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Paper

Composition and electrical properties of ultra-thin SiO_xN_y layers formed by rf plasma nitrogen implantation/plasma oxidation processes

Tomasz Bieniek, Romuald B. Beck, Andrzej Jakubowski, Piotr Konarski, Michał Ćwil, Patrick Hoffmann, and Dieter Schmeißer

Abstract—Experiments presented in this work are a summary of the study that examines the possibility of fabrication of oxynitride layers for Si structures by nitrogen implantation from rf plasma only or nitrogen implantation from rf plasma followed immediately by plasma oxidation process. The obtained layers were characterized by means of: ellipsometry, XPS and ULE-SIMS. The results of electrical characterization of NMOS Al-gate test structures fabricated with the investigated layers used as gate dielectric, are also discussed.

Keywords*—*CMOS, gate stack, oxynitride, plasma implantation.

1. Introduction

According to the ITRS roadmap [1] the thickness of the gate dielectric layer will be dramatically reduced in the near future to 6–8 Å in 2011. Such extremely thin layers generate, however, a lot of problems in terms of processing repeatability and reliability. This, in turn, creates a pressure to substitute silicon dioxide with a single layer of high-*k* material or – more probably – with a gate stack (a combination of high-*k* material and pedestal layer passivating silicon-dielectric interface).

Oxynitride layers seem to be very promising in this respect. This is mostly due to the fact that silicon nitride layers are known to be very resistant to diffusion and thus oxidation (vide their application for LOCOS), while oxide is undisputedly the best possible passivating layer for silicon surface.

Oxynitride layers can be produced with number of methods. The experiments presented in this work are a summary of the study that examines the possibility of fabrication of oxynitride layers for Si structures by nitrogen implantation from rf plasma (denoted hereafter as "as-implanted") or nitrogen implantation from rf plasma followed immediately by plasma oxidation process.

In contrast to the methods presented in the literature so far (e.g., [2, 3]), where the classical implanters or the ion immersion implantation in plasma (IIIP) technique were used for implantation, in this work we used a typical rf plasma planar reactor, usually applied for plasma enhanced chemical vapour deposition (PECVD) – Oxford plasma technology – PlasmaLab 80+.

2. Experimental

In this work ultra-thin oxynitride layers were formed during plasma processes. Ultrashallow plasma implantation of nitrogen ions and low temperature plasma oxidation were used to form the layers. Both these processes were performed, as already mentioned above, in a PECVD reactor. For the purpose of this study, the layers were formed under different conditions. The variable process parameters were: implantation time, rf power, nitrogen source gases, and temperature. A detailed process description may be found in [4–6].

Two-stage analysis of the studied ultra-thin oxynitride layers was performed. In the first stage, the layers formed using nitrogen plasma implantation only (as implanted) were characterized in order to understand the state of the silicon substrate right after plasma implantation. In the second stage, the layers formed using nitrogen implantation followed by plasma oxidation underwent similar analysis, to understand the consequences of the complex process.

Each stage included structural (i.e., optical – ellipsometry, chemical and physical X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and electrical (electrical measurements of NMOS test structures with investigated layer used like a gate dielectrics) analysis. Structural analysis was aimed at independent determination of the chemical composition and thickness of the layers [7–9]. In order to perform electrical characterization of the layers, NMOS Al-gate test structures with ultra-thin dielectric layers formed using the studied method were fabricated. Al gate was chosen to avoid any thermal treatment after the gate dielectric was formed.

The NMOS test structures were then electrically characterized by means of *C-V* and *I-V* measurements in order to evaluate: leakage currents, effective charge density and trapping and breakdown behavior.

3. Results

3.1. Samples with nitrogen plasma implantation only (as-implanted)

In the first step, analysis of the correlation between the ultrashallow plasma implantation and composition and thick-

ness of the affected silicon layer was studied. The following parameters of plasma implantation were of interest: type of nitrogen source gas, rf plasma power, implantation time and sample temperature during implantation.

The XPS studies have revealed that despite using either nitrogen or ammonia plasma during implantation, the implanted substrate region consists mostly of silicon dioxide. This must be the result of a spontaneous oxidation upon the exposure of the samples to the atmosphere when removing them from the plasma reactor. Even though the implantation temperature is only 200°C or 350°C – the results prove that the implantation leaves the silicon surface very prone to oxidation even in such usually unfavorable conditions.

There are, however, small differences in the composition of the studied layers depending on the nitrogen source (see Fig. 1). Marginally higher content of nitrogen is observed for nitrogen implantation from ammonia plasma. Different nitrogen content and/or damage caused to the silicon surface during nitrogen implantation result in significantly different overall layer thickness – lower for implantation from ammonia than from nitrogen plasma. Thus, it seams reasonable to choose ammonia plasma for the purpose investigated in this paper and this choice has been adopted for the subsequent investigation.

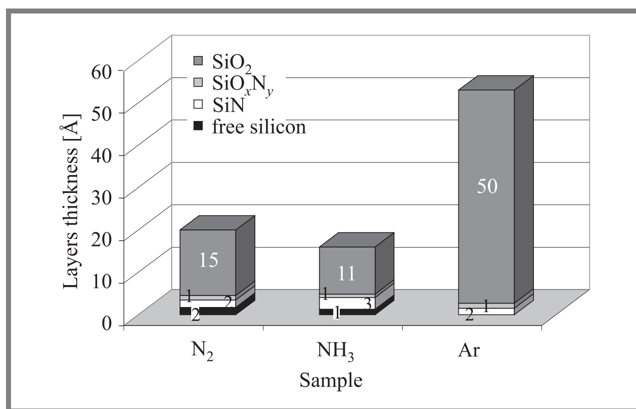

Fig. 1. Chemical composition and thickness obtained from XPS for layers formed in different plasmas (NH_3, N_2, Ar) – normalized to the optical thickness.

From the reference experiment in which the silicon sample was subjected to Ar plasma bombardment (for the same as in case of nitrogen and ammonia plasmas rf power – 100 W) one can evaluate the influence of substrate damage caused by bombarding ions. Comparison of the thickness of spontaneously oxidized layers after exposure to either Ar or nitrogen plasma clearly proves that the nitrogen presence in the surface silicon layer significantly slows down the oxidation rate.

This in turn proves that the presence of nitrogen-rich oxide at the silicon surface may be effectively used to prevent or at least to reduce oxide growth at the silicon interface during high-*k* dielectric deposition and/or source and drain dopant activation annealing.

The next correlation to investigate was the influence of implantation rf power. The analysis based on the example of NH_3 samples shows that rf power is a very important process parameter (see Figs. 2 and 3). Increasing implantation power results in a decrease of the layer thickness and in minor changes of its chemical composition (see Figs. 2a and 2b). It is not obvious if these changes are sufficient to cause the observed reduction of the layer thickness. The other possibility is that changing rf power affects the density of the plasma and thus also the implantation and substrate damage efficiency, which in turn can lead to a change in spontaneous oxidation rate. Additional data for this analysis may be obtained from ultra-low energy SIMS (ULE-SIMS).

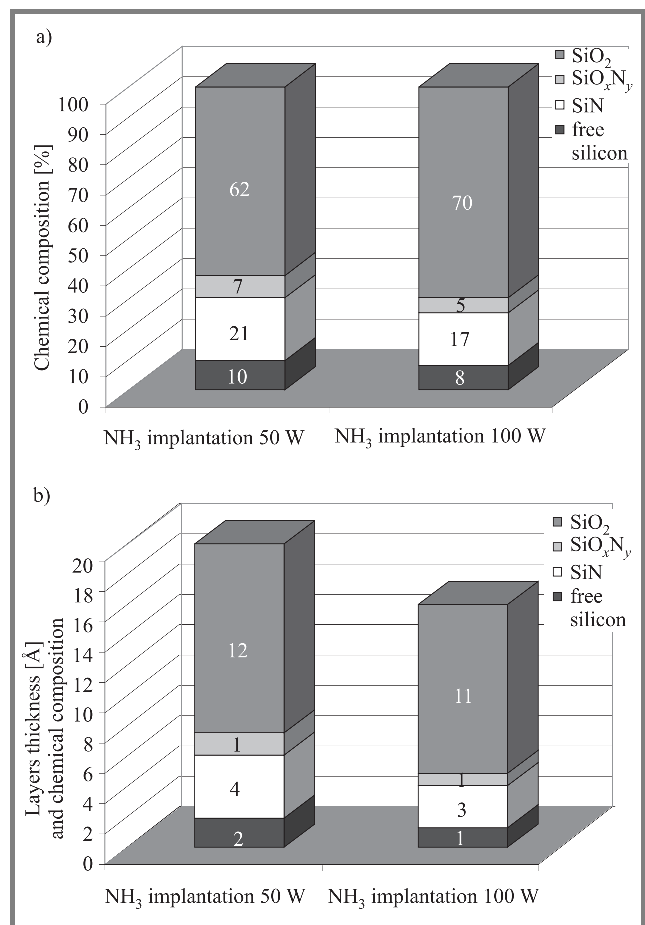

Fig. 2. Chemical composition and thickness obtained from XPS for layers formed in NH_3 plasma for two different levels of rf implantation power (50 W and 100 W) normalized to: (a) 100%; (b) to the layer thickness.

Analysis of ULE-SIMS data yielded similar results to the ones obtained from XPS. They prove that rf power used for nitrogen implantation is a crucial process parameter. Depending on rf power used, the maximum of the nitrogen profile may be located just at the top surface of the layers (for power not higher than 100 W) or within up to 1.0 nm from it (see Fig. 3). It seems, therefore, that the nitro-

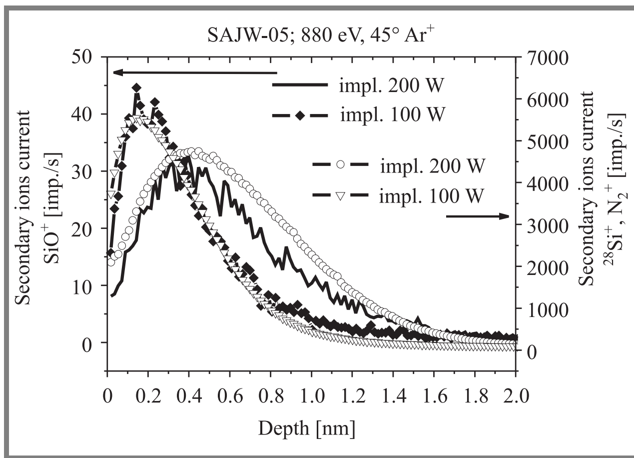

Fig. 3. Examples of ULE-SIMS results – secondary ion current for SiO^+, Si^+, N_2^+ for the samples implanted from NH_3 for two different rf power levels (100 W and 200 W).

gen profile may be optimized by choosing the appropriate rf power for nitrogen implantation.

A profile of this depth is difficult (if not impossible) to obtain by other techniques. The depth correlates well with the desired final thickness of the oxynitride layer. This means that when the formation of ultra-thin oxynitride layer is finished (that is after oxidation) the nitrogen profile will not extend into the device channel region.

The XPS study of the samples exposed to plasma implantation of nitrogen for different time (see Fig. 4) demonstrates that the amount of nitrogen rich phases (oxynitrides and nitrides) reaches a maximum at a certain implantation time. For the studied cases the highest content of nitrogen was observed in layers obtained by 10 min implantation. In practice, however, it may be difficult to use this parameter to optimize nitrogen content since the layer thickness is also dependent on implantation time.

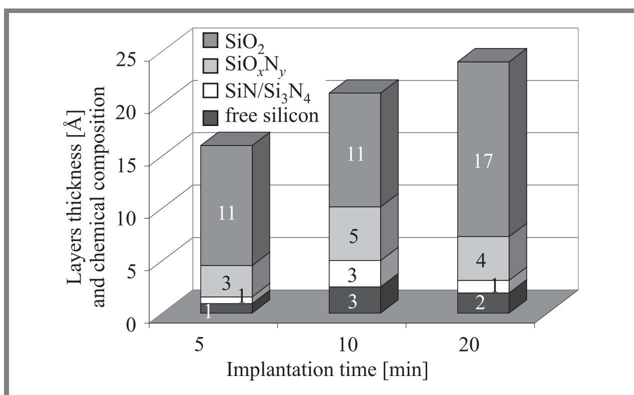

Fig. 4. Chemical composition and thickness obtained from XPS for different times of implantation (5 min, 10 min, 20 min) – normalized to the optical thickness.

The last parameter of nitrogen implantation to be studied was the temperature of the silicon substrate. The surprising result obtained in this study can be seen in Fig. 5a, which demonstrates that no differences in the chemical content are observed between the layer obtained at temperatures ranging from 200°C to 350°C. Interestingly enough higher temperatures promote layer growth (23 Å versus 45 Å for 200°C and 350°C, respectively – see Fig. 5b). The nature of this dependence is not clear. One might speculate

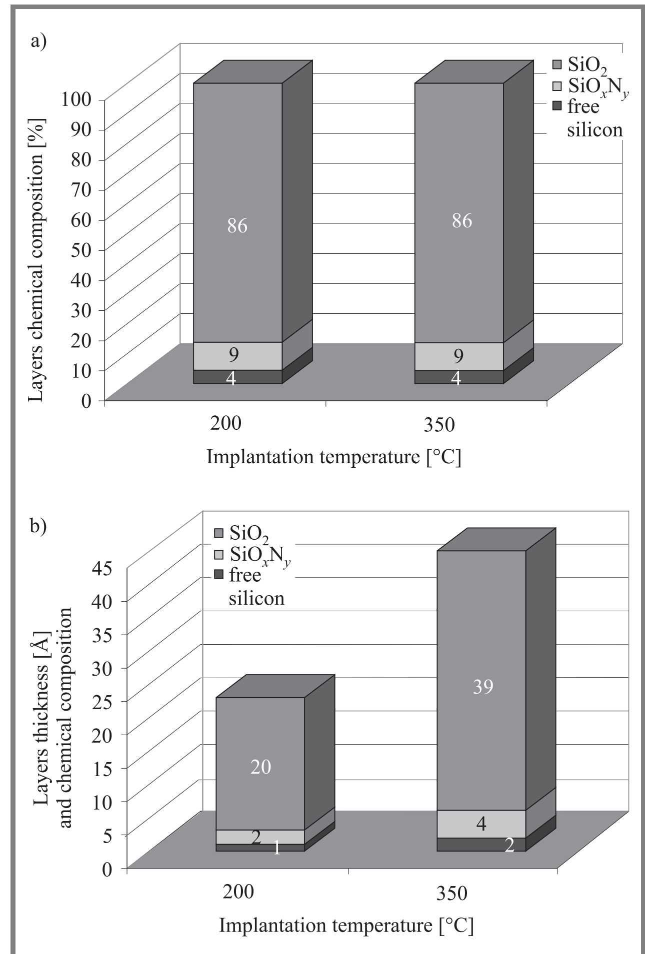

Fig. 5. Chemical composition and thickness obtained from XPS for layers formed at different implantation temperatures (200°C and 350°C) – normalized: (a) to 100%; (b) to the optical thickness.

that higher temperatures allow easier (and faster) formation of nitride bonds, which in turn increases the silicon substrate oxidation rate. Such an explanation would be, however, only true if silicon oxidation took place during implantation and not, as believed until now, exclusively during the exposure to the clean-room atmosphere.

3.2. Samples with nitrogen implantation followed by plasma oxidation

The next stage of analysis refers to the structural investigations of the layers formed using plasma implantation of nitrogen followed by plasma oxidation. Introduction of the second process step – plasma oxidation – has created new parameters to be decided upon. From previous studies

on plasma oxidation alone we have chosen the rf power of 50 W and oxygen pressure of 0.5 Tr for this process. Oxidation time was studied using XPS, similarly to the previous case. From the spectra presented in Fig. 6 we can clearly see that even half minute oxidation after nitrogen implantation is enough to form an oxynitride layer with high silicon dioxide content. Any oxidation, longer than 0.5 min, gives SiO_xN_y layer with similar oxygen content and profile. For the sake of this study, the plasma oxidation time was set to 2 min. The following experiments aimed at checking the influence of plasma oxidation on the composition of the final layer.

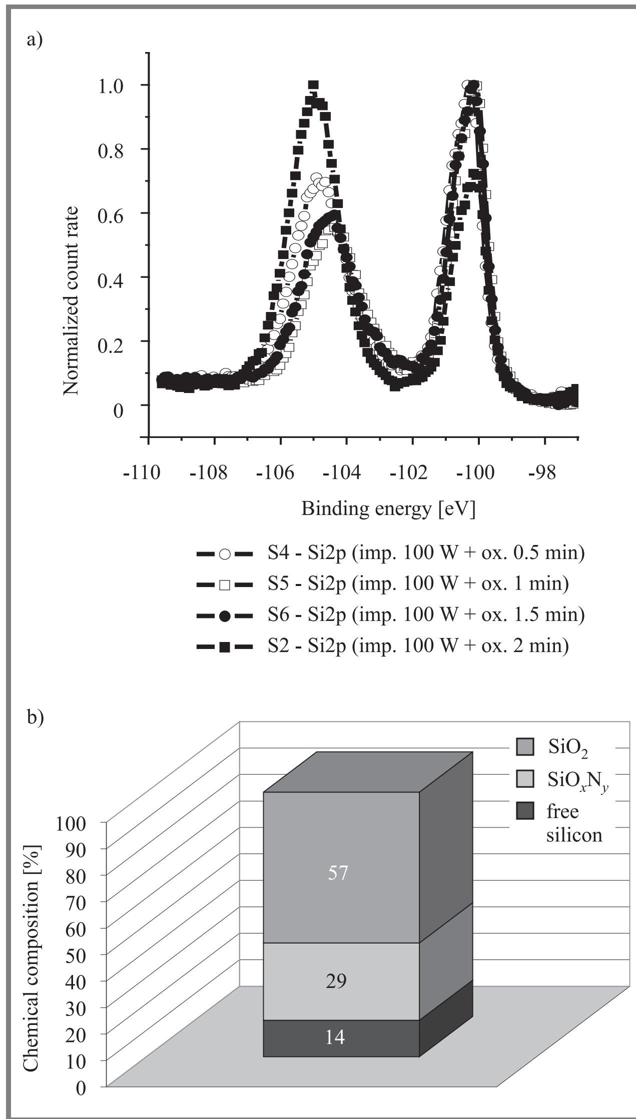

Fig. 6. Results of XPS measurements: (a) Si2p peaks for the samples implanted from NH_3 plasma at 100 W and plasma oxidized for different oxidation times (0.5; 1; 1.5, 2 min); (b) composition of the layer plasma oxidized for 2 min.

The XPS spectra shown in Fig. 7 prove that as a result of plasma oxidation we obtain almost the same composition of the oxynitride layer (as shown in Fig. 6b) regardless of the rf power used for nitrogen implantation.

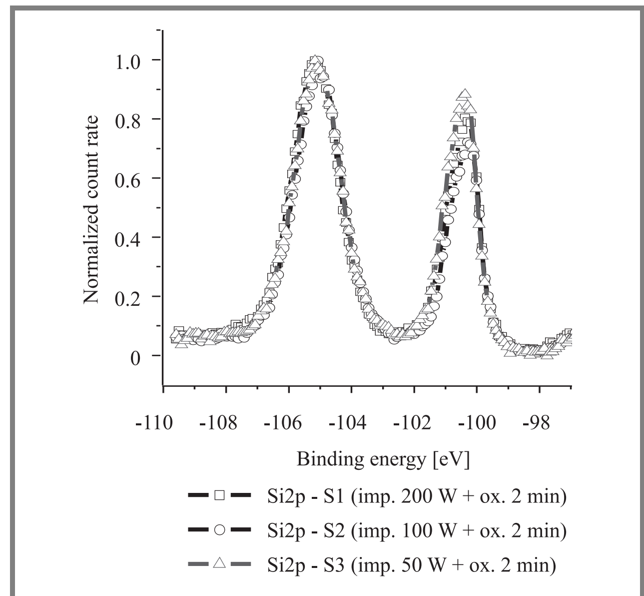

Fig. 7. Si2p peak for samples implanted from NH_3 plasma at three different levels of rf power (50 W, 100 W and 200 W) and oxidized in oxygen plasma for 2 min.

3.3. Electrical characterization

The test structures for the analysis of electrophysical properties were fabricated using different nitrogen implantation conditions. In order to establish the most sensitive relations between the properties of the layers and plasma process parameters the test structures were fabricated using different rf plasma power for plasma implantation. It should be remembered here that this parameter appeared to have the greatest influence on the properties of the layers directly after implantation. Two samples were fabricated using NH_3 as nitrogen source at different levels of rf power (sample 5–100 W and sample 6–50 W). For the sake of comparison, one sample was also produced with the layer formed using N_2 plasma (sample 4). Process parameters and characterization results are summarized in Table 1.

Analysis of electrical characteristics of NMOS test structures has shown strong correlation between plasma process parameters and electrical properties of the layers. This result was rather surprising since XPS analysis revealed that layer composition after plasma oxidation was the same regardless of the initial state after nitrogen implantation.

High frequency *C-V* curves shown in Fig. 8 form two clearly distinguishable groups. One curve (sample 1) is shifted towards negative voltage with respect to all the other curves (including also those obtained from as implanted samples 5 and 6). This voltage shift is the consequence of much higher effective charge concentration Q_{eff}/q (see Table 1). This confirms the results of the XPS analysis, which indicated that implantation at 200 W from NH_3 plasma created significantly more damage than processes carried out at lower values of rf power [4–6].

The differences in maximum capacitance $C_{\max}$ are the obvious consequence of the variation in layer thicknesses,

Table 1
The technological process parameters of oxynitride layer formation and the results of optical and electrical characteristics evaluation for NMOS test structures manufactured in this study

Parameters	Samples					
	1	2	3	4	5	6
Step 1 – nitrogen ions implantation (350°C)						
Power [W]	200	100	50	50	100	50
Gas/plasma	NH_3	NH_3	NH_3	N_2	NH_3	NH_3
Step 2 – plasma oxidation (350°C, 50 W, O_2)						
Optical characterization						
Layer thickness [Å]	33	24	24	52	45	32
Electrical characterization (from *C-V* curves)						
EOT [Å]	59	37	35	41	33	40
U_{fb} [V]	–2.2	–1.1	–1.0	–1.1	–1.2	–1.2
Q_{eff}/q [cm^{-2}]	$4.7 \cdot 10^{12}$	$9.0 \cdot 10^{12}$	$4.9 \cdot 10^{11}$	$7.0 \cdot 10^{11}$	$1.8 \cdot 10^{12}$	$1.1 \cdot 10^{12}$
Q_{eff}/q/optical thickness [cm^{-2}/Å]	$1.4 \cdot 10^{11}$	$3.8 \cdot 10^{10}$	$2.0 \cdot 10^{10}$	$1.3 \cdot 10^{10}$	$4.0 \cdot 10^{10}$	$3.4 \cdot 10^{10}$
D_{itmb} $1/\mathrm{eV\,cm}^2$	$1.8 \cdot 10^{13}$	$1.5 \cdot 10^{13}$	$8.0 \cdot 10^{12}$	$1.2 \cdot 10^{13}$	$9.8 \cdot 10^{13}$	$7.7 \cdot 10^{12}$
Electrical characterization (from *I-V* curves)						
$E_{breakdown}$	17.8	20.4	19.6	10.6	10	–*
* No catastrophic physical breakdown could be detected for these devices.						

compositions, as well as in leakage current for particular wafers. Leakage is related with oxide structure integrity, therefore should also be reflected in the effective dielectric constant of the studied oxynitride layers. These values obtained from $C_{\max}$ (oxynitride thickness was determined independently by ellipsometry) have confirmed the above mentioned relations between samples.

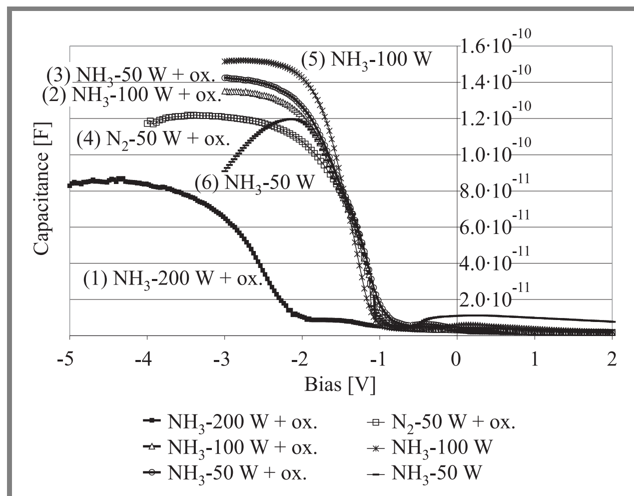

Fig. 8. Typical high frequency *C-V* curves for the studied NMOS test structures with the gate dielectric layers produced with different plasma parameters (varied rf power and nitrogen gas source) [6].

The *C-V* behavior of as implanted samples proves that a dielectric film (identified by XPS as oxynitride layer) is formed on top of the silicon substrate already after nitrogen implantation. This observation confirms that the exposure of the as-implanted silicon surface (please, keep in mind that the wafer temperature is 350°C before the plasma reactor is vented) to the atmosphere is enough to form an oxynitride layer. The quality of such layers (as-implanted) expressed in terms of charge and trap densities in the studied system is, amazingly, comparable to those formed by plasma oxidation only. The significant difference between these two groups (as-implanted and oxidized), as it will be shown below, exists in leakage currents and breakdown properties, which suggests that the main difference between them lays in the integrity of the dielectric layer.

Simple and intuitively obvious dependence between rf plasma power and the densities of the effective charge Q_{eff} and traps D_{itmb} has also been confirmed. The values of both of these parameters rise with the increase of rf power. Taking into consideration different final thickness of the oxynitride layers obtained under different conditions makes this dependence even stronger (see Q_{eff}/q normalized to the layer thickness in Table 1).

It is interesting to realize that although N_2 implanted samples exhibit relatively low Q_{eff}/q values (especially when normalized to the layer thickness) – their interface properties (expressed in D_{itmb}) are worse than those of the 50 W, NH_3-implanted sample.

The typical *I-V* curves (for the purpose of easier comparison drawn in the *J-E* scale) for individual samples studied in this work are presented in Fig. 9. In all of the examined cases (except of sample 6) the breakdown events were

well defined, thus, the Weibull plots could be constructed (see Fig. 10).

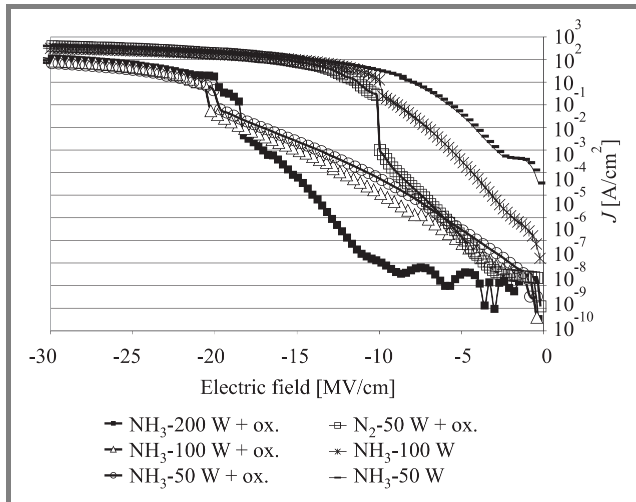

Fig. 9. Typical *J-E* curves for the studied NMOS test structures; gate dielectric layers were produced with different plasma parameters (rf power and nitrogen source gas) [6].

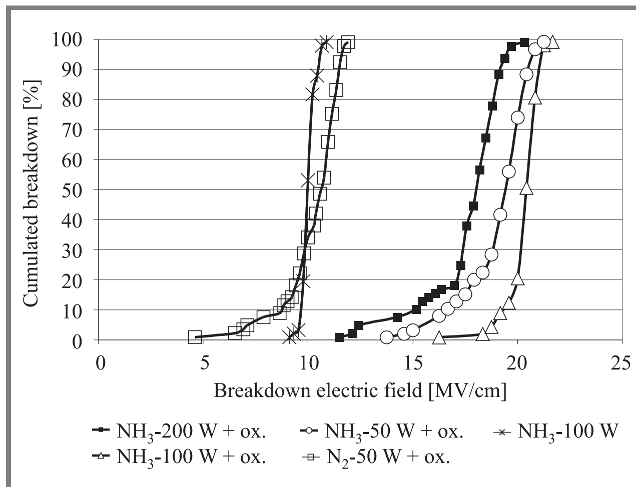

Fig. 10. Weibull's plots for the studied NMOS test structures; gate dielectric layers were produced with different plasma parameters (rf power and nitrogen gas source) [6].

The as-implanted samples (without plasma oxidation) exhibit obviously the highest leakage currents. In the case of the sample implanted at 50 W this current is approximately two orders of magnitude higher than that of the sample implanted at 100 W.

Among the samples which underwent plasma oxidation, N_2 implanted sample proves again to be inferior to the rest. Although its critical electric field is comparable to that typically achieved by thermal SiO_2 layers ($\sim$ 10 MV/cm), other samples exhibited much higher values. The best result (20 MV/cm) was observed in the oxynitride sample formed by implantation from NH_3 at 100 W.

It is interesting to realize that the lowest leakage current is observed for the sample implanted from NH_3 at 200 W, which is the worst among implanted and oxidized samples in terms of charge and trap density In the high electric field region the current for this sample was even a few (up to three) orders of magnitude lower than that for the samples implanted from NH_3 at lower rf power (100 W and 50 W).

The Weibull plots created from the results of *I-V* measurements are shown in Fig. 10. It is interesting to realize that all of them are very steep, proving practically single mode breakdown properties and no (or very little) early, defect related breakdowns.

4. Summary

The nitrogen implantation from rf plasma either alone or followed by plasma oxidation was studied as a potential method to fabricate ultra-thin oxynitrides layers.

It has been proved that nitrogen implantation from NH_3 can be more effective than from N_2. The rf power can be successfully used to control both, the thickness and composition of an ultra-thin oxynitride layer. It can also be used to control the nitrogen profile within the oxynitride layer. The nitrogen penetration depth can be less than 1.0 nm. Thus, no degradation of MOSFET carrier mobility in the device channel should be observed.

The implantation temperature and time are not sensitive parameters, therefore this method offers significant flexibility in this respect.

Plasma oxidation rebuilds the oxynitride layer, the final composition is practically the same regardless of the parameters of the preceding nitrogen implantation. The electrophysical properties of these layers are, however, different (implantation – parameter dependent).

The effective charge and interface trap densities are, so far, hardly acceptable, but no annealing has been used in this study. The breakdown properties of the studied layers are excellent and, hence, give hope for uniform and reliable gate stacks with pedestal oxynitrides formed by this method.

Acknowledgements

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Tomasz Bieniek, **Romuald B. Beck**, and **Andrzej Jakubowski** – for biographies, see this issue, p. 7.

Piotr Konarski and **Michał Ćwil** – for biographies, see this issue, p. 8.