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Dielectric matrix influence on the photoluminescence properties of silicon nanocrystals

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[1]***Abstract* - Photoluminescence properties of silicon nanocrystals embedded in five different oxide matrices are analyzed. Samples are silicon rich oxide and oxynitride produced by PECVD and ion implantation and crystalline and amorphous aluminum oxide implanted with silicon.**

I. INTRODUCTION

Silicon nanocrystals (Si-nc) formed in silicon based dielectrics are an extremely interesting material for optoelectronics. Despite the indirect band gap nature of silicon, the confinement of excitons in a quantum dot has demonstrated a significant enhancement of the luminescence efficiency and the possibility to obtain optical amplification [1-4]. Due to the small size, the surface to volume ratio of Si-nc is very large and their luminescence emission is highly influenced by the surrounding medium. Silicon oxide is widely used as matrix for luminescent Si-nc. Despite the large amount of results on the luminescence of silicon nanocrystals the role of the matrix is still unclear: for example, little is known on the role of nitrogen incorporated into the matrix during the annealing or the PECVD deposition process [5]. Aluminum oxide is also considered an interesting dielectrics for C-MOS technology [6] so it can be interesting to look at the formation of Si-nc in this dielectrics.

In this paper we have performed a comparative photoluminescence analysis of Si-nc embedded in five different sets of samples (Table 1). Three of them are silicon rich oxides (SRO) produced by plasma enhanced chemical vapor deposition (PECVD) and the others are silicon rich aluminum oxides produced by ion implantation. Our purpose is to clarify similarities and differences of the nanocrystals behavior in different matrices.

The first set is composed of PECVD silicon rich oxynitrides (SRON) samples deposited with N_2O as precursor gas, this technique naturally incorporates nitrogen into the matrix, a percentage of 15–17% in the samples under evaluation. The second set is composed of silicon rich oxide (SRO) samples obtained by PECVD using O_2 as precursor gas, this technique is capable of growing nitrogen free samples. The third group is composed of Si implanted silicon oxides to form SRO. While the fourth and fifth sets are crystalline and amorphous Al2O3 implanted with Si ions to form silicon rich aluminum oxide (SRA). The samples sets are indicated respectively with S1, S2, S3, S4 and S5. Si-nc formation is induced by thermal treatments under different conditions as detailed in the following. CW photoluminescence measurements were carried out with the 488 nm line of an Ar laser. Luminescence emission was collected with a double grating monochromator and a photomultiplier tube in a photon counting configuration. Time resolved photoluminescence measurements (TRP) were performed with the 355 nm line of a NdYAG laser (pulse duration 6 ns). Luminescence emission was collected with a monochromator and a streak camera with ps resolution.

TABLE I
Samples characteristics

Set	Material	Process	Excess Silicon
S1	SRON[1]	PECVD + annealing	16-20% (atoms)
S2	SRO[2]	PECVD + annealing	12% (atoms)
S3	SRO[2]	Ion Implant. + annealing	dose $1x10^{17}$ cm^{-2}
S4	Crystalline α-Al_2O_3	Ion Implant. + annealing	dose $1x10^{17}$ cm^{-2}
S5	amorphous-Al_2O_3	Ion Implant. + annealing	dose $5x10^{16}$ cm^{-2}

[1] Silicon Rich Oxynitride
[2] Silicon Rich Oxide

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II. DISCUSSION

Samples S1 and S2 have been annealed in nitrogen at various temperatures for 1 h. Photoluminescence results for samples S1 and S2 are summarized in Figure 1. We have observed for both series a wide emission band, centered at about 800 – 900 nm, red shifting with the increasing of annealing temperature. Luminescence emission is negligible in the as deposited samples.

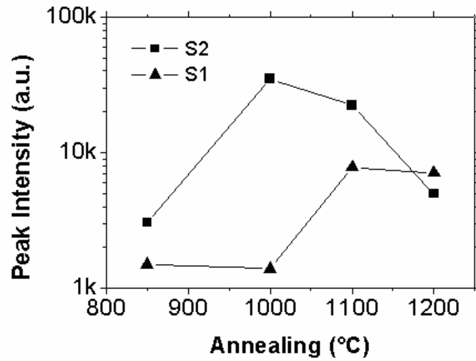

Fig. 1. Comparison between peak intensities vs. annealing temperature for samples of the S1 and S2 series.

Series S1 samples show low luminescence efficiency at annealing temperatures of 850°C and 1000°C that increases by a factor of 8 at 1100°C and 1200°C. The difference between low and high luminescence efficiency could correspond to the temperature at which silicon clusters start to crystallize into Si-nc [7,8] and the dangling bonds, responsible for the presence of nonradiative decay channels, are saturated by the Si-nc reconstruction. The SRO samples S2 show a similar trend shifted towards lower temperatures. For S2 samples at high annealing temperatures the emission intensity decreases once more due to the increase of the Si-nc sizes and hence the reduction of the radiative efficiency. From the comparison between S1 and S2 samples, a critical role played by nitrogen is pointed out. In particular, the presence of nitrogen reduces the emission intensity, likely by means of a general slowing down of the nanocluster crystallization process.

On the other hand, the role of the heavily damaged dielectric matrix, typically induced by high dose implantation processes, is clearly evidenced in the S3 samples series. Their photoluminescence spectra as function of the annealing temperature are reported in Figure 2a. We observe a marked difference in emitted intensity between samples annealed for 1 hour and sample annealed for two hour at 1050°C. It is clear that with the increase of the annealing time a better passivation of nanocrystals surface is reached [9] with the consequent reduction of nonradiative decay channels. This picture is confirmed by the luminescence decay lifetime data presented in Figure 2b. Lifetimes were estimated by fitting the time resolved luminescence with a stretched exponential function [10]. The independence of the lifetime data on the emission wavelength for the short annealed samples (Figure 2b) and the strong dependence (expected for the radiative lifetime [11]) for the long annealed samples demonstrates that one hour annealing is not enough to recover damages introduced into the matrix during the high dose implantation process and hence the emission is dominated by non-radiative energy independent processes.

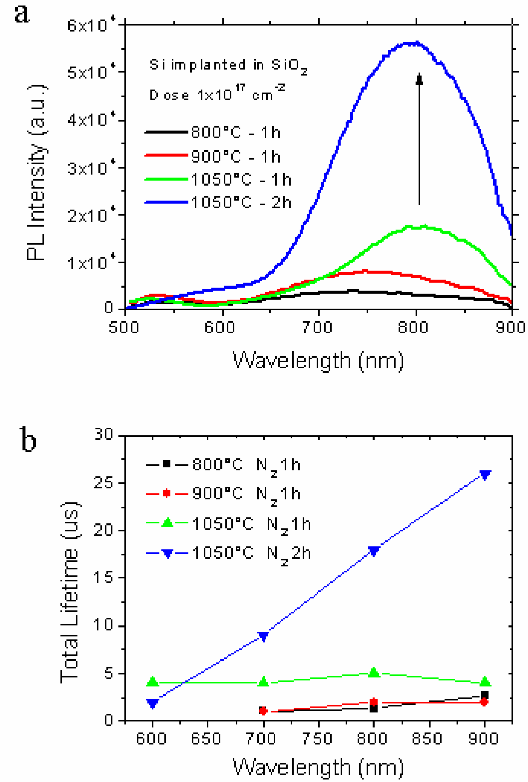

Fig. 2. a) Photoluminescence spectra of Si implanted SiO_2 samples. b) corresponding lifetimes.

A further critical influence of the dielectrics on the optical properties is even more evident when Si-nc in crystalline alumina are studied with respect to the amorphous one. Photoluminescence measurements on Si implanted crystalline Al_2O_3 (S4) samples show a wide photoluminescence band centered at about 750 nm. It does not shift with the annealing temperature and implantation dose and it is also observed in reference samples non-implanted or implanted with Ar ions only. This behavior shows that the origin of the luminescence emission is associated with implantation defects or impurities. In particular, the best suited impurity with an emitting band similar to that observed is Ti^{3+} [12-14]. Si-nc formation in this case is not enough to have emission from them due to a shunting action of the defects providing non-radiative recombination channels. Something very different happens when Si-nc are formed in amorphous Al_2O_3 (samples S5). Figure 3a shows the luminescence spectra of these samples where a wide band extending from 500 nm to 900 nm is observed. The intensity of this band increases by increasing the annealing temperature. In figure 3b it is reported the wavelength shift with the annealing temperature up to 900°C.

We assume the luminescence band to be the superposition of two bands, one due to radiative matrix defect states centered at 550 nm and another due to Si-nc whose emission is red shifting with the annealing temperature.

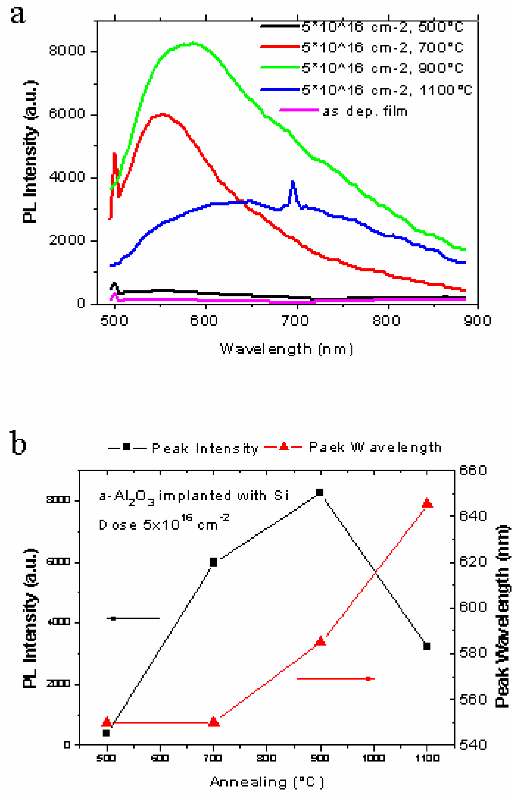

Fig. 3. a) Photoluminescence spectra of silicon Si implanted amorphous Al_2O_3 samples. b) Corresponding intensity and peak wavelength as function of the annealing temperature.

III. CONCLUSION

Many questions are still open regarding the influence of the dielectrics matrix on the luminescence properties of silicon nanocrystals. By comparing Si-nc formed in SRO or SRNO we showed that incorporation of nitrogen can limit the Si-nc density and reduces cluster crystallization or matrix reorganization. Matrix reorganization can occur especially in damaged ones, thus impacting on the Si-nc luminescent characteristics. In this case, longer annealing time allows the dielectrics to rearrange which reduces the non-radiative recombination channels and increases the emission from the Si-nc. The role of the dielectrics is even more evident when crystalline or amorphous alumina are used. We have observed luminescence emission due to silicon nanocrystals in amorphous aluminum oxide samples but not in crystalline aluminum oxide ones. No passivation of implantation defects occurs at the typical annealing temperature used to form Si-nc in crystalline alumina. On the contrary implantation defects anneal out in amorphous alumina and the Si-nc related emission is revealed at high temperatures.

ACKNOWLEDGMENTS

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