A comparative study of O_2/SiH_4 and N_2O/SiH_4 mixtures for SiO_2 deposition in a microwave afterglow

H. DEL PUPPO, J. DESMAISON and L. PECCOUD*

Laboratoire des Matériaux Céramiques et Traitements de Surfaces, CNRS URA 320, 123 avenue Albert Thomas, 87060 Limoges cedex, France

* CENG/DLETI, 85X, 38041 Grenoble cedex, France

ABSTRACT: Silicon dioxide films have been deposited in a microwave afterglow from N_2O/SiH_4 and O_2/SiH_4 mixtures. The effect of the pressure and of the substrate to silane injector distance is investigated, and leads to conclude that the growth mechanism is diffusion limited. In complement to previous studies, the composition of films, obtained at several temperatures and oxidant flow rates, is determined. The gas nature has a low influence on stoichiometry ($O/Si \sim 2$ whatever the conditions are) but has an effect on the impurity content. Indeed, when N_2O is used, nitrogen is incorporated but, at high temperature, the hydrogen content of the films is lower than for those made from O_2 . The impurities are thought to come from uneasily desorbed byproducts.

1 - INTRODUCTION

Silicon dioxide films are widely used in silicon based integrated circuits. Applications such as passivation or insulation require low deposition temperatures ($<450^\circ C$) and also high deposition rates to achieve a suitable throughput in single wafer multichamber systems.

Among the plasma enhanced chemical vapour deposition (PECVD) techniques, those using a microwave excitation provide an elevated electron density useful to obtain high growth rates [1-3].

In a previous paper [4], the microwave downstream deposition of SiO_2 from O_2/SiH_4 and N_2O/SiH_4 mixtures, leading to high deposition rates, was reported. In this technique, the substrate is placed outside the discharge and thus it is not ion bombarded. The results have shown that the deposition temperature and the oxidant gas flow were the two main parameters whereas the silane flow had only an influence on the growth rate. Consequently, for a silane flow of 30 sccm, dense layers could be grown at $300^\circ C$ providing the oxidant flow was greater than 450 sccm. However, the film thickness uniformity was perfectible. As far as the oxidant nature is concerned, no major differences of properties (wet etch rate, refractive index...) have been noticed.

This paper reports on comparative composition analysis of films obtained from O_2 and N_2O . In addition, the effect of two process parameters (pressure and silane injector to substrate distance) is studied in order to improve thickness uniformity. Finally, the growth mechanism is discussed.

2 - EXPERIMENTAL

The reactor has been described elsewhere [4]. The oxidant gas is decomposed in a microwave discharge (surfaguide) while the silane is introduced downstream. The ions are trapped by a grid located at the entrance of the deposition chamber. Therefore, only neutral species are allowed to reach the deposition region.

The substrates used in this study are 4 in. p type Si (100) wafers and 2 in. AsGa wafers. A step is made by etching the layers in a NH_4F/HF solution (1/30). Then the film thickness is measured by profilometry on 10 points of the wafer. Uniformity and wet etch rate are deduced from these measurements.

Chemical bonds present in the films have been characterized by Fourier Transform Infrared spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS). The composition of the layers was obtained by Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA) and the determination of the hydrogen content was performed by Elastic Recoil Detection Analysis (ERDA).

3 - RESULTS

Effect of the pressure and of the silane injector to substrate distance on the deposition uniformity

The downstream PECVD growth mechanisms are closed to those of thermal CVD since no ion bombardment exists. If the deposition is diffusion limited, the pressure and the silane injector to substrate distance (d) will have an effect on the thickness uniformity.

The pressure influence has been investigated from 20 to 600 mTorr for various oxidant to silane ratios (R). The mass weight gain rate ($\Delta m/\Delta t$) increases linearly up to 250 mTorr and then decreases because of gas phase nucleation (Fig.1). At the same time, the thickness uniformity is degraded as shown in Fig. 2. Decreasing the growth rate (i.e. pressure) should lead to a better build up of the oxide network and thus to a lower wet etch rate. In fact, as represented in Fig. 3, the wet etch rate remains constant from 200 to 70 mTorr and then increases with further pressure diminution except for high N_2O to silane ratios. This trend is confirmed by the wet etch rate evolution as a function of the oxidant flow rate at 200 and ~30 mTorr (Fig. 4). Except for N_2O , above 150 sccm, the layers are etched more rapidly at low pressure than at 200 mTorr. So a good film quality together with a satisfactory uniformity cannot be achieved at the same time.

We have tried to overcome this difficulty by varying the silane injector to substrate distance d . As d decreases, the thickness profile over a 4 in. Si wafer changes (Fig. 5). The profile symmetry is circular and when d decreases, there is less deposition in the center of the wafer than on the sides. The best thickness uniformity (5%) is obtained for $d = 2.7$ cm.

Figure 1 : Weight gain rate versus total pressure for several oxidant to silane ratios, 270°C - 300 W.

Figure 2 : Thickness uniformity (%) versus pressure, 300°C - Oxidant/Silane = 600/30.

Figure 3 : Relative etch rate (film wet etch rate/thermal oxide wet etch rate) versus total pressure for various oxidant/silane ratios, 270°C - 300 W.

Figure 4 : Relative etch rate versus oxidant flow for high and low pressures, 270°C - 300 W.

Figure 5 : Film thickness profil versus silane injector to substrate distance,
 $\text{N}_2\text{O}/\text{SiH}_4=300/70$ - 200°C - 300 W.

Film composition

In a previous study [4], the two main parameters of this system were found to be the temperature and the oxidant flow. Their influence on the composition of layers obtained at 200 mTorr from O_2 and N_2O has been determined and the results are reported in tables 1 and 2.

Gas	T ($^\circ\text{C}$)	Ox/SiH_4	O/Si XPS	O/Si NRA	%N NRA	IR	%H ERDA
N_2O	300	60/30	1,5	2,06	0,8	SiOH, SiH, H_2O	11%
		300/30	2,3	2,08	0,6	SiOH, H_2O	17%
		450/30	2,3	2,2	0,7	SiOH, H_2O	11%
		600/30	2,4	2,18*	--	SiOH	8%
O_2	300	30/30	1,8	2,05	--	SiOH, H_2O , SiH	12%
		300/30	2,3	2,02	--	SiOH, H_2O	12%
		450/30	2,3	2,09	--	SiOH, H_2O	0
		600/30	2,5	2,11*	--	SiOH	8%

Accuracy of the value of O/Si : RBS $\pm 0,05$, NRA $\pm 0,14$, XPS $\pm 0,2$.
(O/Si obtained by NRA except * O/Si obtained by RBS).

Tableau 1 : Composition of films = f (D_{oxidant}) : 200 mtorr - 300°C .

Gas	T (°C)	Ox/SiH ₄	O/Si XPS	O/Si RBS	%N NRA	IR	%H ERDA
N ₂ O	450	60/30		2,13	0,1	SiOH, SiH	6%
		300/30		2,05	0,13	SiOH	4,5%
		450/30		2,00	0,07	SiOH	3,5%
		600/30	2,2	2,01	--	--	3,5%
O ₂	450	30/30		2,05	--	SiOH, SiH	7%
		300/30		2,11	--	SiOH	8%
		450/30		2,11	--	SiOH	7%
		600/30	2,2	2,12	--	--	7%

Tableau 2 : Composition of films = f (D_{oxidant}) : 200 mtorr - 450°C.

The use of N₂O as an oxidant gas introduces nitrogen in the films. The N content decreases with temperature, increases with silane flow (i.e. deposition rate) but is independent of N₂O flow below 450 sccm. As already reported nitrogen is mostly unbonded to silicon (XPS analysis).

The hydrogen content decreases with the deposition temperature. This is in agreement with the disappearance of the water peak on IR spectra (i.e. densification). Dense films grown at 450°C from N₂O have less hydrogen (4%) than those grown from O₂ (7%). One can also notice that, at 450°C for an oxidant flow above 600 sccm and in the absence of hydrogen IR related peaks (Si-H, Si-OH), this element is still detected by ERDA. Thus it is incorporated in a non polar form (i.e. H₂, H).

The O/Si ratio is nearly 2 and seems to be independent of the oxidant to silane ratio. Only small differences exist between films grown from O₂ and N₂O. At 450°C, when the oxidant flow increases, the Si-OH bonds disappear from the IR spectra. In the case of N₂O, it is accompanied by a slight decrease of O/Si while the opposite situation occurs with O₂.

4 - DISCUSSION

The variation of the thickness profile with pressure and d shows that the growth is diffusion limited. However, since both the silane and the oxidant injectors were circular, we were unable to determine which of the reactant diffusion is the limiting step. The silane injection symmetry was thus changed to rectangular and it was found that the thickness profile was still circular. So the diffusion rate determining specie should be related to the oxidant.

In fact, as far as the SiO₂ deposition from SiH₄ in an afterglow is concerned, two main growth mechanisms have been proposed. Through gas phase analysis (emission and mass spectroscopies), Lucovsky and al [5] have seen no evidence of silane dissociation so they concluded that SiO₂ is formed from the reaction of silane with metastable molecular oxygen. On the contrary, Horie and al [6] have shown that silane can be decomposed by atomic oxygen to form SiH_x radicals or silanols (SiOH_x). Since O atoms are present in the O₂ and N₂O afterglow [7-10], silane can be dissociated in the gas phase and the reactive species might not only be SiH₄. The adsorption of silane on a Si (100) surface has been studied by Gates [11]. The sticking coefficient (number of adsorbed SiH₄/number of impinging SiH₄) which was 10⁻⁵ on a clean surface decreased when the rate coverage increased. In our case, if all the introduced SiH₄ molecules were impinging on the substrate (i.e. 8.10²⁰ /min for 30 sccm at 200 mTorr) and if the sticking coefficient was maximum (10⁻⁵) the weight gain should be 42.10⁻⁸ mg/min while the experimental one was far bigger (10 mg/min). Thus adsorbed SiH₄ cannot be responsible for the growth rate and the reactive specie should be a radical or a silanol. Furthermore, in a O₂ discharge the atomic oxygen amount decreases when the residence time decreases [7-9] (i.e. pressure at constant gas flow). As the film density and structure are not changed when P decreases, O atoms should have a small importance on the growth mechanism.

This study, in accordance with the previous one [4], has revealed that the evolution of the film properties with the deposition parameters were similar whether O₂ or N₂O was used. In fact, this is not surprising since the oxidant species present in the afterglow are the same for both gases [7-10]. Therefore, the deposition mechanism is not very different from one gas to another. However, the use of N₂O leads to the incorporation of nitrogen in the layers which is for the most part under a chimisorbed form. It was shown [12-13] that the SiN formation in a N₂ afterglow results only from a reaction

between SiH_4 and atomic nitrogen N. Since N is rare in a N_2O downstream because of its quick recombination with NO, only few SiN bonds are present. When the deposition is done directly in the plasma, more nitrogen is incorporated and when R increases the film composition changes from silicon oxynitride to silicon dioxide [14-15]. The constant O/Si value (~ 2), over a wide parameters range and especially with the oxidant to silane flow ratio (R), is in contradiction with the results of several authors. Usually the O/Si ratio is found to depend strongly on R and values from 1.5 to 2 can be achieved [15]. The fact that nitrogen is chemisorbed and that hydrogen is still detected, although there is no IR related peak, leads us to conclude that these incorporations could come from the trapping of byproducts in the layer during the growth. And since the nitrogen content decreases with temperature and increases with the silane flow (i.e. deposition rate), it might come from an uneasy desorption.

5 - CONCLUSION

Previously, we have shown [4] that the influence of temperature and reactant flow on the film properties (wet etch rate, refractive index...) was the same for both oxidant gases (O_2 or N_2O). This behavior is confirmed by the present composition analysis. The O/Si value is ~ 2 over a wide range of parameters whatever the oxidant gas is. The slight composition differences seem to be related to the nature of the reaction byproducts rather than to a change in the growth mechanism. In the present study, the influence of the pressure was investigated. This parameter, through the oxidant species nature, seems to have an influence on the deposition mechanism. For example, with N_2O , decreasing the pressure leads to an improvement of the film density whereas it is not the case with O_2 .

The growth rate is diffusion limited and silane is certainly decomposed in the afterglow. Thus, especially in the case of O_2 , the thickness uniformity improvement should need a new gas injection design since it cannot be done by lowering the pressure.

At this point of the work, the choice of the oxidant gas (O_2 or N_2O) is not yet possible as no great differences in the characteristics of the films are observed. However, in a paper to be published, it will be shown that the electrical properties of the films are highly dependent on the nature of the oxydant gas.

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