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DC and AC electroluminescence in silicon nanoparticles embedded in silicon-rich oxide films

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Abstract

Electroluminescent properties of silicon-rich oxide (SRO) films were studied using metal oxide semiconductor-(MOS)-like devices. Thin SRO films with 4 at.% of silicon excess were deposited by low pressure chemical vapour deposition followed by a thermal annealing at 1100 °C. Intense continuous visible and infrared luminescence has been observed when devices are reversely and forwardly bias, respectively. After an electrical stress, the continuous electroluminescence (EL) is quenched but devices show strong field-effect EL with pulsed polarization. A model based on conductive paths—across the SRO film— has been proposed to explain the EL behaviour in these devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Observation of luminescence in porous silicon [1] seemed to solve the problem of the physical inability of silicon (Si) to act as a light emitter; however, its poor chemical stability, robustness and luminescence degradation [2] have hindered its further development. Silicon nanoparticles (Si-nps) embedded in a dielectric matrix look to be a better alternative for light emitting devices (LEDs) due to their strong, stable luminescence and chemical stability. Nevertheless, among the different techniques to fabricate nanostructured materials, ones compatible with complementary metal oxide semiconductor (CMOS) technology must be used to advance the photonics integration objectives. Low pressure chemical vapour deposition (LPCVD) allows us to obtain silicon-rich oxide (SRO) layers using oxidant species such as nitrous oxide (N_2O) and silicon compounds (SiH_4) as reactant gasses. Silicon excess is easily controlled by changing the partial pressure ratio (Ro) between nitrous oxide (N_2O) and silane (SiH_4). Silicon excess as high as 17 at.% is obtained with $Ro = 3$, and stoichiometric oxide can be obtained for $Ro = 100$ [3–5]. Comparative studies done by our group have shown that SRO films deposited by LPCVD films emit a stronger photoluminescence (PL) than the ones deposited by plasma-enhanced CVD (PECVD) and Si implanted SiO_2 films [6, 7]. Moreover, SRO films deposited by LPCVD (SRO–LPCVD) with low silicon excess have shown more intense PL than that with high silicon excess [5, 6, 8]. The optimum annealing condition where the strongest PL is obtained is 1100 °C for 3 h and the strongest PL is obtained with silicon excess of about 4 and 5 at.%. Spectroscopical analysis has revealed the presence of amorphous Si-nps embedded in SRO films with low silicon excess [5].

Intense investigations of electroluminescence (EL) in Si-nps have been carried out, for example in porous silicon [9–14]. Nevertheless, one of the main problems in obtaining efficient LEDs based on Si-nps is the carrier injection into the dielectric matrix. It is well known that EL intensity is directly related with charge injection to the luminescent centres [9–13]; however, it has been reported that when high current flows

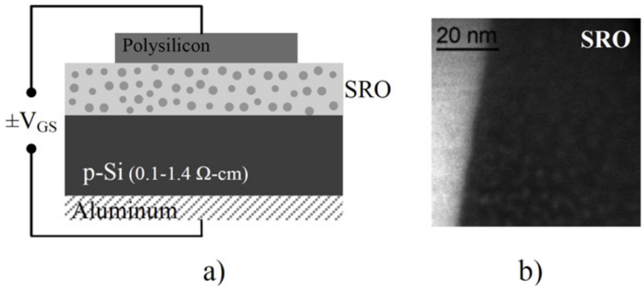

Figure 1. (a) Scheme of the fabricated devices and (b) cross-sectional EFTEM image of Si-nps within the SRO films with 4 at.% of Si excess.

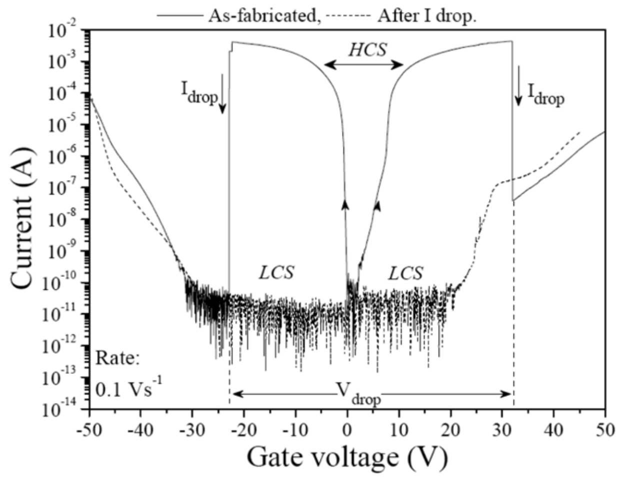

Figure 2. The I–V curve measured on as-fabricated devices and after I_{drop}.

through the active layer, charge trapping or degradation of the matrix could occur, quenching the EL properties [14–16]. Nevertheless, the decay of the EL properties at DC is not necessarily related to those effects, instead of that, the annihilation of unstable Si-nps could be occurring, as reported before [17]. Moreover, the annihilation of such unstable Si-nps could change the way to obtain EL.

In this work, the electro-optical properties of MOS-like structures, using a silicon-rich oxide (SRO) film with 4 at.% of silicon excess as the dielectric layer, is reported. Analyses on these MOS-like devices have demonstrated a quenching of the EL properties after being properly DC biased. However, a partial restoring of the EL emission has been observed from quenched devices biased with AC voltage. A model to explain the results is proposed.

2. Experiment

The SRO films were deposited by LPCVD on (100), 0.1–1.4 Ω cm p-type silicon substrates. The flow ratio ($R_0 = P(N_2O)/P(SiH_4)$) was used to control the silicon excess to be about 4 at.%, as estimated from XPS on equivalent samples [5]. After deposition, SRO films were thermally annealed at 1100 °C for 3 h in nitrogen atmosphere in order to induce a silicon agglomeration by Si and SiO_2 phase separation. The thickness of the annealed SRO films, measured with a Gaertner L117 ellipsometer (incident laser wavelength of 632.8 nm), is about 53 ± 3 nm. A 350 nm thick n+polycrystalline silicon (poly) gate was then deposited on the SRO film. The device area is 9.604×10^{-3} cm^2. The backside contact was a 1 μm thick Al/Cu layer made by sputtering.

The presence of Si-nps within the active layers in these devices was observed on SRO films deposited under the same conditions by energy filtered transmission electron microscopy (EFTEM). Cross-sectional view images were obtained using an electron microscope JEOL JEM 2010F and an Si plasmon of 17 eV.

Current–voltage (I–V) measurements were done with an HP4155B semiconductor parameter analyzer and using a Karl Suss PA200 probes system. EL spectra were measured biasing the devices with a DC gate voltage 'continuous EL'. Light emission was observed with the naked eye as shining spots on the surface of devices. Light emission was collected with an optical fibre with a core of 50 μm, which was located right on single shining spots and connected to a high resolution spectrometer model HR4000 and analysed with a computer. Pulsed EL studies were performed biasing the devices with high voltage pulses using an Agilent 8114A pulse generator. Time resolved electroluminescence was acquired with a photon-counting set-up composed of a Hamamatsu H7422-50 thermoelectric cooled photomultiplier and a Stanford Research SR430 multi-channel scaler. Several devices with the same characteristics were measured and all measurements were done at room temperature.

3. Results

Figure 1(a) shows a schematic of the fabricated devices. The microstructure of the SRO films was analysed using EFTEM. Figure 1(b) shows a cross-view EFTEM image of the SRO films after thermal annealing. In the image, the bright zones are associated with the presence of silicon in the film. Due to the low silicon content in the SRO films, the EFTEM images exhibit a low contrast and sharpness, making it difficult to observe clearly the contour of the Si nanoparticles. Nevertheless, some slightly bright zones are observed, which are evidence of the presence of Si-nps in these films. The average size of these Si-nps is about 1.5 nm, in agreement with some other TEM measurements on similar SRO films [18].

Figure 2 exhibits the typical I–V curve measured in devices at forward and reverse bias (FB and RB respectively), FB and RB refer to negative and positive voltages with respect to the substrate. The devices were measured as-fabricated and then after I_{drop}, (electrically stress). In as-fabricated devices, high current is measured at low voltages at both biases. However, at a voltage $V = \sim -23$ and $\sim +32$ V the current drops from a high conduction state (HCS) to a low conduction state (LCS). Afterwards, for voltages above 30 V the current increases again by Fowler–Nordheim tunnelling [17]. A subsequent I–V measurement on the same devices exhibits a very low current of about 10^{-12} A at small voltages and for both biases. The high current at low voltages is no longer reached and the electrical stress produces charge trapping rather than a recovery of the high current [17]. The HCSs at low voltages have been related to the presence of conductive

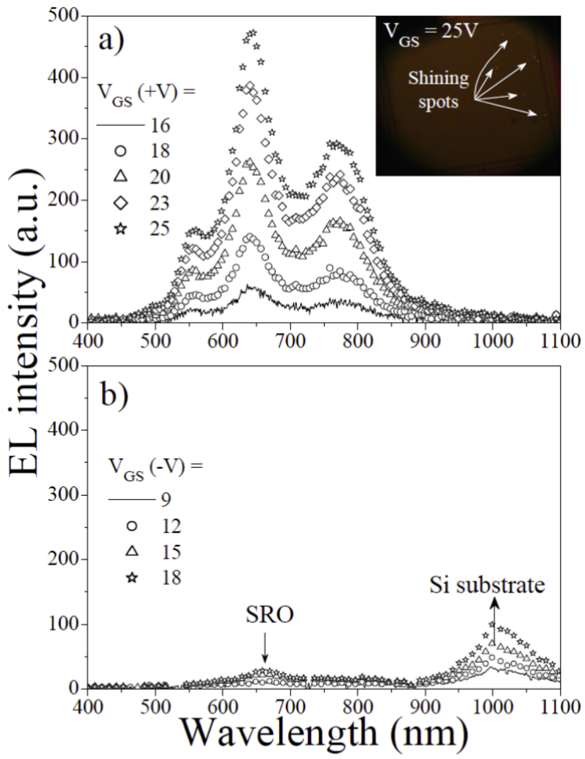

Figure 3. EL spectra measured from as-fabricated devices at (a) reverse bias and (b) forward bias. Inset (a) shows the shining spots in the fabricated devices under DC $V_{GS} = 25$ V.

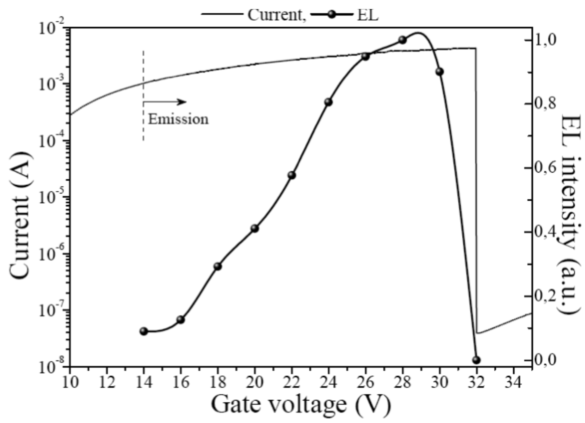

Figure 4. Correlation between current and EL in as-fabricated MOS-like devices.

paths in the SRO films, which connect the polycrystalline silicon gate to the Si substrate. The current drop was explained as a result of the annihilation of such conductive paths [17].

Light emission was observed in as-fabricated devices in the HCS. The EL spectra as a function of the gate voltage at RB and FB are shown in figure 3. At RB, figure 3(a), a broad visible spectrum with various peaks between 450 and 900 nm is observed for all gate voltages. This behaviour of several peaks has been mainly related to the transmittance spectrum of the top polycrystalline silicon electrode [19]. Nevertheless, SRO films with the same silicon excess show a photoluminescent peak with very low intensity at ~470 nm [7, 8]. It is well known that a neutral oxygen vacancy (NOV) defect emits at this wavelength [7, 10]. Due to the low silicon excess, it is possible that these luminescent centres exist in the SRO film. In fact, cathodoluminescence (CL) studies on similar SRO films from this work exhibit an emission band with a maximum peak at about 460 nm and a tail at longer wavelengths [7, 20]. EL emission in this work at that region is not observed due to the zero transmittance of polysilicon at these wavelengths [21], but EL emission with low intensity at 550 nm is observed. Then, it is expected that these films also emit in the blue region and are related to NOV defects. On the other hand, EL is observed with the naked eye as shining spots on the surface of the MOS-like devices, as observed in the inset of figure 3(a). The EL intensity increases with the gate voltage. At FB, figure 3(b), two peaks at about 650 and 1000 nm are observed, but they are very weak. The emission at 650 nm could be produced by the recombination of e–h pairs inside the SRO film; meanwhile the emission at 1000 nm could be due to the Si substrate. The emission at 1000 nm has been reported as a silicon emission [22, 23] in spite of its indirect band. Nevertheless, further studies needs to be done in order to clarify this emission.

Figure 4 shows the reverse *I–V* characteristic and the EL peak intensity at 650 nm as a function of gate voltage normalized to the highest emission measured from as-fabricated devices. As can be seen, when the voltage increases, the current through the SRO film increases and at a certain gate voltage, where the current reaches ~1 mA, the emission starts. As the voltage increases even more, the current and the EL intensity increase. Nevertheless, after a certain gate voltage the current drops, quenching the EL. Therefore, the current decay from the HCS to the LCS is directly related to the EL quenching.

4. Discussion

The tested devices showed high current values even at small voltages, as observed in figure 1. As observed by EFTEM, Si-nps are created inside the SRO films after thermal annealing. Supposing a dispersion on the Si-nps size, a model which involves the presence of Si-nps (size ⩾1 nm) and silicon nanoclusters (Si-ncls, size <1 nm) has been proposed for these metal/SRO/Si structures [17]. In this model, it was assumed that the tunnelling current does not flow uniformly through the whole capacitor area, but instead it passes through discrete conductive paths within the oxide, which are established between adjacent Si-nps and Si-ncls, as shown in figure 5(a). An increase of the total current will result in an increase of the current density in each conductive path, which results, therefore, in a higher number of radiative recombination events.

When the gate is positively biased with respect to the substrate, electrons are attracted to the silicon surface, creating an inverted layer. Electrons from this inversion layer and holes from the poly gate are injected toward the poly/SRO and SRO/Si interfaces through conductive paths, respectively. As a result, emission occurs when e–h pairs recombine within

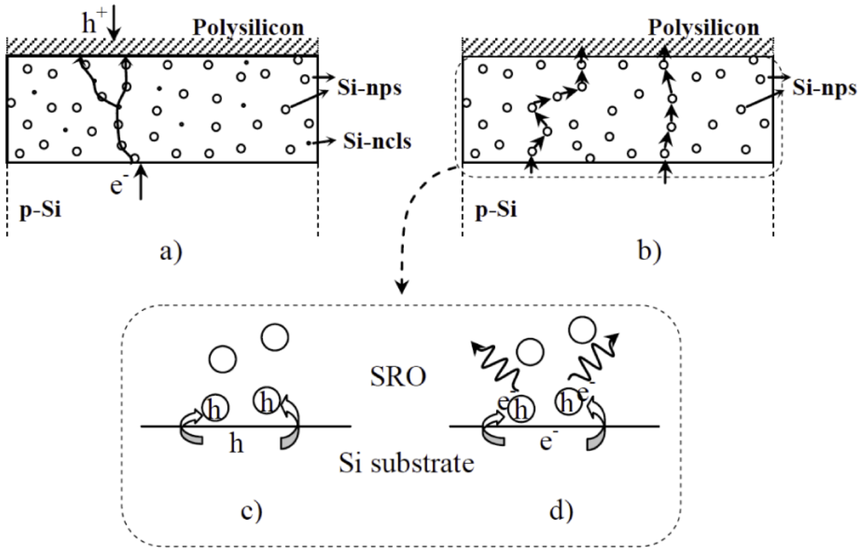

Figure 5. MOS-like structure schematic in (a) as-fabricated and (b) after the current drop. EL mechanism in AC; (c) holes and (d) electrons injection under negative and positive voltages, respectively, after the current has dropped.

the SRO layer. As the gate voltage is increased, the carrier injection toward the SRO and then the EL intensity increase.

The EL peak observed at ∼1000 nm can be explained in a similar way: when a negative gate voltage (FB) is applied to the MOS-like structure, holes are attracted to the silicon surface creating an accumulation layer. Holes from this accumulation layer are injected toward the poly/SRO and electrons from the poly gate to the SRO/Si substrate interfaces. However, since the major contribution of current comes from the tunnelling of electrons instead of holes for MOS on p-type Si [22, 24], the meeting point is closer to the SRO/Si interface and then the recombination happens, both in the SRO film and the Si substrate surface, as reported in other works [22, 23].

As mentioned before, it has been reported that the carriers do not flow uniformly through the whole capacitor area, but they pass through discrete conductive paths within the SRO [17], increasing the emission at their nodes. Therefore, the light is observed as single shining spots on the surface of the MOS structure. As the current (voltage) is increased, more charges that are flowing through the Si-ncls may break off some of the Si–Si bonds (creation of E′ centres) of the nodes, as reported in [17]. In consequence conductive paths become annihilated, resulting in current drops. As a result of that, the flow of charges toward the SRO film and the EL are reduced.

Once the current has dropped, the SRO conductivity changes, then only stable Si-nps can be used as nodes for conductive paths, see figure 5(b). Therefore, higher voltages are required to inject charge through the SRO film. Yet, for gate voltages at DC above +20 V, where the current is activated again, charge trapping is observed, as reported in [17], but no EL emission.

The only way to observe the EL properties in these devices after the current drop is through the field-effect luminescence mechanism proposed by Walters *et al* [13], in which holes and electrons trapped in Si-nps are obtained during the negative and positive pulse, respectively. Simultaneous trapping of both electrons and holes at the very same site may result in radiative recombination.

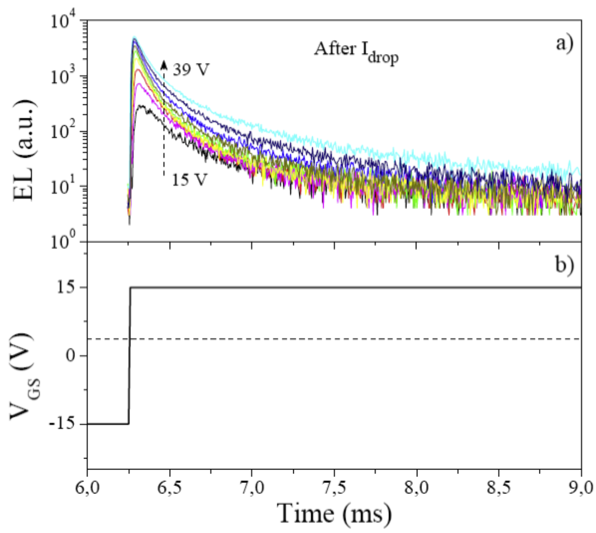

Figure 6. (a) Time resolved EL measured after the current drop and (b) pulse excitation with an amplitude of ±15 V, shown as a reference.

EL measurements at AC were done after the current decay. Figure 6(a) shows the time resolved EL as a function of the AC voltage. The pulse excitation of ±15 V is also shown as a reference in figure 6(b). As we can see, an exponential EL behaviour is observed after alternating the voltage bias from negative to positive. EL is also observed when the voltage bias is changed from positive to negative, but with lower intensity (not shown). It is important to mention that EL intensity at the positive pulse is always similar to and higher than that observed in the negative pulse. There is no exhausting of EL as reported by Linnros *et al* in porous silicon [14]. The EL emission is observed after a threshold voltage of 15 V is reached and it increases as the voltage of the excitation pulse is higher. This emission is related to the injection of holes and electrons from the silicon substrate toward the remaining Si-nps during the negative and positive pulse, as shown in figures 5(c) and (d), respectively [13]. When the pulse excitation is at negative voltage, the substrate surface is strongly accumulated. Holes from the accumulation layer tunnel toward the SRO film where they are trapped. When the pulse changes from negative to positive voltage, an inversion layer is formed. Electrons are injected into the SRO film creating e–h pairs with those holes trapped, e–h pairs recombine and light is emitted. The EL emission is observed until no more holes are inside the SRO film to create e–h pairs, However, electrons from the inversion layer continue to be injected into the SRO film, resulting in a re-charged SRO film, but now it is negatively charged. When the pulse excitation comes back to negative, the accumulation layer is newly created and holes are now injected into the SRO film, so e–h pairs are created again. EL emission is observed, but with a lower intensity. This difference in EL intensities could be due to some electrons back tunnelling to the substrate during holes injection, as reported by other authors [13, 21]. Beside this, due to the Si substrate being highly doped, as the driving voltage is positive a deep inversion will hardly be reached and then electrons in a lower quantity than holes will be injected into the SRO film.

In order to clarify that the EL emission at AC is due to the remaining Si-nps, the mean lifetime was analysed by fitting the EL curves of figure 6 with the equation (1) [15]:

$$I(t) = I_0 e^{(-t/\tau)}. \qquad (1)$$

It has been reported that the typical mean lifetime for systems with Si-nps is in the order of 1–100 μs [13, 15]. A mean lifetime of 91.5 $\pm$ 24 μs has been found for the voltage range reported in figure 6. Therefore, the AC emission observed in the devices after the current decay is due to the remaining Si-nps and it agrees with our proposed model.

5. Conclusion

A broad electroluminescent emission spectrum with maximum peaks was observed in MOS-like devices with SRO films. A maximum and then an EL quenching were observed. The quenching EL was analysed and correlated to a current drop, which results in the annihilation of conductive paths during the charge injection in the SRO films. However, new EL measurements demonstrated EL at pulsed stimulation. This AC emission is due to the remaining Si-nps. Fits on the exponential emission demonstrated a mean lifetime of 91.5 $\pm$ 24 μs, which is typical for Si-nps in agreement with our proposed model.

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