

Nitrogen Influence on the Photoluminescence Properties of Silicon Nanocrystals

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ABSTRACT

We have performed photoluminescence analysis of silicon rich oxide (SRO) and silicon rich oxynitride (SRON) samples deposited by plasma enhanced chemical vapor deposition (PECVD) and thermally annealed to cause the formation of silicon nanocrystals (Si-nc). Our purpose was to investigate the influence of nitrogen embedded into the oxide matrix on the photoluminescence properties of Si-nc. We found a large incorporation of silicon and a decrease of its diffusivity when the oxide is nitrogen rich. As a consequence the rate of crystallization for Si aggregates is slowed down when nitrogen is present in the oxide matrix.

INTRODUCTION

Silicon nanocrystals (Si-nc) are an extremely interesting material for their photonic properties. Despite the indirect gap nature of silicon, Si-nc has demonstrated a significant enhancement of the luminescence efficiency thanks to the quantum confinement effect [1-3]. Many different techniques can be used to produce Si-nc like sputtering [4, 5], ion implantation [6, 7] and plasma enhanced chemical vapor deposition (PECVD) [8, 9]. Among them, CVD techniques seem to be the best suited to develop Si-nc embedded in a homogeneous matrix. Due to the reduced dimensionality, luminescence emission from Si-nc is influenced by their interface with the surrounding matrix and by the composition of the embedding matrix. Radiative and non-radiative interfacial states are often claimed to explain Si-nc photoluminescence properties [10-12]. The matrix composition determines the nucleation and crystallization dynamics as well as the characteristics of the electronic interfacial states. Si-nc are commonly produced by phase separation during a high temperature annealing of a silicon rich oxide (SRO) film. Nitrogen (N) is often present in the SRO as an impurity with variable concentration. In fact, quite commonly, annealing processes are carried out in N and this impacts the Si-nc properties because of the N in-diffusion during the high temperature annealing. Furthermore N can be introduced into the dielectric matrix during the PECVD deposition process if N₂O is used as precursor gas [13]. At present, it is not clear the role of N on the Si-nc structural and luminescence properties [14-17].

This paper is aimed at shining more light on this issue. To this purpose, we report a photoluminescence characterization of two set of samples deposited by PECVD. One set is composed of silicon rich oxide samples (SRO) deposited in nitrogen free ambient and the other of silicon rich oxynitride samples (SRON), where nitrogen is incorporated during the deposition process. In this way, we want to evidence the influence of nitrogen on the luminescence properties of Si-nc embedded in an oxide matrix.

EXPERIMENTAL

Si rich oxides (SiO_x) and Si rich oxynitride (SiO_xN_y) were produced by PECVD using SiH_4 and two different oxidizing gas precursors: O_2 and N_2O . While SiO_xN_y was obtained with a conventional PECVD process, for SiO_x an inductively coupled (IC) PECVD process was used. Samples thickness was about 250 and 300 nm for SiO_xN_y and SiO_x , respectively. Samples were diced in pieces and a sample for each series was covered with a poly-Si capping layer of about 50 nm. Annealing for 1 h in nitrogen atmosphere was performed at different temperatures. The capping layer has the purpose of preventing the diffusion of oxygen and nitrogen during the annealing process. It was then selectively removed by wet etch in order to perform the photoluminescence analysis. N in-diffusion is observed in uncapped samples [13]. SiO_xN_y silicon content was estimated by refractive index measurements and effective medium approximation. It was found a value of 48 % (as percentage of the total atoms) by a three phases Bruggemann model ($\text{SiO}_x + \text{Si}_3\text{N}_4 + \text{Vacuum}$). In the SiO_x samples the silicon percentage is 43%. This value was estimated by the comparison of the measured refractive index with literature data [18]. Nitrogen concentration was measured by secondary ion mass spectrometry (SIMS) [13]. SiO_xN_y samples have a nitrogen concentration of about 15-17% rather independent of both depth and annealing temperature. The as deposited SiO_x samples have a negligible N content. N is incorporated into the samples during the annealing process. Its final concentration depends on the annealing temperature, the higher the temperature, the higher the concentration. However, the maximum N concentration levels are lower than those of the SiO_xN_y samples and are in the range of 2-3%. The annealed samples of both the series show a surface oxide layer, whose thickness is about 80 nm in the SiO_x and roughly 20 nm in the SiO_xN_y samples.

Photoluminescence measurements were performed with the 488 nm line of an Argon laser with 50 mW ($\sim 20 \text{ W/cm}^2$). Emitted light is collected by a double grating monochromator and a photomultiplier tube. Measured spectra are corrected by the instrument response.

DISCUSSION

Photoluminescence spectra from the SiO_xN_y and SiO_x samples are presented in Figure 1. We observe for both series a wide emitting band, centered in the region around 800 – 900 nm, red shifting with the annealing temperature.

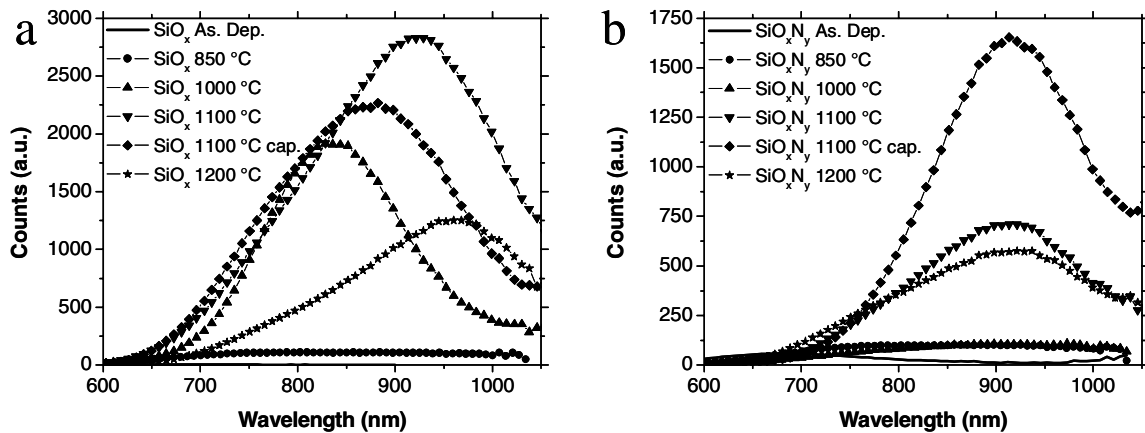


Figure 1: Photoluminescence spectra of a) SiO_x samples and b) SiO_xN_y samples.

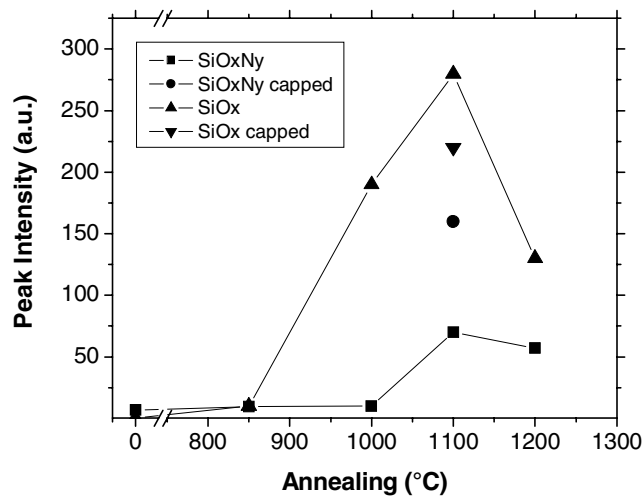


Figure 2: Photoluminescence peak intensity as a function of the annealing temperature.

Luminescence emission is extremely low in the as deposited samples of both series. SiO_xN_y samples (Figure 2) show low luminescence efficiency at annealing temperatures of 850°C and 1000°C increasing at 1100°C and 1200°C . SiO_x samples (Figure 2) have high luminescence efficiency at 1000°C and 1100°C whereas efficiency is low at 850°C and 1200°C . A significant emission intensity increase is observed at 1000°C for SiO_x and at 1100°C for SiO_xN_y . We consider these as the temperatures at which Si clusters crystallize and reorganize their structure and surface so that nonradiative decay channels are removed [9]. The decrease of the emission intensity for the SiO_x sample at 1200°C can be attributed to the reduction of Si-nc density and to the increase of their size due to the growth of the Si-nc (Ostwald ripening effect) or to the out-diffusion of SiO which is known to occur at these high temperatures. This process causes the dissolution of small Si-nc. A weaker luminescence intensity decreases is observed in the SiO_xN_y samples probably because of the reduced mobility of Si in nitrogen rich oxides [14].

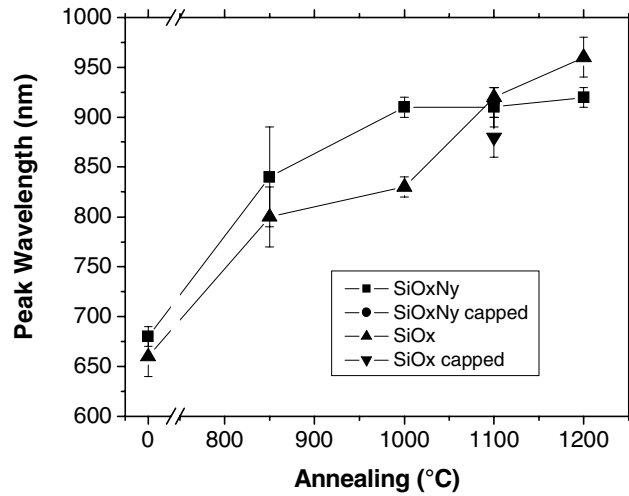


Figure 3: Photoluminescence peak wavelength as a function of the annealing temperature.

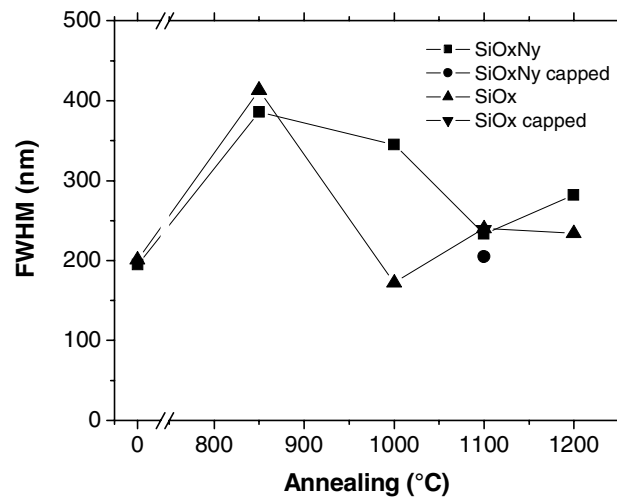


Figure 4: Full width at half maximum (FWHM) as a function of the annealing temperature.

In order to further discuss the luminescence results it is useful to look at the peak wavelengths shown in Fig. 3. The peak wavelengths of the SiO_x sample increase with the increase of the annealing temperature shifting from 600 nm to 960 nm. This behavior is connected with the formation of Si-nc and with the increase of Si-nc size. On the contrary, the peak wavelengths of the samples SiO_xN_y increases with the increase of the annealing temperature up to a value of about 900 nm where it fixes for further temperature increase in the range 1000 °C to 1200 °C. This effect was already observed in high Si concentration oxynitride materials [9] and was attributed to energy migration from small to large Si-nc favored by their high density. While luminescence emission of the SiO_xN_y sample is the result of the emission of a connected population of different size Si-nc, the luminescence from SiO_x sample seems to be

the result of the emission from well insulated large size Si-nc. In Figure 4 it is evident that the formation of Si-nc is characterized by a reduction in the FWHM of the emission.

Literature data [8] for SiO_xN_y show that the passivation / crystallization threshold is fixed at 1200 °C in the case of 42% Si content. Our data, compared with that reported in literature, give clear evidence that the passivation efficiency and the crystallization rate of Si aggregates are slowed down by the presence of nitrogen in the oxide matrix.

CONCLUSIONS

The presented data evidence a strong influence of the nitrogen content on the luminescence properties of silicon nanocrystals embedded in an oxide matrix. The matrix rich in nitrogen shows a larger silicon solubility but a lower silicon diffusivity than a nitrogen poor dielectrics. These conclusions are based on a photoluminescence study where photoluminescence intensities and FWHM data demonstrate the reduction of the rate of crystallization for Si aggregates embedded in a nitrogen rich matrix. The transition between amorphous and crystalline Si aggregates seems to be characterized by a reduction in the FWHM values.

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REFERENCES

1. S. Ossicini, L. Pavesi, F. Priolo, Light Emitting Silicon for Microphotonics, Springer Tracts in Modern Physics.
2. L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzò, F. Priolo, Nature 408, 440 (2000).
3. L. Pavesi, J. Phys.: Condens. Matter 15, R1169 (2003).
4. S. Hayashi, T. Nagareda, Y. Kanzawa and K. Yamamoto, Jpn. J. Appl. Phys., Part 1 32, 3840 (1993).
5. Y. Kanzawa, T. Kageyama, S. Takeoka, M. Fujii, S. Hayashi and K. Yamamoto, Solid State Commun. 102, 533 (1997).
6. T. Shimizu-Iwayama, K. Fujita, S. Nakao, K. Saitoh, T. Fujita, N. Itoh, J. Appl. Phys. 75, 7779 (1994).
7. Jane G. Zhu, C.W. White, J. D. Budai, S. P. Withrow, and Y. Chen, J. Appl. Phys. 78, 4386 (1995).
8. F. Iacona, G. Franzò, and C. Spinella, J. Appl. Phys. 87, 1295 (2000).
9. F. Iacona, C. Bongiorno, C. Spinella, S. Boninelli and F. Priolo, J. Appl. Phys. 95, 3723 (2004).
10. M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, C. Delerue, Phys. Rev. Lett. 82, 197 (1999).

11. M. Luppi and S. Ossicini, *Phys. Rev. B* 71, 035340 (2005).
12. N. Daldosso, M. Luppi, S. Ossicini, E. Degoli, R. Magri, G. Dalba, P. Fornasini, R. Grisenti, F. Rocca, L. Pavesi, S. Boninelli, F. Priolo, C. Spinella and F. Iacona., *Phys. Rev. B* 68, 085327 (2003).
13. V. Mulloni, P. Bellutti, L. Vanzetti, *Surface Science* 585, 137 (2005).
14. T. Ehara and S. Machida., *Thin Solid Films* 346, 275 (1999).
15. E. P. Gusev, H.-C. Lu, E. L. Garfunkel, T. Gustafsson, M. L. Green, *IBM J. Res. Develop.* 43, 265 (1999).
16. G. Santana, B. M. Monroy, A. Ortiz, L. Huerta, J. C. Alonso, J. Fandiño, J. Aguilar-Hernández, E. Hoyos, F. Cruz-Gandarilla, G. Contreras-Puentes, *Appl. Phys. Lett.* 88, 041916 (2006).
17. S. Hasegawa, S. Sakamori, M. Futatsudera, T. Inokuma, and Y. Kurata, *J. Appl. Phys.* 89, 2598 (2001).
18. S. H. Wemple, *Phys. Rev. B*, 7, 3767 (1973).