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# X-ray absorption study of light emitting silicon nanocrystals

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## Abstract

X-ray absorption spectra obtained by total electron yield (TEY) at the Si absorption K-edge have been measured to have chemical and structural information about Si nanocrystals (Si-nc) produced by plasma-enhanced chemical vapour deposition (PECVD). The TEY technique has been employed to investigate the formation of Si-nc and the modification of the silica matrix as a function of annealing temperature (500–1250°C) and of silicon content in the film (35–46 at%). The amount of silicon present in the Si-nc has been evaluated by TEY. Thanks to Rutherford backscattering spectrometry measurements, the amount of Si atoms bonded to oxygen and to nitrogen, incorporated by PECVD, has been assessed. A compositional model that interprets the experimental findings is presented.

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## 1. Introduction

The possibility of obtaining light from silicon in an efficient, tuneable and technological viable way began with the discovery of visible light emission in porous silicon [1]. Only in recent years the development of a Si-based light source has become less unlikely thanks to the high luminescence efficiency, stability and robustness of silicon nanocrystals (Si-nc) embedded in amorphous silica (a-SiO<sub>2</sub>) [2–6]. Pavesi and co-workers [7] have reported experimental evidences of optical gain in Si-nc formed by ion implantation in SiO<sub>2</sub>, where interface radiative states have been suggested to play a crucial role in the gain mechanism. Many reports on both theoretical and experimental results have shown that the details of the

Si/SiO<sub>2</sub> interface have a relevant impact on the optoelectronic properties of Si-nc. In particular, a joint experimental and theoretical study [8] has recently demonstrated the presence of a strained interface region, about 1 nm thick, which coats the Si-nc and which participates in the light emission process. On the other hand, the investigation of the amorphous matrix embedding the Si-nc is functional to understand and control the optoelectronic properties. In addition, the light emission mechanism and the relation between the observation of positive gain values and the structural information are still under debate. Hence, the knowledge of the chemical composition and structure of both amorphous matrix and Si-nc is an important ingredient to clarify all these aspects.

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. The analysis of X-ray absorption spectra

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allows the assessment of the amount of Si atoms clustered in Si-nc, yielding a compositional characterisation of the embedding amorphous matrix.

Silicon nanocrystals have been produced by PECVD of substoichiometric silicon oxide ( $\text{SiO}_x$ ) followed by an high-temperature annealing that induces the formation of Si-nc dispersed in an amorphous matrix [9,10]. Stoichiometric samples ( $x = 2$ ) contain about 33% of Si atoms, while substoichiometric samples ( $x < 2$ ) have an excess of Si atoms available for the formation of Si-nc. By varying the stoichiometry of the film and the annealing temperature, it is possible to change the mean size of Si-nc as observed by transmission electron microscopy (TEM). In qualitative agreement with the variation of the Si-nc mean size, the photoluminescence (PL) peak position red shifts for a given Si content with increasing the annealing temperature, and for a given temperature with increasing the Si content [6,10].

We have investigated two sets of samples: the first characterised by different Si content (35, 37, 39, 42 and 46 at%) and fixed annealing temperature (1250°C in  $\text{N}_2$  atmosphere for 1 h), the second by different annealing temperatures (as deposited and 500°C, 650°C, 800°C, 900°C, 1000°C, 1100°C, 1200°C and 1250°C) and fixed Si content (46 at%).

## 2. Results and discussion

X-ray absorption near edge structures (XANES) 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 absorption edge is at 1839 eV) and Si atoms in the amorphous  $\text{SiO}_2$ , whose absorption maximum is at about 1847 eV. The electronic and structural information obtained by TEY-XANES are related to the local environment of the absorbing silicon atoms regardless they are in luminescent or non-luminescent sites. In order to be selective to the luminescent Si sites, photoluminescence yield (PLY) measurements, which consist in the collection of visible photons emitted as a consequence of X-ray absorption, are necessary. The

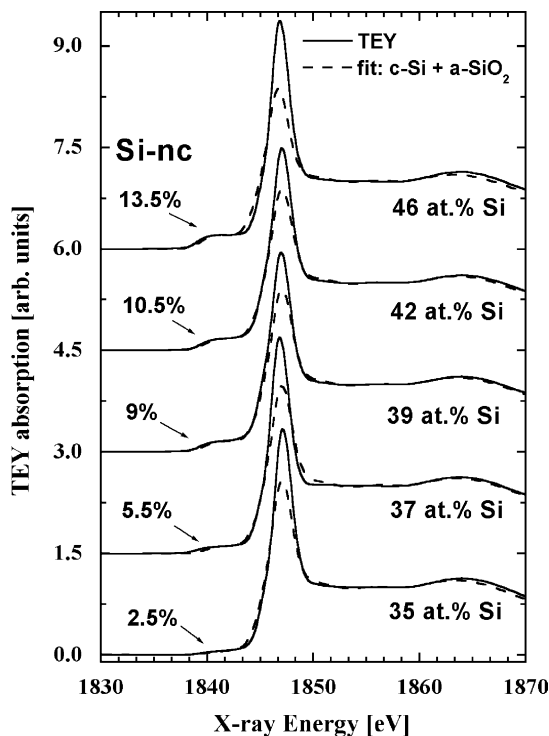


Fig. 1. TEY absorption spectra (continuous lines) at the Si K-edge of a set of PECVD Si-nc obtained with increasing the Si content (35, 37, 39, 42 and 46 at%) and annealed at 1250°C for 1 h in ultrapure  $\text{N}_2$  atmosphere. Simulated spectra (dashed lines) obtained by a combination of c-Si and a- $\text{SiO}_2$  reference spectra.

comparison between TEY and PLY data makes possible to distinguish between luminescent and non-luminescent Si nanocrystals. Structural as well as electronic information were achieved in this way both in porous silicon [11–13] and, more recently, in PECVD-grown samples [6,8].

### 2.1. TEY measurements as a function of Si content

TEY-XANES of different samples prepared by increasing the total Si content (35, 37, 39, 42 and 46 at%) are reported in Fig. 1. For such samples, PL spectra show a red shift (from 760 to 930 nm) with increasing Si content (from 35 to 46 at%), due to the increasing mean size of Si-nc (from less than 1 to 2.1 nm in radius) [6,10]. TEY-XANES show two main features: the absorption of Si nanocrystals, at about 1839 eV (K-edge of Si), and the absorption

of silica, characterised by the sharp peak at about 1847 eV. A fit of the experimental TEY spectra with a linear combination of c-Si and a-SiO<sub>2</sub> reference absorption spectra (dashed lines of Fig. 1) allows us to determine the effective amount of Si atoms clustered into Si-nc as a function of total Si content. Because of the white line of silica at about 1847 eV is very sensitive to small changes to the local environment (strain effects or small chemical bond modifications) [14,15], the silica peak has not been well reproduced, whereas the behaviour of the absorption coefficient at higher energies is well fitted. The results of the fitting procedure indicate that the number of Si atoms clustered in nanocrystals increases (2.5, 5.5, 9, 10.5 and 13.5%,  $\pm 0.5\%$ ) as a function of total amount of Si (35, 37, 39, 42 and 46 at%, respectively). However, not all Si atoms in excess in the substoichiometric films characterised by high Si content form Si-nc after the thermal annealing at 1250°C, but a fraction of excess Si remains in the amorphous matrix. As example, for the sample with 46 at%, a total Si content in the Si-nc of 19% would be expected on the basis of pure stoichiometric arguments. On the contrary, TEY analysis quantifies this content to 13.5%.

Rutherford backscattering spectrometry (RBS) measurements, carried out by using a 1.6 MeV He<sup>+</sup> beam in random configuration, have shown the presence of nitrogen atoms incorporated in the matrix as impurities. Nitrogen incorporation is a consequence of using N<sub>2</sub>O as gaseous precursor in the PECVD procedure. The content of nitrogen atoms changes with increasing the total Si content: 14, 12, 12, 10 and 8 at% ( $\pm 1\%$ ), for the 35, 37, 39, 42 and 46 at% samples, respectively. Hence, the amorphous matrix cannot be simply considered as amorphous SiO<sub>2</sub> but rather as a Si oxynitride phase, characterised by low nitrogen content and weakly dependent on the total amount of silicon. 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<sub>2-x</sub>N<sub>x</sub>. Indeed the Si content in the Si-nc measured by TEY is almost equal to the content one would expect to have on the basis of pure stoichiometric arguments. At high Si content (42 and 46 at%), we suggest that the amorphous matrix assumes a more complex structure. A quantitative compositional description of the amorphous matrix and a deeper discussion about the

role of nitrogen is the object of a recent paper [16]. 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 [17–20].

Good agreement with this compositional picture has been shown by refractive index measurements by the m-line technique [21]. In order to fit the measured refractive index as a function of Si content, Bruggemann effective medium approximation [22] has been used by assuming the presence of Si-nc in a medium composed of both SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> [21]. Despite the rather crude approximation of a complete phase separation between SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, good agreement with experimental results has been found. These results confirm that the presence of nitrogen in the film does influence the optical properties through the formation of a composite matrix.

## 2.2. TEY measurements as a function of annealing temperature

The segregation of crystalline silicon nitride (Si<sub>3</sub>N<sub>4</sub>) or oxynitride (Si<sub>2</sub>N<sub>2</sub>O) phases well separated from the silica network could also be argued in samples with high excess Si atoms. To clarify this, we measured the changes of TEY-XANES as a function of the annealing temperature and compared these with PL spectra.

TEY-XANES of as-prepared SiO<sub>x</sub> film (with  $x = 1.18$ , which corresponds to a total Si content of 46 at%) and of samples annealed at different temperatures are shown in Fig. 2. Besides the absorption features at about 1841 eV, due to Si–Si absorption, and at about 1847 eV, due to a-SiO<sub>2</sub>, 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<sub>x</sub> samples show a broad absorption peak at about 1844–1845 eV, while reference samples of Si<sub>3</sub>N<sub>4</sub> and Si<sub>2</sub>N<sub>2</sub>O present a peak at about 1844 and 1845 eV, respectively. The evolution with the temperature of nitrogen-related features is better pointed out by the analysis of the derivative plots, which show a negligible contribution of absorption

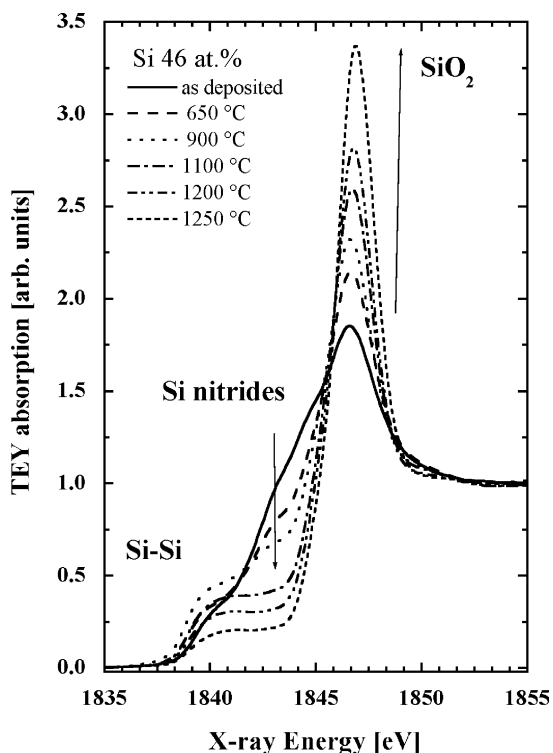


Fig. 2. TEY absorption spectra at the Si K-edge of a set of PECVD Si-nc obtained with fixed Si content (46 at%) and annealed at different temperatures (as deposited, and at 650°C, 900°C, 1100°C, 1200°C and 1250°C) for 1 h in ultrapure N<sub>2</sub> atmosphere. Arrows indicate the trend with increasing annealing temperature.

related to Si oxynitrides for annealing temperatures higher than 1100°C.

From the analysis of Fig. 2 it can be also noted that the intensity of the a-SiO<sub>2</sub> 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 lineshapes.

PL measurements were carried out by using an Ar<sup>+</sup> laser (365 nm emission line) with 50 mW over a circular area of about 1 mm in diameter. The as-prepared and 500°C annealed samples show broad and intense PL at about 600–650 nm. With increasing annealing temperature this band weakens. For temperatures higher than 1100°C, an intense PL peak at about 850–900 nm rises. Small red shift and intensity increases are observed with increasing annealing temperature from 1100°C to 1250°C.

The comparison between TEY and PL spectra suggests that the broad luminescence band at about 600–650 nm is related to Si nitrides segregated in the amorphous substoichiometric film. As a matter of fact, light emission in the range 550–650 nm can be related to defect-radiative states either of Si oxide or Si nitride matrix. Nevertheless, the correspondence of this band with the presence of absorption features of Si nitrides in TEY spectra let us conclude that the as-deposited sample and those annealed at low temperature are characterised by the presence of Si nitrides. As the annealing temperature increases (650–900°C), PL at 600–650 nm disappears. At higher temperatures, Si nanocrystals form and PL emission thus occurs at about 850–900 nm and strengthens after 1100°C. In the mean time the amorphous matrix modifies reducing dangling bonds and forming a Si oxynitride amorphous matrix as previously shown.

### 3. Conclusion

In summary, the analysis of X-ray absorption and RBS data has allowed us to assess the amount of Si atoms clustered in Si-nc and to give a compositional picture of the embedding matrix and of its evolution with thermal annealing and as a function of the film stoichiometry. The incorporation of nitrogen atoms due to the PECVD technique has also been monitored and quantified. In particular, thermal annealing at high temperature favours the formation of a Si oxynitride network, where nitrogen atoms are substitutional of oxygen atoms and whose stoichiometry depends on Si content, rather than the segregation of well-defined Si nitride phases in the Si oxide matrix, as shown in the as-deposited and low-temperature annealed samples.

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