DOWNSTREAM MICROWAVE PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION OF SiO_2 USING O_2/SiH_4 AND $\text{N}_2\text{O}/\text{SiH}_4$ MIXTURES

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Abstract - The deposition of silicon dioxide by downstream microwave plasma-enhanced chemical vapor deposition (PECVD) has been investigated. A comparative study of the properties of oxide layers deposited at a pressure of 200 mtorr with two different oxidizing gases (N_2O or O_2) is reported. Particular emphasis is given to the influence of the substrate temperature and reactive gas ratio $R = \text{oxidant flow/silane flow}$ on the deposition rate, mechanical stress, refractive index and etch rate. The results show that the properties of silicon oxide films are dependent on temperature below 400°C . But for this temperature and a gas ratio $R=1$, films are roughly equivalent and independent of the nature of the oxidizing gas used. Indeed they exhibit similar refractive index (≈ 1.47), etch rate ($\approx \times 3$ current thermal oxide), 2.10^9 dynes/cm² tensile stress, Si-H and Si-OH bonding present in infrared spectra. Nevertheless, the growth rates are very different for O_2 and N_2O , 5 $\mu\text{m}/\text{min}$ and 1.5 $\mu\text{m}/\text{min}$ respectively, but significantly higher than those commonly achieved with classical PECVD methods. Moreover, it is shown that under appropriate process variable conditions, the deposited films are suitable for dielectric passivation applications.

1 - INTRODUCTION

Dielectrics are widely used in microelectronics for silicon integrated circuits, among them silicon dioxide takes an important place (i.e. gate insulator, intermetal dielectric, passivation layer in C-MOS technology). For these applications SiO_2 is often deposited, but high scale integration imposes a low temperature budget in order to minimize temperature related phenomena such as dopant redistribution and hillock formation in metals [1,2]. Plasma enhanced C.V.D. (PECVD) is particularly appropriate because the energy supply needed for deposition is not thermal.

Two PECVD methods can be distinguished : direct PECVD and remote PECVD. In the former, the substrate is placed in the discharge and is thus submitted to charged species bombardment and UV radiation. The plasma is generally created by RF excitation (13,56 MHz) but some authors use low frequency excitation [3,4] and even low frequency together with RF excitation [5]. In the latter method, excited species present in the discharge afterglow are used providing the following advantages : no ion or electron bombardment, no UV radiation, possibility of reactant selective excitation and thus reaction pathway simplification [6]. But, in this case, the use of RF frequency excitation leads to low deposition rates.

For a number of years, microwave frequency (2,45 GHz) has been used in plasma processing because high degrees of ionisation and high dissociation rates are achieved. The classification of microwave reactors is based on the pressure range

used : surfaguide, surfatron, cavity at high pressure (> 100 Torr), ECR, DECR at low pressure ($< 10^{-4}$ Torr). In the latter case, a magnetic field is coupled to microwave energy in order to achieve the electron cyclotron resonance (ECR). In low pressure reactors, the deposition rate is limited by gas flow while high pressure reactors allow high reactant flow and, together with the dissociation efficiency, lead to high deposition rates. However, these type of reactors have not been studied much yet [1,8,9].

Generally, silicon dioxide films are deposited from TEOS/O_2 [5,6,9], SiH_4/O_2 or $\text{SiH}_4/\text{N}_2\text{O}$ [1,3,4,8,10-13] diluted with He or Ar. In the present work, properties of silicon dioxide films, deposited in a high pressure microwave afterglow from $\text{SiH}_4/\text{N}_2\text{O}$ and SiH_4/O_2 mixtures without dilution, are studied.

2 - EXPERIMENTAL

The plasma reactor used in the present work is shown in Fig. 1.

Fig. 1 : The schematic drawing of the microwave downstream plasma reactor.

The microwave (2,45 GHz) power is coupled to the oxidizing gas (N_2O or O_2) that flows through a quartz tube crossing a rectangular wave guide. The generated plasma, sustained by a surface wave, expands along the quartz tube out of the wave guide region. A mobile short cut provides the impedance matching that minimizes the reflected power. In this study, the power is fixed at 300 W. The charged species are

eliminated by a grid placed at the entrance of the deposition chamber. Only neutral species are allowed to reach the deposition region. The rectangular wave guide is about 7 cm above the grid.

The silane is directly fed into the deposition chamber through a specifically designed injector which provides an homogenous division of the gas above the wafer. The samples are placed on a resistance heated hot plate associated with an automatic temperature regulator. The substrate temperature, monitored by a chromel-alumel thermocouple, can be varied in the range of 25°C to 500°C. The substrate holder and the chamber walls can be RF polarised (13.56 MHz). Thus, an in-situ cleaning of the reactor is achieved with a NF_3 reactive discharge.

Before deposition the chamber is evacuated with a turbomolecular pump to a pressure of 10^{-2} mtorr. The pressure during the deposition is set at 200 mtorr.

The substrates used in this work are 4 inch p type Si <100> wafers with a resistivity between 14 and 22 Ω .cm.

The refractive index of the deposited film are measured using a 6328 Angström wavelength ellipsometer. The thickness and homogeneity are obtained with a profilometer after a step being etched in the layers. The chemical structure of the oxide is studied using infrared (I.R.) and X ray photo-electron (XPS) spectroscopies. The film composition and density are obtained by nuclear reaction analysis (NRA).

The stress of the films is calculated from radius curvature measurements. Film texture is studied using a cross-sectionnal observation by scanning electron microscopy (SEM). Wet etch rates of the layers in a $\text{HF}/\text{NH}_4\text{F}$ 1/27 solution are also reported.

3 - EXPERIMENTAL RESULTS

3.1. Temperature effect

3.1.1. Oxide deposited from N_2O

The oxide deposition rates using $\text{SiH}_4/\text{N}_2\text{O}$ chemistry at various substrate temperatures for two $\text{SiH}_4/\text{N}_2\text{O}$ ratios are shown in Fig. 2. The gas flow rate conditions are 300 sccm of N_2O and 30 or 300 sccm of silane. Pressure is set at 200 mtorr and plasma power at 300 W.

The deposition rates (Fig. 2) decrease with temperature and reach a constant value (of 1.1 $\mu\text{m}/\text{min}$ and 0.8 $\mu\text{m}/\text{min}$ for a $\text{N}_2\text{O}/\text{silane}$ ratio of 300/300 and 300/30 respectively). In fact, for a given deposition time, the deposited mass of material remains constant as temperature increases. Therefore the film density increases as can be seen on SEM micrographs. At 300°C the film structure is columnar while at 450°C no texture is visible. The etch rate versus deposition temperature plot, represented in Fig. 2, also confirms this densification effect. As temperature increases the etch rate decreases down to a value 3 times higher than that characteristic of thermal oxide. This densification phenomenon also affects the refractive index. Below 350°C, the refractive index of the film varies between 1.3 and 1.5 from one point of the surface to another. Above 350°C, the index is stable all over the wafer (1.47 to 1.48).

I.R. spectra of films deposited between 25°C and 450°C and with a flow rate ratio $\text{N}_2\text{O}/\text{SiH}_4$ of 300/30 were obtained. In addition to the characteristic bands of SiO_2 (wagging 450 cm^{-1} , bending 810 cm^{-1} , stretching 1050 cm^{-1}) three other absorption bands are present : Si-OH (3650 and 930 cm^{-1}) and adsorbed water 3300-3400 cm^{-1} . The 3650 cm^{-1} band is due to Si-OH in which hydrogen is weakly bonded to a nearby oxygen atom /10/. The 930 cm^{-1} band is attributed to strongly hydrogen bonded silanols /13,14/ and Pliskin /13/ assumed that these Si-OH groups are formed by reaction of water with SiO_2 . This is in agreement in our case with the fact that the 930 cm^{-1} band is always present with the adsorbed water band (3300-3400 cm^{-1}).

When films are prepared at ambient temperature, the absorption due to water is important and the two silanols bands are present. With an increase in temperature the intensity of the adsorbed water band decreases and, above 300°C, the 3300-3400 cm^{-1} and 930 cm^{-1} bands are no longer present. The 3650 cm^{-1} band does not disappear indicating that weakly bonded silanols groups are probably incorporated during film

growth. Therefore, the I.R. behaviour with temperature can easily be explained by the densification of the layers : the more porous the film is, the more adsorbed water is present.

Stress of films are plotted as a function of temperature for two N_2O /silane ratios in Fig. 2. Strain is compressive and rises above $300^\circ C$ (for N_2O/SiH_4 300/30 = 3.10^9 dynes/cm² at $450^\circ C$).

3.1.2. Oxide deposited from O_2

For similar deposition conditions, when N_2O is replaced by O_2 , the same densification phenomenon occurs with increasing temperature. Thus the deposition rate and etch rate decrease and reach a constant value above $350^\circ C$. The maximum deposition rates are $0.75 \mu m/min$ and $5 \mu m/min$ for N_2O/SiH_4 ratios equal to 300/30 and 300/300 respectively. For these two N_2O to silane ratios, the etch rate is 3 times higher than that of thermal oxide (Fig. 3). For $T > 300^\circ C$ the layer structure is no longer columnar, the refractive index becomes stable all over the wafer with values close to 1.46 - 1.47, adsorbed water and strongly bonded silanols disappear in I.R. spectra. Above $200^\circ C$ the compressive stress increases. At $450^\circ C$ the stress value is 4.10^9 dynes/cm².

Fig. 2 : Film properties versus deposition temperature for two SiH_4/N_2O ratios, 200 mtorr, 300 W.

Fig. 3 : Film properties versus deposition temperature for two SiH_4/O_2 ratios, 200 mtorr, 300 W.

3.2. Reactant flow effect

3.2.1. Silane flow

The variation of deposition rate, etch rate and refractive index versus silane flow for a constant oxidant flow (300 sccm) and two temperatures are presented in figs. 4 and 5 for N_2O and O_2 respectively.

With O_2 , the deposition rate increases regularly with SiH_4 flow, while with N_2O , the rate first increases and then stabilizes for a silane flow above 100 sccm ($3 \mu\text{m}/\text{min}$ and $1.6 \mu\text{m}/\text{min}$ at 270°C and 450°C respectively).

This limitation may be interpreted by a lack of oxygen active species. For the same oxidant flow (300 sccm) twice as many oxygen atoms are available in the case of O_2 . Moreover, if the oxidizing sources were equivalent, a limitation of the deposition rate would occur with O_2 for 200 sccm of silane, whereas over this value the deposition rate still increases. An oxygen discharge is thus more effective for oxidant active species production. Under 100 sccm of silane, deposition rates are similar for both gases.

Si-H bands (2280 cm^{-1} and 880 cm^{-1}) appear when the silane flow increases. The threshold value under which no Si-H bonds are detected is 30 sccm for N_2O and 100 sccm for O_2 , but Si-OH groups are present for both gases.

The ratio of the film etch rate to thermal oxide etch rate is reported in Figs. 6 and 7 for N_2O and O_2 respectively. At 450°C , this ratio increases slightly with silane flow while at 270°C it follows the deposition rate variation.

With N_2O , nuclear reaction analysis of layers deposited at 270°C on GaAs shows that, under low silane flow conditions (30 sccm), 0,7% of nitrogen is incorporated while it is 3% under high silane flow condition (300 sccm) (Table I). In the latter case, XPS measurements reveal a nitrogen content of 1,5% with only 13% N atoms silicon bonded. However, the O/Si ratio is close to stoichiometry in both cases although the layer composition is different (Si-H).

Fig. 4 : Film properties versus silane flow at 270°C and 450°C , $N_2O=300 \text{ sccm}$, 200 mtorr, 300 W.

Fig. 5 : Film properties versus silane flow at 270°C and 450°C , $O_2=300 \text{ sccm}$, 200 mtorr, 300 W.

Table I : Nuclear reaction analysis (NRA) of SiO₂ films deposited on GaAs at 270°C, 200 mtorr, 300 W, with various N₂O/SiH₄ ratio.

O ₂ flow (Sccm)	SiH ₄ flow (Sccm)	O ₂ /SiH ₄	Thickness (Å)	Deposition rate (µm/min)	O (x 10 ¹⁷ atm/cm ²)	Si (x 10 ¹⁷ atm/cm ²)	N (x 10 ¹⁷ atm/cm ²)	O/Si	Density (g/cm ³)
30	30	1	990	0,60	5,53	2,68	---	2,06	3
300	30	10	1500	0,85	7,61	3,65	---	2,08	2,5
450	30	15	2600	0,75	13,79	6,26	---	2,2	2,5

3.2.2. Oxidant flow

Data showing the oxidant flow influence on deposition rate, etch rate and refractive index are reported in Figs. 6 and 7 for N₂O and O₂ respectively, the silane flow rate being kept constant at 30 sccm.

For both cases, deposition rates follow an increase-maximum-decrease variation and etch rates match this curve at low temperatures. For oxidant flow rates over 600 sccm film properties are changing. At low temperatures, the etch rate reaches the value of high temperature deposited layers. The refractive index becomes stable (1.47) all over the surface and the film structure is no longer columnar. No adsorbed water is visible in I.R. spectra but Si-OH is still present. At high temperature, no silanol groups are detected.

For both temperatures, SiH bands disappear above 60 sccm with O₂ and 150 sccm for N₂O. For oxidant/silane ratios varying between 60/30 and 450/30 the ratio O/Si is constant (≈ 2).

Fig. 6 : Film properties versus N₂O flow at 270°C and 450°C, SiH₄=300 sccm, 200 mtorr, 300 W.

Fig. 7 : Film properties versus O₂ flow at 270°C and 450°C, SiH₄ = 300 sccm, 200 mtorr, 300 W.

The incorporated nitrogen content is constant (0,8%) when the N_2O flow increases (Table II) while this content increases with the silane flow rate (i.e. the deposition rate). Furthermore, we have previously shown that a great part of nitrogen is unbonded to Si. Consequently, this contamination is probably due to by-product desorption.

Table II : Nuclear reaction analysis (NRA) of SiO_2 films deposited on GaAs at 270°C, 200 mtorr, 300 W, with various N_2O/SiH_4 ratio.

N_2O flow	SiH_4 flow	N_2O/SiH_4	Thickness (Å)	Deposition rate ($\mu m/min$)	O ($\times 10^{17}$ atm/cm ²)	Si ($\times 10^{17}$ atm/cm ²)	N ($\times 10^{17}$ atm/cm ²)	O/Si	Density (g/cm ³)
60	30	2	2000	0,24	10,61	5,18	0,13 i.e:0,8%	2,05	2,6
300	30	10	1800	1,12	9,21	4,55	0,09 i.e: 0,6%	2,02	2,5
450	30	15	2100	0,75	10,71	5,11	0,12 i.e:0,7%	2,09	2,5
300	300	1	-----	3	7,97	4,02	0,39 i.e: 3%	1,98	-----

Accuracy : Silicon and Nitrogen 4%, Oxygen 3%.

Thermal oxide density = 2,2 g/cm³ (i.e. : $4,4 \times 10^{22}$ oxygen/cm³ and 2,2 Silicon/cm³).

4 - DISCUSSION AND CONCLUSIONS

Generally /1,3,10,11/ film properties depend upon process parameters such as oxidant to silane ratio, percentage of silane, power, dilution. But due to the variety of reactor geometries existing it is difficult to establish a comprehensive comparison.

Few authors have published results on the dependence of deposition rates upon temperature. Pai and Chang /9/ have found that, in a microwave afterglow, the deposition rate of oxide from the mixture $SiH_4/N_2O/He$ (8/1000/4640 Sccm) was independent of the deposition temperature between 200°C and 400°C. But their experimental conditions led to a deposition rate of 900 Å/min. In our case, the high rate of deposition enables the species to move on the surface or to desorb. When the temperature is raised, the molecule mobility and the by-products desorption are enhanced, leading to less porous films. Thus the deposition rate decreases and the film properties are changed.

Some authors /1,10/ have reported such a temperature dependence of films properties. Jackson and al. /1/ have deposited SiO_2 films in a quite similar microwave afterglow discharge using $SiH_4/N_2O/He$ chemistry. The refractive index increases until 200°C and then remains constant at 1.46. Above this temperature, the etch rate decreases. Adams and al. /10/ have obtained oxide films from $SiH_4/Ar/N_2O$ mixtures in a direct PECVD reactor and have reported a discontinuity in etch rate, stress and refractive index behavior at 200°C but they did not explain this change by a densification effect.

At 270°C, oxide layers are under compression. For an oxidant to silane ratio = 10, the stress values are $2.5 \cdot 10^9$ and $1 \cdot 10^9$ dynes/cm² for O_2 and N_2O respectively. These values are very close to Jackson's /1/ results ($2 \cdot 10^9$ dynes/cm² at 300°C).

Generally, the reactant flow effect is studied through the following parameters : % SiH_4 and oxidant/ SiH_4 ratio. Dilution makes it possible to keep one parameter constant while the other is varied. In our case, these parameters are linked making the comparison with other studies difficult.

Nevertheless, Jackson et al. /1/ in a similar reactor noticed that at constant temperature of 300°C, a N_2O flow of 380 sccm, a helium dilution of 2000 sccm and a pressure of 630 torr the deposition rate increases slightly when silane is varied from 60 sccm to 140 sccm. This is in agreement with our results in the same range of flow.

As far as composition is concerned, several authors /8,10/ have noticed the dependence of hydrogen content on oxidant to silane ratio (R). For example, using a DECR reactor with N_2O/SiH_4 mixtures, Plais et al. /8/ found by ERDA (electron recoil detection analysis) measurements that the percentage of hydrogen decreases from 22 at % for $R=1$ to 5 at % for $R=10$. They also noticed that nitrogen is incorporated in the layers and that its amount decreases with R : 25 at % for $R=1$ to 2 at % for $R=10$. These values are greater than those found in this study. Like us, they found that the film density (2.4 g/cm^3) was greater than that of thermal oxide.

The independence of the O/Si ratio over a wide range of silane and oxidant flow rates is difficult to understand. Indeed, some authors /8,11/ have noticed that the film composition shifts from oxygen deficient silicon oxide to silicon dioxide as the oxidant/silane ratio increase. Furthermore, IR measurements show the presence of Si-OH in oxygen rich conditions but the stoichiometry is not affected.

In conclusion, properties of oxide films deposited from N_2O/SiH_4 or O_2/SiH_4 in a microwave afterglow reactor have been investigated over a wide range of temperature, silane flow and oxidant flow.

We have shown that good quality oxide films can be obtained at 270°C provided that the oxidant to silane ratio is high enough ($> 600/30$). For this condition, no Si-H bonds are present. Films etch three time faster than thermal oxide, refractive index is 1.47 - 1.48, O/Si ≈ 2 and deposition rate $\approx 6000 \text{ Å/min}$. These results are similar to those of Jackson and al. [1] obtained in the same type of reactor but with helium dilution. The main differences from their films are density (2.2 g/cm^3 against 2.5 g/cm^3) and deposition rate (1000 Å/min against 6000 Å/min).

Using N_2O as oxidizing gas introduces nitrogen in the layers up to 3 at % for silane rich conditions. N atoms are for the most part unbond to silicon. It is probably due to the trapping of by products during high speed growth.

Using O_2 lowers the threshold value of hydrogen incorporation. However, these two gases lead to similar film quality.

In order to gain a better understanding of the reaction mechanism it would be interesting to proceed to a gas phase study in order to correlate film properties and reactive species composition.

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BIBLIOGRAPHY

- /1/ JACKSON R.L., SPENCER J.E., MCGUIRE J.L., Solid State Technol., 30 (4) (1987) 107.
- /2/ HILLS G.W., HARRUS A.S., THOMA M.J., Solid State Technol., 33 (4) (1990) 127.
- /3/ HOLLAHAN J.R., J. Electrochem. Soc., 21 (1979) 930.
- /4/ DRESNER J., J. Vac. Sci. Technol. B, 6 (2) (1988) 517.
- /5/ HEY H.P.W., SLUIJK B.G., HEMMES D.G., Solid State Technol., 33 (4) (1990) 139.
- /6/ LUCOVSKY G., TSU D.V., KIM S.S., MARKUNAS R.J., FOUNTAIN G.G., Appl. Surf. Sci., 39 (1989) 33.
- /7/ MEINERS L.G., J. Vac. Sci. Technol., 21 (1982) 655.
- /8/ PLAIS F., AGIUS B., ABEL F., SIEJKA J., PUECH P., ALNOT P., Proc. of the 8th symposium on plasma processing, Electrochem. Soc. Montreal, May 6-11, 1990.
- /9/ PAI C.S., CHANG C.P., J. Appl. Phys., 68 (1990) 793.
- /10/ ADAMS A.C., ALEXANDER F.B., CAPIO C.D., SMITH T.E., J. Electrochem. Soc., Solid State and Technol. 128 (1981) 1545.
- /11/ PAN P., NESBIT L.A., DOUSE R.W., GLEASON R.T., J. Electrochem. Soc., Solid State and Technol., 132 (1985) 2012.
- /12/ JOYCE R.J., STERLING H.F., ALEXANDER J.H., Thin Solid Films, 1 (1967/68) 481.
- /13/ PLISKIN W.A., in Semiconductor silicon, H.R. HUFF and R.R. BURGESS, The Electro-chem. Soc., Princeton, N.J., 1973, p. 506.
- /14/ VERSAUD P.C., EL RASSI Z., PORTHAULT M., Analisis, 6 (1978) 98.