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LOW TEMPERATURE PLASMA OXIDATION OF SILICON – POSSIBILITY OF APPLICATION IN CMOS –ULSI TECHNOLOGY

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A b s t r a c t. The aim of this work is experimental analysis potential of possibilities of application oxidation in r.f. (13.56 MHz) plasma for the formation of utrathin (<6 nm) gate oxide layers in MOS devices. Process is performed in very low temperature (350°C) in typical planar reactor. The obtained oxidation rate allows relatively easy control of final oxide layer thickness with oxidation time in very wide range, i.e. from 2 nm to approx. 10 nm.
The properties of the obtained layers and systems (silicon-oxide) were characterised by electrical methods using specially designed MOS test structures. Number of electro-physical parameters were determined, e.g.: characteristic charges (fixed and interface traps), critical voltage causing breakdown, defects densities, ... etc. The spectroscopic ellipsometry and XPS measurements allowed independent determination of the dielectric layer thickness and obtaining additional verification of the quality and composition of the ultrathin oxide layer.
The influence of high temperature annealing on properties of the formed layers and systems were also investigated.

K e y w o r d s : silicon oxidation, low-temperature plasma, CMOS-ULSI technology.

INTRODUCTION

Continuous trend in ICs technology development (along with the device miniaturisation) has always been reduction of thermal budget of CMOS ICs production. This requirement means that limits are tightened on temperatures used for high temperature processing and times. Is should be stated however, that quality of the formed by thermal oxidation silicon dioxide (classical gate dielectric layer) depends very much on the temperature of this process. As a consequence we are facing contradictory demands, impossible to satisfy when using conventional high temperature oxidation process.

Already at the beginning of the eighties it was shown [e.g., 1, 2] that silicon dioxide exhibiting quite good properties can be formed by means of plasma anodisation. Only recently, however, the conditions favourable for serious

consideration of its application to CMOS-ULSI ICs fabrication have appeared. Application of standard plasma equipment to plasma oxidation of silicon usually results in too high oxidation rates, which do not allow precise control of ultrathin layers formation. Thus, the first problem to be solved, is finding such values of the process parameters that allow slowing down oxidation rate.

The attempts of to slow down the oxidation process [e.g., 3] (oxidation in microwave O_2 and Kr plasma) do not look very promising due to the radiation damage effects caused by Kr^+ silicon surface bombardment. Thus, other options have to be looked after. Still, final decisions on possible applications of this technique to CMOS-ULSI technology will mainly have to take into account electro-physical properties of the plasma oxides.

PROCESS DESCRIPTION AND ITS OPTIMISATION

Plasma oxidation, on the contrary to all deposition methods, consumes silicon substrate in order to form silicon dioxide layer. The process can take place in very low temperature (even room temperature) due to high reactivity of oxygen ions with silicon atoms at the substrate surface. It is however well known fact, that the properties of the silicon dioxide layer are very sensitive to temperature (very good quality oxide layers cannot be formed in temperatures below 900°C). Therefore, to promote possibly best quality oxide formation, in this study the plasma oxidation was carried on in the highest effectively stabilised temperature allowed by plasma reactor manufacturer, i.e. 350°C.

The processes were carried out in typical planar reactor, typically used for PECVD. The computer controlled system allowed independent control of: substrate temperature, pressure, r.f. power and introduced to reactor chamber gas flows. As a rule, just after each oxidation process, the process gases were evacuated by pump system and short (10 minutes) annealing was performed in vacuum conditions in 350°C (the same temperature as oxidation process).

The optimisation objective was to get parameters of the process allowing formation of utlrathin plasma oxides with reasonable repeatability and good control. Although, due to very low temperature of the silicon samples typical thermally excited oxidation could be neglected, however, in parallel plate reactors powered with r.f. (13.56 MHz) generators the plasma density is usually too high to allow good control of ultrathin layers formation. Few, relatively simple possibilities of decreasing the oxygen plasma density can lead to certain technological problems. For example, decrease of oxygen pressure leads to rise in energy of ions bombarding the silicon surface, which cause radiation damage, thus poor oxide quality is obtained. Decrease of r.f. power, on the other hand, can lead

to poor plasma uniformity, which in turn inevitably causes formation of non-uniform oxide layers.

Hence, true optimisation procedure was needed to reach the set of process parameters fulfilling the optimisation objective. The plasma oxidation parameters, which resulted from the performed in this study optimisation experiments, are show in Table 1.

One of the solutions discussed in the literature is oxidation in mixed plasmas (oxygen mixture with noble gas), e.g. in $Kr:O_2$ plasma [3]. Decreasing density of oxygen reactive ions in dense plasma, allows control of oxidation process by limiting oxidising species in the vicinity of silicon surface. Such an approach can, however, also be dangerous, from oxide properties point of view, as Kr ions can also create a lot of damage in the growing ultrathin oxide.

In our study, the concept of mixed plasma (diluted in noble gas oxygen) was examined experimentally by oxidation in $Ar:O_2$ plasmas, and in parallel – by theoretical calculations of possible radiation damage. The experiments in $Ar:O_2$ plasma were carried out with oxygen flow set exactly as for optimised process (50 sccm), with additionally 100 sccm of argon added [giving $Ar:O_2$ (2:1) volume mixture].

PLASMA OXIDATION KINETICS STUDY

The parameters values show in Table 1 were then used for series of experiments leading to determination of the kinetics of process. Figs 1 and 2 present the kinetics of the process and dependence of refractive index N_f of the formed layers respectively. One can see, that the obtained growth curve shows relatively low oxidation rates for oxides thicker than 2.0 nm, which allows quite precise control of the oxide thickness in the ultrathin thickness range. Performed tests on oxide stability – by high temperature nitrogen anneals (in standard high temperature furnace) after plasma oxidation - show, that up to 800°C the oxide is quite stable (see Fig.1). For annealing in 1000°C, however, the final thickness change considerably proving that some effects take place when plasma oxide is exposed to such high temperature. It is interesting to realise that there is no evidence of these effects on refractive index value (see Fig. 2) and for all these experiments the determined N_f value is well within the range characteristic for stoichiometric silicon dioxide layer (1.46 ÷ 1.47). This, usually sensitive optical parameter remains almost unchanged despite the high temperature annealing. The evaluation of the refractive index from the ellipsometric data was very reliable, due to the fact, that measurements were performed in wide wavelength range (240 nm ÷ 1100 nm) and two incident beam angles (65° and 75°) were used for each

analysis. The fitting of theoretical model to the experimental data was therefore excellent, as can be seen in Fig. 3.

The only results falling away were the refractive index values of all the oxides which were produced in $Ar:O_2$ (2:1) mixture, instead of pure oxygen plasma. The obtained N_f values for these layers are much too low to consider them as pure silicon oxide. Amazingly, the thicknesses of these layers (particularly in the range above 6 nm) are very close to the ones formed in pure oxygen plasma (compare Fig. 1).

The XPS analysis was performed to obtain reliable information on composition of formed by optimised process oxide layers. The atomic concentration profiles of all atoms determined within the layer are shown in Fig. 4. Except for very shallow surface contamination with carbon and very small concentration of fluor (!), only oxygen and silicon were found in significant quantities in the layers. The reason of the presence of fluor is not yet known and will have to be studied in more detail later.

THEORETICAL CALCULATIONS OF POSSIBLE RADIATION DAMAGE

Performed with SRIM model theoretical calculations of the consequences of Ar and O ions bombardment of silicon show (see Figs. 5 and 6), that even for bombarding substrate ions energy as low as 40 eV, some silicon atoms are displaced, while oxygen or argon get implanted, causing defects in the monocrystalline lattice of the substrate. The depth of silicon affected by these changes is of the order of 10 Å for 40 eV, while for 100 eV is almost twice as big. It should be realised that these thicknesses are considerable fraction of the layers to be grown. Thus, these effects certainly affect considerably kinetics of oxide growth as well as properties of the layers formed. From the presented figures it becomes obvious that Ar is more "dangerous" in this respect than O_2. Hence, the second stage of the study concerned only the plasma oxidation in pure oxygen.

ELECTRICAL CHARACTERISATION OF THE ULTRAHIN OXIDE 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 plasma oxide layers. This technology enables fabrication of MOS devices without any high temperature treatment after gate dielectric formation. This way, the properties of the "as formed" and annealed in 600°C and 1000°C in pure nitrogen just after plasma oxidation, could also be compared basing on results obtained by the electrical characterisation methods.

Number of electrophysical parameters was then determined using classical MOS methodology. The results are collected in Table 2. 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. 7. One can see the differences in maximum capacitance, position on voltage axis and slope between these curves.

The C-V shift along voltage axis is attributed to change in effective charge density Q_{eff} (see Table 2). At first glance the Q_{eff} does not decreases (as expected), on the contrary – it slightly increases after annealing in 600°C, and remains practically the same after annealing in 1000°C. However, we have to introduce the oxide thickness changes (due to annealing) into account. If we do so, we can see that annealing in 600°C truly increased the planar density of effective charges, but annealing in 1000°C – has reduced it considerably.

Also the properties of the silicon-oxide interface improved after the annealing in 1000°C (see Table 2). Interface traps density (at the silicon mid band) $D_{it\ mb}$ decreases by approximately factor of two after this annealing.

Very interesting results were also obtained by measurements of dielectric breakdown voltages (under the steps like voltage stress). The examples of J=f(E) curves are shown in Fig. 8. It can be seen there that oxides annealed in 1000°C and plasma oxides formed in 5 minutes process instead of 2 minutes - exhibit much lower leakage currents through the oxide. Thus, also in this case, the annealing in 600°C does not show improvement of the oxide quality. The Weibull plots for the same series of measurements (see Fig. 9) prove however, that even "as formed" plasma oxide exhibits satisfactory resistance to electrical breakdown, while with increasing annealing temperature the critical electric field can rise even to some 17 MV/cm – the values not seen for thermal silicon dioxide.

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.

CONLCUSIONS

In the course of this study, the plasma oxidation of silicon was optimised to enable formation of ultrathin (< 6 nm) layers. The kinetics of the optimised process allows good control and repeatable results of plasma oxidation. The refractive index value of these layers is the same as of stoichiometric thermal oxides. The optical properties of these layers are stable even up to 1000°C.

The introduction of argon to plasma, in order to dilute oxidant, can cause significant radiation damage, as was shown experimentally by refractive index

analysis and theoretically – by using SRIM calculations. Pure oxygen plasma seems to be safer in this respect.

The electrical characterisation methods prove, that annealing in nitrogen in 600°C improves only the oxide integrity (E_{BR}), while annealing in 1000°C, 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 oxide layers (even without annealing) is very good, even when compared with state-of-the-art thermal silicon dioxide.

The nature of these changes in yet known and will have to studied in more detail in the future.

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Table 1. Parameters of the optimised for ultrathin layers formation r.f. plasma silicon oxidation.

Parameter	Value
Process temperature [°C]	350
R.F. power (13.56MHz) [W]	50
Pressure [Torr]	0.5
O_2 flow [sccm]	50
Standard annealing time @ 350°C	10

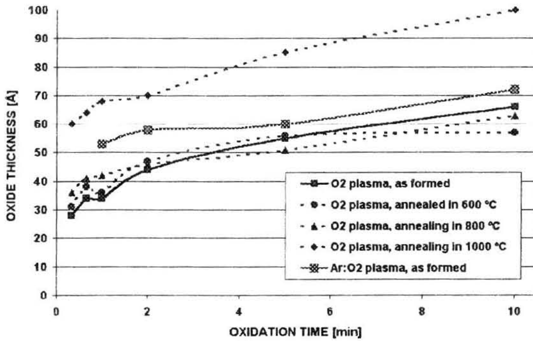

Fig. 1. Kinetics of plasma oxidation for optimised set of parameters and performed in O_2 and O_2:Ar (1:2) mixture plasmas and as formed or annealed in 600°C, 800°C or 1000°C.

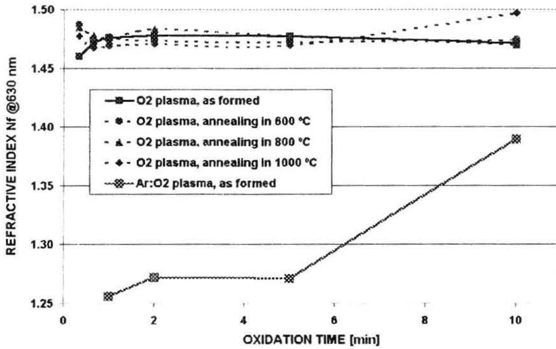

Fig. 2. Dependence of refractive index of the oxidised layer on deposition time for O_2 and Ar:O_2 (2:1) mixed plasma and as formed or after 600°C, 800°C or 1000°C annealing in nitrogen.

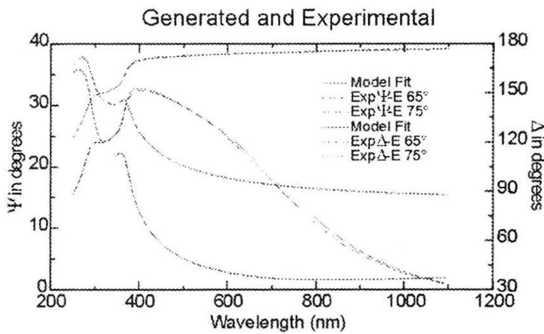

Fig. 3. Result of fitting the theoretical model to experimentally obtained for two incident beam angles (65° and 75°) ellipsometric data.

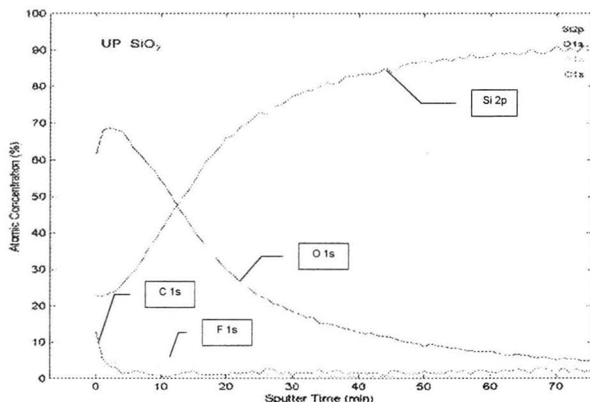

Fig. 4. Obtained by XPS in-depth profile of atomic concentration within the plasma oxide layer.

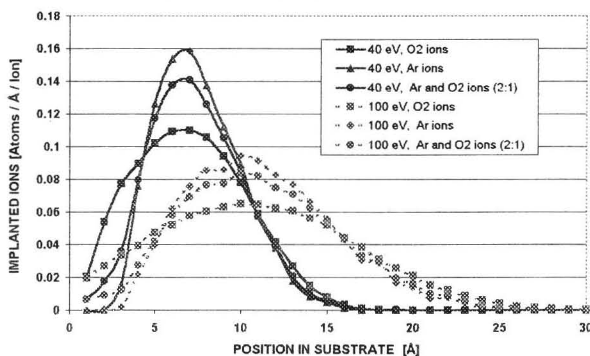

Fig. 5. The distribution of implanted atoms (Ar and O) during plasma oxidation in pure O_2 , Ar and $Ar:O_2$ (2:1) mixture, as calculated with SRIM.

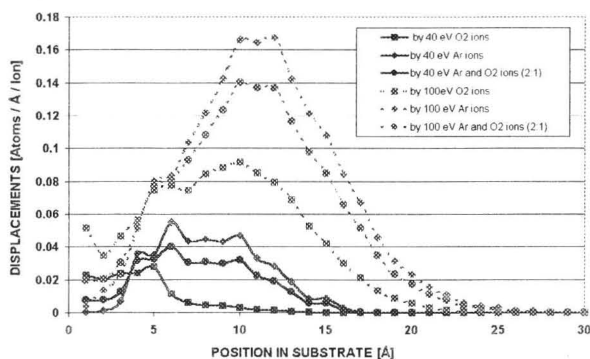

Fig. 6. The distribution of Si atoms displaced by: O_2, Ar or mixture of O_2:Ar (1:2) ions, calculated for 40 eV and 100 eV with SRIM.

Table 2. Parameters evaluated from the analysis of test structures electrical characteristics.

Sample	B4	B1	B5	B2
Oxidation time [min]	2	2	2	5
Process temperature [°C]	350	350	350	350
Pressure [Torr]	0.5	0.5	0.5	0.5
O_2 flow [sccm]	50	50	50	50
Standard annealing time (@350°C) [min]	10	10	10	10
High temperature annealing [C]	-	600	1000	-
High temperature annealing time [min]	-	30	30	-
Optical thickness (by ellipsometry) [A]	44	47	70	55
Electrical thickness [A]	38	35	105	46
Refractive index @630nm	1.476	1.473	1.470	1.477
Q_{eff}/q [cm^{-2}]	2.7e12	3.8e12	3.7e12	2.1e12
$D_{it\ mb}$ [1/eV cm^2]	7.2e12	7.5e12	2.9e12	6.3e12
E_{BR} [MV/cm]	9	13	17.5	13

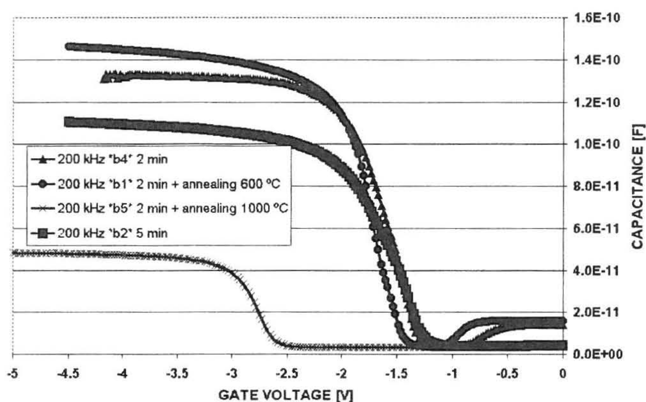

Fig. 7. High frequency C-V characteristics of MOS capacitors with ultrathin plasma oxide films ("as formed" and annealed in 600°C and 1000°C) as gate dielectrics.

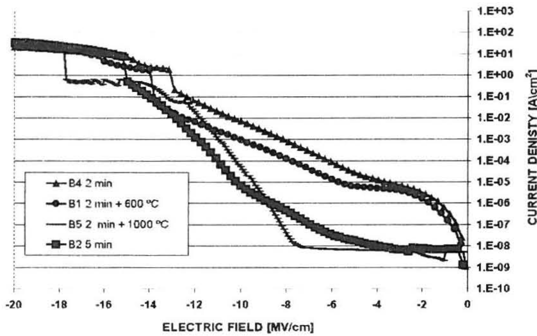

Fig. 8. Comparison of the J=f(E) characteristics for test structures containing as formed and annealed in 600°C and 1000°C plasma oxide layers.

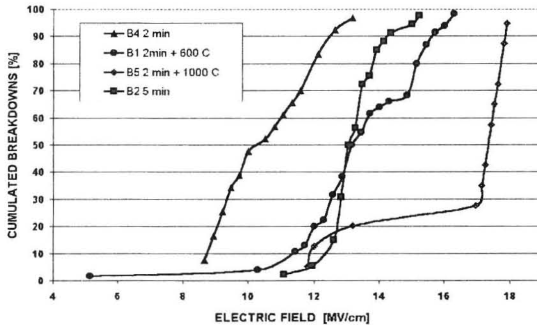

Fig. 9. Weibull plots for breakdowns measured under ramping voltage conditions on MOS structures with "as formed" and annealed in 600°C and 1000°C plasma oxide layers.

UTLENIANIE KRZEMU PLAZMĄ NISKOTEMPERATUROWĄ – MOŻLIWOŚCI ZASTOSOWANIA W TECHNOLOGII CMOS-ULSI

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S t r e s z c z e n i e. Praca poświęcona jest eksperymentalnej analizie potencjalnych możliwości zastosowania procesów utleniania w plazmie w.cz. (13.56 MHz) do wytwarzania ultracienkich (<6 nm) warstw tlenku bramkowego w układach MOS. Proces prowadzony jest w bardzo niskiej temperaturze (350°C), a uzyskana kinetyka pozwala na łatwe sterowanie procesem i uzyskiwanie warstw w bardzo szerokim zakresie (od 2 nm do ok.20 nm). Pomiary za pomocą elipsometrów (także spektroskopowego) pozwoliły na niezawodne wyznaczanie grubości warstw i weryfikację jakości warstwy.

S ł o w a k l u c z o w e : utlenianie krzemu, plazma niskotemperaturowa, technologia CMOS-ULSI.