Size-selecting effect of water on fluorescent silicon clusters

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Abstract

Silicon clusters were produced by gas aggregation in vacuum and co-deposited with water vapour onto a cold target where the water vapour froze. Melting of the ice yielded fluorescent silicon nanoparticles suspended in water which were investigated by photoluminescence spectroscopy (PL) and atomic force microscopy (AFM). The PL spectrum showed a prominent band at 420 nm and other, less intense bands at shorter wavelengths. No fluorescence was observed below 275 nm. The shortest wavelength observed was related to a silicon cluster diameter of 0.9 nm using a simple particle-in-a-box model. Drops of the suspension were also deposited on freshly cleaved HOPG and investigated by AFM. The images showed single and agglomerated clusters with heights of typically 0.6 up to 2 nm. The sizes displayed by our measurements are not correlated to the average sizes that result from gas aggregation, indicating a size-selecting effect of the water suspension. The cluster–cluster interaction in water is governed by repulsion due to thermal energy and attraction due to van der Waals forces. For very small clusters repulsion dominates; at 3 nm diameter the two forces are balanced. We identify this stable phase of small clusters as the origin of exceptionally stable fluorescence. (Some figures in this article are in colour only in the electronic version)

1. Introduction

The specific material properties of crystalline silicon provide a number of advantages responsible for its wide use in semiconductor industries and photovoltaics. Its indirect bandgap, however, is a fundamental obstacle to using crystalline silicon in fluorescence applications. The situation changes on the nanometre scale. Nanoparticles do not possess translational symmetry and silicon therefore turns into a quasi-direct semiconductor that is able to emit light. This phenomenon was first demonstrated by Canham [1, 2] for porous silicon, followed by numerous other examples of nanostructured forms of fluorescent silicon [3–14]. While the prospect of being able to combine microelectronic performance and luminescent activity within the same material is one of the main driving forces in this field of research [15–17], there is increasing interest in using fluorescent silicon nanoparticles for bio-labelling [18] and marking in medical diagnostics and therapy because they are regarded as harmless and bio-compatible. They represent a promising alternative to commonly used fluorescent quantum dots, such as CdTe, as these cannot be used for in vivo applications because of their toxicity [19]. An important aspect is how silicon nanoparticles interact with an aqueous environment because of its biomedical relevance. Generally, water is expected to quench fluorescence because of its dense vibrational spectrum. Also, the interaction with water chemically modifies silicon nanoparticles and, as a consequence, its fluorescence activity degrades [20–23].

We have recently reported on a new production method for fluorescent silicon nanoparticles in water in which silicon clusters are produced in a molecular beam in the gas phase and then co-deposited with a beam of water vapour onto a cold target [24–26]. After deposition the ice is melted which produces a suspension of nanoparticles in water. When illuminated with UV light the liquid fluoresces in the deep blue spectral range. A remarkable feature of the nanoparticle suspension is its optical stability; surveying the fluorescence intensity over more than a year showed a constant fluorescence intensity [25]. Common approaches of achieving stability against degrading of light emission in water involve passivation of the surface with ligands [20–23]. The fact that samples produced by our method achieve exceptional optical
activity without requiring this treatment is very promising for applications, for instance in biomedicine.

The aim of our paper is to elucidate the specific properties that are responsible for this stability. Our focus will be on the size of the nanoparticles. We analyze photofluorescence (PL) spectra using a simple quantum confinement model and compare the findings with atomic force microscopy (AFM) measurements of the heights of nanoparticles that have been deposited on highly oriented pyrolytic graphite (HOPG) by drying the solution. Surveys of large areas of the covered HOPG substrates reveal height distributions around 1.0 nm with maximum heights of 2 nm. This size matches with the findings of our fluorescence data analysis and we conclude that the deposited clusters are identical with the ones that emit light in the solution. Both the fluorescence properties and the narrow size distribution of the deposited clusters show that the sizes are independent of the production conditions of the silicon clusters in the molecular beam, suggesting that the presence of water has a size-selecting effect.

2. Experimental method

The production of the nanoparticles has been described in previous publications [24, 25] and here we give only a brief summary. Silicon clusters were produced in a UHV apparatus by Ar-ion DC sputtering of a p-doped Si target at 80 K at pressures between 1 and 25 mbar. In the Ar atmosphere the Si vapour condensed into clusters, their size depending on the pressure. To produce small clusters He was added as the aggregation gas because the lower mass causes less energy being transferred in collisions with the Si atoms, resulting in slower growth [24]. The clusters then flowed through a differential pumping stage into a chamber where the flux could be measured using a crystal thickness monitor (XTM) mounted on a linear drive which could be moved in and out of the cluster beam. Further downstream, the clusters flowed into another chamber where they hit a liquid-nitrogen-cooled stainless steel target. A capillary was directed at an angle towards the target to allow a beam of water vapour to be co-deposited. Deposition typically lasted 30 or 60 min. Thereafter, the chamber was vented with 99.995% pure nitrogen gas and the target was warmed, whereupon the ice melted and dropped into a dish. The liquid suspension was filled into a quartz cuvette and investigated in a photoluminescence spectrometer (Jobin-Yvon FluroMax-P).

As our set-up did not allow simultaneous flux measurement and deposition it was difficult to produce samples of clusters with different sizes in a systematic way because we observed strong fluctuations in the deposition rate. We investigated the size distribution resulting from different Ar/He ratios in the aggregation chamber [24]. The mean diameters varied between 5.5 and 10 nm but, because of the fluctuations, these sizes can only serve as a qualitative estimate. For the same reason we cannot give an account of the nanoparticle density in the liquid. The difficulty of unstable sputtering of silicon targets was also reported by others [27].

Silicon clusters that had been directly deposited on a glass substrate did not show any fluorescence so we knew that the interaction with water was critical [24, 25]. To record AFM images of the nanoparticles after they had interacted with the water we cleaved a crystal of highly oriented pyrolytic graphite (HOPG) with adhesive tape and placed a drop of the fluorescent liquid sample into the centre of the freshly cleaved crystal. Subsequently, we inserted the crystal into the load lock of the vacuum chamber and dried the sample in vacuum. The sample was then transferred into a variable-temperature AFM/STM (Omicron VL2). By using this simple sample preparation method the nanoparticles remained practically uncontaminated during their transfer into UHV. AFM images were recorded at room temperature in the non-contact-AFM mode (NC-AFM) using a silicon tip (NSC from Mikromasch) with a resonant frequency of 307 kHz and a nominal stiffness of 40 N m⁻¹.

3. Results

3.1. PL spectra

We recorded PL spectra of four liquid samples at various excitation energies. Figure 1 shows three representative spectra, recorded at 308, 270 and 240 nm excitation wavelengths. A prominent fluorescence band is observed in all spectra peaking at 420 nm for 308 and 240 nm excitation energy, but with a slightly shifted maximum at 430 for 270 nm excitation. The band is most intense for excitation at 308 nm.

![Figure 1. Fluorescence spectra of silicon nanoparticles suspended in water recorded at three different excitation wavelengths. For comparison the UV/VIS absorption spectrum as reported earlier [25] is shown (dotted line). The intensity scale for this spectrum is in arbitrary units. The sharp lines are first- and second-order water Raman and Rayleigh lines (see [24]). The spectra have not been corrected for the different spectral excitation intensities. The sample used to obtain all three spectra was the same.](image-url)
of He excitation wavelengths of three further samples where the ratio \( \frac{\text{He}}{\text{Ar}} \) with an He/Ar ratio of 1.4; the total aggregation pressure of sample 3 was 28 mbar. For sample 2 the total aggregation pressure was as high as for sample 1, but the He/Ar ratio was 1. Despite the different He/Ar ratios and different aggregation pressures the differences in the spectral features are small. Figure 2(A) shows almost identical spectra, the only difference being the intensity of the 420 nm band. Samples 1 and 3 were produced at the same He/Ar ratio and the maximum of the 420 nm band in figure 2(B) is in both cases at the same wavelength, but we will later see that this correlation is perhaps coincidental. The maximum fluorescence of the spectrum of sample 2 in figure 2(B) is slightly shifted towards shorter wavelengths. For all spectra an onset region of the fluorescence from 275 to 285 nm can be identified. We have also excited our samples at shorter wavelengths (220 and 200 nm), but also in these cases there is no fluorescence at wavelengths shorter than 275 nm.

3.2. AFM images

Figure 3 shows an AFM image taken in NC-AFM mode (\( \Delta f = -50 \, \text{Hz} \)) of a nanoparticle sample on HOPG that was prepared as described above. Many clusters are agglomerated to chains or to islands. A few clusters are isolated. The sample was prepared from a small drop that was extracted from the upper part of a bottle that was at rest for some days. The image shows regions covered with clusters and clean graphite, with a step. Other images were recorded from samples that were prepared after the bottle was shaken. The AFM images of these samples (not shown) show a higher concentration of nanoparticles, with regions where the HOPG surface is completely covered. Also in these samples single clusters can be identified.

We have measured height profiles of two single clusters and the monatomic step to assess the tip resolution. Two step profiles, A and B, were recorded under an angle of \( \sim 30^\circ \) with respect to the normal incident axis. The profiles show a step length of 5 nm corresponding to 4.3 nm in the normal incidence direction. We assume that the real step length is not larger than the height of an HOPG layer, which is 0.335 nm [28], and attribute the lateral extension of the image to the convolution of the signal with the image of the AFM tip. The apex of the tip has a diameter of approximately 8.6 nm. This value can be taken as our lateral resolution.

The height of the single cluster in figure 3 is 1.1 nm and the width is about 8 nm. This relation between width and height for a single cluster was found throughout the sample. Also the chains showed a minimum height of 7 Å and a minimum width of about 8 nm. As the lateral resolution is limited by the tip it is clear that the profiles do not reflect the cross sections of the nanostructures. It is possible that the clusters have a flat, disc-like structure, but it is more likely that the smallest clusters have a spherical or at least a half-spherical shape because the interaction with HOPG is weak [29–32]. Therefore, we make the approximation that the measured height is reasonably close to the diameter, at least not smaller than the radius of a supposedly spherical/half-spherical cluster. The measured heights of each cluster are identical in the trace and retrace image within a range of 0.6 Å which defines the height resolution of our measurement.

Figure 4 shows a survey over a 400 \( \times \) 400 nm\(^2\) region on a different sample. In this case, 10 \( \mu \text{l} \) of the original bottle was diluted in 200 \( \mu \text{l} \) of deionized water. After the bottle was shaken, a 5 \( \mu \text{l} \) drop was deposited on a clean HOPG surface. The AFM image shows clusters agglomerated to islands and a network of chains. The height distribution extracted from figure 4 displays two peaks, the first peak being assigned to the HOPG substrate and the second to silicon clusters. The
Figure 3. AFM image. (A) and (B) height profile along a monatomic step on the HOPG. (C) and (D) height profiles of a cluster sitting on the step. (E) Same for a cluster sitting on an HOPG terrace.

Figure 4. AFM survey of a 400 nm × 400 nm section (left) of the sample showing height distributions (right). The peak at 0.32 nm is assigned to the HOPG substrate, while the peak at 1.39 nm is assigned to silicon clusters. The widths of the peaks are 0.21 and 0.53 nm, respectively.

difference between the peak maxima reveals an average cluster height of 1.1 ± 0.3 nm, which is close to what we found to the single cluster in figure 3. The height distribution width of the silicon clusters is obtained after subtraction of the substrate width distribution.

We note that the agglomerates of clusters on HOPG seen in figures 3 and 4 are very likely due to the rapid drying process when the drops evaporate in vacuum. The fact that the clusters are agglomerated into two-dimensional structures on the surface does not affect our assessment of the cluster size.

4. Discussion

Figure 1 shows that the peak position of the 420 nm band varies little with the excitation energy. The band is Lorentz-shaped and its spectral width (fwhm) does not change either. This is typical for discrete localized transitions. Regardless of what states are populated in the photoexcitation process energy is transferred radiationlessly to the emitting state. Light emission at 420 nm is a known phenomenon for colloidal suspensions of silicon nanoparticles [33] and silicon nanocrystal films [34], as
well as from silica defects [35–38]. Two possibilities exist: the 420 nm luminescence stems from structural defects that are present in the ground states and in the excited state. A candidate is the $T_1 \rightarrow S_0$ transition of twofold-coordinated Si in SiO$_2$ (O–Si–O). This possibility would straightforwardly explain why the luminescence is only observed after treatment with water in the co-deposition process because the water causes oxidation of the silicon at the surface. The other, weaker bands that are seen at shorter excitation wavelengths are difficult to assign because they are merged with the 420 nm band and one cannot judge whether the band wavelengths are stationary. It is plausible that they also belong to defects. A second possibility is that the silicon nanoparticles undergo structural rearrangement in the excited states and that the luminescence originates from relaxed structures. Such a mechanism would explain the observed Stokes redshift between excitation and luminescence emission [33]. The effect is only expected for small nano-clusters. Larger nanoparticles are too rigid to permit local relaxation of the crystal structure. Our assignment to defect luminescence is further corroborated by the minor variations in the spectral features observed when different samples are investigated (figure 2). One would expect that chemical interaction would, on average, produce similar types of defects, which explains why the fluorescence features are overall similar amongst different samples. Since the water interacts with the surface of the silicon clusters the fluorescent SiO defects are located at the surface and our nanoparticles have an Si/SiO core–shell structure. Transfer of excitation energy from the bulk volume to the surface should become increasingly inefficient with increasing cluster size. This indicates that fluorescence is predominantly expected from small clusters.

We develop this interpretation further using a simple model based on quantum confinement. Quantum confinement relates to the quantum mechanical problem of particle-in-a-box states and is a popular concept for the interpretation of luminescence of nanostructured Si [3, 8, 39] that has been developed for both crystalline [40] and amorphous Si [41]. Usually, the model is applied to the light-emitting levels and predicts how these shift in energy with confinement length, but here we take a slightly different approach by considering the states that are excited in the first place and investigate how the energy gap spanned by the difference between ground and excited states varies with cluster size. We need to do this because our model assumes that the light-emitting levels are stationary. It is plausible that they also belong to structural defects and therefore fixed in energy. We can therefore derive a minimum energy of the bandgap which must be equal to the shortest fluorescence wavelength observed from our samples, because otherwise the light-emitting states cannot be populated. As all of our samples show a threshold wavelength of the fluorescence at 275 nm (4.5 eV) the bandgap cannot be populated. As all of our samples show a threshold from our samples, because otherwise the light-emitting states must be equal to the shortest fluorescence wavelength observed can therefore derive a minimum energy of the bandgap which relates to structural defects and therefore fixed in energy. We because our model assumes that the light-emitting levels are excited states varies with cluster size. We need to do this by the minor variations in the spectral features observed when different samples are investigated (figure 2). One would expect that chemical interaction would, on average, produce similar types of defects, which explains why the fluorescence features are overall similar amongst different samples. Since the water interacts with the surface of the silicon clusters the fluorescent SiO defects are located at the surface and our nanoparticles have an Si/SiO core–shell structure. Transfer of excitation energy from the bulk volume to the surface should become increasingly inefficient with increasing cluster size. This indicates that fluorescence is predominantly expected from small clusters.

Figure 5 shows a schematic of the energy levels and how the fluorescent states are populated. We note that the observation of a fluorescence-onset wavelength at 275 nm coincides with the optical absorption spectrum (UV/VIS) of the nanoparticles in water reported earlier (see the dotted line in figure 1). The transparent region in the absorption spectrum down to 320 nm and the rapidly increasing absorption below this wavelength [25] is further evidence for the existence of an energy gap. As the magnitude of the gap fits neither to bulk Si nor to bulk SiO it must be due to silicon nanoparticles. The onset of absorption at 320 nm shows that the size of the majority of nanoparticles in the suspension—whether they are luminescent or not—is smaller than 1.5 nm. The confinement size of 0.9 nm found by analyzing the fluorescence spectrum represents a upper size limit of a subset of these nanoparticles, that is, those that produce luminescence at 275 nm.

The spectroscopic analysis fits nicely to the cluster heights derived from the AFM images. The measured heights of a number of individual clusters as well as the height surveys vary between 0.7 and 2 nm with an average of approximately 1.1 nm. If we adopt the result of our quantum confinement model the clusters should have a silicon core of 0.9 nm in diameter. This would leave space for an incompletely filled shell of SiO. Li and co-workers found that even the presence of a single doubly bond oxygen site has a stabilizing effect on the fluorescence of silicon clusters [42]. We also note that the quantum confinement model assumes infinitely high potential barriers which does not reflect the real situation, in particular the interface between Si and SiO.

All samples produced by our co-deposition method are stable and show fluorescence over time periods of more than a year (figure 6). Our results show that our apparatus produced in all experiments a sufficiently large quantity of 1.1 nm large clusters, regardless of how the gas aggregation production
parameters were set. We recall that the blueshift of the 420 nm band of sample 2 in figure 2(B) indicates smaller clusters than the spectrum of sample 1, but the gas aggregation production conditions were such that the sizes should relate in the opposite way. This finding suggests that sizes prior to co-deposition are negligible and that the presence of water has a size-selecting effect.

We propose a model of size-dependent agglomeration in water. In liquid water the silicon nanoparticles may agglomerate if their mutual attraction is larger than their thermal energy [43]. At room temperature the thermal energy is 25 meV. The van der Waals attraction between macroscopic bodies can be described by the Hamaker theory [44]. The attractive van der Waals energy $E$ between two spheres of diameters $D_1$ and $D_2$ is given by

$$E = -\frac{H D}{24 z}$$  \hspace{1cm} (1)

where $H$ is the Hamaker constant for silica–silica attraction in water, $0.46 \times 10^{-20}$ J [45], $D = \frac{D_1 D_2}{D_1 + D_2}$ is the reduced diameter and $z$ is the distance between the two objects. As a first approximation for $z$, we consider a value of 0.3 nm, which corresponds to the typical distance of van der Waals interaction. Figure 7 shows the evolution of $E$ with $D_1$ for different values of $D_2$. The van der Waals energy is compared to the thermal energy (grey dotted–dashed line). This simple estimate shows that, in the case of identical clusters (i.e. $D_1 = D_2$) (black line), the thermal energy of clusters smaller than 6.2 nm always exceeds the van der Waals attraction. However, clusters smaller than 6.2 nm can still agglomerate if they interact with larger clusters. The blue dotted line corresponds to the limit when $D_2 \gg D_1$. This gives a size limit of 3.1 nm. The limit of 3.1 nm is already reached for $D_2 = 100$ nm (red dashed line). We note that this limit is in good agreement with the height distribution shown in figure 4, since the maximum height is somewhat more than 2 nm. We note further that in our estimate the greatest uncertainty arises from the distance between the two clusters. For a distance of 1.2 Å instead of 3 Å, corresponding to the typical distance where the Pauli repulsion occurs, the ‘equilibrium diameter’, i.e. the size limit, would decrease to 1.2 nm. This shows that even in this limit a constant fraction of small clusters remains dissolved in the suspension. It is therefore very likely that the 1 nm small clusters are those that fluoresce because it explains straightforwardly the long-term stability.

We finally discuss why the cluster sizes are independent from the production conditions of the gas aggregation cluster source. The gas aggregation technique never produces mono-disperse clusters. One is only able to shift the mean value of a distribution of cluster sizes by changing the production parameters. Under all conditions the molecular beam is accompanied by silicon atoms and small clusters. We believe that the small clusters are responsible for the formation of fluorescent silicon clusters. This can happen when small clusters are co-deposited with the water vapour or when silicon atoms deposited into the ice matrix start to agglomerate when they gain mobility once the ice melts.

In summary, we have produced fluorescent Si/SiO$_2$ nanoparticles in water. The suspension shows exceptional long-term optical stability. Analysis of the photoluminescence and the cluster heights measured after deposition on HOPG show that the nanoparticles in suspension have a very narrow size distribution for which we can find an upper size limit of $\sim$2.5 nm. We interpret our findings in terms of a simple model that relates the thermal energy of dissolved particles in water to their mutual van der Waals attraction. Our model suggests that (i) nanoparticles of 1 nm in diameter and smaller are a stable phase in water. They do not agglomerate because their thermal energy is larger than their size-dependent van der Waals attraction. (ii) Only this phase of very small nanoparticles in water fluoresces. Our work shows that depositing nanoparticles in liquids may provide a general route for obtaining size
selection. Further applications, for instance in catalysis, might be possible.

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References

[20] Li Z F and Ruckenstein E 2004 Nano Lett. 4 1463
[23] Borsella E 2010 Nano Lett. 10 26102