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LPCVD SiO₂ Layers Prepared from SiH₄ and O₂ at 450 °C in a Rapid Thermal Processing Reactor

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Abstract. In this paper experimental results of the silane oxidation kinetics in a rapid thermal low pressure chemical vapor deposition (RTLPCVD) cold wall reactor at 450 °C are presented. For a certain total pressure kept constant in the range of 0.6-4.5 mbar, it is always found a certain threshold silane partial pressure $p(\text{th})_{\text{SiH}_4}$ (decreasing from 0.15 mbar to 0.076 mbar when the total pressure increases) which determines a sharp transition from no film formation to high deposition rates of the SiO₂ layers. Critical partial pressures for lower limits of explosion at room temperature (0.223 mbar) and at deposition temperature (0.17 mbar) are noticed. The film deposition is very sensitive to the changes in the chemical state of the walls. These results may indicate that the silane oxidation process is controlled by the gas phase chain reactions. By keeping constant the total pressure (4.5 mbar), the SiH₄ partial pressure (0.079 mbar) and the total gas flow rate (570 sccm), with the nitrogen varied as a gas balance, an increase-maximum-decrease dependence of deposition rate as a function of O₂/SiH₄ mole ratio is found. Uniform SiO₂ layers (5% around the averaged value) were found for the above CVD conditions and an O₂/SiH₄ ratio equal to 11. Without further process and equipment improvements this process cannot be used in practice.

1. INTRODUCTION

Single wafer rapid thermal processing (RTP) has become an important route for the ULSI technology. At this moment, rapid thermal annealings (RTA), oxidations of (poly)silicon and chemical vapor depositions (RTCVD) of polysilicon are well established processes and represent interlinked steps for the *in-situ* preparation of silicon gate MOS structures [1]. On the other hand, recently, deposited gate oxides thermally annealed in N₂O ambient have shown superior electrical properties with respect to thermally grown oxides, in terms of oxide defect density and hot electron immunity [2-4]. However, a few results were published about the kinetics of low pressure chemical vapor deposition (LPCVD) of SiO₂ films in a cold wall RTP reactor [5]. Moreover, if we take into account the need for low temperature processes applied in the technology of thin films transistors, one can easily understand the motivation for the experimental and theoretical investigation of the reaction between the SiH₄ and O₂ in a cold wall RTP reactor.

The present paper reports experimental results of silane oxidation in a cold wall RTP reactor at 450 °C. It will be shown that the partial pressure of silane plays an essential role in the kinetics of SiO₂ film preparation determining a sharp transition from no film formation to high deposition rate. Moreover, the violent character of the reaction between the two gases in a cold wall chamber is put into evidence by finding the critical SiH₄ partial pressures for lower explosion limit (LEL) at room temperature (0.223 mbar) and at deposition temperature (0.187 mbar).

Based on these results and the experimental observations concerning the sensitivity of the film formation on the chemical state of the reaction walls, a chain reaction mechanism is speculated and discussed in this work in connection with other papers presenting silane oxidation at low pressures [1,6,7]. Although, one can conclude that for the existing RTP reactor configuration this process cannot be used as it is at this moment, we have finally found a narrow region of CVD conditions for preparing uniform layers of SiO₂ films (5% around the average value) with deposition rates in the range of 140 nm/min.

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2. EXPERIMENTAL

The experimental results of SiO_2 film formation presented in this paper are based on the low pressure reaction between the SiH_4 and O_2 at 450°C taking place in a single wafer, load-locked high vacuum rapid thermal multiprocessing reactor. The rapid heating of the wafer (with a heating rate higher than 100°C/sec) is obtained from the light of a LXU-35 arc lamp (Peak Systems) located at the lower side of the reaction chamber. The 3" wafer is positioned on three thin quartz pins (sitting on the quartz window above the lamp) to avoid the thermal inertia phenomena. Within the cylindrical stainless steel reactor with a diameter of 50 cm and a height of 10 cm there is an internal quartz room with the same height and a 30 cm diameter where the wafer is located exactly below the gas injection points. There is no mesh or susceptor in the immediate vicinity of the wafer assuring thus conditions for a real cold wall chamber configuration. The two reactive gases premixed before entering the reactor were injected from the upper side with and without a showerhead. The distance between the wafer and the upper injection area of reactive gases is 90 mm while the distance from the wafer to the quartz window is about 9 mm. Nitrogen was injected into the chamber through a separate port and was used as a gas balance in order to be able to vary the oxygen partial pressure while keeping constant the total pressure, the partial pressure of silane and the total gas flow rate. The temperature received by the wafer from the light flux was used as a reaction switch for the silane oxidation excepting those CVD conditions where a reaction started at the room temperature before any heating process was initialized.

Wafers were cleaned in 100 % HNO_3 acid and boiling 70 % HNO_3 , respectively. Prior any deposition, the wafers were dipped in 1 % HF solution to prevent native oxide increase. The average thickness of SiO_2 layers deposited directly on a bare silicon wafer was obtained by the weighting method with the aid of a microbalance. The thickness uniformity was evaluated with an automatic PLASMOS ellipsometer.

3. RESULTS

Preliminary trials have been initially made to find the CVD conditions for the SiO_2 film preparation in the RTLPCVD reactor. Then, in order to understand the rapid thermal low pressure chemical vapor deposition of SiO_2 films from SiH_4 and O_2 at 450°C , two directions were considered.

First, at a constant O_2/SiH_4 mole ratio equal to 2, different total pressures were established during the deposition process and the deposition rate was represented as a function of the partial pressure of silane.

Second, at a constant total pressure, total gas flow rate and SiH_4 partial pressure, a dependence of the deposition rate as a function of O_2/SiH_4 mole ratio was investigated.

3.1 Preliminary experimental results

Based on earlier results of LPCVD SiO_2 deposition at low temperature in a hot wall LPCVD reactor where thin gate oxides were prepared at very low partial pressure of silane (p_{SiH_4}) [2-4], preliminary experiments were performed for p_{SiH_4} values in the range of 0.0013-0.06 mbar, at a total pressure (P_t) of (0.35-0.4) mbar with the oxygen flow rates (F_{O_2}) decreasing in the range (400-125) sccm while the SiH_4 flow rate (F_{SiH_4}) was increased in the range (1.5-25) sccm. No film formation was obtained for these CVD conditions. First RTLPCVD SiO_2 layers were "seen" for a p_{SiH_4} value of 0.133 mbar ($P_t=0.4$ mbar, $F_{\text{O}_2}=50$ sccm, $F_{\text{SiH}_4}=25$ sccm) and the deposition rate was 5nm/min. By keeping constant the total pressure and the silane and oxygen flow rates, no SiO_2 film formation was noticed again when a flow of 75 sccm of nitrogen was added during deposition, suggesting thus the importance of p_{SiH_4} parameter for the film deposition.

All these experiments were performed with the premixed silane and oxygen injected through only one orifice located at 90 mm above centre of the wafer and thickness nonuniformities were very high with a thicker layer in the centre of the wafer.

When the premixed reactive gases were introduced through a showerhead (a number of small holes distributed on a ring with the diameter of about 20 mm) situated at the same height above the wafer the film nonuniformities remained still as high as before.

3.2 Systematic experimental results

In order to understand the effect of the partial pressure of silane on the kinetics of RTLPCVD SiO_2 film formation, at a certain total pressure, the oxygen and silane flow rates were kept constant and the pSiH_4 was varied by means of the nitrogen flow rate.

In Fig. 1 it is shown a sharp transition from zero deposition rate to high deposition rate for each total pressure used (0.6, 1, 4.5 mbar). For the plot with the total pressure of 0.6 mbar the silane flow rate was equal to 25 sccm and the oxygen flow rate was equal to 50 sccm, while for the plots corresponding to both the total pressure of 1 mbar and 4.5 mbar. the flow rates of silane and oxygen were of 10 sccm and 20 sccm, respectively. From Fig. 1, it is obtained that a threshold partial pressure of silane can be defined for each total pressure used and its value is two times lower (from 0.15 mbar to 0.076 mbar) for an about eight times increase of the total pressure (from 0.6 to 4.5 mbar).

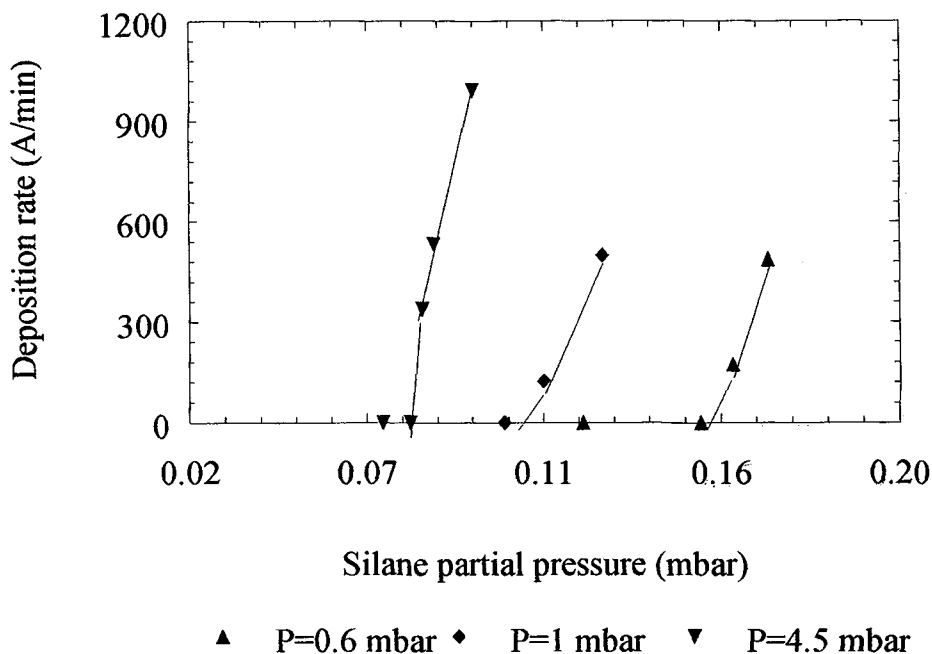


Fig. 1 Deposition rate as function of partial pressure of silane with total pressure as a parameter (0.6, 1 and 4.5 mbar)
Deposition temperature is equal to 450 °C. The oxygen/silane mole ratio is equal to 2.

In Fig. 2, the averaged deposition rate is plotted as a function of the O_2/SiH_4 mole ratio by keeping constant the total gas flow rate (consisting of the sum of flow rates of silane, oxygen and nitrogen) at 570

sccm, the total pressure at 4.5 mbar, the partial pressure of silane at 0.079 mbar (very slightly above the threshold value at that total pressure, according to the Fig. 1) and compensating the oxygen flow rate increase by the nitrogen flow decrease in order to hold constant the above mentioned parameters.

Similar to other results reported for cold wall RTLPCVD systems [5], hot wall LPCVD systems [8], or cold wall atmospheric pressure CVD systems, an increase-maximum-decrease type of dependence is obtained. However, in this case, a slower decrease of the deposition rate at higher O_2/SiH_4 mole ratios is obtained. In fact, the shape of the maximum deposition rate region is very specific to each deposition system. Very interestingly, the thickness uniformity of the SiO_2 films (evaluated by the automatic mapping with the PLASMOS ellipsometer) was quite sensitive to the changes in the O_2/SiH_4 mole ratios. At an O_2/SiH_4 mole ratio equal to 11, the best thickness uniformity, in the range of 5% (around the average value) was obtained if we considered the thickness mapping all over the wafer excepting 5 mm near the wafer edge. Unexpectedly, at O_2/SiH_4 mole ratios higher than 11 the film thickness was lower in the middle of the wafer with respect to edges, revealing a "volcano" thickness profile.

Finally, for the total pressure of 4.5 mbar and the O_2/SiH_4 mole ratio of 2/1 it was checked that the film deposition rate was constant as a function of deposition time in the whole range of deposition time intervals indicating the absence of any incubation time before the film deposition starts.

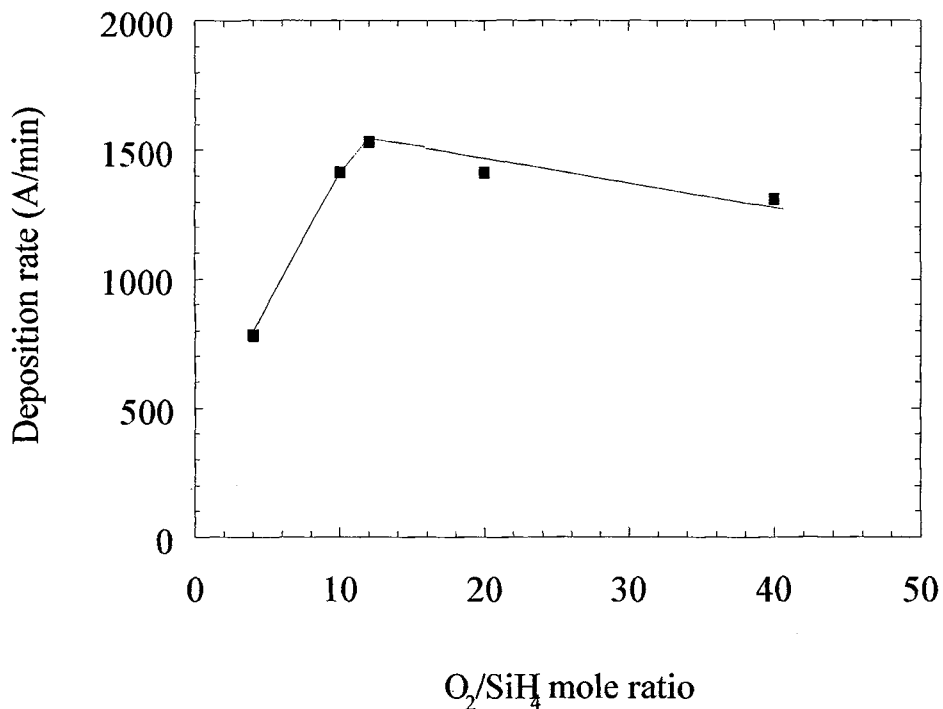


Fig. 2. Deposition rate as a function of the O_2/SiH_4 mole ratio with the following CVD parameters kept constant: Total pressure=4.5 mbar, Total flow rate=570 sccm, Silane partial pressure=0.079 mbar, Deposition temperature=450 °C.

3.3 Experimental observations

During the period of performing the above experiments, different observations have been made as follows.

First, a SiO_2 layer was always formed also on the back of the wafer. The deposition rate on the back of the wafer was about 8% of the deposition rate on the front.

Second, by repeating the same experiments ($P_t=0.4$ mbar, $F_{\text{SiH}_4}=25$ sccm, $F_{\text{O}_2}=50$ sccm) in different days, the deposition rate varied from zero to 50 nm/min.

Third, at a total pressure of 0.56 mbar, $F_{\text{O}_2}=50$ sccm, $F_{\text{SiH}_4}=25$ sccm, a critical silane partial pressure of 0.187 mbar assigned to lower explosion limit (LEL) at 450 °C was noticed being revealed by total pressure variations during deposition.

Fourth, at a total pressure of 0.67 mbar and the same silane and oxygen flows as above, a critical partial pressure of silane of 0.223 mbar corresponding to lower explosion limit (LEL) at room temperature was detected before the lamp was switched on. In this case, in the dark reaction chamber intermittent flames were seen being accompanied by some noises and pressure variations. We consider that this explosion was even more violent than the other one taking place at the deposition temperature.

4. DISCUSSION

The experimental results presented above represent a good starting point for the identification of the CVD conditions that determine SiO_2 film formation from silane and oxygen reaction at 450 °C in a rapid thermal multiprocessing reactor and in same time these data can offer an indication for the reaction mechanism in an open system, cold wall rapid thermal multiprocessing reactor. Unfortunately, at this time as a result of Fig. 1, Fig. 2 and the thickness uniformity evaluation, a very narrow window of CVD conditions for uniform layer deposition has been found ($P_t=4.5$ mbar, $p_{\text{SiH}_4}=0.079$ mbar, $F_{\text{O}_2}=110$ sccm, $F_{\text{SiH}_4}=10$ sccm). The deposition rate corresponding to these CVD conditions was about 130 nm/min with, for a thickness uniformity of 5% on the whole wafer excepting an wafer edge of 5mm.

As shown earlier, the partial pressure of SiH_4 controls the kinetics of SiO_2 film formation. A further argument for this would be that, according to the Fig. 1, the deposition rate variation as a function of partial pressure variation is practically the same at all the total pressures used. The decrease of the threshold SiH_4 partial pressure (determining the SiO_2 film deposition process) while the total pressure is increased and nitrogen is injected during deposition can be connected with the results reported by Emeleus and Stewart [6] where the decrease of the critical SiH_4 partial pressure for explosion at the lower limit is noticed when the nitrogen is present in the reaction chamber. These both results can be explained according to the ref. [6] in terms of branching chain reactions at low pressure where the walls control the reaction kinetics. Poor repeatability of the deposition rate after reactor chamber exposure to room ambient or after longer stand-by periods described above may further suggest that the chemical state of the wall surface affects the deposition kinetics. Therefore, we can consider that the decrease of the threshold partial pressure of silane, in Fig.1 is due to the nitrogen which acts as a "screen" preventing the chain breaking at the walls. Thus, the condition specific to explosion (or film formation in our case) which states that the rate of chain generation is greater (or equal) than the rate of chain breaking is fulfilled even at further decreased SiH_4 partial pressures. It is not the purpose of this paper to present a detailed scheme of the branching chain reactions determining the intermediates responsible for SiO_2 film formation. In fact, in the absence of gas phase composition analysis performed by *in-situ* spectroscopy during deposition process one cannot obtain enough experimental support for the reaction mechanism. So, in agreement with more recent papers [5, 8, 9] studying the SiO_2 deposition kinetics in LPCVD systems with cold wall [5] or hot wall [8,9] one can accept that chain reactions in the gas phase generate one [9] or more intermediates [5] for SiO_2 films, being possible that the final reaction to take place on the film surface. The fact that the ratio between the SiO_2 deposition rate on the back of the wafer and on the front of the wafer (equal to 8%) is approximately equal to the ratio between the volume of the reaction chamber below the wafer and the corresponding volume above the wafer (equal to 10%) can support a gas phase mechanism where the amount of gas phase intermediates is proportional with the volume available for their generation.

Such a sharp transition (see Fig. 1) from zero deposition rate to high deposition was not reported in the work [5] for their type of RTP reactor. We consider that the difference in the experimental results may arise from the fact that a mesh above the wafer was used in their reactor which mainly contributed to the chain breaking and thus limiting the "explosive" character of the reaction. Moreover, may be a warm wall above the wafer was created at longer deposition times, making thus the deposition kinetics milder and much more similar to the LPCVD hot wall reactors [8].

In fact, in an earlier paper [8], it has been also suggested a chain mechanism for LPCVD of SiO_2 films based on an experimental observation where an intense SiO_2 powder formation occurred at a certain O_2/SiH_4 mole ratio and this ratio increased with deposition temperature increase.

Another specific aspect of our experimental results was the detection of the critical SiH_4 partial pressure corresponding to the lower explosion limit (LEL) at the deposition temperature (0.187 mbar) and at the room temperature (0.223 mbar), both of them being higher than the threshold SiH_4 partial pressure. It is believed that near the threshold conditions the chain generation rate is balanced by the chain breaking rate and thus only the film formation takes place, while at the two critical pressures the explosion appears because the chain generation is much higher than their deactivation by the wall breaking process.

The fact that at the room temperature the critical SiH_4 partial pressure for LEL (0.223 mbar) was higher than the corresponding one at the deposition temperature (0.187 mbar) which is opposite to the results of Emeleus and Stewart for monosilane [6] may be explained by the specific geometry of our RTLPCVD reactor and by the presence of the cold walls in this case even at the deposition temperature.

At this moment one cannot explain within the chain reaction mechanism suggested for the SiO_2 film formation the increase-maximum-decrease dependence of the deposition rate on the O_2/SiH_4 mole ratio at a constant partial pressure of silane (Fig. 2). However, the dependence of the thickness uniformity on this ratio may indicate that the spatial distribution of the SiO_2 intermediates generating the film can be changed as a function of the O_2/SiH_4 mole ratio.

As we mentioned earlier, our initial motivation for this research was to obtain low temperature CVD gate oxides by using a rapid thermal multiprocessing reactor.

These experimental results have shown us that further improvements to the process and especially to the equipment should be taken into account in order to develop a safer process and with a lower level of contamination due to the SiO_2 powder generation on the reactor walls.

5. CONCLUSIONS

The kinetics of SiO_2 films preparation from silane and oxygen at 450 °C in a cold wall rapid thermal multiprocessing reactor is mainly controlled by a threshold partial pressure of silane which determines a sharp transition from no film formation to a high deposition rate.

This threshold partial pressure has a slight decrease as the total pressure is increased. The critical SiH_4 partial pressures for lower explosion limits (LEL) were detected experimentally (microexplosions and flames visualised in the reactor chamber at the room temperature (0.223 mbar) and the deposition temperature (0.187 mbar).

The repeatability of the deposition process is poor after reactor chamber exposure to room ambient. These results can be qualitatively explained in terms of branching chain reactions at low pressures where the chemical state of the reactor walls determines the rate of chain breaking (deactivation).

At a constant partial pressure of silane, the deposition rate presents an increase-maximum-decrease dependence on the O_2/SiH_4 mole ratio that cannot be explained at this moment by the above mechanism.

The thickness uniformity is quite sensitive to this ratio and an optimum value equal to 11 was found to give a good film uniformity of about 5% on the whole 3 " wafer excepting an wafer edge of 5 mm.

For the existing configuration of the RTLPCVD reactor where no specific wafer cages and other design elements specific to silane-based systems were considered this process cannot be used as it is due to the reproducibility aspects and even the safety precautions.

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