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On the Deposition Kinetics of the LPCVD Gate Oxides Prepared from SiH₄ and O₂

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Abstract: An experimental study on the deposition kinetics of LPCVD SiO₂ films at 450°C in a hot wall system from SiH₄ and O₂ in the range of very high O₂ / SiH₄ ratios (100-284) and very low SiH₄ partial pressures (3.5-5.2 μbar) is presented. Unexpectedly, a low deposition rate of 1.8 nm/min with a thickness uniformity of less than 6 MAXMIN% on five simultaneously processed wafers is obtained. The results can be explained by a gas phase formation of precursors which dominate the deposition process. This process can be used for different device applications where thin SiO₂ films are required, such as Thin Film Transistors and EEPROMs.

1. INTRODUCTION

The continuous downscaling of electronic devices requires subsequent decreasing film dimensions. Unfortunately, thermal oxides with a thickness below 50 nm suffer from incorporation of contaminants from the oxidation of silicon, leading to inferior oxide quality. Using deposited oxides one can eliminate the incorporation because no substrate material is consumed for the oxide formation. However, usual deposition rates involved are too high to obtain reproducibly thin layers. Hence, the deposition rates have to decrease.

To improve the quality of thin silane (SiH₄) based Low Pressure Chemical Vapor Deposition (LPCVD) oxides the oxide defect density is reduced by decreasing the SiH₄ partial pressure. Kawahara [1] found that a high O₂ / SiH₄ ratio (1-10) can result in a uniformly deposited oxide film when a cage with a tightly designed mesh was used in a cold wall reactor. In another paper we have studied the Rapid Thermal Chemical Vapor Deposition (RTCVD) of SiO₂ films from SiH₄ and O₂ with high O₂ / SiH₄ ratios [2]. This also motivated us to investigate the LPCVD SiO₂ formation at high O₂ / SiH₄ ratios. No detailed kinetic data is known about the combination of a low SiH₄ partial pressure (3.5-5.2 μbar) and very high O₂ / SiH₄ ratios (100-300).

It is the purpose of this paper to study the LPCVD SiO₂ deposition rate and thickness uniformity as a function of the O₂ / SiH₄ ratio, the SiH₄ partial pressure and the total pressure. Based on the dependence of the deposition rate on the inter-wafer distance, a gas phase reaction mechanism generating intermediates, which are responsible for the SiO₂ formation, is supported. The growth rate and edge non-uniformity can be explained by assuming the gas phase precursor formation to be rate determining.

For Thin Film Transistors to be integrated with sensors and/or displays, it is important to have a low maximum process temperature. The sensors and displays are usually fabricated on glass substrates and, in general, both cannot withstand high temperature steps. For Electrically Erasable Programmable Read Only Memories (EEPROMs) the isolating and tunneling properties must be optimized. Here, the low temperature requirement is not so strict, however, the deposition rate should be kept low to reproducibly

deposit thin oxide layers. The implementation of these oxide films in devices such as TFTs and EEPROMs is subject of research in the near future.

2. EXPERIMENTAL

The SiO₂ films were deposited at 450°C in a hot wall LPCVD reactor using 5.0 quality 100% SiH₄ and O₂. See Figure 1 for a schematic presentation. The furnace (1) consists of three separately controlled zones to obtain a flat temperature profile of 30 cm in the center of the reactor. The reactor is equipped with a 11.5cm furnace tube, a wafer “cage” (4) and a cantilever loading system (3), all of them made of quartz. The peculiar aspect of our experimental set-up was that only one orifice injector (2) for silane and oxygen was used, while a simple wafer boat replaced the standard tightly designed cage with orifices. Thirteen 3” wafers were constantly loaded in the carrier (4 dummies in the front and the back and 5 “process” wafers in the middle) for thickness and uniformity control. For a constant flow rate of SiH₄ of 4.4 sccm, the O₂ flow was increased in the range 440-1250 sccm while the total pressure ranged from 0.50 to 1.00 mbar.

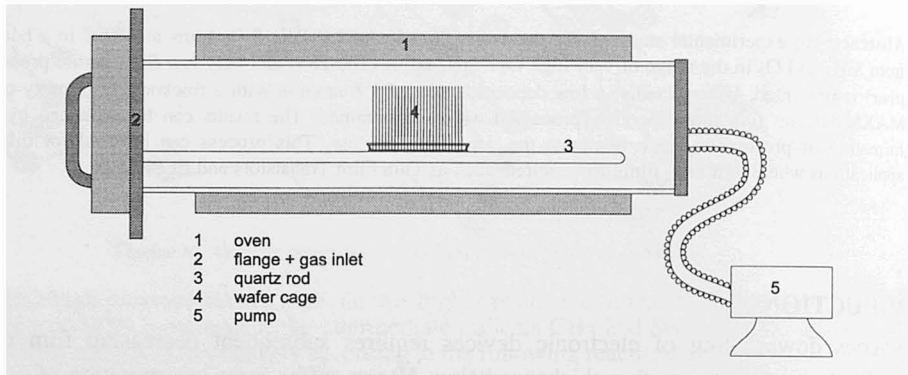


Figure 1: A schematic view of the LPCVD reactor. Dimensions of the tube are: flat zone = 30 cm, diameter = 11.5 cm.

The wafers are cleaned as follows: 10 min in fuming HNO₃, 5 min DI water rinse, 10 min in boiling 70% HNO₃ and DI water rinse. Prior to the actual deposition a 1% HF dip is given to remove the native oxide. The deposition rate is calculated from the mass increase assuming a double-sided deposition. The thickness is also measured with a PLASMOS ellipsometer using a Helium-Neon laser with a wave length λ of 632.8 nm. To eliminate edge effects the thickness uniformity is measured by mapping the thickness across the wafer, taking into account a 10 mm edge. The thickness uniformity is based on statistical analysis performed by the PLASMOS ellipsometer and is defined in terms of MAXMIN% around the MEAN value. Therefore, the thickness uniformity is a deviation from the mean value and should be as low as possible. All deposition rate and thickness uniformity values are averaged over five wafers.

3. RESULTS AND DISCUSSION

From earlier experience it is clear that the O₂ / SiH₄ ratio has an important effect on the uniformity and the deposition rate in other CVD reactors [1,3,4]. So, it is expected that this ratio is also important for the deposition in the LPCVD reactor used in this study. The results will be presented as a function of O₂ / SiH₄ ratio and SiH₄ partial pressure. The primary goal of our research is to find deposition parameters at a low temperature with a good uniformity and a low deposition rate.

Preliminary experiments are performed to see if the simple experimental setup described above fulfils the requirements for very thin SiO₂ deposition. The initial CVD settings are as follows: a deposition

temperature of 450°C, a SiH₄ flow rate in the range of 10-13 sccm, an O₂ flow rate in the range of 1200-1500 sccm and a total pressure in the range of 1.0-1.2 mbar. The inter-wafer spacing is varied between 3-13 mm to evaluate the effect of the wafer distance on the deposition rate and the thickness uniformity.

This resulted in a deposition rate of 4-6 nm/min while it was 4-5 times lower when the inter-wafer spacing was reduced from 13 to 3 mm. The thickness uniformity is 8-10 MAXMIN%. This result proves a proportional dependence of the deposition rate on the inter-wafer spacing. From this it is concluded that the gas phase precursor formation dominates the deposition process. The growth rate is then determined by the area to volume ratio.

The deposition rate found with the setting described above (4-6 nm/min) is still quite high for reproducible deposition of thin SiO₂ films. Therefore, the deposition rate is further reduced by decreasing the SiH₄ partial pressure. In Table 1 the deposition parameters are given.

Table 1: Deposition parameters for the LPCVD oxide from SiH₄ and O₂.

O ₂ flow [sccm]	N ₂ flow [sccm]	SiH ₄ flow [sccm]	O ₂ / SiH ₄ ratio [-]	P(total) [mbar]	P(SiH ₄) [mbar]	P(O ₂) [mbar]	Dep.rate [nm/min]	Uniformity [%]
440	0	4.4	100	0.53	5.2e-3	0.524	2.0	9.4
585	0	4.4	133	0.63	4.7e-3	0.625	2.48	7.3
750	0	4.4	177	0.75	4.4e-3	0.745	2.22	7.0
1000	0	4.4	227	0.90	3.9e-3	0.896	1.87	4.1
1250	0	4.4	284	1.02	3.5e-3	1.016	1.79	5.4
585	750	4.4	133	1.00	3.3e-3	0.436	1.73	8.5

As can be seen the SiH₄ flow rate is kept constant at the minimum level possible with the equipment used in this study. The O₂ / SiH₄ ratio is changed by varying the O₂ flow rate keeping other parameters as constant as possible. However, due to vacuum pump limitations the pressure can not be kept constant at those high O₂ flow rates, thereby changing the partial pressures of O₂ and SiH₄ simultaneously. Because the SiH₄ and O₂ partial pressures cannot be separated, the results of the deposition rate and the thickness uniformity will be presented as a function of O₂ / SiH₄ molar ratio.

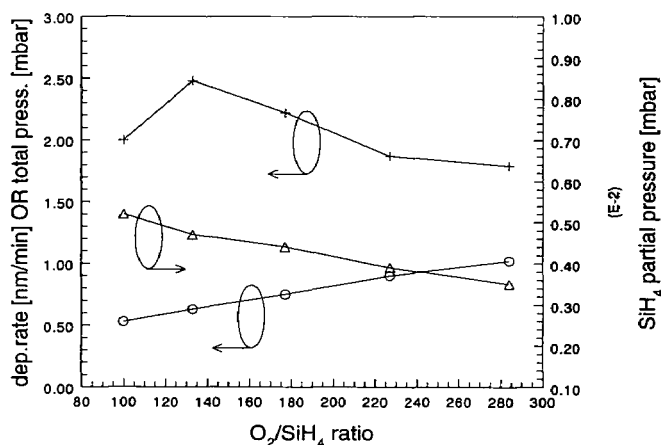


Figure 2: LPCVD SiO₂ deposition rate, total and SiH₄ partial pressure versus O₂ / SiH₄ molar ratio at a constant SiH₄ flow rate of 4.4 sccm and a deposition temperature of 450°C (-+- = deposition rate in nm/min at left Y-axis, -Δ- = SiH₄ partial pressure in mbar at right Y-axis, -o- = total pressure in mbar at left Y-axis).

Figure 2 shows the effect of the O_2 flow rate on the SiO_2 deposition rate at a constant flow of SiH_4 .

As can be seen a slight increase-maximum-decrease behavior is found for the deposition rate as a function of the O_2 / SiH_4 molar ratio, although the variation of the deposition rate is very small (from 2.0 nm/min to 2.5 nm/min and back to 1.8 nm/min), even when the O_2 / SiH_4 molar ratio is increased to as high as 284. The increase-maximum-decrease behavior is also found in earlier work [3,4] at lower O_2 / SiH_4 ratios. It should be noted, though, that the residence time and the SiH_4 inlet partial pressure are also changed when changing the O_2 / SiH_4 molar ratio. At high O_2 / SiH_4 ratios the residence time is short and the effective SiH_4 partial pressure at the wafer position is even further decreased. This results in an extension of the X-axis to even higher values so the increase-maximum-decrease behavior as described above is stretched and therefore diminishes. So, the deposition rate is considered to be not depending on very high values of the O_2 / SiH_4 ratio. The deposition rate is at a level that the control of very thin layers for gate oxide applications is easily obtained.

To eliminate the effect of coupled partial pressures an experiment with N_2 addition is performed. By interchanging N_2 by O_2 the total flow can be kept constant. This can result in a constant residence time and SiH_4 partial pressure while the O_2 partial pressure can be changed. However, this particular experiment has been conducted at such a high total gasflow that only the O_2 / SiH_4 ratio could be kept constant. Still, as can be seen from Table 1, the deposition rate decreases with decreasing SiH_4 partial pressure while the O_2 / SiH_4 ratio remains constant (rows 2 and 6), indicating that the SiH_4 partial pressure is mainly determining the deposition rate. Comparing the experiments described in rows 5 and 6, it is seen that, while the SiH_4 partial pressure is fairly constant and the O_2 partial pressure decreases substantially, the deposition rate is also fairly constant, again indicating that the SiH_4 partial pressure is dominating the deposition rate.

As for the thickness uniformity, one observes a decreasing thickness uniformity, which is good by our definition, for the higher O_2 / SiH_4 molar ratio for the experiments with no N_2 addition. This shows that, even for very high O_2 / SiH_4 molar ratios of 100-284, this ratio affects the thickness uniformity, as was found in earlier works [2-4] for lower ratios.

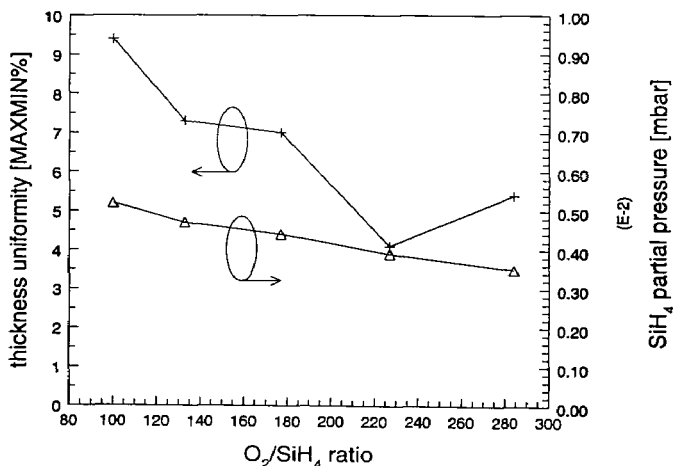


Figure 3: Thickness uniformity and SiH_4 partial pressure versus the O_2 / SiH_4 molar ratio at a constant SiH_4 flow rate of 4.4 sccm and a deposition temperature of $450^\circ C$ (+ = thickness uniformity in %, Δ = SiH_4 partial pressure in mbar).

For thin oxide layers a low deposition rate is necessary for controllable growth. A high O_2 / SiH_4 molar ratio seems interesting since the deposition rate is reasonably constant at a low value. So, for a high O_2 / SiH_4 molar ratio of 227 the thickness uniformity is the most important parameter.

From Figure 3, a trend of improving LPCVD SiO_2 thickness uniformity is observed when the O_2 / SiH_4 molar ratio is increased. The edges are always thicker compared to the center of the wafer, giving information about the deposition mechanism at $450^\circ C$. An increasing O_2 / SiH_4 ratio also increases the total pressure. This usually results in a deterioration of the thickness uniformity. However, for this particular situation of very low SiH_4 partial pressure and high O_2 / SiH_4 molar ratio the uniformity is slightly improving, suggesting that the effect of increasing O_2 / SiH_4 molar ratios on improvement of the thickness uniformity is higher than the deleterious one due to the total pressure increase.

The inter-wafer spacing has a large effect on the deposition rate and the thickness uniformity, in agreement with earlier reports [5,6]. In our case, when the wafer spacing is reduced from 13 mm to 3 mm, the deposition rate decreases by about 5 times. Therefore, a decrease of the deposition rate by the ratio of the distances between the wafers exists. Because of the smaller inter-wafer spacing, any small tilt of a wafer affects the thickness uniformity. From this it can be concluded that the gas phase precursor formation dominates the deposition process. The growth rate is then determined by the area to volume ratio.

4. DISCUSSION

The driving force for the investigation of LPCVD SiO_2 film deposition kinetics under the CVD conditions described above (low SiH_4 partial pressure and high O_2 / SiH_4 molar ratio) is mainly the low deposition temperature required for glass compatibility and the low deposition rate necessary for very thin (gate) oxide applications.

At deposition temperatures higher than $400^\circ C$ the deposition mechanism appears to be mass transport controlled. The deposition mechanism is still under consideration in the literature [3,6]. The dependence of the deposition rate on the wafer to wafer distance in an LPCVD reactor is explained based on the surface reaction mechanism [5]. Later, for LPCVD conditions, a mechanism based on gas phase reactions which provided one [6] or two [1] precursors was suggested. According to the mechanism based on the gas phase precursors and the volume needed to create these, one can easily explain the higher thickness of the oxide layer at the edge of the wafer. Also, the reduction of the deposition rate found when the inter-wafer spacing is decreased can be explained in this way.

A major problem with the theoretical description of the deposition in the system used in this study is the fact that the SiH_4 and O_2 partial pressures are coupled. For the calculation of deposition rate as a function of both SiH_4 partial pressure and total pressure the pressures should be separated. This is not possible due to the vacuum pump limitations.

The main reasons for selecting the deposition temperature of $450^\circ C$ are related to the removal of all Si-H unreacted bonds from the film deposition [7] and a good step-coverage [1]. These are very important from the device point of view. The first property, the elimination of Si-H bonds from the bulk of the dielectric, is necessary to reduce the number of charge carrier traps. The second property, the oxide conformity, is needed for second level poly-silicon overlapping the first level of poly-silicon.

An overall analysis of the experimental results in our laboratory shows only a slight dependence of the deposition rate and thickness uniformity on the deposition parameters. This is very different from earlier results obtained in a standard LTO reactor [3,4], probably due to the much higher O_2 / SiH_4 molar ratios. Moreover, in that paper [3], it is shown that for a higher SiH_4 partial pressure (≈ 3 mbar) at $400^\circ C$, a strong gas phase reaction started when the O_2 / SiH_4 ratio exceeded a certain value. This value is a function of temperature, increasing when the deposition temperature increases. Although in our simple setup the SiH_4

partial pressure is two or three orders of magnitude lower, it can not be excluded that gas phase reactions start to play a role at the higher SiH₄ partial pressures at 450°C.

Some preliminary electrical characterisation is performed on simple capacitor structures after the 50 nm oxide films are annealed in N₂ at 950°C for 15 minutes for densification. The results are promising as a charge-to-breakdown value of 0.5 C/cm² is found for several capacitors. Further electrical characterisation is necessary to assess the properties of these thin oxide layers in devices like thin film transistors and EEPROMs.

The optimum CVD deposition conditions which assure a low deposition rate of 1.8 nm/min and a thickness uniformity (taking into account a 10mm wafer edge) of less than 6 MAXMIN% on five wafers simultaneously are:

1. A SiH₄ flow rate of 4.4 sccm
2. A O₂ flow rate of 1250 sccm (O₂ / SiH₄ ratio of 227)
3. A total pressure of 1.0 mbar
4. A deposition temperature of 450°C

5. CONCLUSIONS

In this work the deposition of thin SiO₂ layers from SiH₄ and O₂ in a standard LPCVD reactor without using complex O₂ and SiH₄ distribution systems is shown. A low deposition rate of 1.8 nm/min with a thickness uniformity of less than 6 MAXMIN% on five simultaneously processed wafers is obtained for a SiH₄ partial pressure of 3.5*10⁻³ mbar and a O₂ / SiH₄ ratio of 227. The results can be explained by assuming the gas phase precursor formation to be dominating the deposition process.

This process can be used for different device applications where thin SiO₂ films are required, the first priority being in the field of Thin Film Transistors and EEPROMs. To meet these requirements, the defect density, step coverage and resistance against hot electron stress and Fowler-Nordheim tunneling must be studied initially. The effect of densification steps will be subject of research in the very near future.

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