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Effect of the annealing treatments on the electroluminescence efficiency of SiO_2 layers doped with Si and Er

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Abstract
We studied the effect of rapid thermal processing and furnace annealing on the transport properties and electroluminescence (EL) of SiO_2 layers doped with Si and Er ions. The results show that for the same annealing temperature, furnace annealing decreases the electrical conductivity and increases the probability of impact excitation, which leads to an improved external quantum efficiency. Correlations between predictions from phenomenological transport models, annealing regimes and erbium EL are observed and discussed.

(Some figures may appear in colour only in the online journal)

1. Introduction

For several years, silicon-based photonic devices have been widely considered in order to develop integrated circuits allowing to overcome the microelectronic bottlenecks. The challenge for silicon photonics is to manufacture high performance and low-cost information processing components using standard and mature CMOS technology. Numerous photonic devices have already been developed in the last years for light propagation, modulation or detection on silicon substrates. The ultimate challenge for the photonic and electronic convergence would be to monolithically integrate powerful Si-based light sources into the CMOS photonic integrated circuits [1, 2].

Among various Si-based materials demonstrated as promising for the fabrication of an electrically driven source, the Er doped silicon-rich silicon oxide (SRSO) system has been studied with great interest in recent years [3–6], mainly to achieve an injection Si-based laser emitting at 1.54 μm. But some efforts have still to be dedicated to understand the underlying physics of injection, transport and Er excitation mechanisms in those layers under electrical pumping. Although some issues on the active material properties have still to be solved [7], getting a more efficient excitation of Er ions at low electrical fluxes is a key to obtain population inversion [8].

In this work we report the study of charge injection and transport in SiO_2 layers doped with Si and Er ions. First, Er-free layers are studied in order to understand the role of the annealing on the charge transport and on the electroluminescence (EL) excitation mechanisms. Then, a layer in which Er has been incorporated is studied. The origin of the Er EL, by direct excitation or by transfer from Si-nc, is addressed.

2. Experiment

The starting materials are 50 nm thick SRSO layers obtained by Si implantation in a SiO_2 layer grown by LPCVD onto a p-type Si substrate. Two different Si excesses have been

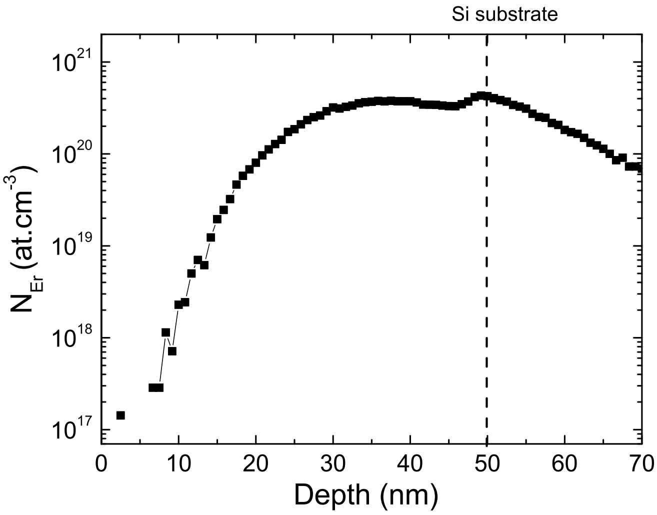

Figure 1. SIMS profile of the Er concentration in our devices.

introduced by varying the dose of implantation. Measurements made by x-ray photon spectroscopy (XPS) show that the Si excess in the layers can be around 9 or 16 at%. To form the Si nanocrystals (Si-nc), the layers were submitted to a thermal treatment. Two annealing processes at 1100 °C in nitrogen ambient are compared, one during 1 h in a conventional furnace and another one by rapid thermal processing (RTP) for 5 min. In the following, the samples with low/high Si excess are labelled L/H, and followed by 1 or 2 if the annealing has been made by RTP or by conventional annealing, respectively. In addition to those four layers, a fifth layer identical to layer L1 has been fabricated, and then implanted with Er ions. The Er concentration in this layer has been measured by means of secondary ion mass spectroscopy (SIMS) to be about 4×10^{20} at cm^{-3} at the peak concentration (see figure 1). After this implantation step, the layer has been annealed at 800 °C for 6 h to activate the Er ions. In the text, this fifth layer is labelled L1Er. To contact the layers a gate electrode has been formed by deposition of an n-type semitransparent polycrystalline silicon layer over an area of 300 μm by 300 μm. In this study the device has been forward polarized (negative voltage on the gate). Current–voltage (I–V) measurements have been carried out with a semiconductor analyser. EL spectra were measured using a spectrometer coupled to a charge-coupled device (CCD) for the visible range, and to a photomultiplier tube (PMT) for the infrared domain.

3. Results and discussion

The current–voltage (I–V) characteristics at room temperature of the four layers are shown in figure 2. An almost exponential growth of the current versus voltage is observed for all layers. Two main trends can be observed. The first one is that larger Si excess results in a larger conductivity, irrespective of the annealing procedure. The second point is that the layers annealed by RTP are much more conductive. This suggests that by means of the annealing one can modulate the transport properties.

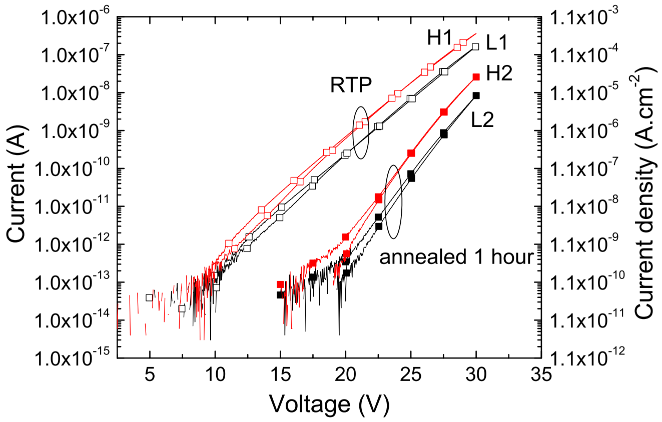

Figure 2. Current–Voltage (I–V) and current density–voltage (j–V) characteristics of the layers L1, L2, H1 and H2.

In order to understand the differences observed in the conductivity in depth, we have applied two models commonly used in the literature to analyse the I–V characteristics in silica and/or SRSOs. Those models are (i) the Poole–Frenkel (P–F) model that corresponds to thermally activated conduction between localized states in the gap assisted by the electric field [9] and (ii) the Fowler–Nordheim (F–N) model that describes the tunnelling of charges through a triangular barrier, from the electrode into the dielectric [10], or between localized states. Note that the localized state may refer to defects in the oxide matrix, or Si nanoclusters. Although those two models are too approximative [9, 10] to describe such a complex system, we will see that they will provide us some insight into the results of EL. The P–F model is described by the relation $I \propto V \exp(e/kT\sqrt{eV/\pi\varepsilon_0\varepsilon_r d})$, where ε_0 is the vacuum permittivity, ε_r the relative permittivity and d the thickness of the layer. For the F–N model, the following relation can be found between I and V: $I \propto V^2 \exp(-(4\sqrt{2m_{ox}\phi_b^3})/3e\hbar V)$, with m_{ox} the effective mass of the electrons in the dielectric, taken such as $m_{ox} = 0.5m_e$ the mass of the electron in vacuum, ϕ_b the potential barrier between Si and SiO$_2$ and $\hbar$ the Planck constant. Each of the experimental I–V curves has been fitted with the help of those relations (see figure 3).

The fitting with both models of the curves provides an interesting evolution of the transport properties with respect to the annealing treatment, which is believed to affect the material microstructure. Indeed, at low voltage the layers annealed by RTP show a current that is too large to be originated from F–N injection. A better agreement with the P–F law is found on a wide range of voltages. However, in layers annealed in the conventional furnace, the overall current is lower, and a better agreement with the F–N law is found. This suggests that for the same annealing temperature (1100 °C), the injection is more difficult when the annealing time is longer, leading to the requirement of larger voltages to promote charge transport. As a consequence, the probability of having hot carrier injection in those layers is higher than in RTP layers. The influence of the annealing treatment on the material properties can have several origins. On the one hand, it is well known that a thermal treatment is required to cure the layer from the defects introduced by the implantation. An annealing of 5 min may

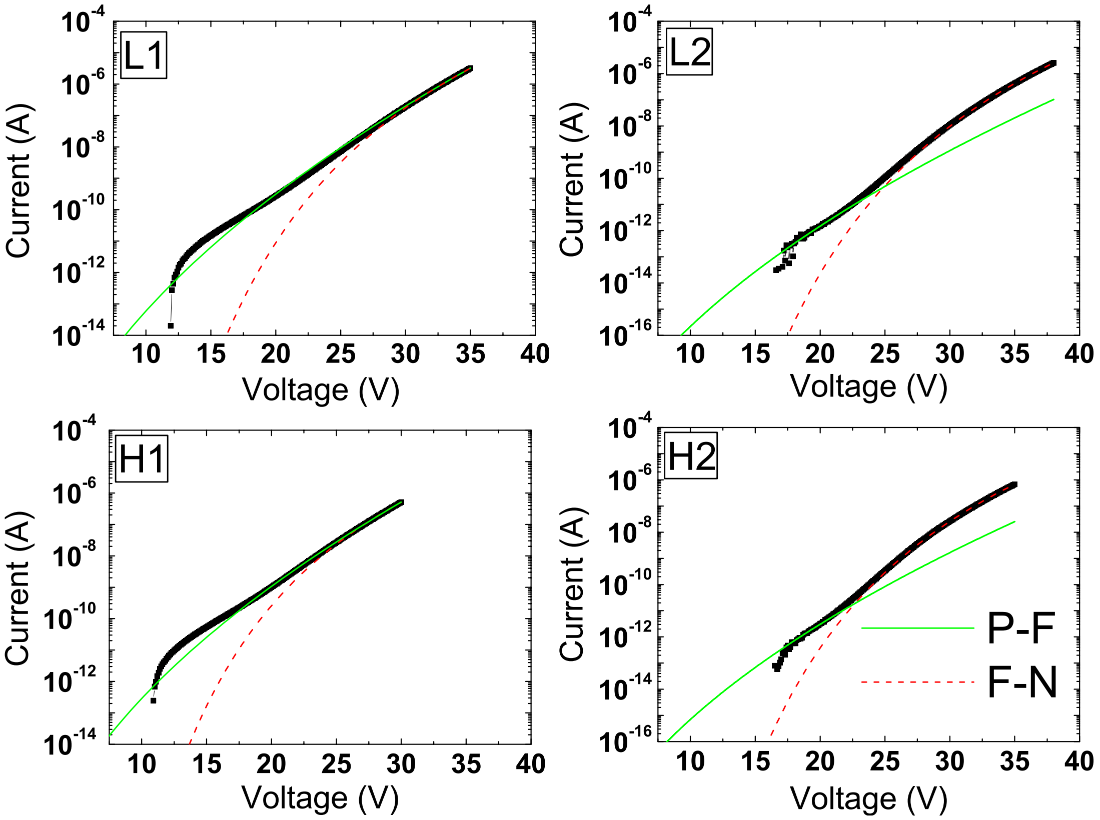

Figure 3. Fits of the I–V curves by the models P–F (green continuous line) and F–N (red dashed line). For layers L2 and H2, the fit with the P–F model is shown by keeping the permittivity found for layers L1 and H1 (see text for details).

Table 1. Injection barrier and permittivity extracted by fitting the I–V by the model F–N and P–F, respectively, on the whole voltage range.

	Barrier height (eV) (F–N)	Relative permittivity (P–F)
L1	1.61	4.52
L2	2.00	2.42
H1	1.32	5.06
H2	1.84	2.49

not be enough for that purpose [11]. On the other hand, at this temperature the formation of Si nanoclusters is expected, as confirmed by the measured large EL band in the visible-near infrared range centered at around 800 nm (see inset of figure 4), that is attributed to quantum confinement or to Si-nc surface states [12, 13]. We suggest that a different nanocluster size and spatial distribution are obtained by each of the annealing processes. However, the Si excess does not seem to have any significant influence on the transport mechanism for the range of Si excesses studied here. We can just observe larger currents when a larger Si excess is introduced. To go further we have looked at the relative permittivity we can extract by fitting the I–V curves with the P–F law, or the injection barrier height that we can extract from the F–N fit. These values are reported in table 1, when fitting the whole voltage range of the I–V of figure 3.

When the P–F model is used to fit the I–V curves at high voltages (larger than 30 V), a permittivity of about 4.5–5 is found for the RTP layers, and less than 2.5 for the layers treated in the conventional furnace. This latter value is too low to be acceptable, while 4.5–5 is an expected value for a Si-rich silicon oxide [14]. In figure 3, the fit by the P–F law has been repeated, this time fixing a permittivity of about 4.5–5, as found for samples L1 and H1, and just adjusting the exponential prefactor. This leads to an agreement with the P–F model at lower voltage, on a reduced range of voltages. Above a threshold voltage, the F–N law is found to reproduce well the I–V curves. Concerning the barrier heights found from the F–N fit, larger values have been found for the layers annealed for 1 h. Those values corroborate that (i) injection is more difficult for those layers than for the RTP ones, and (ii) the transport involves mainly electrons, because hole contribution would have implied a larger barrier height, as holes see a much larger potential barrier than electrons. Note, however, that hole injection in a region close to the Si substrate cannot be discarded [15]. To summarize, in the layers annealed for 1 h in the furnace, the F–N regime is the dominant conduction mechanism at high voltages. In the RTP layers, even if F–N may be activated at high voltages, the current is essentially limited by a P–F-type conduction. Moreover, as the effective barrier in those layers is lower due to a larger amount of defects, injection is favoured and conduction occurs at a lower voltage. This explains why the I–V curves in figure 2 of the RTP layers are shifted towards lower voltages. It is interesting now to observe how the difference in injection and transport affects the EL behaviour. To investigate this point, in figure 4 we have plotted the evolution of the EL intensity versus the electrical current.

A linear dependence is observed between EL and current intensities, implying that saturation of the luminescent centers

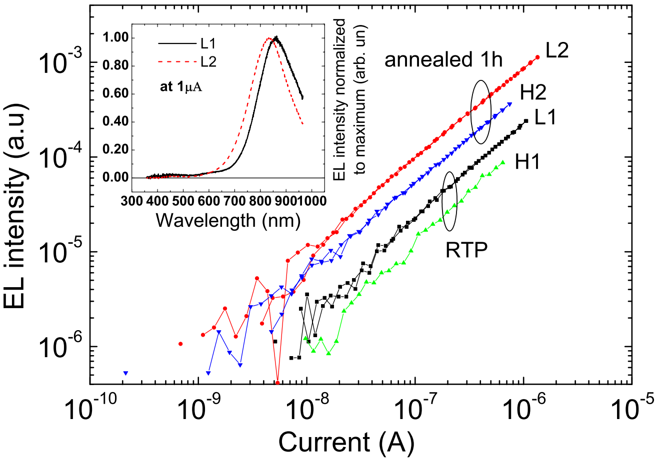

Figure 4. Evolution of the EL intensity versus current. The inset shows the normalized EL spectra of wafers L1 and L2 for a constant current of 1 μA.

still has not been reached. The corresponding EL spectra of devices L1 and L2 under a current of 1 μA are shown in the inset. By comparing the behaviour of the layers treated under the same conditions at a fixed current, one can observe that a lower Si excess results in a brighter emission. This means a larger external efficiency, defined as the ratio between the EL and the current intensities, is obtained for the layers with the lowest Si excess, irrespective of the applied annealing. Regarding the annealing, if we compare the curves at the same current, one can clearly observe that the layers annealed for 1 h are brighter than their counterpart RTP layers. As a consequence, the layers annealed for 1 h present a higher external quantum efficiency than the RTP layers. Looking at the normalized EL spectrum in the inset, we can see that layer L2 is emitting at a higher energy than layer L1. This is in contrast to what can be expected from the quantum confinement theory, as a longer thermal budget should lead to larger Si-nc and thus to a lower energy of emission. This disagreement can, however, be explained by the larger voltage that has to be applied to the L2 layer to obtain the same current, which in turn allows the excitation of smaller Si-nc. Or, as suggested by the I–V curve, this could be due to the larger number of defects present in the matrix of the L1 layer. Indeed, those defects around the Si-nc induce a weaker quantum confinement effect and thus a smaller blueshift of the light emission [12].

Finally, we have studied the possibility of getting EL at 1.54 μm by implanting Er ions in a layer similar to the L1 layer (lower Si excess and with RTP). There are several possible mechanisms of Er excitation, such as (i) direct impact excitation, (ii) impact of Si-nc that transfer their energy to Er ions, and/or (iii) electron-hole injection inside the Si-nc and subsequent energy transfer to the Er ions. In order to observe Er EL due to energy transfer from the Si-nc, we have chosen a layer identical to layer L1 (lower Si excess and RTP), to reduce direct impact excitation of Er that is favoured when the F–N regime is dominant. Figure 5(a) shows the EL obtained in the visible range and at 1.54 μm in the inset. An intense EL is observed at 1.54 μm. If we look at the visible range, we see that the Si-nc broad emission is superimposed to various peaks, whose energy coincides with Er transitions at higher levels [16]. Although a second order mechanism of high level excitation like cooperative up-conversion cannot be discarded [17], the fact that in figure 5(a) we observe at low injection fluxes all the visible emission spectra of Er ions suggests that in those devices, the Er is excited preferentially by direct impact excitation, rather than through indirect excitation of the coupled Si-nc. The excitation of the energy levels of Er in the visible is in agreement with the average energy acquired by the electrons injected by F–N mechanism, of about 2.5–3 eV in those kind of layers, as calculated in [18]. For the layer L1Er, a power efficiency of 10^{-3}% at 1.54 μm has been estimated, a value that is one order of magnitude lower than that already reported for other devices and layers [6, 8]. Note that although the experiment has not been carried out on a L2 type layer (annealed for 1 h) implanted with Er, we expect that, as the F-N regime would be more dominant because of a lower density of traps, the intensity of the Er peaks in the visible and at 1.54 μm should be more intense. As the current would also be lower, this should allow an increase in efficiency, in the same way as described for the EL in the visible range.

As an illustration, we show in figure 5(b) the spectrum, in the visible region, of a layer where the SRSO is grown by LPCVD, annealed at 1100 °C for 1 h as for layer L2 and then implanted with Er with the same implantation parameters as the layer L1Er. The validity of such a comparison can be checked in the inset of figure 5(b), where the I–V curve of this layer is superimposed on the one of layer L2. Both layers have been submitted to the same furnace annealing at 1100 °C for 1 h, and show very similar I–V characteristics, and quite good agreement with the F–N injection model.

The optical transitions of Er ions in the visible range are clearly much more intense. For this layer, a stronger EL intensity at 1.54 μm is found, typically 20 times stronger for the same current, attributed to a larger amount of impact excitation than in layer L1Er. As a consequence, when only one kind of charge—here the electrons—are involved in the charge transport, one has to optimize the hot electrons injection to enhance impact excitation, in order to get higher EL intensity and external quantum efficiency. Nazarov *et al* suggest that a very large Si excess is detrimental for direct impact excitation of Er, as the Si-nc act as scattering centres [3]. Sun *et al* observe that in their LEDs the direct impact of Er for low Si excesses is not efficient [19]. They get a current density of 1.5 A cm^{-2} at 25 V for a 90 nm thick layer. This is several orders of magnitude larger than the density current we have measured (see figure 3). This suggests that the defects that assist transport through a P–F type conduction mechanism in the present case, or a space charge limited current in the case of [19] are responsible for the thermalization of the injected hot electrons, an undesired effect that prevents direct impact excitation. In the case of the layers annealed for 1 h at 1100 °C, the results suggest that most of the electrons are flowing through the SiO$_2$ conduction band at high voltage. An appropriate low Si excess will favour injection at lower voltages, as the effective F–N barrier decreases (see table 1), enhancing the reliability of the layers. Another approach to increase the reliability can be working in the pulsed excitation regime.

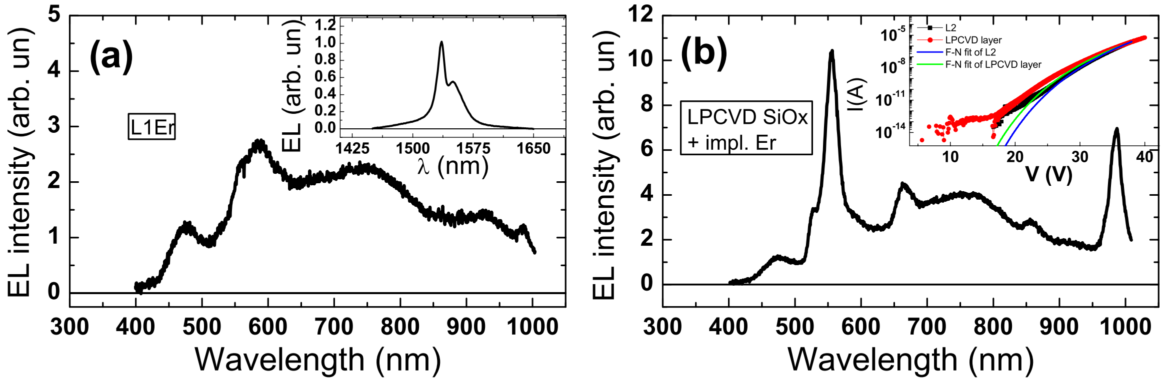

Figure 5. (*a*) EL Spectra in the visible range and at 1.54 μm in the inset, of the layer L1Er, at a forced current of 10 μA. (*b*) EL spectra of an SiO_x layer made by LPCVD annealed at 1100 °C during 1 h and then implanted with Er at the same current for comparison.

Note finally that apart from the Er excited by direct impact, some of the Er may be excited by energy transfer. This fraction could be increased by controlling the hole injection in the active layers. It remains interesting to increase this fraction, as the onset voltage of EL could be reduced, and thus efficiency and reliability would increase. One possibility to do this could be by working in a sequential regime, in the SiO_x system [20] or SiO_x : Er system [21], as no transport inside the layer is required. The other possibility could be to work with a multilayer system SiO_x/SiO_2, in order to control the bipolar current injection, and be able to balance their injection rate by means of a careful engineering of the Si-nc sizes [22]. By introducing Er in the system, one can expect a larger fraction of excited Er by indirect excitation.

4. Conclusion

The effect of RTP and furnace annealing on the transport properties and electroluminescence of Si-nc embedded in SiO_2 layers doped or not with Er ions has been investigated. By changing the thermal treatment, an evolution of the external quantum efficiency is shown, and is correlated with the different transport mechanisms activated. The main excitation mechanism is attributed to impact excitation. The observation of sharp EL peaks of Er in the visible suggests that Er is also excited directly by impact. In this case, the results suggest that the matrix defects promote charge conduction but are detrimental to the electroluminescence, as they lead to an undesired thermalization of the hot electrons injected at high field.

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