An Investigation of Nitrogen-implanted Oxide/nitride/oxide Nanostructures on Silicon with Photoelectron Spectroscopy

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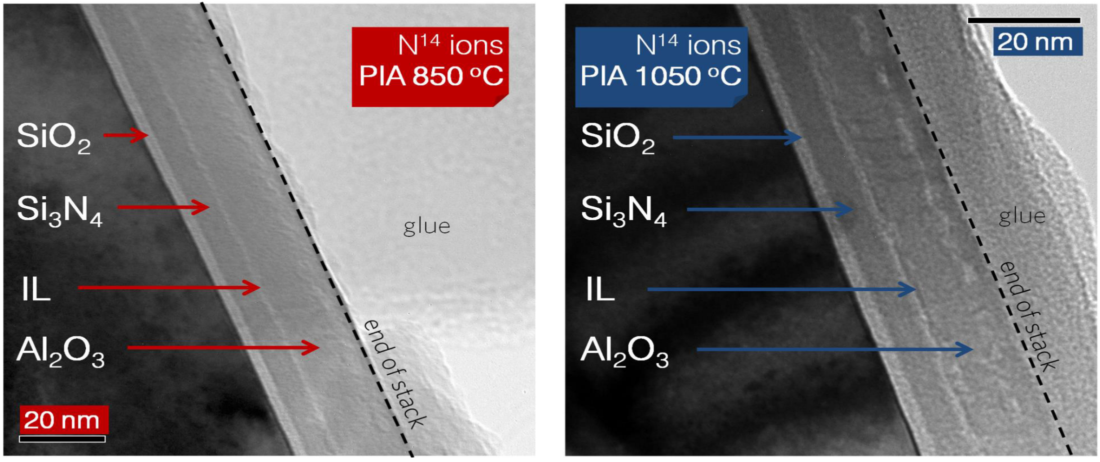
Multilayer nanofilm stacks on silicon are important in many microelectronics applications, including the fabrication of charge-trap memory devices. The memory properties of such devices could be improved by applying various modifications on the prepared stacks, such as ion-beam implantation and post-implantation annealing. The surface and interface properties of the nanofilms, especially their chemical composition, structure and thickness, which determine the electrical performance of the devices, are strongly dependent on the applied treatment conditions. In this work, we used X-ray Photoelectron Spectroscopy (XPS) to investigate the chemical composition, both at the surface and in depth across the layers, of a series of trilayer, $Al_2O_3/Si_3N_4/SiO_2$, stacks grown on silicon wafers and then modified by low-energy nitrogen ion implantation followed by post-implantation annealing (PIA) at three different temperatures, 850, 950 and 1050 °C **(Fig.1).**

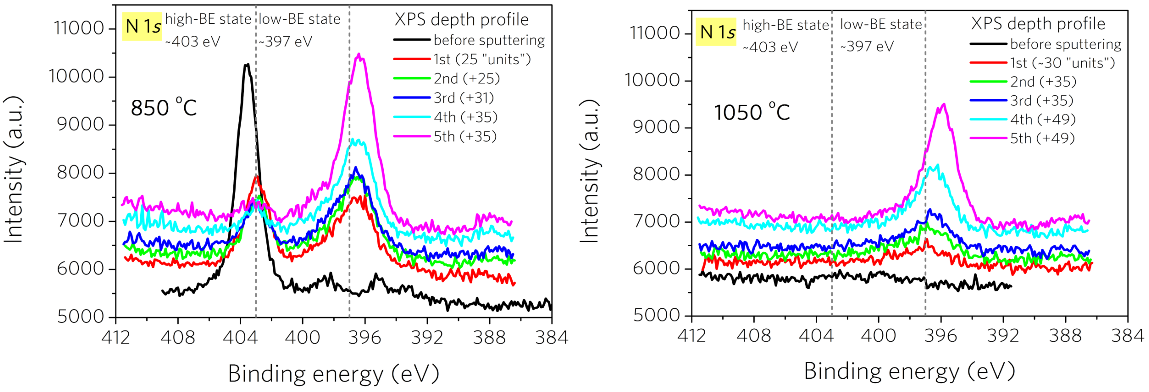
Figure 1 : Transmission Electron micrographs in cross-section for two implanted specimens



Both implanted and non-implanted (reference) specimens subjected to the same annealing treatment were first characterized by XPS in the as-received state at two photoelectron take-off angles. Then, all implanted specimens and two of the reference specimens were subjected to a series of controlled Ar- ion sputtering cycles, each one removing a surface layer to a certain depth of a few nanometers and followed by XPS measurements on the sputtered surface. Although the XPS measurement has a average depth of analysis of the order of several nanometers, the successive XPS spectra yield a useful picture of the in-depth variation of the elemental chemical composition in each specimen.

Of special interest is the distribution of nitrogen across the layers in the implanted samples, which is deduced from the evolution of the N1s spectra, such as those shown in Fig.2 for the lowest and the highest post-implantation annealing temperature. A striking difference between the two annealed samples in the as received state is the predominant presence of a high binding energy (BE) N1s chemical state at ~403 eV at 850 °C and its absence at 1050 °C. The sample annealed at 950 °C exhibits only traces of the high BE state at the surface. This high-BE state, which corresponds to a N^{+3} oxidation state and could be attributed to AlNO$_x$-type compounds [1], is localized at the surface, as it is attenuated fast upon the first annealing cycles. For the implanted specimens annealed at 1050 °C and 950 °C, as well for the subsurface region of the sample annealed at 850 °C , the main, small N1s peak appears near 397 eV BE , which corresponds to nitride-type N in the N^{-3} oxidation state. The N^{-3}/Al atomic ratio in the top , 15nm thick, Al$_2$O$_3$ layer is of the order of 5% at 850 °C and 2% at 1050 °C. After the first three sputtering cycles, the rapid increase of N^{-3} in all samples (both implanted and reference), which is accompanied by the concomitant increase of the Si^{+4} state, results from the expected XPS-'visibility' of the underlying Si$_3$N$_4$ layer, as the sputtering proceeds. Another interesting observation , especially for all as received samples annealed at 950 °C and 1050 °C, is the presence of a small Si4+ peak in the surface region . This might indicate some silicon migration through the alumina blocking layer at high temperatures and needs to be farther investigated.

Figure 2 : The N1s spectra of the specimens in Fig.1 taken normal to the layers, both in the as-received state and following successive cycles of Ar-ion sputtering exposing increasing depths across the layers.



The results of the spectroscopic findings and in particular of the various nitrogen species, as well as their possible correlation with the electrical behavior and the memory characteristics of the devices are currently under discussion.

[1] P.W,Wang, J-C.Hsu, Y-H. Lin, H-L. Chen, Applied Surface Science, **256** (2010) 4211-4214

Key words: nanofilms, ion-implantation, X-ray Photoelectron Spectroscopy