Novel Polymeric Protective Coatings for Hydrofluoric Acid Vapor Etching During MEMS Release Etch

Tingji Tang[1], Curt Planje[1], Ramachandran K. Trichur[1], Xing-Fu Zhong[1], Shelly Fowler[1], Gu Xu[1], Kimberly Yess[1], Xie Shao[1], Daniel J. Vestyck[2]

[1] Brewer Science Inc., 2401 Brewer Dr., Rolla, MO 65401, USA
[2] Primaxx, Inc., 7377 William Avenue, Suite 800, Allentown, PA 18106, USA

Abstract: MEMS release etching of a sacrificial oxide layer plays an important role in fabricating moving parts in MEMS devices. Traditionally, wet chemistries have been used in order to achieve release etching, but their use can create surface tension issues that can cause the MEMS microstructures to stick together. It has been demonstrated that using hydrofluoric acid (HF) vapor release etching can efficiently circumvent the stiction phenomenon because it substantially eliminates surface tension. Inorganic-based films such as silicon nitride, alumina, SiC, polysilicon, etc., have been used as masking materials that are resistant to vapor HF. These materials require very-high-temperature vacuum deposition techniques that are often lengthy, complicated, and costly. This paper presents novel spin-on polymeric HF-resistant blanket coating materials that protect silicon oxide or metals against HF attack during HF vapor etching. These newly developed polymeric coatings can be processed at lower temperatures (< 250ºC) and are applied as thin films (10-15 µm) for extended HF vapor etching periods (longer than 1 hour). Hence, these HF vapor–resistant materials will enable the MEMS industry to significantly lower the cost of manufacturing MEMS devices and will significantly simplify the manufacturing process as well.

Key words: MEMS release etching, HF etching, HF vapor etching, protective coating

Introduction

MEMS devices are increasing in complexity and are finding numerous applications in industrial and consumer products such as cellular phones, micromirrors, radio frequency (RF) devices, microprobes, and pressure sensors.[1] One of the critical processing steps for these devices is release etching. In this step, a sacrificial layer, usually silicon oxide, is removed from certain regions to allow a range of motion of specific features. Occasionally, release etching of a silicon sacrificial layer was carried out using supercritical fluid formulations.[2] The thickness of the materials to be removed may vary from a few hundred angstroms to several microns. Because this sacrificial layer is silicon oxide in most cases, MEMS release etching has been historically performed using wet fluorinated chemistries that tend to produce strong surface tension and lead to stiction, resulting in either device malfunction or a reduction in the final product yield.

Recently, it has been demonstrated that using hydrofluoric acid (HF) vapor for release etching can efficiently circumvent the stiction phenomenon because it substantially eliminates the surface tension that causes the stiction.[3] During HF vapor etching, it is necessary to use masking or protective materials to protect the silicon oxides and metal features from HF attack. Traditionally, inorganic-based films such as silicon nitride (Si_3N_4),[4] alumina (Al_2O_3),[4] SiC,[5] polysilicon,[5,6] and aluminum[4] were used to provide protection during HF vapor etching, but the effectiveness of their protection against HF attack was very limited due to the nature of the materials. Moreover, such inorganic masking layers require high-temperature deposition techniques, which are often lengthy and complicated. It was reported that a polyimide film having a thickness of about 5-11 µm could survive the HF vapor etching process but for only less than 80 seconds, which limits its practical applications.[7] Parylene films used as protective films survived HF vapor etching for longer times, but parylene films were deposited by chemical vapor deposition (CVD).[8] A previously developed polymeric coating (ProTEK®-A2 coating by Brewer Science) can survive 1 hour of HF vapor etching but only after a triple coating is applied to achieve a thickness of 45 µm.[9] Presented in this paper is a novel spin-on polymeric HF-resistant coating material (developed as part of the ProTEK® product line) to provide protection against HF attack during either HF vapor etching or concentrated HF wet etching.

The diffusion of the HF molecules through the polymeric films can be described by the following three-step transport process: 1) dissolution of the HF gas in the organic/polymeric materials; 2) diffusion of the dissolved HF through the organic/polymeric materials; 3) desorption of the dissolved HF gas from the organic/polymeric materials to react with the wafer surface's HF-sensitive features.[8] These three steps happen in a serial manner. Thus, the HF molecule transport rate can be characterized by a permeation coefficient, which is the product of the solubility and diffusion coefficients of the materials. Also, reducing or suppressing each step enhances masking properties of the organic/polymeric materials. The solubility coefficient (steps 1 and 3) will be minimized when the chemical similarity between the HF molecule and polymers is minimized. Because HF is very polar (dipole moment of 1.94 debye), a nonpolar polymeric material is speculated to exhibit much higher HF resistance and thus can provide enhanced masking properties against HF vapor. Polyolefins are hydrocarbon-based polymers having the least polarity along with solubility in hydrocarbon organic solvents. The diffusion coefficient (step 2) can be minimized by using highly crystalline materials or highly crosslinked materials with minimal free volume and dissimilar chemical structure as well. In addition, the overall transport process is inversely proportional to the thickness of the applied protective coatings.

Experimental

Materials. For the protective coating layer, the Polymer 1 platform was made from a blend of commercially available and solvent-soluble polyolefins. Polymer platforms 2 through 4 were made from other commercial available polymer types. Primer layers were used to improve the adhesion between polymers and substates. Concentrated HF solution (ACS grade, 48%-51%, from Alfa Aesar) was used as received. All the polymer solutions were filtered through 0.2-μm filters before being applied onto wafers.

Characterization. The films were applied and baked using a Brewer Science® Cee®-100CB spin-coating and baking tool. The Polymer 1 coating thickness was measured with a Veeco® Dektak® 8 profiler. The primer layer thickness was obtained using either a Gaertner LSE-WS ellipsometer or a Veeco® Dektak® 8 profiler. The oxide thickness was measured using a Metricon® 2010 prism coupler. Scanning electron microscope (SEM) analysis was performed using a LEO Gemini SEM. The concentrated HF wet etchant testing was performed in an in-house HF acid hood. HF vapor tests were done on a Primaxx® CET® tool with anhydrous HF and alcohol (ethanol) as the etching composition at set temperature (45°C). Two recipes were used for testing the HF vapor resistance of our protective coatings: a "mild" recipe and a "medium" recipe with thermal oxide etching rates of 100 Å/min and 350 Å/min corresponding to etch 0.6μm and 2.1 μm of thermal oxide in an hour, respectively.

Results and Discussion

Concentrated HF etching test. It is logical to assume that proving the survival of protective coatings in a concentrated HF solution would be a prerequisite for testing their survival during HF vapor etching for the same period because the vapor etching is done at an elevated temperature under vacuum. Also concentrated HF solution is readily available and is relatively easy to work with if proper personal protective equipment is used. Accordingly, polymer screening was performed in concentrated HF solution for 1 hour with the polymer films coated on either oxide substrates or aluminum-coated silicon wafers. Different kinds of polymers such as polyimides, epoxy resins, polyacrylates, rubbers, polyvinylchloride, polyolefins, block copolymers of styrene with isoprene or butadiene, and even some of their blends were comprehensively investigated. Only several polymer platforms, illustrated in Table 1, can withstand etching in concentrated HF solution for 1 hour when they are applied atop a polymer primer layer (PL-1, PL-2, and PL-3).

Table 1. Polymer platforms resistant to concentrated HF solution.

	Polymer Platform 1	Polymer Platform 2	Polymer Platform 3	Polymer Platform 4
Polymer type	Polyolefin	Specialized rubber	Rubber	Blends of rubber/tackifier

The etching behavior in concentrated HF solution for Polymer Platform 1 with and without the presence of a thin primer layer is shown in Figure 2. Without the primer layer, even Polymer Platform 1, made using polyolefins, cannot survive concentrated HF etching for 1 hour, as indicated by the appearance of blisters formed on the non-patterned blanket oxide wafers after etching (Figure 2a). Once a thin primer layer (60-

70nm) was applied, intact films were obtained after HF wet etching, and no oxide loss was observed by prism coupler measurement. Similar results were also obtained when the protection testing was done on the patterned aluminum wafer. These results provide evidence for the effectiveness of the primer layer by increasing the adhesion as well as helping block the penetrated HF molecules.
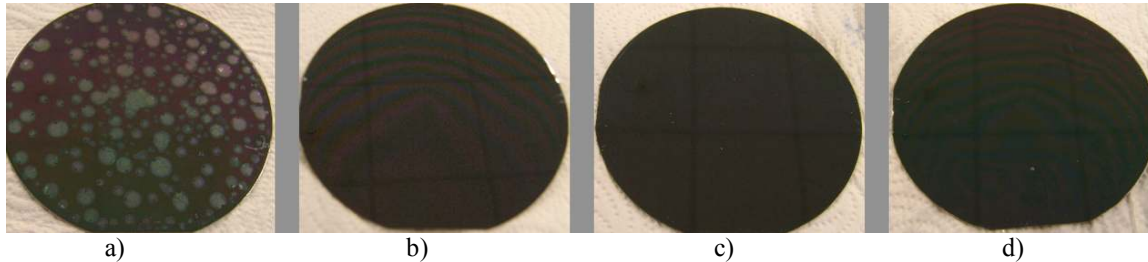

a)   b)   c)   d)

Figure 2. Pictures of 15-µm-thick Polymer Platform 1 coatings with different primer layers after 1 hour of etching in concentrated HF solution: a) No PL; b) PL-1, 72 nm; c) PL-2, 62 nm; d) PL-3, 75 nm.
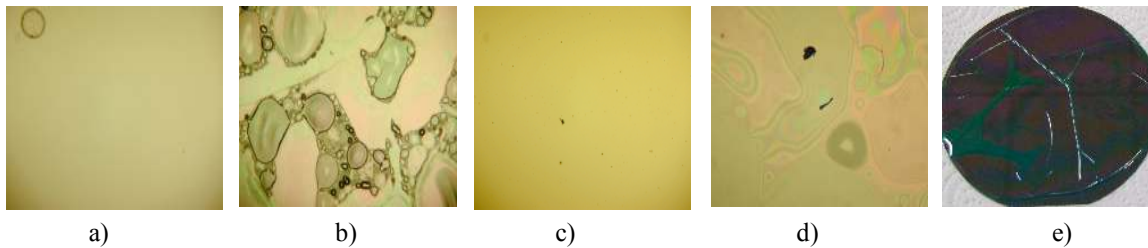

a)   b)   c)   d)   e)

Figure 3. OM graphs (a-d) and picture (e) of different protective coatings at ~10 µm without primer layers after HF vapor etching for 1 hour at mild conditions: a) Polymer Platform 1; b) Polymer Platform 2; c) Polymer Platform 3; d) Polymer Platform 4; e) Polymer Platform 1

HF vapor etching test. Polymer platforms (thickness around 11-13 µm) that survived etching in concentrated HF solution were further tested, without a primer layer under mild conditions using blanket oxide wafers, against HF vapor etching for 1 hour. From Figure 3 and Table 2, it can be seen that only Polymer Platform 1 survived the 1 hour etching without oxide loss after the protective films were stripped. Although Polymer Platform 3 produced very good optical microscope (OM) pictures after etching, an oxide loss of 16.7% was obtained for this platform, which indicates that, when used alone, it failed to effectively protect against HF vapor etching. Also, as for Polymer Platform 1 films, edge lifting occurred or wrinkles developed after HF vapor etching (see Figure 3e), which indicates the need to use a primer layer.

Table 1. Polymer platforms tested towards HF vapor etching.

	Polymer Platform 1	Polymer Platform 2	Polymer Platform 3	Polymer Platform 4
Polymer thickness	13 µm	11 µm	11 µm	12 µm
Oxide Thickness*	1.19 µm	NA	1.00 µm	0.79 µm
Oxide loss	0	NA	16.7%	34.2%

*After HF vapor etching for 1 hour at mild conditions. The thermal oxide thickness was about 1.20 µm before HF vapor etching

Therefore, a primer layer was introduced to supplement the protective film structure, noted as PL/Polymer Platform 1. Because oxide or metals are actually protected by our protective coatings during real device fabrication, we patterned oxide wafers to mimic a real scenario for the protective coatings. The patterned oxide wafers coated with PL-1 layers and Polymer Platform 1 (10-15 µm) were tested under different etching conditions, as shown in Figure 4a-c, respectively. It is clearly seen that the PL-1/Polymer Platform 1 film coatings can withstand both the mild and medium HF vapor etching for up to 2 hours without protective film degradation and oxide attacking (no blisters formed over the oxide patterns). However, if PL-2 is used as a primer layer instead of PL-1, the film coating combination of PL-2/Polymer Platform 1 failed under the mild vapor etching conditions after 1 hour, even though it protects well in concentrated HF solution. These results are evidence of the difference in etching behavior between concentrated HF solution and HF vapor as well as the superior effectiveness of PL-1 as the primer layer. Also noteworthy is the fact

that the bilayer film structure of PL/Polymer Platform 1 can provide much flexibility in tuning the thickness of either the PL or the Polymer Platform 1 top coating for different HF vapor etching recipes and durations as well.
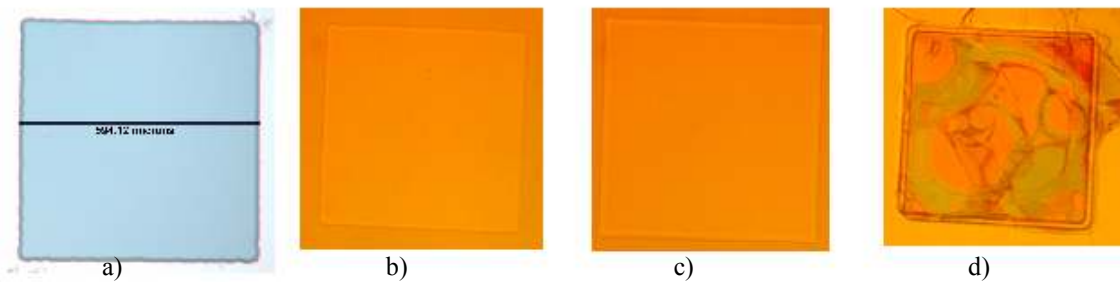

Figure 4. Different PL/Polymer Platform 1 coatings after HF vapor etching under various conditions. a) PL-1 (400 nm) and Polymer 1 (10 µm), mild conditions, 1 hour; b) PL-1 (400 nm) and Polymer 1 (15 µm), medium conditions, 1 hour; c) PL-1 (800 nm) and Polymer 1 (10 µm), medium conditions, 2 hours; d) PL-2 (150 nm) and Polymer 1 (15 µm), mild conditions, 1 hour.
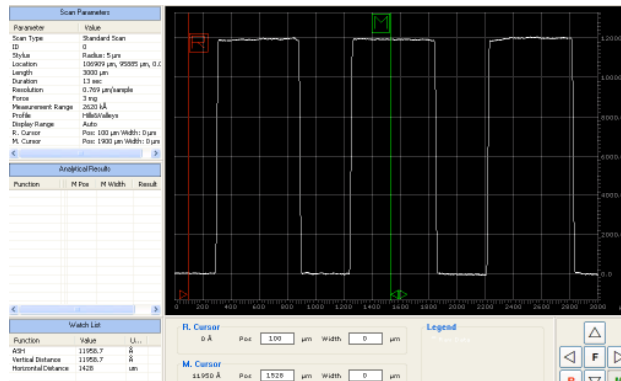

Figure 5. Oxide thickness profile for PL-1 (400 nm) /Polymer 1 (10 µm) coated wafers after HF vapor etching at mild conditions for 1 hour. The original oxide thickness is 1.2 µm.

After removing the Polymer Platform 1 and PL-1 layers through Nanostrip® cleaning, the oxide profile was measured by profilometer to further characterize our protective coating's HF vapor etching resistance performance. Removing through plasma dry etching was also under investigation since MEMS release process has to be performed without wet solvents involved. No oxide loss was observed, and the smooth oxide surface was maintained as well after HF vapor etching, as indicated in Figure 5. However, a slight drop of refractive index from 1.47 to ~ 1.45 was observed by prism coupler measurement. The oxide surfaces before and after HF vapor etching were also characterized by SEM, as shown in Figure 6. Some surface roughness was observed at such high magnification, which might have led to the lower post-vapor-etching refractive index.
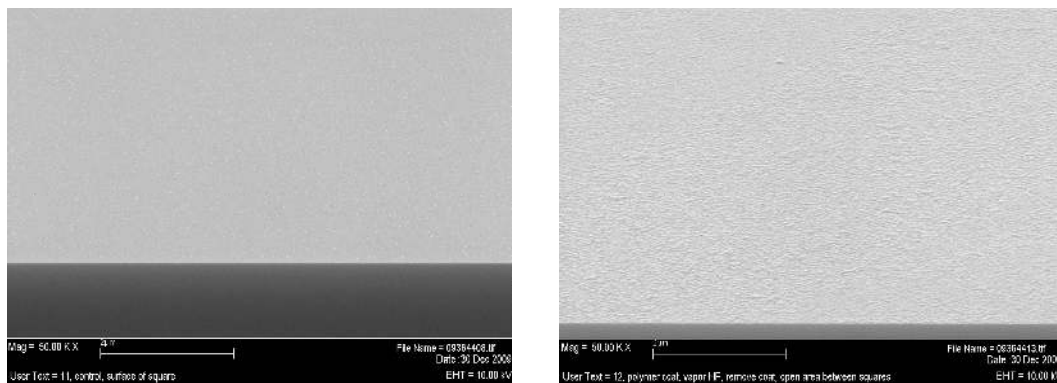

Figure 6. SEM images of oxide surfaces before (a) and after (b) HF vapor etching.

Summary

A spin-on protective polymer coating in combination with a base polymer layer was successfully developed for both concentrated HF solution and HF vapor etching. Our newly developed polymeric coatings can be processed at lower temperatures (< 250 °C) and can be used as thinner films (10-15 µm) for an extended HF vapor etching period. Hence, the newly developed materials that are resistant to HF vapor etching will enable the MEMS industry to significantly lower the cost of manufacturing MEMS devices and will simplify the manufacturing process as well. Currently, work is progressing on making photosensitive materials based on Polymer Platform 1.

References

1. Mahalik N. P. "Principle and Applications of MEMS," *International Journal of Manufacturing Technology and Management*, *13*, **2008**, 324-343.
2. M. B. Korzenski, T. II. Baun, C. Xu, E. G. Gheneiu "Removal of MEMS sacrificial layers using supercritical fluid/chemical formulations," U.S. Patent No. 7,160,815 B2, Jan. 9, **2007**.
3. A. Witvrouw, B.D. Bois, P. D. Moor, A. Verbist, C.Van Hoof, H. B. Bender, K. Baert "A comparison between wet HF etching and vapor etching for sacrificial oxide removal," *Proceedings of SPIE* [MEMS and MOEMS], vol. 3680, **1999**, 956-963.
4. T. Bakke, J. Schmidt, M. Friedrichs, B. Volker "Etch stop materials for release by vapor etching," 16th MME workship, Goeteborg, Sweden, **2005**.
5. M. Wong "Method for vapor release etching of silicon," U.S. Patent No. 5,423,944, June 13, **1995**.
6. J. Chiaroni, H. Grange, O. Pollet, E. Bergman "Characterization of a batch HF vapor processor for MEMS release etching," *Proceedings of 2004 Joint International Meeting on Microfabricated Systems and MEMS VII*, October 308th, **2004**, 127.
7. T. Zhang, J. K. Lee "Polyimide as a mask in vapor hydrogen fluoride etching," U.S. Patent No. 7,128,842 B1, October 31, **2006**.
8. J. Martin, T. J. Brosnihan " Vapor HF etch process mask and method," U.S. Patent No. 7,338,614 B2, March 4, **2008**.
9. a) C. Li, K. Ruben, T. Flaim "Spin-on protective coatings for wet-etch processing of microelectronics substrates," U.S. Patent No. 2006/0240181, October 26, **2006**. b) Brewer Science Inc., internal report.