

Quantum Dot Materials and Devices for Light Emission in Silicon

Maria Eloisa Castagna, Salvatore Coffa, Liliana Caristia, A. Messina
STMicroelectronics, 95121, Catania, Italy,
eloisa.castagna@st.com
Corrado Bongiorno
CNR-IMETEM, 95121 Catania, Italy

Abstract

We report on the fabrication and performances of the most efficient Si-based light sources. The devices consist of MOS structures with erbium (Er) implanted in the thin gate oxide. The devices exhibit strong 1.54 μm electroluminescence at 300K with a 10% external quantum efficiency, comparable to that of standard light emitting diodes using III-V semiconductors. Er excitation is caused by hot electrons impact and oxide wearout limits the reliability of the devices. Much more stable light emitting MOS devices have been fabricated using Er-doped SRO (Silicon Rich Oxide) films as gate dielectric. These devices show a high stability, with an external quantum efficiency reduced to 1%. In these devices Er pumping occurs by energy transfer from the Si nanostructures to the rare earth ions.

1. Introduction

Si is the semiconductor of choice for the fabrication of advanced electronic devices. Hence implementation of efficient optical function in Si would allow us to use the mature and low cost Si Ultra Large-Scale Integration (ULSI) technology for the fabrication of integrated optoelectronic circuits [1], [2]. Si physical properties make it unsuitable for efficient light emission and modulation at room temperature. Generally it is necessary to combine electrical properties of Si devices with the transmission performances of optical communications. Usually Si is used as a convenient substrate where optical devices, realized using direct band gap semiconductors, are hybridly integrated with Si electronic devices. It appears clear that the implementation of efficient optical functions in Si would greatly simplify the integration of electronic and photonic devices.

The first goal is to fabricate efficient and electrically-driven room temperature light emission source in Si. For the application in telecommunication field emission at 1.54 μm is requested

In this paper we propose a Si based light source consisting of a MOS structure with Er implanted in the thin gate oxide. This device shows a 10% external quantum efficiency at room temperature, comparable to

that of standard light emitting diodes using III-V semiconductors. Er ions are excited by impact through hot electrons. Oxide wearout limit the reliability of the devices. To increase the stability of the device the gate dielectric has been replaced with an Er-doped SRO (Silicon Rich Oxide). The deposition characteristics of these films, the nucleation and crystallization of Si nanostructures in a SiO_2 matrix after a post deposition thermal annealing process have been investigated. The devices, that use this film as gate dielectric, show a high stability, with an external quantum efficiency reduced to 1%. In these devices Er pumping occurs by energy transfer from the Si nanostructures to the rare earth ions.

2. Device fabrication

The devices have been fabricated on epitaxial p^- layers (15 μm thick, B-doped with a resistivity of 22 Ωcm) grown on (100) Si p^+ substrates (500 μm thick, B-doped with a resistivity of 0.015 Ωcm). The active area of the devices was defined by a LOCOS structure realized by growing a thin oxide layer (500 Å) and protecting the active area from the following oxidation using a 700Å thick nitride layer properly patterned by standard lithography and etching. Oxidation is performed at 950°C for 2 hrs in a O_2/N_2 ambient such to realize a 1.3 μm thick oxide layer. After LOCOS formation the protective nitride layer and underlying buffer oxide layer are removed. A 620 Å thin oxide, grown using a thermal process in O_2 ambient, or a 1000 Å thin SRO, deposited by PECVD, are used as gate dielectrics in the MOS structure. The samples were implanted with Er at 50 keV to a total fluence of 1×10^{15} ions/ cm^2 . An implantation energy of 50 keV has been selected to have the projected range of the ion distribution roughly in the middle of the gate oxide. After implantation annealing at 1000 °C for 30 minutes was performed under a nitrogen flux. The thermal process is necessary to eliminate implantation defects and to obtain the growth and crystallization of Si nanostructures. The structure of the device is completed by a deposited 3000 Å thick n^+ poly Si layer, doped in-situ using a CVD reactor. The poly Si layer is defined using lithography and reactive ion etching. The poly

layers provide electrical contact on the overall area of the device while being thin enough to allow most of the generated 1.54 μm light to be emitted from the device. Finally, a metal ring consisting on an Al-Si-Cu layer, 3 μm thick, completes the device structure, and allows device bonding on a standard TO₃ package. A schematic of the cross section of the device is reported in Fig. 1. In a single die three MOS devices are present with different active area: 1500x1500 μm^2 , 350x350 μm^2 and 100x100 μm^2 .

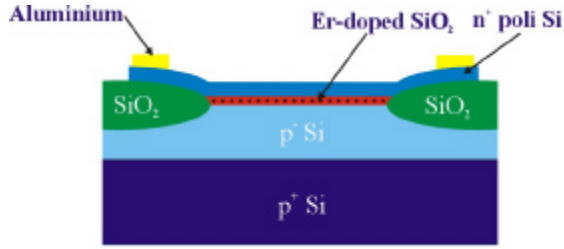


Figure 1: Schematic cross section of the Er-doped light emitting MOS device.

In the scheme the dimensions are not realistic, but we have clearly indicated the gate dielectric that correspond to the emitting area of the device.

3. Electrical characterisation and electroluminescence (EL) spectra of the Er-doped MOS devices.

In Fig. 2 the electro-luminescence (EL) spectra measured on devices having an Er-doped stoichiometric oxide as gate dielectric are reported for a current of 100 μA on an active area of 2.5 mm². Strong room temperature electro-luminescence can be achieved from these devices.

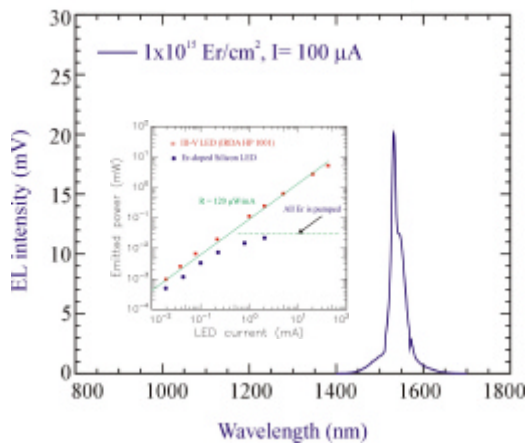


Figure 2: Electro-luminescence spectrum measured on a device having Er-doped stoichiometric oxide as gate dielectric for a current of 100 μA . In the insert the trend of emitted power versus current.

The shape is typical for Er radiative emission in an amorphous matrix. These spectra and the trends of

emitted power versus current density, reported in the insert of Fig. 2, reveal that, at low current density, the EL signal increases linearly with current density while, already at current above 50 μA a saturation of the signal is achieved.

The emitted power from the LED was measured using a calibrated power meter positioned immediately above the device in order to collect most of the emitted light. It is important to take into account that the maximum emitted power from 1×10^{15} Er ions/cm² is extremely close to this value. Hence the observed saturation is caused by the excitation of most of the Er ions. This is of course caused by the long lifetime (3 msec) and the strong cross section of excitation that concur in achieving the saturation already at a low current density. On the same picture we report the measurements performed on a III-V light-emitting device. The device operates at 0.85 μm and presents a linear dependence of the emitted power on the current density. In fact, since in this device light emission originates from electron-hole recombination, the signal could only saturate at larger current densities when Auger-related recombination processes can take place. The fit of the curve allows to estimate a value of 120 $\mu\text{W}/\text{mA}$. It is important to note that standard LEDs have responsivity values comprised between 20 and 60 $\mu\text{W}/\text{mA}$. The high value measured is due to the properly shaped output surface of the device that allows to maximize the extraction efficiency.

The most interesting feature is certainly the fact that before saturation of the Er signal, the two curves basically coincide. This demonstrates that we have fabricated Si-based light emitting devices with external quantum efficiency identical to that of state-of-the art III-V devices. Only the maximum output is limited by the finite density of Er ions and especially by the large value of radiative lifetime. However, applications in integrated devices do not need the use of high powers but only a good efficiency of both the LED and the detector.

The solid line in the insert of Fig.2 represents a fit of the data with the expression:

$$EL = EL_{\max} \frac{\sigma J}{\sigma J + 1}$$

where EL_{\max} is the maximum EL signal at saturation, σ the effective cross section of excitation, τ the overall lifetime (taking into account radiative and non-radiative processes) and J the current density. From the fit a value of $\sigma\tau \approx 3 \times 10^{-17} \text{ cm}^2 \text{ s}$ is obtained. A measure of the time-decay reveals that it is single exponential with a decay time of 3 ms. Hence an effective cross section of 10^{-14} cm^2 characterizes the excitation process.

Measurements of the I-V characteristics, reported in Fig. 3, reveal that, under accumulation conditions (the poly layer is negatively biased with respect to the substrate), the behavior can be described by a Fowler-Nordheim with minor changes for undoped and Er-doped oxide layers. This implies that Er excitation is caused by impact of hot electrons [4] that are injected in

the conduction band of the oxide from the n^+ doped poly Si layer. The devices exhibit also a sharp transition in the green, visible at naked eye. This emission is caused by the direct excitation of the level $^2H_{11/2}$ of Er ions [3]. Hence this Er excited level can be de-excited by emission of a green photon or by emission of a $1.54\ \mu\text{m}$ photon after phonon relaxation from the $^2H_{11/2}$ level to the $^4I_{15/2}$ level. Hot electrons in fact are so energetic to induce the excitation of high energetic level of Er^{3+} ions embodied into oxide.

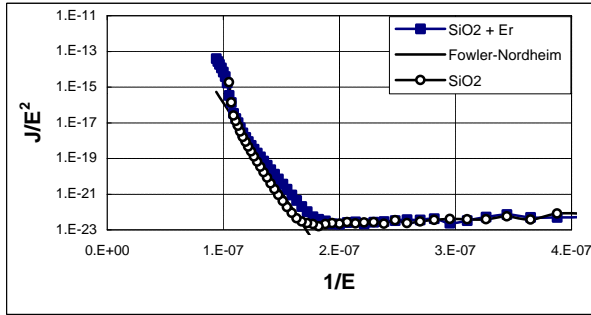


Figure 3: Comparison among electrical characteristics of a MOS with a thermal oxide (circles), of a MOS with Er-doped thermal oxide (squares), and the theoretical curve (line).

We have measured a value of charge to breakdown equal to $13\ \text{C}/\text{cm}^2$ at a current density of $0.004\ \text{A}/\text{cm}^2$ for an Er-undoped gate oxide. Instead for an Er-doped gate stoichiometric oxide we achieved an enhancement of charge to breakdown that is equal to $30\ \text{C}/\text{cm}^2$ for the same current density. When hot electrons impact Er ions, they lose a part of their energy, and are not able to create defects into oxide that are eventually responsible of the oxide breakdown. These devices exhibit then strong internal quantum efficiency, but are not stable, even if are more stable than an undoped oxide. To improve the dielectric stability we have changed the oxide with an SRO.

4. Structural analysis of the SRO film.

Recently it has been demonstrated that by using Silicon-Rich-Oxide (SRO), which consists of Si nanoclusters embedded in a SiO_2 matrix, the cross section for optical excitation of Er^{3+} ions can be enhanced [5]. Si nanoclusters act as classical sensitizer atoms that absorb incident photons and that transfer the energy to luminescent Er^{3+} ions. The absorption cross section of Si nanoclusters is larger than that of Er^{3+} ions by more than 4 order of magnitude. Optical excitation of nano-crystals and energy transfer from nano-crystals to Er^{3+} ions have been largely investigated, even if some mechanisms are not clear nowadays. Our goal is to create e-h pairs into nanocrystals through electrical excitation of the SRO film. SRO (SiO_x , $x < 2$) films have been deposited by rf glow-discharge decomposition of $\text{SiH}_4/\text{N}_2\text{O}$ gas mixture in a PECVD (Plasma Enhanced

Chemical Vapour Deposition) chamber. The flow rate of SiH_4 was 60 sccm and the flow rate of N_2O was 168 sccm. The total pressure in the reactor was kept at 2.8 torr. The rf power was 90 W. The temperature of the chuck, where the wafer was posed, was 400°C . The thickness of the deposited film is 1000 Å. The films are characterized by measuring the refractive index that depends on the Silicon excess against a stoichiometric SiO_2 . Deposited film exhibits a refractive index of 1.72, while in a stoichiometric SiO_2 film the refractive index is 1.46. To obtain the nucleation, growth and crystallization of Si nanoclusters a thermal annealing post deposition of 1000°C for 30 minutes in a flow of N_2 gas is necessary.

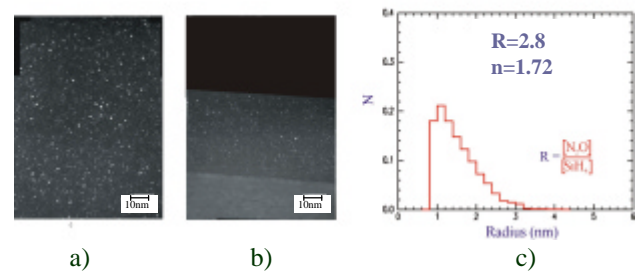


Figure 4: Plan view (a), cross view (b) TEM images, and size distribution (c) of a film containing Si nanocrystals obtained by PECVD.

The nanostructures were characterized by TEM (Transmission Electron Microscopy) analysis. TEM analysis of film were performed in both cross-section and plan-view using a JEOL 200 microscope after proper mechanical thinning of the sample. It's possible to observe nanocrystals as white spots on dark background (figure 4.a). The crystallites are found to be few nanometers in size and to have a spherical shape. From the cross-section, figure 4.b, we derive that nanocrystals are uniformly distributed in the whole film. Figure 4.c shows the grain size distribution of the Si nanoclusters derived by the dark-field plan-view TEM image of the film after annealing. The distribution presents a maximum for a radius of 1.2 nm and an exponential tail extending up to 3 nm, but all the nanocrystals have a size smaller than 4 nm.

The film was successively Er-doped by implantation, as previously reported. MOS structures that use this film as gate dielectric were fabricated. We have investigated electrical behavior of the devices and we have acquired electroluminescence (EL) spectra reported in figure 5.

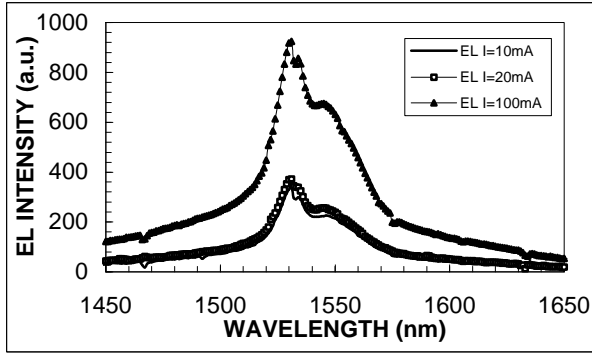


Figure 5: Elettro-luminescence spectra measured on a MOS device having an Er-doped SRO film as gate dielectric for three different currents.

The shape is typical for Er radiative emission in an amorphous matrix.

Measurements of the I-V characteristics, reported in Fig. 6, reveal that, under accumulation conditions, the behavior cannot be described by a Fowler- Nordheim.

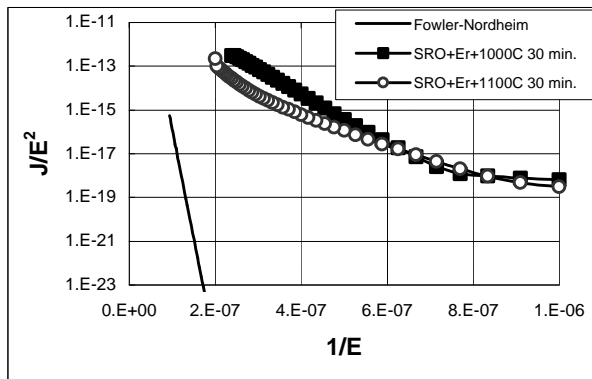


Figure 6: Comparison among electrical characteristic of a MOS with Er doped SRO annealed at 1100°C (cicles), of a MOS with Er-doped SRO annealed at 1000°C (squares), and the theoretical curve for a thermal oxide as gate dielectric (line).

This suggests that Er excitation in these devices cannot be described by a direct hot electron impact. Instead, recombination of electrons (from the n^+ doped poly Si layer) and holes (from the substrate) within the nanocrystals trasfer energy to Er^{3+} ions that emit radiatively. The nanocrystals improve the conductivity of the SRO with respect to a stechiometric SiO_2 . For this reason the current that flows in the gate dielectric does not create damage in the SRO: in fact no defects related to hot electron impact are created. This device is then stable, even if the efficiency, like it will be shown in figure 7, is of 1%.

In figure 7 it is shown the comparison among the emitted power versus current for a MOS with Er-doped SiO_2 annealed at 1000°C and a MOS with Er-doped

SRO, with two different thermal annealing: 1000°C and

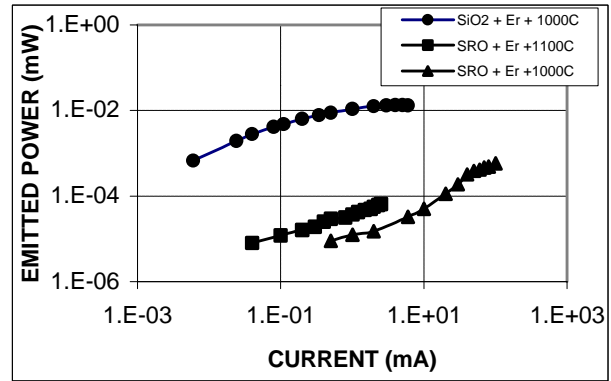


Figure 7: Comparison of emitted power versus current among devices with Er-doped SiO_2 annealed at 1000°C (dots), with Er-doped SRO annealed at 1100°C (squares), and with Er-doped SRO annealed at 1000°C (triangles).

At the same current the emitted power reveals a difference of about three orders of magnitude in the linear regime for the MOS with Er-doped SiO_2 as gate dielectric.

3. Conclusion

We have fabricated Si-based light sources consisting of a MOS structure having an Er-doped SiO_2 or an Er-doped SRO as gate dielectrics. The first one shows a high quantum external efficiency (10%) but his reliability is limited; the second one shows a lower quantum external efficiency (1%), but is much more stable than the first one.

4. References

- [1] Dragoman D., Dragoman M., *Advanced Opto-electronic Devices*, Springer, 2000.
- [2] Zimmermann H., *Integrated Silicon Opto-electronics*, Springer, 2000.
- [3] A. J. Stechl and J.M. Zavada, "Optoelectronic Properties and Applications of Rare-Earth-Doped GaN", *MRS Bulletin* 24 (1999).
- [4] S. Coffa, F. Priolo, G. Franzo', F. A Pacelli and A. Lacaita, "Direct evidence of impact excitation and spatial profiling of excited Er in light emitting Si", *Appl. Phys. Lett.*, vol. 73, 1998, pag. 93.
- [5] S. Libertino, S. Coffa, M. Saggio, "Design Fabrication of Integrated Si-based Optoelectronic Devices", *Materials Science in Semiconductor Processing*, vol. 3, 2000, pag. 375.