Deposition of sacrificial silicon oxide layers by electron cyclotron resonance plasma

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Electron cyclotron resonance plasmas with $SiH_4/O_2/Ar$ mixtures were used for deposition of thin films of silicon oxide, to be employed as sacrificial layers in microelectromechanical system (MEMS) fabrication. The grown films were characterized by Fourier transform infrared and ellipsometry. Optical emission spectroscopy and Langmuir probe were used for plasma characterization. It has been shown that OH molecules generated in the plasma play an important role in formation of films suitable as sacrificial layers for MEMS fabrication. Extremely high etch rates of grown oxide films (up to 10 μm/min) were obtained, allowing fabrication of high quality poly-Si suspended structures. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2746331]

I. INTRODUCTION

Thin sacrificial layers are used in micromachining to obtain suspended membranes or cantilevers using the surface micromachining technique.[1–6] In this process, after the deposition of a structural layer, a suspended structure can be formed removing the sacrificial layer by appropriate enchants. High selectivity etch is required in order to produce high quality suspended structures. Silicon oxide films can be etched with high selectivity over silicon and other materials and are widely used in microelectromechanical system (MEMS) applications.[3,7]

Silicon oxide films can be deposited by low-pressure chemical vapor deposition (LPCVD) or plasma enhanced chemical vapor deposition at temperatures higher than 550 and 200 °C, respectively.[5] High-density plasma techniques, such as electron cyclotron resonance chemical vapor deposition (ECR-CVD),[8,9] allow film deposition at a room temperature and thus can be an attractive alternative.

This work reports the use of an ECR plasma for deposition of silicon oxide films with properties that make them suitable as a sacrificial layer material for MEMS applications. The physical and chemical characteristics of the SiO_2 films, such as BHF and KOH etching rates, composition, refractive index, and deposition rates were analyzed. Plasma parameters were measured during the deposition to complement the *ex situ* film analysis. Extremely fast etch rates of the oxide films ($\sim$10 μm/min) were obtained. This is an important advantage of the method, allowing the reduction of the etching time and the exposure of a structural layer to chemical attack. Finally, high quality suspended polycrystalline silicon structures were successfully obtained, showing the applicability of ECR-CVD oxide films as sacrificial layers.

II. EXPERIMENTAL DETAILS

The procedure to fabricate suspended structures is shown in Fig. 1. In the first step, the *p*-type ⟨100⟩ Si substrates were cleaned by the RCA method, and a silicon nitride (SiN_x) layer, which presents high resistance to BHF solution etching, was deposited by ECR-CVD. This layer is used for electrical isolation between the suspended structure and the substrate. Then (step 2), sacrificial silicon oxide layers were deposited by ECR-CVD on the SiN_x surface. In the step 3, a lithography process followed by a SiO_2 BHF etching was used to define the structural layer (polycrystalline Si) support area. Following, 1 μm poly-Si was deposited by LPCVD at 800 °C in step 4. Then (step 5), a second lithography process followed by the poly-Si dry etching was performed to define the suspended structure area. As in the previous etching process, an organic cleaning was carried out to remove the photoresist. In the last step, the sacrificial SiO_2 layer was etched away in a BHF solution (for about 2 min) to finish the fabrication of suspended poly-Si membranes and cantilevers.

The ECR-CVD system was used to produce high-density plasma with a microwave (2.45 GHz) power fixed at 1000 W. The plasma was generated in an upper chamber, and the deposition processes were carried out in a downstream region (20 cm below) where the plasma density is three to five times lower. An additional rf power of 3 W was used to control the bias of the sample holder. The rf power was fixed at the relatively small level as higher powers (and thus stronger ion bombardment[9]) lead to enhanced hydrogen removal and formation of denser films, more resistant to etching. On the other hand, better uniformity of film deposition over the wafer is achieved when rf power is applied.[10] The substrate temperature was kept at 20 °C. The sacrificial oxide layers, about 1 μm thick, were deposited using SiH_4 and O_2 gases strongly diluted in Ar. The 200 SCCM (SCCM denotes cubic centimeter per minute at STP) gas mixture (2% of SiH_4 in Ar) was injected near the deposition region, while Ar (20 SCCM) and O_2 were injected in the upper plasma chamber. Depositions were performed with different

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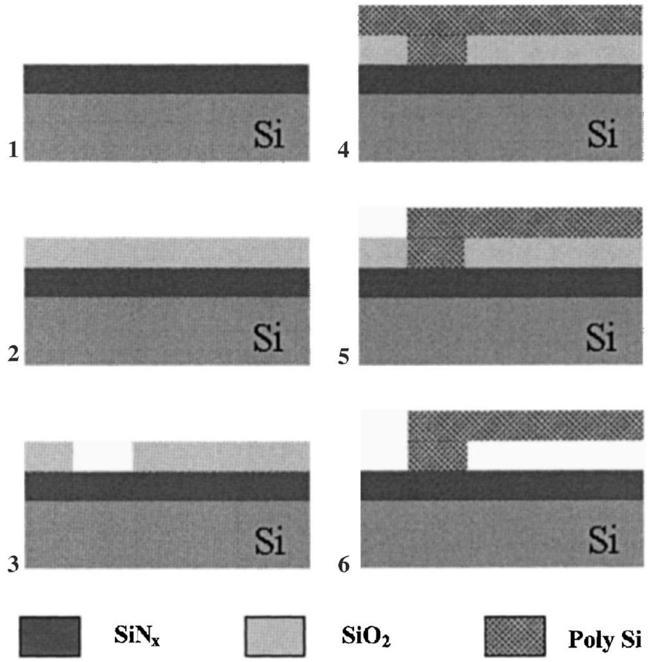

FIG. 1. Process steps for a membrane fabrication.

TABLE I. Ellipsometry results for the deposited silicon oxide films. Process conditions: (1) Variable pressure of 5–30 mTorr, gas flows $Ar/O_2/(2\% SiH_4$ in Ar$)=20/40/200$ SCCM; (2) Variable O_2 flow of 10–40 SCCM, pressure of 20 mTorr, gas flows $Ar/(2\% SiH_4$ in Ar$)=20/200$ SCCM.

Variable process parameter	Deposition rate (nm/min)	n	KOH etch rate (nm/min)
Pressure (mTorr)=5	16	1.49	2
7.5	17	1.48	2
10	18	1.47	5
15	20	1.46	13
20	23	1.46[a]	>90
30	25	1.45	>100
O_2 Flow (SCCM)=10	20	1.64	1
20	22	1.46	3
30	23	1.48	5
40	23	1.45[a]	>70

[a] The data are obtained under the same process conditions for two different runs. The difference between the n values is within the precision of measurements.

O_2 flow rates (10, 20, 30, and 40 SCCM) and gas pressures (5, 7.5, 10, 15, 20, and 30 mTorr). For the processes performed varying the O_2 flow rates, a constant pressure of 20 mTorr was used. For the processes varying the pressure, the O_2 flow rate was fixed at 40 SCCM.

The silicon oxide films were analyzed *ex situ* by ellipsometry (fixed wavelength of 632.8 nm and an incidence angle of 70°) and Fourier transform infrared (FTIR) spectrometry. During the film deposition, the plasma was analyzed by optical emission spectrometry (OES) in the 200–900 nm spectral range. A Langmuir probe was used to measure the main characteristics of electrons (density and temperature) in the plasma region just near the electrode/sample holder.

III. RESULTS AND DISCUSSION

Ellipsometry measurement results for the films deposited under different conditions are shown in Table I. Note that oxide deposition rates increase only slightly with pressure ($\sim$56% with a six-fold rise of the pressure) and with O_2 flow ($\sim$15% with a four-fold rise of the O_2 flow), being in the range of 16–25 nm/min. Langmuir probe measurements, performed near the sample holder (4 cm above), have shown that the plasma density is quite high in the process chamber for all the pressure range studied. The maximum electron density was measured to be as high as $4\times 10^{10}\ cm^{-3}$ at intermediate pressures (10 mTorr), reducing to about half of this value ($\sim 2\times 10^{10}\ cm^{-3}$) for 5 and 30 mTorr. The electron temperature was measured to fall gradually with pressure, being about 3.5 and 2.5 eV for the pressures of 5 and 30 mTorr, respectively. The small changes of the deposition rate with O_2 flow indicate that the SiH_x radical supply is likely to be the rate limiting process. Higher process pressures result in stoichiometric oxide films (refraction index n is close to 1.46). Higher O_2 flow rates also lead to nearly stoichiometric films, while the lowest (10 SCCM) O_2 flow apparently result in a Si-rich film.

The BHF etch rate of the oxide films, the key characteristic for their use as a sacrificial layer, is extremely high for all deposited films. In fact, it was difficult to measure it. However, estimates give values exceeding 10 μm/min, being much higher than that for a conventional oxide.[7] Another important characteristic is the etch rate in KOH solution. As can be seen in Table I, this parameter can vary widely with the pressure or O_2 flow. It starts to grow quickly for pressures exceeding 15 mTorr or for O_2 flows higher than 30 SCCM. Note that these changes in most cases are not accompanied by the significant refractive index variation. For example, when the pressure rises from 10 to 30 mTorr (the first group of processes in Table I), the refractive index changes only slightly, from 1.47 to 1.45, indicating that the changes in the film composition are relatively small. Therefore, the observed rise of the KOH etch rate (from 5 to more than 100 nm/min) is probably due to increase of the oxide porosity, which is usually caused by enhanced hydrogen incorporation in the films. Note that under the present conditions, the KOH etch rate varies roughly two orders of magnitude, revealing significant changes of the film properties. This is an interesting result indicating that films with significantly differing properties can be obtained by ECR-CVD, at room temperature, which can be suitable for different micromachining processes. For example, films with low resistance to KOH etching could be used as sacrificial layers in situations where BHF etching is not appropriate because of the structural material characteristics.

The results of FTIR measurements of the oxide films absorption spectra are shown in Fig. 2. An increase of the O–H bonds density (at $\sim 3500\ cm^{-1}$) at higher pressures can be observed. For higher O_2 flows, similar results were obtained

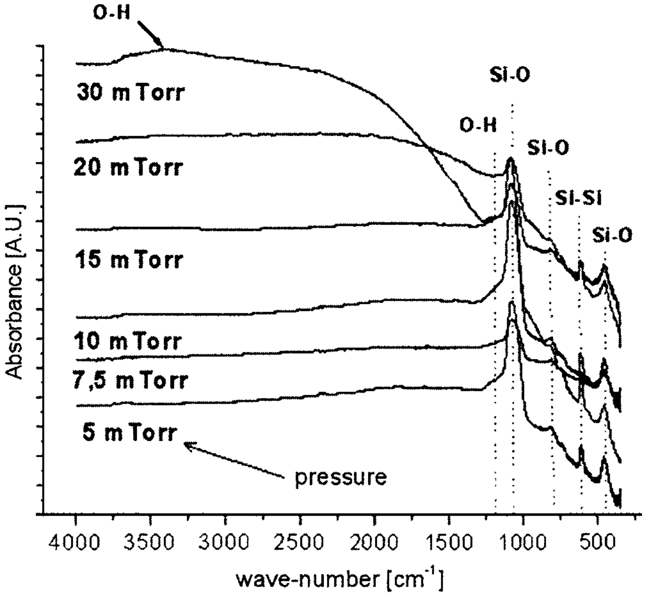

FIG. 2. FTIR spectroscopy results for different process pressures.

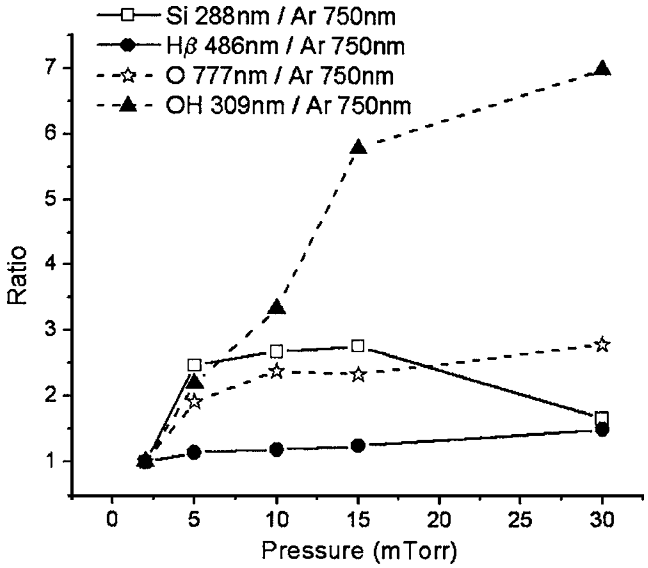

FIG. 3. Relative intensities of selected emissions for different pressures.

(not shown). So, the reduced resistance of oxide films to KOH etching (Table I) is correlated with higher concentration of O–H bonds in the films. This observation corroborates with the hypothesis that the observed changes of the film properties are due to higher hydrogen incorporation.

To explain the reduced resistance of the films to KOH etching observed for higher gas pressure or O_2 flow, four possible mechanisms could be supposed: (1) an increase of the density of highly unsaturated SiH_x radicals ($x \leq 2$) in the plasma; (2) direct incorporation of H atoms from the plasma into the growing film; (3) generation in the plasma of another Si precursors besides SiH_x; and (4) direct incorporation of OH molecules, generated in the plasma, into the growing film.

To evaluate the relative importance of these mechanisms, the results of the plasma diagnostics were utilized. SiH_x radicals with $x \leq 2$ are known to have high sticking coefficients and low surface mobility.[9] So, plasmas with high content of these radicals lead to formation of less dense films. Thus, if the concentration of these radicals rose with pressure and O_2 flow rate, this fact could explain the higher film porosity. However, the Langmuir probe measurements have shown that the plasma density in the process chamber is the highest at intermediate pressures (10 mTorr) and falls for higher pressures. The electron temperature was measured to reduce gradually with pressure, as expected.[11] Therefore, the rate of silane dissociation by electron impact should be lower for higher pressures, and thus the first mechanism is unlikely to apply. This is also confirmed by OES measurements, where Si radical ($x=0$) density appears to be at maximum for intermediate pressures (see below).

In Fig. 3, emission intensities of various plasma species, normalized to the 750 nm Ar line, are shown. The normalization of species' emission by a rare gas line emission is known as the actinometry technique,[12] and the obtained relative intensities characterize (at least, semiquantitatively) the density of species in the plasma. The 750 nm Ar line is frequently used for actinometry measurements, as it is known to be predominantly excited directly from the ground state.[12] As seen in Fig. 3, the relative H atomic emission almost does not change with pressure. This is in contrast to the behavior of OH molecules, whose emission increases fast (almost linearly) with the pressure. Thus OH molecules, rather than H atoms, can be responsible for the observed increase of the film porosity for higher pressures. Note that the same correlation was also observed in the measurements with different O_2 flows: for higher O_2 flows, a decrease of H emission was detected, in contrast to the continuous rise of OH emission. For example, as the oxygen flow increases from 20 to 40 SCCM (with a notable increase of the KOH etch rate, Table I), the relative intensity of the H_β emission decreases 30%, while the OH of 309 nm emission grows almost 100%.

Another possible mechanism could be related to generation of radicals with Si–O bonding (besides SiH_x), in particular, silanols such as SiH_3O or SiH_2O.[1,2,13] These radicals, together with OH molecules, could be produced in gas-phase or surface catalyzed reactions of silane oxidation. This mechanism was found plausible by Kushner for conditions of remote plasma activated CVD of SiO_2.[13] One of the reactions leading to silane oxidation is

$$SiH_4 + O_2(^1\Delta) \rightarrow SiH_3O + OH. \qquad (1)$$

However, the experiments discussed in Ref. 13 were performed at higher pressures and much lower plasma density compared with the present work. Note that OH molecules are by-products in the reaction of silane oxidation [Eq. (1)]. Then, if the contribution of mechanism [Eq. (1)] to the oxide deposition was significant, the seven fold rise of OH emission with pressure (Fig. 3) would indicate also a proportional increase of silanol generation. However, as the deposition

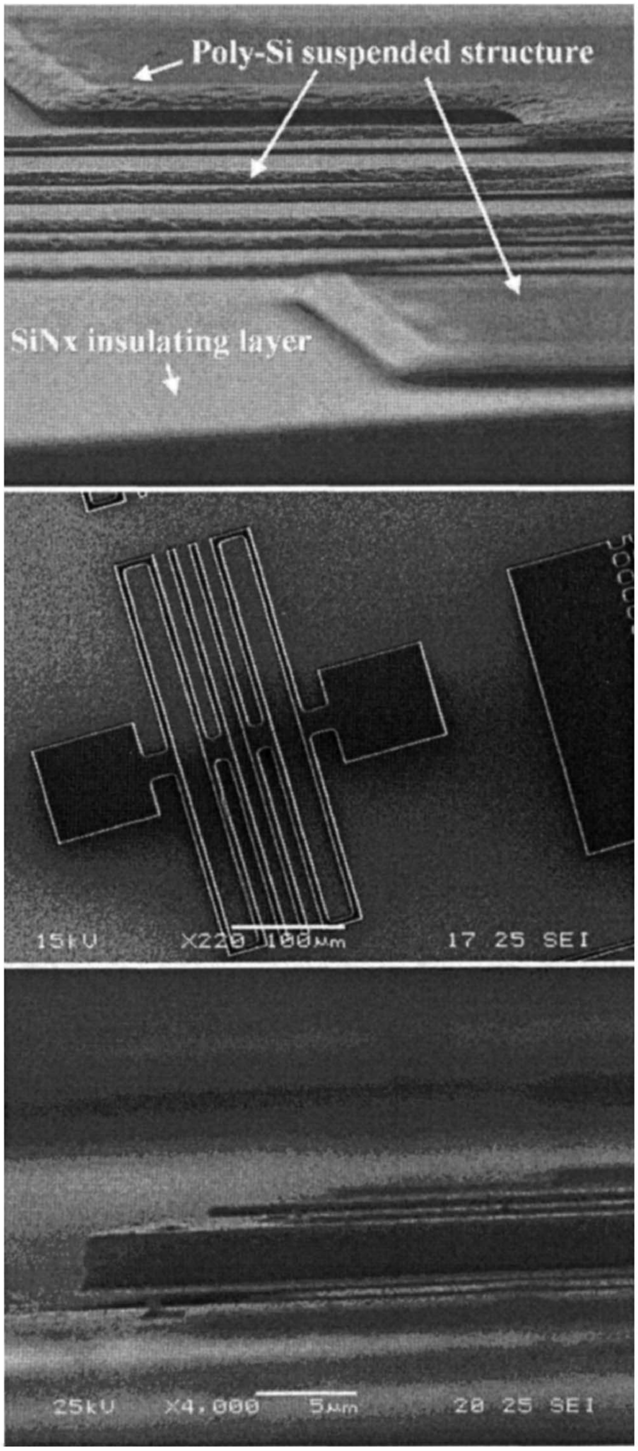

FIG. 4. SEM images of suspended poly-Si structures after sacrificial silicon oxide etching; oxide growth conditions: 20 mTorr, 40 SCCM O_2 flow, and 2 min of BHF etch.

rate, in fact, grows only slightly, it is unlikely that silanols such as SiH_3O play significant role as oxide deposition precursors under the present conditions. Furthermore, OH molecules generated in the plasma are mainly produced in reactions other than Eq. (1), most probably in reactions between H atoms and O_2 or between excited oxygen atoms [mainly $O(^1D)$ and $O(^3P)$] and SiH_4.[13] Note that OH molecules can further react with SiH_4 producing H_2O, which can be also incorporated in the growing oxide film.

So, the plasma diagnostic and FTIR results strongly indicate that direct incorporation of OH (or H_2O) molecules from the plasma is likely to be responsible for reduced film resistance to etching observed for higher pressures and O_2 flows. Similar results were obtained in a previous work analyzing the NH molecules in silicon nitride depositions.[14]

Finally, some examples of successful applications of the CVD grown sacrificial oxide layers for MEMS fabrication are shown in Fig. 4. Structures with different sizes were obtained using 1 μm thick oxide layers. The rate of oxide lateral etching beneath the poly-Si structural layer was estimated to be as high as ~10 μm/min (10 μm wide structures were released after 30 s of etching), being an order of magnitude higher than that for conventional oxides.[1–3,7] Note that this fast etching was achieved after the oxide film annealing at 800 °C that occurs during the growth of poly-Si structural layer. It is important that the fast removal of the sacrificial layer reduces the mechanical degradation of a structural layer during exposure to BHF, and thus is beneficial for fabrication of high quality suspended structures.[1]

IV. CONCLUSIONS

A high-density plasma ECR reactor was employed for sacrificial oxide film deposition at room temperature. By changing experimental conditions, films with considerably differing properties were produced. In particular, the experiments have shown the possibility to control the resistance of grown oxide films to wet etching. Films deposited at higher pressures or high O_2 flow rates presented much higher KOH etch rate (possible indication of a high film porosity) and hydrogen incorporation. Plasma diagnostics were utilized in order to compare contributions from different mechanisms possibly responsible for enhancement of the oxide porosity. Our analysis has shown that OH molecules generated in the plasma are likely to be responsible for the reduced resistance of the films to wet etching. Etch rates of oxide films in BHF as high as 10 μm/min were obtained. Finally, the grown films were successfully used as sacrificial layers to produce various suspended structures. The results obtained demonstrate that porous oxide films produced by ECR-CVD can be used for different MEMS applications, yielding high quality suspended poly-Si structures.

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