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Low temperature deposition: properties of SiO$_2$ films from TEOS and ozone by APCVD system

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Abstract. An Atmospheric Pressure Chemical Vapor Deposition (APCVD) system was implemented for SiO$_2$ nanometric films deposition on silicon substrates. Tetraethoxysilane (TEOS) and ozone (O$_3$) were used and they were mixed into the APCVD system. The deposition temperatures were very low, from 125 to 250 °C and the deposition time ranged from 1 to 15 minutes. The measured thicknesses from the deposited SiO$_2$ films were between 5 and 300 nm. From the by Fourier-Transform Infrared (FTIR) spectra the typical absorption bands of the Si-O bond were observed and it was also observed a dependence on the vibrational modes corresponding to hydroxyl groups with the deposition temperature where the intensity of these vibrations can be related with the grade porosity grade of the films. Furthermore an analytical model has been evoked to determine the activation energy of the reactions in the surface and the gas phase in the deposit films process.

1. Introduction
Interlayer dielectric film formation technology is essential for multilevel interconnection in ULSI devices. Low temperature deposition has been required. Organosilicon materials such as tetraethoxysilane (TEOS), Si[OCH$_2$CH$_3$]$_4$ have increasingly been used as a silicon source because it provides a better film quality and excellent step coverage compared to the conventional silane method [1]. Desirable aspects of TEOS as a silicon source are safety, easy of handling, and chemical stability. However, conventional thermal CVD TEOS processes require temperatures higher than 600°C. The CVD reaction of TEOS with ozone yields silicon dioxide thin films with excellent characteristics at unusually low process temperatures (300°C to 400°C) [2-6]. However, its deposition mechanism is not well understood yet. The chemistry of this process has not been definitively characterized yet and the process therefore presents an excellent opportunity to evaluate our approaches.

In this work, SiO$_2$ films by APCVD using TEOS and ozone were deposited at very low temperature on silicon substrates and their optical properties were investigated. An analytical model for the deposition rate was used to obtain the activation energy of the reaction at the film.

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2. Experimental Procedure
A schematic draw of the APCVD system is shown in figure 1 [7]. The reactor is composed by a graphite heater element into a closed quartz chamber. The deposition temperature is controlled by a k type thermocouple and a temperature controller (Eurotherm model 2416). TEOS is introduced into the reactor by flowing N₂ through a bubbler containing the precursor at 25 °C. Also an O₃/O₂ flow was introduced into the reactor. The partial pressure of the TEOS was 1.1 Torr and the ozone concentration in the oxygen was controlled to be 5%.

![Figure 1. Schematic diagram of the APCVD system.](image)

The SiO₂ films were deposited on n-type (100) silicon substrates of 5 Ω-cm at a pressure of 590 Torr. Prior to the deposit process, the substrates were cleaned by a standard process (RCA) to eliminate organic and inorganic moistures on their surface and the silicon wafers were introduced into the reactor. After the temperature on the substrate was stabilized the TEOS and Ozone was flowed into the chamber. The oxide films were deposited at temperatures from 125 to 250 °C having deposition time between 1 and 15 minutes. The final film thicknesses were from 5 to 300 nm as measured from a Rudolph 439L633P ellipsometer. The films were etched in a chemical solution, composed by 15:10:300 of HF (48%): HNO₃ (70%): DI water, in volume, to determine the etch rate in the films. Film microstructure was examined by a FTIR Bruker vector 22 system.

3. Results and Discussion
The main absorbance peaks expected from SiO₂ films from an infrared spectroscopy are rocking (450 cm⁻¹), bending (800 cm⁻¹) and asymmetric stretching (1072 cm⁻¹) originated from the vibration modes of Si-O bonds. In the figure 2 a serie of absorbance spectrum are presented for SiO₂ films obtained at different temperatures and from where those main peaks are observable. Also, in some cases, additional bands corresponding to hydroxyl groups (920 cm⁻¹) and other residual groups (ethoxy groups at 1395-1837 cm⁻¹) are exhibited.

When the deposition temperature was increased from 125 to 250 °C the intensity of those absorption bands decreased, this means that the quantity of residual groups incorporated in the film decreases [8]. This could signify that the film porosity is decremented principally as a consequence of the reduction in the number of the hydroxyl groups [9]. The higher etch rate values found in the films deposited at lower temperature (table 1) shown a decrease in the film density. It is known a decrease in the Si-OH bonds in the film resulted in a more dense silicon oxide film [9, 10].

The refractive index has been reported to be inversely proportional both to etch rate and the number of hydroxyl groups in the film [9-11]. Hence, the silicon oxide films obtained at low temperatures with high number of Si-OH bonds lead to low values for the refraction index. The refraction index of the as-deposited silicon oxide films increased from 1.400 to 1.461, as the deposition temperature rise from 125 to 250 °C.
Figure 2. Absorbance spectra for SiO₂ films obtained by APCVD at different temperatures and 10 min of deposition. The flow of N₂ and O₂ were 100 and 500 sccm respectively.

Table 1. SiO₂ films TEOS-Ozone parameters.

<table>
<thead>
<tr>
<th>Deposition temperature [ºC]</th>
<th>Deposition rate [nm/min.]</th>
<th>Refraction index</th>
<th>Etch rate [nm/sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>5</td>
<td>1.400</td>
<td>1.73</td>
</tr>
<tr>
<td>150</td>
<td>12</td>
<td>1.420</td>
<td>1.46</td>
</tr>
<tr>
<td>175</td>
<td>20</td>
<td>1.445</td>
<td>1.17</td>
</tr>
<tr>
<td>200</td>
<td>19</td>
<td>1.457</td>
<td>0.84</td>
</tr>
<tr>
<td>225</td>
<td>16</td>
<td>1.460</td>
<td>0.71</td>
</tr>
<tr>
<td>250</td>
<td>9</td>
<td>1.461</td>
<td>0.66</td>
</tr>
<tr>
<td>Thermal SiO₂</td>
<td>8</td>
<td>1.46</td>
<td>0.59</td>
</tr>
</tbody>
</table>

On the other hand, was found that the film deposition rate was dependent on the deposition temperature. From Table 1 can be observed that the minimum value for this parameter is found at 125°C. For higher temperatures it reaches a maximum and after it decreases. To explain this behavior the model of Kim and Gill [12] was taken.

The kinetic mechanism includes parasitic gas phase reactions. Thus, the deposition rate is given by [12]

\[
R_{SiO_2} = \frac{Q_{in}[O_3]_{in}}{V} \frac{[TEOS]_{in}}{1 + k_G [O_3]_{in}},
\]

where \(Q_{in}\) is the volumetric flow rate, \([O_3]_{in}\) and \([TEOS]_{in}\) are the concentration of ozone and TEOS at the reactor input respectively, \(V\) is the reactor volume and \(k_S, k_G\) are the reaction rate constant in the surface and in gas phase respectively. The equation (1) contains the surface reaction (numerator) and the gas phase reactions (denominator). For our APCVD system the values for \(Q_{in}, [O_3]_{in}\) and \([TEOS]_{in}\) were

\[
[TEOS]_{in} = 1.2x10^{-6} \text{ mol/cm}^3
\]

\[
[O_3]_{in} = 1.5x10^{-5} \text{ mol/cm}^3
\]

\[
Q_{in} = 26.6 \text{ cm}^3/s
\]

\[
V = 1021.4 \text{ cm}^3
\]

Substituting those values en equation (1), it is found;
\[ R_{\text{SiO}_2} = \frac{4.69 \times 10^{-13} k_s}{1 + k_g \cdot 1.5 \times 10^{-3}}, \quad (2) \]

where \( k_s \) and \( k_g \) have the form [7]

\[ k \propto e^{\frac{B}{RT}}, \quad (3) \]

here, \( T \) is the temperature, \( R \) is the Boltzmann constant and \( B \) is the activation energy of the reaction.

Taking into account just the reactions in the surface, the second term in the denominator of equation (2) can be neglected and it becomes,

\[ R_{\text{SiO}_2} = 4.69 \times 10^{-13} k_s \quad (4) \]

If the experimental values of the deposition rate from table 1 vs. the inverse of the deposition temperature are plotted, it is possible to obtain the value of the activation energy for the reactions in gas phase and on the surface. In figure 3 such characteristic is presented.

In that figure, it is observed that in the temperature range 125 to 175 °C, a straight line is obtained according to the equation (4), signifying that the deposition rate is increased with the increase in the deposition temperature because the value of the \( k_s \) in equation (3) increases with temperature.

After reach a maximum, a decrease in the deposition rate can be observed around 200 °C. This fact can be explained by the effects in gas phase reactions. At higher temperatures (>175°C), where the gas phase reactions are significant the second term in the denominator of equation (2) becomes important and therefore the theoretical deposition rate must be decrease. The deposition rate of the TEOS–Ozone process is limited by reactions in the gas phase and this cause the decrease in the deposition rate. This behavior has been also found in systems LPCVD to 30 Torr, where the maximum is located around of 400°C [7, 12, 13].

Using the experimental values of the deposition rate and numeric analysis with regard to equation (2), the values of \( k_s \) and \( k_g \) and therefore the activation energy in the surface and in gas phase were obtained. These values were 8744.0 and 27925.9 cal / mol respectively. Substituting the values in equation (1) it becomes;

\[ R_{\text{SiO}_2} = \frac{4.75 \times 10^{-4} \ e^{\frac{8744}{RT}}}{1 + 4.5 \times 10^{12} \ e^{\frac{27925.9}{RT}}}. \quad (5) \]

A plot of equation (5) is shown in figure 3. It can be seen that the experimental data fits well with the theoretical ones calculated from equation (5). A little difference observed around the maximum of the deposition rate in figure 3 can be due to a change in the predominant reactions, that is, the dominant processes are initially the reactions in the surface and later the dominant processes changes and it leads to reactions in gas phase to be dominant [7]
4. Conclusions

An APCVD system was implemented to deposit SiO₂ films on silicon substrates. The deposition temperatures ranged from 125 to 250 °C, temperatures range not reported in APCVD systems. The film thickness ranged from 5 to 300 nm. The absorption bands corresponding to the vibration modes of the SiO₂ were observed. It was also observed additional absorption bands belonging to hydroxyl groups (Si-OH bonds). It could be observed from those spectra that the composition of the silicon dioxide films changes with the film deposition temperature. Increasing the temperature, from 125 to 225 °C the quantity of hydroxyl groups incorporated in the film reduces. These produce a change in the value of the refraction index film and as consequence a decrease in the film porosity. A theoretical model was fed with parameters calculated from our APCVD system to determine the activation energy of the reactions in gas phase and on the surface. The experimental data for the film deposited rate fitted well with the ones found from that theoretical model.

5. References:

[7] Pacio M. 2004 M. D. Thesis: Modeling, design and developed an APCVD system, to obtained SiO₂ nanometrics films on silicon substrates (Puebla, México: CIDS-ICUAP, University of Puebla)

