Influence of rapid thermal vacuum annealing and high temperature treatment on the properties of PSG films

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Abstract. The effect is presented of rapid thermal annealing (RTA) in vacuum and thermal annealing in water vapor at 850 °C on the properties of phosphosilicate glass (PSG) films deposited in PECVD and μPCVD reactors. The films were characterized by etch rates and XPS and AES analyses. The RTA was carried out at 800 – 1400 °C at annealing times varying from 15 to 180 sec. The RTA caused a significant decrease in the etch rate, which is indicative of structural changes. The XPS and AES analyses showed that the PECVD PSG films contain excess Si due to the lower oxidation activity of N2O. The excess Si can be oxidized in water vapor at high temperatures. The excess Si leads to a decrease in the etching rate of the PECVD PSG layers as compared to that of the μPCVD films.

1. Introduction
Phosphosilicate glass (PSG) films prepared in different chemical vapor deposition (CVD) systems are widely used in microelectronics. They are employed as passivating layers to provide mechanical protection and gettering of impurities and as inter-metal insulating layers for conformal step coverage. The PSG layers are usually subjected to high-temperature treatments, which are part of the technological process. Many authors have investigated structural, morphological and electrical changes in the films properties after different temperature treatments [1, 2].

The aim of this work is to present the changes in the properties of PSG films after rapid thermal annealing (RTA), as well as annealing in water vapor at 850 °C. Films deposited by two methods: Plasma Enhanced Chemical Vapor Deposition (PECVD) and Micro-pressure Chemical Vapor Deposition (μPCVD) were studied. The PSG films were characterized by etch rate measurements, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

2. Experimental
The PSG layers were deposited on (100) oriented p-type silicon wafers with resistivity of 4-6 Ω.cm. Before deposition, the wafers were cleaned chemically in boiling H2SO4:H2O2 (1:1) for 30 min, rinsed in deionized water and etched in HF:H2O (1:10) for 10 sec. The deposition of the layers was carried out in industrial type reactors: ASM PECVD and ASM μPCVD. The optimized deposition conditions are given in table 1. The phosphorus content was determined with electron microprobe analysis.
Phosphosilicate glass films with two phosphorus contents were studied, namely, 4.5% wt% and 7.5 wt%, the respective PH3 flows are presented in table 1.

### Table 1. Technological conditions of PSG layers deposition.

| Reactor type | T [°C] | SiH4 [sccm. min⁻¹] | O2 [sccm. min⁻¹] | N2 [sccm. min⁻¹] | N2O [sccm.min⁻¹] | PH3 4.5 wt% | PH3 7.5 wt% | P [Torr] | RF [W] |
|--------------|-------|---------------------|------------------|-----------------|-----------------|-------------|-------------|---------|-------|
| μPCVD        | 430   | 100                 | 200              | 500             | -               | 3           | 14          | 0.25    | -     |
| PECVD        | 380   | 135                 | 16               | -               | 2500            | 7.5         | 15          | 1.00    | 30    |

A part of the samples were submitted to RTA in vacuum for different times and temperatures. The RTA system raises the temperature from room temperature to the required temperature for 2 seconds. For a silicon substrate with a thickness of 300 μm, the cooling down from 1200 - 1400 °C to T < 700°C (sensed by an optical pyrometer) is carried out in 6-7 seconds. Another part of the deposited PSG samples were annealed for 30 minutes in water vapor at 850 °C.

The etch rate was measured at 21 °C in 20:1 buffered oxide etch (BOE) with the following composition: 20NH4F (40 wt %):1HF (49 wt%).

The XPS spectra were measured by Escalab MK II (VG Scientific) equipment with Al Ka (1486 eV) X-ray source.

The Auger spectra were acquired by a Riber Auger spectrometer.

### 3. Results and discussion

The effect of RTA on the film properties was studied by following the changes in the chemical etch rate at different annealing parameters. The mechanism of PSG etching in the chosen BOE etch is connected with the breakage of siloxane (Si=O) bonds and =Si-O-P- and P=O bonds, which result from the incorporation of phosphorus in the glass network. Furthermore, cations such as NH~ have also a catalytic effect on the dissolution reaction of Si-O and P-O, with the rate of breakage of P-O bonds being higher compared to that of the Si-O bond [3].

The etch rate decreases with the increase of the RTA temperature and depends on the process duration (figure 1 and figure 2). The change is very fast for the first 60 seconds, particularly for the high annealing temperatures (1200 - 1400 °C); a tendency for saturation is then observed. This is evidence that the RTA induces significant structural changes in short time intervals. The etch rate decrease is mainly due to densification of the film and effusion of impurities [4].

**Figure 1.** Etch rate of μPCVD PSG films (P=4.5 wt%) vs. time of RTA at different temperatures.

**Figure 2.** Etch rate of PECVD PSG films (P=4.5 wt%) vs. time of RTA at different temperatures.
In order to study the effect of RTA on the PSG composition and structure, XPS analysis was carried out on both layer types. The influence of RTA on the position of the Si2p characteristic peak and on the silicon elemental composition was followed for the different treatments (table 2). The peak positions of Si2p for as deposited \( \mu \)PCVD PSG films coincide with the values characteristic for SiO\(_2\). The peaks for the PECVD PSG samples show a low energy broadening of the Si2p peak, which is characteristic of elemental Si (99 eV), i.e. some fraction of the silicon is not oxidized or not fully oxidized (excess silicon). The latter is confirmed also by the silicon content in the layer (table 2) and can be explained by the lower oxidation activity of N\(_2\)O. The increased silicon content is also the cause of the lower PECVD PSG films etch rates as compared to those of \( \mu \)PCVD films. The peaks of as-deposited films and those that underwent RTA at 800 and 1000 °C are shifted to lower binding energies, as compared with the \( \mu \)PCVD films, which corresponds to lower degree of oxidation. After the longest annealing time (3 min) at 1400 °C, the silicon content increases for both layer types, which is due to a partial destruction of the layers. The latter is more weakly expressed for the \( \mu \)PCVD PSG films, because of their higher thermal stability and stoichiometric composition.

Table 2. XPS data on Si2p peak position and silicon content.

| Si2p peak position | Si at% | \( \mu \)PCVD PSG films | PECVD PSG films | \( \mu \)PCVD PSG films | PECVD PSG films |
|--------------------|--------|--------------------------|-----------------|--------------------------|-----------------|
| As-deposited        | 104.0  | 103.4                    | 23.4            | 24.6                     |
| 15 sec at 800°C     | 103.7  | 103.8                    | 24.0            | 22.5                     |
| 1 min at 1000°C     | 103.8  | 103.9                    | 23.8            | 23.5                     |
| 1 min at 1400°C     | 103.7  | 103.7                    | 23.9            | 25.5                     |
| 3 min at 1400°C     | 103.8  | 103.5                    | 24.2            | 25.9                     |

Figure 3. Etched-off PECVD PSG film thickness versus etch time.

Phosphosilicate glass films (7.5 wt% phosphorus) are used as an interlayer dielectric in the fabrication of integrated circuits. They are subjected to additional high temperature treatment in oxidizing ambient – reflow. During the high temperature annealing in water vapor, the oxygen reacts with unoxidized species in the film (Si-H, OH, P-H, free Si, etc.) [5]. We studied the effect of high temperature annealing of PECVD PSG films at 850 °C for 30 minutes in water vapor. The homogeneity along the film thickness was studied by step-by-step etching of as-deposited and
annealed layers. The etch was performed in 20:1 BOE at 21°C. Figure 3 shows the etched-off film thickness ($d$) as a function of the etch time ($\tau$). The annealed sample has a lower etching rate. The almost linear graphics is an indication that the layers are homogeneous in depth. However, a difference is observed in the surface layer. A lower etch rate for as-deposited layers is observed there (region 1) and increased values after the annealing (region II). During the high temperature water vapor treatment an additional oxidation of silicon and phosphorus follow [6], which leads to an increased etching rate. These results are supported by AES analysis.

In figure 4 the concentration depth profile, obtained from AES spectrum of a PECVD PSG film, 100 nm thick is shown. A surface film about 22 nm thick, deficient in oxygen and rich in silicon is registered. The oxygen deficiency is could be explained by the lowered RF plasma during the switch off. The layer in depth has constant composition with silicon to oxygen ratio 1:1.81.

![Figure 4. Concentration-depth profile obtained from an AES spectrum for a 100 nm PECVD PSG film.](image)

4. Conclusion
PECVD PSG layers are not fully oxidized and contain excess, not fully oxidized silicon. In the temperature range 800 – 1000 °C RTA leads to a decrease in the PSG etch rate due to layer densification. At 1400 °C RTA induces a partial destruction. The effect is weaker at µPCVD PSG, because they are thermally more stable, which is due to the higher temperature of the process and the absence of plasma in the system.

Acknowledgments
This study was supported by the National Science Fund of Republic of Bulgaria under Grant X-1505.

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