# The Influence of process parameters on the electrical behavior of silicon oxide thin films deposited by PECVD-TEOS

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## Abstract

*This paper deals with the optimization of silicon oxide deposition process by plasma-enhanced chemical vapor deposition based on TEOS pyrolysis. We focused the analysis on the effect of the oxygen/TEOS ratio during the deposition and on the influence of the rapid thermal annealing process used to densifiy the film at the end of the process. The films were physically analyzed by FTIRS and AFM techniques and electrically characterized through MOS capacitors, fabricated with TEOS silicon oxide. We found that using pure oxygen plasma at the beginning and at the end of the deposition step followed by densification process by rapid thermal annealing improves significantly the electrical behavior of these films.*

## 1. Introduction

The Plasma Enhanced Chemical Vapor Deposition process, based in pyrolysis of the Tetra-ethyl-orthosilicate (PECVD-TEOS), is widely applied in the microelectronic industry. [1,2,3] Using this high deposition rate process, the obtained silicon oxide films can be involved in several ways: first, as multilevel metallization dielectrics because it gives good step coverage and low void formation,[4] second as a sacrificial layer in the micro-machining technology because it combines high deposition and high etching rates,[5] and finally as a dielectric in the thin film transistor (TFT) technology, thanks to its low temperature process, compatible with glass substrates.[6,7]
The PECVD-TEOS deposition process is a radio frequency (RF) plasma based technique, in which a mixture of oxygen and TEOS is used as process gas to deposit silicon oxide thin films.
In this paper, we present the results about the optimization of the deposition process, in order to minimize the defect densities and to get the best electrical behavior. For as-deposited films and densified ones using two depositions procedures, several characterizations were performed such as Fourier Transform Infra Red Spectroscopy (FTIRS), Atomic Force Microscopy (AFM) and capacitance-voltage and current-voltage electrical measurements. A discussion about the results ends the paper.

## 2. Experimental procedure

The deposition reactor was already described in previous work.[8] We based our experimental conditions on the results obtained in previous experiments[9]. To deposit the silicon oxide thin films, two different process procedures were performed aiming at the observation of the electrical behavior of the films. The basic deposition conditions are described in the Table I.

| | |
|---|---|
| Total oxygen flux (sccm) | 500 |
| TEOS flux (sccm) | 5 |
| Process pressure (Torr) | 1 |
| RF power (W) | 400 |
| Temperature (°C) | 360 |
| Distance between electrodes (mm) | 15 |

**Table I: Deposition Conditions**

In the first procedure, we started the deposition process with an oxygen plasma without TEOS addition. After few seconds (10 s) the TEOS flux is injected into the chamber without breaking the plasma. The deposition process was carried out during 5 min and the TEOS flux was interrupted 10 s before the end of the process. We call this procedure as intermittent.
In the second procedure, the silicon oxide thin films were deposited using process parameters described in the table I. We call this procedure as normal.
The samples, with the deposited silicon oxide in both cases, were split into two parts. One part was densified in a RTP furnace at 1000ºC during 120 s in nitrogen ambient. The other part was maintained as-deposited.
The samples were analyzed by FTIRS and AFM. C-V-HF and I-V curves were obtained from MOS capacitors. The deposited films were characterized using FTIRS to analyze the chemical state of the film. The roughness of the film surface was analyzed by AFM.

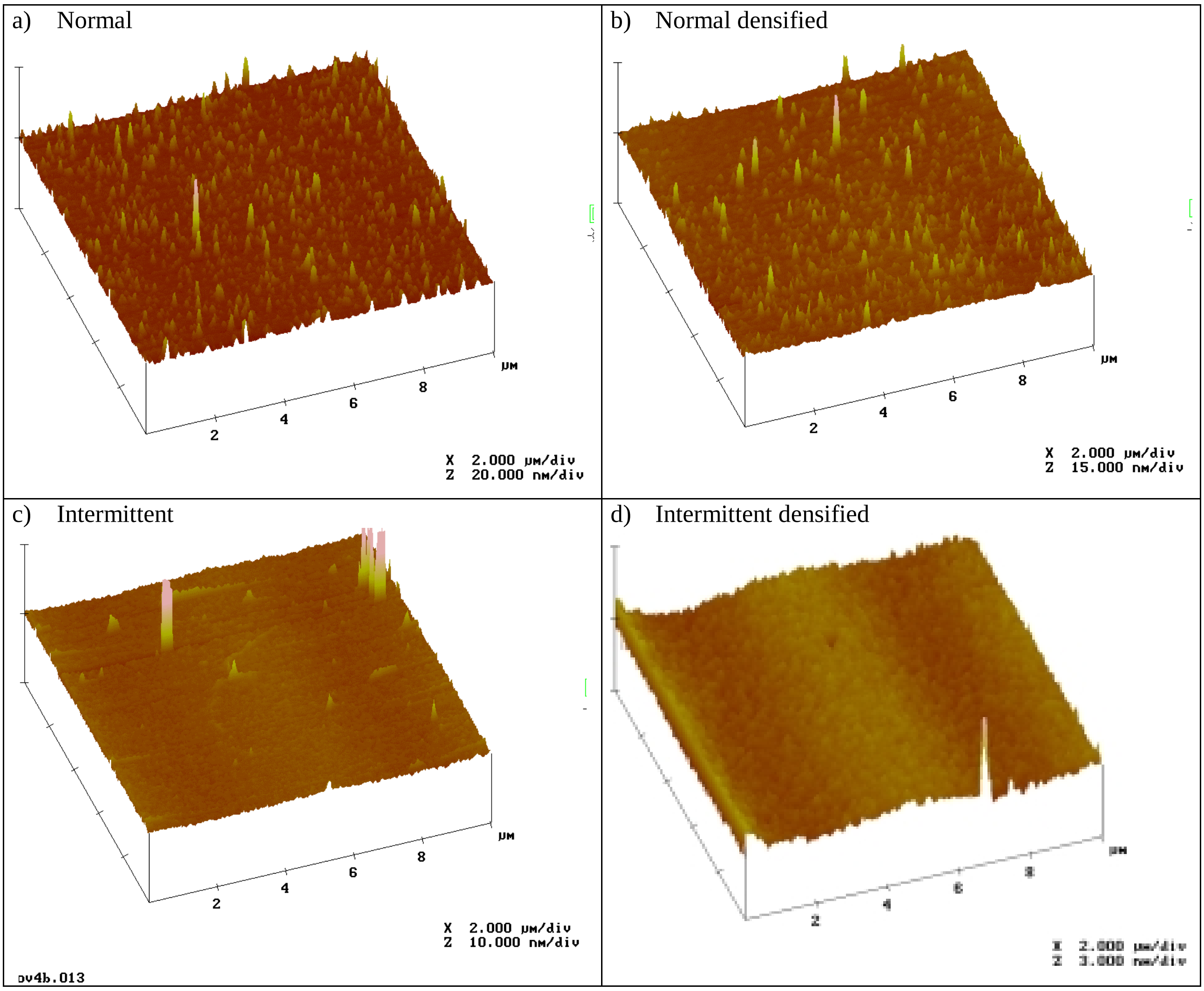


**Figure 1: AFM images for the four types of sample: a) normal processed sample before densification, b) densified normal sample, c) intermittent processed sample before densification, d) densified intermittent processed sample. For the last one, we can observe that peaks present mainly at the surface of the normal process samples have disappeared.**

## 3. Results and Discussions

The results, obtained from physical analysis and electrical measurements of MOS capacitors, are presented for the as-deposited and densified films.

### 3.1 Physical Characterization

The FTIRS analysis showed the regular Si-O bonds. There is no evidence of Si-OH and OH bonds on both films.

From AFM analysis it is observed that the roughness is large for the films deposited in the so-called normal process and it increases after the rapid thermal annealing process. The images on Figure 1 show small peaks at the silicon oxide surface. These peaks can be attributed to TEOS fragments that are not oxidized, and which remain at the surface. For the films deposited with the intermittent process, the density of peaks is lower, suggesting that when the deposition process ends in presence of an oxygen plasma without TEOS, the TEOS fragments adsorbed at the surface are fully oxidized, leading to a smoother surface. Moreover, the images of the densified intermittent process samples do not exhibit any peak; suggesting that these peaks are because of volatile subproducts.[10]

The roughness values for all the samples are reported in Table II, in which RMS is the root mean square roughness expressed in nanometers, $R_{max}$ the peak-valley roughness, $R_a$ the average roughness also expressed in nanometers. It is clear that the roughness is lower using the so-called intermittent process. But a deeper analysis shows that if the effect of the peaks is eliminated, there is no significant variation of the roughness for all the samples. This means that the films can be used in an advanced process.

### 3.2 Electrical Measurements:

#### 3.2.1 Normal Procedure

Figure 2 shows the C-V-HF curves obtained from the MOS capacitors with silicon oxide film deposited in the normal procedure. The capacitor area is 300x300 $\mu m^2$. For the densified MOS capacitors C-V-HF curves present a shift towards negative values, suggesting that the annealing process increases the charge concentration into the silicon oxide film and that these charges are positive[11]. The observed stretching in both C-V-HF curves is an indication of the presence of interface charges.

| | Normal | | Intermittent | |
|---|---|---|---|---|
| | As-deposited | Densified | As-deposited | Densified |
| **RMS (nm)** | 0.95 | 1.00 | 0,22 | 0.22 |
| **$R_{max}$ (peak-valley) (nm)** | 42.86 | 38.41 | 4.64 | 6.27 |
| **Ra (nm)** | 0.49 | 0.49 | 0.18 | 0.17 |

**Table II: AFM measurements**

The process parameters and the TEOS/$O_2$ ratio were chosen to result in silicon oxide films with the best composition. The oxygen concentration was high enough to promote the TEOS fragmentation in the gas phase and the oxidization process of TEOS fragments in the solid phase[12]. So, the density of charges should be negligible into the films but, because the C-V-HF curves exhibit a shift, these charges must be present mainly at the interface. These charges can be because of the Si-OH bonds and the non-oxidized TEOS fragments even if there were not detected by FTIRS measurement. [15]

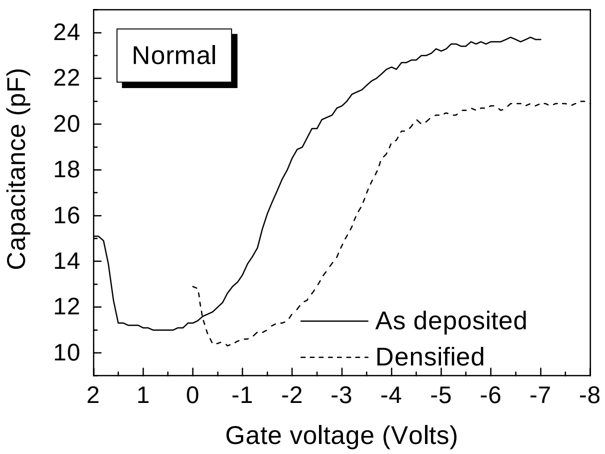


**Figure 2: C-V-HF curves obtained from capacitors fabricated with the silicon oxide deposited in the normal procedure. The shift of the curve, towards negative voltages, is observed; suggesting that the charges into the oxide or at the interface are positive.**

It was reported by G. Raupp[5], that in the deposition processes, performed with an excess of oxygen, the deposition surface is saturated with oxygen ions which avoid the elimination of volatile subproducts. The decrease of the maximum capacitance value after the densification step may be an indicator of a variation of the electrostatic permittivity, because the film thickness has no significant decrease.[15]

Figure 3 shows current versus calculated electric field curves. The electric field is deduced of the applied voltage considering an average oxide thickness. The non-densified structure curve indicates an apparent breakdown electric field near 1 MV/cm. This rather low value is because of the presence of local high electric field at the level of the peaks detected by AFM measurements. As previously mentioned, these peaks are partially eliminated after the densification process that explains the much higher breakdown electric field after this densification.

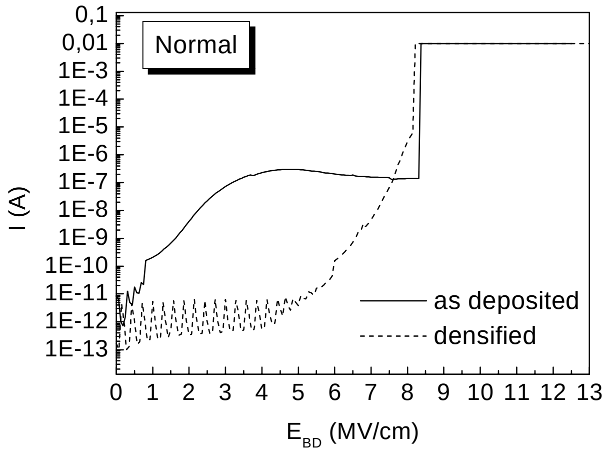


**Figure 3: Current versus electric field of the capacitors with silicon oxide films deposited in the normal procedure.**

The leakage current also decreases after the densification process. These results give evidence that the charges are mainly due to volatile subproducts trapped at the interface and unsatisfied bonds, which are partially eliminated after the thermal process.

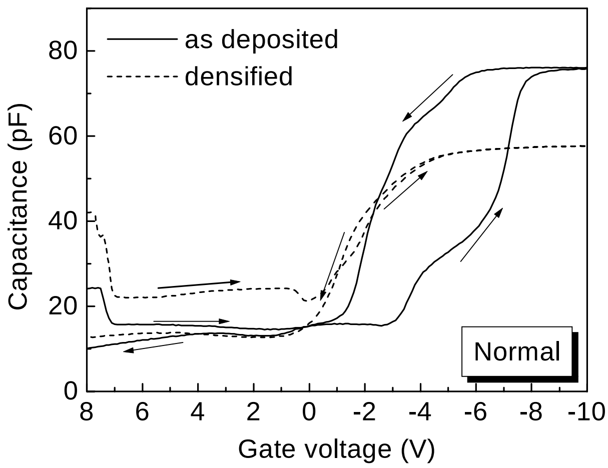


**Figure 4: Hysteresis in the CV-HF curves**

These results are confirmed by the hysteresis present in the C-V-HF curves as shown in Figure 4. The origin of the shift of the C-V -HF curve is the presence of charges and unsatisfied silicon bonds trapped into the film. After the densification process this hysteresis is lower than for the films as-deposited. The remaining hysteresis near the maximum capacitance may be because of charges located near the Fermi level.[13]

The deep depletion observed in the C-V-HF curves may be attributed to the interface states that are not able to follow the applied voltage.

#### 3.2.2 Intermittent Procedure

Figure 5 shows typical C-V-HF curves obtained from the MOS capacitor with silicon oxide deposited with the intermittent procedure. It is observed that there is a shift of the curve towards the positive values after densification. The maximum capacitance decreases after the densification, suggesting also variation in the permittivity.

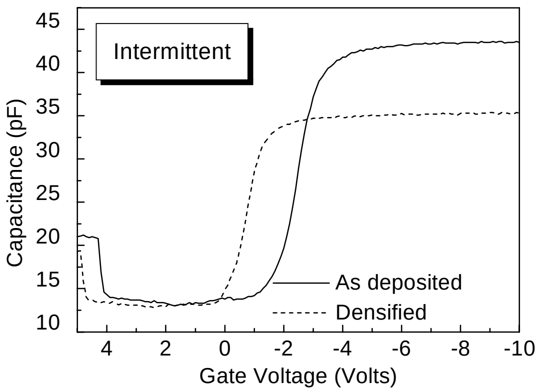


**Figure 5: C-V-HF curves obtained from capacitors fabricated with the silicon oxide deposited with the intermittent procedure.**

Beginning the deposition process, with an oxygen plasma, results in a bombardment of the sample surface with ions that probably etch the initial native oxide but, also create a new “native” oxide. When the TEOS is added to the gas flux the oxidation reactions at the surface results in fewer charges at the silicon/oxide interface.

When the TEOS flux is interrupted at the end of the deposition process, the remaining non-oxidized species, adsorbed at the surface, are oxidized by the oxygen ions without adsorption of new species. Also, the surface bombardment by the oxygen ions removes the subproducts.[514]

Figure 6 shows a calculated breakdown electric field close to 2 MV/cm that is rather low similarly to the samples as-deposited. The leakage current is determined at 3 MV/cm. The leakage current increases with the applied voltage up to $10^{-7}$ A and then stabilizes. The total breakdown occurs at 9.5 MV/cm.

This behavior is not observed after the densification, confirming that mainly the volatile subproducts create the charges. The breakdown electric field reaches 11 MV/cm and the leakage current remains lower than $10^{-11}$ A up to 9 MV/cm. This behavior is confirmed by capacitance-voltage measurement.

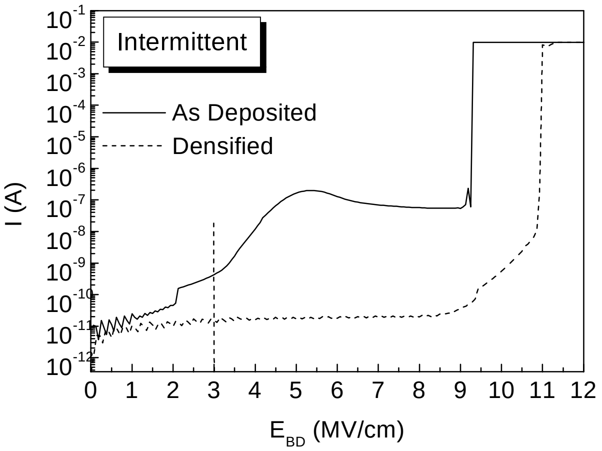


**Figure 6: Current versus calculated electric field curves of the capacitors with silicon oxide films deposited in the normal procedure. The breakdown electric field is close to 9 MV/cm before densification and 11 MV/cm after. The leakage current is much higher before densification.**

Figure 7 shows a strong decrease of the hysteresis in comparison with the curves of Figure 4. After densification, the shape of this curve indicates a potential application of this oxide as gate insulator.

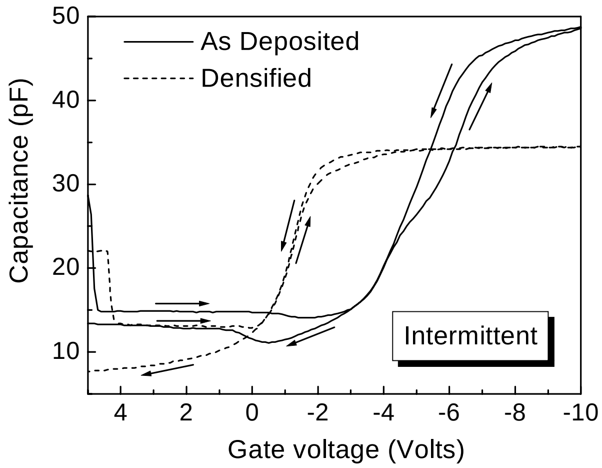


**Figure 7: Hysteresis in the CV-HF curves**

## 4. Discussion and conclusions

We have optimised the process to deposit silicon oxide involving a plasma-enhanced chemical vapour deposition of TEOS. FTIRS, AFM, and electrical analyses showed that a pure oxygen plasma at the beginning and at the end of the deposition step and a rapid thermal annealing process to densify the films, improve significantly the electrical behaviour of these films. Thanks to AFM analysis, we observed a decrease of the punctual defect density at the surface. Electrical measurements on MOS capacitance indicated that the defects are mainly located at the interface and are significantly reduced by the oxygen plasma followed by the rapid thermal annealing. Table IV shows a comparison of different results of the literature with ours. One can note that the breakdown electrical field is much higher than previous ones that open the spectrum of applications.

Table III: Comparison of different results of the literature with ours.

| | $N_{ss}$ ($cm^{-2}$) | | $E_{BD}$ (MV/cm) | |
|---|---|---|---|---|
| | **As Deposited** | **Densified** | **As Deposited** | **Densified** |
| **This work (intermittent)** | 5.31E11 | 1.53E10 | 9.5 | 11 |
| **Ray et all.**[3] | 2.00E11 | *1.3E11 | 3-5 | *4-5 |
| **Pavalescu *et al*.**[15] | 6.16E11 | #2.37E11 | § | § |
| **Patrick *et al*.**[16] | 1.75E11 | § | 5-6 | § |

***** Densified in $N_2$ 900ºC, 30 min, conventional furnace
[#] Densified in $N_2$ 500ºC, 10 h
[§] not given

The C-V characteristics are also good enough to expect fabrication of thin film transistors or more generally MOS devices involving this TEOS oxide.

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