Plasma nitridation of silicon by N$_2$ and NH$_3$ in PECVD reactor

V S Bakardjieva$^{1,4}$, Z I Alexieva$^1$, G D Beshkov$^2$ and E S Mateev$^3$

$^1$Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
$^2$Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, Sofia 1784, Bulgaria
$^3$Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, Sofia 1784, Bulgaria

E-mail: vlabakar@phys.bas.bg

Abstract. The effect was investigated of nitrogen and ammonia plasma treatment of monocrystalline Si wafers. The experiments were carried out in a plasma-enhanced chemical vapor deposition reactor. The wafers were subjected to N$_2$ and NH$_3$ plasma treatment for varying times at temperature of 380 °C. The plasma treated surfaces were studied by transmission electron microscopy with C-Pt replicas, reflection high-energy electron diffraction and Auger electron spectroscopy. The results point to the growth of an amorphous layer on the surface. The Auger electron spectroscopy depth profiles obtained by sputtering show the presence of an oxynitride layer with varying composition depending on the time of plasma treatment. The Auger electron spectroscopy analysis shows that after 60 s of treatment in N$_2$ plasma, the nitrogen content is 8 at.%, while after 300 s it is 22 at.%, the thickness of the oxynitride nanolayer being 2.5-7.2 nm. In the case of NH$_3$ plasma the thickness calculated from the sputtering time (from 50 s to 15 min) varies between 2 and 12 nm, and the nitrogen content, between 5 and 35 at.%.

1. Introduction
In order to reduce the thermal budget in the fabrication of current and future microelectronic devices and integrated circuits, high-temperature process steps must be minimized in number and duration, and low-temperature alternatives, such as plasma-enhanced chemical-vapor deposition (PECVD), applied [1]. The basic advantages of this method consist in the possibility of activating the operating gas and the substrate and depositing device-quality film in a single run process at low temperature [2]. Exposing the substrate to a controlled N$_2$ plasma atmosphere is effective in reducing the hydrogen content in silicon nitride films and improving its dielectric properties [2]. Compared to thermal processes at same substrate temperatures, film growth rates are accelerated by the plasma-enhanced generation of reactive chemical species or by the presence of electric fields to assist the charged-particle transport during plasma processes [1]. In this study, nitrogen (N$_2$) or ammonia (NH$_3$) plasma nitridation of monocrystalline Si was performed in a PECVD reactor using radio-frequency (RF) plasma at low temperature.

$^4$ To whom any correspondence should be addressed.
2. Experimental

All plasma treatments were carried out in a capacitively-coupled parallel-plate ASM RF plasma reactor operating at a frequency of 13.56 MHz, and RF power of 60 W. Polished p-type (100) oriented silicon wafers, with resistivity of 10 - 15 Ohm.cm were used. They were subjected to a standard chemical surface cleaning and then placed in the reactor and subjected to N₂ (99.999%) plasma treatment for 15, 30, 60 and 300 s at a temperature of 380°C, nitrogen flow-rate of 1.2 standard liter per minute (slm) and working pressure of 0.2 Torr. The influence of the NH₃ plasma on the silicon surface was also investigated. The conditions were the same but for the working pressure, which was kept at 1.52 Torr. The plasma treated surfaces were studied by transmission electron microscopy (TEM) with C/Pt replicas, reflection high energy electron diffraction (RHEED) and Auger electron spectroscopy (AES). The AES depth profiles were obtained by grazing-incidence Ar-ion sputtering at 15º to the surface. In order to minimize the depth of the damaged surface layer, the Ar ion energy was chosen to be 1 KeV. The AES spectra were taken in dN(E)/dE mode with a modulation amplitude of 4 V. The calculations were made using the element sensitivity coefficients obtained at the same experimental conditions for Si LVV line – 92 eV from monocrystalline Si, taken as a reference sample, Si LVV - 79 eV and O KLL from SiO₂ and Si LVV - 86 eV and N KLL – from Si₃N₄ stoichiometric layers. The inaccuracy of the calculations is estimated to be ±3 at.% for N and O content and as ±5 at.% for Si.

3. Results and discussion

TEM of C/Pt replicas is superior at resolving nanoscale surface structures, including the development of new faces and the different microtopography of individual particles [3]. The TEM images did not show any changes induced by the plasma treatment when the duration of treatment was less than 30 s. Cone-like defects were detected on the surface when the N₂ plasma treatment was prolonged. Figure 1 shows the surface morphology prior and after plasma treatment for 300 s. Defects as high as 3 nm with density of 2.5×10⁸ cm⁻² are observed in figure 1 b). RHEED studies were carried out on the same surfaces. The electron pattern of the clean silicon surface prior to plasma treatment showed Kikuchi lines characteristic for a monocrystalline surface. After the treatment, the sharpness of the lines decreased and a halo pattern was observed indicating a process of amorphization. The mechanism of initial defect formation is not quite clear but probably active nitrogen atoms, which are the dominant active species, can react with the silicon [3-6]. The AES analysis showed that after 60 s treatment in N₂ plasma, the nitrogen content was 8 at.%, while after 300 s, 22 at.%, the thickness of the SiₓOᵧNz nanolayer being 2.5 - 7.2 nm.

![Figure 1. Surface morphology of a clean Si monocrystalline wafer a) prior to plasma treatment and b) after N₂ plasma treatment for 300 s.](image-url)
The influence of NH$_3$ plasma on the silicon surface morphology was also investigated by TEM with C/Pt replicas. Figure 2 shows the silicon surface after 1 min. and 15 min. The roughness is due to an increased layer growth in defect sites, as well as to erosion in the vicinity of the defects caused by the ion bombardment.

![Image](Figure 2. Surface micrograph of a NH$_3$ plasma treated silicon wafer after a) – 1 min and b) – 15 min.)

Figure 3 shows the AES profiles of the silicon surface after different times of NH$_3$ plasma treatment (the sputtering rate is 1 nm/min). The concentration is shown of O, Si and N measured in at.% as a function of the sputtering time.

![Image](Figure 3. AES depth profile of a Si wafer after NH$_3$ plasma treatment for a) – 5 min and b) – 15 min.)

The comparison of the figures shows that as the plasma treatment time is increased (5 min. and 15 min) the maximum nitrogen concentration rises and moves away from the outer surface. The thickness of the nano-layers obtained can be calculated from the sputtering time – they are respectively about 7 nm and 12 nm. The AES results indicate that N$_2$ and NH$_3$ plasma treatment induces a growth of oxynitride layers on the silicon surface. Direct growth of pure nitride layers onto silicon is difficult for two reasons. In spite of the preliminary etching for native oxide removal, the latter grows rapidly in air during the wafer loading in the reactor. In addition, there are trace amounts of oxygen and water vapors in the N$_2$ or NH$_3$ gas, which lead to the presence of oxygen in the nitride bonding structures during plasma growth processes [4-8].

The layers grown by N$_2$ plasma treatment are thinner and with lower N content than the layers grown by NH$_3$ gas. This is due to the fact that N$_2$ has higher dissociation energy than the NH$_3$ molecule. As a result, a lower density of active particles is achieved at the same plasma conditions. The higher pressure of NH$_3$ in the discharge acts in the same direction.
4. Conclusion
The effect of nitrogen and ammonia plasma treatment of silicon surfaces for varying times was investigated. The results indicate an amorphous layer growth on the surface. The AES depth profiles obtained by sputtering show the presence of a SiO$_x$N$_y$ layer with varying composition according to the time of N$_2$ and NH$_3$ plasma treatment. The layers grown by N$_2$ plasma treatment are thinner and with less N content than the layers grown by NH$_3$ plasma treatment, because N$_2$ has higher dissociation energy than the NH$_3$ molecule, resulting in lower density of active particles.

Acknowledgments
This work was supported by the National Science Fund at the Ministry of Education and Science of Bulgaria under Grant X 1505.

References
[1] Heiss D W 1999 IBM J. Res. Development 43 127
[2] Franco C, Cioffi N, Ditaranto N, Vitiello M, Sibilano M, Torsib L and Scamarcio G 2008 J. Mater. Process. Tech. 206 462
[3] Chien Y, Mucci A, Paquette J, Sears S and Vali H 2000 Microsc. Microanal. 12/4 302
[4] Nakae M; Hayakawa R; Yoshimura T; Fujimura N; Kunugi S and Uehara T 2007 J. Appl. Phys. 101 023513
[5] Wong S and Oldham W 1984 IEEE Electron Device Lett. EDL-5 175
[6] Hirayama M, Matsukawa T, Arima H, Ohno Y, Tsubouchi N and Nakata H 1984 J. Electrochem. Soc. 131 663
[7] Hirayama M, Matsukawa T, Arima H, Ohno Y and Nakata H 1985 J. Electrochem. Soc. 132 2494
[8] Reisman A, Berkenblit M, Ray A and Merz C 1984 J. Electron. Mater. 132 505