The Radiation Effects on Structural Defects and Reliability of High-k MOS Gate Dielectrics

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***Abstract* — The effects of γ – irradiation on the physical and electrical properties of ZrO_2 and HfO_2 based high-k MOS structures were studied. The doses of γ –irradiation applied have been up to 80 Gray. The C-V characteristics seeing as the flat-band shift when exposed to γ – irradiation showed high reliability of the structures. Raman scattering spectra of the ZrO_2 thin films grown by RF magnetron sputtering on silicon substrate have been investigated. The impact of γ –irradiation doses on the ZrO_2 thin films Raman spectra was analyzed. The intensity of the Raman signal originating from monoclinic ZrO_2 is found to decrease with increasing gamma radiation.**

***Index Terms* — ZrO_2, HfO_2, Gamma Rays, MOS structure, Raman**.

I. INTRODUCTION

Traditionally silicon dioxide for the gate dielectric, SiO_2, has to less than acceptable limits (<20A) [1] where the gate leakage current are a substantial detriment to device operation [2,3]. The continued decrease of the SiO_2 thickness is no longer possible for future MOS-CMOS devices and therefore replacement dielectrics need to be found. The high-k materials can be more thicker to reduce the leakage current while increasing the capacitance, via a higher dielectric permittivity special the following Al_2O_3 [4-7], ZrO_2 8-11], HfO_2 12,13,14,15]. By using these high-k dielectric materials for gate insulator, it will be possible to build devices with an equivalent oxide thickness (EOT) of 10nm that have significantly reduced leakage current compared to similar devices build using SiO_2 [13].

Have been investigated different effects in this materials: effect of radiation and charge trapping on the reliability of high –k gate dielectrics [12,14,15], hysteresis in metal insulator semiconductor structures with high temperature annealed ZrO_2/SiO_x layers [14]; the radiation effects in high-k HfO_2 and Al_2O_3 as MOS gate dielectric [17], effect of γ –irradiation on ZrO_2 properties [16], radiation sensors based on high-k ZrO_2 [18].

Despite the large amount of ongoing research into alternative dielectrics, very little work has been done to understand the low dose γ- radiation responses of ZrO_2 and HfO_2 materials, on structural defects and reliability. In this paper we examine the γ- radiation effects on charge structural defects and reliability of high-k ZrO_2 and HfO_2 materials as MOS gate dielectrics.

II. RESULTS AND DISCUSSION

2.1. Specific properties of high-k dielectrics

The silicon dioxide SiO_2 is the best material for MOS-CMOS integrate circuit producing. But for new generation of nano-devices with nanoscale of gate thickness lower than 1- 2nm this dielectric with low k-permittivity (3.9) can not be used due to the gate large tunneling current, low threshold voltage, high concentration of interface defects and low radiation reliability Therefore replacement dielectrics need to be found. Zirconium oxide (ZrO_2) and hafnium oxide (HfO_2) with high-k permittivity (20-25) and high band gap energy (3.2-3.5) eV are the main candidate for replacement of SiO_2.

The replacement of SiO_2 by high-k dielectrics can be selected on the base of relation of equivalent oxide thickness [5-8]:

$$EOT=3.9\times t_{hk}/\varepsilon_{hk}, \qquad (1)$$

where 3.9 is permittivity of SiO_2, t_{hk}, ε_{hk} – thickness and permittivity of high-k dielectric. In Table 1 are presented the calculated values of t_{hk} for different high-k dielectrics and EOT=10.

TABLE 1. THE CALCULATE VALUES of t_{hk} FOR DIFFERENT HIGH-K/Si DIELECTRICS as a GATE-MOS and EOT=10.

Material/ Parameters	**SiO_2/ Si**	**Al_2O_3/ Si**	**ZrO_2/ Si**	**HfO_2/ Si**	**TiO_2/ Si**
ε_i	3.9	8	23	25	49
EOT	10	10	10	10	10
t_{hk}	10	20.5	58.9	64	125.4

As follows from this data, dielectric SiO_2 with thickness of 1nm -10nm can be replaced by ZrO_2 with thickness of 6nm – 110nm, or by HfO_2 with thickness of 6.4nm-64nm, or by Al_2O_3 with thickness of 2.0nm- 20nm. Another advantage is in technological compatibly of this MOS structures with conventional MOS technology in microelectronics. But till now this new material are not all satisfactory properties and quality for industrial implementation.

In this paper we analyze the result of γ-radiation effect on Raman spectra and CV characteristics of structures

ZrO_2/SiO_2/nSi and HfO_2/SiO_2/nSi and impact of Rapid Photothermal Processing (RPP) on composition and CV characteristics of these structures related to there radiation reliability. The technology of investigated structures elaboration we have previously presented in [13,14,17,18]

2.2. Effect of γ-radiation on Raman spectra and CV characteristics of ZrO_2/SiO_2/nSi

The effect of γ-radiation dose on the chemical composition and phase of ZrO_2 (Zr-O bonds) and Si-substrate (Si-Si bonds) where determined by Raman spectroscopy, carried out at room temperature [18,19]. Have been observed the peak at 616cm^{-1}corresponding to the Zr-O phonon mode confirming the monoclinic zirconia dioxide formation after thermal annealing at 850°C for 1 hour in O_2. Decrease of Raman spectra intensity is duet o the decrease of the number of Zr-O bonds broken by γ-radiation with 0.1 and 20.0 Gy dose. The ZrO_2 spectra broadening after γ-radiation (80Gy) is likely to result from the increase of local compressive stress [18].

The influence of γ-radiation on CV characteristics of ZrO_2 at different dose (0.1, 2.0, 20, 80) Gy, and HfO_2 at dose (0.1-16)Gy have been investigated in our works [17,18]. For ZrO/SiO_2 have been shown that the CV characteristics under radiation shifts to negative threshold voltage from -1.3V to -1.63V as results of increasing concentration of positive trap-charge defects. Some results are presented in Table 1 and Fig. 1. The obtained results for HfO_2/nSi shown the bidirectional shift of CV characteristics presented in Table 2 and Fig. 1.

TABLE 2. THE RADIATION DEPENDENCE of THRESHOLD VOLTAGE V_T for ZrO_2/nSi and HfO_2/nSi

Dose, Gray	V_T **ZrO_2/nSi**	V_T **HfO_2/nSi**
0.1	1.3	2.0
0.5		1.75
1		1.5
2	1.33	1.1
4		1.2
8		1.4
16		1.6
20	1.35	
40	1.40	
60	1.55	
80	1.62	
$\Delta V_T/\Delta D_\gamma$;	4.1×10^{-3} V/Gy=4.1× 10^{-6} V/rad	3.7×10^{-3} V/Gy=3.7× 10^{-5} V/rad

As is shown in Fig. 1 and Table 2, for HfO_2/nSi under low dose of 0.1Gy - 2Gy the CV characteristics shifts to positive threshold voltage from -2V to -1.1V, but at higher dose from 2Gy to 16Gy the CV characteristics returned to -1.6V. The estimated γ - radiation sensitivity for ZrO_2/nSi is equal to 4.1×10^{-6}V/rad and for HfO_2/nSi is equal to 3.7×10^{-5} V/rad. The estimated radiation sensitivity of HfO_2 to X-rays from data presented in [12] is ~4×10^{-6}V/rad.

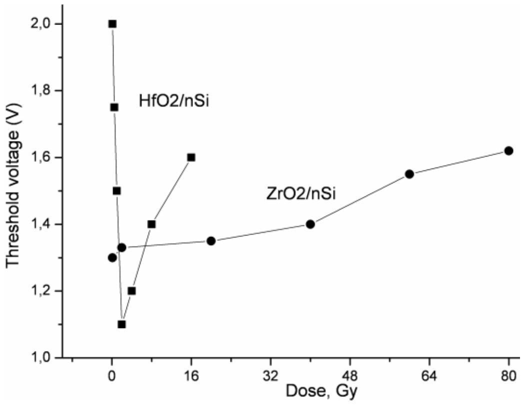

Fig. 1. The radiation dependence of threshold voltage, V_T, for ZrO_2/nSi and HfO_2/nSi.

These values are not exact because they depend on different factors as technology of growing, post growing thermal treatment, thickness of multilayer structures etc. But, in any case, these estimated values are very high in comparison with the radiation of sensitivity of the best quality SiO_2/Si structures (~mV/1Mrad). Therefore the problem of radiation reliability and radiation degradation of high-k dielectrics is very important and need the future investigation, higher material quality leads to higher reliability. For improvement of quality and reliability of ZrO_2/Si and HfO_2/Si, as well as SiO_2/Si, can be used different methods - the new technologies, the optimal regime of post growing thermal treatment, structure design, impurity compositions etc. In our case for improvement of quality of ZrO_2/nSi we used the post growth Rapid Photothermal Processing (RPP) in temperature interval from 200°C to 600°C.

2.3. Impact of RPP on composition, Raman spectra and CV characteristics of ZrO_2/SiO_2/Si structures

The reliability of structures ZrO_2/SiO_2/Si can be improved by different methods: by improvement of growing technology, by optimization of post growing thermal treatment in forming gases etc. Our experiments showed that by Rapid Photothermal Processing is possible to improve the composite (Zr, O, Si), Raman specter and CV characteristics of these structures. The influence of Rapid Photothermal Processing (RPP) on morphology and composition of structures ZrO_2/SiO/nSi have been studied by EDX. For illustration in Fig. 2 are presented the EDX composition of ZrO_2/SiO_2 and in Fig. 3 - concentration of elements (Zr, O, Si) after RPP at different temperatures. These data confirm the presence in ZrO_2 layers only Zr and O elements. At the same time the morphology of ZrO_2 layers becomes more homogeny with minimum surface defects.

In Fig. 3 are presented the concentration of Zr and O elements after RPP at different temperatures in the structure ZrO_2/SiO_2/nSi. The samples in this experiment have been prepared at magnetron power 250W, pressure 1.5Pa (Ar/O_2) and temperature 300°C.

Fig. 4 shows that before RPP the intensity of Raman shift for Zr-Zr bond (300 cm^{-1}), Zr-O bond (616 cm^{-1}) and Si-Si substrate bond (520 cm$^{-1)}$) were minimal. But after RPP the intensity of Zr-Zr bonds and Zr-O bonds increased to maximum at T=400°C and the intensity of Si-Si bonds increased to maximum at 450-500°C; after RPP at 600°C intensity of Zr-Zr, Zr-O and Si-Si bonds returned to minimum. These experimental results demonstrated that by rapid photothermal processing at temperature ~ 400°C in the time of ~60 sec is possible to improve the structure of $ZrO_2/SiO_2/Si$ by increasing the number of he bonds (Zr-Zr, Zr-O and Si-Si).

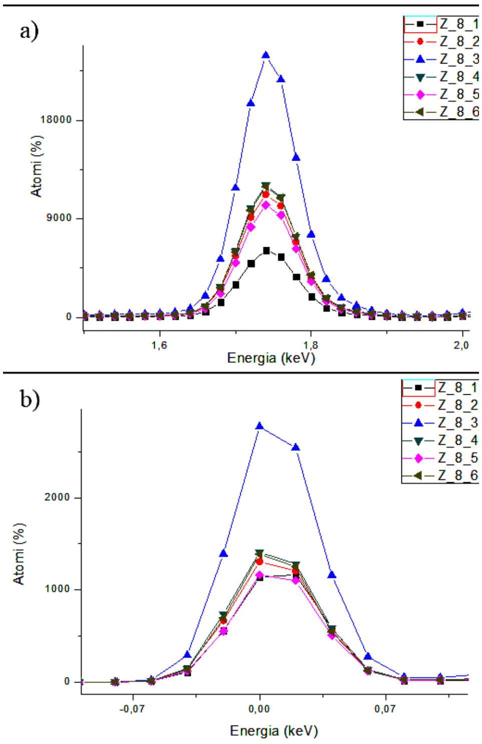

Fig. 3. The concentration of Zr (a) and O (b) after RPP at different temperatures at t=60sec: 1) T=200°C;2) T=300°C; 3) T=400°C; 4) T=450°C; 5), T=500°C.

Fig. 3 shown the that highest concentration of Zr and O is after RPP at 400°C. In Fig. 4(a,b,c,d) are presented the Raman spectra of ZrO_2/Si after RPP at different temperatures.

The optimal temperature and time of RPP depend of technology and composite of these structures. Also we studied the CV characteristics of structures $ZrO_2/SiO_2/Si$, measured at different frequencies (10kHz, 100kHz, 1MHz) after RPP at 200°C (a), 300°C (b), 400°C (c) and 450°C (d). After RPP at 400°C the CV characteristics shifts to negative midgap voltage (V_{mg}): small shift at 1MHz, average at 100kHz and high at 10kHz (about $\Delta V_{mg} = -1.5$V). This means that under RPP at 400°C the concentration of positive charge defects have been increased, $\Delta N^{+} = \Delta Q^{+}/qA = C\Delta V_{mg}/qA$, where C and A is dielectric capacity and aria, q – electron charge.

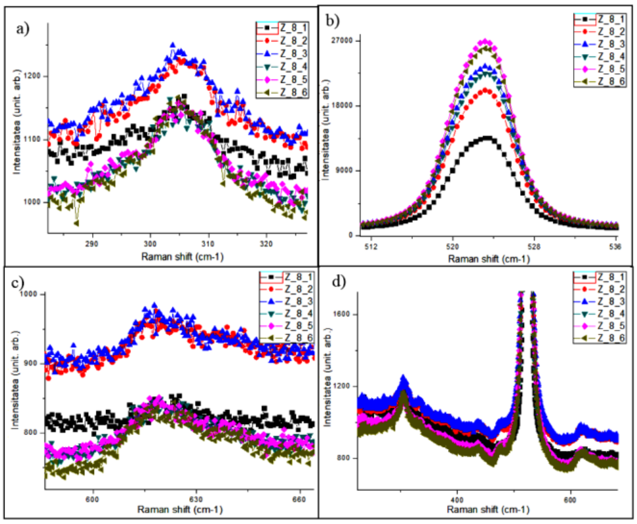

Fig. 4. Raman spectra of ZrO_2/Si after RPP at different temperatures: a) Zr-Zr bonds (300 cm^{-1}), b) Si-Si bonds (520 cm^{-1}); c) Zr-O bonds (616 cm^{-1}), d) Full range Raman spectra; temperature – 1) T=200°C; 2) T=300°C; 3) T=400°C; 4) T=450°C; 5) T=500°C; 5) T=600°C; t=60s.

At the same time the CV at 10kHz shows the minimum at region of flatband voltage (ΔV_{fb} = 0-0.5)V, which can be due to presence of negative charge – trap defects.

The obtained results shown that the low dose γ-radiation response and instability of structures $ZrO_2/SiO_2/Si$ and $HfO_2/SiO_2/Si$ is due to the radiation excitation of the different interface trap-charge defects in these structures.

The experimental results are explained by model of interface trap-charge defects. We consider the presence at list three type of interface trap-charge defects in this structure: the positive charge interface defects Q_0^{+} $(SiO_x)^{+}$- conventional defects in SiO_x/Si, positive trap-charge interface defects like donor centers Q_d^{+} $(ZrSi_xO_y/SiO_x)^{+}$ and negative trap-charge interface defects like acceptor centers Qa^{-} $ZrO_2/ZrSi_xO_y$. In this case the total defect charge in structure is $Q_T = Q_0^{+} + Q_d^{+} - Qa^{-}$. The effect of improvement of quality of ZrO_2/Si by RPP is as results of dissociation of slow energy defects (Q_d^{+}), (Q_a^{-}) and formation of the new Zr-Zr, Zr-O and Si-Si bonds.

III. CONCLUSION

Have been investigated the radiation effects on structural defects and reliability of high-k MOS gate dielectrics ZrO_2/Si and HfO_2/Si. The response of this materials to the low dose γ-radiation (Raman spectra and CV characteristics) and low reliability compare to SiO_2/Si is attributed to excitation of presented positive charge defects like donor centers (Q_d^{+}) and negative charge defects like acceptor centers (Q_a^{+}).

By RPP at optimal temperature and duration (in our case T=400°C and t=60sec) is possible to increase the number of bonds (Zr-Zr, Zr-O, Si-Si) and to improve the quality and reliability of high-k MOS gate dielectrics (ZrO_2/Si and HfO_2/Si.).

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