Process characterization for LPCVD TEOS-ozone based SiO₂ films

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ABSTRACT

Process characterization of 400 nm thick LPCVD-SiO₂ films based on TEOS-Ozone chemistry was performed. Films were deposited on six inch silicon wafers using a single wafer cluster system. The process characterization was carried out starting from a standard process taken as reference, around which the main process parameters, temperature (300-430°C), pressure (50-80 torr), and gas ratio (3:1-7:1), were varied one at a time whilst keeping the remainder fixed. The effect of process parameters on deposition rate, thickness uniformity within wafer, film stress, etch rate and refractive index was investigated. On the basis of these results the optimum working conditions for the industrial implementation of the process were determined and proven for sidewall spacer formation and 1Mbit EPROM devices. An interpretation of the data of deposition rate is provided in terms of the elementary processes involved.

1. INTRODUCTION

Silicon oxide films, deposited from tetraethoxysilane (TEOS) liquid precursor using a plasma enhanced chemical vapor deposition (PECVD) technique, are widely used in the manufacture of very large scale integrated (VLSI) electronic devices, such as LOGICs and non volatile memories utilizing multilevel metallization. These films are usually employed in combination with spun, cured and sacrificial spin on glass (SOG) layer to get good interlevel dielectric (ILD) planarization. ILD film main requirements are: i) conformal step coverage; ii) low temperature growth to avoid hillocks formation on the underlying aluminum lines; iii) proper electrical insulation both intermetal and intra-metal (low dielectric constant, low defect density, etc.).

In the last few years there was an increase of interest in TEOS and ozone (O₃) based oxides deposited with atmospheric [1,2], sub-atmospheric [3,4], and low pressure [5,6] chemical vapor deposition techniques, whose typical working pressures are 760 (1atm), 600 and 60 torr respectively. Indeed, their high conformal step coverage properties allow void-free filling of high aspect ratio trenches between metal strips and development of new planarization methods (integrated, with oxide deposition and subsequent etch back, in situ [7] or using multichamber tools [8], mechanical polishing, and self-planarizing).

The main shortcoming of thermal TEOS-O₃ oxide is its low film quality, due to its low density, low moisture resistance, high dielectric constant (around 5, depending on the process conditions), weak cracking resistance, when it is directly deposited on metal lines, due to its high tensile stress.

Nevertheless, TEOS-O₃ oxide can be used for sidewall spacer formation process, and also as intermetal dielectric used in combination with two PECVD-TEOS based oxides.

Sub atmospheric and atmospheric pressure CVD techniques are also used to deposit boron and phosphorus doped TEOS-O₃ films (BPSG) with better (as deposited) step coverage properties than those obtained with similar layers based on silane chemistry. The most utilized liquid source precursors for boron and phosphorus doping are trimethylborate (TMB) and trimethylphosphite (TMPi) respectively.

This paper is concerned with the general process characterization (deposition rate and thickness uniformity across the wafer) of a Low Pressure CVD technique.

Furthermore, data concerning the main film properties, i.e. refractive index, stress, density, and wet etch rate are also reported. From this evaluation it was possible to define the process window to obtain proper TEOS-O₃ oxide film that had been tested in sidewall spacer formation.

In addition, deposition rate data have been analyzed on the basis of a qualitative modelling of the deposition kinetics.

2. EXPERIMENTAL

P-type, 150 mm diameter, 675 μm thick, [100] oriented Czocharalski silicon wafers, with 16-24 Ωcm resistivity were used as substrate for film depositions. All the oxide layers were deposited in a single wafer, multichamber cluster system; detailed information about the system configuration are provided in references [8, 10]. The deposition chamber has a parallel plate configuration and the silicon wafer was lying face up under the shower head from which TEOS vapor, O₂ and O₃ gas flow comes out. The wafer, situated on the wafer holder back heated by halogen lamps, was maintained fixed at 0.74 cm below the shower head. TEOS vapor was delivered by He bubbling in an ampulla kept at the constant temperature of 42 °C ($\pm 0.5^\circ\text{C}$), situated in a thermostatic on-board cabinet. The O₃ concentration coming from the ozonator cells was nominally 8 % in O₂. The helium flow rate, to get the desired recipe TEOS flow set point, was found depending on the (O₂+O₃)/TEOS ratio and process chamber pressure, but no temperature dependence was observed. This dependence is due to the back pressure from the deposition chamber to the bubbler [6].

All the analyses were performed on as deposited 400 nm thick films.

Process conditions for their deposition are reported in Table 1. Gas ratio (R), temperature and pressure deposition parameters were varied one at a time keeping the others fixed. (O₂+O₃)/TEOS gas ratio R was varied only from 3:1 to 7:1. Higher gas ratios (e.g. > 20:1) were not evaluated, although the films obtained in these conditions, using atmospheric and sub atmospheric pressure CVD techniques, reveal better film properties [4]. Using the low pressure CVD tool utilized for this work a too low deposition rate is obtained for such R values. Furthermore, assuming that the in situ plasma cleaning of the process chamber has roughly the same duration as the deposition time, serious problems of hardware degradation can occur due to addition of the NF₃ gas in this cleaning.

These two findings lead to an unacceptable low process throughput, incompatible with industrial application.

Temperature set point was changed from 300 to 430 °C (effective wafer temperature is around 30 °C less) and pressure was varied from 50 to 80 torr.

Thickness uniformity and refractive index were measured on 4000 Å thick film by a Gaertner ellipsometer at 632.8 nm wavelength, with ± 0.005 instrumental accuracy.

The film density was measured by weighing the wafer before and after deposition.

The wafer bow was measured by Tropel Autosort Mark II laser flatness tester and the stress calculated with the standard formula [9].

Wet etch rate measurements were performed in 10:1 D.I. water diluted HF (40%) solution at room temperature.

3. DEPOSITION RATE: RESULTS AND DISCUSSION

Details on mechanism of SiO_2 film deposition from TEOS-ozone chemistry are still unknown, but it is commonly assumed that in this case the depositing species are silicon oxides and hydroxides, as obtained by the partial oxidation of the TEOS molecule and that they are then subject to surface migration and hydrogen release processes. The gas phase reactions between TEOS and ozone or oxygen are characterized by a much larger activation energy with respect to the diffusion process of the products toward the film surface or their subsequent deposition so that they represent the limiting step for the overall process in the low temperature range where the deposition rate significantly increases with temperature (Fig.1). On the contrary, for higher value of the process temperature, the equilibrium is reached for the gas phase reactions and the deposition rate is determined by the velocity of the diffusion-adsorption processes. The latter are mainly influenced by the gas phase partial pressure of the products of TEOS oxidation which, on the other hand, varies with temperature and pressure as imposed by the equilibrium condition for the gas reactions. Because of the exothermic nature of the oxidation reactions, an increase of temperature corresponds to a decrease of equilibrium concentration of the products thus resulting in a reduction of the overall velocity of the process.

A maximum value is then observed for the deposition rate as function of the process temperature; the value of the temperature corresponding to the maximum deposition rate changes according to the process conditions, and in particular to the value of the pressure. All data reported in Fig.1 refers to 60 torr and the maximum deposition rate is reached at 390 °C. The maximum deposition rate is obtained for higher value of the temperature if lower reactor pressures are considered, as reported, for example, by Nguyen et al.[10]. Correspondingly for atmospheric pressure reactors, where similar trend is observed for the temperature dependence of the deposition rate, the maximum value is found for much lower temperatures [11].

Those data indicate that a pressure increase produces different effects on the velocity of the limiting steps governing the deposition rate in the higher and lower temperature range. In particular an increase of the reactor pressure results in a larger increase of the deposition rate at lower temperatures.

That can be understood in terms of the above mentioned hypothesis on the limiting steps. Indeed in the high temperatures range, where the equilibrium for the TEOS oxidation reaction is attained, the

obvious increase in the product concentration due to the pressure increment is reduced because the pressure itself has a negative effect on the equilibrium molar fraction of the reaction products.

In view of the previous consideration, and remembering that the chosen standard temperature ($T=390^{\circ}\text{C}$) corresponds to a maximum value for the deposition rate on an isobaric curve at 60 torr one may argue that different limiting steps characterize the deposition process for lower and higher pressure at the same temperature.

Indeed, when the pressure decreases below 60 torr the deposition rate decreases according to the velocity of the reactions of TEOS oxidation. On the other hand, when the pressure increases above 60 torr the deposition rate increases according to the velocity of the adsorption of the silicon oxides on the film surface.

On the basis of the above reported analysis, at the constant temperature of 390°C weaker variations of the deposition rate are expected as function of reactor pressure in the range above 60 torr with respect to the lower one. Experimental data, reported in Fig.2, confirm that expectation.

The influence of the oxidants/TEOS feed ratio on the deposition rate was finally considered, as obtained by varying the flow of TEOS while keeping constant the flow of $\text{O}_3 + \text{O}_2$ mixture. The results, reported in Fig.3, indicate that an increase of the deposition rate is obtained when the TEOS flux increases so that the $(\text{O}_3 + \text{O}_2)/\text{TEOS}$ ratio decreases from 7:1 to 3:1. Remembering that, for the temperature and pressure conditions used, the equilibrium of the oxidation reactions is reached, it can be concluded from the data in Fig.3 that for the standard case ($R = 5:1$) TEOS results to be the limiting reactant. That means that the average stoichiometric ratio oxidant/TEOS in the reactions actually taking place in this case is lower than 5:1, corresponding to only a partial oxidation of the TEOS molecules as is widely assumed in the literature [10].

4. FILM PROPERTIES: RESULTS AND DISCUSSION

Table 1 reports the obtained values for within wafer thickness uniformity, refractive index, stress, and etch rate measurements.

Thickness uniformity was calculated with the standard formula: $Th_{unif} = (Th_{max} - Th_{min}) / (2 Th_{av})$ and was found in the range from 2.4 % to 3.5 %, the best case corresponding to samples obtained for the run conditions n°6 in table 1, while the worst corresponds to sample obtained for the run conditions n°3 in the same table.

Refractive index is mainly affected by gas ratio variations; indeed it varies linearly from 1.448 to 1.454 in the range of 3:1 to 7:1 R values.

Density values obtained for as-deposited films lie in the range of 2 to 2.1 g/cm³. These data are in good agreement with those reported in the literature [4], but the variations in density values are within the experimental error so that no significant influence of the process parameters on the value of the film density has been revealed.

All the deposited films show a tensile stress in the order of magnitude of 10⁸ dyne/cm², in agreement with data reported in the literature [6]. The set of stress values concerning gas ratio variations was collected for as-deposited films measured immediately after the deposition and a clear trend of stress increasing with gas ratio can be observed. On the other hand, the data for temperature and pressure variations were collected after a few days of storage in a clean room environment. The values are clearly influenced by the stress release due to the moisture absorption.

The etch rate variation of TEOS films with temperature and gas ratio are similar; in both cases the etch rate decreases with an increase of the process parameter and the etch rate values range from 210 to 270 nm/min. On the other hand, the effect of pressure variation is both less evident and restricted to a narrower range.

Table 1. Film properties as function of the process conditions.

RUN	R	TEOS flux (sccm)	P (torr)	T (°C)	Th _{unif} (%)	R.I.	Tensile Stress (10 ⁸ dyne/cm ²)	Wet E.R. (nm/min)
1	5:1	530	60	390	3.3	1.451	4.8	231.3
2	3:1	883	60	390	2.7	1.448	4.0	269.4
3	7:1	371	60	390	3.5	1.454	5.4	217.2
4	5:1	530	60	365	2.6	1.448	1.4	270.6
5	5:1	530	60	415	3.1	1.452	0.4	212.4
6	5:1	530	50	390	2.4	1.449	0.4	232.8
7	5:1	530	70	390	3.0	1.452	1.3	210.9

5. DEVICE INTEGRATION

TEOS-O₃ films deposited in the conditions of run 1 (Table 1) were tested as sidewall spacer in 1 Mbit EPROM device cells (1 μ m technology). The complete spacer formation process, consisting of a 400 nm thick TEOS-O₃ film deposition followed by a blanket dry etch-back, was performed in sequence in the same cluster tool in two different process chambers. A run of 12 wafers was processed with the standard production flow and was split only at the sidewall spacer film deposition and etching step. Four wafers were used for comparison following the standard industrial flow and 8 wafers were run on an integrated process. The TEOS-O₃ film performances have been evaluated in terms of electrical wafer sort (EWS) yield on EPROM cells. Three EWS testing levels were used: the first one at the end of the device fabrication to write the cells, the second after a storage of 24 hours at 250 °C in N₂ environment (standard EWS testing), and the third after thermal treatment at 430 °C in N₂ for 15 min (belt test). The last EWS step was performed to simulate the thermal budget of the ceramic packaging operations and to find out eventual contamination (charge loss) through the TEOS-O₃ spacers. Both the reference and the integrated processes had a comparable 2nd EWS yield (>68%), but after 3rd EWS testing the devices processed with the integrated process showed an electrical yield improvement of 10 %. This can be attributed to the fact that the devices manufactured with TEOS-O₃ oxide spacers were not exposed to the air between TEOS-O₃ oxide film deposition and subsequent blanket oxide etch, reducing the particulate contamination. Reliability tests, which are necessary to obtain a complete validation before industrial applications, were not performed on these devices.

6. CONCLUSIONS

The characterization of a Low Pressure CVD process for the deposition of SiO₂ films from TEOS-Ozone system in a single wafer reactor has been performed. The effects of temperature, pressure, (O₂+O₃)/TEOS ratio in the inlet gas stream on the deposition rate and several film properties were analyzed. A single parameter was varied each time keeping the other fixed to the values of the "standard process" [T = 390°C, p = 60 torr, (O₂+O₃)/TEOS = 5:1].

Experimental data show that the deposition rate uniformly increases with the reactor pressure and the TEOS inlet flux while for temperature variations a maximum value of the deposition rate is observed corresponding to the "standard" value of 390°C. That behavior is here explained assuming that equilibrium conditions are attained in the gas phase with respect to the oxidation of TEOS molecules for high values of the temperature. The same hypothesis can help to understand the different sensitivity shown by the deposition rate to the pressure variations above and below the value of 60 torr.

With regard to the film properties, the refractive index is mainly influenced by the value of the ratio between TEOS and oxidants species in the inlet gas while no appreciable differences were found for the density of the film as obtained in the various conditions considered in this work. Also thickness uniformity within wafer varies in a narrow range from a lower limit of 2.4% to an upper limit of 3.5% according to the values of the process parameters. Stress data indicates relatively low tensile values for the film deposited in all cases and the etch rate decreases when either the reactor temperature or $(\text{O}_2+\text{O}_3)/\text{TEOS}$ ratio in the inlet gas increase.

TEOS-Ozone oxide films obtained in the process conditions of run 1 were tested as sidewall spacers for 1 Mbit EPROM devices, providing electrical yield results similar to those achieved with the standard flow.

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