



# Visible electroluminescence from silicon nanoclusters embedded in chlorinated silicon nitride thin films

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## ABSTRACT

Visible electroluminescence (EL) has been obtained from devices with active layers of silicon nanocrystals embedded in chlorinated silicon nitride (Si-nc/SiN<sub>x</sub>:Cl) thin films, deposited by remote plasma enhanced chemical vapour deposition, using SiCl<sub>4</sub>/NH<sub>3</sub>/H<sub>2</sub>/Ar. The active nc-Si/SiN<sub>x</sub>:Cl film was sandwiched between Al contacts and a transparent conductive contact of ZnO<sub>x</sub>:Al deposited by the pyrosol process. White EL centred at around 600 nm was observed, with a turn-on voltage of 5 V, and the intensity increasing as a function of voltage. Recombination between electron–hole pairs generated in the Si-nc by electron impact ionization is proposed as the EL mechanism.

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## 1. Introduction

The preparation of silicon-based electroluminescent (EL) devices is very important for the development of low cost optoelectronic integrated circuits (OIC). Since the observation of strong photoluminescence from porous silicon (PS) [1], several EL devices based on PS have been developed [2–7]. However their application to the development of OICs is still limited due to the mechanical fragility of PS and the incompatibility of its fabrication process with the conventional processes used in the silicon integrated circuits technology. EL devices have also been prepared using silicon dioxide films containing tiny silicon particles or silicon nanocrystals [8–13], which are usually prepared by techniques more compatible with the integrated circuits technology such as: chemical vapour deposition (CVD) and plasma enhanced CVD (PECVD). Nevertheless, the application of these structures is limited by the difficulty in carrier injection, due to the wide band gap of the SiO<sub>2</sub> layers. Because of its narrower band gap, silicon nitride (SiN<sub>x</sub>) films containing amorphous silicon quantum dots or silicon nanocrystals (Si-nc) have been proposed as a better option to prepare EL devices with lower operation voltages [14–19]. In most of these cases the Si-nc/SiN<sub>x</sub> active film of silicon nanoclusters or nanocrystals embedded in silicon nitride has been prepared by PECVD using SiH<sub>4</sub> as silicon source gas, and N<sub>2</sub> or NH<sub>3</sub> as nitrogen source [14–17]. A variety of EL structures with different EL characteristics (operation voltage, peak, width and intensity of emission) have been prepared using indium tin oxide (ITO) [15,16,18,19] or Au/NiO

[14,17] as a transparent electrode. Here we report the visible electroluminescence of an EL structure that uses an active layer of Si-nc embedded in chlorinated silicon nitride (Si-nc/SiN<sub>x</sub>:Cl) deposited by remote plasma enhanced chemical vapour deposition (RPECVD) using SiCl<sub>4</sub>/NH<sub>3</sub>/H<sub>2</sub>/Ar, and a transparent conductive contact of aluminium doped zinc oxide (ZnO:Al) deposited on glass by the pyrosol process. The motivation and advantage of the use of SiCl<sub>4</sub> in place of SiH<sub>4</sub>, is that previous works have demonstrated that the SiCl<sub>4</sub>/H<sub>2</sub> mixture plasma favors the formation of silicon nanocrystals (Si-nc) at low deposition temperatures [20–22] and that the addition of NH<sub>3</sub> in the SiCl<sub>4</sub>/H<sub>2</sub> plasma generates the formation of these Si-nc embedded in a silicon nitride matrix [23,24]. Other advantages of using SiCl<sub>4</sub>/H<sub>2</sub> plasmas is that the SiCl<sub>x</sub> radicals promote chlorine-terminated Si-nc surfaces, which have a better chemical stability than the hydrogen-terminated surfaces, and that the amount of chlorine and hydrogen atoms incorporated in the growing film can be mutually controlled through the formation of volatile HCl [21,23].

The motivation to use ZnO:Al as a transparent conductive contact is that it is an n-type wide band gap semiconductor (~3.3–3.6 eV), with properties very similar to that of ITO, such as good optical transmission in the visible region and low electrical resistivity, but with the advantages that the ZnO:Al is a non-toxic, inexpensive, a more abundant material, and chemically and thermally more stable than ITO [25–27].

## 2. Experimental details

The starting solution for the pyrosol deposition of the ZnO:Al layer was made with 0.2 M of zinc acetate (ZnAc) and 3 at.% of aluminium acetylacetonate (AlAAC) dissolved in 170 ml of anhydrous methanol

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plus 20 ml of water and 4 ml of acetic acid. This solution was ultrasonically sprayed on glass substrates at 500 °C, using air as carrier and director gas at flow rates of 2 and 1.5 l/min, respectively. After a deposition time of 30 min, under these conditions, a ZnO:Al film with a sheet resistance of  $\sim 60 \text{ Ohm}/\square$  was obtained. The transmittance of this ZnO:Al film was about 70–80% in the visible spectrum. The Si-nc/SiN<sub>x</sub>:Cl film, with a thickness about 80 nm, was deposited on the ZnO:Al-coated glass, using the RPECVD system whose characteristics are reported elsewhere [23,28]. The source gases were SiCl<sub>4</sub>, H<sub>2</sub>, and NH<sub>3</sub>, introduced at constant flow rates of 5, 20 and 40 sccm, respectively. A flow rate of Ar of  $\sim 100 \text{ sccm}$  was added in order to have a deposition pressure of 300 mTorr. The substrate temperature was 200 °C, and the deposition was activated using 200 W of input RF power. Under these conditions we had the evidence from HRTEM results that the as-grown Si-nc/SiN<sub>x</sub>:Cl film contains Si-nc with diameters in the range of  $\sim 1$  to 4 nm [23,24]. In order to complete the EL device structure depicted in Fig. 1, Al electrodes with circular areas of 0.07 cm<sup>2</sup> and thickness of 275 nm were thermally evaporated on the top of the Si-nc/SiN<sub>x</sub>:Cl film, and on an uncovered part of the ZnO:Al film. The EL of these devices was investigated under both, forward and reverse bias. The EL signal was collected using a quartz optical fiber, and measured with a Spex-Fluoromax spectrometer sensitive in the range 200–850 nm.

### 3. Results and discussion

Since the ZnO:Al film is n-type, we defined the polarity shown in Fig. 1 as the forward bias. However, currents of the same order of magnitude were also measured under the reverse bias, indicating that there is no rectification effect in these devices, and that in both polarities there is only electron injection from the electrodes. Prior obtaining the final EL spectra shown in Fig. 2, the devices were given an “electrical healing” process, which consisted in applying increasing voltages from 1 to 15 V, in steps of 1 V during 5 min, once in forward bias and once in reverse polarity. During this healing process the EL signal was detected above 11 V in the forward bias and, both, the electrical currents and the EL signals were unstable. After this healing process the current and EL became stable and when the forward bias voltage was 5 V and the current density was about 29 mA/cm<sup>2</sup>, EL was clearly observed with the naked eye in a dark room. The EL spectra of the EL devices measured at different forward bias voltages are shown in Fig. 2. From this figure we can see that the EL intensity enhances rapidly when the bias voltage increases. For the maximum forward voltage of 15 V, the EL could be observed with the naked eye in a medium bright room. Although no significant changes in the shape of the EL spectra are observed, the peak position is slightly blueshifted

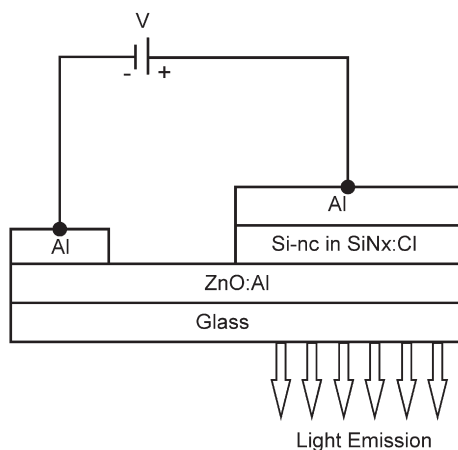


Fig. 1. Schematic illustration of the ZnO:Al/(Si-nc/SiN<sub>x</sub>:Cl)/Al EL structure under the forward bias condition.

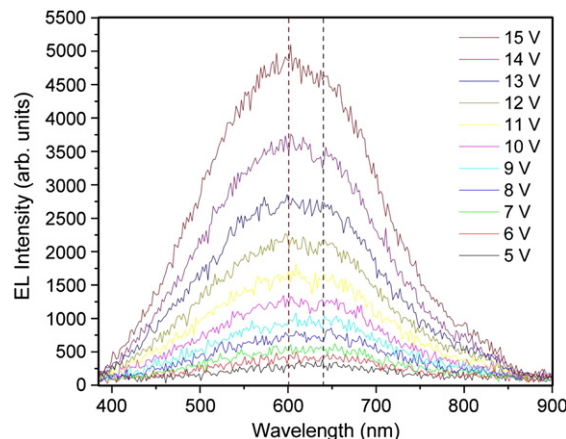


Fig. 2. EL spectra of the Si-nc/SiN<sub>x</sub>:Cl EL device as a function of the forward biased voltage. The dashed lines indicate the approximate peak position for the first (5 V) and last (15 V) spectra.

from  $\sim 635 \text{ nm}$  ( $\sim 1.95 \text{ eV}$ ) to  $\sim 600 \text{ nm}$  ( $\sim 2.07 \text{ eV}$ ), as the bias voltage increases from 5 to 15 V, respectively.

Fig. 3 shows the plot of current density vs voltage ( $J$  vs  $V$ ) during operation of the EL device, under forward bias. The fit of these data was tried with the relationships of Pool-Frenkel (PF) and Fowler-Nordheim (FN), given by the equations:  $J_1 = C_1 V \exp(-a + bV^{1/2})$  and  $J_2 = C_2 V^2 \exp(-\beta/V)$ , respectively, which describe well the conduction mechanisms in silicon-based gate dielectrics [29]. Although the conduction mechanisms in our films are much more complicated due to the presence of the silicon nanocrystals in the silicon nitride matrix, as Fig. 3 shows, at low voltages the PF process dominates, as it is expected to happen in silicon nitride films. On the other hand, at high voltages the probability of having FN tunneling of electrons through triangular barrier into the silicon nitride conduction band, increases, and the current transport behavior includes both mechanisms. This behavior is consistent with the mechanism of electron injection proposed to explain the electroluminescence of other silicon-nanostructured systems, which involve direct tunneling and Fowler-Nordheim tunneling between the nanocrystals that are separated from each other by dielectric distances of the order of some units of nm [6,8,10,12].

Based on the above discussion we can propose a simplified band model of our ZnO:Al/SiN(Si-nc) EL device under a strong electric field, such as that shown in Fig. 4, where the ZnO:Al/SiN interface can be regarded as a Schottky-like junction and the Si-nc are connected together via the wider-gap regions of SiN (silicon nitride). When a high forward bias voltage is applied, a stronger electric field is built up in the wider band gap SiN regions and energetic electrons can be

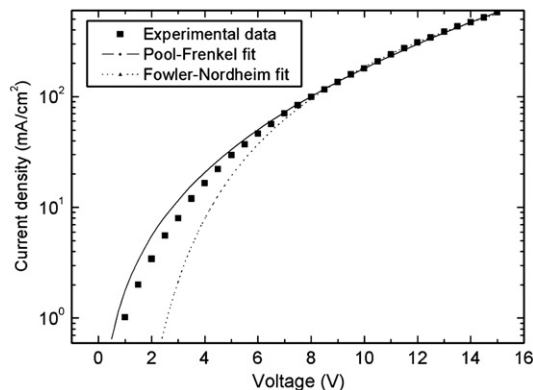


Fig. 3. Plot of the experimental data of  $J$  vs  $V$  during operation of the EL device under forward bias.

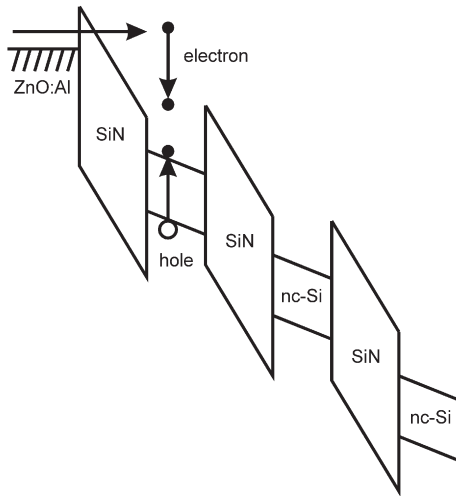


Fig. 4. Band model of the ZnO:Al/SiN(Si-nc) EL device under a sufficiently high forward bias voltage.

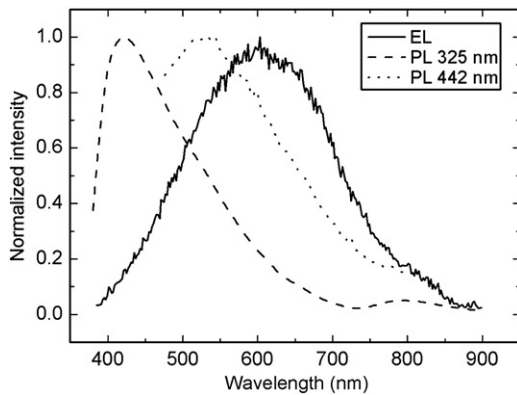


Fig. 5. Normalized EL spectrum obtained at 15 V, and normalized PL spectra of Si-nc/Si<sub>x</sub>:Cl thin films, obtained with the unfocused 442 and 325 nm lines of a He–Cd laser.

injected, by the tunneling effect, from the ZnO:Al transparent conductive contact into the Si-nc regions.

Fig. 5 shows the normalized PL spectra of the active Si-nc/Si<sub>x</sub>:Cl film, excited with the two wavelengths (325 nm and 442 nm) of a Kimmon He–Cd laser, and the normalized EL spectra of the device obtained at 15 V. As this figure shows, the normalized PL spectrum excited with photons of 442 nm (2.8 eV) is shifted to lower wavelengths (peak at ~527 nm) with respect to the normalized EL spectrum (peak at ~600 nm), and the PL spectrum excited with photons of 325 nm (3.81 eV) is much more shifted (peak at ~420 nm).

Based on our results and previous discussion, the electroluminescence in our EL devices can be explained by assuming that electron–hole pairs are generated within the Si-nc by energetic electron impact ionization, and then, they recombine radiatively. This proposed EL mechanism is consistent with the small shift of the EL peak toward shorter wavelengths (or higher energies) with increasing the applied voltage, observed in the spectra of Fig. 2, since the energy of the tunneled electrons increases with the voltage, favoring the excitation of smaller Si-nc, which emit at higher energies due to their larger band gap [10]. Under this model, and considering the wavelength peak position of the EL spectra of Fig. 2, we can infer that the average energies of the hot electrons that create the electron–hole pairs within the Si-nc, are of the order or slightly higher than 1.95–2.07 eV. The assumption that the light emission, either by EL or PL, is due to electronic radiative transitions between discrete energy levels created

in the Si-nc by quantum confinement effect also explains the further shift of the PL peaks toward shorter wavelengths or higher energies with respect to the EL peaks (see Fig. 4), with increasing energy of the exciting photons, since this favors the excitation and light emission of smaller Si-nc. We assume that the good EL emission, peaked at ~2.0 eV, of the Si-nc in the Si<sub>x</sub>:Cl matrix is due to an enhancement of the quantum confinement effect, because their surface results well passivated with chlorine and nitrogen atoms, which reduces the non-radiative recombination [23]. It is also possible the oxidation of SiCl bonds, which can leave some Si-nc passivated with oxygen atoms and generate localized radiative centers near the nc-Si/SiO<sub>x</sub> surface, however, they are reported to emit at lower energies (1.38–1.48 eV) [22].

#### 4. Conclusions

In summary, visible EL emission was obtained from electroluminescent (EL) devices prepared with active layers of silicon nanocrystals embedded in chlorinated silicon nitride thin films and ZnO:Al as transparent conductive contact. The EL mechanism is interpreted as a result of radiative recombination of electron–hole pairs generated, by electron impact ionization, within the well passivated Si-nc in the Si<sub>x</sub>:Cl matrix.

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