RF Sputter Deposition of Poly(tetrafluoroethylene) Films as Masking Materials for Silicon Micromachining

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ABSTRACT: Polymers have been studied extensively because of their wonderful array of properties. Their properties can be tailored by many means and can be made useful in many ways. Polymers can be crosslinked or branched and can provide different properties, such as conduction and passivation. This study dealt with the RF sputter deposition of poly(tetrafluoroethylene) (PTFE) films with the aim of using them as masking materials during the fabrication of various micromachined structures. The films were deposited on silicon substrates at different plasma powers (100, 150, and 200 W) for a constant deposition time (60 min). To test the masking properties, the deposited films were immersed in a 20 wt % aqueous KOH solution at 80°C for 60 min. The films showed lower contact angles and interfacial tension, and this indicated good adhesion of the films to the silicon substrates. Good adhesion is an essential quality of masking materials during micromachining. The structural properties of the as-deposited and etched films were studied with Fourier transform infrared and X-ray photoelectron spectroscopy. These indicated that the bonding groups and binding energies of C—F and C—CF matched the reported values well. Furthermore, the presence of C—F and C—CF bonds, even after the etching of silicon substrates in highly alkaline KOH solutions for 60 min, showed that the PTFE films remained unchanged in the etchant and, therefore, could function as good masking materials during the fabrication of micromachined structures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1183–1192, 2004

Key words: structure; X-ray; FT-IR

INTRODUCTION

Polymers have evolved over the past century to become seminal materials in a wide variety of industrial, electronic, and research applications.[1–3] Because of the incredible range of characteristics displayed by polymeric materials, their potential applications appear to be unlimited. Their surface-layer properties have recently received great attention in practical applications, such as biomaterials, adhesives, and paintings.[4] This unique class of compounds find uses in products as varied as photoresist materials during microfabrication processes, materials for masking during the fabrication of MEMS structures,[5] contact lenses, artificial organs, structural materials, food packaging, and potential substrates for flexible circuit fabrication.[1,6] Moreover, the properties of polymers can be tailored according to requirements by the doping of some other materials or the making or breaking of long-chain compounds. The other way is the crosslinking and branching of polymers. Because so many iterations are possible, polymers happen to be the most suitable, easy to use and handle, and easily available materials. The properties of polymers can be governed by different processes, such as RF sputtering, magnetron sputtering, plasma polymerization, and ion bombardment and implantation.

In a previous study,[7] we carried out sputter deposition, structural characterization, and masking-property determination for poly(methyl methacrylate) films in KOH solutions for MEMS applications. Along the same lines, here RF sputtering of poly(tetrafluoroethylene) (PTFE) was carried out on silicon substrates. PTFE was selected because it is a chemically inert material, is easily available, and can be cast into films. The films were intended to be used as masking materials during the fabrication of silicon micromachined structures and were expected to replace conventionally used silicon dioxide and silicon nitride masking materials. The RF-sputter-deposited PTFE films were immersed in 20 wt % KOH solutions at 80°C for 60 min to study the masking properties for the fabrication of various microstructures. KOH at 80°C was used as an anisotropic etchant for silicon at an etching rate of 86 μm/h;[8] at higher KOH temperatures, the undercutting of silicon can take place, and the line width of the structure is spoiled. It was, therefore, necessary to study the structural and adhesive properties of the films on the silicon substrate. The deposited films (before and after etching) were character-

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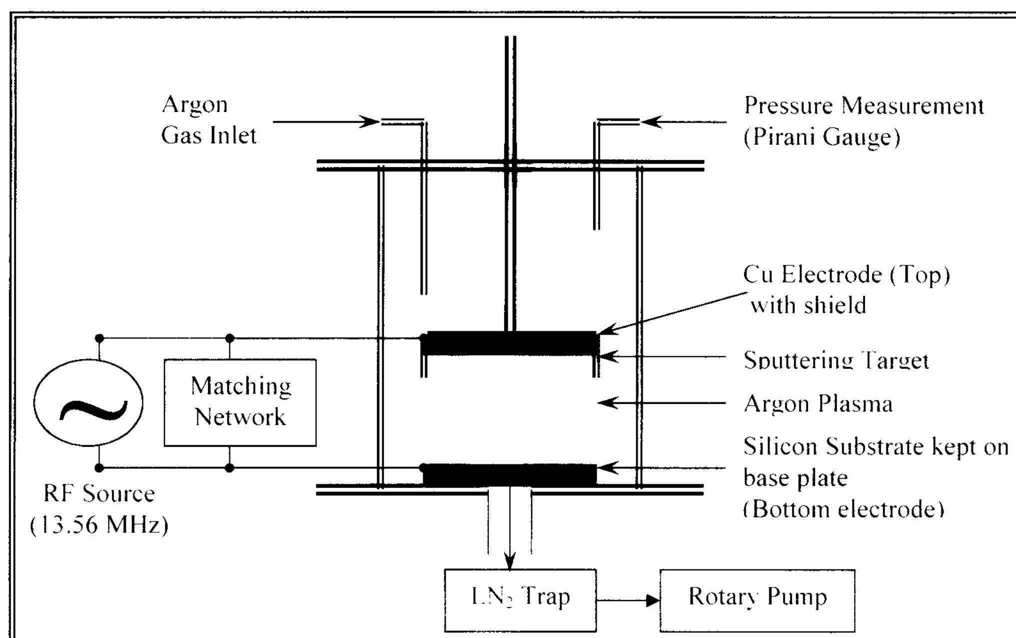


Figure 1 RF plasma sputtering system.

ized by different characterization techniques, such as Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), to observe the changes taking place on the surface during the deposition and after etching in KOH. Contact-angle measurements were performed to check the adhesion of the films to the substrates. Furthermore, the variations of these properties with the power during the deposition were studied.

EXPERIMENTAL

Materials

A commercially available PTFE (DuPont, Ltd.) sheet was used as the sputtering target. The target was 1 mm thick and was clamped to a copper electrode (excitation electrode). The depositions were carried out on an n-type, ⟨100⟩-orientation, 500-μm-thick silicon substrates; 20 wt % KOH (analytical-reagent-grade) at 80°C was used as an anisotropic etchant for the silicon.

Deposition process

PTFE thin films were prepared in an in-house-fabricated parallel-plate sputtering system schematically shown in Figure 1. The sputtering system consisted of a quartz chamber (24 cm in diameter), feed-throughs for gas inlet and pressure measurements, and an electrode assembly. Parallel plates made of copper were used as electrodes for plasma excitation. The bottom electrode was mounted on a tripod and kept on the base plate. The bottom plate was connected to the outer conductor of an RF cable and was grounded. The diameter of the copper electrodes was 13 cm. A PTFE sheet (the target) of the same diameter (13 cm) as that of the copper electrode and approximately 1 mm thick was attached to the top electrode (Fig. 1) with pressure clips. This electrode was shielded with an Al sheet placed approximately 2 mm away from the electrode. Argon was used as a carrier gas. Silicon substrates on which deposition was performed were kept on the bottom plate. The distance between the two plates (anode and cathode) was 5 cm. An RF power supply (13.56 MHz) was connected between these two plates for plasma excitation through the matching network. Before the silicon substrates were loaded into the system, they were cleaned by a conventional cleaning procedure.[9]

The system was evacuated to 0.133 Pa (10^{-3} Torr) with a rotary pump. The rotary pump was connected to the reactor through a liquid nitrogen trap to avoid contamination by the pump oil. The pressure was measured with a Pirani gauge. The reactor was flushed afterwards by the passage of argon gas for 10–15 min for the removal of the residual gas contents. The water vapor was also removed by the argon, which was passed at a high flow rate. During the deposition, the pressure of the system was set to 26.66 Pa (0.2 Torr) through control of the argon gas flow. The deposition was performed at three different RF plasma powers (100, 150, and 200 W) at the constant deposition time of 60 min.

Characterization techniques

The deposited films were structurally characterized by FTIR and XPS techniques, and the adhesion properties were determined through contact-angle measurements.

FTIR spectroscopy

The FTIR spectra of the deposited films were recorded with a PerkinElmer 2000 FTIR spectrometer. The spectrum was recorded over a wave-number range of 400–4000 cm^{-1}.

XPS

An ESCA-3000 electron spectrometer with twin anodes [Al Kα (1486.6 eV) and Mg Kα (1253.6 eV)] was used to characterize the surfaces of the films, which were deposited on single-crystal silicon. The vacuum in the analyzing chamber was greater than 10^{-9} Torr. The multichannel detectors were used to detect the photoelectrons. The spherical sector analyzer was used to detect the photoelectrons energywise. An X-ray flux of 200 W was used. The XPS spectra were acquired with a 50-eV pass energy, a 5-mm slit width, and a take-off angle of 55°. Because of the large number of channeled electrons, the detection limit was increased. The spectrometer was calibrated by the determination of the binding energy values of $Au4f_{7/2}$ (84.0 eV), $Ag3d_{5/2}$ (368.8 eV), and $Cu2p_{3/2}$ (932.8 eV). All these values were in good agreement with the literature.[10,11] Details about the electron spectrometer are given in our earlier article.[12] The instrumental resolution under this condition was a 1.6-eV full width at half-maximum for the $Au4f_{7/2}$ level. The thin films were mounted on a suitable conducting sample holder, which was used for recording the XPS spectra.

Contact-angle measurements

The contact-angle measurements were carried out to determine the adhesion of the PTFE films to the silicon substrates, the work of adhesion, the surface free energy, and so forth. A drop of deionized water or diiodomethane was placed on each film, and the angle was measured with a Ramé Hart 100 contact-angle goniometer.

RESULTS AND DISCUSSION

The depositions of the PTFE films were carried out on silicon substrates in an in-house-fabricated parallel-plate RF sputtering system, as shown in Figure 1, at different plasma powers (100, 150, and 200 W) for a fixed deposition time of 60 min. The thicknesses of the films, measured with a Talystep, were 1500, 1700, and 2100 Å for plasma powers of 100, 150, and 200 W, respectively. The corresponding deposition rates were 25, 28, and 35 Å/min. This deposition rate was low because of the high pressure (0.2 Torr) at which the depositions were carried out. Although there was an increasing trend observed with an increase in the RF power, the increase was not significant. An observed small change in the deposition rate may be attributed to the incorporation of water vapor; however, it should be mentioned that OH groups were not found in the films during the FTIR characterization, as discussed later.

For testing the adhesion and determining good masking properties, we performed contact-angle measurements of the deposited films. The angles were approximately 50° with water and 44° with diiodomethane, indicating the presence of highly hydrophilic groups on the film surfaces.[13] The lower contact angle may be attributed to the polar groups present on the surfaces of the films. The films in this work were deposited in a plasma environment. In this process, deposition and etching took place simultaneously. This created more dangling bonds on the surfaces of the films. During exposure to the atmosphere, oxygen was adsorbed onto the surfaces of the films, creating polar groups on the film surfaces. The polar groups interacted readily with water, and this led to the decrease in the contact angle. A contact angle of less than 60° was reported by Yu et al.[14] for PTFE films treated with a low-temperature cascade arc torch. They attributed the observed low contact angle to the combination of the introduction of oxygen groups, which created polar groups, and defluorination on the film surface. The interfacial tension of the film was calculated[13,15] to be, on average, 0.76 dyn/cm for all the power levels. This lower interfacial value indicated very good adhesion with the silicon substrate.[7,16] There was negligible variation (± 2°) of the contact angle for the films deposited under different power levels; this was within in the error bar of the instrument used. The contact angles measured after the etching of the silicon in KOH did not show any change. This shows that the deposited PTFE films were present on the surfaces of the silicon substrates, even after they were dipped in KOH for a long time.

Figure 2 shows the FTIR spectra of as-deposited PTFE films at three different plasma powers (100, 150, and 200 W). The peaks observed at 678, 742, 970, 1095, 1272, and 1442 cm^{-1} correspond to CF_2 wagging, amorphous PTFE, CF_3, CF, and CF_2 symmetric and asymmetric stretching, respectively.[6,17,18] The Si—Si bonding peak can be observed at 610 cm^{-1}. The additional peaks at 812 and 884 cm^{-1} are attributed to bonding between silicon and fluorine atoms.[19] An OH peak was not detected, even though the deposition was carried out at a high pressure. No new peaks were introduced into the spectrum of the film due to the

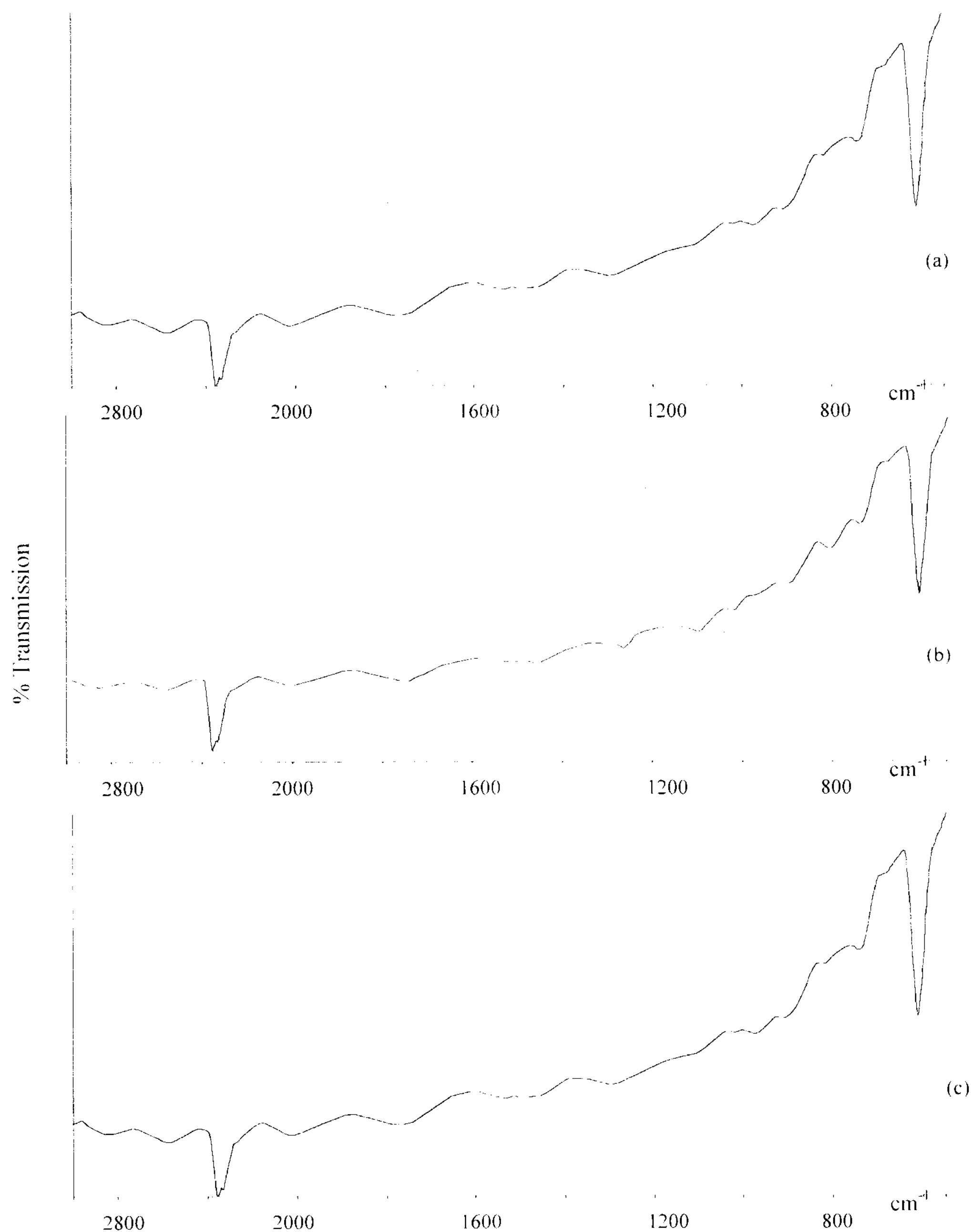


Figure 2 FTIR spectra for the RF sputter deposition of PTFE films at plasma powers of (a) 100, (b) 150, and (c) 200 W for a deposition time of 60 min.

power variation. This indicates that the deposition of the films at all power levels had no large effects on the thickness and structure of the films. Similar absorption bands were observed by Biederman et al.[17] They attributed the important peak at 1288 cm^{-1} to the CF_x group for their RF-magnetron-sputtered PTFE films, whereas the peak at 980 cm^{-1} was attributed to C—F stretching by Han et al.[18] for their plasma-polymerized films of pentafluorostyrene.

Furthermore, to observe the changes in the films after their subjection to 20 wt % KOH at 80°C for 60 min, we again recorded FTIR spectra, which are shown in Figure 3. The FTIR spectrum shows a decrease in the intensity for all previously observed peaks. Moreover, additional peaks at 1080 and 3300 cm^{-1}, corresponding to SiO_2 and OH, respectively, can be observed for the films after etching. The films were subjected to the action of KOH (a highly alkaline solution). In the process, silicon might have reacted with KOH, forming SiO_2 and OH groups,[8,20] which were adsorbed onto the film surfaces; therefore, the respective peaks can be observed in the FTIR spectrum. The decrease in the peak intensity was due to the removal of the unreacted fluorine and other

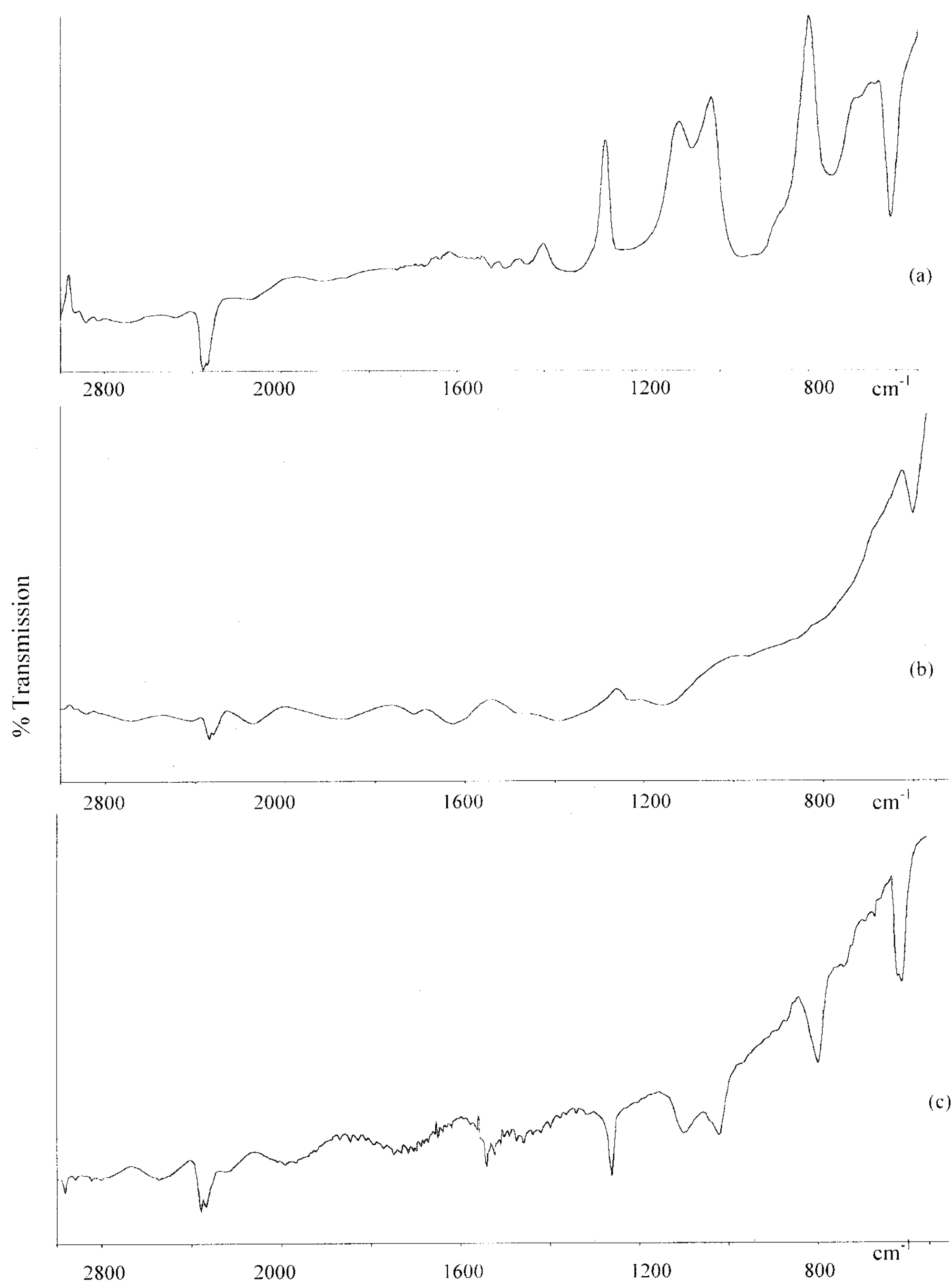


Figure 3 FTIR spectra for PTFE films etched in 20 wt % KOH at 80°C at RF plasma powers of (a) 100, (b) 150, and (c) 200 W for a deposition time of 60 min.

loosely bound molecules from the surface. The presence of all the PTFE peaks (discussed previously) in the FTIR spectra of the etched films (Fig. 3) indicates that the PTFE films remained on the silicon substrates even after etching for 60 min.

The compositions of the films deposited at plasma powers of 100, 150, and 200 W on silicon substrates were further investigated with the XPS technique. This is an analytical technique that features high sensitivity for surface chemical analysis and bonding because of the short escape depth of the emitted photoelectrons.[21] The technique is particularly suitable for fluoropolymer analysis because photoelectrons emitted by C1s display large chemical shifts on account of fluorine electronegativity, and so it was used in this study.

We corrected all the XPS spectra for charging effects that may have arisen by referencing them to C1s at 285.0 eV as an internal standard, which was present in the samples. XPS spectra of the constituent elements revealed carbon and fluorine as the main elements and

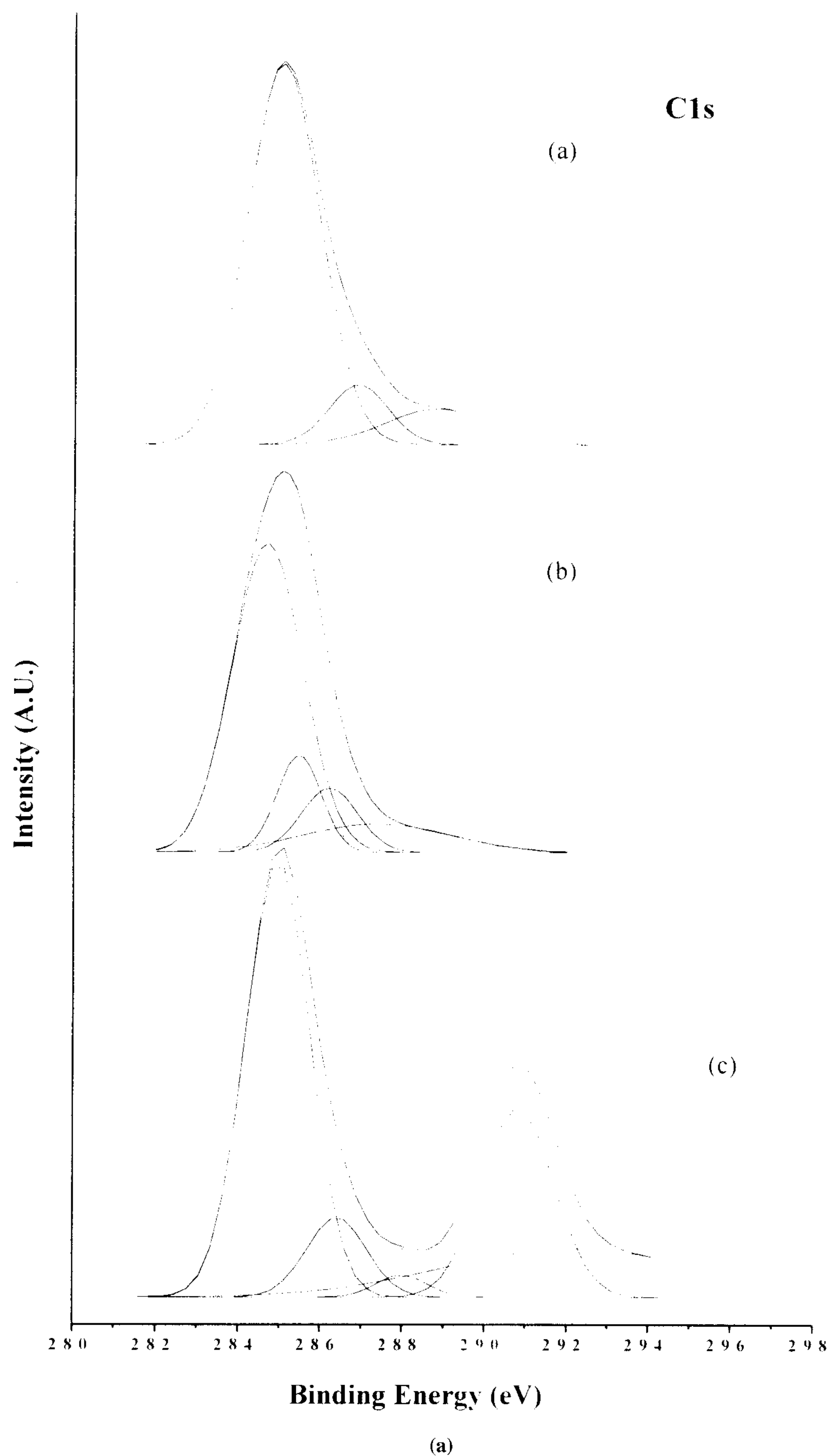
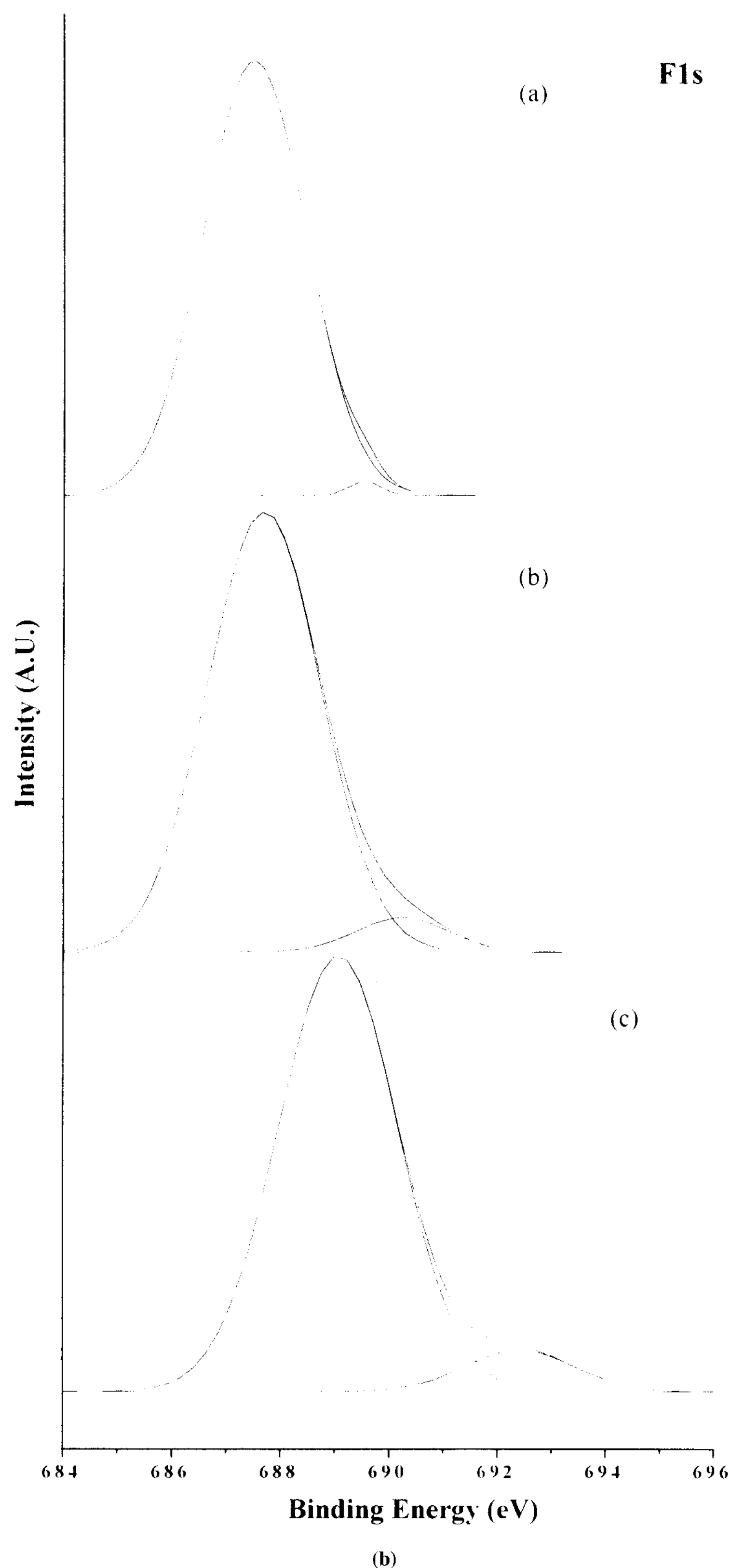


Figure 4 (a) XPS C1s spectra and (b) XPS F1s spectra of sputter-deposited PTFE films for RF plasma powers of (a) 100, (b) 150, and (c) 200 W for a deposition time of 60 min.

oxygen as a trace element, indicating a uniform deposition of the films on the substrates. No nitrogen was detected by XPS. The XPS data analysis showed no argon detected at the background level, even though the depositions were carried out in an argon atmosphere. The C1s and F1s spectra were deconvoluted with a Gaussian curve-fitting technique into different moieties. These chemically distinct carbon atoms, as shown in Figure 4(a) for a 100-W plasma power, were assigned to C—F at 288.8 eV and to C—CF at 286.8 eV. For 150 W, the peaks were assigned to C—F at 288.3 eV and to C—CF at 286.6 eV, and for 200 W, the



(b)

Figure 4 (*Continued from the previous page*)

assignments were CF_3 at 292.2 eV, CF_2 at 290.8 eV, C—F at 288.0 eV, and C—CF at 286.4 eV. Similarly the chemically distinct fluorine atoms, as shown in Figure 4(b), were assigned to F—C and F1s bonding at 687.4 and 690 eV, at 687.6 and 690.2 eV, and at 687 and 690.4 eV for 100, 150, and 200 W, respectively.[4,14,19,20]

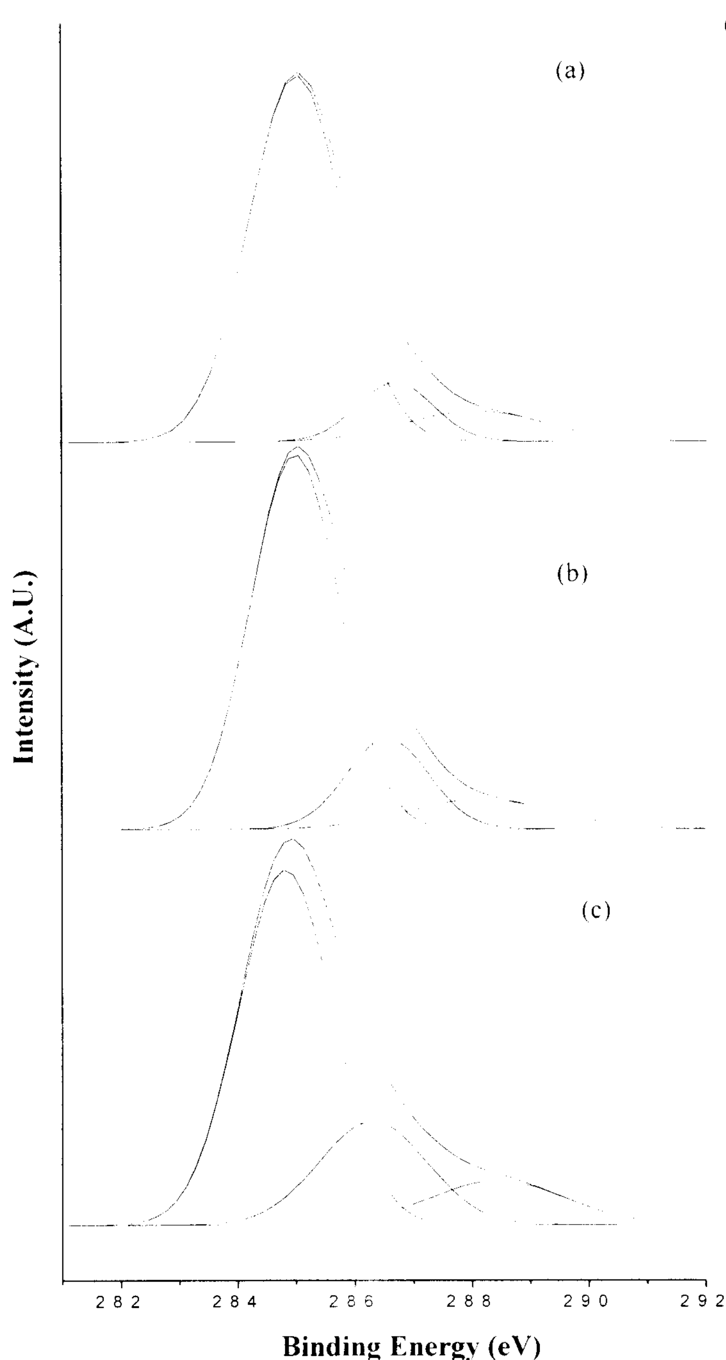
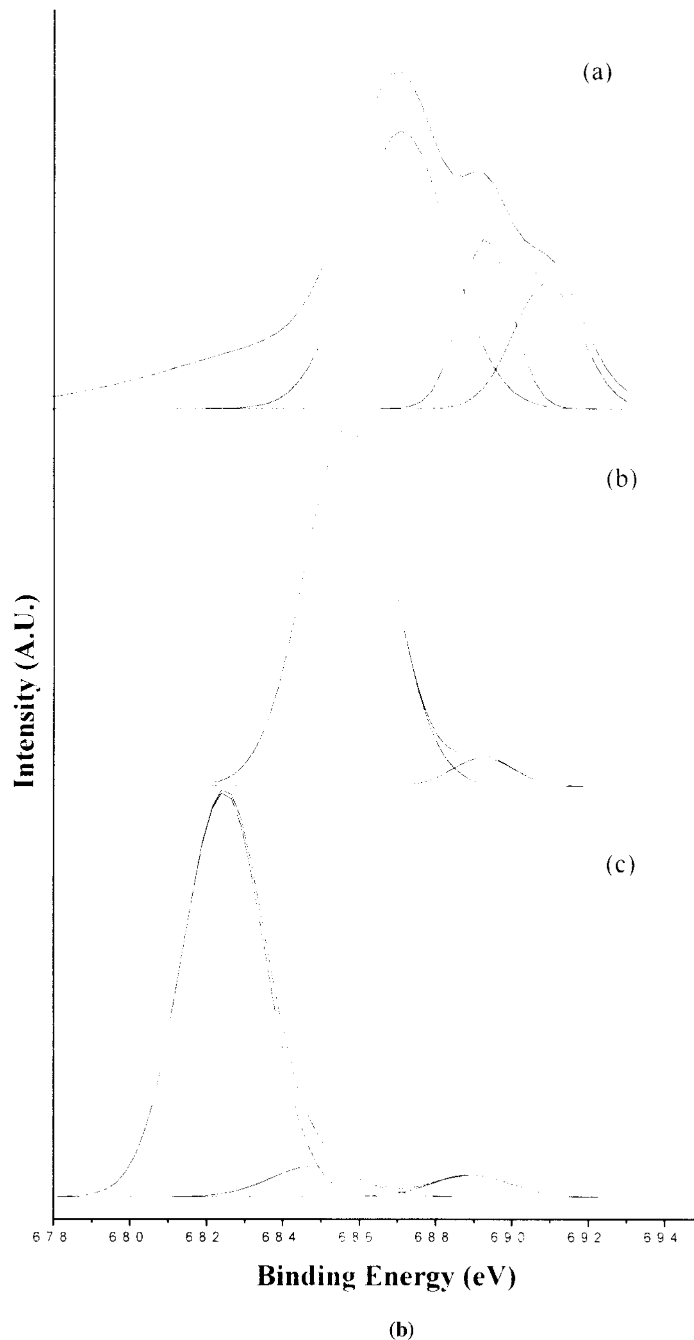


Figure 5 (a) XPS C1s spectra and (b) XPS F1s spectra for PTFE films etched in 20 wt % KOH at 80°C for RF plasma powers of (a) 100, (b) 150, and (c) 200 W for a deposition time of 60 min.

As shown in Figure 4(a), the intensity of the C—F peak appearing at 288–288.8 eV decreased with an increase in the plasma power, and the intensity of the C—CF peak increased with an increase in the plasma power. Furthermore, the films deposited at 200 W showed the appearance of two additional peaks of CF_3 and CF_2 at 292.2 and 290.8 eV, respectively. The binding energy values for bulk PTFE were 292 and 294 eV for CF_2 and CF_3, respectively.[3,17] A comparison of the XPS data for bulk PTFE samples and the films in this work shows that the peak value shifted to a lower binding energy side. This shift could be attributed to the lower thicknesses of the films and the different deposition processes. F/C ratios of 0.51, 0.98, and 1.2 were calculated for plasma powers of 100, 150, and 200 W, respectively. These increased with the plasma



(b)

Figure 5 (*Continued from the previous page*)

power, and this indicated the formation of stoichiometric PTFE films at higher plasma powers. The high intensity of the peaks indicated a highly crosslinked network in the deposited films. Wang et al.[22] reported an XPS investigation of polymer surfaces modified by CF_4/Ar and CH_4/Ar plasmas. They attributed peaks at 293.2, 291.2, and 288.9 eV to CF_3, CF_2, and C—F, respectively; these are close to values of the films in this study with an F/C ratio of 1.2. Furthermore, Jaszewski et al.[23] reported the deposition of ion-sputtered PTFE-like films with CHF_3 as the sputtering gas at an RF plasma power of 50 W. They attributed the XPS binding energy corresponding to CF_3, CF_2, CF, CCF, and CCC at 293.2, 291.4, 289.0, 286.9, and 284.8 eV, respectively. These reported XPS binding energy values well matched those observed in this study.

For further investigation, XPS spectra were recorded for the films after their immersion in 20 wt % KOH solutions for 60 min to test the masking properties [Fig. 5(a,b)]. The chemically distinct carbon atoms after etching, as shown in Figure 5(a), were assigned to C—F and —C—CF at 288.0 and 286.7 eV, at 288.1

and 286.5 eV, and at 288.6 and 286.4 eV at plasma powers of 100, 150, and 200 W, respectively. The peak intensity of C—F and —C—CF increased with the plasma power after etching. The chemically distinct fluorine atoms, as shown in Figure 5(b), showed no appreciable changes in the composition. The F/C ratios for the etched films were 0.2, 0.25, and 0.86 for 100, 150, and 200 W, respectively. This decrease in the F/C ratio with respect to the as-deposited film may have been due to the removal of the unreacted fluorine atoms sitting on the surfaces of the films in highly concentrated KOH solutions.

The results obtained by XPS supported the results obtained by FTIR. XPS indicated that the PTFE groups were still present on the film surfaces even after etching in highly alkaline solutions. There were differences in the intensities and F/C ratios of the films, indicating that the unreacted fluorine sitting on the film surfaces was etched out. The same observation was made with FTIR. The presence of all the PTFE peaks in etched FTIR spectra (Fig. 3) indicated that PTFE films remained on silicon substrates even after etching for 60 min. This showed that the PTFE films worked well as masking materials. The whole silicon substrate was etched out in 300 min at the temperature and concentration of KOH used, but the PTFE films were present on the substrates. This was expected because PTFE is a chemically inert material. PTFE, therefore, is expected to serve as a good mask during MEMS device fabrication.

CONCLUSIONS

PTFE films were deposited by RF sputtering on silicon substrates. The surface characteristics, determined by FTIR and XPS studies of the deposited and etched films, showed that more stoichiometric PTFE was deposited at higher power levels of plasma and stayed on silicon substrates even after etching in 20 wt % KOH solutions at 80°C for a 60-min exposure. Furthermore, the contact-angle measurements and lower interfacial tension (0.76 dyn/cm) showed that greater adhesion of the deposited films with the silicon substrates was achieved. This was further supported by the action of highly alkaline solutions such as KOH on the films. The films after the action of KOH did not show marked differences in composition. Therefore, it can be said that RF-sputtered PTFE films work well as masking materials.

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