Silicon Nanocrystal Nucleation as a Function of the Annealing Temperature in SiO_x Films

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ABSTRACT

Si nanocrystals (Si-nc) embedded in amorphous silica matrix have been obtained by thermal annealing of substoichiometric SiO_x films, deposited by PECVD (plasma enhanced chemical vapour deposition) technique with different amount of Si concentrations (42 and 46 at.%). Both nucleation and evolution of Si-nc together with the changes of the amorphous matrix have been studied as a function of the annealing temperature. The comparison of x-ray absorption measurements in Total Electron Yield (TEY) mode at the Si *k*-edge with photoluminescence (PL), FTIR and Raman spectra, allowed clarifying the processes of Si-nc formation and structural evolution as a function of the annealing temperature and Si content.

INTRODUCTION

The research of Si-based light emitting systems has increased due to the high luminescence efficiency, stability and robustness of silicon nanocrystals (Si-nc) embedded in amorphous silica (a-SiO_2) [1,2,3,4,5], and more recently to experimental evidences of optical gain [6,7]. However, because of the various techniques and experimental conditions used to prepare Si-nc, the interpretation of the light emission mechanism given by different authors is often controversial. It is fundamental a comprehensive characterization of the Si-nc and the embedding matrix about the amount of Si atoms segregated in the Si-nc, the evaluation of size and distribution of the clusters, and the chemical composition and structure of the host matrix.

In this work, we report on x-ray absorption measurements performed on a set of plasma enhanced chemical vapour deposition (PECVD) grown Si-nc samples and on FTIR, Raman, and photoluminescence (PL) measurements, whose comparison yields to a better comprehension of the embedding amorphous matrix and the evolution of Si-nc with the annealing temperature.

EXPERIMENTAL

Silicon nanocrystals have been produced by PECVD of substoichiometric silicon oxide (SiO_x) followed by high-temperature annealing in order to induce the formation of Si-nc dispersed in an amorphous matrix [5,8]. We have investigated the evolution of different sets of samples characterised by different Si content (42 and 46 at.%) as a function of the annealing temperature (from as deposited to high annealing temperatures).

X-ray absorption spectra were measured at Super-ACO (LURE) on the SA32 soft x-ray beamline by detecting the total yield of electrons escaping from the sample (TEY mode) at the Si *k*-edge. By scanning the x-ray energy it is possible to probe the different Si local environments characterised by different Si-bonded species: for example, Si atoms in the nanocrystals (whose *k*-edge is at 1839 eV) and Si atoms in the amorphous SiO_2, whose absorption maximum is at about 1847 eV. The sampling depth of TEY-XAS technique at Si *k*-edge energy is about 100 nm for both c-Si and SiO_2 [9], i.e. comparable to the thickness of samples but not too long to detect the contribution of the Si substrate.

Fourier Transform Infrared (FT-IR) spectra were recorded at room temperature in the spectral range between 4000 and 500 cm^{-1} with a Jasco (model 660 plus) operated in transmission mode, using a Si wafer as reference.

Raman scattering measurements were carried out at room temperature by means of a micro-probe. The spectra were excited in true backscattering geometry by the 488.0 nm line of an Ar^+ ion laser, while the scattered radiation was filtered by a double-monochromator and detected in photon counting mode. For all of measurements the instrumental band-pass was 2.5 cm^{-1}, the spectral resolution being 0.33 cm^{-1}.

PL measurements were carried out by using an Ar^+ laser (488 nm emission line) with 50 mW over a circular area of about 1 mm in diameter and a visible spectrometer with a CCD detector.

RESULTS AND DISCUSSION

In a recent work [10] we have shown how the intensity of the x-ray absorption coefficient of Si in Si-nc increases with the Si content of the samples, confirming that excess Si atoms form Si-nc after the thermal annealing at 1250 °C, although not all Si atoms. In fact, a fraction of excess Si remains in the amorphous matrix bonding with N atoms, which have been incorporated in the substoichiometric film during the PECVD procedure [10]. This reveals that the amorphous matrix cannot be simply considered as amorphous SiO_2 but rather as Si oxynitride amorphous phase, characterised by low nitrogen content and weakly dependent on the total amount of silicon. In particular, we have shown that at low Si content (35, 37 and 39 at.%) the nitrogen can be simply considered as substitutional of oxygen in the formation of tetrahedra participating to a silica-like network $SiO_{2-x}N_x$. At high Si content (42 and 46 at.%), the amorphous matrix assumes a more complex structure SiO_yN_x. It is worth noting here that the presence of amorphous Si oxynitride plays a fundamental role both in modifying the optical properties and in lowering structural strains with respect to Si oxide [11,12], as also confirmed by refractive index measurements on the same samples [13]. Moreover, it is known that the presence of nitrogen could influence the precipitation of Si-nc in SiO_yN_x thin films [14].

To investigate the formation and evolution of Si-nc we have planned a series of measurements as a function of the annealing temperature on samples characterised by different Si content.

<u>TEY measurements</u>

TEY absorption spectra (figure 1) show two main features at about 1841 eV, due to Si-Si absorption, and at about 1847 eV, due to *a*-SiO_2, characterized by a sharp peak (white-line). These two features are present for all the annealing temperatures, although they are quite clear and separated at high annealing temperatures. Besides these absorption features, the as-deposited sample shows two broad absorption structures at about 1843.5 and 1844.6 eV. These structures decrease in intensity (without showing any significant energy shift) with increasing the annealing temperature. On the basis of TEY measurements of reference samples, we can assign these structures to Si nitride species: in fact, SiN_x samples show a broad absorption peak at about 1844-1845 eV, while reference samples of Si_3N_4 and Si_2N_2O present a peak at about 1844 and 1845 eV, respectively.

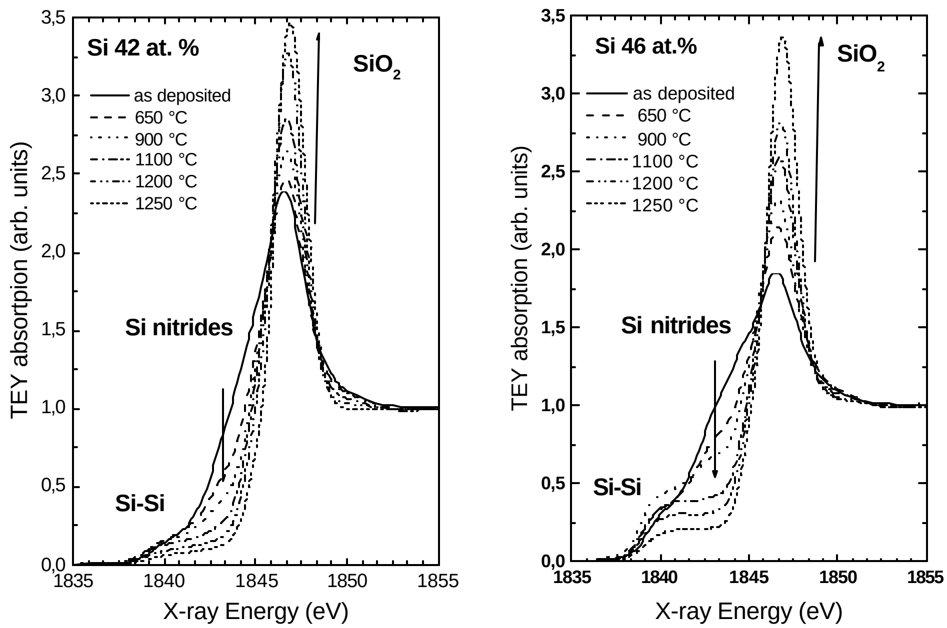
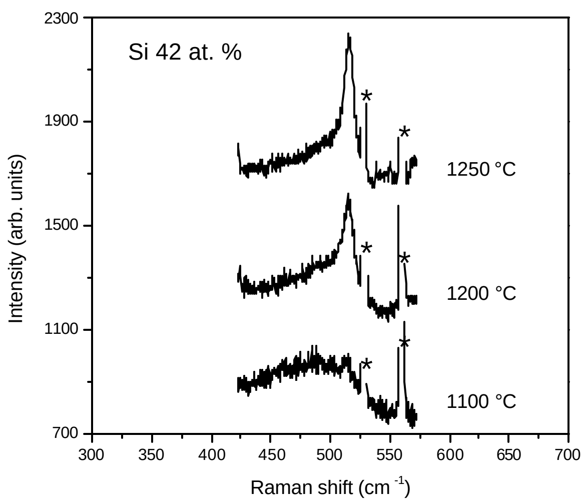


Figure 1. TEY absorption spectra at the Si *k*-edge of SiO_x samples containing 42 and 46 at.% of Si as a function of the annealing temperature. Arrows indicate the trends with increasing annealing temperature.

The evolution with the temperature of nitrogen-related features is also pointed out by the analysis of the derivative plots, which shows a negligible contribution of absorption related to Si oxynitrides for annealing temperatures higher than 1000 °C. By comparing the evolution of these absorption features in the 42 and 46 at. % samples, it is clear that for higher Si concentration the presence of these compounds is more relevant, but the trend is the same. For annealing temperatures higher than 1000 °C these absorption features disappeared suggesting the complete phase separation between Si-nc and the matrix, which consists in a Si oxynitride amorphous phase as previously shown [10]. It can be also noted that the intensity of the a-SiO_2 absorption peak increases with increasing the annealing temperature. Moreover, small shifts of its maximum energy towards higher values are observed together with more symmetric absorption lineshape. Another relevant fact is the presence of Si-Si absorption feature for samples annealed at low temperatures and also in the as-deposited film. It should be noticed that the absorption contribution at about 1841 eV is related to Si atoms bonded to Si atoms in the basic tetrahedra but without any information about the crystallinity of the Si aggregates. Moreover, TEY spectra performed on reference samples of Si_3N_4 and Si_2N_2O present a small contribution at about 1840 eV. This complicates the interpretation of the TEY analysis, but it can be supposed the presence of Si aggregates also in the as deposited film, which results in Si-Si, Si-N, Si-O bonded phases. The thermal annealing induces a phase separation allowing the formation of Si-nc and Si oxynitride matrix.

FTIR and Raman measurements

FT-IR spectra collected on as-deposited samples (not reported here) show the typical absorption bands of Si-rich a-SiO_x films doped with H and N: a main absorption band at 1060 cm^{-1} due to the Si-O stretching mode, an absorption band at 2250 cm^{-1} due to the Si-H stretching mode and an absorption band at 3380 cm^{-1} due to the N-H stretching mode [15]. FT-IR spectra recorded on films annealed above 900 °C exhibit the typical absorption bands of silica-based glasses at 1076 cm^{-1} (Si-O stretching), but not the Si-H stretching band at ≈2250 cm^{-1} which suggests that H has been completely removed during the annealing process above 800 °C.
FTIR absorption spectra cannot show clear evidence of Si precipitation in silica matrix. The formation of Si-nc within the thermally annealed films can be evidenced by Raman scattering. Raman spectra of Si-rich samples treated above 1000 °C show typical features (spectral intensity, peak position and shape) of Si-nc formed in dielectric matrices, with a pronounced asymmetric peak at ≈ 515-517 cm^{-1} and a linewidth of ≅ 8-10 cm^{-1} [16]. These spectral features on both sets of samples show, at first sight, a common trend vs the annealing temperature.



	Peak (cm^{-1})	FWHM (cm^{-1})	Int. (a.u.)
42 at. %			
1100 °C	515.6	11.5	113
1200 °C	516.2	8.7	326
1250 °C	516.4	9.0	472
46 at. %			
1100 °C	515.0	9.5	522
1200 °C	515.8	8.3	874
1250 °C	515.5	7.9	1210

Table 1

Figure 2. Experimental Raman spectra carried out at room temperature from SiO_x samples (Si content of 42%) treated at three different annealing temperatures. The asterisks (*) label the positions of two plasma lines used as energy standards (560.7 cm^{-1} and 529.5 cm^{-1}). The table summarizes the main data deduced by Raman scattering studies.

The spectral intensity and the peak positions of samples treated at increasing temperature above 1000 °C reveal the progressive formation of Si-nc following a phase separation between Si and SiO_2 matrices. This general trend vs annealing temperature shows some differences in the two sets of samples due to the occurrence of a different structural rearrangement, as it can be inferred from the values of spectral parameters quoted in Table 1.

In the 42 at. % sample annealed at 1100 °C, an amorphous Si component, evidenced by the broad Raman band around 470 cm^{-1}, coexists with the Si-nc, seen as a weak peak at 517 cm^{-1}, (Figure 2). When the annealing temperature raises the density of Si-nc increases with a small increment of their size. This is inferred by the negligible energy-shift of the Si-nc peak in the Raman spectra. It seems that the number of Si-nc increases through the coagulation of finely dispersed Si precipitates (forming the a-Si-like phase observed at 470 cm^{-1} in the Raman spectra), rather than via the enlargement of Si-nc already formed at lower annealing temperatures (800-900 °C). The nano particle mean size estimated by phonon confinement model (mean size: from about 5nm to 5nm+10%) is a bit higher than the size estimated by TEM because this model doesn't account for the possible compressive stress due to glass matrix. A similar behaviour to form Si-nc is also observed in the 46 at. % sample, but for this sample no contribution of the a-Si-like phase is observed in the Raman spectrum of sample treated at 1200 °C because the structural changes occurred at lower temperatures. In any case, in the quantitative interpretation of the Raman spectra the strain effects should be considered, too. A study is under-way to investigate the strain effects in Si-nc and their temperature evolution.

PL measurements

PL measurements have been performed as a function of the annealing temperature. The as-prepared and 500 °C annealed samples show broad and intense PL at about 550-600 nm. With increasing annealing temperature this band weakens. For temperatures higher than 1100 °C, a PL band at about 850-900 nm rises. Small red shift and intensity increases are observed with increasing annealing temperature from 1100 to 1250 °C.

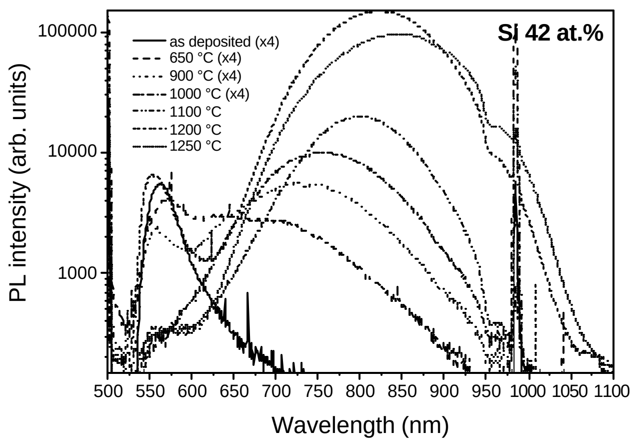


Figure 3. PL spectra of 42 at.% Si SiO_x sample as a function of the annealing temperature.

The comparison between TEY and PL spectra suggests that the broad luminescence band at about 550-600 nm is related to Si nitrides segregated in the amorphous substoichiometric film. As a matter of fact, light emission in the range 550-600 nm can be related to defect-radiative states either in the Si oxide or Si nitride matrix. The measure of absorption features of Si nitrides in TEY spectra supports the presence of Si nitrides in the as-deposited and low temperature annealed samples. As the annealing temperature increases (650-900 °C), the PL emission at 550-600 nm disappears. At higher temperatures, Si nanocrystals form and PL emission occurs at 850-900 nm. In this annealing temperature range, the amorphous matrix modifies reducing dangling bonds and forming a Si oxynitride matrix.

CONCLUSIONS

The analysis of x-ray absorption, FTIR, Raman, and PL data has allowed us to assess that the nucleation of Si-nc produced by PECVD as a function of the annealing temperature is not a simple phase separation between Si-nc and a-SiO_2 but follows a more complicated scheme where nitrogen plays a role that depends on the Si content. We found that amorphous Si aggregates as well as Si-N related species are present in the as deposited film. The annealing induces the nucleation of Si-nc and allows migration of N in the matrix forming a Si oxynitride network, where N is substitutional of O. At high annealing temperature, the formation of oxynitride is observed, whose stoichiometry depends on Si content, rather than a phase separation of Si nitride phases in the Si oxide matrix. The Si content of the embedding matrix is larger than the one which could be deduced by the presence of SiO_2 alone, due to the presence of the oxynitride.

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