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Technical Note

Vapor etching to avoid micro-masking by gas-bubbles in wet release of MEMS

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Abstract

We report on the formation of gas bubbles during the release of MEMS devices using buffered oxide etch. Several approaches to mitigate the problem are proposed and tested together with a qualitative study of the phenomenon. The chemical reaction behind such phenomenon and the influence of defects and topography is discussed. Finally, a comparison with the HF-vapor release technique is shown.

Keywords: wet etching, bubbles, micro-masking, MEMS

(Some figures may appear in colour only in the online journal)

1. Introduction

Most micro-electromechanical systems (MEMS) devices are made of a structural silicon layer and a sacrificial silicon oxide layer which is removed during the release. MEMS fabrication requires the release of the moving parts of the device by removal of the sacrificial layer underneath the structural one. SiO_2 is usually etched by exposure to hydrofluoric acid in the form of either liquid, vapors, or gas. The use of gaseous hydrofluoric acid (HF) is nowadays the most used approach; indeed, gaseous HF avoid several problems such as stiction and problems related to capillarity. On the other hand, gaseous HF is very aggressive to many materials. The gaseous form of HF can lead to problems such as metal blistering or galvanic reactions [1, 2]. This can pose problems in the integration of new materials in the MEMS fabrication chain if not properly passivated. The alternative to vapor and gaseous HF is the wet-etch of SiO_2, this step is usually performed using buffered oxide etch (BOE), a mixture of ammonium fluoride and HF. BOE allows to use photoresist as passivation layer and a better control of the etch rate with respect to concentrated HF. As previously reported [3], the wet etching can pose problems of stiction during the drying of the devices after the release. This problem can be reduced by proper design of the MEMS structure, use of stoppers and drying techniques such as the critical point drying.

Unfortunately, problems related to the use of BOE are not only related to stiction. In this paper, we discuss a specific problem encountered during the fabrication of MEMS devices by means of wet etch which, to the best of our knowledge, seems not to be mentioned in literature regarding release of MEMS devices and might be of interest to research groups working with this technique. The problem we encountered during the release of MEMS devices is the formation of bubbles of gas which remain attached to the substrate hindering or blocking the complete release of the structure. The etching of silicon oxide in BOE should not produce gas

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[4, 5], on the other hand undesired etching of silicon might lead to gas formation. Si(100) is etched in NH_4F/HF based solution when the *pH* is above 5 [6] and in general in NH_4F solutions [7, 8]. Etching of silicon in fluoride solutions can also be induced by exposure to light [9]. The etching of silicon is associated with the formation of H_2(g) bubbles which tend to form in the presence of defects [7, 10, 11]. Moreover, doping of silicon can also increase the etch rate in HF solutions [12]. In this work we tried to investigate the different reasons behind the formation of gas bubbles and possible approaches to reduce this phenomenon in MEMS application.

The paper is divided as follows: first, the device geometry, fabrication and the experimental setup are presented. Second, different solution approaches are shown, followed by a discussion of the results.

2. Methods

2.1. Test structure design

The device used for our investigation is reported in figure 1. The mechanical structure is composed of a moving frame, suspended by four folded-beam springs. The frame is divided in cells and within each cell there is a fixed pad. The features are separated by gaps which are about 2 μm wide, similar to those usually found in MEMS [13–15]. The thickness of the movable part of the device (5 μms) is however smaller than a standard process for inertial MEMS (typically above 20 μm). This particular layout is linked to the realization of a peculiar MEMS magnetometer [16].

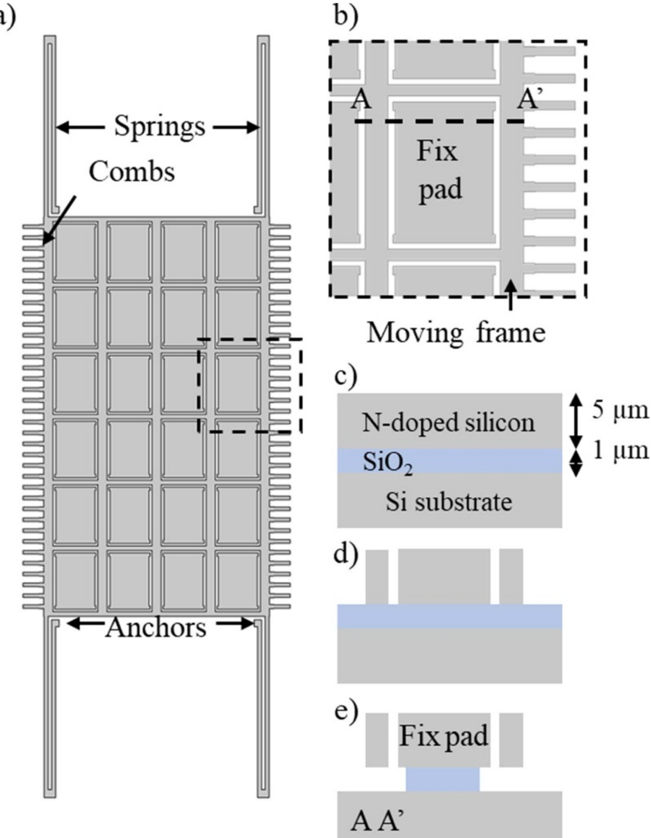

Figure 1. (a) Schematic view of the device, fixed anchor points are not represented; (b) zoom in of the device, showing the fixed pads within the moving frame (c) SOI stack used to fabricate the device (d) Schematic view of the device patterning; (e) Schematic A–A' cross-section view of the final device after release.

2.2. Test structure fabrication

The fabrication of the test structure starts with a silicon on insulator (SOI) wafer having 5 μm-thick silicon mechanical layer doped with phosphorus on top of 1 μm of thermal silicon dioxide. The silicon layer is grown epitaxially with the addition of dopants starting from a thinner silicon seed layer of an SOI, final doping is 2e18 cm^{-3}. The silicon layer is patterned using a maskless photolithographic process (employing the AZ5214 photoresist and the MLA100 laser writer from Heidelberg) to protect with a resist the parts not to be etched and reactive ion etching (RIE, Oxford plasma lab) with a Bosch-like process. The chip is exposed to a bath of BOE in different conditions and its then dried using a critical point dryer (Tousimis 815 B series).

Finally, for comparison purpose, the same geometry is released using vapor HF in the commercial system provided by Idonus VPE100 [17].

3. Results

3.1. Release step—fabrication issue

A very uniform etching is required over all the surface of the device to grant all parts of the moving frame are released at the same time. This would yield a clean and uniform gap under all segments of the frame. Accordingly, BOE was preferred to HF as etching agent due to its chemical composition stability that enhances repeatability, its mild *pH* that is compatible with the resist and its limited etch rate, that enhances etching stop time control. We would like to point out that the resist is not removed before release; this is because the final goal of this process is to use photoresist as protecting layer for additional functional materials previously added on the surface of the MEMS device. This condition will be a limiting factor during the release test, as explained later.

During the wet release two critical phenomena are observed. The first is the generation of gas bubbles. These bubbles, that become evident as the etch proceeds, follow the arrangement of devices in the substrate (figure 2). Bubbles tend to be centered in the moving frame, where the gas is formed, and suitable anchor points are present.

Figure 3 reports SEM and optical images of the device after release in static BOE (1:6) (J.T.Baker) for 40 min. From the images it is clearly visible how the etching of the silicon oxide is not uniform. The dark area of the optical image clearly visible in figure 3(c), corresponding to unetched SiO_2, is found on different devices with a random position.

However, all observed dark areas share a common ovoidal shape, congruent with the shape of the bubbles. The composition of the unetched sample features was studied

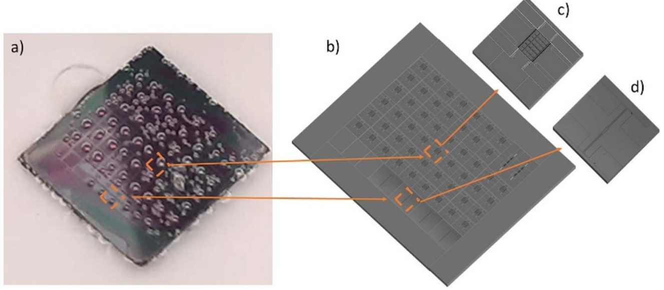

Figure 2. (a) Image of the chip during release. (b) Schematic representation of the chip highlighting (c) the matrix-like structure and (d) the clamped-clamped cantilever. It can be seen how several bubbles are formed and how they dispose on a regular pattern according to the layout. The clamped-clamped layout shows smaller bubbles which form on the side, not hindering the release.

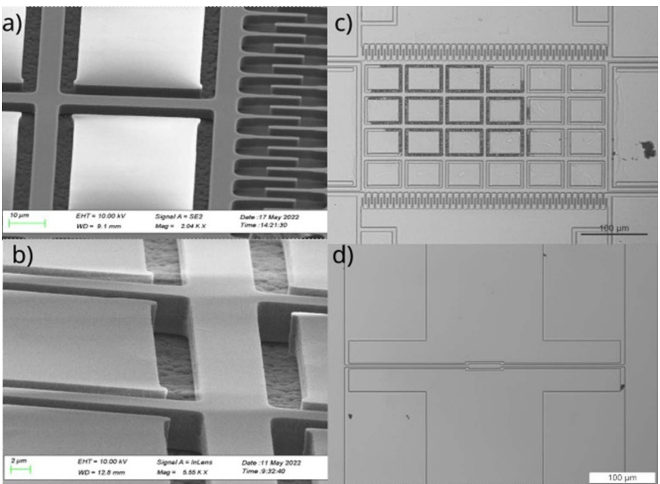

Figure 3. SEM (a) and (b) close-view of the device gaps and optical images (c) and (d) of the devices after release in static BOE. Clamped-clamped beam geometry (d) does not show traces of oxide, while the matrix-like geometry suffers from bubble shadowing.

using energy dispersive x-ray(EDX), confirming the presence of oxygen and the hypothesis of unetched SiO_2. Moreover, the residual areas were successfully etched using a second dip in BOE, this also confirmed that the residual layer was indeed unetched silicon oxide. Noteworthy, devices with a more elongated geometry (figures 2(d) and 3(d)) do not suffer from this problem. In these devices bubbles tend to form close to the anchor of the cantilever and do not hinder the release. Thinner elements, like comb-fingers and springs of the resonator are also unaffected by the masking problem.

Once formed, bubbles with a size in the range of tenths to a few hundreds of microns (as observed in figure 2) may induce significant localized micro-masking that prevents the required uniformity of the etching process (as the stains observed in figure 3(c)). This is not uncommon in alkaline etching of silicon [7, 18, 19] or in metal assisted etching of silicon [20]. In our case (i.e. BOE etching of SiO_2), bubble micro-masking leads anyway to an unsuccessful release of the moving parts.

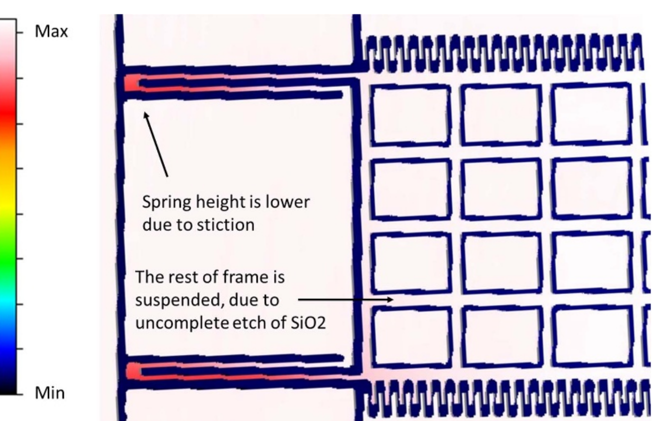

Figure 4. Optical profilometer image of a suspended device after prolonged wet etching in BOE to release areas previously masked by bubbles. Part of the device is collapsed (springs) while other parts are held in place by the unetched silicon oxide layer.

Table 1. Test conditions performed during the release.

Test condition	Qualitative results
BOE (1:6) $T = 20$ °C	Masking
BOE (1:6) $T = 20$ °C + stirring	Masking
BOE (1:6) at $T = 30$ °C	Masking
BOE (1:6) + added surfactant	Reduced size masking
BOE (1:7) surfactant (commercial solution including surfactant)	Masking
Diluted BOE 1:2	Masking
HF vapors	No masking

As a result, the moving frame is completely released just in some parts, thus impeding the free motion of the resonator. In this case longer etching time would not solve the problem properly, creating excessive under-etching in the clamps, elastic distortions or even major damage (figure 4).

3.2. Proposed solutions

In order to solve this issue several approaches have been tested as reported in table 1. Most of these approaches are used for wet-etching steps in order to obtain improved uniformity and remove residuals which could lead to masking [21]:

The first approach consisted in the use of a stirrer in the bath to promote the detachment of the bubbles or hinder their formation. The transport of fresh solution close to the bubble nucleation zone is not able to avoid bubble formation because the solution is not able to incorporate the gas produced (solubility effect) nor it is able to drag the bubble away (hydrodynamical effect) in agreement with previous [13].

The second approach was to perform the release at higher temperature. The rationale behind this point is that etching at higher temperature could change surface tension of the liquid increasing the contact area between solid and liquid and reducing the one between solid and gas, therefore promoting the detachment of the bubble [22]; on the other hand

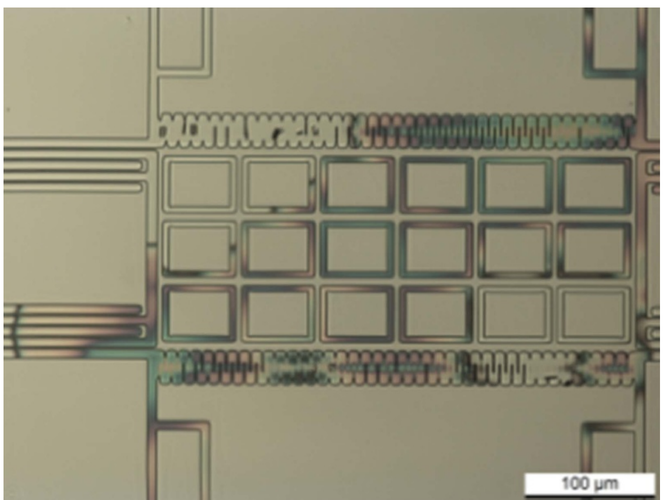

Figure 5. Surfactant spoiling (after intense rinsing). Residuals are found on the substrate in the narrow tranches of the device likely due to limited access of rinsing agent or to accumulation of surfactant above the precipitation limit in those regions.

it also reduces gas solubility increasing bubbles formation. Experimentally, we verified that the change of temperature did not improve the detachment of bubbles, leading to unchanged masking.

The third approach was the use of surfactant. This approach was carried out in two ways. First by adding a surfactant to the BOE (Aluminum etch surfactant from Fujifilm containing Dimethylamine oxide), second by using a commercially available BOE with surfactant already present in the solution (BOE 7:1 from MicroChemicals). Both approaches had the goal to improve wettability of the silicon surface i.e. to reduce the contact area between gas and solid promoting bubbles detachment from the device by buoyancy forces that are proportional to bubble volume. The former approach slightly reduced the size of the bubbles, but micro-masking effect remained. Besides, the concentration of surfactant must be tuned precisely due a trade-off between bubble reduction and surfactant residues: too low concentration would not reduce bubble formation effectively; too high concentration would damage the device due to the difficulty to remove residuals of surfactant that spoil the device [22] (figure 5).

The use of commercial BOE with surfactant was less effective than BOE with added surfactant. The reason might be in the different chemistry of the surfactant (not provided by MicroChemicals).

The final test in wet environment was performed in diluted formulation of the BOE bath (1 part of DI water and 1 part of BOE): this alternative approach aims to dilute the generated gas, maintaining a reasonable etch rate. Notwithstanding, also this approach was not able to reduce bubble formation.

Three approaches were discarded. The use of alcohols (i.e. isopropyl alcohol (IPA) or similar), although very effective to reduce the contact angle [21], is precluded in our case due to its incompatibility with the polymeric resist mask required by our process. Ultrasound [7] was discarded as not compatible with fragile MEMS devices. Finally, we excluded the option of periodically removing the sample from the bath to eliminate the bubbles [7, 19] as this would cause stiction of the MEMS structures. For structures with anti-stiction bumpers, this option could be a viable solution to reduce of the masking phenomenon.

4. Discussion

4.1. Study of the reaction

In the introduction of this work we mentioned how the origin of the bubbles is most likely related to the etching of silicon and not to the etching of SiO_2.

Silicon oxide etching forms SiF_4 gas which is usually soluble in water forming SiF_6H_2 (aq) [4]:

$$SiO_2\,(s) + 6HF\,(l) \rightarrow SiF_6H_2\,(aq) + 2H_2O\,(l)\,.$$

On the other hand, hydrogen gas formation is observed in the first step of silicon etching that follows the reaction [7]:

$$\equiv Si - H + OH^- + H_2O \rightarrow \equiv Si - OH + H_2 + OH^- \,(\text{Ox.})$$

$$(\equiv Si)_3 Si - OH + 3HF \rightarrow 3\,(\equiv Si - H) + SiF_3OH (\text{Etch.})$$

The hydrogen terminated surface of silicon is oxidized by the OH group and the hydrogen atom of the termination recombines in the form of gas; this is the limiting step in the etching rate of silicon. The OH terminated silicon is then etched by HF restoring an hydrogen terminated surface.

This reaction is usually observed in 40% NH_4F or NH_4F/HF solutions and dramatically increases when the pH is above 8, however the etching of silicon is still present for lower pH [6, 23]. The pH of our solution was controlled to be almost neutral ($pH = 7$) using litmus paper. Bubbles formation is usually not visible on plain silicon when immersed in BOE, therefore we decided to fabricate a testbed sample to mimic the MEMS device. We created a set of grooves in a single crystal silicon substrate (Si(100)) and immersed the substrate in the BOE solution for 15 min. Figure 6, reports the evolution of bubbles on the test sample. It is clear how bubbles are formed in proximity of defects and trenches. These areas offer suitable anchor points and might present defects in the crystal structure which might lead to an increase of reactivity [10]. The defects are not only anchor points, but nucleation points as the bubbles grow in the same spot. The circular traces left by the bubbles are similar to those reported in literature during this type of etching (figure 6(d)) [7]. We have also verified that similar samples, immersed in deionized water do not show any bubbles after 40 min, confirming the hypothesis of gas formation as reaction product and not as gas already diluted in the solution. Moreover, samples etched in both fresh and already used BOE baths do not present gas evolution differences, thus ruling out solubility effects. Those tests also helped us in understanding that silicon is most likely the main source of gas production, as no silicon oxide layer was present in this case. However, we cannot exclude that any byproduct of the etching of the sacrificial silicon oxide might also contribute to the increase of bubbles size in the real

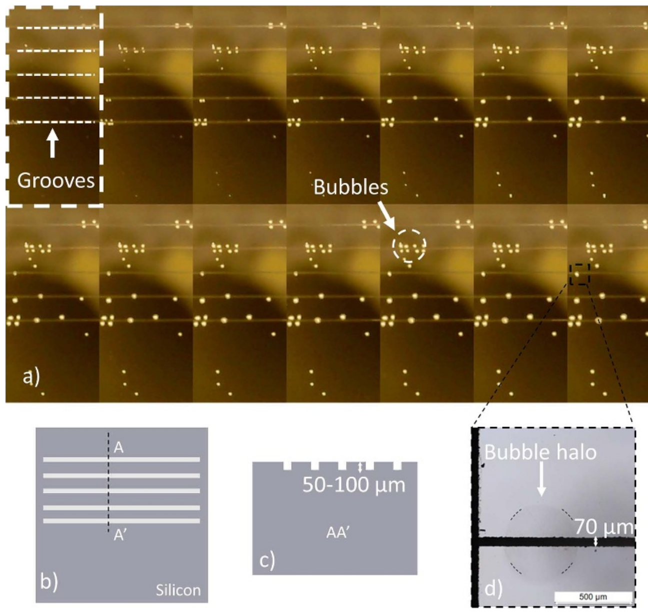

Figure 6. (a) Bubble evolution on a silicon substrate with several grooves (highlighted with the white dashed lines in frame 1) which were etched using saw dicing. It is clearly visible how the bubbles tend to form in the presence of defects or topography. Images are taken with a time interval of 1 min, from left to right, top to bottom. The different colors of the substrate are due to reflection of the microscope used to acquire the images; (b) schematic top-view of the chip; (c) schematic cross-section of the chip; (d) optical image of one trench after the exposure to BOE: a halo is left from the gas bubble. Dashed lines are used to highlights part of the halo.

device case (SiF_4 gas). We also tend to exclude light inducted etching of silicon in fluoride solution [9] as no specific difference was observed between tests performed in light and dark conditions on similar samples. We can therefore conclude that BOE is etching silicon and the reaction is producing gas, which is most likely hydrogen. MEMS fabrication intrinsically requires strong topography and introduction of defects induced by the RIE of the silicon layer. These features are the ideal environment for the nucleation and propagation of gas bubbles which lead to micromasking in the etch of the sacrificial oxide. Geometrical features like clamped-clamped beams, suspension springs and comb-fingers do not seem to suffer from masking. On the other hand, matrix-like geometries, with a dense and regular distribution of trenches seem to offer the ideal substrate for bubble growth. In such structures, the large, exposed silicon surface offers several nucleation and anchoring points. Locally, bubbles can grow homogeneously in all directions maximizing solid–gas interface without increasing the liquid–gas interface. Finally, the presence of dopants in the structural silicon or defects emerging during the epitaxial grow might further enhance the etching of the structural substrate. On this point several works have already reported how doped silicon and polycrystal silicon suffers the exposure to BOE [24, 25].

Finally, as a reference, the same geometry was exposed to HF vapor. The results are visible in figure 7. The etch is uniform and the structure is suspended without any stiction

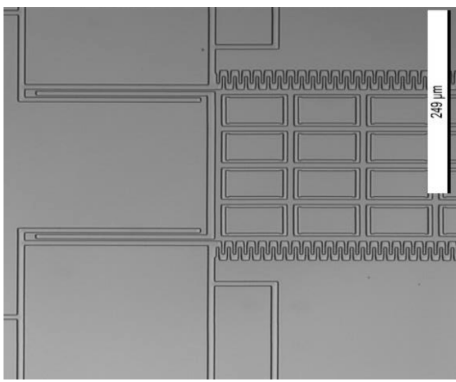

Figure 7. Optical image of the device released in vapor HF. The etching is uniform, and the structure is fully released.

problem. As mentioned before, this technique does not allow the use of photoresist as a masking layer, requiring the deposition of a proper passivation layer to protect any metal surface on top of the device. Interestingly enough, the etching rate can be affected by the deposition of passivation layers as well as by the density and even depth of the etching structure, which can locally alter the sample hydrophilicity and thus make unfavorable the absorption of water acting as catalyzer for the Si etching by HF. Even though release by vapor HF can definitely solve the problem of stiction and micro-masking encountered in wet-etching, other issues related to passivation layers must be solved with reference the specific layout for optimal and uniform release.

5. Conclusions

Persistent bubble formation during SiO_2 etching in BOE was observed during the release of MEMS devices fabricated on SOI substrates. Several mitigation approaches have been used, showing no specific improvement. The most promising approach remains the use of surfactant, although the chemistry and dosing of this molecule should be optimized.

The formation of bubbles is most likely related to the etching of silicon and the topography of the samples and the defects induced by the silicon etching offer nucleation points and anchor sites for the bubbles grow. Also, the device geometry seems to play a role in the gas bubbles formation and masking, with elongated structures being less prone to micro-masking. Nevertheless, adopting a geometry that minimizes bubbles formation can be an unacceptable constrain for designers.

Despite the need of a more complex passivation layer, vapor HF seems to be the most effective way to release MEMS structure and avoid micro-masking.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

The authors declare no competing financial interest.

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