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Structural and optical characterization of size controlled silicon nanocrystals in SiO_2/SiO_xN_y multilayers

J. López-Vidrier[a,*], S. Hernández[a], A.M. Hartel[b], D. Hiller[b], S. Gutsch[b], P. Löper[c], L. López-Conesa[a], S. Estradé[a], F. Peiró[a], M. Zacharias[b], B. Garrido[a]

[a]*MIND, Departament d'Electrònica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain*
[b]*IMTEK, Faculty of Engineering, Albert-Ludwigs-University Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany*
[c]*ISE, Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany*

Abstract

We offer a complete structural and optical study of samples containing silicon nanocrystals (Si-NCs) embedded in SiO_2/SiON multilayers, varying the oxynitride layer thickness from 2.5 to 7 nm. Using energy-filtered transmission electron microscopy we have determined the size distribution of the precipitated Si-nanoaggregates. Raman scattering measurements were used to investigate the Si-NC size and crystalline quality. By combining both techniques, the nanoaggregate crystalline degree has been evaluated, with values around 50% for all the samples. Photoluminescence spectroscopy has shown a blueshift of the emission at smaller NC sizes, presenting the sample with Si-NCs of 3.9 nm the best emission properties.

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Keywords: Silicon Nanocrystals; Oxynitride; EFTEM; Raman Scattering; Photoluminescence

* Corresponding author. Tel.: +34 93 4039175; fax: +34 93 4021148.
E-mail address: jlopezv@el.ub.es.

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1. Introduction

Silicon solar cells have attracted the attention of science and industry for years for their low fabrication and commercialization costs and their favourable electrical properties. However, silicon is an indirect bandgap semiconductor, with a bandgap energy of 1.12 eV. Its absorption of solar radiation is very poor as the associated energies of most photons coming from sun lay much above the silicon energy gap. Moreover, as a consequence of the indirect bandgap electronic transitions require the intervention of a phonon to couple the momenta and accomplish the conservation law, notably decreasing the transition probability. Because of these extremely poor optical properties of bulk silicon, the efficiency of these photovoltaic devices is far from the desired one [1]. However, by means of the reduction in size of crystalline silicon, a strong localization of the carriers can be reached and the bandgap energy of these nanostructures can be tuned by controlling their size [2]. Therefore, a good determination of the Si-NC size, distribution and optical properties is fundamental in order to reliably characterize the grown samples, thus optimizing the fabrication process. In this paper, a complete structural and optical characterization of Si-NCs embedded in oxynitride matrices is presented, using widely developed techniques such as energy-filtered transmission electron microscopy and Fourier-transform infrared, Raman scattering and photoluminescence spectroscopies.

2. Experimental Details

Silicon rich oxynitride (SRON) films were deposited on (100) Si substrates at 375 °C with a composition of $SiO_{1.1}N_{0.25}$, by means of plasma-enhanced chemical-vapour deposition (PECVD). Samples consist of 20 bilayers of $SiO_2/SiO_{1.1}N_{0.25}$, with different thickness of the latter from one sample to another and keeping the oxide barrier thickness constant at 4 nm for all the samples. After deposition, an annealing of the films at 1100 °C was carried out in a quartz tube furnace for 1 hour in N_2 ambient, in order to precipitate the Si excess. A reference sample containing only a 200 nm thick SRON layer was also prepared under the same conditions, with the aim of checking the unconfined precipitation of Si.

Fourier-transform infrared (FTIR) spectroscopy measurements were performed by means of a BOMEM DA.3 with a spectral resolution of 1 cm^{-1}. A good phase separation between the SiO_2 and SiON matrices has been observed after annealing, as corroborated by the presence of the Si-O-Si asymmetric stretching modes in the two different matrices, at 1065 and 1094 cm^{-1}, respectively [3, 4]. The thickness of the SRON layers, NC size and distribution of the Si nanoaggregates have been measured by means of energy-filtered transmission electron microscopy (EFTEM) using a JEOL 2010 (200 keV FEG) equipped with a Gatan image filter (resolution of 0.8 eV). The silicon contrast was enhanced by energetically filtering the electron energy-loss spectra around the Si plasmon energy (E_{Si} = 17 eV).

Regarding the optical properties, Raman scattering spectra were obtained by exciting the samples using the 325 nm line of a He-Cd laser and analyzed through a LabRam spectrometer, coupled to a high sensitive CCD. The large absorption coefficient of this system at the employed wavelength ($\alpha \approx 10^4$ cm^{-1} [5]) ensures that the probing depth is limited close to the sample surface, allowing the characterization of samples deposited on Si substrates. Nevertheless, some contribution to the Raman spectra from the Si substrate is expected. Photoluminescence (PL) spectra were acquired in the visible range by a combination of a GaAs photomultiplier tube and a CCD, using a standard lock-in technique and exciting the samples also with the 325 nm line.

3. Results and Discussion

3.1. Energy-Filtered Transmission Electron Microscopy

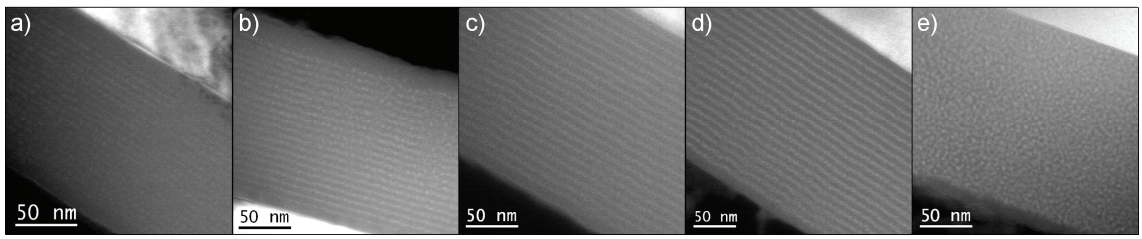

Fig. 1. Cross-section energy-filtered transmission electron microscopy images of the samples with different nominal thickness values of the SiON layers: (a) 2.5 nm, (b) 4.0 nm, (c) 5.5 nm, (d) 7.0 nm and (e) 200 nm bulk SRON.

Energy-filtered transmission electron microscopy measurements were performed for all the samples in order to ensure the correct growth of the Si-NCs within the SRON layers. The obtained images are presented in Fig. 1, and show a excellent quality of the multilayer structure for all the samples. In the images, both SRON and SiO_2 barrier layers can be distinguished as a bright and dark pattern, respectively. A gradual increase of the thickness of the SRON layers can be seen from one sample to another. In addition, the SRON layers present a discontinuity in the brightness, which indicates the presence of Si nanoaggregates, thus corroborating a good precipitation of the Si excess during the annealing process. This observation can easily be checked by observing Fig. 1(e), the sample containing a bulk SRON layer, where the aggregates appear randomly distributed as bright dots. Another feature that can be observed is the waviness present at the interfaces between layers, which cannot be due to the effect of temperature during the annealing process, since as-deposited samples (not shown here) also presented this side effect; the waviness, then, can only be due to the substrate, which propagates the effect to the deposited upper layers.

The high resolution of the employed set-up allowed for a precise measurement of the thickness of the SRON layers as well as the size of Si-NCs, whose values are shown in Tab. 1. The size of NCs was found to follow a Gaussian distribution around a mean value, with an associated dispersion. As can be seen in the table, the nominal thickness of the SRON layers perfectly agrees with the measured size of the precipitated Si-NC for the samples with a nominal thickness of 2.5 and 4.0 nm, while they are slightly larger than the mean size of the NCs for thicknesses larger than 5 nm. Therefore, the size control based on the superlattice for layer thickness is excellent for thicknesses below 5 nm, providing a deviation of the average NC size of only 0.2 nm (with respect to the measured layer thickness), which corresponds to only ± 1 atomic layers in deviation. The rather large dispersion of the size distribution could be an artefact from the cross-section preparation; the images still average over a depth of 30-50 nm, which could result in the observation of apparently larger NCs because of nanocrystals laying behind each other. The size distribution measured this way provides information about the radiative centers delivering energy, and represents an initial point for the discussion of the crystalline quality of the grown nanostructures.

3.2. Raman Scattering

The Raman spectra of the samples are presented in Fig. 2(a). In all the samples we have observed a broad band between 480 and 520 cm^{-1}, whose intensity scales with the SRON layer thickness, and a sharp peak at ≈ 521 cm^{-1}, increasing for thinner SRON layers. The broad structure is related to disorder activated modes, either coming from the SiO_2/SiON matrix or Si, while the sharp peak is attributed to

crystalline Si, as previously reported [6]; their observation indicates that some Si has precipitated in amorphous or crystalline states. Nevertheless, the central frequency and lineshape at high frequencies of the crystalline feature are similar to the ones observed in crystalline bulk Si. Actually, the low thickness of the layers (around 200 nm at most) allows the penetration of light beyond the layers, resulting in a Raman contribution from the Si substrate, whose phonon is superimposed with those originated in the crystalline Si-aggregates (it explains the increasing intensity of the crystalline peak for thinner layers).

Assuming that the substrate contribution corresponds to a lorentzian peak centered at 521 cm^{-1} with a full-width at half-maximum (FWHM) of 4.0 cm^{-1} and deconvoluting it from the SRON layers contribution, we could isolate the information of the latter [see the inset of Fig. 2(a)]. Due to the low volume of the NCs of the thinnest sample (2.5 nm), a low population of phonons are excited (only a few atoms can vibrate), being their Raman efficiency much lower than in larger Si-NCs, and no reliable information of the size for these small NCs can be extracted using this method [7]. Once the Si-substrate contribution is removed, a peak at frequencies slightly lower than 521 cm^{-1} remained visible that comes from the Si-NCs present in the layers, being both its frequency and lineshape strongly dependent on the size of the nanostructures [7]. In Fig. 2(b) we isolated this contribution from the one obtained from disorder modes. It is clearly observed that, on one hand, the crystalline Raman contribution from Si-NCs presents an intensity reduction as the SRON layer thickness is reduced and, on the other, its lineshape also varies with the sample, obtaining a blue shift and a broadening of the peak at lower thicknesses.

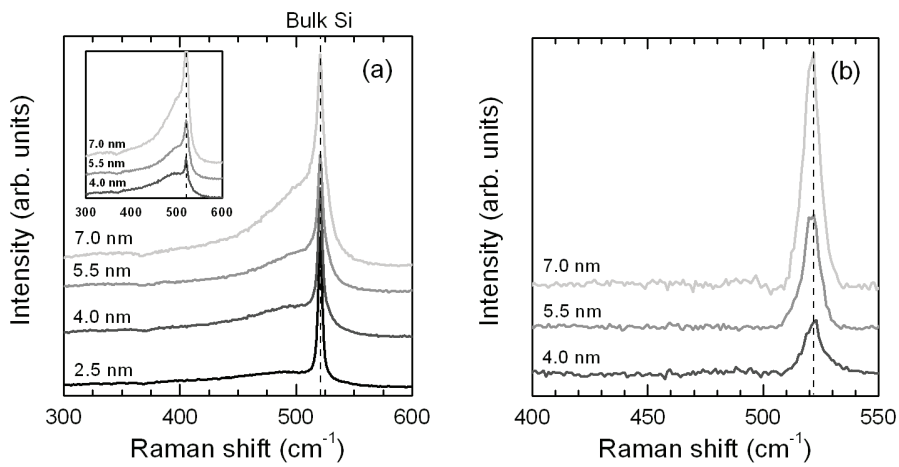

Fig. 2. (a) Raman scattering spectra for the measured samples (the inset shows the spectra after substracting the Si substrate contribution) and (b) the Raman Si-NC peak, once removed the substrate and disorder-modes-related contributions.

We used a previously developed phonon confinement model to analyze the crystalline Raman feature of Si-NCs and to extract their crystalline size (see Ref. [6]). The results obtained by fitting our model to the crystalline Raman peak of the Si-NCs are presented in Tab. 1, showing an increase of the crystalline Si-NC size with the thickness of the SiON layers. We observed that Raman sizes are smaller than the ones obtained by EFTEM measurements. The discrepancy is about 1 nm, which perfectly agrees with previously reported studies using EFTEM and dark-field TEM, where a core-shell model is assumed (a crystalline core surrounded by an amorphous shell) [8]. Our experimental energy resolution in the EFTEM measurements cannot distinguish between amorphous or crystalline silicon states. Consequently, by means of EFTEM we observe the whole Si-nanoparticle while only the crystalline part is evaluated when using the aforementioned confinement model. Considering this kind of structure, it is possible to

estimate the crystalline fraction of the Si-NCs (Γ_c, see Tab. 1), keeping a value around 50% for all of the samples.

Table 1. Nominal and measured thickness of the SRON layers by means of EFTEM, the NC sizes obtained by both EFTEM measurements (expressed as a mean value with an associated dispersion, considering a Gaussian distribution) and from the fitting of the Raman peak (whose errors are associated to data treatment), and their corresponding crystalline fraction.

Nominal thickness (nm)	Thickness measured by EFTEM (nm)	NC size by EFTEM (nm)	Si-NC size by Raman (nm)	Γ_c (%)
2.5	2.5	2.3 ± 0.4	-	-
4.0	4.1	3.9 ± 0.7	3.0 ± 0.3	45 ± 15
5.5	5.0	4.3 ± 0.6	3.3 ± 0.2	45 ± 10
7.0	5.7	4.6 ± 0.6	3.7 ± 0.2	50 ± 10
200 (bulk layer)	184	3.5 ± 0.5	-	-

3.3. Photoluminescence Spectroscopy

In Fig. 3(a) we display the PL spectra of the samples under study, once scaled to their corresponding SRON layer thickness. The spectra show a peak emission in the near-infrared and visible ranges that shifts to longer wavelengths with the Si-NC size, which corroborates the precipitation of Si-NCs [9]. We observe a redshift from approximately 710 to 860 nm for the samples with 2.5 to 7.0 nm SRON layer thickness, respectively [see Fig. 3(b)], as well as a clear dependence of the PL intensity on the thickness of the SRON layer, being maximum for the sample with 4.0 nm SRON layer. The emission of the bulk SRON layer sample is very similar to the one of the thickest sample, suggesting a saturation of the growth process of Si-NCs for the used annealing conditions. The emission from samples with a SRON layer thicker than 4.0 nm presents a FWHM of about ≈ 0.3 eV, associated to both the size dispersion observed by EFTEM and the indirect nature of the recombination process in this system. A rough estimation of the dispersion of the Si-NC sizes can be evaluated by monitoring this parameter. On the contrary, the sample with SRON layers of 2.5 nm presents the largest FWHM and the lowest intensity, probably due to a more pronounced growth of the amorphous phase of NCs instead of the crystalline one.

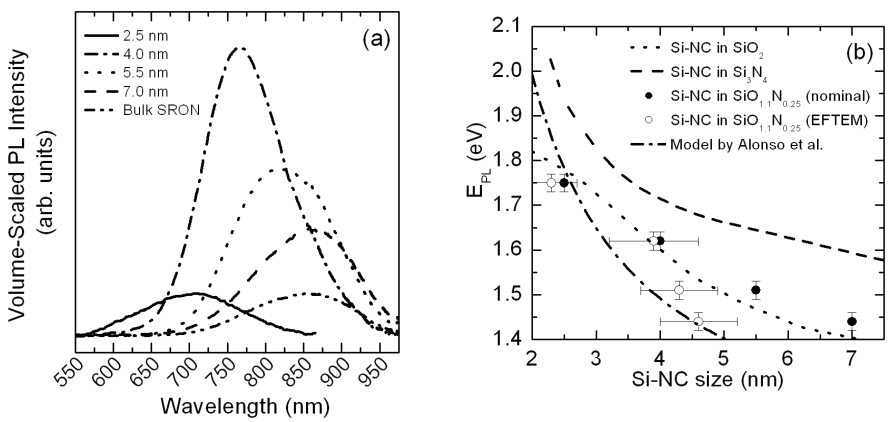

Fig. 3. (a) PL spectra of the studied samples, scaled to the thickness of the SRON layers. (b) Comparison between our PL values, considering the nominal (black points) and the EFTEM (green points) NC sizes, and the ones obtained by other authors, in SiO_2 [10] (blue dashed line) and Si_3N_4 [11] (red dashed line) matrices. Green dot-dashed line represents the calculations by Alonso *et al.* [9].

As can be seen in Fig. 3(b), our PL results from Si-NCs embedded in a SiON matrix lay within the already reported ones for SiO_2 [10] and Si_3N_4 [11] matrices, when the nominal value of the SRON thickness is considered as the Si-NC size. However, a sizeable discrepancy exists when considering the sizes of the nanostructures obtained by EFTEM: lower energies are observed for all Si-NC sizes with respect to previously reported values. Therefore, an overestimation of the Si-NC sizes would be obtained through the previously reported relations [10, 11]. Nevertheless, a reasonable good agreement is found when comparing our results with recently published theoretical calculations of electronic transitions in Si-NCs embedded in SiO_2 [9], establishing a direct relation between the size and the PL emission energy.

4. Conclusions

In summary, we have characterized the structural and optical properties of Si-NCs grown in SiO_2/SiON multilayers deposited by PECVD on Si substrate and annealed at 1100 ºC for different SRON layer thicknesses. The thicknesses of the multilayers and the Si-NC sizes have been determined by EFTEM, in good agreement with their nominal values. Raman scattering was used to evaluate the size and the crystalline fraction of the Si-NCs. The estimated crystalline fraction is found to be in good agreement with previous reports, performed by combining EFTEM and dark-field TEM measurements in PECVD grown samples. PL spectra show a blueshift of the emission up to ~ 1.7 eV (sample with 2.3 nm NC size) with decreasing NC size, being the 4 nm sample the one which shows the highest PL intensity. The comparison of the PL results with recently published theoretical models has allowed us to establish a direct relation between the size and the optical properties of Si-NCs.

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