased from 26.7 N cm⁻² for pristine PTFE to 583 N cm⁻² for plasma treated PTFE. There is a increase in adhesion strength by a factor of 22 which indicates that plasma treatment is rather effective for modifying the surface properties of PTFE and could meet the requirements for practical use. This decrease in contact angle indicates that the H₂O/Ar plasma treatment is much more effective than the chemical treatment, ion irradiation and various plasma treatments with pure gases. There was an increase in contact angle from 23.6 to 60 ° after storage of the film for 10 h. This might be due to the polymer chain reorientation of the oxygen and fluorine species from the bulk to the surfaces. After the plasma treatments, F/C ratio decreased to 0.41 from 1.68. This indicates that plasma treatments introduce a great amount of oxygen resulted in substantial defluorination. The XPS spectra showed peaks at 292.4, 288.8, 286.2 and 284.6 eV for CF₂, C=O, C-O and CH bonding respectively for plasma treated films. It is seen that the chemical environment of the carbon on the PTFE surface changed significantly with the defluorination and the introduction of oxygen during the plasma treatment, which contributed to the improvement of the PTFE surface properties. The FTIR spectra indicated peak values at 2882.8 and 2931.9 cm⁻¹ for sp³ CH vibration, 3031.1 cm⁻¹ for sp² CH vibration and 3554.4 cm⁻¹ for OH stretching vibrations. It is seen that many hydrophilic groups were introduced to the PTFE surface during the plasma treatment, which contributed to the wettability of the samples.

Zhang Y et al. have carried out surface modification of PTFE films by Ar⁺ ion beam irradiation with varying ion energy and ion dose. The treatment was carried out a 2 KeV Ar⁺ ion beam at ion current density of 0.30 mA/cm² and different fluence values. XPS of the modified film showed peaks at 286.2, 288, 290 and 294.1 eV corresponding to C-O, C(CF₃), C-F and CF, respectively. The incident energetic species react initially with the PTFE chain and give rise to chain scission and defluorination of the CF₂ group. The F and CF₂ free radicals formed, further, react to form the CF group and the CF group in the polymer chain. The CF group may further breakdown to generate a quaternary carbon free radical, which can react with the CF₂ species to form the cross...
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linked PTFE chains. Higher Ar⁺ ion fluence will result in more chain scissions on the PTFE surface, hence leading to a decrease in CF₂-CF₂ specie concentration on the surface of the Ar⁺ ion beam treated PTFE film. The reduction in CF₂ group concentration in the Cls core level spectra is probably attributable, in part, to the etching effect on the PTFE surface caused by the incident Ar⁺ ion beam. It have been reported that ion beam can lead to the chain scission, cross-linking, carbonization and other chemical processes. Authors have also suggested that the increase in hardness of a polymer is a manifestation of the cross-linking reactions. Another evidence of presence of free radicals on the Ar⁺ ion beam treated PTFE surface is the increase in oxygen concentration of the surface after it has been exposed to air. Etching and defluorination effects also lead to the formation of some active species, such as free radicals, on the surface of the PTFE substrate. Further, decrease in F/C ratio from about 1.9 to 1.5 of PTFE substrate before and after atmospheric exposure suggests that the reaction of the reactive species (such as free radicals) with oxygen in the air.

4.1.3 Sputtering of PTFE

Beiderman H et al.⁴ carried out deposition of fluorocarbon plasma polymer films by means of RF sputtering of PTFE in argon, nitrogen and in a self sputtering mode. Static contact angles of 100 and 105 were measured in N₂ and Ar atmosphere respectively. The sputtering was done at a RF power of 125 to 200W. The XPS spectra show peaks at 294, 292, 290.2, 289.2, 285.6 and 285 eV corresponding to CF₃, CF₂, CF-CF₅, CF, CCF₂ and C-C bonding for argon treated/deposited/sputtered film. FTIR show absorption peaks at 1722 cm⁻¹ for C=CF₂, 1288 cm⁻¹ for CF₂, 1100 for CF₂ groups for Argon sputtered films. The static contact angle was measured for PTFE films sputtered in argon plasma. Contact angle was found to be 105°.

Beiderman H et al.⁹ reported study of an RF polymeric material such as PTFE and polyethylene (PE) deposited by RF magnetron sputtering technique. The input power for PTFE sputtering was 220 W and for PE was 80 W. The F/C ratio calculated from the XPS analysis gives a value of 1.3. The PTFE film seem to amorphous with featured of densely packed fibers perpendicular to the substrate, when viewed under SEM. FTIR shows bands due to C-F and C-C stretching in range of 1100 and 1300 cm⁻¹ (doublet with maxima at 1152 and 1207 cm⁻¹) for bulk PTFE. The strongest absorption bands for the bulk PTFE at 502, 625 and 638 cm⁻¹ are due to deformation vibrations of CF₂ groups.
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Zhang Y et al. deposited dielectric polymer films of about 40-300 nm in thickness were deposited on Si <100> substrates via RF plasma sputtering of PTFE target using different sputtering gases viz. Ar, N₂, CF₄, H₂. Composition of the deposited material, dielectric constant and deposition rate were found to be dependent on the gas used. Ar, CF₄ and N₂ plasma gave rise to PTFE like films. Non reactive Ar plasma gave rise to highest deposition rate. C1s spectra of PTFE-Si in Ar can be curve fitted into 7 components with BE's at 284.6 eV for C-H species, at 286.2 eV for CH₂-CF₂ species, at 287.4 eV for C-CF₃ species at 288.6 eV for CFH species, at 290.0 eV for CF species, at 292.0 eV for CF₂ species and at 294.1 eV for CF₃ species. The FTIR of the pristine PTFE displays the characteristic absorption bands CF₂ at 514, (CF₂ wagging), 640 (CF₂ rocking), 1152 (asymmetric CF stretch) and 1208 (symmetric CF stretch). The argon sputtered PTFE films exhibit a strong broad band at about 1230 cm⁻¹ (an overlap of CF₂, CF₃, and CF₄ vibrations), and relative weak absorption bands at 740 and 991 cm⁻¹ (CF₃ vibrations). Medium intensity absorption band at about 1520 cm⁻¹ (aromatic C-F stretch) is observed in the PTFE.

Surface morphology is of great importance to the application of deposited polymer films as dielectric barriers or passivation films of silicon wafer surfaces. A uniform defect free surface is preferable in the planarization process. AFM images of sputtered PTFE on silicon surface in argon atmosphere show a slightly rough silicon substrate. This indicates that the technique can produce almost molecularly flat surfaces. Results of the film thickness measurement also indicate that the uniformity in thickness of the sputtered PTFE film falls within ±5%. Physiochemical characterization indicated that the argon sputtered sample gave rise to highest deposition rate compared to H₂ or O₂ gas. This is due to the fact that Ar is a non reactive gas; the sputter generated active species are not consumed by the argon plasma. On the other hand, some of the active species are consumed by the other sputtering gas plasmas. Thus argon plasma gives rise to the highest deposition rate among the gases used.

Surface hydrophobicity is another important property of the polymers used as barrier films and as dielectric materials. The water contact angles 108° and 20° is obtained for the pristine PTFE surface and of the pristine silicon surface respectively. The water contact angle decreases slightly to a value 106° for sputtered PTFE in argon plasma. The hydrophobic nature of the sputtered PTFE in argon plasma is consistent with the high F/C ratio of the fluoropolymer films. F/C ratio obtained for the pristine PTFE and sputtered PTFE in argon plasma are 2 and 1.6 respectively. The interaction of the
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Sputtered PTFE films with the plasma preactivated silicon substrates was evaluated by the 180° peel adhesion test. Copper foil adhesive tapes were applied to the various sputtered PTFE surfaces and subsequently peeled off on the tensile tester. The sputtered PTFE sample deposited in argon plasma has 180° peel adhesion strength of about 3.3 N/cm. This value indicates a good adhesion to silicon surfaces.

Zhang Y et al. have deposited fluoropolymer thin films on <100> oriented single crystal silicon substrates via argon plasma sputtering of a PTFE target and plasma polymerization of 1H, 1H, 2H-heptadecafluoro-1-decene (HDFD). The surface composition and molecular structure of the deposited fluoropolymer films were analyzed by XPS, SIMS and FTIR. RF magnetron sputtering and deposition of PTFE films on silicon substrates was carried out at a RF power of 350 W for 1200 s. An s-PTFE (sputtered PTFE) film of 240 nm thickness was reported by the authors. The XPS spectrum of pristine-PTFE film showed one distinct peak at 292.0 eV corresponding to CF₂ species. The s-PTFE film showed peaks at 284.6 eV (C-H), 286.2 eV (CH₃-CF₃), 287.4 eV (C-CF₃) 288.6 eV (CFH), 290.0 eV (CF), 292.0 eV (CF₂) and 294.1 eV (CF₃).

The F/C ratio of 1.57 was obtained for the s-PTFE films. Decrease in CF₂ and CF₃-CF₂ species and increase in CF, CHF and CF₃ species is observed with increase in RF power for the plasma polymerized film. Also there was decrease in F/C ratio due to increase in RF power. The FTIR spectra indicated peak values at 514, 640, 1152 and 1208 cm⁻¹ corresponding to CF₂ wagging, CF₂ rocking, asymmetric CF stretching and symmetric CF stretching respectively for pristine PTFE films. The s-PTFE films showed a broad band at 1230 cm⁻¹ corresponding to CF, CF₂ and CF₃ overlapping vibrations, 740 cm⁻¹ corresponding to C-F stretching deformation, 1520 cm⁻¹ corresponding to aromatic CF stretch and 1720 cm⁻¹ corresponding to CF = CF stretching vibrations. The plasma polymerized film showed peaks at 640, 1152 and 1208 cm⁻¹ corresponding to CF rocking, asymmetric CF₂ stretch and symmetric CF₂ stretching. The XPS and FTIR results suggested that the surface composition and chemical structure of the plasma polymerized films deposited at higher RF power were closer to those of the s-PTFE.

Water contact angle showed values of 108° for pristine PTFE, 106° for s-PTFE films. Water contact angle measurements indicated that both s-PTFE and plasma polymerized films could give rise to highly hydrophobic surfaces with good uniformity. Peel adhesion test suggested that both the s-PTFE and plasma polymerized films were strongly tethered to the surface of silicon. Adhesion strength of 3.3 N/cm is obtained for sputtered PTFE deposited on silicon substrate.
4.1.4 Applications of fluorocarbon films in micromachining

The use of silicon in micromachining is limited primarily to single crystal and polycrystalline silicon systems. Most recently there is an increasing trend towards utilization of polymer materials in microelectronics and biomedical fields due to the range of properties exhibited by polymers. Ample references are available in the literature. Few related to the present work are given here.

Lee LP et al. have reported high etching selectivity of different fluoropolymers for the fabrication of high aspect ratio polymer (HARP) microstructures. They developed transparent fluoropolymer based free standing cantilever for use in microfluidic devices. 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 photoresist (PR) on the family of fluoropolymers including PTFE, Tefzel®, FEP and Teflon® AF. Satisfactory pattern transfer capability down to sub-micron dimension is achieved through low energy ion beam technology. Successful surface modification was demonstrated for the adhesion of photoresist on the fluoropolymers. The optimum selectivity of etch rates between fluoropolymers and photoresists is determined through the 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 oblique angle of incident beam. The results have large applications in MEMS community. These polymer cantilevers have direct applications as bio-chemically functionalized tips for an AFM or near field probes within integrated microfluidic system.

PTFE is degraded by radiation with low dose through the main chain scission. This property of PTFE is utilized by Yamaguchi D et al. in micromachining of PTFE. Authors have carried out micromachining of cross linked PTFE using synchrotron radiation direct photo etching method. High aspect ratio microfabrication was carried out. The experiments were performed using SR microfabrication beam line (BL-4) for the compact normal conducting electron storage ring, AURORA-2S. The samples were placed perpendicular to the SR beam in the vacuum chamber. The photon flux of the SR beam through the Be filter was $3.2 \times 10^{11}$ photons/smA$m^2$. A Ni mesh was set on the sample to transfer the pattern. The proximity X-ray masks was also used in some cases. The temperature of the samples was controlled by a hot plate (from room temperature to 473 K).
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The microstructures created by SR direct photoetching were observed under SEM and the etching depth was measured by optical microscope. The surfaces of the samples were analyzed by FTIR for the investigation of SR etching mechanism. Microfabrication of the cross linked PTFE by SR photo etching was carried out successfully. It was confirmed from SEM that the quality of micromachining of cross linked PTFE is as good as that of non-cross linked PTFE. Through the etching rate measurements of various samples, it was found that synchrotron radiation etching rate of cross linked PTFE only depends on the degree of cross linking, neither molecular weight nor crystallinity of the film.

In order to investigate SR induced reaction and desorption mechanism, authors analyzed the surface of SR irradiated sample of thickness of 50 μm by FTIR. The band at 1784 cm\(^{-1}\) is assigned to the terminal double bonds. The bands at 1729 and 1716 cm\(^{-1}\) are attributed to internal double bonds. The appearance of these bands indicates that SR induces main chain scission and dissociation of CF bond in the region which is penetrated by SR. Moreover, the weak absorption band at 1671 cm\(^{-1}\) can be observed. This band is due to CF= C which originates from defluorination around CF. This result suggests that crosslinking reaction is also induced by SR. SR modifies inner region, in which crosslinking reaction is induced much below the melting temperature due to SR high dose rate. These findings might be suitable for the development of microcomponents and other applications taking advantages of crosslinked PTFE, which is available not only in electronics or medical fields, but also in radiation fields.

Yoshida A et al.\(^{14}\) carried out experiments on etching of PTFE films by synchrotron radiation (SR). Authors have deposited PTFE thin films both from the PTFE target by using synchrotron radiation (SR) beam and from PTFE emulsion by spin coating process. PTFE films were deposited through Ni mesh mask with a hole of 7.5 x 7.5 μm on the silicon <100>, glass and metal substrates. The substrate temperature was varied from room temperature to 483 K. The spin coating of PTFE emulsion was carried out at 4000 rpm rotational speed for 60 s. The wafers were baked at 513-673 K for 10 min. The deposited films were characterized by XRD, FTIR and XPS. The etching of the PTFE films was done by SR photoetching process. For the SR beam deposited PTFE, FTIR absorption data shows peaks due to CF\(_2\) and small peaks from CF\(_3\) bonding. XPS analysis showed only C & F components with no trace of impurity. All the properties of both SR induced and spin coated PTFE thin films were almost the same and the authors concluded that the films deposited by both methods were purely PTFE. Etch rate of
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Around 6 μm/min was observed. Nanostructured PTFE is easily fabricated and such a microfabrication process is promising.

Matsumoto Y et al. have studied several deposition techniques and their characteristics of fluorocarbon films. They have developed novel methods for deposition of fluorocarbon films with applications for bulk and surface micromachined devices. First, a fluorocarbon (FC) film is spin coated from cyclic perfluoro polymer (CPFP), which is commercially known as CYTOP is studied. Because of its excellent durability for alkalis or acids, the FC film is used for protection of the circuit area of an integrated accelerometer from a silicon alkaline etching process by 25 wt% TMAH at 90 °C. Secondly FC films are formed on a field free zone with capacitively coupling type plasma polymerization equipment using perfluorinated liquids, as monomer species. The deposition rates and thermal stability have been investigated and reported by the authors.

The morphology of CPFP is fully amorphous due to the ring structure in the polymer main chain. CYTOP was spin coated on silicon wafer at a speed of 2000 rpm. Thickness of the film was around 0.5 μm. The film was pre-baked at 50 °C and post-baked at 200 °C for 60 min respectively. A water contact angle of 110 ° was obtained even after 1 h aging test at 400 °C. Etch rate selectivity of the FC films under 25 wt% TMAH was 500. Direct patterning of the FC film with photoresist is usually impossible because of its low surface energy and high wetting angles. However, Ar or O₂ plasma ashing process facilitated the use of photolithography. The water contact angle after the ashing process at 100 W for 2 min was reduced from 110 to 90 ° due to the surface roughness of the FC films. The FC film shows good adhesion from the result of the Scotch tape test. A 0.5 μm FC film can be etched by O₂ plasma ashing (100 W for 30 min). However, when the patterned FC film was subjected to TMAH solution or HF solution, peeling was observed in the solution, therefore the patterned FC film cannot be used as an etch mask.

Plasma polymerization of FLUORINERT was carried out by Matsumoto et al. at 100 W power. The deposition rate of the FC film was about 150 nm/h at a pressure of 0.6 Torr. If the molecular weight of FLUORINERT becomes large the F/C ratio approaches 2. XPS showed peaks at 291.5, 293.5, 290.6 and 285 eV corresponding to CF₃, CF₂, CF and CH respectively. A poor etch selectivity of 50 was observed for plasma polymerized films. A contact angle of 105 ° was obtained after the aging temperature of 250 °C. Though the properties of the plasma polymerized FC films were poor compared to the spin coated FC film, the surface energy is expected to be much lower than that of
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the silicon substrate. Therefore, these films can be used for the elimination of in use stiction for surface micromachined devices.

Normand P et al have reported a new masking method for protecting silicon surfaces during anisotropic etching. A room-temperature silicon masking approach based on the exposure of silicon to CHF$_3$-based plasma is reported. This plasma treatment leads to ultra-thin (2-5 nm) films that consist of a fluorocarbon top layer and a sub-oxide lower layer and are appropriate for anisotropic wet etching masks. Exposure of silicon to CHF$_3$ plasma generates a composite material referred to as CMPL (composite material by plasma). Normand et al found this material protecting silicon against EPW solution. They further found that films formed under appropriate plasma conditions remain resistant to such solutions at elevated temperatures typically applied for residue free etching of bulk silicon.

In their subsequent paper, Normand et al have seen the resistance of CMPL mask to EPW and KOH as a function of plasma duration, silicon surface preparation and aging. CHF$_3$ plasma exposure of Si surfaces was performed in a Nextra RIE parallel plate plasma reactor with a radio frequency (RF) of 13.56 MHz and a CHF$_3$ gas flow rate of 50 sccm (standard cubic centimeters per minute). The RF power density and the total pressure were fixed at 0.5 W/cm$^2$ and 10 mTorr, respectively (1 Torr=133.322 Pa). The CHF$_3$ plasma exposure time of Si surfaces was selected from 10-120 s range. The conventional fabrication of silicon structures in a silicon wafer through anisotropic wet etching involves the two preliminary steps of formation and patterning of a masking material such as SiO$_2$, Si$_3$N$_4$, or metal films. A 'lift-off'-type of process is used for the CMPL-based patterning. Fluorocarbon plasma under different conditions, leads to the formation of an etchant-resistant CMPL film only onto the silicon surfaces exposed to the plasma energetic-ion flux defined by the lithographic pattern in resist. Such a selective formation of the CMPL film allows micromachining by anisotropic wet etching of the vertical sidewalks. CHF$_3$ plasma treatments of silicon lead to ultrathin masks for versatile micro- and nano-machining using EPW etching solutions. The etch resistance and destruction mode of the films varies within wide limits. Short (e.g., 20 s) plasma treatments are appropriate for fine patterning with depths up to ca. 10 μm, while long (e.g., 120 s) plasma treatments are suitable for deeper (by an order of magnitude) but coarser patterning. The new masks compare favorably with common masking materials such as SiO$_2$ or Si$_3$N$_4$, in terms of achievable patterns and processing options.
4.2 RESULTS AND DISCUSSION ON STRUCTURAL AND PHYSICAL CHARACTERIZATION OF PTFE FILMS

In the present work, PTFE films are deposited on silicon substrates by RF sputtering techniques (see Section 2.2). Ar is used as a carrier gas. The depositions are carried out at different RF powers and for different time durations. Physical parameters such as adhesion and thickness are measured. Structural characterization of the films is done using FTIR and XPS techniques. The performance of the films as masking material is studied by subjecting them to wet chemical etchants such as KOH and TMAH. The results obtained are presented here and analyzed. The results are compared with the ones available in the literature and discussed.

4.2.1 Deposition of PTFE by RF sputtering

The fact that RF sputtering increases adhesion and increases the cross linking densities in the films was utilized to get adherent films of PTFE on silicon substrate. PTFE was selected as it is a chemically inert material. PTFE sheet of thickness 5 mm from DuPont was used as sputtering target. RF sputtering is carried out in argon plasma in parallel plate plasma reactor. The experimental details are given in Section 2.2. PTFE was sputtered on the silicon substrate under following deposition conditions:

- Base pressure: 10^{-3} Torr
- Deposition pressure: 0.2 Torr
- Sputtering gas: Argon
- Argon flow rate: 4.6 sccm
- RF power: 100, 125, 150, 175, 200 W
- Time of deposition: 15, 30, 45, 60, 90 min
- Distance between anode and cathode: 12 cm

In each deposition cycle 7 - 10 samples were prepared for thickness, contact angle, FTIR, XPS and SEM studies. Depositions under certain condition were repeated for 5 - 6 times. The results given here are the average over the repetition cycles.

The thickness of the film was measured by Tally step technique. Figure 4.1 shows graph of the variation of thickness with the deposition power at different deposition times. From Figure 4.1 it can be seen that the thickness of the film increases with increase in power as well as time. However, the variation is larger with time than for power. For example, if one looks at the curve at a constant deposition time of 15 min. It is seen that as the deposition power increases the thickness increases gradually from 500 - 750 Å. Next, the range of thickness at constant deposition power of 100 W with varying time is 500 - 1900 Å. It was observed that even after keeping the longer deposition times (> 90 min) the thickness does not increase much. It is known that
during the plasma processes deposition and etching of the film takes place simultaneously. Negligible increase in thickness beyond certain time duration may be because of the possible equilibrium established between deposition and etching of the film. Hence deposition times above 90 min were not tried in the present study. Maximum thickness of ~2100 Å is obtained at the power of 200 W for deposition time of 90 min.

4.2.2 Structural Characterization of PTFE films

Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) technique are used for structural characterization of RF sputtered PTFE films. Scanning electron micrographs are taken of the sputtered films to know topography, uniformity of pin hole density. Experiments done and the results obtained on FTIR, XPS and SEM studies are given and discussed in this article. The results are compared with the standard results and with those available in the literature.

4.2.2.1 FTIR Analysis

FTIR spectra on the films deposited at different RF power and for different time durations were taken. Figure 4.2 gives representative FTIR spectra of the sputtered PTFE samples at constant deposition power of 200 W for different deposition time durations. Figure 4.3 gives representative FTIR spectra of sputtered PTFE samples at constant deposition time of 90 min and for different deposition powers used. The peak positions observed in the spectra are given in Table 4.1. The peak values of pristine bulk PTFE and the ones reported in literature are also given in the Table 4.1.
Figure 4.2: FTIR spectra of RF sputtered PTFE film at a constant deposition power of 200 W at deposition time of (a) 90 min, (b) 60 min, (c) 45 min, (d) 30 min, (e) 15 min.
Figure 4.3: FTIR spectra of RF sputtered PTFE film at a constant deposition time of 90 min at deposition power of (a) 200 W, (b) 175 W, (c) 150 W, (d) 125 W, (e) 100 W.

Table 4.1: FTIR spectral values observed in present work and compared with those available in literature

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Pristine</th>
<th>Present work</th>
<th>Ref 10, 11</th>
<th>Ref 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_2$ wagging</td>
<td>650</td>
<td>679</td>
<td>-</td>
<td>640</td>
</tr>
<tr>
<td>Amorphous PTFE</td>
<td>740</td>
<td>733</td>
<td>740</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 4: PTFE as an masking material: Results and Discussion

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si – F</td>
<td></td>
<td>805, 812</td>
<td></td>
</tr>
<tr>
<td>CF_{3}</td>
<td>980</td>
<td>968</td>
<td>991</td>
</tr>
<tr>
<td>CF</td>
<td>1030</td>
<td>1020</td>
<td></td>
</tr>
<tr>
<td>CF_{2} symmetric stretch</td>
<td>1160</td>
<td>1103</td>
<td>1152</td>
</tr>
<tr>
<td>CF_{2} asymmetric stretch</td>
<td>1220</td>
<td>1263</td>
<td>1230</td>
</tr>
<tr>
<td>CF_{2} asymmetric stretch</td>
<td>1450</td>
<td>1456</td>
<td></td>
</tr>
<tr>
<td>Aromatic C– F Stretch</td>
<td></td>
<td>1531</td>
<td>1520</td>
</tr>
<tr>
<td>C = CF stretch</td>
<td>1725</td>
<td>1730</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from the Figure 4.2 and 4.3 that the peak intensity decreases with deposition power as well as deposition time. As can be seen from Figure 4.2 there is slight shift in the peak values with deposition time duration at constant deposition power of 200 W. At a lower deposition time peak at 1531 cm\(^{-1}\) is shifted to a higher wave number to 1560 cm\(^{-1}\). The peak at 679 cm\(^{-1}\) is missing in initial stages of deposition. There is an intensity change in the peaks at 1263, 1103, 1020 cm\(^{-1}\) etc. Also the peaks corresponding to the silicon fluorine bonding at 882 cm\(^{-1}\) seems to be having larger intensity for larger deposition time.

Similar peak values are observed for spectra with constant deposition time of 90 min with power variation (see Figure 4.3). There is a marked decrease in peak intensity with power variation. No additional peaks are observed due to power variation.

In Table 4.1 the average values obtained from the present work are given. The values are in the error range of ± 10 cm\(^{-1}\) which is an instrumental error. It can be seen from the Table 4.1 that most of the peak values of absorption bands of the present work and bulk PTFE matches well.

Similar peak values are reported by Zhang Y et al\(^{10}\) for dielectric polymer films of about 40 300 nm in thickness deposited on Si (100) substrates via RF plasma sputtering of PTFE target using different sputtering gases. The argon sputtered PTFE films exhibit a strong broad band at about 1230 cm\(^{-1}\) (an overlap of CF, CF\(_{2}\), and CF\(_{3}\) vibrations), and relative weak absorption bands at 740 and 991 cm\(^{-1}\) (CF\(_{3}\) vibrations). Medium intensity absorption band at about 1520 cm\(^{-1}\) (aromatic CF stretch) is observed in the PTFE. Zhang Y et al\(^{11}\) have reported a broad band at 1230 cm\(^{-1}\) corresponding to CF, CF\(_{2}\) and CF\(_{3}\) overlapping vibrations, 740 cm\(^{-1}\) corresponding to CF\(_{2}\) stretching deformation, 1520 cm\(^{-1}\) corresponding to aromatic CF stretch and 1720 cm\(^{-1}\) corresponding to CF=CF stretching vibrations for sputtered PTFE films in argon plasma. Smasuz T et al\(^{2}\) have
reported FTIR spectral values at 1207 and 1151 cm$^{-1}$ for CF$_2$ asymmetrical and symmetrical stretching, 640 and 626 cm$^{-1}$ for CF$_2$ wagging modes; as well as the PTFE bending and rocking modes at 553 and 507 cm$^{-1}$ for PTFE films prepared from pressed powder pellets via pulsed laser deposition using ArF excimer laser.

The variation is observed in the absorption peak values of the doublet observed at 1220 and 1160 cm$^{-1}$ in case of bulk PTFE. This doublet is a characteristic of stoichiometric PTFE. This doublet is seen to be shifted to 1263 and 1103 cm$^{-1}$ in the FTIR spectrum in the present work. This shift may be attributed to the deposition condition of PTFE. The shift observed may be due to the simultaneous etching and deposition process of the PTFE film. The process of simultaneous etching and deposition leads to cross linked structures. This leads to decrease defluorination of the film. Hence the peak seems to be shifted in the film observed in the present case. As can be seen from Table 4.1, the doublet is also reported by different researchers to be present at 1230 and 1152 cm$^{-1}$, and 1207 and 1151 cm$^{-1}$, and 1207 and 1151 cm$^{-1}$, and 1207 and 1151 cm$^{-1}$, and 1207 and 1151 cm$^{-1}$. The shift may be attributed to the different deposition conditions used. It must be mentioned that Zhang Y et al., and Smasuz et al., prepared PTFE films via pulsed laser deposition using ArF excimer laser.

Additional peaks observed in the film other than those observed in bulk PTFE sample are the absorption peaks at 805, 812 and 1531 cm$^{-1}$ corresponding to the silicon and fluorine bonding and aromatic CF stretch. These peaks observed in the film, indicate good adhesion of the film and the silicon substrate onto which depositions are carried out. The presence peak at 1531 cm$^{-1}$ indicates the presence cross linked networks in the film which obviously cannot be observed in bulk PTFE sample.

Other than these peaks, the peak value at 640 cm$^{-1}$ matches with the present value. Other peaks are not reported by the author. The value of 1520 and 998 cm$^{-1}$ has been reported by Zhang et al.,, and are attributed to aromatic CF stretch and CF$_3$, respectively which match well with the present work.

The above discussion suggests that though there are variations in the intensities and positions in the peak values, the overall structure of the PTFE is retained even at higher power and longer deposition times.
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4.2.2.2 XPS Analysis

XPS technique is an analytical technique which features high sensitiveness for surface chemical structure because of the short escape depth of emitted photoelectrons.

Composition of the PTFE films deposited on silicon was further investigated with the help of XPS technique. The technique is particularly suitable to fluoropolymer analysis since photoelectrons emitted by Cls display large chemical shifts due to fluorine electro-negativity. Cls and Fls spectra of the sputtered PTFE films for constant deposition power of 200 W and variation in deposition time and constant deposition time of 90 min and variation of deposition power is shown in Figure 4.4 (i) and (ii) and Figure 4.5 (i) and (ii) respectively. All these spectra are corrected for any charging effects that may arise, by referencing them to Cls (285.0 eV) present in the sample. XPS spectra of the constituent elements revealed carbon and fluorine as main elements and oxygen as trace element indicating uniform deposition of the film on the substrate.

The Cls and Fls spectra were deconvoluted using Gaussian curve fitting technique into different moieties as indicated in Figure 4.4 and 4.5. Table 4.2 (A) and (B) give the different peak values observed in the present study under constant deposition power and constant deposition time respectively as well as those obtained from bulk PTFE and those available in the literature.
Figure 4.4 (i) and 4.4 (ii): C1s and F1s spectra for constant deposition power of 200 W and variation of deposition time (a) 15 min (b) 45 min and (c) 90 min
Figure 4.5 (i) and 4.5 (ii): C1s and F1s spectra for constant deposition time of 90 min and variation of deposition power (a) 200 W (b) 150 W and (c) 100 W.
Table 4.2: XPS peak values obtained in present study compared with those observed in bulk PTFE and ones available in literature

(A) Deposition power 200 W

<table>
<thead>
<tr>
<th>Assignment</th>
<th>15 min</th>
<th>45 min</th>
<th>90 min</th>
<th>Bulk PTFE</th>
<th>Ref \textsuperscript{5}</th>
<th>Ref \textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - CF</td>
<td>286.6</td>
<td>286.4</td>
<td>286.4</td>
<td>287.3</td>
<td>286.5</td>
<td>285.6</td>
</tr>
<tr>
<td>C - F</td>
<td>289.1</td>
<td>288.6</td>
<td>288.0</td>
<td>289.5</td>
<td>289</td>
<td>289.2</td>
</tr>
<tr>
<td>CF\textsubscript{2}</td>
<td>-</td>
<td>-</td>
<td>290.8</td>
<td>292.1</td>
<td>291.8</td>
<td>292</td>
</tr>
<tr>
<td>CF\textsubscript{3}</td>
<td>-</td>
<td>-</td>
<td>292.6</td>
<td>294.0</td>
<td>293.5</td>
<td>294</td>
</tr>
<tr>
<td>F - C</td>
<td>687.2</td>
<td>687.3</td>
<td>687</td>
<td>687.7</td>
<td>687.7</td>
<td>687.6</td>
</tr>
<tr>
<td>F1s</td>
<td>690.1</td>
<td>690.5</td>
<td>690.4</td>
<td>690</td>
<td>689</td>
<td>690</td>
</tr>
<tr>
<td>F/C ratio</td>
<td>0.5</td>
<td>0.89</td>
<td>1.2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(B) Deposition time 90 min

<table>
<thead>
<tr>
<th>Assignment</th>
<th>100 W</th>
<th>150 W</th>
<th>200 W</th>
<th>Bulk PTFE</th>
<th>Ref \textsuperscript{5}</th>
<th>Ref \textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - CF</td>
<td>286.6</td>
<td>286.6</td>
<td>286.4</td>
<td>287.3</td>
<td>286.5</td>
<td>285.6</td>
</tr>
<tr>
<td>C - F</td>
<td>288.8</td>
<td>288.3</td>
<td>288.0</td>
<td>289.5</td>
<td>289</td>
<td>289.2</td>
</tr>
<tr>
<td>CF\textsubscript{2}</td>
<td>-</td>
<td>-</td>
<td>290.8</td>
<td>292.1</td>
<td>291.8</td>
<td>292</td>
</tr>
<tr>
<td>CF\textsubscript{3}</td>
<td>-</td>
<td>-</td>
<td>292.6</td>
<td>294</td>
<td>293.5</td>
<td>294</td>
</tr>
<tr>
<td>F - C</td>
<td>687.4</td>
<td>687.6</td>
<td>687</td>
<td>687.7</td>
<td>687.7</td>
<td>687.6</td>
</tr>
<tr>
<td>F1s</td>
<td>690</td>
<td>690.2</td>
<td>690.4</td>
<td>690</td>
<td>689</td>
<td>690</td>
</tr>
<tr>
<td>F/C ratio</td>
<td>0.51</td>
<td>0.98</td>
<td>1.2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from Table 4.2 (i) and (ii) that the peak values of the present and the bulk PTFE are compared. The values corresponding to C - CF and CF are obtained at 286.4 and 288 eV respectively for deposition power of 200 W and deposition power of 90 min. These values are observed at 287.3 and 289.5 eV in bulk PTFE. There is shift of 1.5 eV observed in the CF peak value when compared with bulk PTFE. The shift of 1.3 eV is observed in the peak value of CF\textsubscript{2}. This peak is obtained at 290.1 eV in present work where as bulk PTFE show this peak at 292.1 eV. Similarly there is shift of 1.4 eV observed in the peak value for CF\textsubscript{3} which is observed in the present work at 292.6 eV. These shifts can be attributed to the defluorination of the PTFE films in argon plasma. At longer time duration a equilibrium is established between the etching and deposition of the films. Due to the etching defluorination takes place and hence the shift in peaks is...
observed in the present study. As can be seen from the Table 4.2 (a), for lower deposition powers, the shift in peak for CF is less as compared to the 200 W deposition power. The peak observed for 100 W deposition power is 288.3 eV and for 150 W deposition power is 288.3 eV. This indicates that at lower deposition powers the cross linking or in other words the making and breaking of bonds is less. Similarly for deposition times of 15 min and 45 min there is a less shift observed for the CF peak. This peak is obtained at 289.1 eV for 15 min deposition time and 288.6 eV for 45 min deposition time. The same reason as in case of lower deposition power can be given for depositions carried out at lower deposition times. For lower depositions time and lower deposition powers the peaks corresponding to CF$_2$ and CF$_3$ are not observed. This indicates an un-complete formation of PTFE at these parameters.

As seen from the Table 4.2 (A) and (B) the F1s spectra for 200 W at deposition time of 90 min, reveal two peaks at 687 and 690 eV where as the bulk PTFE spectral values are observed at 687.7 and 690 eV. There is 0.7 and 0.4 eV shift observed in the spectral values obtained in present work when compared die bulk PTFE values. When the values obtained at lower deposition powers and lower deposition times are considered it is observed that the spectral values show a less shift in the F1s spectra. This effect again indicates that in the earlier stages of deposition at lower time and at lower power, there is less amount of cross linking.

The F/C ratio observed for the variation in deposition power of 100, 150 and 200 W with constant deposition time of 90 min is 0.51, 0.98 and 1.2 respectively. The F/C ratio for bulk PTFE is 2. The lower value of F/C in case of lower deposition powers indicates an un-complete deposition. As in case of 200 W the F/C ratio is 1.2 which is much closer to the bulk PTFE value. Similar trend is observed in case at depositions carried out at constant deposition power of 200 W with variation in deposition times for 15, 45 and 90 min. The deposition time of 90 min give a closer F/C ratio when compared with the bulk PTFE value.

These results are in accordance with the results obtained by FTIR spectroscopy where in at higher deposition time the spectra show higher peak intensity. As the deposition time increases there is an increase peak broadening and peak intensity. This indicates that there is a cross linking or branching of the films.

When spectral values are compared with those available in literature (See Table 4.2 (A) and (B)), it is seen that the values reported by Wilson D et al. for C – CF and CF are in close comparison with those obtained in present work. There is a shift in
spectral values observed in the case of CF$_3$ and CF$_2$ bonds. Shift in these peak values can be attributed to the different deposition conditions. Wilson D et al. have carried out treatment of PTFE which showed peaks at 293.5, 291.8, 289, 286.5 and 285 eV corresponding to CF$_3$, CF$_2$, CCF, O-C=O, C=O, C=O and C-H moieties respectively. These compare well with the peaks obtained in present study.

Zhang Y et al. have carried out surface modification of PTFE films by Ar$^+$ ion beam irradiation with varying ion energy and ion dose. The treatment was carried out a 2 KeV Ar$^+$ ion beam at ion current density of 0.30 mA/cm$^2$ and different fluence values. XPS of the modified film showed peaks at 286.2, 288, 290 and 294.1 eV corresponding to C-O, C(CF$_3$)$_n$, C-F and CF$_3$ respectively. The incident energetic species react initially with the PTFE chain and give rise to chain scission and defluorination of the CF$_2$ group. The F and CF$_2$ free radicals formed, further, react to form the CF$_3$ group and the CF group in the polymer chain. The CF group may further breakdown to generate a quaternary carbon free radical, which can react with the CF$_2$ species to form the cross linked PTFE chains. Higher Ar$^+$ ion fluence will result in more chain scissions on the PTFE surface, hence leading to a decrease in CF$_2$-CF$_2$ specie concentration on the surface of the Ar$^+$ ion beam treated PTFE film. The reduction in CF$_2$ group concentration in the Cls core level spectra is probably attributable, in part, to the etching effect on the PTFE surface caused by the incident Ar$^+$ ion beam.

Jaszewski RW et al. have also reported the deposition of ion sputtered PTFE-like films using CHF$_3$ as the sputtering gas at the RF plasma power of 50W. They have attributed XPS binding energy corresponding to CF$_3$, CF$_2$, CF, CCF and CCC at 293.2, 291.4, 289.0, 286.9 and 284.8eV respectively. These reported XPS binding energy values match well with those observed in the present study. Similar deposition conditions result in similar peak values obtained in the present work.

Above discussion and comparison suggests that the films prepared by RF sputtering of PTFE target in the present work resemble the bulk PTFE characteristics.

4.2.2.3 SEM Analysis

In order to check the pin hole free nature of the film they were observed under Scanning Electron Microscope (SEM). The SEM micrographs showed smooth pin hole free films for all deposition conditions. Such a film is requirement for use as a masking material. Figure 4.6 shows an indicative SEM for PTFE film for 200 W deposition.
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power and time duration of 90 min. Also an SEM of PTFE film deposited for a deposition power of 200 W for deposition time of 15 min.

Figure 4.6: SEM of sputtered PTFE film at deposition power of 200 W at deposition time of (a) 15 and (b) 90 min

4.2.3 Physical Characterization

One more important property desirable for good masking materials is better adhesion between the film and the substrate. An elementary tape test was done to check the adhesion qualitatively. The films deposited under all the conditions mentioned in the Section 4.2.1 could not be removed indicating good adhesion of the film to the substrate.

For quantitative measurement of adhesion between the film and the substrate, contact angle measurement technique was used (see Section 2.5 for details). Contact angle measurement was carried out with two different liquid systems. Polar liquid, water and nonpolar liquid, di-iodomethane were used in the present study. Formaldehyde instead of di-iodomethane can also be used. From the contact angle data interfacial tension and work of adhesion between the film and the substrate were calculated (for details see Section 2.5).

Figures 4.7 (a) and (b) give the variation of interfacial tension and work of adhesion of the RF sputtered film respectively as a function of deposition time at different powers. As can be seen from Figure 4.7 (a) there is a decrease in the value of interfacial tension with increase in deposition time. The interfacial tension also decreases with increase in deposition power. A value of 0.72 dyne/cm is obtained for deposition power of 200 W when deposited for 90 min. This indicates that RF sputtered PTFE films adhere nicely to the substrate. This value is also comparable to that obtained by Ilie et al. [36] (0.746 dyne/cm) for their adherent PMMA layer.

The work of adhesion which is another important criteria for determining adhesion follows the same trend as in case of spin coated samples [35, 39]. There is an increase in work of adhesion with deposition time and deposition power. A maximum
value of work of adhesion obtained is 93.68 dyne/cm (for films deposited at 200 W for 90 min) which is high compared to the value of 82.09 dyne/cm obtained for DC sputtered PMMA samples. The interfacial tension obtained is very high as compared to the work of adhesion of the adherent PMMA layer obtained by Ilie et al (20.8 dyne/cm). This indicates that there is a better adhesion between the RF sputtered PTFE and the silicon substrate.

It may be mentioned that FTIR spectra (Figure 4.2) support the result of good adhesion of the film with substrate. The spectra show a peak related to Si-F (at 805 and 882 cm$^{-1}$) for all RF sputtered films, which indicates bonding between the silicon substrate and PTFE film. Increase in peak intensity as well as peak broadening is observed with increase in deposition power as well as deposition times (Figure 4.2 and 4.3). This proves that better adhesion of the sputtered PTFE film with the silicon substrate at higher power of deposition and for larger time of deposition.

From the results of better adherent characteristics and the retention of PTFE structure of RF sputtered films it is expected that these films will prove equal or better masking materials for bulk silicon micromachining compared to the conventional masking materials.

The variation of the interfacial tension and work of adhesion Vs thickness graphs are plotted as shown in Figure 4.8 (a) and (b). It can be clearly seen that there is a decrease in interfacial tension and increase in work of adhesion with thickness of the film. It can be concluded that films with higher thicknesses adhere better with the substrate. The thickness in turn depends on the deposition power and deposition time. The higher thickness is obtained at a power of 200 W for 90 min. It can be concluded that at higher power the film bonds better than that for lower power. This is also seen
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from the FTIR spectra which show a higher intensity peak (peak at 882 cm⁻¹) for films deposited at higher power and for greater deposition times.

![Figure 4.8: Variation of (a) interfacial tension and (b) work of adhesion with thickness of the film](image)

Adhesion strength of 2.1 MPa was obtained by Smasuz T et al. for their excimer laser deposited PTFE samples. The films were deposited at 500 °C for 30 min. The authors have reported this value of great significance for protecting coatings. Zhang Y et al. 10, 11 have reported peel of adhesion strength of 3.3 N/cm for argon plasma deposited PTFE samples. They have reported contact angles of the order of 106 ° for their samples deposited by magnetron sputtering at RF power of 350 W for 1200 s. The lower contact angles of ~ 50 ° obtained in the present work can be attributed to the different deposition conditions employed.

4.2.4 Performance of PTFE films as a mask: Results and Discussion

After confirming the structure of the deposited films and adherent nature of these films the films deposited under different conditions were then subjected to the wet chemical etching in KOH and TMAH. Etching at various concentrations viz. 10, 20, 30, 40 wt% for KOH & 15, 20, 25 wt% for TMAH and different temperature conditions viz. 60, 70, 80, 90 °C was carried out.

The etching performance is measured in terms of masking time. The masking time of the film is defined as the time required to etch the PTFE film from the silicon substrate. PTFE film was coated on the mirror finished side of the silicon substrate and back side was allowed to etch in etchant solution. The time of start of etching of silicon front side was noted as the masking time of the PTFE film. This time was considered as
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the time taken to completely etch the PTFE film. Figures 4.9 and 4.10 give the masking time of the RF sputtered PTFE film at various conditions of deposition. The variation of deposition power was from 100 – 150 W and for deposition times for 15 – 45 min. Substrates were checked after every 10 – 15 min for front side etching. Therefore the results may be in error by 10 – 15 min. Etching experiments were done at different etchant temperatures but in Figure 4.9 and 4.10 the plots of masking time at KOH temperature of 80 °C and TMAH temperature of 90 °C only are given at various concentrations. Plots at these temperatures are given as the silicon micromachining using SiO₂ and Si₃N₄ as masking materials is typically carried out at these temperatures. The plots of masking time Vs concentration of etchant at various deposition conditions viz. 100, 125 and 150 W deposition power and 15, 30 and 45 min deposition time are given.

![Figure 4.9: Masking time Vs Concentration of Etchant (KOH) for RF sputtered PTFE films at different deposition conditions (KOH Temp. = 80 °C)](image)
From Figure 4.9 (a, b and c) for KOH as etchant, it can be seen that for films deposited at different powers 100, 125 and 150 W, the masking time decreases as the concentration of the etchant is increased. This is obvious because at higher concentration of the etchant the etching rate is higher. Further, the masking time is more for the films deposited for longer time. This may be attributed to the higher thicknesses of the deposited films for longer deposition time (see Figure 4.1). The maximum masking time of 300 min is obtained at the deposition power of 150 W at deposition time of 90 min. as can be seen from Figure 4.9 (a) - (c) for KOH etchant. Arguments similar to the one made in case of PMMA is true here also (see Section 3.2.3.2). Silicon was not coated from the backside and the etchant etches silicon substrates from back side. At 10 wt% concentration the PTFE films is etched and therefore starts etching from side of silicon substrate in 300 min (for 150 W deposition time), but for 20 wt%, the silicon wafer etches completely within 300 min and not PTFE. This is because the thickness of silicon used in the study was 500 μm. KOH etchant at concentration 20 wt% at 80 °C temperature etches 500 μm silicon in 300 min (at 1.4 μm/min). Hence masking times
above 300 min were not obtained. At higher concentration however the masking time is less.

When results on variation in deposition power are considered it is found that there is an increase in masking time with increase in deposition power. In Figure 4.9 (a - c) dotted lines are shown for concentration of 20 wt% and deposition time of 45 min. The increase in masking time with power can be attributed to better adhesion of the PTFE film at higher power and also higher thickness of the film.

Similar trend for variation of masking time with concentration of etchant and variation of masking time with deposition power and deposition time is observed in the case of TMAH etchant at 90 °C (see Figure 4.10 (a - c)). The minimum masking time of 150 min is obtained for the deposition condition of 100 W deposition power at 15 min deposition time (see Figure 4.9 (a)). The minimum masking time obtained for the films deposited under same conditions when KOH is used as etchant is 150 min. It shows that there is not much difference in etching characteristics of KOH and TMAH etchants.

Sufficiently longer masking times of RF sputtered PTFE films indicated that PTFE adheres nicely to silicon substrate. This is found to be due to bond formation with silicon. Also due to cross linking network formed in the film structure, the films do not get etched in etchant solution easily.

Etch rates of RF sputtered PTFE films were calculated for KOH and TMAH for different deposition conditions. Etch rate Vs temperature of etchant graph for PTFE films subjected to etchants viz. KOH and TMAH is given in Figure 4.11 (a) & (b) respectively.

The graph of etch rate Vs temperature indicate clearly a decrease in etch rate with decrease in concentration and temperature of the etchant. The etch rate of 0.0004 μm/min at 20 wt% and 80 °C for KOH and that of 0.0005 μm/min at 10 wt% at 90 °C for TMAH are obtained. These etch rates are sufficiently smaller than that for silicon (1.4 μm/min) and therefore thought to be suitable for micromachining. 1.4 μm/min is the maximum etch rate of silicon at these concentration and times. For micromachined structures concentration of 40 wt% for KOH and 25 wt% for TMAH at 90 °C are used. At these conditions PTFE show an etch rate of 0.0006 & 0.0007 μm/min. which is better than PMMA (0.0005 & 0.0006 μm/min). The etch rate of SiO₂ & Si₃N₄ is 0.005 & 0.0005 μm/min which are of the same order or larger compared with the etch rate of PTFE.
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The advantage of using PTFE as a masking material is that the films can be deposited at room temperature and require less time (~90 min) to deposit. This is unlike SiO₂ & Si₃N₄ which require 800-1000 °C temperature and 8 hours of deposition time. Moreover, the present study requires a simple sputtering system, which is cost-effective than the system required for SiO₂ and Si₃N₄. At these conditions, the masking time obtained for PTFE is greater than 300 min. In this time, 500 µm silicon gets completely etched out at an etch rate of 1.4 µm/min at 20 wt% and 10 wt% concentration of KOH and TMAH, respectively, at 90 °C. The etch rate of PTFE is lower as compared to PMMA.

FTIR and XPS spectra were recorded after etching in KOH and TMAH etchants to confirm the presence of PTFE on the substrate. Figure 4.12 (a, b and c) shows FTIR spectra of RF sputtered PTFE film etched in KOH (20 wt% concentration at 80 °C temperature) for 3 hours. This concentration and temperature of KOH is selected as micromachining of silicon is carried out at this concentration above 80 °C. Also, the silicon has the highest etch rate at 20 wt% concentration of KOH. All the FTIR spectra show the similar peak values, hence indicative FTIR spectra are shown in the Figure 4.12 with variation in power at a constant deposition time of 90 min. The presence of all PTFE peaks (discussed above) in etched film FTIR spectra indicates that, PTFE film remains on silicon substrate even after etching of 3 hours. The FTIR spectrum shows a decrease of intensity in all previously observed peaks. Moreover, additional peaks at 1080 and 3300 cm⁻¹ corresponding to SiO₂ and OH respectively are observed in the film after etching. It may be mentioned that the film is subjected to the action of KOH (highly alkaline solution). In process, silicon might have reacted with KOH forming SiO₂ and OH group which get adsorbed on the film surface and hence the respective peaks are...
observed in the FTIR spectrum. The decrease in peak intensity in all spectra are due to the removal of the unreacted fluorine and other loosely bound molecules from the surface.

The XPS Cls and Fls spectra were also recorded to check the presence of PTFE film after 3 hours of etching in 20 wt% KOH at 80 °C. The XPS spectra for the film deposited at a constant deposition time of 90 min with variation in power after subjecting them to etching is shown in Figure 4.13. The chemically distinct carbon atoms after etching are assigned to G-F and -C-\(\text{CF}\) at 288.0 & 286.7 eV, 288.1 & 286.5 eV and 288.6 & 286.4 eV at 100, 150 and 200 W plasma power respectively. The peak intensity of G-F and -C-\(\text{CF}\) increases with plasma power after etching. The chemically distinct fluorine atoms show no appreciable change in the composition. The F/C ratios for etched film were 0.2, 0.25 and 0.86 for 100, 150 and 200 W respectively. This decrease of the in F/C ratio with respect to the as deposited film may be due to the removal of the unreacted fluorine atoms sitting on the surface of the film in highly concentrated KOH solution. This confirms that the PTFE stays on the silicon substrate after 3 hours of etching. The etch rate of the PTFE film is also negligible in the both the etchant solutions. This proves that PTFE can be used as a mask in silicon micromachining process. Also better masking properties of PTFE than conventional masking materials like SiO\(_2\) and Si\(_3\)N\(_4\).
Figure 4.12: FTIR spectra for PTFE films etched in 20 wt% KOH at 80 °C for RF plasma powers of a) 100W, b) 150W and c) 200W for 90 min deposition time
Figure 4.13 (a) and (b) Cls and F1s spectra for constant deposition power of 200 W and variation of deposition time (a) 15 min (b) 45 min and (c) 90 min after etching in KOH.

4.2.5 Transfer of pattern in the mask layer and removal of mask layer after completion of fabrication process

RF sputtered PTFE film was used for the transfer of pattern as it resulted in a better etch rate as compared to the spin coated PMMA and sputtered PMMA film. A simple diaphragm pattern was transferred through the PTFE layer on the silicon substrate. A lift off process was used in order to transfer the pattern into the PTFE layer. Procedure of transfer of pattern was same as in case of sputtered PMMA film. Detailed process steps are given in Figure 3.22, only change is that the masking layer is PTFE instead of PMMA. The silicon substrate with diaphragm pattern on it was then
etched in 40 wt% KOH at 90 °C temperature to get a diaphragm thickness of around 80 μm. PTFE layer was deposited on the back side to protect the back side from etching.

The diaphragm etched in silicon using PTFE film as a masking material is shown in Figure 4.14. The dimensions of the diaphragm are 1 x 1 mm and the thickness of diaphragm is around 80 μm. The etching of silicon was carried out in KOH anisotropic etchant at the concentration of 40 wt% at a temperature of 90 °C which are normally used parameters for micromachining. The etching is around 5 hours.

Removal of mask layer after the completion of micromachined structure was not tried out with PTFE. References suggest that PTFE can be removed by plasma etching using a H/N, (70:30) mixture. Chemical route to remove PTFE is also available. Etchant known as Fluoroetch, basically mixture of sodium and naphthalene known as sodium naphthanilide is used. These processes are very hazardous and should be used under utmost care. Due to unavailability of etchant and gases the removal was not tried.

Figure 4.14: Diaphragm etched in silicon using PTFE as a etch mask
3.3 CONCLUSIONS

Deposition of PTFE was carried out on silicon substrates by RF sputtering of PTFE. Thin films of PTFE were deposited on silicon substrates with variation in deposition power (100 - 200 W) and deposition time (15 - 90 min). Thin films of maximum thickness of order of 2100 Å were obtained. FTIR spectroscopic studies revealed peaks related to standard bulk PTFE in addition to peaks related to bonding between silicon and fluorine. This indicated increase in adhesion between the silicon substrate and the PTFE film. RF sputtering showed cross linked structures of PTFE film. Decrease in peak intensity was observed with decrease in sputtering time as well as deposition power, which also indicated that higher thicknesses were obtained for higher deposition power and/or deposition times. XPS showed an increase in C – CF groups and C – F groups with increase in power indicating increase in thickness of PTFE. At higher power peaks of CF$_2$ and CF$_3$ are visible indicating stoichiometric deposition at higher power levels of plasma. XPS spectroscopy showed results in agreement with FTIR spectroscopy.

Studies on contact angle measurements showed better adhesion of the RF sputtered PTFE films than the sputtered PMMA films. The interfacial tension of the order of 0.72 dyne/cm was obtained for RF sputtered PTFE which was in good agreement with the reported value of 0.74 dyne/cm. Decrease in contact angle values from the standard value of 110 ° indicated that there is an increase in cross linking densities and increase of hydrophobic structures. This result supports the results obtained from FTIR and XPS spectroscopic studies.

Performance of PTFE as masking material was tested in conventionally used etchants viz. KOH and TMAH at various concentrations and temperatures. The masking times obtained RF sputtered films are of the order of 300 min. FTIR and XPS were again recorded to prove the presence of masking material after 3 hours of etching in KOH and TMAH etchants. FTIR and XPS showed peak of PTFE indicating its presence after immersing in etchant solution. The etch rate of the RF sputtered films is observed to be 0.0004 μm/min which is better than that for the conventional masking materials viz. SiO$_2$ (0.006 μm/min). This proves the candidature of PTFE thin films as masking material. The next important step of transfer of pattern in masking material was successfully demonstrated. A diaphragm of size 80 mm was successfully etched using KOH as etchant.
It can be concluded from this study that RF sputtered PTFE can successfully replace the conventionally used masking materials. The RF sputtered PTFE sample is a better masking material than DC sputtered PMMA as the etch rate of PTFE films is less than that for PMMA films. The RF sputtered PTFE has many advantages over the conventional masking material like chemical resistance, easy availability, easy deposition, cost effective deposition systems, less possibility of contamination, less time consuming deposition process and better etch rate in etchant solutions.

The microstructure created by Yamaguchi et al. with the help of SR direct phototetching was carried out successfully. It was confirmed that the quality of micromachining of cross linked PTFE is as good as that of non cross linked PTFE. Through the etching rate measurements of various samples, it was found that synchrotron radiation etching rate of cross linked PTFE only depends on the degree of cross linking. The etching rate of 6 μm/min was determined by Yoshida A et al. for PTFE film etched by synchrotron radiation. Authors have deposited PTFE films through Ni mesh with a hole of 7.5 x 7.5 μm on silicon <100>.

Matsumoto Y et al. have studied several deposition techniques and characteristics of fluorocarbon films. The fluorocarbon films show good adhesion from the result of Scotch tape test. The patterned fluorocarbon subjected to TMAH etching observed peeling hence patterned fluorocarbon film was cannot be used as etch mask. Normad P et al. have reported new masking method for protecting silicon surfaces during anisotropic etching. A room temperature silicon masking approach based on the exposure of silicon to CHF₃ plasma is reported. A lift off process is used for pattern transfer as used in present case. KOH and EPW based etchants were used to test the resistance of CMPL mask. The authors have reported the use of these masks for micro and nano machining using EPW solutions. Further, they report that these masks allow anisotropic wet etching of the vertical side walls. They have reported that the new masks compare favorably with common masking materials such as SiO₂ or Si₃N₄ in terms of achievable patterns and processing options.

However, similar to PMMA experiments on process integrity with other fabrication process need to be carried out extensively.
References


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