HF ETCHING OF SI-OXIDES AND SI-NITRIDES FOR SURFACE MICROMACHINING

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Abstract

In this work the etching of Si-oxide, Si-nitride (LPCVD and PECVD) and Si-oxide/Si-nitride stacks in HF/H_2O 26.3:73.7 and vapour HF is studied. Special attention is given to the residues, which were found to form during vapour HF etching of Si-nitride, PECVD Si-oxide and Si-oxide/Si-nitride stacks. These residues are not encountered during wet etching. Their origin and possible removal procedure are investigated.

Keywords: surface micro-machining, vapour HF, sacrificial etching

1. Introduction

Many surface micro-machined Micro Electro Mechanical Systems use poly-Si or poly-SiGe [1-2] as a structural layer, an oxide layer as the sacrificial layer and Si-nitride as the etch-stop and/or as the protection layer for the underlying structures. The sacrificial layer can then be selectively etched by the use of hydrofluoric acid (HF). The most widespread method of HF based etching is the wet etching in a mixture of HF and water [3-4].

Drying of released wet etched structures however causes stiction of the devices. Different methods to avoid stiction have been proposed [5-6]. A rather new processing is vapour HF etching, where a high yield can be obtained for surface micro-machined structures, particularly when the wafer temperature during the release is raised above 35 °C [1-2,7-9].

2. Experimental procedure

2.1. SAMPLE PREPARATION

The blanket layers that were etched in this work are five different Si-oxides and two different Si-nitrides. The Si-oxide layers are 1200 nm wet thermal oxide grown at 975

°C, 1000 nm TEOS (tetraethoxysilaan) deposited by a CVD process at 670 °C, the same film annealed for 30 min. at 900 °C, 1000 nm PSG (phosphosilicate glass) with 4.5 wt.% P grown at 550 °C and annealed for 30 min at 750 °C and two different types of PECVD oxide deposited in two different systems. In PECVD system 1 a 1000 nm thick Si-oxide film was deposited at 400 °C. In PECVD system 2 a 1200 thick Si-oxide film was deposited at a wafer temperature of 450 °C. The Si-nitride layers are a 200 nm thick LPCVD nitride layer deposited at 770 °C and a 1000 nm PECVD nitride layer deposited at 400 °C.
Also a stack of 1200 nm TEOS Si-oxide on 300 nm LPCVD nitride, both annealed at 1050 °C, was investigated.

2.2. DESCRIPTION ETCH PROCEDURE

For the wet chemical etching experiments a solution of one part HF (49%) and one part DI water is used. The experimental procedure is as follows: after etching a piece of a wafer for a certain time, the sample is put in a beaker with DI water for a few seconds after which it is rinsed in streaming DI water. After drying with a nitrogen gun, the film thickness is measured by a spectrometer on at least five different places on the sample.
The vapour HF etching is done in a commercially available system for wafer cleaning, that was adapted according to custom specifications to enable stiction-free surface micro machining [7]. To get a vapour of HF in the reaction hood nitrogen is bubbled through a 49% HF solution. The nitrogen flow can be adjusted between 0.1 and 1 l/min. In order to get reproducible etching results, the preparation of the sample is important [7]. The 2cm*2cm samples are first cleaned with water, then dried with a nitrogen gun and then baked out in a furnace at 120 °C for 30 minutes. This result in a clean sample, which is then preheat for 10 min. in the system before the etching with a nitrogen flow of 1 l/min. starts. Layer thickness measurements are done in the same way as for the wet chemical etched samples.
The reaction equations both for wet and vapour HF etching can be found in several references [3-4,7-9]. For vapour HF etching of Si-oxides it is important to note that water is needed as an initiator for the reaction.

3. Wet chemical etching

The Si-oxide and Si-nitrides etch rates for wet chemical HF etching are constant over the etched thickness. This etch rates are listed in tables 1 and 2.

3.1. SI-NITRIDES

LPCVD nitride is etched slower than PECVD nitride due to his higher processing temperature and consequently higher density (Table 1) [7].

TABLE 1. Etch rate in HF/H_2O solution

Material	PECVD nitride	LPCVD nitride
Etch rate (nm/min)	98 ± 7	12,8 ± 0,6

3.2. SI-OXIDES

PSG, TEOS and PECVD oxide 1 have more or less the same etch rate (Table 2). The PECVD oxide 2 has a lower etch rate compared to PECVD oxide 1, which is probably due to a higher deposition temperature. Annealing a film results in a slower etch rate. The etch rate for the slowest etching Si-oxide is at least 3 times higher than the etch rate for the fastest etching Si-nitride.

TABLE 2. Etch rate in HF/H_2O solution

Material	PSG annealed	TEOS	PECVD-oxide 1	Thin PECVD-oxide 2	TEOS annealed	Thermal oxide
Etch rate (nm/min)	3300 ± 100	3110 ± 80	3080 ± 100	2580 ± 80	1180 ± 10	410 ± 20

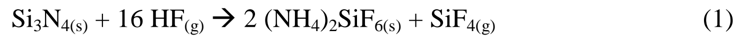
4. Vapour HF

Etch rates in vapour HF are determined from a linear square fit through al data points for one material.

4.1. SI-NITRIDES

4.1.1. Residues of Si-nitrides

During the vapour HF etching of Si-nitride, residues are created according to equation (1) [10]:



$$Si_3N_{4(s)} + 16\ HF_{(g)} \rightarrow 2\ (NH_4)_2SiF_{6(s)} + SiF_{4(g)} \qquad (1)$$

These residues form a white, non-transparent film and cause an apparent increase in film thickness (Figure 1), which in extreme cases can lead to a cracking of the structural layer on top. If almost all the nitride is etched, the film can peel off (Figure 2).

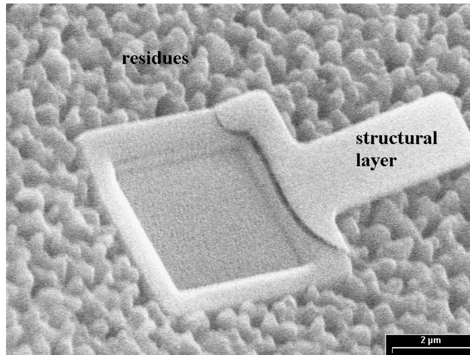


Figure 1. Residues of the nitride film

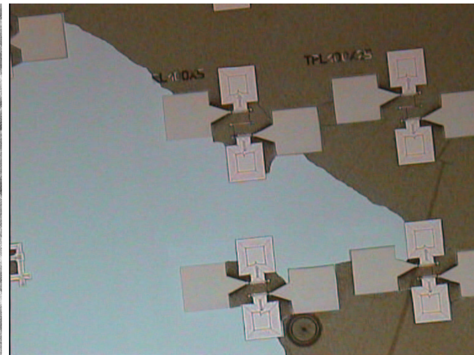
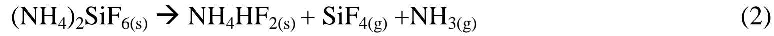


Figure 2. Peeling of the etched nitride

These residues can be removed by a water rinse after vapour HF etching, but this will give stiction. Therefore another solution had to be found to remove the residues.

Above a temperature of 100 °C, the following decomposition takes place [3] (Eq. 2):



$$(NH_4)_2SiF_{6(s)} \rightarrow NH_4HF_{2(s)} + SiF_{4(g)} + NH_{3(g)} \quad (2)$$

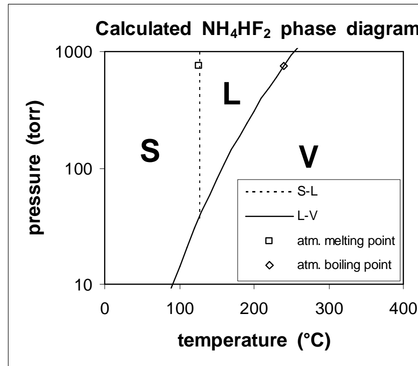


Figure 3. Approximate phase diagram of NH_4HF_2

In order to avoid problems of stiction, $NH_4HF_{2(s)}$ should be sublimated. According to calculations (Figure 3), the liquid phase can be avoided when heating in a vacuum below 30 Torr (1 Torr = 133,32 Pa).
From experiments at different temperatures and times, we found that the best results are obtained with a 30 minutes vacuum anneal (10 Pa) at 180 °C after vapour HF etching.

4.1.2. Etch rate of Si-nitride

PECVD nitride has the highest etch rate (Table 3). Unlike for vapour HF etching of Si-oxide (see also 4.2.3.), the influence of the temperature in the vapour HF system is not so important. This is because condensed water is not an element in the etching reaction.

TABLE 3. Etch rate of nitrides in vapour HF at different temperatures

Material	PECVD nitride at 35 °C	LPCVD nitride at 50 °C	LPCVD nitride at 75 °C	LPCVD nitride at 35 °C
Etch rate in (nm/min)	31 ± 5	6,3 ± 0,6	5,5 ± 0,5	5,4 ± 0,6

4.2. SI-OXIDES

4.2.1. Residues of Si-oxides

As PECVD Si-oxides films contain some nitrogen (Table 4), similar residues as for Si-nitride films are formed during vapour HF etching. Because the amount of nitrogen is smaller then in nitride films, fewer residues are formed.
These residues can be removed in the same way as the one from the nitride.

TABLE 4. XPS data of PECVD Si-oxide films before and after vapour HF etching. After etching only residues remain on the Si-wafer.

	C (%)	**F (%)**	**Si (%)**	**O (%)**	**N (%)**
PECVD oxide 2 non-etched	11.7	1.6	31.8	64.9	1.6
PECVD oxide 2 etched (residues)	6.9	47.8	17.6	21.1	13.5
PECVD oxide 1 non-etched	11.1	1.0	32.0	65.8	1.3
PECVD oxide 2 etched (residues)	4.3	37.5	20.8	31.8	9.9

4.2.2. Etch rates of the Si-oxides

The temperature of the vapour HF system has an important influence on the etch rate of Si-oxides. The etch rate decreases with increasing the temperature as the amount of

condensed water decreases. When increasing the temperature from 35 °C to 50 °C, the etch rate of TEOS annealed decreases from 100 nm/min to 15 nm/min [7].
PSG oxide has the highest etch rate (Table 5), but it results in a wet residue (phosphoric acid) [7] on the surface making this oxide unsuitable as sacrificial layer material because stiction will be unavoidable. Annealing the oxide film decreases the etch rate. When using PECVD oxide as sacrificial layer, residues need to be removed as explained above.

TABLE 5. Etch rate of Si-oxides in vapour HF at 35°C

Material	PSG annealed	PECVD oxide 1	TEOS	PECVD oxide 2	TEOS annealed	Thermal oxide
Etch rate at 35 °C (nm/min)	290 ± 20	230 ± 30	22O ± 40	210 ± 40	100 ± 10	15 ± 1

4.3. SI-OXIDE/SI-NITRIDE STACKS

When there is an oxide layer above a nitride layer, residues will be formed during the vapour HF etching of the stack. The chemical composition of these residues is not yet determined. They cannot be removed in the same way as the residues from the nitride and the PECVD oxide. If a Si-oxide sacrificial etching with a Si-nitride etch stop needs to be done, a combination of wet and vapour etching is a solution. Alternatively the residues can be removed by underetching them if it is allowed to etch away 100 nm or more of the Si-nitride layer.

5. Discussion

Vapour HF etching of Si-oxide has the advantages of a high yield of released structures can be obtained when the wafer temperature during the release is raised above 35 °C and a very high selectivity towards aluminium. It has, however, also a few disadvantages comparing to wet etching. When using Si-nitrides and PECVD oxides an additional vacuum anneal has to be done to remove the residues. Moreover, PSG cannot be used as sacrificial layer and the formation of the residues when using a Si-nitride/Si-oxide stack is still not well understood. Also the selectivity with respect to Si-nitride is not very high compared to wet etching, this selectivity however improves with decreasing temperature (Table 6).

TABLE 6. Selectivity between Si-oxide and Si-nitride

	selectivity of the etch rates of annealed TEOS Si-oxide with respect to LPCVD Si-nitride	selectivity of the etch rates of annealed TEOS Si-oxide with respect to PECVD Si-nitride
HF/H_2O	92.8	12.0
vapour HF @ 35 °C	21.7	3.1
vapour HF @ 50 °C	2.6	

6. Conclusion

In conclusion, the wet and vapour HF etching of different Si-oxide and Si-nitride layers was studied. It was found that a Si-nitride layer is not such a good etch stop layer for Si-oxide sacrificial etching in vapour HF, as the selectivity is worse compared to wet etching and one has to deal with the residues that form.
However, as for wet etching one need to solve the stiction problems, a combination of wet and vapour HF etching is a possible solution.

7. Acknowledgements

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8. References

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