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#### Erratum

Editorial Board of the journal apologizes to our readers and authors for the error that occurred when publishing the paper by A.N. Nazarov et al. "Electrical and light emitting properties of silicon dioxide coimplanted by carbon and silicon ions" placed in the fourth issue of Vol. 11, N 4, P. 319-323, 2008. It was printed without figures that should be inserted to its text. The amended version of this paper has been placed below.

## Electrical and light-emitting properties of silicon dioxide co-implanted by carbon and silicon ions

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**Abstract.** In this paper, we explore the electrophysical and electroluminescence (EL) properties of thermally grown 350 nm thick  $SiO_2$  layers co-implanted with  $Si^+$  and  $C^+$  ions. The implanting fluencies were chosen in such a way that the peak concentration of excess Si and C of 5-10 at.% were achieved. Effect of hydrogen plasma treatment on electroluminescence and durability of  $SiO_2$  (Si,C) - Si-system is studied. Combined measurements of charge trapping and EL intensity as a function of the injected charge and current have been carried out with the aim of clarifying the mechanisms of electroluminescence. EL was demonstrated to have defect-related nature. Cross-sections of both electron traps and hole traps were determined. EL quenching at great levels of injected charge is associated with strong negative charge capture, following capture of positive charge leading to electrical breakdown of SiO<sub>2</sub> structures.

Keywords: electroluminescence, MOS - structure, implantation, EL quenching.

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### 1. Introduction

Silicon-based light emission is a promising approach to design and realize optoelectronic inter- and intrachip communication in future computer systems. Additionally, there is a great interest in multifunctional microsystems (e.g., lab-on-chip applications). Since a lot of these microsystems are based on standard SiO<sub>2</sub>-Si technology, there is also a strong demand for Si-based light emitters, especially to achieve low-cost production processes. One method for the formation of the Si-based light-emitting structures is ion beam synthesis. Electroluminescence (EL) from the Ge-rich SiO<sub>2</sub> layers was found to be in the red/infrared and in the blue/violet spectral regions [1]. The Si-rich SiO<sub>2</sub> layer emits red light [2]. Ion-beam implantation using a few co-implants is of interest from two standpoints. At first, this procedure allows to expand spectral range of light emission. Secondly, co-implantation can create more stable precipitates and/or stable impurity distribution inside SiO<sub>2</sub>. Using this approach, white

photoluminescence and electroluminescence of coimplanted  $SiO_2$  by silicon and carbon ions have been observed in [3] and [4], respectively. However, from our knowledge the study of electrical characteristics and degradation of electrical and luminescent properties during operation of such light-emitting devices was performed insufficiently. Thus, this paper addresses the electroluminescence, electrical characterization and their degradation in the Si/C co-implanted SiO<sub>2</sub> structures.

#### 2. Samples and experimental technique

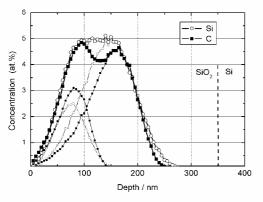
The SiO<sub>2</sub> layers with 350 nm thickness were thermally grown on  $\langle 100 \rangle$ -oriented n-type Si-substrates at 1000°C. First, the oxide films were doubly-implanted with Si<sup>+</sup> ions at the energy of 90 keV followed by a the second Si<sup>+</sup> implantation at 47 keV. Three sets of samples with different implanted dose were prepared. The doses were chosen in such a way that a broad implant profile with a nearly constant concentration of excess Si about 5%, 7.5% and 10% at the depth of 60–180 nm below the

oxide surface was formed. Fig. 1 shows the implantation profile calculated with the TRIM code [5]. After these implantations, the devices were furnace annealed at 1100°C for 30 min in a N<sub>2</sub> ambient. This annealing step was carried out in order to initiate the formation of first Si nanoclusters that have to be acted as seeds for the final clusters. Then, C<sup>+</sup> ions at the energy 43 keV were implanted, then followed by the second C<sup>+</sup> implantation at 22 keV. A post-implantation heat treatment at 800° C for 60 min followed by a final annealing step at 1100° C for 60 min was employed.

The investigation of the EL requires transparent and conductive gate electrodes. On the top of oxide, an indium-tin-oxide (ITO) layer, a special kind of transparent conductive oxide, was deposited using a sputtering process. The thickness of the layers was 80 nm. The gate electrode was processed using standard lithography. The sizes of the devices were 0.5 mm in diameter in a periodic pattern of 2 mm pitch.

A portion of so fabricated MOS Light Emitting Devices (MOSLEDs) had been subjected to RF plasma treatment (13.56 MHz) in a low pressure, diode type reactor, with the ITO electrode being exposed to the plasma discharge. The plasma working gas was a mixture of 90% nitrogen and 10% hydrogen. The plasma power density was in the range of 0.5 - 1.5 W cm<sup>-2</sup>. Additional substrate pre-heating from a heat source independently of the plasma discharge was used over the temperature range 100° to 300°C, and elevated temperature was maintained during the plasma treatment. The plasma treatment duration was 15 min. Details of the plasma reactor and the used processing parameters were published in [6].

EL spectra were measured on MOSLEDs with a circular ITO at a constant current supplied by a sourcemeter Keithley 2410. The EL signal was recorded at room temperature with a monochromator Jobin Yvon Triax 320 and a photosensor module Hamamatsu H7732-10 in the range of wavelengths between 300 and 750 nm.



**Fig. 1.** TRIM-profile of a Si/C co-implanted SiO<sub>2</sub> layer. Two implantations at different energies were carried out for both Si and C. The small symbols are related to each single implantation.

The measurement was performed with electron injection in the constant-current mode from ITO electrode into the SiO<sub>2</sub>. The typical current density for EL excitation was  $10^{-3}$  down to  $10^{-5}$  A/cm<sup>2</sup>. The charge trapping during EL excitation was studied by analysing the applied voltage at constant current injection ( $V_{CC}$ ) from the ITO to the SiO<sub>2</sub>.

### 3. Results and Discussion

### 3.1 Current-voltage characteristics of $SiO_2$ coimplanted by $C^+$ and $Si^+$ ions

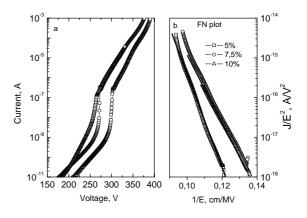
Current-voltage (I-V) characteristics for the case of electron injection from ITO into implanted  $SiO_2$  are represented in Fig. 2. The constant current regime used for the EL excitation corresponds to high-field portions in the I-V characteristics of the MOS structures. As it can be seen, cut-off injection voltage (manifested as a sharp bend in the I-V curve) shifts to lower value when dose of implantation increases; that is, EL emission arises at lower electric fields.

Actually, section of the I-V curve corresponding to the EL processes is rectified well in coordinates  $J/E^2$ -1/E, where E is the electric field in oxide (see Fig. 2 b). Therefore, charge transport in Si/C implanted SiO<sub>2</sub> is governed by Fowler-Nordheim (FN) tunneling, that is to say, by tunnel injection of carriers in the conduction band of oxide through the triangular shaped barrier. The current density of FN tunneling may be expressed, as

$$J_{FN} = \frac{q^3}{8\pi h \varphi_B} E^2 \exp\left(-\frac{8\pi \sqrt{2m * q}}{3hE} \varphi_B^{3/2}\right), \qquad (3.1)$$

where  $\phi_B$  is the barrier height, m<sup>\*</sup> is the effective mass of electron, other quantities are common accepted.

For the Si-SiO<sub>2</sub> structures with 5% of Si/C implants, from the slope of linear part of the  $\ln(J/E^2) - f(1/E)$  - dependence the barrier height has been obtained as 3,05  $\Rightarrow$ B (in assumption of m\* = 0.52m<sub>0</sub>).



**Fig. 2.** The current –voltage characteristics of MOSLEDs (injection from ITO) (a); The same characteristics converted to the Fowler-Nordheim coordinates (b).

When the dose of Si/C implantation increases up to 10% the barrier height falls up to 2.8 eV (at the same value of the effective mass). It is worth noting that the value is significantly lower than the injection barrier for electrons in pure SiO<sub>2</sub> (3.15 eV [7]). This phenomenon is evidence of enhancement of the electron injection into SiO<sub>2</sub> due to the increasing concentration of SiC-related complexes and associated with trap-assisted tunneling mechanisms [8].

# 3.2 Charge trapping in the SiO<sub>2</sub> co-implanted by $C^+$ and Si<sup>+</sup> ions

Changes of the voltage (V<sub>CC</sub>), applied to the MOS structure, in the constant current regime of high-field electron injection from ITO as a function of injected charge are depicted in Fig. 3. The decrease of the voltage during high-field electron injection (up to  $\sim 9 \cdot 10^{14} \text{ e/cm}^2$ ) suggests positive charge trapping in the oxide at the distance longer that the tunneling length from the injected ITO-SiO<sub>2</sub> interface. Then, the voltage tends to steady increasing, which is indicative for negative charge trapping.

Assuming the first-order trapping kinetics the trapped charge (both negative and positive ones) versus injected charge can be described by following the expression [9]

$$Q_t = Q_t^{\max}[1 - \exp(-\sigma_i Q_{inj})], \qquad (3.2)$$

where  $Q_t$  is the trapped charge,  $Q_t^{max}$  is the maximal trapped charge and  $\sigma_i$  is the effective capture cross-section of the trap.

If the trapping efficiency (P) is presented as the first derivation with respect to the injected charge in Eq. (3.2), then we obtain

$$P = \frac{dQ_t}{dQ_{inj}} = \sigma_i Q_t^{\max} \exp\left(-\sigma_i Q_{inj}\right).$$
(3.3)

From Eq. (3.3), it is easy to understand that for every trap the plot of ln(P) vs.  $Q_{inj}$  will consist of linear part with the slope corresponding to  $\sigma_i$ . The extrapolation to  $Q_{inj}=0$  for this plot provides  $\sigma_i Q_t^{max}$ . Thus, using the proposed method [10], the number and main trap parameters can be estimated. Our calculations have demonstrated that three kind of electron traps with the average value of the capture cross-section ( $\sigma_e^1 =$  $3.6 \times 10^{-16}$  cm<sup>2</sup>,  $\sigma_e^2 = 8 \times 10^{-18}$  cm<sup>2</sup> and  $\sigma_e^3 = 2 \times 10^{-19}$  cm<sup>2</sup>,) and two kind of hole traps ( $\sigma_h^1 > 1x 10^{-14}$ cm<sup>2</sup>,  $\sigma_h^2 = 6.6x 10^{-15}$  cm<sup>2</sup>) can be found by the proposed method. It should be noted that hole traps with  $\sigma_h^2 = 6.6x 10^{-15}$  cm<sup>2</sup> are typical for Si-SiO<sub>2</sub> structures with excess Si content in SiO<sub>2</sub>, which subjected to rapid thermal annealing [11].

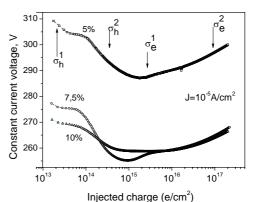


Fig. 3. Constant current voltage  $(V_{cc})$  as a function of the injected charge.

#### 3.3 The features of the EL spectra

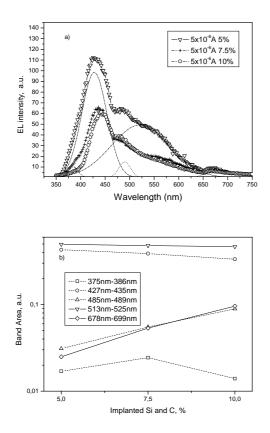
Fig. 4 represents EL spectra for the MOSLEDs fabricated at different implanted doses. In this experiment, the MOSLEDs were operated under electron injection from ITO at the current density 2.5.10<sup>-3</sup> A·cm<sup>-2</sup>. As seen from Fig. 4a, the EL spectra are relatively broad and consist of several peaks. There is visible correlation between EL spectra and the concentration of implants. The multy-Gaussian deconvolution of all the spectra was performed, and the set of band positions have been determined. For the lowest concentration (5%), clear double-peak structure is observed with maxima close 425...435 nm and 515...525 nm. The latter maximum belongs to a relatively broad peak that consists of two sub-peaks on its shoulders. The integral intensity of EL spectra falls down when the concentration of implanted Si and C increases, the high-energy peak decreases too, but relative intensities af broad peaks are nearly constant (Fig. 4b). Similar characteristics of photoluminescence (PL), showing a decrease of the high energy tail (340....410 nm) for higher Si/C concentration, have been observed earlier [4].

Additional measurements were carried out in order to investigate the influence of the injection current density on the shape of the EL spectrum (Fig. 5). Basically, no changes occur in the spectrum with increasing the current density and consequently also with increasing the electric field. This means that the difference in the shape of the spectra for different Si/C concentrations is only related to the different microstructure and not to the distribution of hot electrons, but effect of the injected charge on the EL spectra demands further investigations.

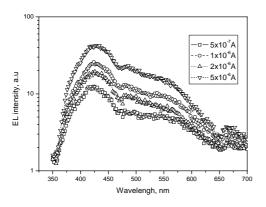
Thus, we have analyzed variation of the EL spectra at high levels of injected current employing the multiscanning regime: that is EL spectra have been recorded repetitively one after another (Fig. 6). It should be noted that about  $3.725 \cdot 10^{18}$  e/cm<sup>2</sup> are injected during one EL scan. As one can see, the high energy band (within the range 390 to 400 nm) is suppressed strongly when the number of EL scans is increased, during which the

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integral EL intensity decreased just linearly (see insert in Fig. 6). That is, EL quenching is observed at the used current density.



**Fig. 4.** EL spectra of the Si and C co-implanted SiO<sub>2</sub> layers as a function of the implantation dose. Dashed line presents multy-Gaussian fitting for 5% Si/C implants. (Current of  $5 \cdot 10^{-6}$  A was used for all the samples) (a); Variation of the EL intensity sub-peaks (see Fig. 4a) as a function of the implanted dose (b).



**Fig. 5.** EL spectra of Si/C co-implanted MOSLEDs operating at different currents (dot area: 0.2 mm<sup>2</sup>).

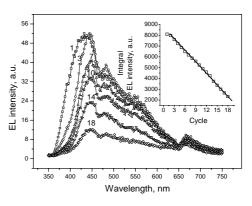


Fig. 6. EL spectra of 7.5% Si/C co-implanted MOSLED obtained in multi-scanned procedure at the current density  $5^{\cdot}10^{-3}$ A/cm<sup>2</sup>. Scan numbers are shown near curves. Insert: variation of the integral EL intensity as a function of scan numbers.

The mechanism of the MOSLED operation is believed to be based upon impact ionization of specific defect-type luminescent centers (LCs) by hot electrons moving in the conduction band of oxide [1]. It follows from the literature that the observed line of 520 nm is attributed to  $E_{\delta}$  center [12], lines of 385 nm and 490 nm are related to the Si-C bonds [13] and the Si/C/O complexes [14] correspondingly, and the line at 390-400 nm - to the oxygen deficiency centre ( $\equiv$ Si-Si $\equiv$ ) [15] or two-fold coordinated silicon (=Si) [16]. The line of 440... 450 nm can be ascribed both to SiC pricipitats [17, 18] and neutral oxygen vacancy [12]. On the low energy shoulder, one can see increase of the line 620 nm for the largest current density. This line is attributed to the nonbridging oxygen hole center [19].

# 3.4 Effect of RF plasma treatment on light-emitting characteristics

As it was considered earlier in [20-22], the radiofrequency (RF) plasma treatment (PT) of ion-implanted MOS structures may result in considerable modification of their structural and electrical properties. Especially, it is regarded to post implanted defects both in Si and SiO<sub>2</sub>. Low temperature defect annealing in SiO<sub>2</sub> under PT can be explained within the framework of the recombination enhanced defect reactions [23, 24] caused by alternate injection both electrons and holes and there recombination at the defects.

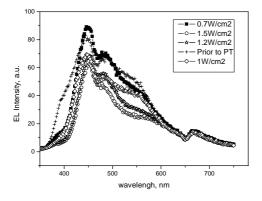
Analysis of the hydrogen plasma effect on the  $SiO_2$  MOS structures co-implanted by C<sup>+</sup> and Si<sup>+</sup> ions allows us to reveal the following peculiarities in light-emitting and electrical properties.

1. There is an optimal regime of the hydrogen plasma treatment (~0.7 W/cm<sup>2</sup>) that results in improvement of the lifetime inherent to the device without changing its EL intensity and spectrum (see Fig. 7);

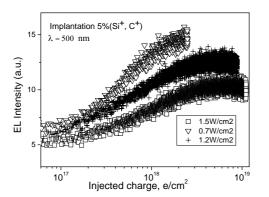
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- 2. Exceeding the optimal power density resulted in reduction of the integral EL intensity and transformation of the EL spectrum, namely, the high energy shoulder is considerably suppressed;
- 3. The increase in the power density resulted in an increase of device operation durability (Fig. 8).

The observed phenomena can be explained taking into account an effective annealing and hydrogen passivation of point defects and defect complexes in SiO<sub>2</sub> during hydrogen plasma treatment [6]. The complicated EL spectrum of SiO<sub>2</sub> (Si,C)-Si-structures in a wide range of a wavelength is associated with both nanoinclusions (such as Si<sub>X</sub>C<sub>Y</sub>O<sub>Z</sub> [14]) and different kinds of defects, as mentioned above. Probably, availability of high concentrations for different types of defects in the SiO<sub>2</sub> matrix shifts the reactions ordering of amorphous network towards the higher power densities used in the hydrogen plasma treatment, and ordering the SiO<sub>2</sub> network occurs simultaneously with annealing of the defects determining the EL spectrum in our devices.



**Fig. 7.** Influence of plasma treatment on the EL spectra of Si/C co-omplanted MOSLED.



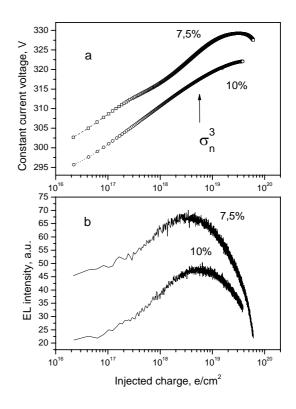
**Fig. 8.** EL intensity at the wavelength 500 nm as a function of electron-injected charge after hydrogen plasma treatment of the  $Si^+$  and  $C^+$  co-implanted  $SiO_2$ .

# 3.5 Interrelation between EL and charge trapping in the $SiO_2(Si,C)$ - Si-structure

In order to study the relationship between the EL intensity and charge trapping in the dielectric, combined measurements of the EL intensity at the settled wavelength and the  $\Delta V_{CC}$  versus the injected charge (Q<sub>inj</sub>) at high constant current levels were studied. The injected charge is simply calculated from the measurement time using the expression:

$$Q_{inj} = \int_{0}^{t} J(t) dt$$
 (3.4)

Fig. 9 demonstrates direct correlation between the EL intensity and value of the constant current voltage up to the injected charge ~  $2 \cdot 10^{18}$  e/cm<sup>2</sup>, that is, excitation of EL is governed by impact ionization. When the injected charge reaches  $3 \cdot 10^{19}$  e/cm<sup>2</sup>, the EL intensity tends to decrease, though the applied voltage increases. The dependence  $V_{cc}$  as a function of  $Q_{inj}$  manifests strong electron capture by the traps with the cross - section as estimated above:  $\sigma_e^3 = 2 \times 10^{-19}$  cm<sup>2</sup>. This process is clear seen on the  $V_{cc} - Q_{inj}$  curve for 7.5% Si/C co-implantation (see Fig. 9).



**Fig. 9.** Constant current voltage ( $V_{cc}$ ) as a function of the injected charge (a); the EL intensity ( $\lambda = 440$  nm) as a function of the injected charge (b). Injection is performed from ITO, the current density is  $1 \times 10^{-3}$  A/cm<sup>2</sup>.

It was shown in the paper [25], that small capture cross-sections of the negative charge correlating with quenching some EL lines, are associated with a probability of defect luminescent centers reconstruction during their excitation by electron impact ionization and have to be designated for clarity as the quenching crosssection,  $\sigma_q$ , for given EL line. So the value of  $\sigma_e^3 \equiv$  $\sigma_{q,\ 440nm}$  has to be linked with a probability of reconstruction and/or destroying the EL center. revealing a light emission at 440 nm, with following electron trapping in the new generated defect. Since the EL at 440 nm in SiO<sub>2</sub> can be associated with excitation of the neutral vacancy (O<sub>3</sub>=Si-Si=O<sub>3</sub>) or two-fold coordinated silicon (=Si), the quenching process can be described by the following reactions

$$O_3 \equiv Si - Si \equiv O_3 + e(hot) \rightarrow$$
  

$$\rightarrow O_3 \equiv Si^{(-)} \cdots Si \equiv O_4$$
(3.5)

$$O - Si - O + O_3 \equiv Si - O - Si \equiv O_3 +$$
  
+ 2e(hot)  $\rightarrow O_3 \equiv Si^{(-)} + O_3 \equiv Si^{(-)}$  (3.6)

The reaction (3.5) assumes a breakup of Si-Si bond by a hot electron and relaxation of Si atom at the distance longer than 4Å with bonding to the neighboring oxygen atom. These four-fold coordinated Si and the silicon dangling bond can represent the electron trap [26]. In case of the reaction (3.6) two-fold coordinated Si interacts with broken Si-O bond in neighbouring Si-O-Si fragment that results in formation of two silicon dangling bonds ( $O_3 \equiv Si$ ) that can work as electron traps.

Further electron injection (more than  $3 \times 10^{19}$  e/cm<sup>2</sup>) leads to positive charge generation and drastic EL quenching (see Fig. 9). It should be noted, that capacitance-voltage characteristics of these structures demonstrate a shift along the voltage axis towards negative values, which corresponds to positive charge accumulation in oxide near the SiO<sub>2</sub>/Si interface (not shown here). Obtained results testify to positive charge accumulation/generation in the bulk and oxide interface [26]. The observed positive charge accumulation occurs jointly with electrical breakdown of the MOSLEDs.

### 4. Conclusion

Fowler-Nordheim tunnelling offers the main mechanism of charge transport in the Si/C co-implanted Si-SiO<sub>2</sub> structures in actual for the EL voltage range.

Combined studies of the MOSLED EL intensity and charge trapping vs. time for high field electron injection into the Si/C implanted SiO<sub>2</sub> have shown for the first time that EL correlates well with charge trapping governed by that three kind of electron traps with the average value of the capture cross-section ( $\sigma_e^{1}$ = =3.6×10<sup>-16</sup> cm<sup>2</sup>,  $\sigma_e^2$ = 8×10<sup>-18</sup> cm<sup>2</sup> and  $\sigma_e^3$ = 2×10<sup>-19</sup> cm<sup>2</sup>,) and two kinds of hole traps ( $\sigma_h^1$  > 1x10<sup>-14</sup> cm<sup>2</sup>,  $\sigma_h^2$ =6.6x10<sup>-15</sup> cm<sup>2</sup>). The EL quenching caused by electron impact ionization resulting to reconstruction of defect LC with following electron trap generation. The quenching cross-section for the observed process is  $\sigma_{q,440nm} = 2 \times 10^{-19} \text{ cm}^2$ . Positive charge generation arises at high levels of charge injection leading to electrical breakdown.

Hydrogen plasma treatment of implanted  $SiO_2$  layers containing of the nanoinclusions results in increase of the lifetime inherent to light-emitting devices and improvement of their stability without reduction in EL intensity.

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