

Defect engineering in the MOSLED structure by ion implantation

S. Prucnal^{a,b,*}, A. Wójtowicz^a, K. Pysznik^a, A. Drozdziel^a, J. Zuk^a, M. Turek^a, L. Rebohle^b, W. Skorupa^b

^a Maria Curie-Skłodowska University, Pl. M. Curie-Skłodowskiej 1, 20-035 Lublin, Poland

^b Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

ARTICLE INFO

Article history:

Available online 20 February 2009

PACS:

72.20.Jv

73.40.Qv

78.60.Fi

Keywords:

MOSLED

Ion implantation

Defect engineering

Electroluminescence

ABSTRACT

When amorphous SiO₂ films are bombarded with energetic ions, various types of defects are created as a consequence of ion–solid interaction (peroxy radicals POR, oxygen deficient centres (ODC), non-bridging oxygen hole centres (NBOHC), E' centres, etc.). The intensity of the electroluminescence (EL) from oxygen deficiency centres at 2.7 eV, non-bridging oxygen hole centres at 1.9 eV and defect centres with emission at 2.07 eV can be easily modified by the ion implantation of the different elements (H, N, O) into the completely processed MOSLED structure. Nitrogen implanted into the SiO₂:Gd layer reduces the concentration of the ODC and NBOHC while the doping of the oxygen increases the EL intensity observed from POR defect and NBOHC. Moreover, after oxygen or hydrogen implantation into the SiO₂:Ge structure four-fold or fifth fold increase of the germanium related EL intensity was observed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Great efforts are currently undertaken worldwide to achieve efficient light emission from Si-based structures and devices with the aim of developing an integrated optoelectronic platform on Si [1]. One of the most promising candidates are metal–oxide–silicon light emitting devices (MOSLEDs) containing Si nanoclusters embedded in SiO₂ co-doped with rare earths (RE) [2], SiO₂ layers doped with RE's only or Ge-implanted silica [3–6]. Due to the excellent dielectric properties of SiO₂ and the large electron barrier at the Si/SiO₂-interface, electroluminescence from the MOS light emitters is normally excited by hot electrons injected by Fowler–Nordheim (F–N) tunnelling at high electric fields in the range of 6–8 MV/cm [7]. Charge trapping leading to breakdown and quenching of the EL intensity during the operating time of the MOSLED devices are a key problem limiting the broad spectrum of potential applications of such devices. Defects generated in the oxide matrix by the ion implantation and hot electrons injected during F–N tunnelling are responsible for the charge trapping. Charge trapping and carrier transport in Ge⁺ implanted blue light emitting MOS devices were studied by Gebel et al. [8]. Nazarov et al. explained the charge trapping mechanism in Er-doped Si-rich SiO₂ films containing silicon nanoclusters [9] and proposed an EL quenching mechanism in Ge implanted SiO₂ layer [10]. Recently,

we have shown the correlation between the charge trapping during electron injection process and the specific luminescent defects such as: ODC, E' centres and NBOHC [11]. Therefore, in order to increase the operating time of the MOSLED devices it is necessary to reduce the number of defects in silica. In this paper we present the enhancement of the EL intensity and the reduction of the point defects concentration in a SiO₂ layer by the low dose ion implantation of hydrogen, nitrogen and oxygen into the full processed MOSLED devices. The MOSLEDs containing Ge co-implanted with O (fluence 5×10^{12} ion/cm²) or H (fluence 5×10^{13}) show a fourfold or fivefold increase of the ultraviolet EL intensity with a maximum at 380 nm related to Ge centres, respectively. Additionally, four times weaker EL intensity related to NBOHC and twice in case of the E'_o centres were observed. Similar effects are shown by samples co-implanted with oxygen. Nitrogen co-implantation enhances twice the EL intensity related to Ge centres simultaneously reducing the number of the NBOHC at about 25%. In case of the MOSLED devices containing RE (Gd or Tb) the best results after nitrogen co-implantation were observed. The EL intensities observed from the ODC and E' centres were reduced by about four and three times, respectively.

2. Experimental details

Electroluminescence devices are prepared by standard silicon MOS technology on 4 in. n-type silicon wafers with a resistivity of 2–5 Ωcm. Thermally grown 100 nm thick SiO₂ layers with a 1000 nm field oxide frame were processed in LOCOS (LOCAl

* Corresponding author. Address: Maria Curie-Skłodowska University, Pl. M. Curie-Skłodowskiej 1, 20-035 Lublin, Poland.

E-mail address: prucnal@tytan.umcs.lublin.pl (S. Prucnal).

Oxydation of Silicon) technology and implanted by RE (Gd and Tb) and Ge ions with an energy of 100 and 50 keV, respectively and subsequently annealed at 900 °C for 1 h in the nitrogen ambient. In order to protect the oxide layer against breakdown, a 50 nm SiON layer was deposited on it (ratio between O and N is 1:1). The SiON layer was deposited by plasma-enhanced chemical vapour deposition and the atomic composition of the SiON layers was confirmed by scanning Auger electron spectroscopy (AES Microlab 310F). The maximum concentration of rare earths (Gd and Tb) and Ge atoms was 1.5%. The fluence of the co-implanted elements (hydrogen, nitrogen and oxygen) were ranging from 5×10^{12} to 5×10^{14} ion/cm². The depth profile of implanted elements was calculated using the SRIM 2003 code [12]. Hydrogen, nitrogen and oxygen were implanted into full processed MOSLED structure with an energy of 25 keV, 110 keV and 120 keV, respectively. Whereas the current density of the ion beam during implantation of the RE and Ge atoms was around 4 $\mu\text{A}/\text{cm}^2$, the ion current density of the co-implanted elements was around 0.5 $\mu\text{A}/\text{cm}^2$. The gate and bottom electrodes consist of 100 nm thick indium–tin–oxide (ITO) deposited by rf sputtering and a 300 nm thick evaporated Al layer, respectively. The EL measurements were performed using electron injection mainly from the silicon substrate. The EL spectra and the quenching of the EL intensity were measured at room temperature on MOS structures with a circular ITO electrode of 200 μm diameter at constant current supplied by a source meter (Keithley 2410). The EL signal was recorded with a TRIAX 550 single grating monochromator and a photomultiplier (Hamamatsu R943-02).

3. Results and discussion

Fig. 1. shows EL spectra from unimplanted and Gd or Ge implanted SiO₂ layer at an injection current of 1 μA . The maximum concentration of the implanted elements was 1.5%. A weak EL spectrum taken from an unimplanted sample is shown for comparison. Fig. 1 shows the EL spectra taken from the pure and implanted with Gd or Ge SiO₂ layers during constant current electron injection at 1 μA . The Gd-implanted SiO₂ layers show a strong EL with a peak at 314 nm arising from the transition of the lowest excited state of $^6\text{P}_{7/2}$ to the ground state $^8\text{S}_{7/2}$ of Gd³⁺ ions [13]. After Ge implantation the MOSLED structures exhibit a violet luminescence with maximum at 385 nm corresponding to the Ge oxygen deficient centres (GODC's), a peak at 650 nm corresponding to the NBOHC and a weak green luminescence at 550 nm observed from

the E' centres. In case of the unimplanted SiO₂ layer two weak bands with maximum at 450 (ODC's) and 650 nm (NBOHC) were observed. The EL taken from unimplanted samples at the same level of the excitation current is almost three orders of magnitude lower than those observed from the Gd-implanted oxide. The EL spectrum of Gd-implanted samples consists of a single monochromatic line at 314 nm emitted by the Gd³⁺ ions which is unique compared to other RE's in SiO₂. Therefore it gives the opportunity to investigate the properties of the defects created in the oxide layer during both ion implantation and electron injection.

Recently Nazarov et al. [11] have found that after Ge implantation into the SiO₂ layer and subsequent annealing only 0.01% of the Ge implanted atoms are involved in the formation of optically active centres (GODC's), while the major part of implanted Ge is incorporated in Ge clusters. Fig. 2 shows the change of the maximum EL intensity observed from the Ge implanted silica as a function of the fluence of the implanted hydrogen (open symbols) and oxygen (solid symbols) ions during constant current electron injection of 1 μA . Square symbols correspond to the GODC's, circles to the E' centres and the maximum EL intensity observed from the NBOHC is marked as triangles. In order to increase the concentration of optically active Ge atoms the low fluence ion implantation was performed. After oxygen implantation to a fluence of 5×10^{12} ion/cm² a fourfold enhancement of the EL intensity from GODC's and only two times higher defect related (E' centre and NBOHC) luminescence were observed. An increase of the fluence of implanted oxygen up to 5×10^{13} ion/cm² reduces the concentration of the E' centres and NBOHC five and three times, respectively. Similar effect after nitrogen implantation (not shown here) with the same fluences was observed. Much more spectacular results after hydrogen implantation were obtained. The EL intensity observed from the NBOHC defects does not depend on the hydrogen content up to 5×10^{13} ion/cm². Further increase of the fluence of the hydrogen implanted into the SiO₂ layer up to 5×10^{14} ion/cm² reduces the number of the NBOHC defects. In case of the E' centres only a slight increase of the EL intensity for the medium dose of the hydrogen implanted samples was observed. Moreover sixfold enhancement of the violet electroluminescence emitted from GODC defects due to hydrogen implantation to a fluence of 5×10^{13} ion/cm² takes place. An increase of the H dose up to 5×10^{14} ion/cm² does not change the maximum EL intensity related to the GODC defects. Simultaneously the concentration of the E' centres and NBOHC defects is reduced by factor of two and

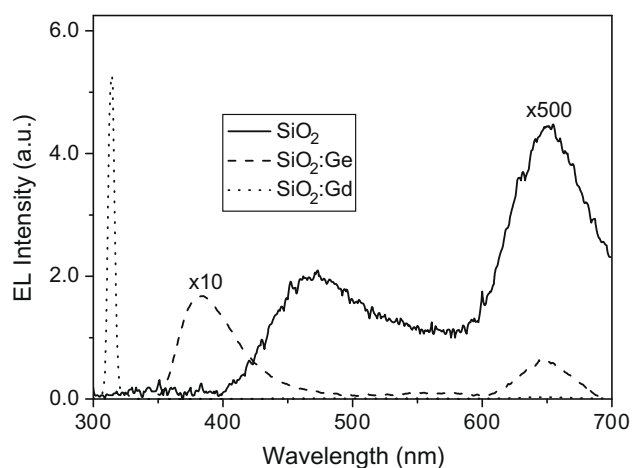


Fig. 1. EL spectra from unimplanted and Gd or Ge implanted SiO₂ layer at an injection current of 1 μA . The concentration of the implanted elements was 1.5%. A weak EL spectra taken from unimplanted sample is shown for comparison.

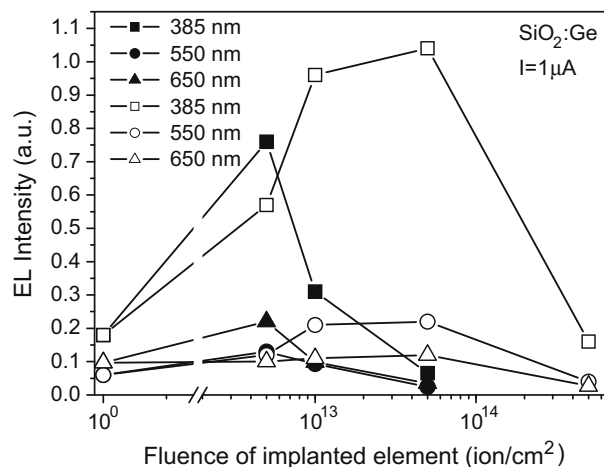


Fig. 2. Change of the maximum EL intensity from the GODC's (385 nm), E' centres (550 nm) and NBOHC's (650 nm) in the Ge implanted SiO₂ as a function of the fluence of the implanted oxygen (solid symbols) and hydrogen (open symbols) ions. For constant current excitation 1 μA was used.

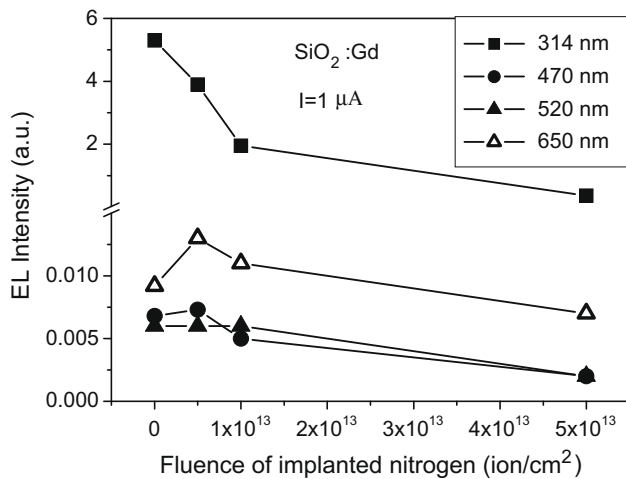


Fig. 3. Maximum EL intensity of the major peaks observed from the $\text{SiO}_2:\text{Gd}$ layer as a function of fluence of the implanted nitrogen. Squares, circles, solid and open triangular corresponds to Gd^{3+} (314 nm), ODC's defect (470 nm), E' centres (520 nm) and NBOHC's defects (650 nm), respectively.

five, respectively. The enhancement of the Ge related luminescence in the blue–violet range of the spectra observed after hydrogen or low fluence oxygen or nitrogen co-implantation is due to the destruction of the Ge clusters. This phenomenon increases the number of the Ge related optically active luminescence centres. Ion implantation of H, N or O to fluence above $5 \times 10^{14} \text{ ion/cm}^2$ introduces new defects into the silica matrix such as radiative damage on which the hot electrons injected by F–N tunnelling are scattered. Therefore the yield of the EL excitation is diminished.

We have investigated an influence of the H, N and O low dose co-implantation on the MOSLED structure containing rare earths (Gd or Tb) as well. Fig. 3 shows the change of the maximum EL intensity at the peak corresponded to the Gd^{3+} ions (314 nm), ODC defects (470 nm), E' centres (520) and NBOHC (650 nm) as a function of the nitrogen fluence. In contrary to the Ge implanted samples, the modification of the MOSLED structure by the low fluence of ion implantation, independently on the type of ions, decreases the UV EL intensity. The concentration of the ODC and NBOHC defects increases for the lowest implanted fluence of the nitrogen ($5 \times 10^{12} \text{ ion/cm}^2$), whereas the nitrogen implantation to a fluence above $1 \times 10^{13} \text{ ion/cm}^2$ decreases the EL intensity observed from the ODC and NBOHC.

The E' centres band with the maximum peak at 520 nm initially does not depend on the nitrogen content but the increase of the nitrogen fluence up to $5 \times 10^{13} \text{ ion/cm}^2$ decreases the EL intensity related to the E' centre more than two times (see Fig. 3). The same influence of the oxygen co-implantation on the quenching of the UV EL intensity at 314 nm was observed. But contrary to the nitrogen co-implantation oxygen co-implanted samples exhibit the reduction of the ODC related electroluminescence, whereas the red electroluminescence intensity at 650 nm corresponded to the NBOHC defects continuously increases with the fluence of oxygen.

Finally Fig. 4 shows the change of the EL intensity observed from the reference SiO_2 layer implanted with hydrogen, nitrogen or oxygen to a fluence of $5 \times 10^{13} \text{ ion/cm}^2$ measured at constant current injection. Both nitrogen and oxygen implanted into the SiO_2 layer do not change the total EL intensity observed from the ODC defects at about 470 nm. However, the red luminescence with

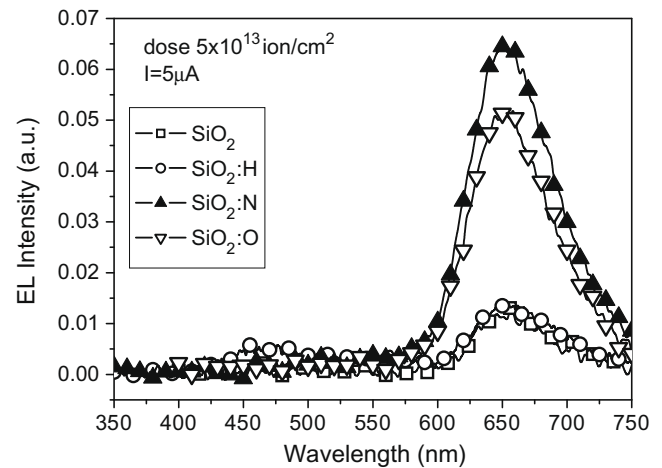


Fig. 4. Defect related electroluminescence from the SiO_2 layer modified by ion implantation. The experiments were performed at a constant current injection of $5 \mu\text{A}$.

a peak at 650 nm (NBOHC) increases five times after oxygen implantation and above six times after nitrogen implantation. Ten times increase of the fluence of the implanted O or N ions only gives rise to about 40% higher red EL intensity in comparison with low implanted fluence. In turn, hydrogen implanted into SiO_2 layers increases the number of the ODC defects and an enhancement of the ODC related EL is proportional to the hydrogen content.

4. Conclusions

It was found that co-implantations of light elements like hydrogen, nitrogen or oxygen to the full processed MOSLED structure containing Ge atoms enhance violet electroluminescence observed from the GODC's up to six times due to the increase of the number of optical active Ge centres. Simultaneously, the number of defects such as E' -centres and NBOHC are reduced. In case of the $\text{SiO}_2:\text{Gd}$ layer the co-implantation of the H, N or O at a fluence above $1 \times 10^{13} \text{ ion/cm}^2$ reduces both the number of the defects and UV EL intensity.

References

- [1] S. Ossicini, L. Pavesi, F. Priolo, *Light Emitting Silicon for Microphotonics*, Springer Tracts in Modern Physics, Springer, Berlin, 2003, 194.
- [2] A. Polman, *Nature Mater.* 1 (2002) 10.
- [3] M.E. Castagna, S. Coffa, M. Monaco, A. Muscara, L. Caristia, S. Lorenti, A. Messina, *Mater. Sci. Eng. B* 105 (2003) 83.
- [4] J.M. Sun, W. Skorupa, T. Dekorsy, M. Helm, A.N. Nazarov, *Opt. Mater.* 27 (2005) 1050.
- [5] J.M. Sun, W. Skorupa, T. Dekorsy, M. Helm, L. Rebohle, T. Gebel, *J. Appl. Phys.* 97 (2005) 123513.
- [6] S. Prucnal, J.M. Sun, W. Skorupa, M. Helm, *Appl. Phys. Lett.* 90 (2007) 181121.
- [7] D.J. DiMaria, J.W. Stasiak, *J. Appl. Phys.* 65 (1989) 2342.
- [8] A.N. Nazarov, J.M. Sun, I.N. Osiyuk, I.P. Tjagulskii, V.S. Lysenko, W. Skorupa, R.A. Yankov, T. Gebel, *Appl. Phys. Lett.* 86 (2005) 151914.
- [9] A.N. Nazarov, I.N. Osiyuk, J.M. Sun, S. Prucnal, R.A. Yankov, I.P. Tyagulskii, V.S. Lysenko, T. Gebel, L. Rebohle, W. Skorupa, *Appl. Phys. B* 87 (2007) 129.
- [10] S. Prucnal, J.M. Sun, A. Muecklich, W. Skorupa, *Electrochem. Solid-State Lett.* 10 (2007) H50.
- [11] S. Prucnal, J.M. Sun, A.N. Nazarov, I.P. Tjagulskii, I.N. Osiyuk, R. Fedaruk, W. Skorupa, *Appl. Phys. B* 88 (2007) 241.
- [12] J.F. Ziegler, *Nucl. Instr. and Meth. B* 219&220 (2004) 1027.
- [13] J.M. Sun, W. Skorupa, T. Dekorsy, M. Helm, L. Rebohle, T. Gebel, *Appl. Phys. Lett.* 85 (2004) 3387.