Comparison of composition of ultra-thin silicon oxynitride layers' fabricated by PECVD and ultrashallow rf plasma ion implantation

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Abstract—In this paper differences in chemical composition of ultra-thin silicon oxynitride layers fabricated in planar rf plasma reactor are studied. The ultra-thin dielectric layers were obtained in the same reactor by two different methods: ultrashallow nitrogen implantation followed by plasma oxidation and plasma enhanced chemical vapour deposition (PECVD). Chemical composition of silicon oxynitride layers was investigated by means of X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). The spectroscopic ellipsometry was used to determine both the thickness and refractive index of the obtained layers. The XPS measurements show considerable differences between the composition of the fabricated layers using each of the above mentioned methods. The SIMS analysis confirms XPS results and indicates differences in nitrogen distribution.

Keywords—ultra-thin dielectrics, oxynitride, SIMS, XPS, PECVD.

1. Introduction

Silicon oxynitride has been investigated extensively for several years as an alternative for silicon dioxide (e.g., [1]). This is mainly due to the fact that the dielectric constant of oxynitride is slightly higher than that of SiO_2, the reliability of the oxynitride/silicon system is better and boron and phosphorus diffusion is reduced. Moreover, the diffusion of atomic hydrogen is also suppressed by silicon oxynitride (e.g., [2]).

Nowadays, as the thickness of the gate dielectric layers has reached the scale of a few nanometers, understanding the chemical composition of such thin layers is of extreme importance. For appropriate characterization of such ultra-thin layers ultra-low energy secondary ion mass spectroscopy (ULE-SIMS) and XPS can be used [3, 4].

In this paper ultra-thin silicon oxynitride layers were fabricated in a planar rf plasma reactor. The dielectric layers were obtained in the same reactor using two different methods: ultrashallow nitrogen implantation followed by plasma oxidation (referred to hereafter as implantation/oxidation) and plasma enhanced chemical vapour deposition (PECVD). The source of plasma used during nitrogen implantation was either ammonia (NH_3) or pure nitrogen (N_2).

Chemical composition of silicon oxynitride layers was investigated by means of XPS and ULE-SIMS. Spectroscopic ellipsometry was used to determine the thickness and refractive index of the obtained layers.

2. Experimental

Two-inch $\langle 100 \rangle$ p type silicon substrates of the resistivity 4–7 Ωcm were used in this study. The silicon oxynitride films were fabricated in an Oxford plasma technology PlasmaLab 80+ system. The silicon substrates were cleaned using the standard RCA method. A schematic view of the equipment used is shown in Fig. 1.
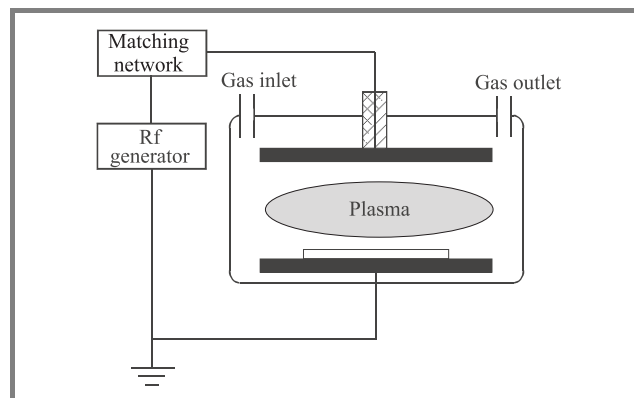

Fig. 1. Schematic view of the parallel plate reactor.

Process parameters necessary for ultra-thin oxynitride to be formed are presented in Table 1.

The properties of the obtained layers were studied by ellipsometric, XPS and ULE-SIMS analysis. A J.A. Woollam Co. ellipsometer allowing measurements at different angles with the wavelength ranging from 250 nm to 1400 nm was used to determine the thickness and refractive index of the investigated layers.

The XPS and ULE-SIMS measurements were used to investigate differences in the chemical composition and profiles of SiO_xN_y layers. XPS measurements were performed at 1254 eV at the Brandenburg University of Technology in Cottbus. SIMS measurements were done at the Industrial Institute of Electronics in Warsaw using

SAJW-05 system equipped with 06-350E Physical Electronics Ar+ gun (ultra-low energy 880 eV Ar^+ beam) and Balzers QMA-410 quadrupole mass spectrometer. Ar^+ beam (100 μm in diameter) was rastered over an area of 2 mm $\times$ 2 mm in order to get low ion current density and appropriate sputtering rate during ion bombardment. With this high in-depth resolution could be obtained.

Table 1
Process parameters allowing formation of ultra-thin dielectric layers

Parameters	Ultrashallow ion implantation		PECVD	
	Step 1 – plasma nitridation	Step 2 – plasma oxidation		
Power [W]	50		10	
Pressure [mTr]	500		300	500
SiH_4 (2%): N_2 flow [sccm]	–		150	
N_2O flow [sccm]	–		16	
NH_3 or N_2 flow [sccm]	50	–	32	
O_2 flow [sccm]	–	50	–	
Temp. [°C]	350		350	

Quantitative atomic concentration of nitrogen and oxygen was calculated based on Si_2N^+, Si_2O^+ and Si_2^+ secondary ion currents.

3. Results and disscusion

Thickness and refractive index of the obtained ultra-thin silicon oxynitride layers are presented in Table 2. These results combined with those of XPS measurements (to be discussed below) strongly indicate that the amount of silicon nitride phase is higher in the PECVD layers than in those fabricated using the implantation/oxidation technique. The refractive index of PECVD layers is significantly higher than that of implantation/oxidation ones. Additionally, its values are practically independent of process pressure (see Table 2). Moreover, the refractive index of oxynitride fabricated by means of implantation/oxidation depends on the plasma source used during implantation. In the case of pure nitrogen source the refractive index is very close

Table 2
Thickness and refractive index of ultra-thin silicon oxynitride layers evaluated from spectroscopic ellipsometry

Thickness [Å]	Ultrashallow plasma ion implantation		PECVD	
	NH_3 implantation	N_2 implantation	300 mTr	500 mTr
	36	36	30	38
N_f	1.63	1.44	1.95	1.98

to that of silicon dioxide ($N_{f\,layer} = 1.44 \approx N_{f\,SiO_2} = 1.46$) while the refractive index of layers obtained from ammonia source is between silicon dioxide and silicon nitride ($N_{f\,SiO_2} = 1.46 < N_{f\,layer} = 1.64 < N_{f\,Si_3N_4} = 2$).
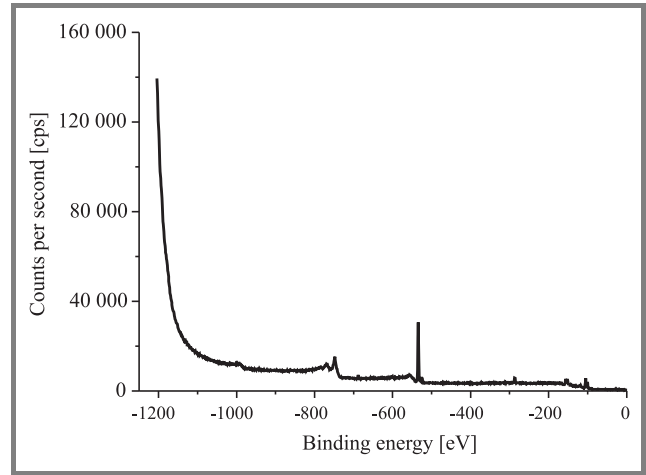

Fig. 2. The XPS spectrum of silicon oxynitride layer obtained by means of implantation/oxidation from ammonia source.

Comparison of composition and structure of ultra-thin silicon oxynitride layers was made using XPS analysis. Photoelectron spectra were taken at 1254 eV. In Fig. 2 a survey spectrum of an implantation/oxidation layer (ammonia source) is presented. Si2p ($\sim$100 eV) and significant O1s ($\sim$532 eV) peaks can be seen, while the N1s peak ($\sim$398 eV) is not noticeable. It means that the nitride phase in this layer is practically absent.
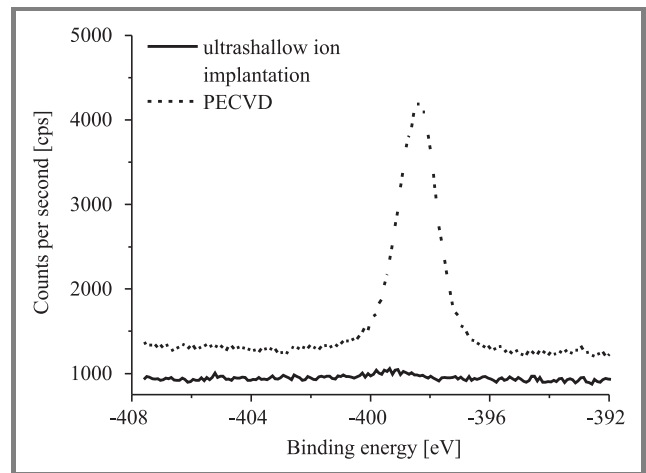

Fig. 3. Comparison of N1s spectra of PECVD and implantation/oxidation layers.

A comparison of N1s spectra obtained from PECVD and implantation/oxidation layers is shown in Fig. 3 confirming that the N1s peak of the implantation/oxidation layer is practically invisible, while it is very strong in the PECVD layer. This result might indicate that there is no nitrogen in the implantation/oxidation layers that consist of sil-

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icon oxide only. One could argue then, that the implantation step failed at implanting nitrogen into the silicon subsurface region.

It is interesting to compare the nitrogen content in the fully formed implantation/oxidation layer with that directly after implantation [5]. We can clearly see that plasma oxidation, although taking place at low temperature, is extremely effective in removing nitrogen from the formed layer. Lower energy of nitrogen bonding with silicon than that of oxygen bonding with silicon is a well known reason for such an effect. However, this type of behavior has been so far reported in the case of high-temperature oxidation. In this work we have found evidence that this effect is also true for plasma oxidation at 350°C. As it will be shown below, some nitrogen remains in the oxide-silicon system.

In the PECVD layer, in turn, the amount of bonded nitrogen is significantly higher than implantation/oxidation layers – the nitrogen peak is clearly visible (see Fig. 3).

A comparison of O1s spectra of both types of ultra-thin silicon oxynitride layers is presented in Fig. 4. The concentration of bonded oxygen in implantation/oxidation layers is three times higher than in PECVD ones. These results
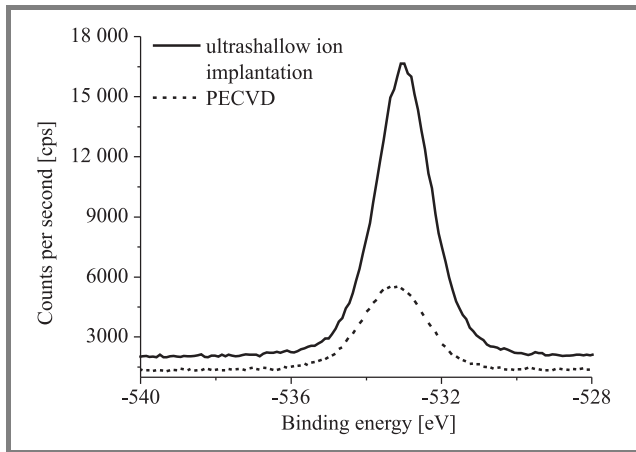

Fig. 4. Comparison of O1s spectra of PECVD and implantation/oxidation layers.
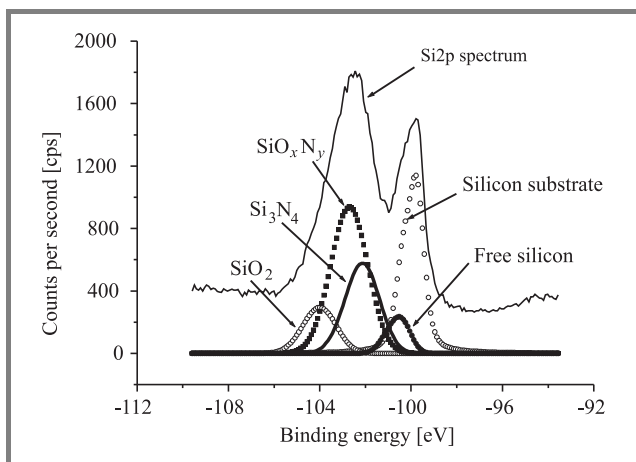

Fig. 5. Si2p line decomposition (PECVD sample, 500 mTr).

will be discussed in more detail below using Figs. 6 and 7, where chemical composition of both types of silicon oxynitride is presented.
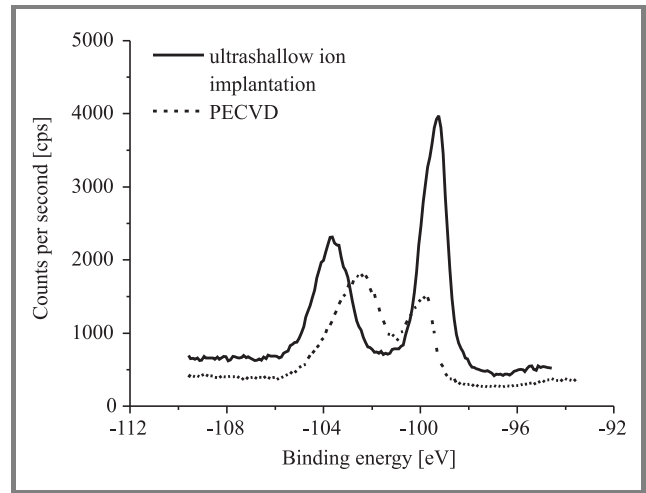

Fig. 6. Comparison of Si2p spectra of layers PECVD and implantation/oxidation layers.

The obtained emission lines were analyzed using curve-fitting procedure. An example of Si2p line deconvolution for a PECVD layer is shown in the Fig. 5. Since every single line may be attributed to a particular compound due to its unique binding energy, chemical composition of each layer may be determined.

The Si2p spectra of both types of ultra-thin silicon oxynitride layers are compared in Fig. 6. Si2p spectra of implantation/oxidation layers are characteristic for silicon dioxide layers. Similar spectra of thermal silicon dioxide may be found, e.g., in [6].
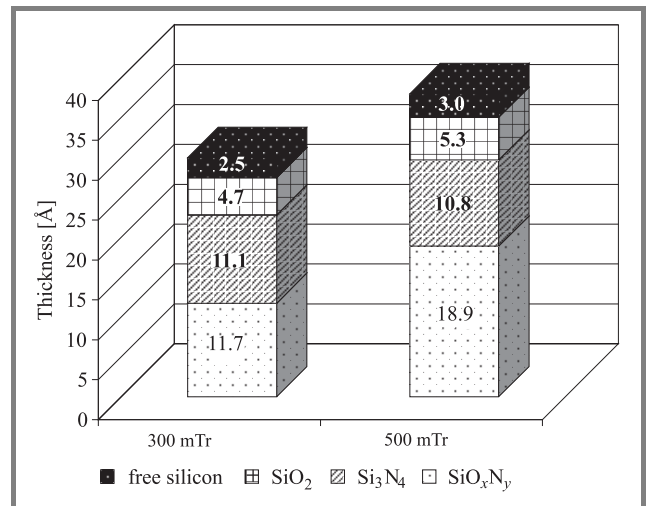

Fig. 7. Comparison of chemical composition (obtained from XPS spectra and expressed as thickness) of PECVD ultra-thin silicon oxynitride layers.

Chemical composition (as determined from the Si2p line) of PECVD and implantation/oxidation layers is shown in Figs. 7 and 8, respectively. The influence of process pres-

sure (300 mTr and 500 mTr) on the composition of PECVD layers is illustrated in Fig. 7. It should be noted that although SiO_xN_y and Si_3N_4 phases are the dominant compounds in the PECVD layer in both cases, increasing process pressure results in significant increase of SiO_xN_y only. The influence of nitrogen source (N_2 or NH_3) on the composition of implantation/oxidation layers is shown in Fig. 8. As seen, oxygen is present in implantation/oxidation layers in the form of silicon dioxide, which confirms the earlier conclusion that this type of oxynitride is almost classical silicon dioxide.
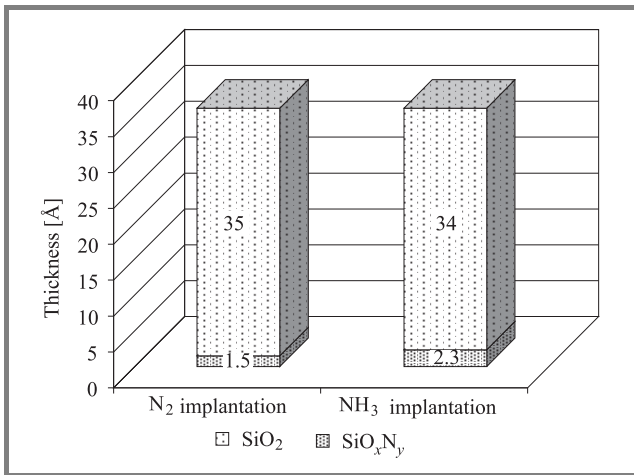

Fig. 8. Comparison of chemical composition (obtained from XPS spectra and expressed as thickness) of implantation/oxidation ultra-thin silicon oxynitride layers.

Comparison of Figs. 7 and 8 indicates that the composition of PECVD layers is more complex than that of implantation/oxidation ones. Furthermore, the chemical composition of the implantation/oxidation layers is characteristic of "classical" silicon dioxide.

The ULE-SIMS profiles of silicon, oxygen and nitrogen within the PECVD layers are shown in Fig. 9. No significant difference in the atomic profiles obtained from layers formed under different process pressure is observed. More-
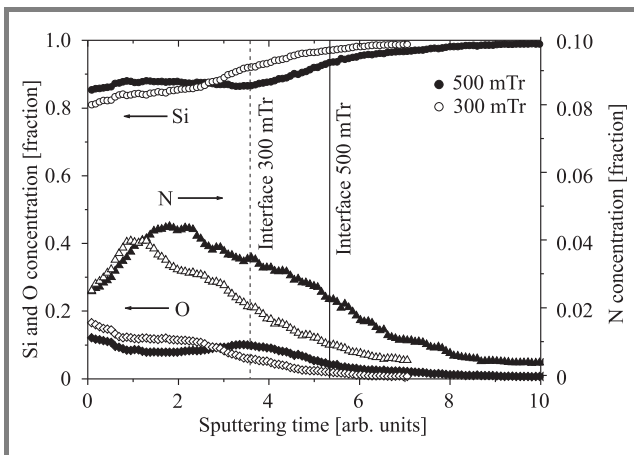

Fig. 9. Comparison of composition profiles (obtained by ULE-SIMS) of PECVD ultra-thin oxynitride layers.

over, the maximum concentration of both oxygen and nitrogen in the layers is almost the same for both PECVD conditions.
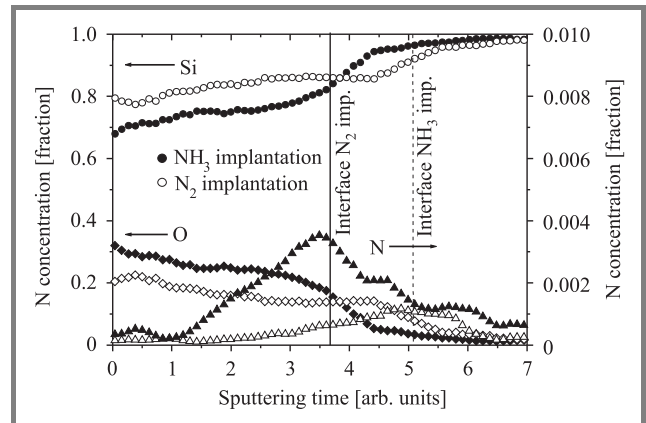

Fig. 10. Comparison of composition profiles (obtained by ULE-SIMS) of implantation/oxidation ultra-thin oxynitride layers.

Profoundly different conclusions may be drawn from Fig. 10, which shows profiles of silicon, oxygen and nitrogen in implantation/oxidation layers. Different profiles may be achieved depending on the source nitrogen ions. Maximum concentration of both oxygen and nitrogen is lower in oxynitride layers obtained by means of implantation from pure nitrogen plasma than in those formed using ammonia source. When the concentration of nitrogen in the bulk of the layer is taken into account, it becomes obvious that ammonia source is more effective than pure nitrogen source.
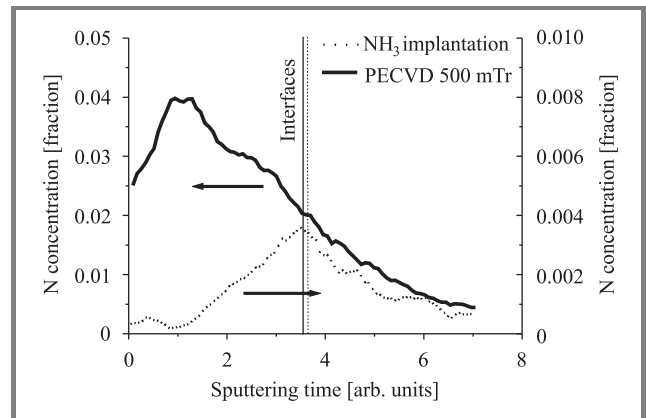

Fig. 11. Comparison of nitrogen profiles (obtained by SIMS) in oxynitride – silicon systems fabricated by means of PECVD and implantation/oxidation.

A direct comparison of nitrogen profiles obtained from PECVD and implantation/oxidation layers is shown in Fig. 11. It should be noted that nitrogen pile-up is observed at a certain depth in PECVD layers while the highest nitrogen concentration in implantation/oxidation is located near the dielectric-silicon interface. Moreover,

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the nitrogen content in PECVD layers is one order of magnitude higher than implantation/oxidation layers. In the literature published so far it is commonly agreed that nitrogen incorporation not exceeding a certain limit (~ 0.1 at. %) at or near the Si channel interface improves device performance, while higher amounts of N near this interface make device properties deteriorate [7]. It is also known that introduction of nitrogen near the dielectric/poly-Si interface prevents boron penetration if the p^+-poly-Si gate is used [8]. Taking into account these findings and the results presented in this paper, it can be concluded that nitrogen profile may be engineered using a multi-stage process combining PECVD and implantation/oxidation steps. Moreover, unlike the approach of Mian and Flora [9], who demonstrated a technique to engineer the nitrogen profile in an ultra-thin oxide by changing the oxidation sequence in O_2 and N_2O by RTP, low temperature processing in the standard planar rf plasma reactor is compliant with the requirement to keep silicon nanotechnology thermal budget low.

4. Conclusions

In this paper differences in chemical composition of ultra-thin silicon oxynitride layers fabricated in standard rf planar reactor were studied.

The investigations carried out in this work showed that the two investigated methods of ultra-thin silicon oxynitrides fabrication result in completely different chemical composition.

The PECVD SiO_xN_y layer composition is more complex than that of oxynitride formed by means of implantation/oxidation. Moreover, ultra-thin silicon oxynitride obtained using the latter method is almost a "classical" silicon dioxide (SiO_2) which is proved not only by chemical composition but also by refractive index value.

The two studied methods result also in different nitrogen profiles. In the PECVD oxynitride the highest concentration of nitrogen is located near the metal gate/dielectric interface, while for the implantation/oxidation oxynitride – at the dielectric/Si interface. These differences may be used to our advantage in particular devices. Additionally, using a multi-step process combining both methods, the required nitrogen profile may be achieved. It should be remembered that this variety of nitrogen profiles may be obtained using very low temperature processes, which is of great importance to next generations of ULSI-CMOS technology.

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Robert Mroczyński – for biography, see this issue, p. 19.

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