Fluorescence of Silicon Nanoparticles Suspended in Water

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Following the discovery of intense fluorescence of porous silicon [1] there is recent interest from the semiconductor industry to implement silicon light emitters in integrated electronic circuits. This interest stems from the ongoing miniaturisation of integrated circuits which has reached a size regime where serious performance losses due to signal transmission delay are expected. These delays are caused by the increasingly longer interconnects in high-density integrated electronic circuits and it has therefore been suggested to replace electric signal transmission by optical transduction [2]. A second, similarly important, field for application of fluorescent silicon nanoparticles are thin film solar cells. These types of cells use only a limited fraction of the solar light spectrum and to improve their conversion efficiency it has been suggested to employ fluorescent nanoparticles to down-convert ultraviolet light into a wavelength to which the solar cell responds to [3].

The present paper is motivated by these needs. Our method to achieve luminescent silicon is to generate quantum confinement using cluster beams because the degree of confinement can be controlled by changing the average cluster size. Free silicon clusters are known to exhibit dangling bonds that quench fluorescence and therefore we passivate the cluster surface in a second step. In first experiments silicon clusters have been co-deposited with water onto a cold target. Melting of the ice yielded a suspension that fluoresces in the deep-blue when excited with UV light. The silicon nanoparticles produced in this way show a number of remarkable properties, for instance, their fluorescence remains stable in intensity for more than a year [4]. In this paper, we report on the spectroscopic characterisation of the nanoparticles. We observed water Raman emission and we found that the intensity of the Raman lines were enhanced by the presence of nanoparticles.

Experiment

Here, we give only a brief description of the experiment. Silicon clusters are produced in a gas-aggregation source in a He/Ar atmosphere using DC sputtering of a doped silicon target. The silicon clusters fly through a three-stage aerodynamic lens system and a differential pumping stage into a UHV chamber where they are co-deposited with water vapour onto a liquid nitrogen cooled target. Typical deposition times are 30 minutes. Thereafter the target is heated up to room temperature whereupon the ice layer melts and drops into a dish. The liquid suspension is then bottled and investigated by photo-fluorescence spectroscopy. More details and a schematic of the experiment are given in ref. [4] and ref. [5].

Results and Discussion

Figure 1 shows fluorescence spectra of the liquid samples recorded at different excitation wavelengths. The most prominent band is located at 420 nm. The intensity maximum varies slightly in wavelength within 20 nm between different samples as well as with age of the samples. Fresh samples show the band maximum shifted to somewhat shorter wavelengths and also a rugged structure on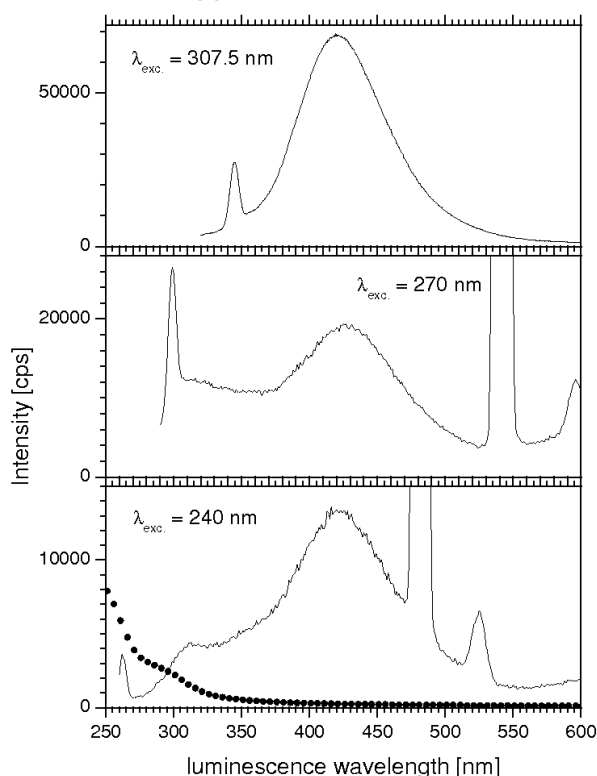 the short wavelength side from the maximum. We also recorded photo luminescence excitation (PLE) spectra for the 420 nm emission (shown elsewhere [4]). The PLE spectrum shows that the 420 nm emission is most efficiently excited at a wavelength of 307.5 nm. When excited with shorter wavelengths additional bands emerge between 320 and 380 nm. We note, that further to these bands, sharp lines are observed at 480 and 540 nm in two of the spectra in figure 1. These lines are the second order of the Rayleigh line of the excitation light that becomes scattered by the nanoparticles and the silica cell. Other sharp features are observed at 345, 300 and 260 nm, respectively. At longer wavelengths the second order of these lines are also visible. These lines are due to Raman emission of water and will be discussed later.

Fig. 1: Fluorescence and UV/VIS (dots) spectra

We assigned the fluorescence at 420 nm to the $T_1 \rightarrow S_0$ defect fluorescence of twofold coordinated silicon in (O-Si-O) in a SiO_2 layer at the surface. This assignment is based on the similarity with the peak wavelengths of the well-known defect luminescence of bulk SiO_2 reported in the literature and also on the fact that the rugged features of the fresh samples change into a smooth band with time, which is indicative for a defect-healing process. No fluorescence is observed below 275 nm. This cut-off at short wavelengths coincides well with the onset of UV/VIS absorption which is shown in figure 1 as filled circles (note that the intensity scale does not apply to this spectrum). This behaviour would be expected for particles with a band gap energy corresponding to 275 nm. Bulk SiO_2 has a much larger band gap energy than 4.5 eV and thus we interpret our observation as showing the presence of a silicon core. Quantum confinement is well known to increase the effective band gap energy and according to theoretical work the diameter of the core should be approximately 1.5 nm [6,7].

Fig. 2: *spectrum of diluted sample*

In the following we will discuss the sharp lines on the short wavelength side of the prominent fluorescent band. In contrast to the 420 nm fluorescence these lines shift with the excitation energy and have been assigned to Raman Stokes emission of water. The energetic difference between the wavelength of excitation at 307.5 nm and the Stokes line at 345 nm is 3535 cm^{-1} and this value is close to the v_1 symmetric stretch vibration of water in the gas phase (3657 cm^{-1}, [8]) and in the liquid pha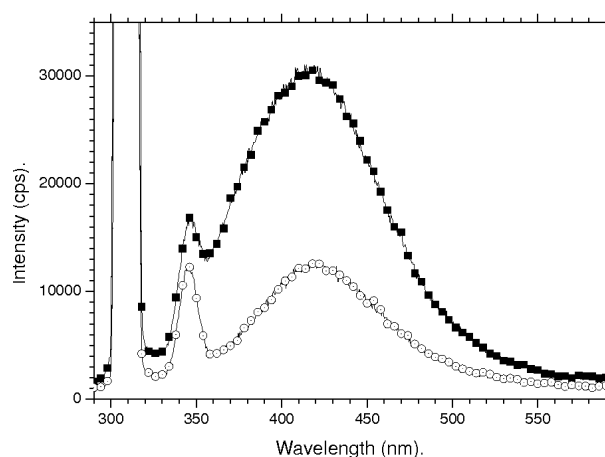se (3280 cm^{-1}, [9]). The difference between liquid and gas-phase frequencies results from the additional coupling of the O-H stretch vibration to hydrogen bonds in the liquid and the fact that the frequency of the Stokes line of the nanoparticle suspension lies between those two values can be explained by a reduced water-coordination of those water molecules that are adsorbed at the surface of the nanoparticles.

A remarkable observation is that the intensity of the Raman line is correlated with the concentration of the silicon nanoparticles. Figure 2 shows the emission spectrum for 307.5 nm excitation (solid squares) together with the spectrum of the same sample, but diluted with water by a factor of 10 (open circles). It can be seen that with increasing nanoparticle concentration the Raman intensity rises. Enhancement of Raman emission is a well-known effect for molecules adsorbed onto rough metal surfaces. Recently, SERS from non-metallic surfaces was reported [10] and exp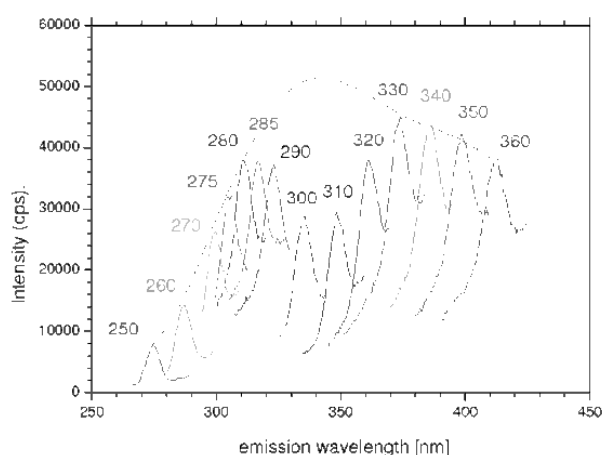lained by charge transfer from filled adsorbate levels to empty InAs/GaAs quantum dot levels. Here, we observe an enhancement effect due to the presence of nanostructured semiconductors as well, however, the effect is caused by the oscillators involved in the fluorescence process. In a previous publication we pointed out that the fluorescence evolves in different steps, notably by excitation of excitons located at the Si/SiO$_2$ interface followed by an energy transfer to the defected fluorescent SiO$_2$ sites [4].

Figure 3 shows a series of Raman spectra recorded for the same sample but with different excitation energies. The line intensity increases

Fig. 3: *Raman spectra*

with decreasing excitation energy, passes through a maximum with a dip for excitation energy of 307.5 nm, and decreases at longer excitation wavelengths. To better visualise the intensities the envelope of these curves has been marked by a dotted line. This envelope shows that the Raman intensity becomes enhanced when the excitation energy approaches values where the fluorescence is maximum.

The dip around the maximum fluorescence excitation is probably a consequence of the coupling between the two relaxation channels. Within the electronically excited nanoparticles the two relaxation channels compete and ultimately the fluorescence is more efficient. The fact that the envelope of the Stokes line intensities in figure 3 follows the PLE spectrum [4] shows that the origin of the enhanced Raman emission is very likely linked to the field of the oscillators that are involved in the fluorescence process, presumably the state that is excited by the absorption of 307.5 nm photons in the first step. This effect may have more general implications for the assessment of radiative and non-radiative relaxation processes.

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