Poly(methyl methacrylate) as Masking Material for Microelectromechanical System (MEMS) Fabrication

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ABSTRACT: In the present study direct current (dc) sputtered poly(methyl methacrylate) (PMMA) films deposited on silicon substrates were evaluated as masking materials for anisotropic etching of silicon in aqueous potassium hydroxide (KOH) and tetramethyl ammonium hydroxide (TMAH) solutions. Sputtered PMMA films were characterized by FTIR to ascertain the bonding, by X-ray photoelectron spectroscopy (XPS) for the elemental composition, and by the contact angle for measuring the adhesion of the film with the substrate. FTIR and XPS data showed the presence of a poly(tetrafluoroethylene)-like film on the silicon substrate. The interfacial tension was calculated from the contact angle value, which was 0.82 dyne/cm, confirming good adhesion of the film and the substrate. A pattern was lithographically transferred through the masking material on the silicon substrate, and the etch rate of the masking layer was calculated from the masking time data of the films. The etch rate value of 4 Å/min obtained for the masking material is low compared to the etch rate of the conventional masking materials (60 Å/min for SiO_2 and 8 Å/min for Si_3N_4). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2094–2098, 2006

Key words: poly(methyl methacrylate); direct current (dc) sputtering; X-ray photoelectron spectroscopy; masking materials; potassium hydroxide

INTRODUCTION

In microelectromechanical system (MEMS) technology, new ways and means for the fabrication of microelectromechanical devices and systems are being developed. For the fabrication of 3-dimensional (3-D) high aspect ratio precision structures, silicon micromachining is carried out by anisotropic etching of silicon by etchants such as potassium hydroxide (KOH), ethylenediamine pyrocatechol water, tetramethyl ammonium hydroxide (TMAH), and so forth[1,2] through the pattern transferred in the masking material. A good masking material is one that stays on the substrate until the process of micromachining is complete, that is, until the end of fabrication of the required structure. The commonly used masking materials are SiO_2 and Si_3N_4.[1,2] Thermal treatment is required to grow SiO_2 on clean silicon substrates and for Si_3N_4 a low stress layer has to be deposited by sophisticated processes such as low presssure (LP) and plasma-enhanced chemical vapor deposition.

These processes are costly and time consuming. Polymers have attracted much attention as promising masking materials because of their inherent properties like easy availability, temperature resistance, ability to sustain the action of an anisotropic etchant, and easy procedures for deposition without contaminating the silicon substrate. Polymers such as poly(vinyl difluoride), poly(tetrafluoroethylene), and poly(methyl methacrylate) (PMMA) have been reported as masking materials.[2–4]

The interest in polymer films[5–7] has increased because of their excellent mechanical and chemical properties. PMMA is widely used in coatings, painting, biomaterials, and now microfabrication, especially in microfluidics. Various deposition methods such as plasma polymerization, radio frequency, direct current (dc), and magnetron sputtering have been employed to deposit thin films of PMMA. This work describes the results of the application of a PMMA thin film on silicon as a mask for anisotropic etching in aqueous KOH and TMAH solutions.

EXPERIMENTAL

PMMA thin films were prepared in an in-house fabricated parallel plate dc sputtering system.[8] The sputtering system consisted of a quartz chamber, feedthroughs for a gas inlet, and a pressure measurement and electrode assembly. Parallel plates made of copper were used as electrodes for plasma excitation, and argon was used as a carrier gas. PMMA sheets (with holes) comprising top electrode and silicon substrates on which deposition was done were kept on the bottom plate. A dc power supply was connected between the two plates for plasma excitation. Before loading the silicon substrates in the system, the substrates were cleaned by the conventional RCA cleaning procedure.[9] The system

Figure 1 SEM photos of the PMMA film.

was evacuated to 0.133 Pa (10^{-3} Torr) using a rotary pump to the reactor through a liquid nitrogen trap to avoid contamination of the pump oil. The pressure was measured using a Pirani pressure gauge. The reactor was flushed by passing argon gas through it for 10–15 min to remove the residual gas contents and water vapors. During deposition the pressure of the system was set to 26.66 Pa (0.2 Torr) by controlling the argon gas flow. The deposition was carried out with 35-W dc plasma power at a constant deposition time of 35 min. FTIR and X-ray photoelectron spectroscopy (XPS) characterization was carried out for confirmation of PMMA films on the silicon substrate, and contact angle measurements were performed out to measure the adhesion between the PMMA film and silicon substrate.

RESULTS AND DISCUSSION

The deposition of the PMMA films was done in the radio frequency sputter system for 35 min at 35 W and at a gas flow rate of 15 sccm. The thickness of the PMMA film was 1800 Å as measured with a mechanical stylus profiler (Talystep).

For testing the adhesion and to find the good masking properties, contact angle measurements were carried out using a Ramé–Hart contact angle goniometer. It showed angles on the order of 65° with water and 56° using diiodomethane, indicating the presence of highly hydrophilic groups on the film surface.[10] The lower contact angle value compared to bulk PMMA (105°) may be attributed to the polar groups present on the surface of the film as the deposition was done in a plasma environment. When exposed to the atmosphere, oxygen is adsorbed on the surface of the film, creating polar groups on the film surface. The polar groups interact readily with water, hence the decrease in the contact angle. The interfacial tension of the

film was calculated,[10–12] which showed a value of 0.82 dyne/cm. This lower interfacial value indicates very good adhesion with the silicon substrate.[2,4] The scanning electron microscopy (SEM) micrograph provided in Figure 1 was recorded for dc sputtered PMMA film to observe pinholes in the film, which revealed that the film is pinhole free.

Structural characterization of the deposited films was done using FTIR and XPS techniques. Figure 2 shows the FTIR spectra of the as deposited PMMA film at a plasma power of 35 W. The FTIR peak values that were obtained are 2532, 1725, 1472, 1271, 1060, 917, and 765 cm^{-1}, which are attributed to carboxylic acid, carbonyl group (C=O), C—CH$_3$, C—C—O asymmetric stretch, Si—O, SiOCH$_3$, and CH$_2$ rocking vibrations, respectively. The important peaks of bulk PMMA reported previously[13,14] are at 1729, 1483, 1272, 750, and 2850–3000 cm^{-1}. All peaks except in the range of 2850–3000 cm^{-1} observed in the bulk PMMA spectra were observed in the sputtered PMMA film. Additional peaks found in the present study are the peaks at 1060 and 917 cm^{-1}, corresponding to Si—O and SiOCH$_3$ bonding, respectively. These peaks indicate bonding with the silicon substrate onto which the depositions were carried out.

The composition of the film was further investigated with the help of the XPS technique. This analytical technique features high sensitivity for surface chemical analysis and bonding because of the short escape depth of emitted photoelectrons.[15] All XPS spectra are corrected for charging effects that may arise, referencing them to C1s at 285.0 eV as an internal standard, present in the sample. XPS spectra of the constituent elements revealed carbon and oxygen as the main elements, indicating uniform deposition of the film on the substrate. Other impurities were not observed. The C1s spectra of the sputtered PMMA film with a 35-W constant deposition power and 35-min deposition time are revealed in Figure 3. The C1s is deconvoluted using the Gaussian
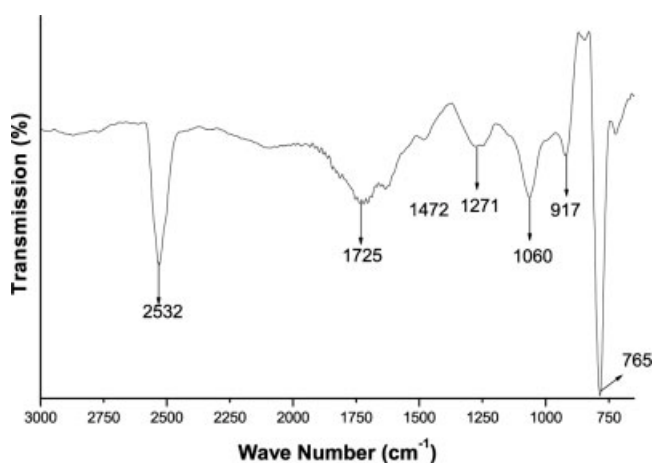

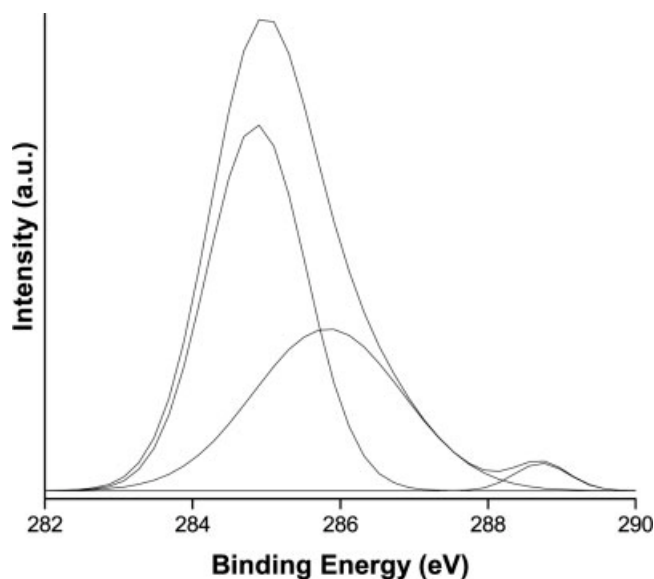**Figure 2** The FTIR spectrum of the dc sputtered PMMA film.

Figure 3 The XPS spectrum for the PMMA film.

curve-fitting technique into different moieties. Table I gives the peak values of the C1s spectra from Figure 3 and their assignments. Standard peak values[16] for bulk PMMA and those available from the literature[17,18] are also provided in Table I for comparison.

Similar peak values obtained in this work as standard peak values and those obtained from the literature confirm the presence of PMMA film on the substrate. The elemental composition of the sputtered PMMA film is the same as that of the bulk.

The PMMA film deposited on the silicon substrate was subjected to etching under standard conventional anisotropic etchants (KOH and TMAH) to test the masking characteristics of PMMA. The etch rate was also calculated for the PMMA film.[19] The rate versus temperature of the etchant profile is given in Figure 4(a,b) for KOH and TMAH, respectively. The etch rate increases as we increase the temperature of the etchant. It is obvious that as the temperature of the etchant increases, the etching of the film increases. There is also a similar increase in the etch rate with an increase in the concentration of the KOH and TMAH etchants. Etch

TABLE I
Cls Spectra Assignments and Peak Values
for Bulk PMMA

Assignment	Present study (eV)	Std. peak values[a] (eV)	Literature[b] (eV)
Cls	285	285	285
C=O	286.2	286.6	286.6
O—C=O	288.7	289.0	289.0

[a] Standard peak values are from Briggs and Seah.[16]
[b] Literature values are from Schulz et al.,[13] Groning et al.,[17] and Ben Amor et al.[18]
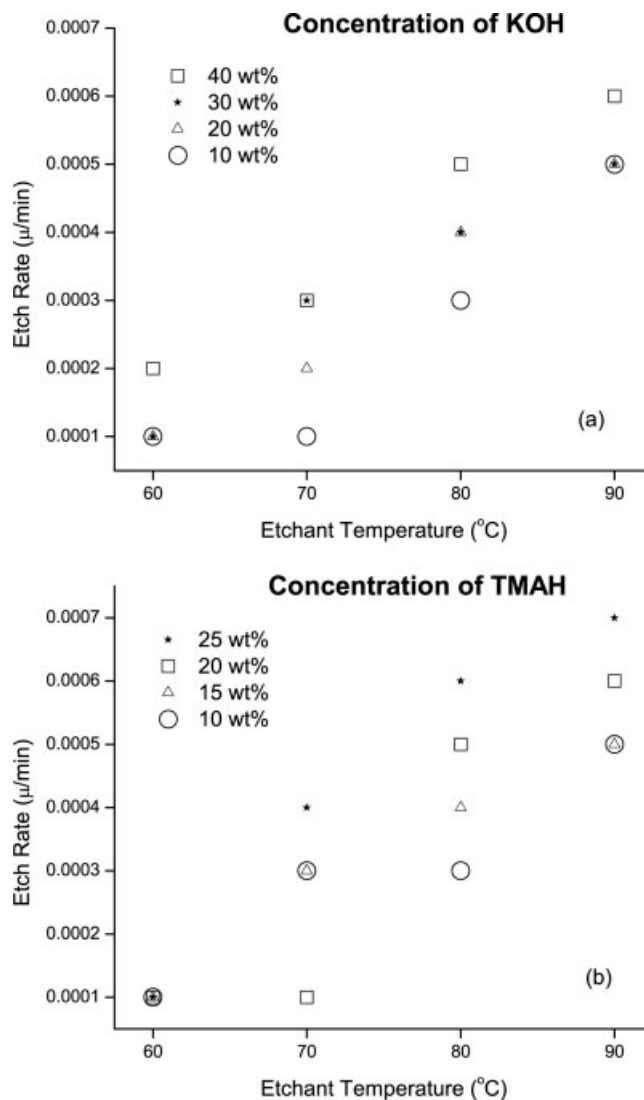

Figure 4 The etch rate of PMMA film in (a) KOH and (b) TMAH etchants.

rates of 4 and 3 Å/min were obtained with 20 and 10 wt % KOH and TMAH, respectively, at 80°C. These etch rates are sufficiently smaller than that for silicon (1.4 μm/min) and are therefore thought to be suitable for micromachining. The etch rates of SiO_2 and Si_3N_4 are 60 and 8 Å/min, respectively, which are on the same order as the etch rate of PMMA. The advantage of using PMMA as a masking material is that the films can be deposited at room temperature and require less time to deposit. This is unlike SiO_2 and Si_3N_4, which require 800–1000°C and 8-h deposition. Moreover, the present study requires a simple sputtering system that is more cost effective than the system required for SiO_2 and Si_3N_4. At these conditions the masking time obtained for PMMA is greater than 300 min. In this time the 500-mm thick silicon substrate gets completely etched out at a etch rate of 1.4 m/min at a 20 wt % concentration of KOH at 90°C.[1] PMMA can withstand higher
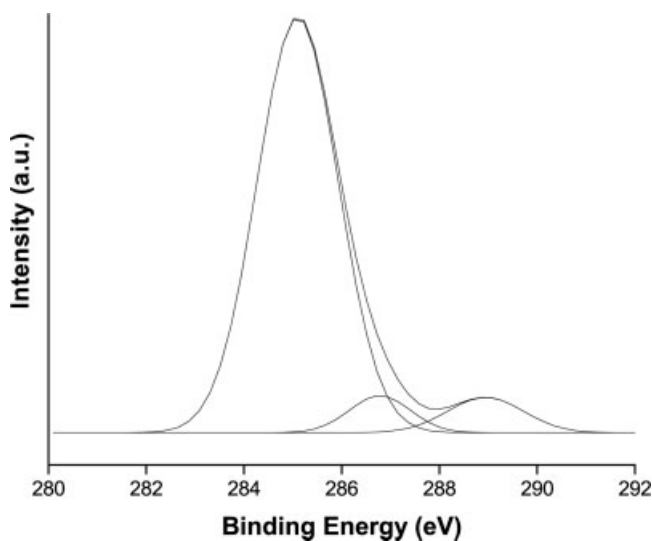
Figure 5 XPS spectra for the PMMA film etched in KOH for 4 h.

Figure 7 The cantilever beam etched in silicon.

concentrations of KOH and TMAH for larger time periods compared to conventional masking materials. PMMA film was tested for over 4 h in 20 wt % KOH at 80°C. The XPS (Fig. 5) spectrum obtained after the etching of KOH shows the presence of PMMA on the silicon substrate. XPS shows a decrease in intensity of the 286.6- and 288.7-eV peaks without any shift, which confirms that the PMMA stays on the silicon substrate after 4 h of etching. This proves the better masking properties of PMMA than conventional masking materials like SiO_2 and Si_3N_4. Details of some decomposition of the film are found from the XPS spectrum (Fig. 5), but that might be attributed to the surface removal of PMMA film.[4] In addition, there is no pinholing effect observed because of the etching action. If there were pinholes
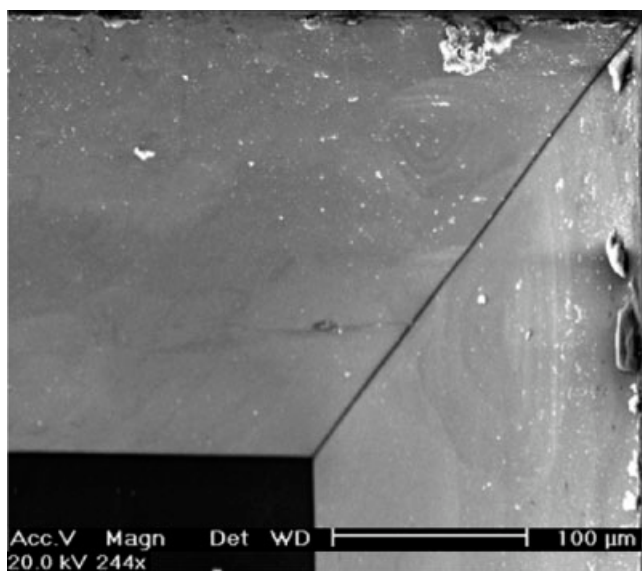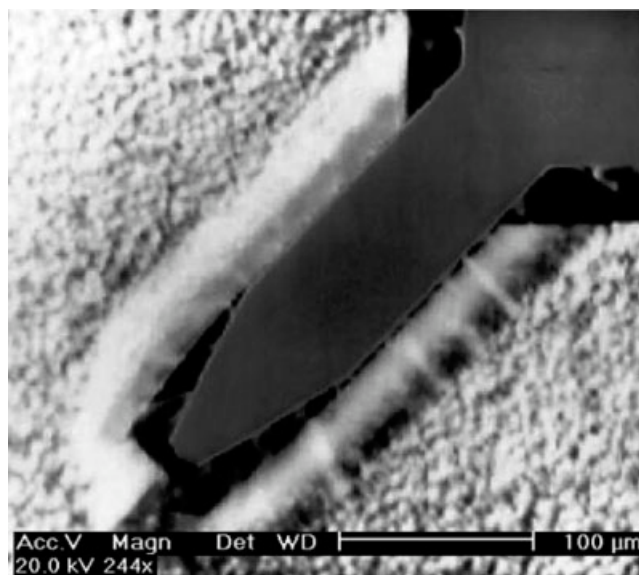
the etching on a particular plane would not have been possible. An SEM photograph was recorded to confirm this.

A transfer of pattern was carried out to fabricate a diaphragm structure in silicon using PMMA as a masking material. The process steps for the transfer of pattern are reported elsewhere.[19] This silicon substrate was then etched (420 μm) in 40 wt % KOH at 90°C to attain a diaphragm thickness of around 80 μm. The etching was carried out for around 400 min at a silicon etch rate of 1 μm/min. Figures 6 and 7 provide the SEM micrographs of the etched diaphragm and cantilever beam in silicon using PMMA as a masking material. This proves that PMMA can be used as a masking material and can replace the conventional SiO_2 and Si_3N_4 masking materials. Fabrication of complex structures and the study of the removal of PMMA after the completion of the etching process is underway.

CONCLUSION

PMMA films were deposited by dc sputtering on a silicon substrate. The surface characteristics such as FTIR and XPS studies of the deposited and etched film showed that more stoichiometric PMMA was deposited. It was also shown that the PMMA stayed on the silicon even after etching in 20 and 10 wt % KOH and TMAH solutions, respectively, at 80°C for 60 min. Further, the contact angle measurement and lower interfacial tension (0.82 dyne/cm) demonstrated that good adhesion of the deposited film with the silicon substrate was achieved. Etch rates of 4 and 3 Å/min with KOH and TMAH etchants, respectively, and the diaphragm etched in silicon proved the better masking characteristics of PMMA. Thus, we demonstrated that

Figure 6 The diaphragm (~ 80 μm) etched in silicon.

PMMA can be a good substitute for conventional masking materials (SiO$_2$ and Si$_3$N$_4$).

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