Colloidal Solutions with Silicon Nanocrystals: Structural and Optical Properties

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Abstract

In this work, colloidal solutions with silicon nanoparticles using different solvents were synthesized. Structural, morphological and optical characterizations were realized, and these were studied. X-ray diffraction (XRD) was used to measure the diffractograms of the colloidal solutions, which are composed of silicon nanocrystals (Si-ncs), with an average size of approximately 3 nm, and a preferential crystalline orientation (311). Atomic force microscopy (AFM) images show that the morphology of silicon nanoparticles (Si-nps) is agglomerated in a big amount, which is corroborated by means of the roughness. On the other hand, high resolution transmission electronic microscopy (HRTEM) images show on average size of the Si-nc ranging from 1.5 to 10 nm, which depends on the solvent used. Also, different preferential crystalline orientations of the Si-nc such as (311), (220) and (111) were obtained. A correlation between the optical and structural properties was realized in colloidal solutions with silicon nanoparticles and different solvents.

Keywords: silicon nanocrystals, colloidal solutions, porous silicon, XRD, AFM, HRTEM

1. Introduction

In the last years, the synthesis of the silicon nanostructures has been developed in grand manner, due to both by their interesting quantum effects that these structures present and also by their interesting optical and unique electrical properties. A fundamental result that has been found in the silicon nanocrystals (Si-ncs) is that they make a contribution to the shifting in the

prohibited energy band. Thus, we observed in the measurements that the energy band gap increases when decreasing the Si-nc size [1–3]. Other interesting result is related to the emission efficiency of light in the visible range, which is linked to the energy band gap of the Si-nc, which in turn depends strongly on the size of the Si-ncs, and when they have lesser size than the Bohr exciton radius in the silicon, the spatial confining of the carriers in the nanocrystal is greater, which gives rise to a strong overlap of the wave functions in the k -space in both electrons and holes. Therefore, the nanocrystals can absorb and emit light with different energies by controlling only their size [4]. Silicon nanocrystals have been widely exploited in electronics and other areas, due to their low toxicity, and they exhibit the ability to be doped in order to become either an n -type or p -type material [5]; this fact allows generating new technologies such as sensors [6–8], biosensors [9–12], magnetic materials [13], photodiodes [14], Bragg reflectors [15], photonic applications [16–21], nonvolatile storage devices [22–24], solar cells of third generation [25–29] as well as tandem solar cells [30–35], among other devices [35, 36].

Actually, it exists a big interest in the topic of photovoltaic energy, due to Queisser-Shockley theory limit, in one standard solar cell of Si where there is a loss of efficiency due to the phonon scattering phenomenon that is produced by the hot electrons. To eliminate such undesirable effects, it has been proposed two alternatives for improving the efficiency of such Si cell. The first one consists of making heterostructures with materials of different energy band gaps; in each layer forming the heterostructure, the energy will be absorbed and transformed into electric energy. The second one is based on the down conversion process that consists of depositing one layer on the solar cell and using the photoluminescent effect to reduce the energy of incident photons. These photons make a more efficient conversion of the solar energy into electric energy. These two ways proposed require a careful control of the size of the nanocrystals [4].

Today, there are a lot of methods for obtaining silicon nanocrystals, namely Stober, pulsed laser, controlled precipitation, emulsions, oxidation, silane combustion, gas evaporation, co-sputtering and thermic degradation [37–48], chemical vapor deposition (CVD) [49, 50], low pressure chemical vapor deposition (LPCVD) [51], ionic implantation [52, 53] and other ones. Unfortunately, such methods are very expensive. As an alternative, a method consisting of using colloidal solutions for obtaining Si-ncs may be used. We have reported somewhere previously how to obtain these colloidal solutions [54]. In this chapter, we report the observed structural and morphological properties of silicon nanocrystals in different organic solvents as colloidal solutions with Si-ncs, and we quantify the exact size of these nanocrystals.

2. Experimental method

The first step to obtain the silicon nanocrystals consisted on obtaining the porous silicon (PSi). To synthesize the PSi, we used the electrochemical etching process for which was used hydrofluoric acid (HF) with different electrical current densities. The obtained PSi samples were subjected to a scrapped-off process, and after this, a grinding process was carried out in an agate mortar.

After the latter process a fine powder was obtained, it was mixed with organic solvents (acetone, methanol and ethanol) and then a process of decanting over the larger particles found in the solution was done. Finally, almost transparent solutions were obtained as observed at a glance, but when they were exposed under UV radiation, they showed an efficient photoluminescence lying between green and blue colors. The obtaining of nanocrystals by means of colloidal solutions was previously reported by the authors [54]. Therein, the process used to obtain the nanocrystals is explained in detail.

The structural properties of the silicon nanocrystals were determined by the high resolution transmission electronic microscopy (HRTEM) technique with a JEOL-2010 HRTEM (Jeol, Tokyo, Japan) system with a potential of 200 kV. The X-ray diffractograms were obtained with Discover Bruker D8 equipment operated at 40 kV and at 40 mA using a CuK α radiation (1.5406°), with a Lynxeye detector and a 0.2 mm divergence grid as primary optics and a grid of 3 mm anti-dispersion as secondary optics. The morphological properties were studied by atomic force microscopy (AFM) with a JEOL JSPM-5200 team.

3. Results and discussion

3.1. X-ray diffraction (XRD)

To obtain the diffractograms of the colloidal solutions, we deposited a colloidal solution on silicon substrates with crystalline orientation (100), so that they functioned as support to the Si-ncs. The diffraction pattern peaks obtained in the diffractogram are localized near those that have been reported in Ref. [55]; the case of crystallographic planes is also similar [56–59]. This result indicates clearly that there are silicon nanocrystals in our silicon substrate. On the other hand, the XRD data show that Si-ncs have a preferential crystalline orientation (311). However, in some samples (M₀₉ and M₁₅), additional peaks were found around $2\theta = 28.52^\circ$ (111), 47.31° (220), and this may be due to the existence of some type of metastable state of the silicon nanocrystals on the silicon substrate as indicated in **Figure 1**. By using the average width of the diffraction peak (FWHM), the average size of the nanocrystals could be calculated by applying the Scherrer equation [60, 61]. **Table 1** shows a comparison between the diffracted peaks of JCPDS card 27–1402, with respect to the diffracted peaks belonging to our samples obtained.

Some papers report that these diffraction peaks are originated by the core/shell structures, where such structures are formed from the combination of silicon nanocrystals coated by an oxide layer [57], due to the etching process in which HF was utilized to obtain the PSi and the subsequent atmospheric exposure.

It was observed that the average size of the nanocrystals varied from 2.88 to 3.67 nm according to the data reported in **Table 1**. In the work that was reported in Ref. [54], it is possible to observe that the nanocrystals have the tendency to orientate themselves in the crystallographic plane (111), but with nanocrystals having a larger size. However, when the nanocrystals were directly measured, it was found that their preferential orientation changed to (311) with smaller sizes. This can be attributed to the fact that the sizes of larger crystals

Figure 1. XRD diffractograms of the colloidal solutions obtained.

are due to the agglomerations of small crystals, thus producing a preferential orientation as a consequence of this agglomeration. When we carry out the measurement of the smallest crystal dimensions, in a certain way we measure the crystal dimensions individually; therefore, we can say that we are measuring the true natural orientation of the nanocrystals which is possibly because of the way of preparation of the colloidal solution samples, contrary to other works where they have different orientation tendencies of the crystals such as (111)

Ref. [57]	Sample M_09		Sample M_10		Sample M_11		Sample M_14		Sample M_15		Sample M_19	
	PP	Size (nm)	PP	Size (nm)	PP	Size (nm)	PP	Size (nm)	PP	Size (nm)	PP	Size (nm)
28.44	28.52	4.88	N/A	N/A	N/A	N/A	N/A	N/A	28.62	2.19	N/A	N/A
47.30	47.31	4.19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
56.12	56.09	2.88	55.64	3.18	55.84	3.24	55.74	3.06	55.84	3.67	55.59	3.62

Table 1. XRD peaks position and nanocrystal size obtained from the samples.

[60] or an orientation (220) [4]. An important feature which is noteworthy to emphasize is the intensity of the diffraction peaks; such intensity is attributed to the thickness formed by the silicon nanocrystals on the substrate [4]. Therefore, we suggest that the intensity of the peaks depends strongly on the amount of nanocrystals found.

3.2. AFM characterization

The characterization by atomic force microscopy was realized in all colloidal solutions with Si-ncs, in order both to know the roughness of the samples and to demonstrate the existence of silicon nanocrystals by using another characterization technique. The colloidal solution samples were deposited on p-type silicon substrates with orientation (100). The results were the following: all the samples presented particles with spherical shapes well-defined and sometimes irregular shapes, similar to particle agglomerations. The sample M_09 exhibited a set of particles forming several geometries, as can be seen in the XY scale of the image. In this scale, the dimensions of such particles lie in the micron order, but in the Z scale, we find that they have a maximum of 186 nm. Therefore, we can say that there are agglomerates of crystals in the XY plane with micrometric dimensions which have along the Z direction nanometric dimensions. The largest particles have a height of 186 nm and it decreases until finding particles with a height approximately of 18 nm. The 3D image shows the roughness surface of the substrate due to the layer of the colloidal solution that was deposited as shown in **Figure 2**.

By taking a specific area of the image, it was possible to locate an area where particles with heights approximately from 1 to 2.3 nm were found. On the other hand, nanometric particles could also be found in the X-Y plane. Besides, there are agglomerated particles whose size is around 100 nm in the XY plane with a height of approximately 30 nm. This dispersion in size that occurs between the images is due to the sections that are reviewed in the sample as is shown in **Figures 2** and **3**. However, with this information obtained from these images, we can determine and verify that we really have particles of nanometric size.

Similar situation happened for samples M_10, M_11, M_14, M_15 and M_17 because they also had particles with different geometric shapes which in general exhibit a tendency to be spherical. At first glance, it was observed in a large area comprising micron-sized dimensions, but

Figure 2. AFM image and 3D image obtained from the sample M_09.

it was also possible to see agglomerated particles with dimensions in the order of hundreds of nanometers, with similar heights. This occurred for some areas studied as shown in **Figure 4**.

On the other hand, by observing specific areas of the samples, particles of smaller sizes could be detected. We could also reduce the scanning area, and we could find a quantity of nanometric particles in the X-Y-Z space with a size of approximately 1.8 nm. These images clearly demonstrate the existence of silicon nanoparticles.

Figure 5 shows the contrast between individual particles that can be found and agglomerates that are produced by the junction of individual particles. The origin of the agglomeration process is not yet clear; we assume that this mechanism may be due to several factors, such as the preparation of the samples, the deposition of the colloids on the substrate or the density of suspended particles in the solvents.

Figure 3. The X-Y plane of the sample M_09 with agglomerations of nanometric size.

Figure 4. The X-Y plane and 3D image of the colloidal solution sample with Si-ncs.

Figure 5. Junction of individual particles generating an agglomeration process.

It is clear that we can corroborate the X-ray diffraction data with these results because in XRD there are average crystal sizes between 1.5 and 3 nm, and it is clear that we are obtaining similar crystal sizes by means of this characterization technique.

For sample M₁₄, a remarkable fact happened, it consisted of agglomerations of particles, but in a particle image there were longitudinal agglomerations, similar grooves, and on these grooves more particles appeared. The approximate height of these grooves is 100 nm. By closing up these grooves, some particles of the order of 10 nm were found in the X-Y plane having an approximate Z-height of 15 nm (Figure 6).

The results obtained in this work are similar to those that have been reported in the literature [61–64]. Most of these works report morphologies similar to those found in this work, including those we reported in the sample M₁₄, with the formation of grooves, that was similar to that reported by Jasmin et al. [64], because in an image of phase shows a similar behavior, due

Figure 6. Longitudinal agglomerations, similar grooves, and on these grooves more particles appeared.

to an interference between the sample and the cantilever. However, this behavior is due to the magnetic properties of the particles. Now, in our case, we do not have that kind of properties so we can attribute this behavior to a kind of longitudinal agglomerations of the particles.

3.3. TEM characterization

The results of the HRTEM images of the colloidal solutions show the size, shape and preferential orientation of the silicon nanocrystals immersed in the colloidal solution. This

characterization is presented only for three samples with different solvent (ethanol, methanol and acetone). We could note nanocrystals of different diameter sizes in a range from 1.5 to 8 nm and different geometrical shapes; some of which were circular, ellipsoidal and some others with not well defined shapes. Ray Mallar et al. [57] also reported nanocrystals of size close to those obtained in the present work (1.5 nm), with shapes and crystalline orientations similar to the present work.

The three images in **Figure 7** correspond to a sample of colloidal solution with acetone solvent; in two of such images, we can notice a large number of spherical and ellipsoidal nanocrystals and other ones similar to agglomerations (irregular shapes); a few more are not clearly perceived because the scale of the image is very large. Possibly the lack of magnification in this image hid the clearer vision of the nanocrystals, although other works have shown areas with spots or black marks as nanocrystals formation [64]. These black marks correspond to the fact that the nanocrystals have been wrapped in an oxide layer. Then, according to what has been reported in the scientific literature, our sample of acetone is immersed with nanometric nanocrystals. We stress that nanocrystals with dimensions larger than 10 nm were also found. In the image, 6 and 7 nm nanocrystals were found, and in the inserted images, the diffraction patterns are indicated where crystalline orientations were found to be (220). This result agrees with some orientations that were presented in the X-ray diffractograms. Finally, from the third image, we can identify a black spot; the latter is originated because the thickness of that agglomerate impedes the electrons from penetrating into the sample. Consequently, they are bounced in such a region, forming an image similar to an scanning electron microscopy (SEM) one. However, smaller particles were found, which were detached from this agglomerate; this event is consistent with the AFM images, where there are nanocrystals forming agglomerate (**Figure 7**) [54].

The second image of **Figure 8** corresponds to a colloidal solution with ethanol solvent. It could be noted that only a few dark spots were found. This may be possible because either there exists a smaller amount of nanocrystals or there are a lot of nanocrystals but without the oxidant coating. These nanocrystals were found having an average size between 4 and 5 nm, exhibiting circular shapes and other irregular ones. The inserted images of the diffraction patterns depict preferential crystalline orientations corresponding to (220) and (311). This fact confirms us and at the same time proves that the crystal orientations in X-ray diffraction are similar to those obtained by HRTEM. In relation to the third image of **Figure 8**, we find that there is agglomerate, but a little thinner, which allows observing the crystallinity of the agglomerate. On the other hand, dark spots were observed here, but the crystal arrangement could be appreciated. This is because the oxide layer is thinner than the crystal. This proves what was mentioned in the acetone images. It leads one to think that core-shell crystals are formed, where the silicon crystals play the role as a core and the oxidizing layer functions as a shell.

The last images corresponding to **Figure 9** are attributed to a colloidal solution with methanol solvent, where no dark spots were found. In this case, the resolution scale was far better. It allowed that in this image we could find a larger quantity of nanocrystals with a much smaller size than those found in the previous images, showing sizes from 1.4 to 3.4 nm, with a more circular tendency. In fact, making an approach, it was possible to notice that the whole image was full of nanocrystals with different orientations. In the figures inserted with diffraction patterns,

Figure 7. The HRTEM images of colloidal solution with acetone solvent.

Figure 8. The HRTEM of the colloidal solution with ethanol solvent.

Figure 9. The HRTEM of the colloidal solution with methanol solvent.

they were found with crystalline preferential orientations of (220) and (111). With this image, we can verify and compare that the results of XRD are similar to those obtained with HRTEM, as well as with the results presented by Mallar et al. [57]. Even in the last image, one can see different regions with nanocrystals shape not well-defined, but with sizes of 1 nm or less.

The HRTEM images showed the approximate size of the nanocrystals (1.5 nm to 10 nm) and a roughly circular shape, Mallar et al. [57] according to their results mention that the HF apparently produces a decrease in the size of the nanocrystals; we can see this in the methanol sample because there are nanocrystals up to 1.4 nm. They also mention that there is a formation of spherical isolated crystals [64]. This is also compatible with our results, since these isolated crystals can be clearly seen in all the samples. According to the diffraction patterns shown in each of the HRTEM figures, some of these image insertions show almost continuous rings. This indicates that there are random orientations of neighboring crystals, that is, a polycrystalline composition. Such presence can also be noticed by diffuse halos which are indicators of an amorphous background that may be due to some type of silicon oxide or even amorphous silicon [57]. According to Mallar et al. [57], HF etching is more effective in the formation of isolated crystals, with regular shapes and nanometric sizes.

We can correlate the size of the nanocrystals with the solvent used. Such fact can be seen in the HRTEM images where the size of the nanocrystals decreased when the solvent was changed. More exactly, for the case of acetone solvent sample, the nanocrystal size was from 7 to 10 nm, with a large number of nanocrystals and core-shell structures. On the other hand, nanocrystal sizes between 4 and 6 nm were found for the ethanol sample, besides a reduction in the number of nanocrystals and amount of nanocrystals with sizes from 1 to 3 nm for the methanol sample was found. We attribute this event to the molar mass of each solvent; the molar mass of acetone is 58.08 g/mol, for ethanol we have a molar mass of 46.06 g/mol, and for methanol we have a molar mass of 32.02 g/mol. Due to the differences in the molar masses among the solvents, the formation of nanocrystals and agglomerates is possible.

Figure 10 shows histograms about the distribution of nanocrystals versus diameter. As can be seen, the sample contained in acetone possesses nanocrystals of larger size at 5 nm, while the sample contained in methanol has nanocrystals whose sizes are smaller than 5 nm. Finally, the ethanol sample contains intermediate nanocrystals whose size lies between the two mentioned samples. This can verify in a certain way, the proposed theory, the influence that the solvent has on the size of the nanocrystals.

In the article previously reported by the authors, photoluminescence spectra [54] were shown, which also correlate with PL intensity and nanocrystal size, where acetone samples (M_16 [54]) have a higher PL intensity, but a luminescent emission of longer wavelength; ethanol samples (M_14 [54]) had a lower PL intensity, but with a shift to lower wavelengths and methanol samples (M_09 [54]) had lower PL intensity, but with a higher energy luminescent emission than the previous samples. This can show that the solvent affects the size of the crystals, the luminescent emission and the emission energy. In this case, photoluminescence is affected by quantum confinement and by defects. The emission energy is originated by the nanocrystal size, while the emission intensity is attributed to the presence

Figure 10. The histograms of the nanocrystals distribution vs. diameter.

of defects which are present in the nanocrystals due to the bonds that are formed with the solvent. From the HRTEM images, it was possible to verify that the different solvents affect the nanocrystal size.

4. Conclusions

We have demonstrated in this work that the synthesis of silicon nanocrystals by means of colloidal solutions is a technique very cheap and so good for controlling the Si-ncs size. By the XRD technique, it was possible to observe the Si-ncs obtained in the colloidal solutions. The AFM images depicted that the colloidal solutions with Si-ncs deposited on silicon have roughness, and it was observed that the Si-ncs possess a process of agglomerations, but it is indubitable that Si-ncs are present. The HRTEM images showed that colloidal solutions with Si-ncs have different agglomerations which exhibit a variable number of such nanocrystals depending on the solvent type. The Si-ncs sizes were possible to obtain in these images, and also, it was possible to observe a clear influence of the solvent type used in the solution. In this study, we were capable of controlling the Si-ncs size without having to use another technique more expensive. Finally, we confirmed the existence of core/shell type particles generated by the oxidated layers formed around the nanocrystal surface, such event may be controllable provided that the appropriate oxidant is selected, in this case the suitable solvent.

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Conflict of interest

The authors declare that they have no competing interests.

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