# Improvement of SiO2(Ge)SiO2/Si Nanostructures by Low Dose γ-radiation

S.T. SHISHIYANU[1] , T.S. SHISHIYANU[1], E. YILMAZ[2], R. TURAN[3], N.A.P. MOGADDAM[3]

[1]*Department of Microelectronics, Technical University of Moldova, 2004 Chisinau, Moldova*
[2] *Department of Physics, Abant Izzet Baysal University, 14280 Bolu, Turkey*
[3]*Department of Physics, Meddle East Technical University, 06531Ankara, Turkey*
*sergeteo@mail.utm.md*

***Abstract* – Effect of γ – radiation on $SiO_2$(Ge)$SiO_2$/Si nanostructures structural defects was investigated by C-V measurements characterization. The obtained results demonstrated that by low dose γ-radiation (0.1Gy÷150Gy) have been essentially reduced the negative charge defects in the nanocomposite structures $SiO_2$(Ge)$SiO_2$/Si. At higher doses (350Gy÷4000Gy) the concentration of positive charge defects slowly increased and C-V characteristics moved to the position of the C-V characteristics of pure $SiO_2$ (without nc-Ge) having the same curves configuration. At the average doses (200Gy÷350Gy) the concentration of negative charge defects and positive charge defects were approximately equal and the radiation stability of samples was the highest.**

***Index Terms* – Ge nanocrystal, $SiO_2$/Si, structural defects, γ –radiation.**

## I. INTRODUCTION

The investigation of radiation effects on nanocrystals Ge and Si embedded in $SiO_2$ has the major importance, first of all, to know the specific of radiation stability and degradation of nanocrystals in comparison with monocrystalline materials (semiconductors – Ge, Si); secondly, for elaboration of the new methods of radiation-nanotechnology for the nanoelectronic device fabrication, and third, for the implementation of these new nanostructured and nanocomposite materials for radiation sensor fabrications.

Nanocrystals of Si and Ge embedded in $SiO_2$ - matrices have attracted much attention due to their possible applications in integrated opto-nano-electronics as nanolasers, nano-flash memory and multifunction nanodevices [1-3]. Many authors have been elaborated different methods of Ge- nanocrystal obtaining: molecular beam epitaxy on the thin $SiO_2$ layer on Si(001) [1], implantation of $Ge^+$ ions into $SiO_2$ films with subsequent annealing [2], chemical vapor deposition (PECVD)[3,4], magnetron sputtering [5,6]. In [7] are presented the comparative study on photoluminescence from Ge/PS, (PS - porous silicon) and Ge/$SiO_2$ thin films; the photoluminescence peaks of Ge/PS were located at 517nm and peaks of Ge/$SiO_2$ at 580nm. In [8] the samples of Ge/$SiO_2$,obtained by sol/gel method , after annealing at 700°C under $H_2$ reduction, by UV light excitation was observed tree peaks of photoluminescence at room temperature 392nm(3.12 eV), 600nm(2.05eV) and 770nm(1.6eV). The peak of 1.6eV is attributed to Ge monocrystals, peak of 2.05 eV – to defect $GeO_x$ and peak of 3.12eV – to $GeO_2$. The unreduced sample shows only on peak of 3.12eV attributed to $GeO_2$. These results are different of other authors: 570nm(2.16eV) in Ge/$SiO_2$, obtained by rf-magnetron co sputtering method [9]; 510-680nm (2.42 ÷ 1.81 eV) at 77K temperature in Ge/$SiO_2$, prepared by sol-gel method: 680nm (1.8eV) at room temperature [10]; 689nm (1.8eV) at room temperature [11].

From these data we can conclude that in the samples of Ge/$SiO_2$, in dependence of growth methods and thermal annealing in different ambient ($N_2$, $H_2$), can be formed not only nanocrystals of Ge, but and different defects as $GeO_x$, $GeO_2$, GeSi, which have direct impact to properties of $SiO_2$Ge/SiO2/Si –nanostructures.

By another hand radiation methods can bee efficiently used for defect monitoring of structural defects for improvement of fundamental properties of nanostructured and nanocomposite materials [12-15]. It is shown in [12] that by the ion irradiation is possible to change of the number, size and distribution of the silicon nanocrystallites and improve the photoluminescence intensity. This results are in accordance with publication [13] where is indicated that after irradiation with 400kev electrons or 30-130kev $He^+$ ions and the post-irradiation annealing at 1000°C, the photoluminescence intensity of Si-nanocrystals became several times stronger than that from the initial samples prepared at 1150°C. These results are assumed to be a sum of the intensities from the initial nanocrystals and from the new ones that appeared due to irradiation [13]. In [14] it was shown that the low-dose of γ- irradiation ($5\times10^4 \div 10^5$rad.) leads to remarkable (up to 40%) increase of photoluminescence band (1.33eV) intensity. Infrared spectra demonstrated that composition and structure of the nanocomposite matrix were not changed by radiation. The effect was explained by radiation induced structural ordering nanocrystal-matrix interface [14]: low-dose irradiation partially eliminated defects (recombination centers) at nc-Si-$SiO_2$ interfaces that resulted in enhancement of nanocrystal luminescence. The impact of low-dose γ- radiation on nc-Ge in $SiO_2$ has been studded in [15].

The main objective of this paper is investigation of the effect of ionizing γ- radiation on C-V characteristics and radiation defect monitoring in $SiO_2$(Ge)$SiO_2$/Si.

## II. EXPERIMENTAL

The samples used in this work were 100nm Ge rich $SiO_2$ layer sandwiched between two $SiO_2$ films deposited on n-type Si<100> substrate by RF magnetron co-sputtering from two independent target materials with powers of $P_{SiO2}$= 300W, $P_{Ge}$= 20W [15]. The bottom SiO2 layer with the thickness of about 100 nm was deposited on Si to restrain Ge atoms from growing epitaxially on the Si substrate in the post-annealing process. The top $SiO_2$ layer with the thickness of about 40 nm was deposited to impede the diffusion of Ge atoms out of the surface.

In our experiments have been investigated the C-V characteristics of the nanocomposite structures, $SiO_2$(nc-Ge)$SiO_2$/nSi, prepared by different post-grown thermal treatment: Set-1 - as grown, Set-2 – after 1 hour annealing at 900°C in $N_2$, Set-3 – after 1 hour annealing at 1000°C in $N_2$ and Set 4 – after 1 hour annealing at 1000°C in a $N_2$, RTA 15 min $H_2$+$N_2$. In general, the formation mechanism for Ge nanocrystals embedded in $SiO_2$ matrix goes through the familiar sequence of nucleation and growth, followed by coarsening of nanocrystals due to Ostwald ripening [16].

The C-V characteristics gave information about state and dynamic charged defects of investigated MOS structures under influence of ionization γ- radiation. All C-V curves have been measured before and after radiation at dose from 0.1Gry to 4000Gry at frequencies - 1MHz.

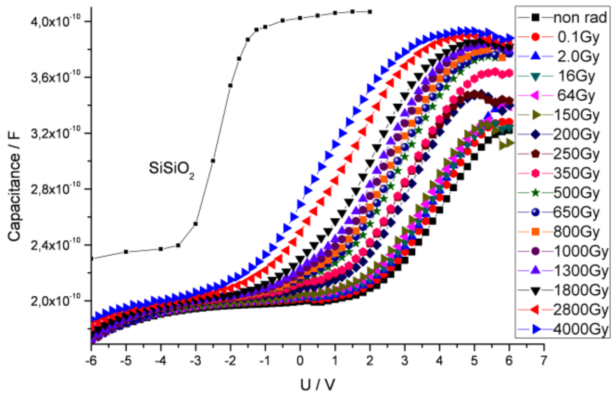

Fig. 1 The C-V characteristics 1MHz before and after γ- irradiation at different doses (0.1 Gy ÷ 4000Gy), Set 4.

## III. RESULTS AND DISCUSSION

The C-V characteristics have been measured of the samples from different Sets - 1, 2, 3, 4 before and after γ-radiation at dose from 0.1Gy to 4000Gy. For illustration in Fig. 1 are presented the C-V characteristics for Set- 4.

The samples of Set 4 after growth have been 1 hour annealed at 1000°C in $N_2$ + RTA for 15 min in forming gas $H_2$+$N_2$. This regime was used for Ge nanocrystals formation in $SiO_2$ [15].

In Fig.1 are presented dynamics of C-V characteristics of nanostructured samples of $SiO_2$(Ge)$SiO_2$/nSi (Set 4) under γ-irradiation of dose from 0.1Gy to 4000Gy (a); (b) –C-V characteristics of conventional $SiO_2$/nSi –structure (without nc-Ge).

As shown in Fig. 1, there are some specific properties of these C-V characteristics: (1) all curves have typically form as MOS structures; (2) the C-V characteristics of nanostructured samples, SiO2(Ge)SiO2/nSi, are situated at positive voltages (V>0) to opposite to conventional MOS structure ($SiO_2$/nSi curve, without nc-Ge) which is situated at negative voltages (V<0); (3) - the accumulation regime corresponds to positive high voltage of +(4÷5)V and depletion- inversion regime corresponds to small positive-negative voltage of ± 2V; (4)-after cumulative irradiation from 0.1Gy to 4000Gy the C-V characteristics moved from positive threshold voltage (+3V) to negative threshold voltage (-1V) corresponding to the decreasing of negative charge defects or increasing the positive charge defects in these structures ($\Delta Q = \Delta V \times C$). After high dose γ- irradiation (2800Gy÷4000Gy) the C-V characteristic tend to conventional C-V characteristics (SiSiO$_2$ curve), but there incline is higher due to high concentration of charge defects.

These experimental results indicate that all C-V characteristics in fig.1 can be deviated in two groups: (i) - low-dose (0.1Gy÷150Gy) characteristics and (ii) – high dose (200Gy÷4000Gy) characteristics.

The low-dose (0.1Gy÷150Gy) characteristics, in accumulation regime at $V_{fb}$= +(5÷6)V, have a smaller capacitance and accumulated electrons than that of middle and high radiation dose.

The high dose irradiation in interval of 350Gy÷4000Gy moved the C-V characteristics to negative voltage: flat band voltage ($V_{fb}$) decreases from $V_{fb}$ = +4V to $V_{fb}$ = +1.7V and middle gap voltage removed from $V_{mg}$ = +2.2V to $V_{mg}$ = -0.45V.

The middle dose radiation (200Gy÷350Gy) removed very slowly C-V characteristics: flat band voltage from $V_{fb}$= +4V to $V_{fb}$= +3.9V and middle gap voltage from $V_{mg}$ = +2.2V to $V_{mg}$ =+2V; the C-V characteristics have not specific properties, but they look more radiation stable (characteristics after 250Gy and 350Gy coincide).

Using the values of $\Delta V_{mg} = V_{mg}(0) - V_{mg}(U)$ and $\Delta V_{fb} = V_{fb}(0) - V_{fb}(U)$ we estimated the net oxide trap/charge densities ($\Delta N_{ot}$) and the net interface trap-charge density ($\Delta N_{it}$) by relations [17]:

$$\Delta N_{ot} = -\frac{C_{ox}\Delta V_{mg}}{qA}; \tag{1}$$

$$\Delta N_{it} = \frac{C_{ox}\left(\Delta V_{fb} - \Delta V_{mg}\right)}{qA}, \tag{2}$$

where $C_{ox}$ is the oxide capacitance measured in accumulation, $-q = (1.602\times10^{-19}C)$ electron charge and $A$ is the area of capacitor.

The C-V characteristics of other samples (Set 1,2,3), as well as Set 4, have specific differences at low dose irradiation (0.1Gy - 64Gy) and many similarities at high dose irradiation (350Gy - 4000Gy). Therefore we will analyze in details the effects of low-dose irradiation.

The charged defect concentration in volume ($\Delta N_{ot}$) and the interface charge stats ($\Delta N_{it}$) calculated from the experimental results of flat band voltage ($V_{fb}$, $\Delta V_{fb}$) and middle gap voltage ($V_{mg}$, $\Delta V_{mg}$) and are presented in Fig. 2.

In Fig.2(a,b) are presented the dependences of the volume charged defect concentration ($\Delta N_{ot}$) and interface charge stats concentration ($\Delta N_{it}$) vs dose of γ-radiation for samples Sets 2,3,4.

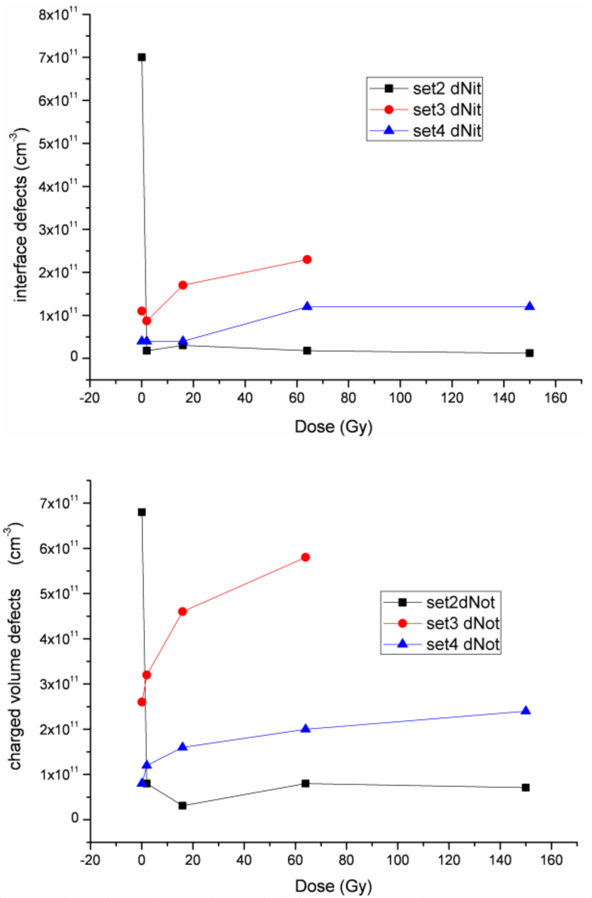

Fig. 2 (a,b). The volume charged defect concentration ($\Delta N_{ot}$) and interface charge stats concentration ($\Delta N_{it}$) vs dose of γ-radiation, Sets 2, 3, 4.

We can see in Fig.2 that flat band voltage($V_{fb}$) and middle gap voltage ($V_{mg}$), as well as concentrations ($\Delta N_{ot}$) and ($\Delta N_{it}$), changed more rapidly after low-dose (0.1Gy÷2.0Gy) and slowly changed after dose of 16Gy ÷150Gy.

As it is shown in Fig. 2, for the samples of Set 4, as result of γ-irradiation at low-dose (0.1÷150Gy) the flat band voltage ($V_{fb}$) changed from +5.1V to 4.2V, the middle gap voltage ($V_{mg}$) - from +3V to +2.4V; the concentration of volume charged defect ($\Delta N_{ot}$) – from $8.0\times10^{10}$ cm$^{-3}$ to $2.4\times10^{11}$cm$^{-3}$ and the interface charge stats ($\Delta N_{it}$) – from $4.0\times10^{10}$cm$^{-3}$ to $1.6\times10^{11}$cm$^{-3}$. Respectively, the concentration of volume negative charged defects ($Q^-$) have been reduced at low-dose radiation and concentration of positive charge defects ($Q^+$)slowly increased at high dose to $\Delta N_{ot} = 1.7\times10^{12}$cm$^{-3}$ and $\Delta N_{it}$=$1.6\times10^{11}$cm$^{-3}$ at 4000Gy.

The specific properties of the C-V characteristics of samples Set 2 are: 1) for non radiation, C-V characteristic are situated in the region of positive voltage (+2V÷-0.8V); 2) at low-dose radiation (0.1÷16Gy) the CV characteristics where instable with some deviation voltage (±0.2V); but at dose up to 64Gy the C-V characteristics become stable at region of negative voltage that corresponds to minimum negative charge defect concentration; 3) at higher dose of 200÷4000Gy the C-V characteristics moved slowly to negative voltage in correspondence with slow increase of the positive charge defect concentration. Calculation demonstrated that concentration of volume negative charge defects changed in interval of ($\Delta N_{ot}$=$3.1\times10^{10}$cm$^{-3}$ ÷ $1.1\times10^{12}$cm$^{-3}$) and interface charge stats – in interval of ($\Delta N_{it}$= $1.2\times10^{10}$cm$^{-3}$ ÷$1.9\times10^{11}$cm$^{-3}$). Respectively, the concentration of negative charged defect ($Q^-$) have been reduced at low-dose radiation and concentration of positive charge defects ($Q^+$) slowly increased at high dose to $\Delta N_{ot}$ =$1.2\times10^{12}$cm$^{-3}$ and $\Delta N_{it}$=$6.5\times10^{11}$cm$^{-3}$ at 4000Gy, Fig. 2.

For all samples of Set-3 the C-V characteristics were situated at negative voltage at 0.2V÷1.0V in accumulation regime and at -1.0V÷3.2V in depletion regime. After radiation at low-dose (0.1Gy÷150Gy) the flat band voltage ($V_{fb}$) changed from +0.2.1V to -1.0V, the middle gap voltage ($V_{mg}$) - from -1.0V to -3.0V; the concentration of volume charged defect ($\Delta N_{ot}$) – from $2.6\times10^{10}$cm$^{-3}$ to $5.8\times10^{11}$cm$^{-3}$ and the interface charge stats ($\Delta N_{it}$) – from $1.1\times10^{11}$cm$^{-3}$ to $2.3\times10^{11}$cm$^{-3}$. Respectively, the concentration of negative charged defect ($Q^-$) have been reduced at low-dose radiation and concentration of positive charge defects slowly increased at high dose to $\Delta N_{ot}$=$7.2\times10^{11}$cm$^{-3}$ at 4000Gy, Fig.2.

The C-V characteristics of Set 1 (without post-growth thermal annealing) were situated in region of positive threshold voltage corresponding to very high concentration of negative charge defects ($Q^-$), having a complicate shape and were non stable during the measurements.

We explain the obtained results on the base of model of negative-positive charge defects correlation at low- and high dose of radiation. In accordance with this model, it is supposed that in investigated samples Set 1,2,3,4, before irradiation existed at least three types of charge defects: negative charge volume defects ($Q_a^-$) like acceptor centers $(GeO_x)^-$, slow negative interface stats ($Q_s$-) like structural defects $(GeSi)^-$ and conventional positive charge defects ($O_b^+$) like $(SiO_x)^+$ in pure $SiO_2$.

In this case the charge neutrality of material can be expressed by relation:

$$Q_b^+ - \left(Q_a^- + Q_s^-\right) = 0 \tag{3}$$

Before irradiation, samples of Set 1, 2, 3, 4, have the C-V characteristics situated in region of positive voltage (+$V_{fb}$, +$V_{mg}$) due to majority of negative charge defects:

$$Q_a^- + Q_s^- \succ Q_b^+ \tag{4}$$

Under the influence of low-dose γ-radiation (0.1Gy÷ 200Gy) have been decreased of the negative charge defect concentration to level of charge neutrality ($Q_a^-$ + $Q_s^-$ = $Q_b^+$). In this case the instability and the abrupt change of charge defect concentration at very low dose (0.1Gy) is due to the rapid concentration decrease of slow negative charge states - structural defects $(GeSi)^-$. At higher γ-radiation (350Gy÷ 4000Gy) have been increased slowly the concentration of positive charge defects and have been improved the linearity of C-V characteristics, which become comparable with the C-V characteristics of pure $SiO_2$/nSi structures with the same configuration.

These results of improvement of C-V characteristics of nanocomposite structures ncGe/$SiO_2$ are in accordance with data of photoluminescence improvement of silicon nanocrystals ncSi/$SiO_2$ after low dose ion radiation [12], electron radiation [13] and gamma radiation [14].

## IV. CONCLUSIONS

The obtained results demonstrated that by low dose γ-radiation (0.1Gy÷150Gy) have been essentially reduced the structural negative charged defects in the nanocomposite structures $SiO_2(Ge)SiO_2/Si$ investigated by the C-V characteristics. At higher doses (350Gy÷4000Gy) the concentration of positive charge defects slowly increased and C-V characteristics shown the properties of the pure $SiO_2$ (without nc-Ge) with the same configuration. At average doses (200Gy÷350Gy) the concentration of negative charge defects and positive charge defects were approximately the same and the radiation stability of the samples was the highest.

## REFERENCES

[1] N.L. Rowell, D.J. Lockwood, A. Karmous, P.D. Szkutnik, I.Berhezier, Supperlattices and Microstrucrures, 44, p.305, 2008.

[2] A. Singha, P. Dhar, A. Roy, "A nondestructive tool for nanomaterials: Raman and photoluminescence spectroscopy," Am. J. Phys. vol.73, n.3, pp. 224-230, 2005.

[3] A. Dana, S. Agan, S. Tokay, A. Aydinli, T.J. Finstad, "Raman and TEM studies of Ge nanocrystal formation in SiOx:Ge/SiOx multilayers," Phys. Stat. Sol., (C), vol. 4, n.2, pp.288-291, 2007.

[4] S. Agan, A. Dana and A. Aydinli, "TEM studies of Ge nanocrystals formation in PECVD grown $SiO_2$:Ge/$SiO_2$ multilayers," J. Phys: Condens. Matter, vol.18, pp. 5037-5045, 2006.

[5] K. Salamon, O. Milat, M. Buljan, U.V. Desnica, N.Radic, P.Dubcek, S.Bernstorff, "X-ray study of Ge nanoparticle formation in Ge:$SiO_2$/$SiO_2$ multilayers," On-line Journal of E-MRS Fall Meeting, 2007.

[6] U.V.Desnica, M.Buljan, K.Salamon, N.Radic et al., "Formation of germanium nanocrystals in $SiO_2$ using RF magnetron sputtering," http://www.science24.com/paper/15584.

[7] X.J. Sun, S.Y. Ma, J.J. Wei, X.L. Xu, "Comparative study on photoluminescence from Ge/PS and Ge/$SiO_2$ thin films," http://www.ncbi.nlm.nih.gov/pubmed/19093555.

[8] Yu Ying, at al., "New Photoluminescence of Ge/$SiO_2$ Glass Synthesized by Sol/gel Method," Chinese Chemical Letters vol.15, n.12, pp.1505-1508, 2004.

[9] Y.Maeda, N.Tsukamoto, Y.Yazawa, Appl.Phys.Lett. vol.59, n.24, p.3168, 1991.

[10] M. Nagami, Y. Abe, Appl. Phys. Lett., vol.65, n.20, p.2545, 1994.

[11] K.S. Min, K.V.Shcheglov, C.M. Yang and H.A. Atwater, Appl.Phys.Lett., vol.68, n.18, p.2511, 1996.

[12] I. Antonova, V. Scuratov, M. Gulyaev, D. Marin, J. Jedrzejewski, I. Balberg, "Improvement of the nanocrystals embedded in dielectrics and nanostructures," IBMM2008.org 16th International Conference on Ion Beam Modification of Materials, Dresden, Germany, 31 September, 2008.

[13] G.A. Kaciurin, et al., "The influence of Irradiation on Subsequent Annealing on Si Nanocrystals Formed in $SiO_2$ Layers," Semiconductors, vol.34, n.8, pp.965-970, 2000.

[14] I. P. Lisovskyy, I.Z. Indutnyy, M.V. Muravska, V.V. Voitovych, E. G. Gule, P.E. Shepelyavyi. Fizika i Tekhnika Poluprovodnikov, vol.42, n.5, pp.591-594, 2008.

[15] S.T. Shishiyanu, N.A.P. Mogaddam, E. Yilmaz, R. Turan, "Effect of Gamma Radiation on Raman Spectra of Ge Nanocrystals embedded in $SiO_2$," Proc. of 5th Nanoscience and Nanotechnology Conference NanoTR5, Eskişehir, Turkey, pp.67-69, 2009.

[16] J.H. Yao, K.R. Elder, H. Guo, M. Grant, "Theory and simulation of Ostwald ripening," Phys. Review B, vol. 47, n. 21, pp.14 110-14 125, 1993.

[17] F.B. Ergin, R.Turan, S.T. Shishiyanu, E.Yilmaz. "Effect of γ-radiation on $HfO_2$ based MOS capacitor," Nuclear Instruments and Methods in Physics Research Section B; vol.268, n.9, 2010, pp.1482-1485.