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O. Jambois, B. Garrido, P. Pellegrino, Josep Carreras, A. Perez-Rodriguez, et al.. White electroluminescence from C- and Si-rich thin silicon oxides. *Applied Physics Letters*, 2006, 89 (25), pp.253124 - 253124. 10.1063/1.2423244 . hal-01745047

**HAL Id: hal-01745047**

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Citation: [Appl. Phys. Lett.](#) **89**, 253124 (2006); doi: 10.1063/1.2423244

View online: <https://doi.org/10.1063/1.2423244>

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## White electroluminescence from C- and Si-rich thin silicon oxides

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(Received 22 September 2006; accepted 16 November 2006; published online 22 December 2006)

White electroluminescence from carbon- and silicon-rich silicon oxide layers is reported. The films were fabricated by Si and C ion implantation at low energy in 40 nm thick SiO<sub>2</sub>, followed by annealing at 1100 °C. Structural and optical studies allow assigning the electroluminescence to Si nanocrystals for the red part of the spectrum, and to C-related centers for the blue and green components. The external efficiency has been estimated to 10<sup>-4</sup>%. Electrical characteristics show a Fowler-Nordheim behavior for voltages above 25 V, corresponding to the onset of electroluminescence. This suggests that light emission is related to the impact ionization of radiative centers. © 2006 American Institute of Physics. [DOI: 10.1063/1.2423244]

During the last decade, intense investigations have been devoted to the development of an efficient silicon-based optically active material that could enable integration of photonics with Si microelectronics. Several materials have been synthesized, showing light emission in different spectral regions. For example, silicon nanocrystals (Si-ncs) embedded in SiO<sub>2</sub> emit in the red and near infrared spectral regions. In this system, light emission has been attributed to quantum confinement or surface states.<sup>1-3</sup> Incorporation of rare earth such as Er<sup>3+</sup>, Tm<sup>3+</sup>, or Gd<sup>3+</sup> into Si-rich SiO<sub>2</sub> allows sharp light emission from the infrared up to the ultraviolet region.<sup>4,5</sup> Recently, a few studies have reported broad photoluminescence (PL) in the whole visible domain, by doping Si-rich SiO<sub>2</sub> layers with carbon.<sup>6-9</sup> Blue electroluminescence (EL) emission from such a material has been already reported,<sup>10</sup> but efficient EL covering the whole visible spectrum has still to be developed. White light sources compatible with Si technology are interesting for several applications, such as biological and chemical sensors, that need a broad spectral detection, optical interconnects, or color display.

We have previously reported white PL of 400 nm thick SiO<sub>2</sub> layers by coimplanting Si and C.<sup>9</sup> The PL spectrum is the convolution of emission bands located in the red, green, and blue spectral regions. The structural and optical studies reported for this layer attributed the red band to Si-nc, and the blue and green bands to C-related nanophase such as SiC- or graphitic-like nanoaggregates. Furthermore, the green band shows lifetimes of the order of 50–100 ps,<sup>11</sup> which gives interest to this system for telecommunication applications where fast modulation is required. This material looks thus very promising as a complementary metal-oxide-semiconductor compatible light source once electrical excitation is achieved.

This work reports the observation of white EL achieved by adapting the Si and C implantation procedure previously developed in Refs. 9 and 11 for thick materials to thin SiO<sub>2</sub>

films (40 nm). Reduction of the thickness of the active layer is required to allow injection and conduction of electrical charge across the dielectric layer at relatively low voltages. The profile of the implanted atoms has been determined by x-ray photoelectron spectroscopy (XPS). White EL has been observed, clearly showing the contribution of Si-nc in the red and of C-rich nanoparticles in the blue-green region. Finally, the analysis of electrical conduction points to impact ionization as the predominant mechanism responsible for the observed EL.

The samples have been prepared by sequential implantation of Si<sup>+</sup> and C<sup>+</sup> in a 40 nm thick SiO<sub>2</sub> layer grown by dry oxidation at 1000 °C on a *p*-type <100> Si wafer. The implantation parameters (energy, dose) were obtained by means of TRIM simulations. A uniform profile of 10 at. % Si excess in SiO<sub>2</sub> has been obtained by means of a four step implantation. In order to obtain a distribution of Si-ncs close enough to the SiO<sub>2</sub> surface, very low implant energies (down to 1 keV) have been required. In addition, the higher energy implant was chosen to obtain the Si projected range at the SiO<sub>2</sub>/Si interface region, which is desirable to allow direct tunneling of electrons and holes from the substrate region to the nanocrystals.<sup>12</sup> Subsequently, a single C<sup>+</sup> ion implantation was carried out to a nominal dose of 10 at. % at the peak, i.e., equal to the Si excess. The C implant energy was selected to locate the distribution at the center of the Si rectangular profile to block the outdiffusion of C, and to favor the formation of SiC and C compounds in the implanted layer. A sample without C<sup>+</sup> implantation was also fabricated as a reference sample. All the implantations were performed at room temperature, and details are summarized in Table I. To synthesize the Si and C nanophases, the samples were annealed in a N<sub>2</sub> atmosphere at 1100 °C in two steps: the first one was performed in a rapid thermal processing system (1 min) to ensure the reproducibility of the nucleation step, while the second one was in a conventional furnace (4 h). Finally, metal-oxide-semiconductor structures were fabricated by a standard photolithographic process, with an electrode active area of 9.6 × 10<sup>-3</sup> cm<sup>2</sup>. For the gate electrode, a

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TABLE I. Implantation energy and doses of Si<sup>+</sup> and C<sup>+</sup> for the silicon-rich silicon oxide enriched with C (SRSO:C). A reference sample without the C<sup>+</sup> implantation has also been fabricated, noted as SRSO in the text.

Si implants		C implant	
Energy (keV)	Dose (cm <sup>-2</sup> )	Energy (keV)	Dose (cm <sup>-2</sup> )
1	$1.4 \times 10^{15}$		
3	$3.4 \times 10^{15}$		
10	$7.5 \times 10^{15}$	6.5	$2 \times 10^{16}$
25	$2.7 \times 10^{16}$		

semitransparent 100 nm thick *n*-type polycrystalline silicon contact was deposited. The device was polarized by applying a negative voltage on the gate, allowing injection of electrons from the gate and hole injection from the *p*-type substrate. Details about the XPS and PL experiments are given in Ref. 9 EL excitation has been obtained using an Agilent 8114A pulse generator, and the collected signal was processed with a Stanford Research SR830 lock-in amplifier. The spectra have been corrected for the spectral response of the system. Current-voltage (*I*-*V*) characteristics were measured using an HP4140B picoamperimeter.

The inset of Fig. 1 shows the XPS concentration profile of the Si-rich silicon oxide sample enriched with C (SRSO:C), once annealed at 1100 °C. The figure shows an almost uniform Si profile, as expected from TRIM simulation. Note that the strong increase of the Si signal at 30 nm is due to the interface with the substrate. Moreover, the C distribution is located as expected at the center of the layer. At the maximum of the peak, its content is a little bit less than the expected 10 at. %, meaning that some C might have outdiffused during the annealing process. Note that the increase of the C concentration from 2 to 0 nm corresponds to surface contamination. In order to check that the introduced carbon is optically active, PL measurements have been made and they are represented in the main part of Fig. 1. Two spectra are included from both the SRSO:C and the SRSO reference sample (without C). The latter shows a PL band centered at 760 nm, characteristic of the light emission coming from Si-nc. For the SRSO:C spectrum, the two Gaussian peak deconvolution enables us to show that in addition to the band due

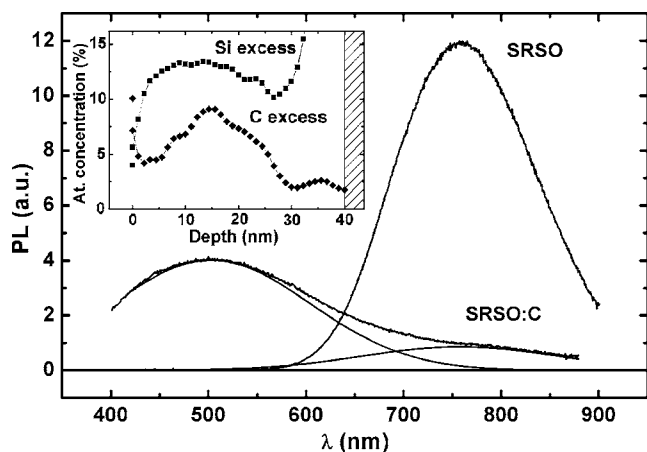


FIG. 1. PL spectra of the SRSO and SRSO:C samples. The two Gaussian fits are a guide for the eyes to analyze the luminescence of the Si-nc in the SRSO:C sample. Inset shows Si and C excess vs layer depth, as measured by XPS.

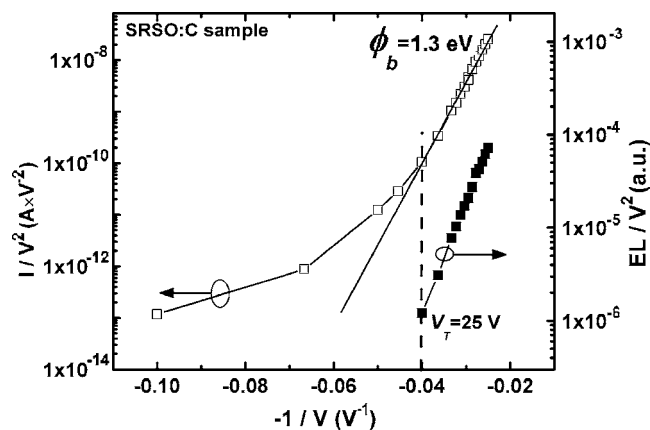


FIG. 2. *I*-*V* and EL-*V* in Fowler-Nordheim plot.  $V_T$  indicates the threshold voltage where both Fowler-Nordheim regime and EL start to appear, while  $\phi_b$  is the deduced injection barrier.

to the Si-nc, another band appears, attributed to the C-containing nanoaggregates, similarly to what was observed in thicker layers in previous works.<sup>9</sup>

Electrical characterization of both samples was performed in forward polarization. Further details are reported in Ref. 13. For voltage larger than 20 V, the *I*-*V* curve shows a Fowler-Nordheim dependence. This mechanism is related to the tunnel injection of carriers in the conduction band of the oxide through a triangular shaped barrier.<sup>14</sup> The Fowler-Nordheim regime is governed by the following law:  $I = (BV^2/\phi_b) \exp[-(\lambda d \phi_b^{3/2}/V)]$ , with *I* the electrical current, *V* the applied voltage on the oxide of thickness *d*,  $\phi_b$  the injection barrier,  $B = 1.1e^2/4\pi h$ ,  $\lambda = 23\pi m^{1/2}/6he$ , the other parameters having their usual physical meaning. For the SRSO sample, the onset of this regime is observed at 20 V, whereas for the SRSO:C sample, it appears at higher voltage, i.e., 25 V. The Fowler-Nordheim plot for the carbon-containing sample is depicted in Fig. 2. Assuming a uniform voltage drop across the layer and equal effective masses for both structures, similar injection barriers of about 1.3 eV are deduced. This value is significantly lower than the injection barrier of electrons for pure SiO<sub>2</sub> (3.1 eV). This shows an enhancement of the injection of carriers due to the presence of Si-nc,<sup>15</sup> or of C-rich nanoaggregates in the case of the C-rich sample.

EL has been observed for both samples. The spectra are represented in Fig. 3, from the onset voltage of EL up to before breakdown voltage, i.e., from 23 to 27 V for the SRSO sample and from 30 to 40 V for SRSO:C sample. For both samples, the EL is visible by naked eye. The overall EL external efficiency of SRSO:C has been estimated to be around 10<sup>-4</sup>%. This value is of the same order of those reported in Ref. 10, where efficiencies between 10<sup>-4</sup>% and 10<sup>-3</sup>% have been obtained for layers coimplanted with different Si and C contents. In the same reference, indium tin oxide electrodes were used with a transmission of about 80% in the blue range. This value strongly differs from the very low transmission in the blue (about 6%) for the polycrystalline silicon used in this work. According to this, a significant improvement of the external quantum efficiency can be attained by optimizing the transparency of the gate electrode in our devices.

In both samples of the present work, the red EL band from Si-nc can be easily identified. Moreover, appearance of

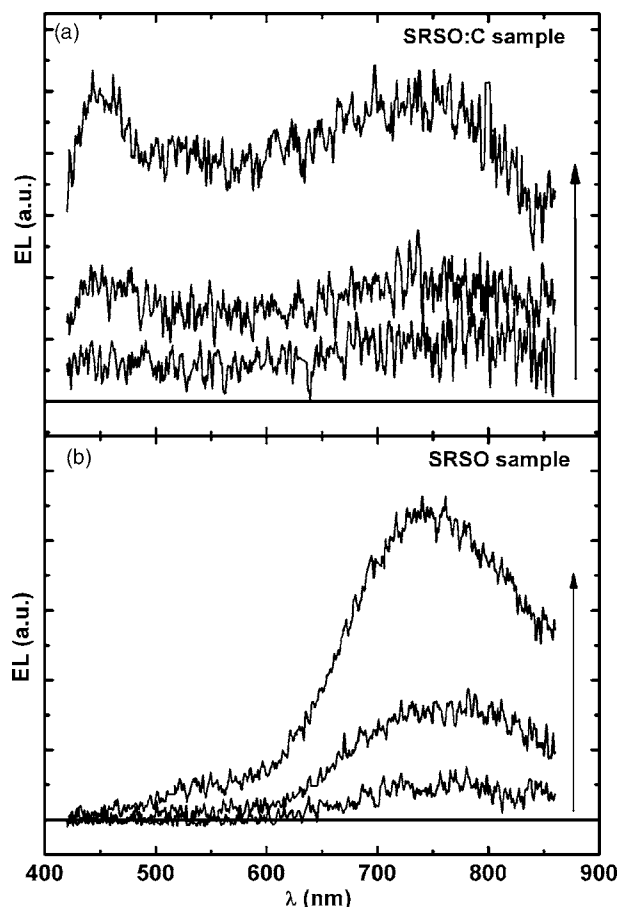


FIG. 3. EL of (a) the SRSO:C sample and (b) the SRSO sample. The substrate is biased positively with respect to the gate electrode. The applied voltages are given in the text. The arrows show the increase of applied voltage.

bands at higher energies is clearly observed, leading to a white EL. In particular, one can note a peak at 450 nm. Gebel *et al.* have studied the EL of SiO<sub>2</sub> layers implanted with Si and C.<sup>10</sup> They have observed a peak of luminescence at this wavelength that, according to their previous PL analysis reported in Ref. 6, has been attributed to Si<sub>y</sub>C<sub>1-y</sub>O<sub>x</sub> complexes. This is in agreement with our previous structural analysis,<sup>9</sup> where experimental evidences were reported relating this emission to Si- and C-related centers. Consequently, even though it is difficult to assign the exact microstructural origin of the broad white EL, we can state that this latter is the sum of the emission from Si-nc and from C-related complexes in the matrix. Note that since the upper electrode has a progressively lower transmission at shorter wavelengths, the true EL due to the C centers is stronger than what is observed. This can partly explain the difference observed between PL and EL spectra in the green to the blue spectral region. Additionally, in EL, the excitation rate of a luminescent center may also be different for each kind of center, as it deals with injection and trapping of carriers. As this material consists of different emitting species, it is not surprising that the EL does not match the PL for the SRSO:C sample. In this sense, the experimental data point out the existence of a higher EL excitation efficiency for the centers responsible for the 450 nm peak.

In order to describe the mechanism responsible for the EL, |EL|-V characteristics have been added to the Fowler-Nordheim plot in Fig. 2. For this purpose, the light was not spectrally resolved, to increase the collection of light. This figure shows that the onset of detection of EL (25 V) correlates with the setting of the Fowler-Nordheim regime. Moreover, the functional dependence is found to be proportional, suggesting that the Fowler-Nordheim regime is the primary transport mechanism responsible for the observed EL. It appears thus that the mechanism involved in the EL is radiative impact ionization,<sup>16</sup> meaning that a hot electron, injected in the conduction band of SiO<sub>2</sub>, is trapped by a Si-nc or a C-related center. The electron releases its kinetic energy by the formation of an electron-hole pair inside the luminescent center, in a mechanism similar to avalanche breakdown mechanism. Then, this electron-hole pair recombines radiatively.

In conclusion, very thin Si- and C-rich layers have been synthesized by high dose ion beam synthesis. The use of low energy implants has allowed growing a uniform distribution of light emitting nanoparticles. The C-related centers give rise to a significant luminescent contribution in the high energy region of the visible spectrum. Together with the well known red light coming from the Si-ncs, this leads to a white (to the eye) characteristic emission. The electro-optical characterization of these systems has allowed demonstrating the existence of an intense, white EL emission, which correlates with the PL behavior. Radiative impact ionization of the emitting centers is proposed as the main mechanism responsible for the EL emission. These interesting results open a perspective to the possibility of exciting the C-related centers by sequential injection of carriers.

This work was supported by the Spanish project TIC2003-07464 and the "Acciones Integradas-Picasso" French-Spanish collaborative program HF2003-72.

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