Silicon nitride multi nanolayer system fabricated in one reactor

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Abstract. **The silicon nitride nanomultilayer structure (5 layers, thickness of each around 12 nm) was fabricated in one reactor. The structure had less oxygen concentration against the monolayer one having the same thickness. The oxygen and its originated centers were identified because of XPS, prethershold photoelectron emission spectroscopy and FTIR measurements. Oxygen connected electrically active centers decreased an electrical capacitance of the silicon nitride based capacitors.**

Key words – electron emission, optical absorption, silicon nitride, nano layer, electrical capacitance

I. Introduction

Silicon nitride (Si_3N_4) nanofilms (SiN) are widely in use to fabricate nanoelectronic circuits like memory systems, nanocapacitors, etc. The world solid electronic industry trends to decrease dimensions of electronic devices (Moor's law). However, a thickness (d) of the SiN is limited because of its inhomogeneity increasing, when the $d \rightarrow 0$. To enhance the homogeneity the SiN are assembled as a multi layer system that consists of the nanolayer by nanolayer deposited films. In this case interfaces between the layers avoid inhomogeneous penetration from one layer to the other one. To reach this a following technological scheme is employed usually: deposition of SiN layer, functionalization of its surface for the next SiN deposition, next SiN deposition, etc. In this case several reactors and transportation systems between them are employed usually [1]. To increase the cost effectiveness of the scheme the deposition of the SiN films and their functionalization could be done at the same reactor.

The present article is aimed to verify a possibility to employ one reactor based technique for both deposition and functionalization of SiN to reach a multynanofilm SiN system having improved electrical properties against the single silicon nitride layer.

An electrical capacity of the multynanofilms SiN system (MSiN) was is use to identify its electrical properties. Higher capacity corresponds to the enhanced homogeneity of the MSiN. The capacity could be increased, if an electrical charge inserted in SiN during its fabrication is minimized. Therefore the inserted electrical charge should be identified as an MSiN fabrication quality index. As the contact measurement of electrically active centers are able to damage the nanolayer a contact less instrumentation was employed.

II. Fabrication of MSiN

The MSiN were fabricated in two ways: to reach the MSiN based capacitors for electrical tests and to provide a capacitor MSiN satellite for contact less measurements.

The MSiN capacitors were fabricated on the Si wafer (111 wafer surface). Next:

1) the wafer (∅76 mm) was oxidized at 1130 °C in the oxygen environment during 2 h; a thickness of SiO_2 was 1 mcm;
2) deposition of the conductive polycrystalline Si layer to reach an electrical contact of the capacitor; the deposition was done in SiH_4 and N_2 gases atmosphere during 40 minutes at 900 C; the layer was doped with phosphorus (gases: $POCl_3$, O_2+N_2; 15 minutes; 900 C); a thickness of the layer was 0.4 mcm;
3) photolithographic configuration of the windows for SiN deposition;
4) Low Pressure Chemical Vapour Deposition of SiN (gases SiH_4 + NH_3 at 800°C); the thickness of the layer was ~12 nm;
5) functionalization of the SiN layer because of the SiH_4 and NH_3 gases flow modulation;
6) the steps 4) and 5) were repeated to reach 5 SiN layers for the MSiN having the 60 nm thickness;
7) photolithography and aluminum layer deposition for the electrical contact of the capacitor.

The MSiN satellites having a thickness 60 nm were fabricated by the above scheme, however, the steps 2), 3) and 7) were not provided. Alongside the specimens having only one 60 nm monolayer SiN (MNL) were prepared, too.

III. Measurement technique

The chemical composition of the fabricated MSiN was verified because of the XPS (x-ray photoelectron spectroscopy) measurements. The PHI VersaProbe III (Physical Electronics) spectrometer was in use. The Ar^+ ions (1 keV) were employed for spattering of the specimens aimed for depth profiling.

It is generally known that the inserted charges are supplied because of local states situated at the energy gap of a dielectric that SiN is. Therefore, to identify the presence of the inserted charges the local states could be filled with electrons/holes because of their excitation from a valance band or local bands containing charge carries and located in the energy gap. As the

SiN energy gap is around 5-6 eV [2] the charge carriers are easily available for excitation by weak electrons (energy <1000 eV) and ultraviolet radiation (UV) supplied in normal atmospheric conditions (~5…6 eV).

The 1000 eV electrons are able to excite the layers having a thickness around 34 nm [3]. UV, compare with the electrons, delivers wavelengthes ~200…250 nm and therefore is absorbed by the approximately same thickness of the layer.

Therefore, the weak electrons were in use to excite the first (counting from the MSiN surface) SiN layers, UV was employed to stimulate the entire MSiN.

A thickness (R) of the surface layer, where electrons were absorbed was estimated following the formula [3]:

$$R = \frac{115}{\rho} E^{1.35} \quad , \text{ nm}$$

ρ - density of the radiated material, g/cm^3; the ρ value of 3.44 g/cm³ was applied for Si_3N_4 [4];

E – energy of the radiating electrons, keV.

The 300, 500, 800 eV E values were selected to get the electrons into the first and second SiN single layers of the MSiN sandwich (the selected energies corresponded to the R values 6.5 , 13.3 and 25.5 nm, accordingly).

The weak electrons were supplied from the thermocathode hand made gun in vacuum conditions (10^{-5} Pa). The distance between the cathode and the specimen as well the cathode current were 4 cm and 2 A, correspondingly. In these conditions the electron current density was ~1 mcA/cm^2.

A prethreshold photoelectron emission (PE) spectroscopy was employed to identify electron traps filled in because of weak electron radiation. The PE was detected in vacuum conditions 10^{-5} Pa immediately after radiation with weak electrons. A hand made spectrometer described in details in [5] was in use.

The UV was supplied from the Hamamatsu Photonics Lightningcure LC8 light source equipped with a 200 W mercury-xenon lamp L10852 (240–450 nm, the central wavelength 365 nm, UV irradiance at 10 mm distance from the light guide output was 4.5 W/cm2 at 365 nm). The highest energy of the photons delivered from the UV source in air was 5.12 eV. The specimens were located at a distance 20 cm from the source optical guide and were exposed during 20 minutes in normal atmospheric conditions.

An optical absorbance of the reflected beam was measured for UV radiated specimens immediately after they were excited by UV photons. The infrared Bruker FTIR Tensor II spectrometer was employed for this. ATR (Diamond) FTIR method was applied [6]. The incident light beam was directed to the surface of the specimen and reflected beam was detected. The ratio of incident and reflected light beams intensities identified the surface layer optical absorbance. Because the UV photons excited both SiN and SiO_2 layers, and the thickness of SiN was significantly less that of SiO_2 the absorbance by the latter was in use as the reference. The SiO_2 spectra were subtracted from both the MNL and MSiN ones. An uncertainty of the subtracted spectra was < 10%.

The electrical capacitance of the prepared capacitors was measured at a frequency range of 25 Hz to 1 MHz in room conditions. The capacitor meter E7-25 was in use. The contact needles from "ACCUPROBE" company were applied. The capacitor structures located at the wafer were selected randomly for measurements. To avoid an influence of the wafer edge on quality of the capacitors they were designated within a circle of ∅40 mm.

IV. Results and Discussion

The SiN chemical elements depth XPS profiling is presented in Fig 1. The ratios of Si/N and Si/O were equal to 0.83 and 0.46, correspondingly. These data related to the stoichiometric coefficients ratios for Si_3N_4 and SiO_2: 0.75 and 0.5, respectively.

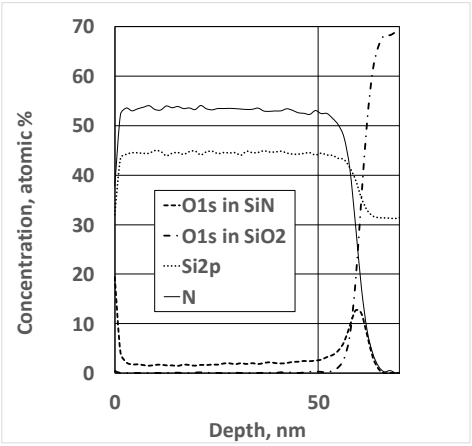

Fig. 1. SiN chemical elements depth profiling.

The XPS analysis identified presence of the oxygen both in mono and multi layers silicon nitride films (Fig 2). However, the oxygen profiling of the MSiN demonstrated oxygen concentration irregularities having a width related to the thickness of SiN single layers. Because the minimums of the oxygen appeared only for MSiN one assumed that they were supplied by the functionalization procedure of the SiN surface. In other words, the minimums were connected with the interfaces between the SiN single layers.

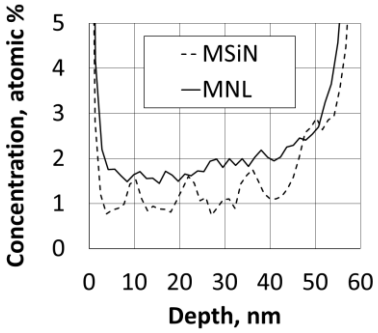

Fig. 2. SiN chemical elements depth profiling.

The PE current (I) spectra (regularities of I on the photon energy hv) of the radiated with electrons MNL and MSiN are presented in Fig. 3

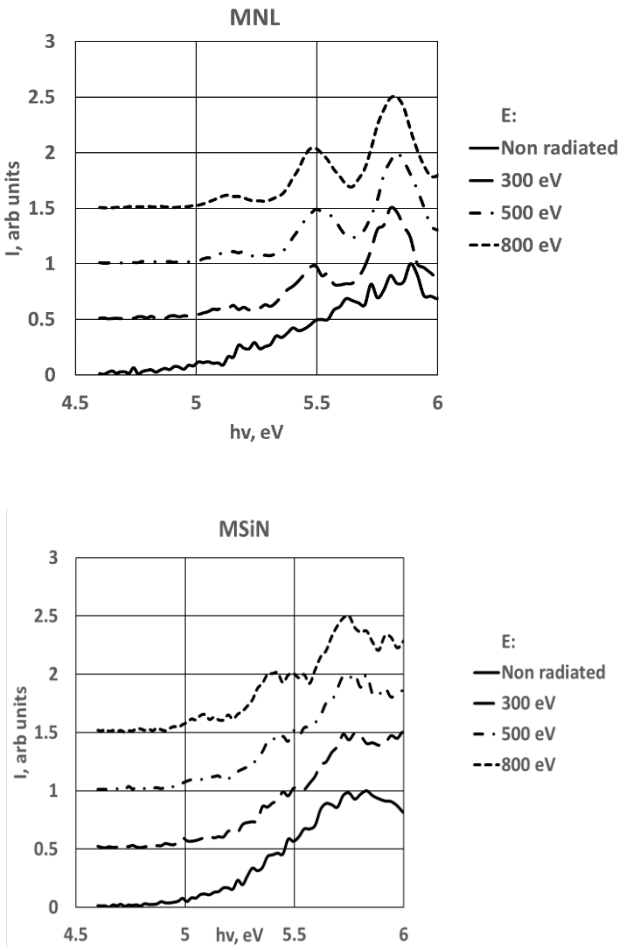

Fig. 3. PE spectra of MNL and MSiN radiated with electrons.

Following [7] the maximums of *I* are connected with recharging of the emissions centers during PE measurement (the centers were charged because of the electron radiation before PE detection).

Development of the specific maximums for the MNL specimens, when E increased (deeper penetration of the electron radiation) could be connected with rising of both electron absorption cross section (σ) by the local states and their concentration in the direction of MNL surface to its bulk.

It is generally known that the weak electrons are in use to compensate a positive electrical charge deposited onto the dielectric surface, for instance by ion, etc radiation employed for spectroscopy (secondary ion mass spectroscopy, etc) purposes. This means, that the weak absorption by dielectric (SiN) charges it negatively. Therefore, one could assume that the increase of E did not rise σ. If so, the specific maximums developed, when E grown were connected with enlargement of the local states concentration in the direction from the surface of SiN to its bulk.

The PE spectra of MSiN do not demonstrate the specific maximums at E<800 eV. Absence of the maximums evidenced in the favor of the electrically active centers less concentration in MSiN against MNL. This is connected with existence of the interfaces between SiN single layers of MSiN, the oxygen concertation at the interface being less that in SiN layer.

When E=800 eV, the weak electron radiation excited two SiN layers, the total amount of oxygen is higher that in a case of the single SiN layer. As the result scattered like maximums peculiarities appeared at 5.1 and 5.4 eV.

Following the above the local states could be provided by chemical compositions including oxygen. Si-O could be a probable candidate of such the composition because of the oxygen presence in SiN.

The measured PE spectra of SiO_2 are presented in Fig. 4

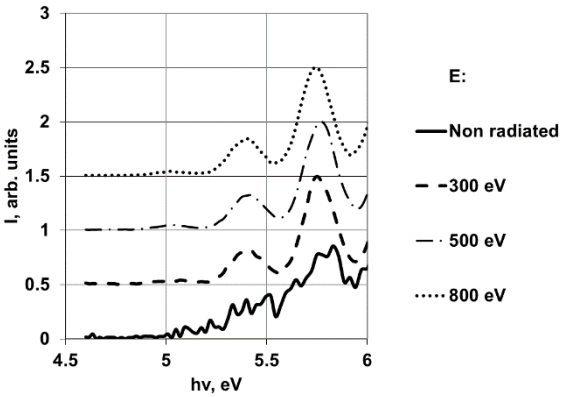

Fig. 4. PE spectra of SiO_2 radiated with electrons.

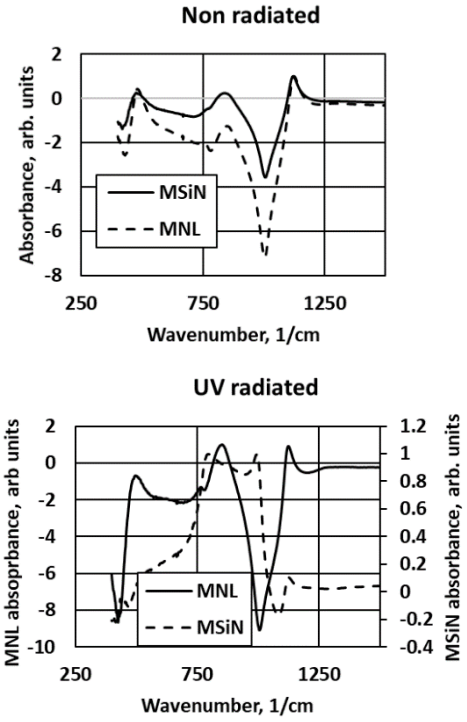

Fig. 5. FTIR spectra of MNL and MSiN .

In spite of the slight (~0.1 eV) shift to the lower energies the PE maximums detected for SiO_2 the SiO_2 and MNL spectra are very alike (Fig 3 and 4). Therefore, one could suppose that PE maximums detected for MNL were provided by the Si-O composition(s).

ATR FTIR spectra are presented in Fig. 5. The spectra of non radiated MNL and MSiN specimens are alike. However, UV radiation made them different: the maximum at 500 cm^{-1} detected for MNL did not appear for MSiN. This meant that the absorption center at 500 cm^{-1} was UV sensitive and electrically active perhaps (UV excited electrons via the energy gap and they were trapped by center, that was displayed in FTIR spectra). The absence of the centers for MSiH was connected with the less concentration of oxygen in MSiH interfaces against MNL that did not have internal boundaries.

The results of the electrical capacitance measurements are presented in Fig 6.

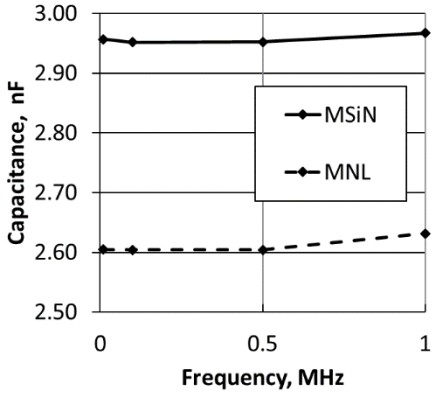

Fig. 6. Electrical capacitance of MNL and MSiN.

Because the standard deviation of the capacitance was not wider that 0.6% the MSiN differed from MNL significantly. Therefore, the lower concentration of the oxygen originated electrically active centers in MSiN increased electrical capacitance of the latter compare with MNL.

CONCLUSION

1. The silicon nitride nanomultilayer structure fabricated in one reactor has less oxygen concentration against the monolayer one.
2. Oxygen delivers electrically active centers that decreases the electrical capacitance of the silicon nitride based capacitors.

ACKNOWLEDGMENT

This work has been supported by the European Regional Development Fund within the project "Multilayer Silicon Nanocapacitor with Improved Dielectric Layers" No.1.1.1.1/16/A/203.

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