Effects of γ – irradiation on ZrO_2 properties

Sergiu T. Shishiyanu[1] , Valentin K. Gueorguiev[2], Ercan Yilmaz[3], Rasit Turan[4], Teodor S. Shishiyanu[1]

[1]*Department of Microelectronics, Technical University of Moldova, 2004 Chisinau, Moldova*
[2]*Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria*
[3]*Department of Physics, Middle East Technical University, 06531Ankara, Turkey*
[4]*Department of Physics, Abant Izzet Baysal University, 14280 Bolu, Turkey*

Abstract

The effects of γ – irradiation on the physical and electrical properties of ZrO_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 sensitivity.
Raman scattering measurements of the undoped 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. We also observed peak shift with the gamma radiation dose.

Keywords: ZrO_2, Gamma Rays, MOS structure, Raman.

1. Introduction

Silicon dioxide for the gate dielectric, has to less than acceptable limits (< 20A) [1] where the gate leakage currents are a substantial detriment to device operation [2,3]. The continued decrease of the SiO_2 thickness is no longer possible for future CMOS and therefore replacement dielectrics need to be found.
The new dielectric materials must emulate as many of the good SiO_2 qualities as possible. The high-k materials, which can be made thicker to reduce the leakage current while increasing the capacitance, via a higher dielectric permittivity, high-k, are required and notably Al_2O_3 [4-6], ZrO_2 [7-10].

Zirconium oxide (ZrO_2) is one of the most promising high-k dielectric for applications gate oxides for future generation of CMOS with low tunnel leakage current and as insulators in memory capacitors of dynamic random excess memory [11,12]. Lately, this dielectric was proposed as blocking oxides for silicon-oxide-nitride-oxide-silicon electrically erasable read only memory (FLASH EEPROM) for the future generation high-speed and low-power-consumption FLASH, including those based on silicon quantum dots [13]. The electronic and atomic structure of silicon oxide SiO_2, has been extensively studied during last four decades. However, much less is known about ZrO_2.

2. Experimental

Metal-oxide-semiconductor MOS structures were fabricated on *n*-type (100) silicon wafers with phosphorous doping of about 1×10^{15} cm^{-3}.

Chemical silicon oxide layer on the top of silicon wafers for MOS structures was grown in H_2SO_4:H_2O_2 (3:1) mixture at temperature of 40°C, for 20 min. The thickness of the chemical silicon oxide layer was 2 nm.
Zirconia with thickness of 80nm was deposited by radio frequency magnetron sputtering from Zr target (Lesker Co. with purity 99.7%). The sputter gas was Ar/O_2 (90/10) mixture at a pressure 0.5 Pa. The samples were annealed at 850 °C in dry oxygen for 1 h.
Top aluminum contacts on the oxide were deposited by thermal evaporation. The area of the fabricated capacitors was of about 1×10^{-4} cm^2. Finally, all samples were annealed at 425°C for 30 min in forming gas.
The obtained capacitors were electrically studied using HP impedance meter to obtain the C–V characteristics. The HF C–V measurements were performed at 1 MHz.

The formation mechanism for ZrO_2 oxide goes through the sequences of nucleation and growth. The formation of ZrO_2 and evolution of nanostructures upon gamma radiation were studied by Raman spectroscopy measurements. Raman scattering spectra were taken on a confocal micro-Raman (HR800, Jobin Yvon), attached with Olympus microanalysis system and a charge-coupled device (CCD) camera providing a resolution of ~1 cm^{-1}. The spectra were carried out in backscattering geometry with the 632.8nm line of He-Ne laser at room temperature. The effect of γ-radiation dose on the chemical composition and phase of the Zr nanocrystals were determined by Raman spectroscopy, carried out at room temperature.

The obtained ZrO_2 MOS structures have low leakage currents (1e−7 A/cm^2) with highest k –value (~20) for 80nm ZrO_2 layer RF-magnetron deposited at 310°C.

The Si substrates Raman spectra of the non radiated and irradiated by γ-Raya are shown in Fig. 1. The Si substrates Raman spectra it is narrowed and the peak at 521cm^{-1} is right shifted to 522 cm-^{1} while increasing the dose of γ-radiation shown in Fig. 1. The Raman scattering spectra intensity dependence on the γ-radiation dose from 0.1 to 20 Gy was found to decrease as shown in Fig. 2.

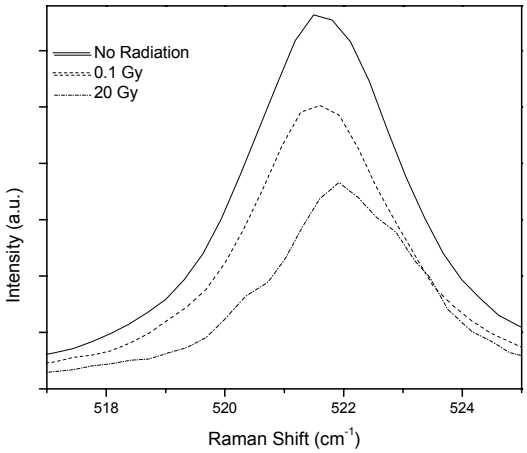

Fig. 1. Raman scattering spectra of the Si-Si bonds of the substrate: non irradiated and irradiated with 0.1 and 20.0 Gy doses.

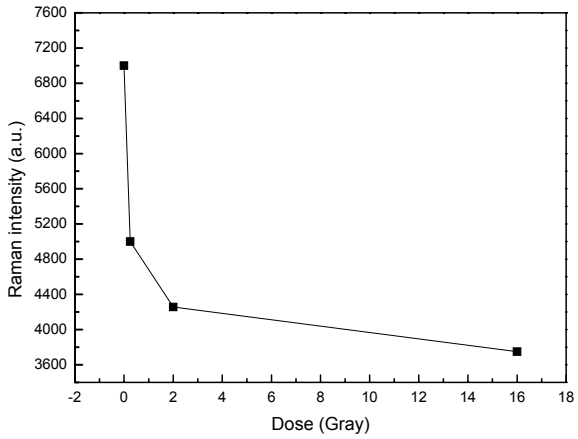

Fig. 2. Raman spectra intensity vs γ–radiation dose.

Raman spectra of the ZrO_2 embedded in the SiO_2 matrix show a 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 [14,15].

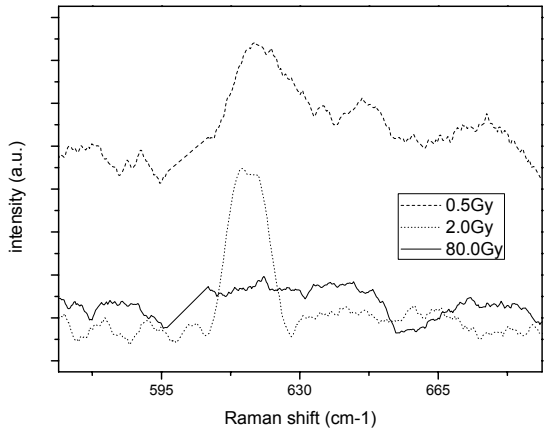

Fig. 3. Raman scattering spectra of the ZrO_2: γ-radiated with 0.5, 2.0 and 80.0 Gy doses.

Raman spectra of the ZrO_2 embedded in the SiO_2 matrix show a 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 [14,15]. The decrease of Raman spectra intensity is due to the decrease of the number of Zr–O bonds broken by high–energy γ-radiation. The ZrO_2 spectra broadening after γ-radiation (80 Gy) is likely to result from the increase of local compressive stress [16].

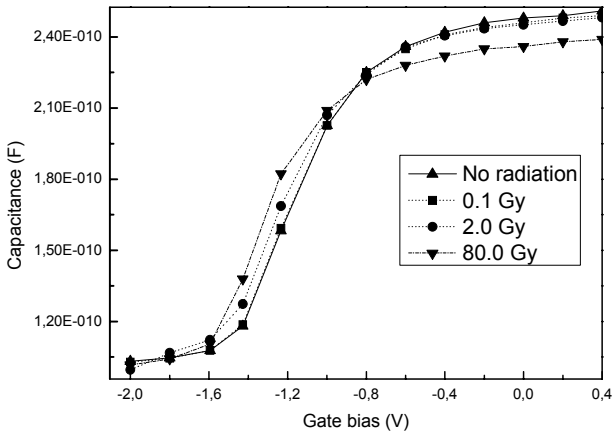

Fig. 4. C-V curves for capacitors irradiated by γ -rays with doses from 0.1 to 80.0 Gy.

Fig. 4 shows the measured flat band shift upon exposure as a function of γ -ray dose from 0.1 to 80 Gy. This shift to the negative direction is attributed to trapping of holes generated by radiation.
Electrons generated during ionization disappear into the metal contact and the substrate leaving behind a hole in the oxide. The generated holes are trapped at some oxide and interface defects.

Conclusions

We have fabricated Zr nanocrystals embedded in SiO_2 layer by RF magnetron sputtering.
$ZrO_2/SiO_2/Si$ nanostructures response to gamma radiation studied by Raman spectroscopy and C-V flat band shift measurements shown the possible application as the radiation sensors.

[1] R. H. Dennard, et al. IEEE J. Solid-State Circuits SC-9, p.256, 1974.
[2] D.A.Buchanan. IBM J. Res. and Develop. 43, p.245, 1999.
[3] S. H. Lo, D. A. Buchanan, and Y. Taur, IBM J. Res. and Develop. 43, p.327, 1999.
[4] V.V.Afanas'ev, et al. J. Non-Crys. Sol. 303, p. 69, 2002.
[5] L. Manchanda, et al. IEDM Technical Digest, p.605 1998.
[6] E. Yılmaz, I. Dogan, R. Turan. Nuclear Instruments and Methods in Physics Research B, 266, Iss 22, pp. 4896-4898, 2008.
[7] S. Ramanathana, P. C. McIntyre, S. Guha, E. Gusev, Appl. Phys. Lett. 84, pp. 389-391, 2004.
[8] J. Robertson, K. Xiong, B. Falabretti, IEEE Electron Device Lett., p.19, 2004.
[9] M. Houssa, J. L. Autran, A. Stesmans, M. M. Heyns. Appl. Phys. Lett. 81, p.709, 2002.
[10] T.S. Kalkur, Y.C. Lu. Thin Solid Films 207, pp. 193-196, 1992.
[11] G.D. Wilk, R.M. Wallace, J.M. Anthony, J. Appl. Phys. 89, 10, pp. 5243-5274, 2001.
[12] J. Robertson, Euro. Phys. J. Appl. Phys. 28, pp. 265-291, 2004.
[13] V.A. Gritsenko, et al. Solid-State Electronics 47, pp.1651-1656, 2003.
[14] B-K.Kim, H.Namaguchy. Phys. Stat. Sol. (b), 203, p. pp.557-563, 1997.
[15] J.E.Maslar et al. J. of Nuclear Materials 298, pp.239-247, 2001.
[16] U. Serincan, G. Kartopu, A. Guennes, T.G. Finstad, R. Turan, Y. Ekinci, S.C. Bayliss. Semicond. Science Technol. 19 pp. 247-251, 2004.