Experimental and Theoretical Joint Study on the Electronic and Structural Properties of Silicon Nanocrystals Embedded in SiO_2: active Role of the Interface Region

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ABSTRACT

The local environment of light emitting silicon nanocrystals (Si-nc) embedded in amorphous SiO_2 has been studied by x-ray absorption spectroscopy (XAS) and by ab-initio total energy calculations. Si-nc have been formed by PECVD deposition of SiO_x with different Si content (from 35 to 42 at.%) and thermal annealing at high temperature (1250 °C). The comparison between total electron yield (TEY) and photoluminescence yield (PLY) spectra has allowed the identification of a modified region of SiO_2 (about 1 nm thick) surrounding the Si-nc, which participates to the light emission of Si-nc. Total energy calculations, within the Density Functional Theory, clearly show that Si-nc are surrounded by a cap-shell of stressed SiO_2 with a thickness of about 1 nm. The optoelectronic properties show the appearance of localized states not only in the Si-nc core region but also in the modified SiO_2 region.

INTRODUCTION

The interface region between silicon and silicon oxide is a fundamental subject of investigation because of the technological importance of thin silicon oxide films in semiconductor devices. Moreover the possibility of getting relevant optoelectronic properties from Si nanocrystals (Si-nc) has enhanced the hope in the integration of Si low-dimensional structures showing appropriate optoelectronic properties with the well-established silicon microelectronics present technology. The question of surface effects, in particular oxidation, on the optoelectronic properties of Si-nc has been recently addressed in various experimental and theoretical studies. Both first principle calculations and experimental observations have been applied to investigate the influence of the interface on the optoelectronic properties of Si-nc and many different models have been proposed [1,2,3,4,5]. Moreover, interface radiative states have been shown to play a key role in the optical gain in Si-nc [6,7].

Here we present a joint experimental and theoretical study of light emitting Si-nc embedded in SiO_2 to achieve a structural characterization of the luminescent Si-nc and of their environment and to understand the light emission mechanism.

SAMPLES, EXPERIMENTAL AND THEORETICAL METHODS

Si-nc were produced by plasma enhanced chemical vapour deposition (PECVD) of 200 nm thick substoichiometric SiO_x on a Si substrate followed by a high-temperature annealing at 1250 °C for 1 h in ultrapure nitrogen atmosphere. The excess silicon atoms contained in the films, due to the high temperature, diffuse inside the oxide matrix and forms nanometric silicon aggregates. Experimental evidences that the formation of Si-nc does not depend on the film depth are provided by Rutherford backscattering spectrometry (RBS) and transmission electron microscopy (TEM) [8].

A set of SiO_x films with different total atomic content of Si (35%, 37%, 39% and 42%) was investigated. At increasing Si content, TEM measurements showed an increase of the Si-nc mean radius (from less than 1.0 to 1.7 nm) and photoluminescence (PL) measurements a red-shift (from 790 to 910 nm) of the emission band [8,9].

X-ray absorption near edge structures (XANES) at the *k*-edge of Si were measured at Super-ACO (LURE) on the SA32 beam line in two detection modes: total electron yield (TEY) and PL yield (PLY). TEY measures the electrons escaping from the sample, it is sensitive to the local environment of all absorbing Si atoms regardless they are in luminescent or non-luminescent sites and its sampling depth at Si *k*-edge energy is about 100 nm for both c-Si and SiO_2 [10], i.e. comparable to the thickness of samples but not too long to detect the contribution of the Si substrate. PLY measurements consist in the collection of visible photons emitted as a consequence of x-ray absorption and are selective only to the luminescent Si sites. The comparison between TEY and PLY data has allowed to achieve structural and electronic information both in porous silicon [11,12] and in Si-nc samples [9].

TEY and PLY measurements were done simultaneously, hence the relative positions of edge and XANES features are not affected by monochromator uncertainties or resolution effects.

Theoretical calculations have been performed building up a simple model for a Si cluster embedded in a SiO_2 cage. From a cubic cell (side length: 1.432 nm) of crystalline β-cristobalite (BC) SiO_2, we obtained a small Si cluster simply deleting some O atoms of the SiO_2 matrix and linking together the Si atoms left with dangling bonds, resulting in a supercell of 64 Si and 116 O atoms with 10 Si bonded together. Total energy ab-initio calculations were based on the plane wave pseudopotential code CASTEP [13] using ultrasoft pseudopotentials [14]. The geometry optimization was performed leaving atom positions and cell dimensions free to move (keeping fixed the cell angles). To understand the character of the states involved in the optical transitions, we calculated the spatial distribution of the Kohn-Sham orbitals square modulus.

EXPERIMENTAL RESULTS

Figure 1 compares the normalized TEY and PLY XANES spectra of samples with 35 and 39% at. Si. Two well separated absorption edges for Si atoms are present, depending on the chemical bond: the first one, starting at 1839 eV, is the *k*-edge of Si atoms bonded to Si; the second one, due to Si in SiO_2 environment, is characterized by the white peak with maximum at about 1847 eV, followed by a flat region before the beginning of the EXAFS oscillations.

A quantitative analysis of the amount of Si atoms composing the Si nanodots has been done by the present authors in a very recent paper, thanks to a careful comparison between TEY-XAS and Rutherford backscattering spectrometry data [15].

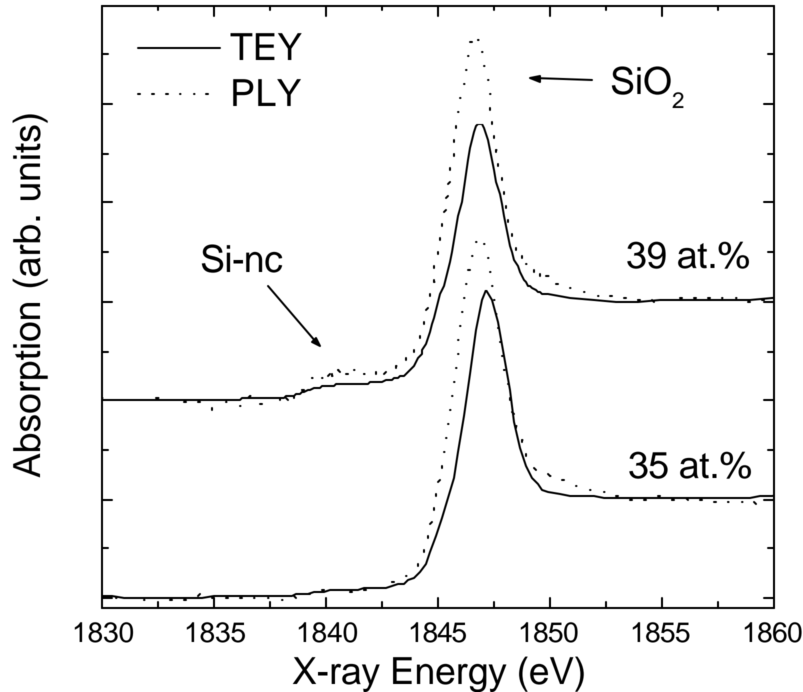

Figure 1. X-ray absorption spectra measured in TEY (continuous line) and PLY (dotted line) mode on 35 and 39 at. % of Si.

The analysis of spectra in figure 1 indicates that in PLY-XANES the luminescence is a consequence of x-ray absorption in both Si-nc and SiO_2. This is a noticeable difference with respect to porous Silicon (PS). In fact, for PS, even in aged or slightly oxidized samples, the PLY-XANES spectra obtained by monitoring the red XEOL band do not show any positive contribution at the SiO_2 absorption edge; only with anodically oxidized PS samples, we were able to detect a small positive contribution, while samples with a much thicker oxide layer showed a decreasing intensity and a typical reverse-edge behavior [16].

In principle, the PLY signal might be due to the x-ray absorption within the entire SiO_2 matrix. However, our data strongly suggest that this is not the case, because TEY and PLY XANES spectra measured on the same sample show remarkable differences. A first difference is that the PLY signal in the absorption region only due to Si-nc is significantly higher than the TEY one and this difference grows with increasing the Si content. This means that the concentration of Si-nc in the luminescent sites is larger than in the whole sample.
The most interesting differences are shown by the SiO_2 white peak at about 1847 eV: the PLY XANES signal grows up at lower energy and the energy difference is about 0.4-0.5 eV. Moreover, a remarkable difference in the relative intensity of the peak is evident and a small contribution at 1850 eV is often present in the PLY-XANES spectra. It is worth noting that a shift towards lower energy of the SiO_2 absorption threshold was experimentally obtained in densified silica, accompanied by an intensity reduction of the peak [17]. This experimental observation was interpreted as a reduction of the mid-range Si-Si interatomic distances.

In summary, we attribute these differences to the presence around the Si-nc of a modified SiO_2 region participating to the light emission process, but not extending to the whole silica matrix: otherwise no difference in PLY and TEY spectra would have been observed. Thus we propose a structural model, where the Si-nc are capped by a modified SiO_2 region, which plays an active role in the luminescence. The model involves three regions: the core Si-nc, the capping

modified SiO_2 shell and the embedding bulk SiO_2. The size of this intermediate region has been evaluated about 1 nm considering the ratio between the maximum of the PLY_{Si-nc} absorption (measured at 1841 eV) and the absorption PLY_{tot} at 1855 eV (which accounts for Si-nc and the SiO_2 cap-shell).

THEORETICAL RESULTS

The final relaxed supercell structure after the geometry optimization for the Si_{10} nanocrystals in SiO_2 shows that the skeleton is still crystalline-like, with a Si-Si bond length reduced from 3.1 Å to 2.67 Å, which means a strain of 14% respect to the bulk case. This rearrangement caused a deformation of the SiO_2 matrix around the dot both in bond lengths and angles. Nevertheless the deformation doesn't affect the SiO_2 matrix. It is actually possible to find still a good BC crystalline structure, in terms of angles and bond-lengths, at a distance from the dot's atoms of about 0.8-0.9 nm. This means that the dot is surrounded by a cap-shell of stressed BC SiO_2 which goes towards a pure crystalline BC matrix.
Moreover, the calculated results for the electronic properties of the relaxed structure (figure 2) present now a E_g of 2.07 eV, that must be compared with the calculated value of 5.84 eV for the E_g of the BC SiO_2. The strong reduction is originated by the presence, at the valence and conduction band edges, of confined, flat, states completely related to the Si-nc, whereas deep inside the valence and conduction bands the more k-dispersed states related to the SiO_2 matrix are still present.

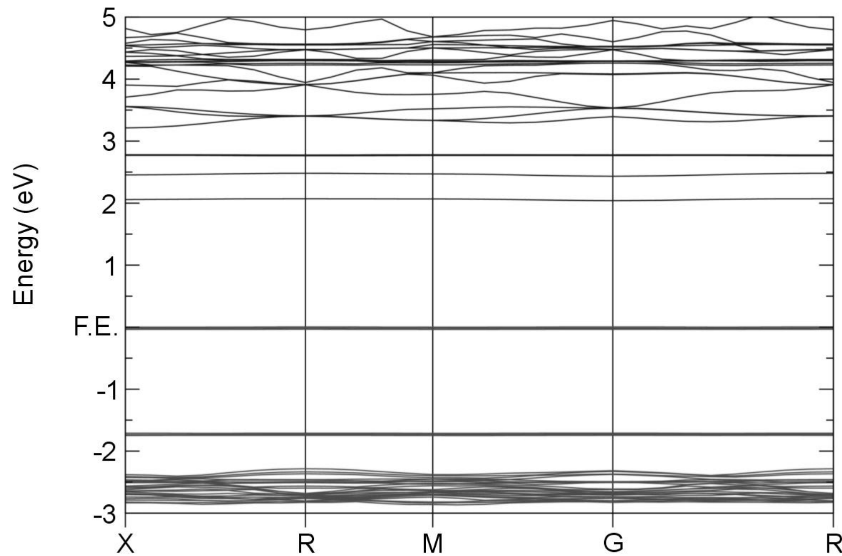

Figure 2. Band structure along high symmetry points of the Brillouin Zone for the Si-nc in SiO_2 at relaxed geometry.

In figure 3 the isosurfaces relative to fixed value of the square modulus of highest occupied (HOMO) and lowest unoccupied (LUMO) Kohn-Sham orbitals for the Si-nc in the SiO_2 matrix are reported; we clearly see that the distribution is totally confined in the Si-nc region with some weight on the interface O atoms. These dot-related states originate strong absorption features in

the optical region. These features are entirely new and can be at the origin of the PL observed in the red optical region for Si-nc immersed in a SiO_2 cage.

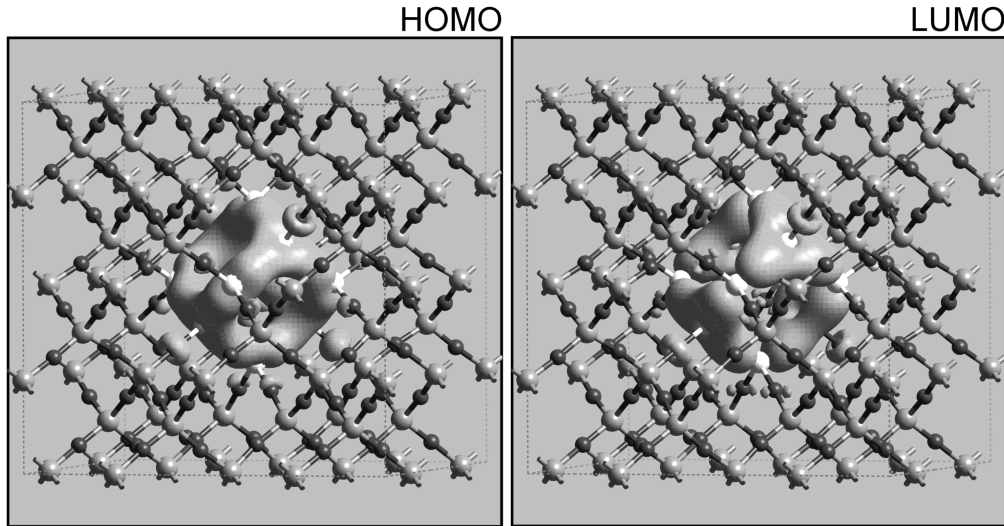

Figure 3. Isosurfaces at fixed value (25% of max. amplitude) of the HOMO and LUMO for the Si-nc in the SiO_2 matrix.

These results concerning the role of both Si-nc and the interface region with respect to the absorption process are in close agreement with the x-ray absorption measurements that indicate the presence of an intermediate region between Si-nc and the SiO_2 matrix that participates to the light emission process.

CONCLUSIONS

We have provided evidence of the presence of modified oxide region around Si-nc embedded in SiO_2. The experimental x-ray studies show that luminescent Si-nc are coated by an about 1 nm thick SiO_2 region with a different structure with respect to the rest of the matrix, and that it participates to the light emission process. The ab-initio density functional calculations indicate the presence of a strained SiO_2 shell of similar thickness around the Si-nc, which introduces optically active states.

These experimental and theoretical analyses clearly point out, for the first time, the important role played not only by the Si-nc but also by a modified silica host region in determining the optoelectronic properties of this system. Its relevance for the observed optical gain in Si-nc is under investigation.

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