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FORMATION BY PECVD OF VERY THIN SILICON OXYNITRIDE (SIO_XN_Y) LAYERS (TECHNOLOGY AND CHARACTERISATION)

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A b s t r a c t. In this work, results of PECVD process optimisation aiming in repeatable formation of oxynitride layers below 10 nm and possibly the best electro-physical properties (which in the near future would allow their application for ULSI-CMOS ICs production) are presented. The processing was performed in very low temperature process (350°C) and typical parallel plate reactor. As a result of performed optimisation procedure it appeared feasible to form repeatedly oxynitride layers of very low thickness (below 10 nm).
The influence of high temperature annealing on the properties of the formed layers and systems has also been studied.
The properties of the obtained layers and systems (silicon-oxynitride) were characterised by electrical methods using specially designed MOS test structures (MOS capacitors, MOSFETs and gated diodes). Number of electro-physical parameters were determined, e.g.: characteristic charges (fixed and interface traps), critical voltage causing breakdown, defects densities, ... etc. The test structures were fabricated in NMOS technology with aluminium gate. The spectroscopic ellipsometry measurements allowed independent determination of the dielectric layer thickness and approximate (primary information) on stoichiometry (silicon nitride to silicon oxide bonds rate).

K e y w o r d s: silicon oxynitride, thin layers, PECVD process, process optimisation.

INTRODUCTION

„*ITRS Roadmap*" [1] suggests the necessity of working out processing methods allowing formation of ultrathin dielectric layers with higher than for silicon dioxide dielectric permittivity value. In most cases, the application of different than SiO_2 materials results in deterioration of silicon-insulator interface properties. The silicon oxynitride layers (SiO_xN_y) seem to be the most natural compromise. Still, as it was proved in report [2], none of high temperature methods used for its formation cannot be seriously considered as final solution for future ULSI-CMOS ICs production due to the inevitable formation of nitride monolayers just at the silicon-insulator interface. In consequence, all hopes have become located in CVD techniques, particularly (due to very low temperatures) in PECVD. Classical PECVD, however, offers too high deposition rates to allow its application for ultrathin layers formation.

The aim of this work was, therefore, to find the process parameters of the PECVD allowing to form, under very low temperature (<400°C) conditions, very thin silicon oxynitride layers (<10nm) exhibiting promising for application in CMOS technology electro-physical properties.

The properties of the obtained layers and systems (silicon-oxynitride) were characterised by spectroscopic ellipsometry, XPS and electrical methods using specially designed MOS test structures (MOS capacitors, MOSFETs and gated diodes).

PROCESS OPTIMISATION

The PECVD process is difficult to optimise due to large number of process parameters with each of them changing its value in wide range. In order to find PECVD process parameters that allow possibly precise control of very thin oxynitride layers deposition in reasonable number of experiments - orthogonal tables approach (Taguchi's method [3]) has been used. The method allows determination of defined output parameters dependence trends on the process parameters. This enables quick and reliable determination of most sensitive parameters of the process and their values giving satisfying process results (i.e. reaching optimisation objective).

In the technological experiments, the typical parallel plate, powered with 300 W r.f. (13.56 MHz) generator, type of reactor (*Oxford Plasma Technology Plasmalab 80Plus*) was used. The parameters of the process were following: pressure, r.f. power, flows of three reactive gases (SiH_4, NH_3, N_2O), and temperature of the substrate.

Our optimisation objective was to reach possibly smallest deposition rate, while obtaining the silicon oxynitride layers exhibiting the electro-physical properties suitable for their application as MOSFET gate dielectrics. The possibility to control composition - the nitride to oxide ratio - of the oxynitride layer was also of interest, as the trend towards higher dielectric permittivity promotes the layers with higher concentration of silicon nitride.

The spectroscopic ellipsometer (Woollam) was used for independent thickness and refractive index N_f determination. Number of individual measurements per wafer were done (in wide wavelength spectrum and two angle of incidence) along the wafer radius, allowing the statistical approach not only to obtain the reliable mean values, but also – standard deviations of the determined parameters (thickness and refractive index). The values of standard deviation gave us information on overall uniformity of the thickness and composition across the whole silicon wafer.

As a result of the performed few stages optimisation process, the deposition rate was finally decreased from the standard value of the order of 50 nm/min to some 18 nm/min. The uniformity of the thickness (or deposition rate) was better than 0.2 %. The parameters resulting in such deposition process are listed in Tab. 1, while kinetics of oxynitride deposition is shown in Fig. 1. It can be noticed that the deposition rate changes around deposition time equal to 1.5 minutes (decreases almost by a factor of two).

In the course of the optimisation process it became clear, that the composition does not change considerably in the range of PECVD process parameters which allow very thin layers deposition. The obtained for optimised for very thin oxynitride layers processing conditions N_f value of about 1.75 (see Fig. 2). This value seems to be satisfying for the gate dielectric layer applications (compare it with 1.46 for SiO_2 and 2.0 for Si_3N_4). For the optimised process the refractive index value shows standard deviation below 0.5 %, which proves very good overall uniformity of the deposited layer.

OPTICAL CHARACTERISATION OF THE VERY THIN OXYNITRIDE LAYERS

For optimised processing conditions some more elaborated ellipsometric measurements' analysis as well as the XPS studies, were performed. The problem of thermal stability appears to be a crucial problem preventing application of many dielectric layers in real CMOS technology. In order to study these effects in case of our PECVD oxynitride layers, the rest of experiments (including also the electrical characterisation using semiconductor test devices described in next paragraph) were performed using split experiment approach. Half of the samples characterised contained the oxynitride layers "as deposited", while another half – layers annealed in high temperature in 600°C in nitrogen for 30 min. just after deposition process.

Fitting of the theoretical optical model to the experimental data obtained by spectroscopic ellipsometry measurements in wide range of wavelengths allowed independent determination of the layers thickness and effective refractive index. The use of another type of optical model resulted, in turn, in evaluation of approximate composition of the oxynitride films. In case of both types of models we obtained excellent fitting, as can be seen on the example presented in Fig. 3.

In Table 2 mixed layer model (consisting of SiO_2 and Si_3N_4) analysis for both, "as deposited" and annealed in 600°C in pure nitrogen layers, are presented. It can be seen that the evaluated thickness, refractive index and composition do not differ significantly for both splits, which obviously means that annealing up to 600°C in N_2 does not affects significantly the properties of the oxynitride layers.

The spectrum taken at the layer surface and in-depth composition profile of the exemplary 6.0 nm oxynitride layer as studied by XPS method are show in Figs 4 and 5, respectively. Except for very shallow surface contamination with carbon (compare with Fig. 5), only the peaks of oxygen, nitrogen and silicon spectrum can be seen. From the in-depth atomic concentration profile it becomes clear that the ratio of oxide vs. nitride does not change much along the layer's depth.

ELECTRICAL CHARACTERISATION OF THE VERY THIN OXYNITRIDE LAYERS

The NMOS technology of the test structures was used to manufacture the MOS test devices, which can be used for electrical characterisation of the PECVD oxynitride layers. This technology enables fabrication of MOS devices without any high temperature treatment after gate dielectric formation. This way, the properties of the "as deposited" and annealed just after oxynitride layers PECVD deposition, could also be compared basing on results obtained by the electrical characterisation methods.

Number of electro-physical parameters was then determined using classical MOS methodology. The results are collected in Table 3. The exemplary curves of measured high frequency capacitance-voltage (HF C-V) characteristics of MOS capacitors manufactured in this split experiment can be seen in Fig. 6. One can see the differences in maximum capacitance, position on voltage axis and slope between these curves. As the ellipsometric measurements of these layer thickness prove almost no change takes place in oxynitride layer thickness due to annealing – the whole effect has to be attributed to change in dielectric permittivity of the ultrathin insulating layer. The evaluated this way effective dielectric permittivity of the "as deposited" and "deposited and annealed" oxynitride layers are 2.59 and 1.78, respectively. The change of these values is so significant that it becomes obvious that although (as mentioned above) during annealing no significant changes of the optical properties are observed - some chemical state or composition changes must take place.

The C-V shift along voltage axis is attributed to change in effective charge density Q_{eff} (see Table 3). The Q_{eff} decreases considerably (approx. 5 times) after annealing in 600°C. This obviously means significant improvement in the quality of the oxynitride layer volume (e.g. less non-saturated bonds). This effect is also confirmed by difference in threshold voltage determined from test MOSFETs measurements performed on these samples (see Fig. 7).

Also the properties of the silicon-oxynitride interface become improved after the annealing. Interface traps density (at the silicon mid band) $D_{it\ mb}$ decreases by a factor of two after the annealing.

Very interesting results were also obtained by measurements of dielectric breakdown voltages (under the constant voltage stress). The resulting Weibull plots are shown in Fig. 8. For "as deposited" oxynitride layer the critical electric field value (approx. 12 MV/cm) is comparable to those usually obtained for thermal silicon dioxide (believed to be almost ideal dielectric for silicon technology). Thus, the value of 28 MV/cm obtained for oxynitride layer has to be considered as excellent result, proving capability of PECVD oxynitrides to be used as gate dielectrics in ULSI-CMOS technology. The Weibull plots allow also evaluation of density of the defects in the formed dielectric layers. This parameter is, however, the only one among those, determined by electrical methods, which did not show improvement after annealing. On the contrary, the density of defects has slightly increased after this high temperature treatment.

It is too early to speculate the nature of these changes – some additional experiments and characterisation will have to be done.

It is also interesting why all the discussed above improvements realised by electrical methods are not noticed by such a sensitive method as spectroscopic ellipsometry.

CONCLUSIONS

In the course of this study, the PECVD process of silicon oxynitride deposition was optimised to enable formation of very thin (<100 Å) layers. The kinetics of the optimised process changes for deposition times below 1 minute, while processes below 20 seconds result in unstable refractive index values.

The layers obtained with the chosen technological parameters seem to be stable up to 600°C if characterised by optical properties.

The electrical characterisation methods prove, however, that annealing in 600°C in nitrogen causes significant improvements, in both, volume properties (decrease in Q_{eff} and defect density, while increase in critical electric field E_{br}) and interface properties (characterised by $D_{it\ mb}$).

The integrity of the obtained oxynitride layers (even without annealing) is excellent, even comparing with state-of-the-art thermal silicon dioxide.

The nature of these changes in yet known and has to studied in more detail.

REFERENCES

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3. **Peace G.S.**, "Taguchi methods – a hands-on approach", Paris, Addison-Wesley Publ. Comp. 1996.

ACKNOWLEDGEMENTS

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Table 1. Optimised PECVD process parameters values.

Pressure [mTorr]	300
R.F. power [W]	10
Substrate temperature [°C]	350
SiH_4:N_2 flow [sccm]	300
NH_3 flow [sccm]	16
N_2O flow [sccm]	16

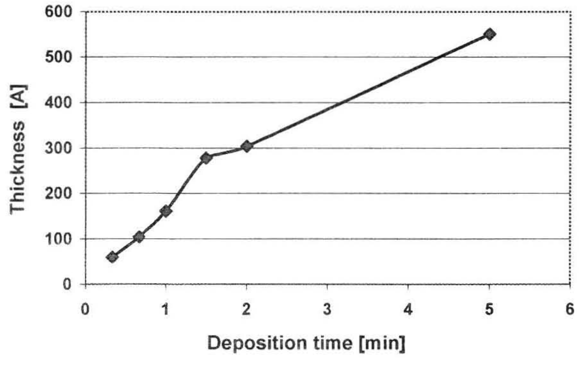

Fig. 1. Kinetics of PECVD deposition for optimised set of parameters (shown in Table 1).

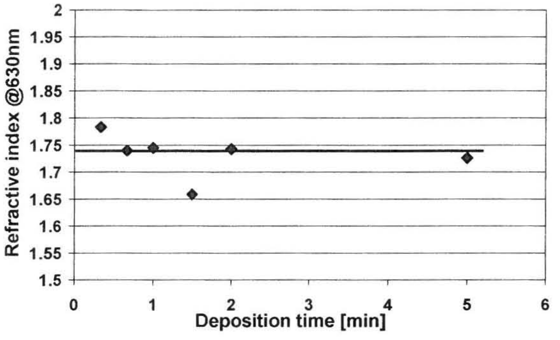

Fig. 2. Dependence of refractive index of the deposited layer on deposition time (for optimised parameters shown in Tab. 1).

Table 2. Parameters of the "as deposited" and annealed in 600°C oxynitride layers determined by spectroscopic ellipsometry.

Oxynitride layer	"As deposited"	Deposited + annealed
Temperatures [°C]	350	350 + 600
Deposition time [s]	20	20
Thickness [A]	60	59
Refractive index @630nm	1.783	1.748
Ratio Si_3N_4/SiO_2 [%]	41	47

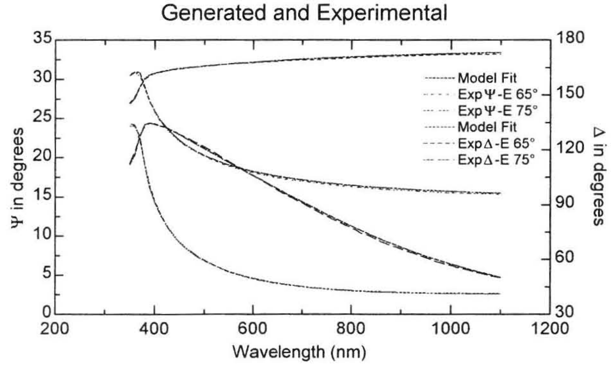

Fig. 3. Result of fitting the theoretical model (two components mixture) to experimentally obtained ellipsometric data.

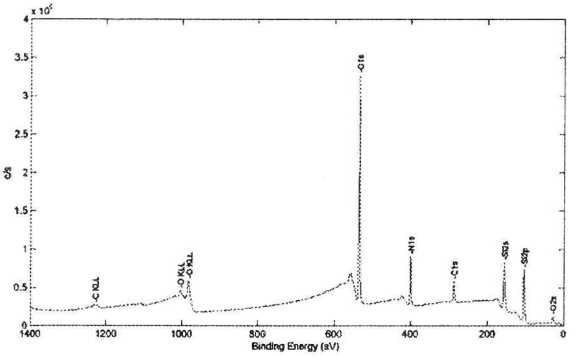

Fig. 4. Obtained by XPS method spectrum of the oxynitride surface.

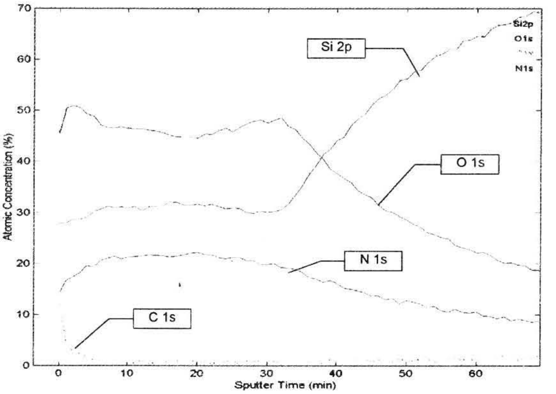

Fig. 5. XPS in-depth profile of atomic concentration within the PECVD deposited oxynitride layer.

Table 3. Parameters evaluated from the analysis of test structures electrical characteristics.

Oxynitride layer	As deposited	Deposited and annealed
Temperature [C]	350	350 + 600
Final thickness [A] by ellipsometry	59,7	59,4
Refractive index Nf by ellipsometry	1,7829	1,7484
Cmax [pF]	58,3	40,4
Dielectric permittivity	2,59	1,78
Ufb [V]	-4,005	-1,846
Ditmb(*Terman) [1/Vcm2]	4,39E+12	2,41E+12
Qeff/q [1/cm2]	7,86E+12	1,54E+12
Deffect density [1/cm^2]	180	225
Uth (5umx5um) [V]	-3,9	-1,25

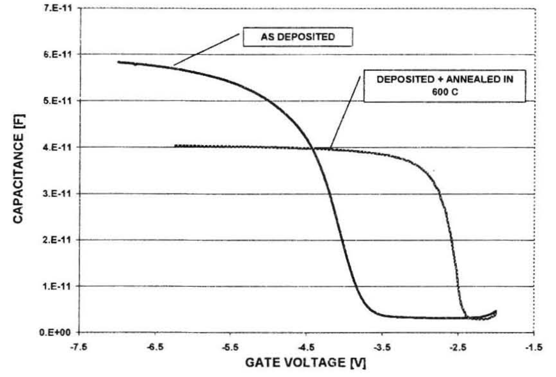

Fig. 6. High frequency C-V characteristics of MOS capacitors with very thin oxynitride films ("as deposited" and annealed) as gate dielectrics.

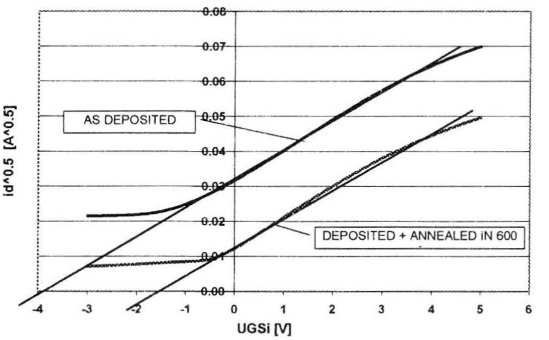

Fig. 7. Determination of test MOSFETs threshold voltages for "as deposited" and annealed oxynitride layers.

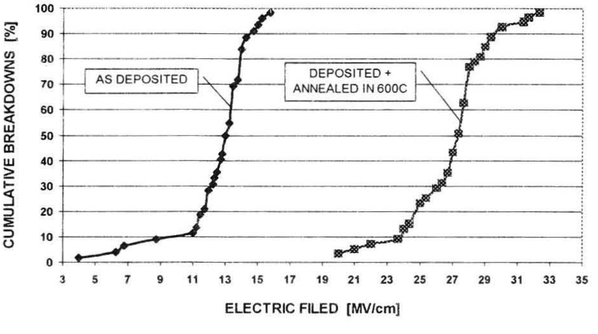

Fig. 8. Weibull plot for breakdowns measured under ramping voltage conditions on MOS structures with "as deposited" and annealed oxynitride layers.

WYTWARZANIE BARDZO CIENKICH WARSTW TLENKO-AZOTKÓW KRZEMU (SIO_XN_Y) METODĄ PECVD (TECHNOLOGIA I CHARAKTERYZACJA)

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S t r e s z c z e n i e. W pracy przedstawiane są wyniki optymalizacji procesów PECVD warstw tlenko-azotków krzemu pod kątem zmniejszenia szybkości osadzania tych warstw do poziomu umożliwiającego kontrolowane wytwarzanie warstw poniżej 10 nm oraz uzyskania możliwie najlepszych właściwości elektrofizycznych, które pozwoliłyby zastosować te warstwy i tę metodę w produkcji układów scalonych ULSI-CMOS. W wyniku przeprowadzonych eksperymentów optymalizacji okazało się możliwe otrzymywanie powtarzalnych bardzo cienkich (> 10 nm) warstw tlenko-azotków. Badano również wpływ temperatury wyżarzania na własności powstających warstw.

S ł o w a k l u c z o w e : tlenko-azotki krzemu, cienkie warstwy, proces PECVD, optymalizacja procesu.