MNOS structure: towards efficient and reliable silicon nanocrystal-based LEDs

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Abstract—Efficiency and reliability improvement of silicon nanocrystals in silicon oxide light-emitting devices is reported. The emission power efficiency is enhanced up to ~1 % by depositing a ~15-nm silicon nitride buffer onto the active layer. The presence of this additional layer reduces the leakage current through the structure, leading to an effective increase of the power efficiency without significant effects on the operation voltages. Furthermore, the silicon nitride cools down the electrons that reach the top electrode. Both effects lead to a device degradation reduction of up to 50 %.

I. INTRODUCTION

Silicon nanocrystal based materials are attractive for electronic and optoelectronic applications thanks to their tunable emission in the red-NIR (near infrared) range and their compatibility with the current CMOS (complementary metal oxide semiconductor) technology [1]-[3]. In the last years, many studies on electroluminescence (EL) from Si-nc (silicon nanocrystals) in silicon oxide (SiO₂) have been published. Some authors reported emission under DC excitation [4] that usually leads to fast device degradation and poor emission efficiencies. Others authors apply the concept of field-effect luminescence (AC excitation) and demonstrate that under this mechanism the device durability and the emission power efficiency are enhanced [5],[6]. In spite of this, the leakage current level is still quite large, even under AC operation, so the emission efficiency improvement is not significant [5]. The achievement of efficient Si-nc based sources appears to be related to the reduction of the current flow and the optimization of the carrier injection into the Si-nc. In this framework, the addition of a thin silicon nitride (Si₃N₄) buffer in a MNOS (metal nitride oxide semiconductor) scheme is presented as a very promising solution [7]-[9]. The presence of the nitride layer reduces the effective field in the silicon-rich oxide, giving rise to a reduction of the current flow that, in our case, is strongly field dependent (Fowler Nordheim, FN, injection). The additional barrier next to the top electrode hinders the carrier injection from the gate (that is not involved in the field effect mechanism) without significantly affecting the injection from the Si substrate. Moreover, if the nitride layer is thin enough, thanks to its relatively high dielectric

constant the overall thickness increase has not a remarkable influence on operation voltages. The device durability is also improved as the buffer layer cools down the carriers from the oxide reducing the damage at the top electrode interface.

In this work, we report an increase of the emission power efficiency of Si-nc based field-effect light emitting devices through the addition of a ~15-nm Si₃N₄ control layer within a MOS (metal oxide semiconductor) stack. MNOS and MOS structures were prepared with a ~55-nm silicon rich oxide (SRO) fabricated by PECVD (plasma enhanced chemical vapour deposition). The power efficiency increases up to ~1 % that represents an improvement of, at least, one order of magnitude with regard to similarly processed MOS structures. The device degradation is reduced down to 50%.

II. EXPERIMENTAL

The MNOS structure consists of a pure nitride ~15 nm-thick control layer deposited onto a ~55-nm Si-nc/SiO₂ layer with approximately ~20 % of Si excess. The MOS structure was fabricated with similar oxide thickness (~55 nm) and Si excess. The SRSO (Silicon-Rich Silicon Oxide) layers were fabricated on a p-type Si-substrate (0.1-1.4 Ω ·cm) by PECVD (plasma-enhanced chemical-vapor-deposition) and submitted to high temperature annealing. More details about the SRSO deposition can be found in Ref. [5]. In MNOS structures, the silicon nitride is fabricated by LPCVD (low-pressure CVD) at 800°C and 26.66 Pa with a NH3 (ammonia) and SiH2Cl2 (dichlorosilane) mixture. In both kinds of samples, N-doped semitransparent polycrystalline silicon (poly-Si) 350-nm-thick was deposited as a top-electrode. Its transparency was checked by transmittance spectroscopy of poly-Si layers deposited onto fused silica substrates. The field-effect luminescence is achieved by biasing with bipolar square waves from an Agilent 8114A Pulse Generator. Time-resolved EL measurements were performed by a photon-counting set-up basically composed of a Hamamatsu H7422-50 photomultiplier and the EL spectra were measured by a Princeton Instruments 100B-LN CCD camera and an Oriel MS257 1/4 m Monochromator. Quasi-static I-V (currentvoltage) characteristics were measured by an Agilent B1500 semiconductor device analyzer.



Fig. 1. Schematic cross-section of MNOS (a) and MOS (b) devices. (c) Representation of some basic principles of the MNOS structures. (i) The presence of the silicon nitride reduces the electric field in the oxide layer, leading to an increase of the oxide barrier height. (ii) and (iii) show the probability of electron injection from the gate and the substrate, respectively, that are proportional to the inverse of the lighted areas.

III. RESULTS AND DISCUSSION

Figs. 1(a) and 1(b) show schematic cross sections of the two different devices fabricated (the layers are not scaled): first, the MNOS structure where a ~15-nm nitride buffer is clearly seen between the active layer and the top electrode. The figure on the right shows a typical MOS structure with a similarly prepared SRO layer. Fig. 1(c) represents the basic principles of operation of Si-nc based MNOS devices. The silicon nitride reduces the electric field across the oxide layer, which translates into a barrier height increase and, consequently to a decrease in the current density (i). The diagrams (ii) and (iii) show the probabilities of electron injection from the gate and the substrate respectively that are related to the inverse of the lighted areas. Whereas the nitride barrier strongly hinders the carrier injection from the gate, (ii), its influence on the responsible of substrate injection, the field-effect luminescence, is negligible (iii). Fig. 2(a) shows the field effect luminescence of MOS and MNOS devices under application of 26 V square wave voltages. The spectra were normalized to their own maxima in order to easily compare the peak positions and spectral shapes. The field-effect mechanism entails the sequential injection of electrons and holes from the substrate, in a process assisted by the Coulomb field attraction from the previously stored carriers. Note that during the second carrier injection a sizeable percentage of the trapped charge tunnels back to the substrate. Therefore the achievement of an efficient emission depends on both the retention time of the first carrier injected and the tunneling time of the incoming second carrier. With respect to Fig. 2(a), it should be noted that the emission range is in accordance with the typical emission observed from Si-nc/SiO₂ systems [2]. In spite of this, the spectral shapes appear to be narrower than typically reported values under optical excitation [10]. This is attributed to interference phenomena from the poly-Si,

as revealed by transmittance measurements (not shown). The small peak shift observed in Fig. 2(a) is attributed to the difference refractive index contrasts at the poly-Si interface that modifies the interference pattern. In both cases the onset of the emission is placed at about 20 V. As expected, thanks to its higher dielectric constant and the thinness of added layer, the silicon nitride does not have a noticeable effect on the operation voltage, which represents one of the most important features of the nitride-oxide stacks. It should be noted that the emission intensity measured from the MNOS structure is approximately one order of magnitude higher than that in MOS devices. Therefore, it becomes clear that the addition of the nitride layer not only reduces the power consumption of the device (as discussed later on), but also leads to a better profit of the injected charge. Fig. 2(b) shows an example of the time-resolved field effect luminescence of Si-nc based devices. For sake of clarity, in this case, the figure only depicts the results from the MOS structure (similar behavior is observed in MNOS devices). Note that most of the emission is triggered by the rise edge of the driving signal i.e. when the electrons are injected from the substrate into hole-charged nanocrystals. In contrast, the contribution to the emission when the voltage switches from positive to negative values (hole-triggered or fall-edge emission) is very weak [not



Fig. 2. (a) Normalized EL spectra of MNOS and MOS structures. (b) Time resolved EL of the MOS structure. (c) Integrated EL as a function of the frequency of the driving signal.



Fig. 3. (a) Comparison of the current-voltage curves of the different structures. (b) Degradation of the EL intensity with the time of operation.

resolved in Fig. 2(b)], which is attributed to the shorter retention times of the previously stored electrons. The EL transients are characterized, in both structures, by typical rise times of about 0.2 µs. The radiative recombination is of about 10 μ s, in good agreement with previous results [5]. Fig. 2(c) depicts the integrated EL of the MNOS structure as a function of the driving frequency (similar behavior is observed in MOS devices). The plot reveals that as the integration time is held constant, the EL initially increases due to the increasing number of integrated cycles [2]. The EL intensity peaks at ~100 kHz, a frequency that is determined by the radiative decays of the Si-nc (driving periods of $\sim 10 \ \mu s$). Therefore, to obtain the maximum EL intensity achievable for MOS and MNOS devices we polarized at the maximum frequency. These measurements resulted in typical output powers of ~ 1 nW and ~10 nW, for MOS and MNOS devices, respectively.

Fig. 3(a) represents the comparison of the J-V (currentvoltage) curves of both kinds of devices. Due to the presence of the Si₃N₄, a strong reduction of the current is observed in MNOS devices above 20 V. These low current levels imply a reduction of the device power consumption, which translates into an enhancement of the emission power efficiency of one order of magnitude (~1 % as opposed to ~0.1% in MOS devices). Fig. 3(b) depicts the results of the accelerating aging studies performed on MNOS and MOS structures. The degradation of the emission is reduced down to 50 % by the presence of the control layer. The damage of the structure is reduced first by the decrease of the current level and on the other hand, by the low electric field in the silicon nitride (higher dielectric constant) that contributes to cool down the carriers that reach the top electrode.

IV. CONCLUSIONS

Si-nanocrystal based field-effect light-emitting devices fabricated with a MNOS configuration exhibit a power efficiency of ~1 %, which represents an enhancement of one order of magnitude with regard to similarly prepared MOS structures. The silicon nitride reduces the power consumption of the device and, at the same time, induces a better profit of the injected charge. Furthermore, due to the thinness of the silicon nitride, the overall increase of the device thickness does not have an observable impact on the operation voltages. It has been also demonstrated that the silicon nitride increases the endurance of the Si-nc devices, reducing the degradation of the emission down to ~50%. In the light of our results, it becomes clear that the MNOS structure represents a very promising solution in order to achieve efficient and reliable Sinc based devices.

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REFERENCES

- Josep Carreras, J. Arbiol, B. Garrido, C. Bonafos, and J. Monserrat, "Direct modulation of electroluminescence from silicon nanocrystals beyond radiative recombination rates," *Appl. Phys. Lett.* 92, 091103 (2008).
- [2] R.J. Walters, H. Atwater, and G. Bourianoff, "Field-effect electroluminescence in silicon nanocrystals," *Nature Materials* 4, 143-146 (2005).
- [3] M. Porti, M. Avidano, M. Nafría, X. Aymerich, J. Carreras, O. Jambois, and B. Garrido, "Nanoscale electrical characterization of Si-nc based memory metal-oxide semiconductor devices," *J. Appl. Phys.* 101, 064509 (2007).
- [4] A. Irrera, F. Iacona, G. Franzo, S. Boninelli, D. Pacifici, M. Miritello, C. Spinella, D. Sanfilippo, G. Di Stefano, P.G. Fallica, and F. Priolo,"Correlation between electroluminescence and structural properties of Si nanostructures," *Opt. Mat.* 27, 1031 (2005).
- [5] M. Perálvarez, C.García, M.López, B.Garrido, J.Barreto, C.Domínguez, and J.A.Rodríguez,"Field-effect luminescence from Si nanocrystals obtained by plasma-enhanced chemical vapor deposition," *Appl.Phys.Lett.* 89, 051112 (2006).
- [6] R. J. Walters, J. Carreras, T. Feng, L. D. Bell, and H. A. Atwater, "Silicon Nanocrystal Field-Effect Light-Emitting Devices," *IEEE J. Sel. Top. Quantum Electron.* 12, 1647 2006.
- [7] P. Gentil, "Instabilities in Silicon Devices" Silicon Passivation and Related Instabilities, edited by G. Barbouttin and A. Vapaille (Elsevier Science Publishers B.V., Amsterdam, 1986) Vol. 2, p. 659.
- [8] A. Sudhakar Reddy, P.R.S. Rao, K.N. Bhat and Nandita Das Gupta,"Lower Leakage and Higher Breakdown Voltage for MNOS (Metal-Sin-SiO2-Si) Structure," *Proc. SPIE* 3975, 357 (2000).
- [9] M. Perálvarez, Josep Carreras, J. Barreto, A. Morales, C. Domínguez, and B. Garrido, "Efficiency and reliability enhancement of silicon nanocrystal field-effect luminescence from nitride-oxide gate stacks," *Appl.Phys.Lett.* 92, 241104 (2008).
- [10] F. Iacona, G. Franzò, and C. Spinella," Correlation between luminescence and structural properties of Si nanocrystals," J. Appl. Phys. 87, 1295 (2000)