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Development of SiN_x LPCVD processes for microtechnological applications

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Abstract: Various silicon rich silicon nitride SiN_x films have been deposited by low-pressure chemical vapour deposition (LPCVD) from dichlorosilane SiH_2Cl_2 and ammonia NH_3. Deposition rate, refractive index, residual stress and SiN_x stoichiometry are studied as a function of deposition parameters, evidencing the main influence of the NH_3/SiH_2Cl_2 gas ratio. However, as such SiN_x layers have special applications for micro-opto-electro-mechanical systems (MOEMS), the influences of the deposition conditions are more precisely studied for improving the uniformity properties along the load. In order to achieve this goal, different load configurations are tested and the use of non-isothermal furnace profiles is proposed in order to develop the LPCVD deposition technique of SiN_x films for industrial microtechnological processes.

1. INTRODUCTION

The fabrication and the optimisation of micro-opto-electro-mechanical systems (MOEMS) have required the advantages brought forth by silicon rich silicon nitride SiN_x as construction or detection material. Indeed, through variations of the SiN_x stoichiometry, a wide range of properties (optical, electrical, mechanical, chemical...) is obtained for many microtechnological applications [1-5]. In order to deposit these films, chemical vapour deposition (CVD) has commonly been used and different gaseous sources, i.e. dichlorosilane SiH_2Cl_2 or silane SiH_4 mixed with ammonia NH_3, have been studied, evidencing different drawbacks [6-11]. For example, for a given SiN_x stoichiometry, the SiH_2Cl_2/NH_3 gaseous mixture is responsible for better thickness uniformity on a wafer but also for higher stress than the SiH_4/NH_3 one. However, in all cases, the use of low-pressure chemical vapour deposition (LPCVD) processes for the obtaining of SiN_x films is characterised by consumption effects and therefore non-uniformity phenomena along the load.

In this work, we report the deposition of (silicon rich) silicon nitride films SiN_x by low-pressure chemical vapour deposition (LPCVD) from dichlorosilane SiH_2Cl_2 and ammonia NH_3. Deposition rate, refractive index, residual stress and SiN_x stoichiometry are studied as a function of deposition parameters (temperature, total pressure, gas flow ratios...). However, in order to propose solutions for the development of SiN_x LPCVD industrial processes, the non-uniformity phenomena along the load must be solved. Therefore, special cares are more precisely given for testing the LPCVD deposition technique (moving the load back in the furnace or using non-isothermal profiles) and finally improving the uniformity along the load.

2. EXPERIMENTS

Growth experiments were carried out in a conventional hot-wall horizontal LPCVD reactor accommodating up to 12.5-cm substrates. SiN_x films were deposited from dichlorosilane (DCS) SiH_2Cl_2 and ammonia NH_3 on 10-cm diameter, (100) silicon wafers. Two deposition temperatures, i.e. T = 750°C and 800°C, were chosen while total pressure P was kept constant around 500 mtorr. Various NH_3/SiH_2Cl_2 gaseous ratios were tested in order to obtain various SiN_x stoichiometry. Isothermal (± 1°C) profiles were controlled along the load (flat zone length: 1 m). However, according to deposition experiments (see hereafter), non-isothermal profiles were also realised by increasing the temperature (up to 830°C) of the furnace rear zone.

A full load of 29 wafers (including 4 screen wafers) was used for each deposition experiment. Test wafers were situated at the position 1, 13 and 25. Films thickness and refractive index were measured by ellipsometry at an 830-nanometer wavelength. Profilometry was used to check the ellipsometric results, and to determine films residual stress through wafer curvature measurements before and after removal of the backside deposition by chemical etching into fluorhydric acid HF [11-12]. The accuracy of the whole experimental procedure has been estimated to ± 0.5% for the thickness and refractive index measurement and to ± 5% for the residual stress determination.

3. RESULTS AND DISCUSSION

3.1 Optical and structural properties

In previous works, by applying the Bruggeman theory to the mix of polycrystalline silicon p-Si and silicon nitride Si_3N_4, a relation between the N/Si ratio and the refractive has been evidenced for SiN_x films deposited at high temperature (T > 600°C) from the SiH_4/NH_3 gaseous mixture [13-14]. Figure 1 represents the variations of the refractive index n (assessed at an 830nm wavelength) of SiN_x films as a function of the N/Si ratio x. A quasi-parabolic relation is evidenced by interpolation of the theoretical curve (error lower than 1%):

$$n = 3.70 - 1.83x + 0.42x^2 \qquad (1)$$

Ellipsometric measurements (assessed at an 830nm wavelength) of the various deposited SiN_x films are resumed for the two deposition temperatures, i.e. 750 and 800°C (table 1). A rather wide range of refractive index, i.e. $2 \le n \le 2.5$, is obtained as a function of the NH_3/SiH_2Cl_2 gaseous ratio.

Table 1: refractive index versus NH_3/SiH_2Cl_2 gaseous ratio

NH_3/DCS	6	1.18	0.59	0.29	0.24	0.16	0.08
n (T = 750°C)	2	2	2	2.025			2.25
n (T = 800°C)	2			2.05	2.15	2.35	2.5

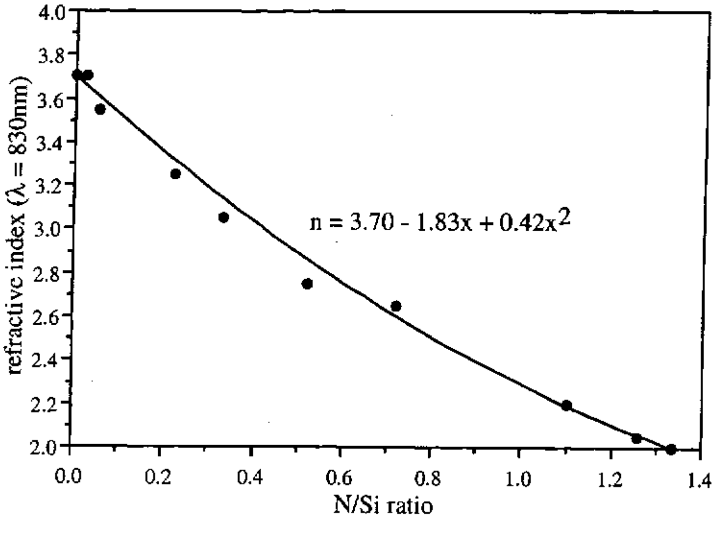

Figure 1: refractive index versus SiN_x stoichiometry

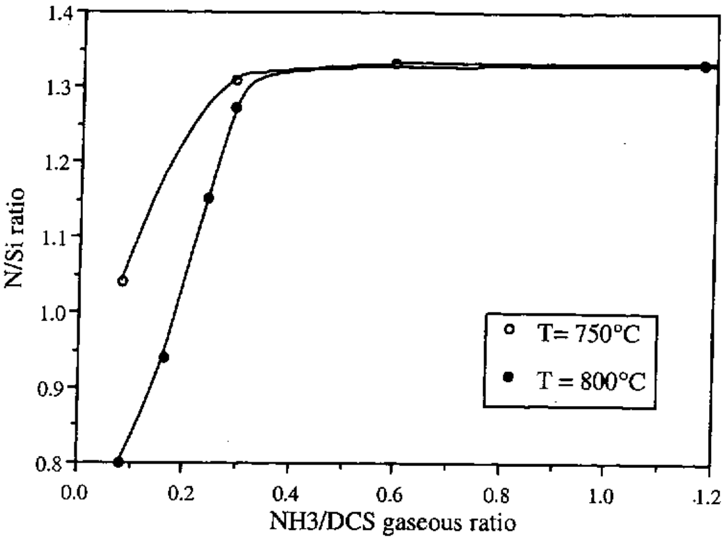

Figure 2: N/Si ratio versus gaseous ratio for different temperatures

According to equation (1), the N/Si ratio of the deposited SiN_x films has been estimated from its refractive index. Figure 2 represents the variations of the N/Si ratio as a function of the NH_3/SiH_2Cl_2 gaseous ratio. Whatever the deposition temperature, stoichiometric Si_3N_4 (n = 2) and silicon rich silicon nitride SiN_x (n > 2) are obtained for gaseous ratios respectively higher and lower than 0.3.

In order to explain such results, the chemical system of the SiH_2Cl_2/NH_3 gas mixture must be studied. It can be briefly described thanks to the following global equations:

$$SiH_2Cl_2 + NH_3 \text{ -----> } Si_3N_4 \quad (2)$$
$$SiH_2Cl_2 \text{ -----> } Si \quad (3)$$

For high gaseous ratio (R > 0.3), ammonia NH_3 is in excess and controls the deposition mechanisms. Therefore, the pyrolysis of dichlorosilane SiH_2Cl_2 (equation 3) is completely inhibited and stoichiometric silicon nitride Si_3N_4 is obtained (equation 2).

For low gaseous ratio (R < 0.3), ammonia is no longer controlling the deposition mechanisms. The pyrolysis of dichlorosilane SiH_2Cl_2 is responsible for the adsorption of silicon atoms in excess and therefore for the obtaining of silicon rich silicon nitride SiN_x. For such deposition conditions, the temperature favours the pyrolysis of dichlorosilane SiH_2Cl_2 (equation 3) rather than the direct deposition of silicon nitride from dichlorosilane SiH_2Cl_2 and ammonia NH_3 (equation 2). Therefore, its increase is responsible for the decrease of the N/Si ratio of the deposited film.

3.2 Mechanical properties

Mechanical properties have been studied through residual stress measurements, considering stress as an algebraic data, a compressive and tensile stress being negative and positive respectively. Furthermore, the residual stress σ into SiN_x films is considered as the sum of the intrinsic and the thermal stress σ_i and σ_{th}. σ_i is related to the deposition conditions while σ_{th} is caused by the differences between the thermal expansion coefficients of the silicon substrate α_s and the deposited film α_f and between the ambient temperature T_a during stress measurement and the deposition temperature:

$$\sigma = \sigma_i + \sigma_{th} \quad \text{with} \quad \sigma_{th} = G_f(\alpha_s - \alpha_f)(T_a - T) \quad (4)$$

where G_f is the film elastic modulus.

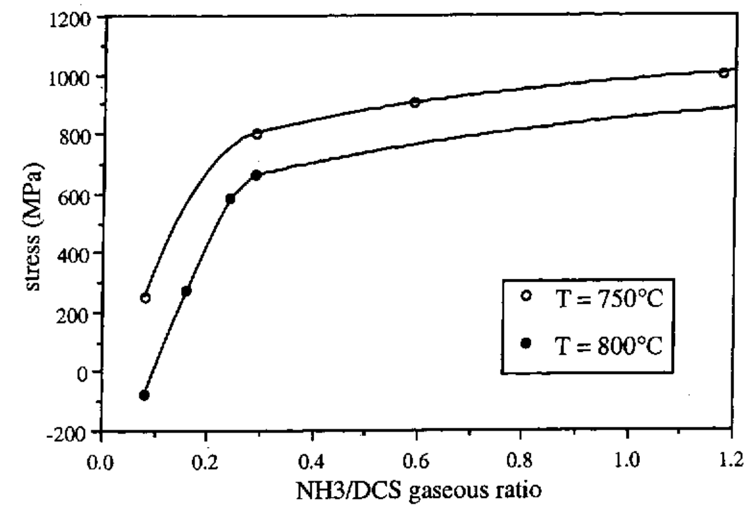

Figure 3: residual stress versus gaseous ratio for different temperatures

Although the thermo-mechanical properties of silicon Si(111), polysilicon p-Si and silicon nitride Si_3N_4 are known ($G_{Si(100)} \approx G_{p\text{-}Si} \approx 175$ GPa, $G_{Si3N4} \approx 190$ GPa, $\alpha_{Si(100)} \approx \alpha_{p\text{-}Si} \approx 2.5 \times 10^{-6}$ K^{-1}, $\alpha_{Si3N4} \approx 3 \times 10^{-6}$ K^{-1}), those of the SiN_x material are still being discussed. However, by considering that silicon rich silicon nitride SiN_x is a mix between polysilicon p-Si and silicon nitride Si_3N_4, the thermal stress σ_{th} of the deposited films can be roughly estimated by the following equation (where stress and temperature are respectively measured in MPa and °C):

$$0 < \sigma_{th} < 0.1(T - T_a) \qquad (5)$$

Figure 3 represents the stress variations as a function of the NH_3/SiH_2Cl_2 gaseous ratio. Whatever the deposition temperature (750 and 800°C), the gaseous ratio decrease is responsible for the stress decrease from highly tensile stress (higher than 1 GPa for stoichiometric silicon nitride Si_3N_4) to compressive stress. Since, this decrease is enhanced for gaseous ratio lower than 0.3, explanations of such phenomena must be related to the SiH_2Cl_2/NH_3 chemistry.

According to literature, tensile stress into silicon nitride Si_3N_4 is caused by the hydrogenation during the film deposition and more precisely to the shrinkage of the film caused by the dissociation of Si-H and N-H bonds and the rearrangement of the dangling bonds to stable Si-N bonds [6]. Therefore, such tensile stress must be related to the global reaction between dichlorosilane SiH_2Cl_2 and ammonia NH_3 (equation 2). As the NH_3/SiH_2Cl_2 gaseous ratio becomes lower than 0.3, the pyrolysis of dichlorosilane SiH_2Cl_2 (equation 3) is responsible for the adsorption of silicon atoms in excess and for the decrease of the N/Si ratio. As more Si-Si and less Si-N bonds are formed, silicon rich silicon nitride SiN_x is deposited and residual stress decreases quickly from tensile to compressive values.

According to equation 5, the temperature increase is responsible for tensile thermo-mechanical stress σ_{th}. In fact, experimental results demonstrate that this influence is negligible and that the temperature increase is finally responsible for compressive (intrinsic) stress σ. Such results are always explained by considering the SiH_2Cl_2/NH_3 chemistry. As already shown, the temperature favours the dichlorosilane pyrolysis (equation 3) rather than the direct reaction between dichlorosilane SiH_2Cl_2 and ammonia NH_3 (equation 2). Therefore and as already shown, its increase leads to compressive stress.

Finally, residual stress of SiN_x films has been represented as a function of the N/Si ratio and compared with previous results obtained with the SiH_4/NH_3 gaseous source [11] (figure 4). Similar behaviours are evidenced whatever the deposition temperature or the silicon precursor. However, more investigations are necessary to define a direct relation between stoichiometry and residual stress.

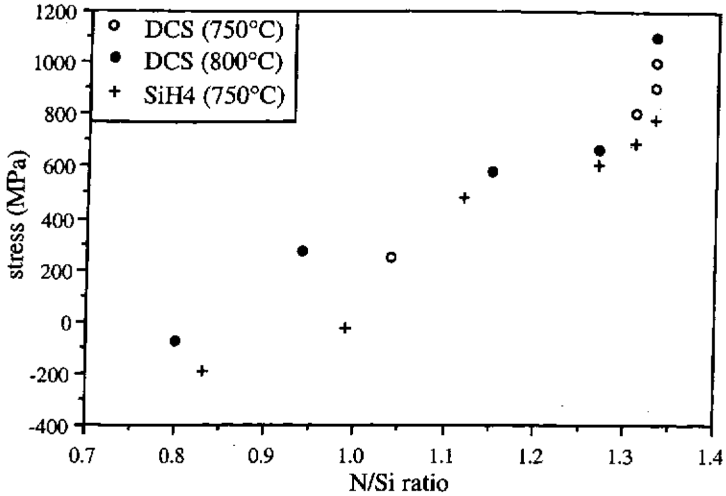

Figure 4: residual stress versus SiN_x stoichiometry

3.3 Deposition rate and thickness non-uniformity

Variations of deposition rate V_d (measured on the 13th wafer of the load) with gaseous ratio evidence a maximal value around $R \approx 1$ whatever the deposition temperature (figure 5). Such phenomenon has already been shown by Gardeniers et al. [7]. It has been related to the dependence of the deposition rate with the partial pressure P_{DCS} and P_{NH3} of dichlorosilane and ammonia into the gaseous phase:

$$V_d \;\alpha\; (P_{DCS})^a\,(P_{NH3})^b \;\alpha\; (R)^b\,(1+R)^{-(a+b)} \qquad (6)$$

According to equation 6, the maximal deposition rate is obtained for R = 1 only when a and b are equal. Such result demonstrates that dichlorosilane SiH_2Cl_2 and ammonia NH_3 have similar behaviour for the deposition of silicon rich silicon nitride films SiN_x.

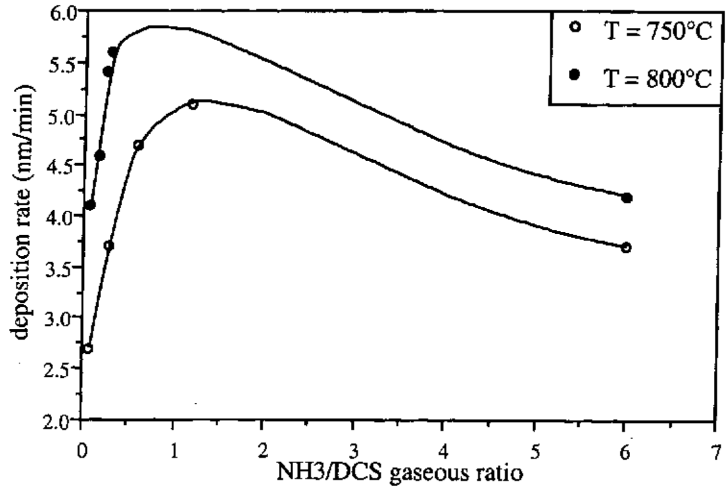

Figure 5: deposition rate versus gaseous ratio for different temperatures

3.4 Optimal deposition conditions for microtechnological applications

The optimisation of the LPCVD deposition technique for the development of micro-opto-electro-mechanical systems (MOEMS) has been performed by considering non-uniformity on the wafer and on the load. However, since very good uniformities, i.e. lower than 3%, have been obtained on the wafer whatever the deposition conditions, non-uniformities on the load will only be investigated hereafter. Thus, thickness and refractive index relative variations δe/e and δn/n have been estimated from the ellipsometric and profilometric measurements on the 1st and 25th wafers. Typical results (given in percent) are presented in table 2.

Table 2: thickness and refractive index relative variations versus NH_3/SiH_2Cl_2 gaseous ratio

NH_3/DCS	6	1.18	0.59	0.29	0.24	0.16	0.08
δe/e (T = 750°C)	± 1%	± 1.3%	± 2.8%	± 5.7%			± 8.9%
δn/n (T = 750°C)	± 0.5%	± 0.5%	± 0.5%	± 0.5%			± 0.5%
δe/e (T = 800°C)	± 1.5%			± 10.1%	± 11.2%	± 14.5%	± 16%
δn/n (T = 800°C)	± 0.5%			± 0.5%	± 0.5%	± 1.1%	± 1.8%

According to these results, the refractive index relative variation δn/n does not depend on the deposition temperature and on the NH_3/SiH_2Cl_2 gaseous ratio. Non-uniformities can be considered as constant (equal to the measurement error: ± 0.5%) even if a small increase is evidenced for the highest temperature and the lowest gaseous ratio.

The study of the thickness relative variations is more interesting since it appears that δe/e increases with both the temperature increase and the gaseous ratio decrease. Such result should be related to consumption phenomena and more precisely to the exhaustion of the SiH_2Cl_2/NH_3-deviated chemical species along the load.

For silicon nitride depositions (R > 0.3), ammonia is in excess and has been shown to control the deposition mechanisms. Therefore, consumption phenomena have no real influence and uniform Si_3N_4 films have been obtained whatever the deposition temperature.

For silicon rich silicon nitride SiN_x films (R < 0.3), neither dichlorosilane are in excess and consumption phenomena occur along the load. According to figure 2, the N/Si ratio, i.e. the refractive index, is roughly related to the NH_3/SiH_2Cl_2 gaseous ratio. Thus, if ammonia and dichlorosilane are characterised by similar consumption phenomena, refractive index should not vary along the load and low δn/n values should be obtained as shown in table 2. On the contrary and according to equation (6), the deposition rate, i.e. the film thickness, is related to the product between the dichlorosilane and ammonia partial pressure. Thus, consumption phenomena of both gases cumulate and high thickness non-uniformities δe/e are evidenced. Of course, when temperature increases, deposition rate and consumption phenomena also increase, leading to higher thickness non-uniformities.

For microtechnological applications, low stress (silicon rich) silicon nitride films and high deposition rates are widely used. For all these requirements, increasing the temperature towards 800°C and more is a good solution. However according to our results, a compromise can hardly be found while taking into account the obtaining of low thickness non-uniformities (lower than ± 5%). Several solutions are therefore proposed in order to tackle this problem.

Table 3: thickness and refractive index relative variations for different load configurations

NH_3/DCS	#1	#2	#3
δe/e	± 11.2%	± 14.8%	± 16.6%
δn/n	± 0.5%	± 1%	± 1.5%

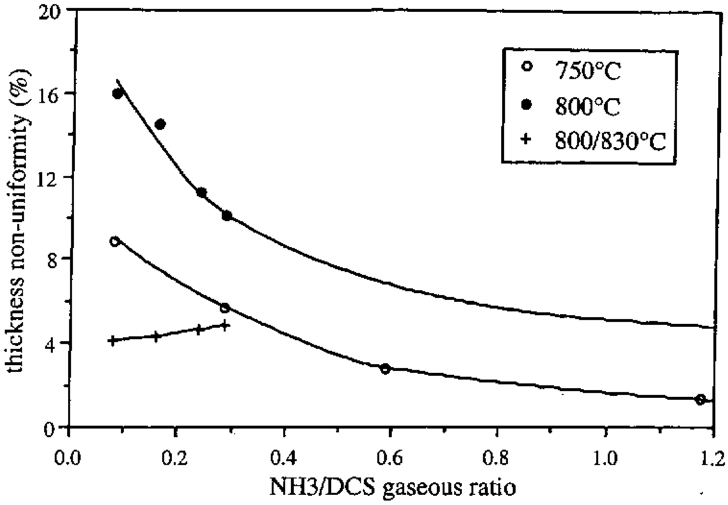

Figure 6: thickness and relative variations versus gaseous ratio for different temperatures

First, different load configurations have been tested. Compared to the standard one (configuration #1: boat at the furnace centre, use of 25 5mm-spaced wafers), the boat has been moved 24 cm towards the rear of the furnace (configuration #2) or the wafer spacing has been fixed at 10 mm increasing the load length (configuration #3). Results confirm, if necessary, that non-uniformities are actually related to consumption phenomena (table 3). Since the total deposition surface has been increased for configurations #2 and #3, higher thickness and refractive index relative variations are obviously evidenced. From these results, it may be concluded that non-uniformities could be improved by moving the boat towards the front of the furnace. Unfortunately, this solution is not conceivable and has therefore not been tested: films with good uniformities cannot be deposited in the entrance zone where dichlorosilane SiH_2Cl_2 and ammonia NH_3 are not fully mixed into the gaseous phase.

Since consumption phenomena are related to the exhaustion of chemical species along the load, their effects must be balanced by increasing the temperature at the rear of the furnace [15]. Thus, in a second time, the temperature at the front, the middle and the rear of the deposition zone have been respectively fixed at 800°C, 815°C and 830°C in order to have a temperature ramp along the load. Deposition experiments have been performed with such non-isothermal profile. Thickness non-uniformities are given as a function of the NH_3/SiH_2Cl_2 gaseous ratio for different temperature profiles (figure 5). The previously shown δe/e decrease with the gaseous ratio and the deposition temperature is thus represented and the improvement brought forth by the non-isothermal profile is clearly evidenced.

Finally, thickness and refractive index relative variations are given in table 4. It appears that the δe/e decrease is related to the δn/n increase. In fact, if the temperature increase has effectively balanced consumption phenomena, it also favours the pyrolysis of dichlorosilane SiH_2Cl_2 (equation 3) and is responsible for the refractive index increase along the load. However, with the 800°C/830°C non-isothermal profile, both relative variations remain lower than ± 5%, evidencing the deposition of silicon rich silicon nitride films SiN_x with a high uniformity on a 25-wafer load.

Table 4: thickness and refractive index relative variations for the 800/830°C non-isothermal profile

NH_3/DCS	0.29	0.24	0.16	0.08
δe/e (T = 800/830°C)	± 4.8%	± 4.6%	± 4.3%	± 4.1%
δn/n (T = 800/830°C)	± 1.8%	± 1.3%	± 1.5%	± 2%

4. CONCLUSION

A study of the influence of the deposition parameters on the deposition rate, refractive index and residual stress of LPCVD SiN_x films deposited from dichlorosilane SiH_2Cl_2 and ammonia NH_3 has been performed, evidencing the main influence of the NH_3/SiH_2Cl_2 gaseous ratio. The Bruggeman theory has been used to have a relation between the refractive index and the SiN_x stoichiometry and the obtaining of varied N/Si ratios and of low stress silicon rich silicon nitride films has been shown.

Special investigations have been performed in order to develop industrial LPCVD processes for the fabrication of micro-opto-electro-mechanical systems. Consumption phenomena have been shown to be responsible for high thickness non-uniformitities especially for silicon rich silicon nitride films. Solution to this problem has been found by increasing slightly the temperature at the rear of the furnace. Thus, the use of such non-isothermal profiles has allowed the deposition of varied SiN_x films with good thickness and refractive index uniformities on a 25-wafer load.

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