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Sensitization of the Blue-green Electroluminescence by Gadolinium Coupled to Si Nanocluster Embedded in a SiO_2 Matrix

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In this work an enhancement of the blue and green electroluminescence (EL) related to silicon inclusions into SiO_2 layer by gadolinium co-doping was investigated. The blue (460 nm) and green (550 nm) EL corresponds to the oxygen-deficient-centres (ODC) and Si nanoclusters with average diameter around 1 nm, respectively. After gadolinium co-doping a fourfold increase of the total EL intensity was observed. It was found that the increase of the blue and green EL is due to the energy transfer from Gd^{3+} ions to the ODC defects and amorphous silicon nanoclusters. Moreover, the gadolinium co-doping increases the concentration of the small silicon nanoclusters.
Keywords: electroluminescence, Gd, Si-nanocrystals, MOSLED, energy transfer.

1. INTRODUCTION

During the last two decades, big effort was undertaken to achieve efficient light emitters based on silicon or related materials like silicon dioxide, silicon nitride or SiC [1 – 3] with the aim of developing an integrated optoelectronic platform on Si. Several materials have been investigated showing electroluminescence (EL) with bands in different spectral regions. It was shown that metal-oxide-semiconductor (MOS) structures containing different rare earth elements can emit light from ultraviolet to the infrared spectral range related to their specific energy level structure [4 – 7]. Silicon nanoclusters (Si-nc) embedded in the oxide layer can emit light from green to IR due to quantum confinement effects [8]. The Si-nc's are commonly used as sensitizers for Er due to an energy transfer from the Si-nc to the Er^{3+} ion [9]. Recently, Jambois et al. reported [10] white light emitters based on SiO_2 implanted with carbon and silicon.

In this paper we present an enhancement of the blue (460 nm) and green (550 nm) EL obtained from the SiO_2 layer containing Si nanoclusters by gadolinium co-doping. The detailed study of the optical properties of our samples shows that the blue EL is emitted by the oxygen deficient centres (ODC) and it is enhanced due to an energy transfer from the Gd^{3+} ions to the ODC. The green EL at around 550 nm is emitted by small silicon nanoclusters with average diameters around 1 nm. The number of small Si-nc can be significantly enhanced by ion implantation and subsequent annealing at temperatures higher then 800 ºC [11].

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2. EXPERIMENTAL

Electroluminescence devices – MOSLED – are prepared by standard silicon MOS technology on 4 inch, *n*-type silicon (100) wafers with a resistivity of (2 – 5) Ωcm. Thermally grown 100 nm thick SiO_2 layers with a 1000 nm field oxide were processed using local-oxidation of silicon (LOCOS) technology and Si and Gd implantation. Two different sample sets were performed (see Table 1).

Table 1. Ion implantation and annealing parameters of investigated samples

	Step 1	Step 2	Step 3	Step 4
	Si impl.	Annealing	Gd impl	Annealing
Sample A	20 keV	1000 ºC, 30 min	140 keV	900 ºC, 30 min
Sample B	25 +55 keV	1000 ºC, 30 min	160 keV	900 ºC, 30 min

The atomic concentrations of Si and Gd varying from 3.5 % up to 12.5 % and from 0.4 % up to 3 %, respectively. The depth profile and the atomic concentration of the implanted elements (Si and Gd) was calculated using the SRIM 2003 code. In order to protect the oxide layer against the breakdown, a 200 nm (sample A) or 100 nm (sample B) thick SiON layer was deposited on top of it (O : N = 1 : 1) by plasma-enhanced chemical vapour deposition. The gate and bottom electrodes consist of a 100 nm thick indium-tin-oxide (ITO) layer deposited by rf sputtering and a 300 nm thick evaporated aluminium layer, respectively. The EL measurements were performed using electron injection mainly from the Si substrate. The EL spectra and the quenching of the EL intensity were measured at room temperature on MOSLED structures with a circular ITO electrode of 300 μm diameter at a constant current supplied by a source meter (Keithley 2410). The EL signal was recorded with a monochromator (Jobin Yvon Triax 320) and a photomultiplier (Hamamatsu H7732-10). Photoluminescence (PL) experiments were conducted at room temperature with an excitation wavelength of 325 nm from an He-Cd laser (laser power – 20 mW).

3. RESULTS

We have investigated the influence of the Gd co-doping on the optical and electrical properties of the SiO_2 layers containing silicon nanoclusters. For this purpose two different sample sets were performed. In case of “sample A” silicon and gadolinium were implanted with an energy of 20 keV and 140 keV which generates Si and Gd profiles with a maximum concentration at 30 nm and 60 nm below the surface of the SiO_2 layer, respectively. Such a distribution of the implanted elements provides the possibility for an effective excitation of both silicon nanoclusters and Gd^{3+} ions. In case of “sample B” the depth profiles of the implanted Si and Gd were completely overlapping. In order to have homogeneously distributed silicon nanoclusters in the SiO_2 silicon was implanted with two energies of 25 keV and 55 keV producing rectangular depth profile of Si in the range of 20 nm to 90 nm. The Gd atoms were implanted with an energy of 160 keV with the maximum peak concentration around 65 nm below the SiO_2 surface. Due to such implantation conditions gadolinium atoms are either incorporated into Si-nc or are in the close surrounding of the Si-nc which provides the possibility of the energy transfer from Gd^{3+} ions to the Si-nc.

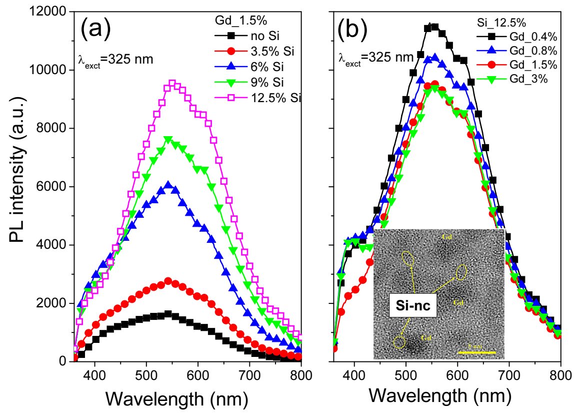

Fig. 1. Room temperature PL emission obtained from “sample B” containing different concentrations of silicon (a) or gadolinium (b). Inset in (b) shows HRTEM image of Si-nc and Gd clusters

The optical properties of the MOSLED structures containing Si and Gd were investigated by PL and EL measurements. Fig. 1 shows the PL emission observed from the samples containing a fixed concentration of either Gd (see Fig. 1, a) or Si (see Fig. 1, b) and varying the concentration of the second element. The PL signal shows a broad spectrum with three bands centred at about 550, 610 and 750 nm, and the intensity of the PL signal strongly increases with increasing silicon concentration (see Fig. 1, a). Samples containing 12.5 % of silicon and doped with different concentrations of Gd exhibit a slight decrease of the PL intensity with increasing Gd concentration (see Fig. 2, b) due to the partial degradation of the Si-nc during Gd implantation.

EL spectra taken from the same samples show a completely different behaviour. The electroluminescence measurements were performed under constant current excitation of 10 μA. The EL spectra exhibit two main bands at about 450 nm and 550 nm related to the ODCs and Si nanoclusters with average diameter around 1 nm, respectively [12]. The high-resolution TEM (HRTEM) measurements have been performed to check the Si-nc formation keeping the electron beam along [110] zone axis. Inset in Fig. 1, b, shows the HRTEM image of Si-nc and Gd clusters obtained from sample B containing 12.5 % of Si and 3 % of Gd. Only Si-ncs with average diameter around 2 nm are visible and they are located in close vicinity of amorphous Gd cluster with diameter of about 4 nm ±1 nm [13]. Since the contrast of Si nanocrystals is relatively low with respect to the surrounding amorphous SiO_2 smaller Si-nc than 2 nm are not distinguishable. The maximum EL intensity in the visible range was observed from the sample containing 1.5 % of Gd and 6 % of Si (see Fig. 3, a). An increase of the Si content above 6 % quenches the EL efficiency. It is worth to notice that the silicon co-doping strongly quenches the UV EL observed from the Gd^{3+} ions with the peak at 316 nm (see inset Fig. 2, a). The UV EL corresponds to a radiative intra-4f transition in the Gd^{3+} ions [7]. The same influence of the Si co-doping on the EL intensity obtained from Er^{3+} was presented by Sun et al. [4]. The rare earth’s luminescent centers are excited by hot electron impact excitation [5].

High concentration of the silicon nanocluster causes direct tunnelling of electrons between them, thus reducing the population of hot electrons for impact excitation of Gd^{3+} ions. If the visible EL is obtained only due to hot electron impact excitation the same rate of the quenching process should be observed.

The different behaviour of the UV and visible EL with increasing the Si concentration suggests that the UV EL observed from the Gd^{3+} ions is diminished by both the reduction of the hot electron population and an energy transfer from the Gd^{3+} ions to the ODC and Si-nc.

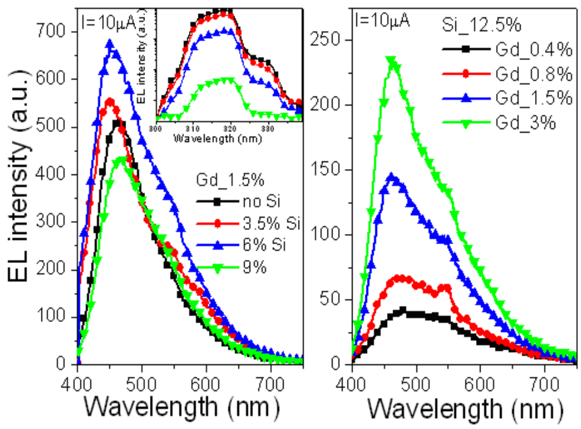

Fig. 2. EL intensity observed from samples containing different concentration of Si (a) or Gd atoms (b). The inset shows the UV EL observed from the Gd^{3+} ions. The EL measurements were performed under constant current excitation of 10 μA

Moreover, an increase of the Gd concentration from 0.4 up to 3% causes a sixfold enhancement of the visible electroluminescence intensity. In case of “sample A” the MOSLED structure containing Si-nc and Gd atoms shows a fourfold increase of the EL power efficiency (up to $3\cdot10^{-3}$ %) compared to the sample containing Si-nc only.

In order to clarify the EL excitation mechanism of the main luminescence centres the time resolved spectroscopy and the investigation of the EL intensity as function of the excitation current density was performed. Fig. 3, a and b, show the change of the blue (450 nm) and green (550 nm) EL intensity as a function of the injected current density (sample B), respectively. The EL-*J* curves marked by symbols and solid lines present the experimentally and theoretically obtained results, respectively.

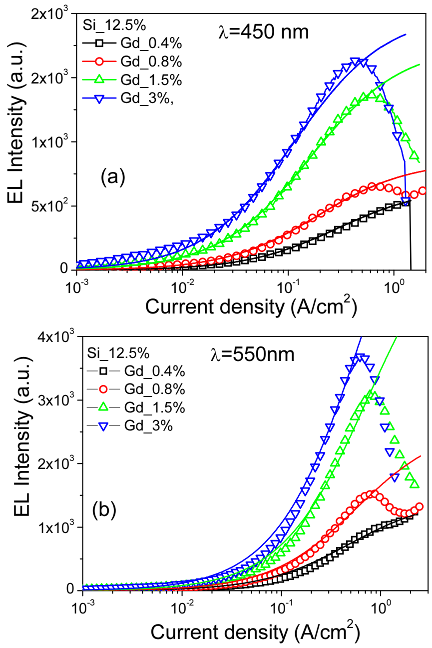

Fig. 3. EL intensity of the 450 (a) and 550 nm line (b) as function of the injected current density (sample B)

Initially, the EL intensity has a linear relationship with the injected current density, than it saturates and quenches for the high injection current. The saturation point (maximum EL intensity) is achieved when all optically active centers are excited or a steady state between excitation and de-excitation process is achieved. Finally, the quenching of the EL intensity is due to the deactivation of the luminescence centres by hot electrons (with energy above 7 eV). In order to examine the excitation process of the ODC defects and Si-nc in presence of Gd^{3+} ions the experimentally obtained EL-*J* curves were fitted by the following equation:

$$I_{EL} = I_{max}\frac{J/q}{J/q+1/\sigma\tau}$$

where I_{max}, J, σ, q and τ are the maximum EL intensity, the injection current density, the excitation cross section, electron charge and the total life time of the excited level, respectively [14]. The life time of the excited levels τ was obtained from single exponential fitting of the decay time curve. The product of $\sigma\tau$ is evaluated by fitting the dependence of I_{EL} vs. injection current density. Since the decay time is known we can calculate the excitation cross section for Gd^{3+} ions, ODC and Si-nc. The decay time of the 316 nm line decreases with increasing the Si concentration from 1.3 ms for the sample containing only Gd down to 0.74 ms for Gd codoped with 12.5 % of Si (sample B) and from 2 ms down to 0.95 ms (sample A). Additionally, in presence of Si-nc the decrease of the decay time of the UV EL from 0.97 ms down to 0.71 ms with increasing the Gd concentration up to 3 % was observed as well. The decrease of the decay time with increasing the Gd content is due to a concentration quenching [5]. The decay time of the blue EL decreases from 5 ms to 2.1 ms ±0.1 ms with increasing the Si concentration and was almost not dependent on the Gd content. The decay time of the 550 nm line observed from sample containing 1.5 % of Gd and different concentration of Si shows similar behaviour. With increasing the Si concentration up to 9 %, the τ_{550nm} decreases from 1.7 ms down to 0.92 ms while the samples with 12.5 % of Si and different concentrations of the Gd show the τ_{550nm} of about 1.2 ms ±0.2 ms. Moreover the excitation cross section σ of the ODC defects and Si-nc increases with increasing the Gd concentration from 2.05 cm^2 up to 6.65×10^{-16} cm^2 and from 3.6 cm^2 up to 8.3×10^{-16} cm^2, respectively. In case of “sample A” the Gd co-doping causes a fourfold increase of the maximum EL intensity at 450 nm and more than one order of magnitude in comparison with “sample B” containing 12.5 % of silicon. The decrease of the UVEL decay time and an increase of the excitation cross section of the main luminescence centres (ODC and Si-nc) can be taken as an evidence for the energy transfer from the Gd^{3+} ions to the ODC defects and silicon nanoclusters.

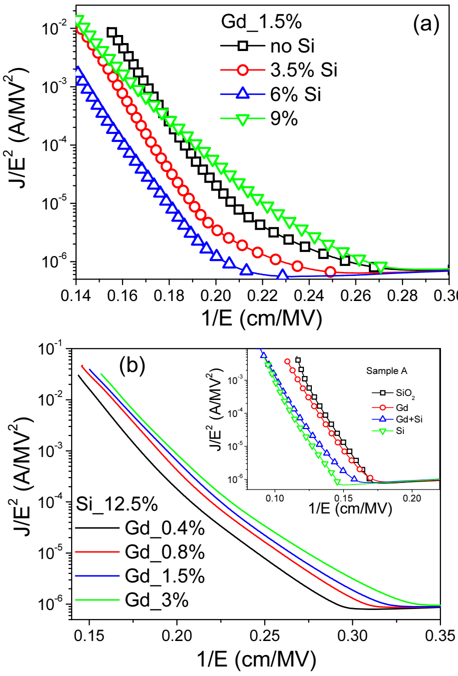

Fig. 4. Injected current density divided by the square of the electric field as the function of the reciprocal electric field in the MOSLED structure of the “sample B” containing different amounts of Si (a) or Gd (b). Inset (b) shows the $J/E^2(E^{-1})$ data measured from “sample A”

The current vs. electric field characteristics for the electron injection from the Si substrate were measured for samples containing different values of the Si or Gd content. Fig. 4 shows the dependency of the current density, on the average electric field, E, plotted in Fowler-Nordheim (FN) coordinates [$\ln(J/E^2) - 1/E$] for samples containing either 1.5 % of Gd and different concentration of Si (Fig. 4, a) or 12.5 % of Si and different concentration of Gd atoms (Fig. 4, b). The inset of Fig. 4, b, shows the $J/E^2(E^{-1})$ curves obtained from "sample A" containing only Gd or Si atoms or both elements together. The current-field (*I-E*) characteristics reveal that up to 6 % excess of Si the current injection into the dielectric is due to FN tunneling mechanism. Higher content of the Si atoms decreases the effective potential barrier for electron injection and the slope of the current-field curves decreases. In case of samples containing 12.5 % of Si and different concentrations of the Gd atoms the electron injection through the dielectric layer can be described by trap-assisted-tunnelling (TAT) mechanism [15].

An increase of the Gd content from 0.4 % up to 3 % does not affect the slope of the $J/E^2(E^{-1})$ characteristics but the *I-E* curves are shifted towards lower electric field. For the same value of the electric field with increasing the Gd concentration from 0.4 % up to 3 % the current density increases five times. It is known that Gd implanted into SiO_2 and subsequently annealed forms the Gd_2O_3 or $Gd_xSi_yO_z$ nanoclusters with a certain number of defects in the close vicinity of nanoclusters [16]. Such defects may create donor or acceptor levels in the SiO_2 band gap increasing the conductivity of the oxide layer which causes the shift of the *I-V* curve to the lower electric field. The inset of Fig. 4, b, shows the *I-V* characteristics obtained from "sample A" implanted by Gd or Si, or containing both Gd and Si atoms. The Si-nc's embedded close to the SiO_2 surface did not affect significantly the conduction mechanism through the oxide layer. The Gd implanted sample shows the same behaviour as sample B, the *I-V* curves were shifted towards lower electric fields which proves that defects created in the oxide layer by Gd implantation increase the conductivity of the SiO_2 and the conduction mechanism can be described by F-N tunneling. In case of samples containing both elements the slope of the *I-V* curve increases and the conduction mechanism can be described by TAT conduction due to high number of charge traps distributed in the oxide layer.

4. CONCLUSIONS

We have shown that the visible EL from the silicon rich SiO_2 layer can be significantly enhanced by Gd co-doping. The blue EL corresponding to the ODC defects increases by a factor of four with increasing the Gd concentration up to 3 %. The energy transfer from the Gd^{3+} ions to the ODC and Si-nc was confirmed by time resolved spectroscopy. The study of the conduction mechanism in the SiO_2 layer containing Gd atoms and Si-nc shows F-N tunneling for samples containing up to 6 % of Si and TAT for a higher content of silicon.

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