High-precision determination of silicon nanocrystals: optical spectroscopy versus electron microscopy

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Abstract

We evaluate different approaches to determine the diameter of silicon nanoparticles in the regime of ultra-small particle sizes \(d < 5 \text{ nm}\). The nanocrystals are fabricated using a plasma-enhanced chemical vapor deposition (PECVD) process and are embedded in a matrix of SiO\(_2\). For characterization, different experimental techniques can be used, ranging from optical measurements such as photoluminescence or nonlinear optical response over transmission electron microscopy. An extensive analysis leads to a high-precision size determination and a good agreement between most of the techniques. Apart from the particle size, additional information can be derived depending on the method of choice, such as exciton fine structure splitting energy, width of the particle size distribution etc. While the nonlinear signal shows the expected enhancement for smaller nanoparticle sizes, it turns out to be inadequate for determination of particle sizes with a high accuracy.

Keywords: silicon nanocrystals, silicon nanoparticles, photoluminescence, size determination, band gap, excition

(Some figures may appear in colour only in the online journal)

1. Introduction

Silicon is one of the most important semiconductor materials in both microelectronics [1–3] and photovoltaic technology [4–6]. The great advantages of silicon are that it is low-priced, abundant and non-toxic. At the same time it shows excellent electronic properties, such as—among others—high conductivity by doping. By reducing the size of silicon crystals down to the nanometer range, additional highly interesting properties can be achieved, such as efficient optical emission [7, 8], tailoring of the band gap energy [9] and control over vibronic states [10, 11].

Since the 1980s, there has been continuing interest in nanocrystals. In 1981, the first paper on the quantum mechanical confinement in nanocrystals was published, demonstrating a blue shift of exciton absorption lines in microscopic crystals [13]. In addition, efficient light emission in the visible and near infrared spectral region was discovered in both silicon nanocrystals [14–17] and porous silicon [18–20]. Since then, nanocrystal research has grown enormously. By reducing the size of the crystals to a few nanometers, a large number of new features is revealed that are still not fully understood in detail. Due to the reduction of the crystal size, the electronic states become localized and the momentum distribution gets spreaded. This is a consequence of the Heisenberg uncertainty principle, so the nanocrystals become quasi-direct [21–24], resulting in a higher probability of radiative recombination. Silicon nanoparticles embedded in thin films of SiO\(_2\)/Si\(_3\)N\(_4\) are of great interest due to their compatibility with planar technology as used for silicon-based photonics [25]. However, for such particles, size-control cannot be achieved by classical techniques which are well-established such as the
The silicon nanocrystals (NCs) used in the present study are fabricated in multiple, separated layers by a PECVD process. The layer stack consists of 40 alternating layers of SiON and SiO\textsubscript{2} and a cladding and capping layer of 10 nm SiO\textsubscript{2} (figure 1(a)).

The overall thickness is 435 nm in one sample and 271 nm in the second sample. The overlayer matrix of SiO\textsubscript{2} serves as a diffusion barrier for the Si atoms in the SiO\textsubscript{2} layers, a chamber pressure of 450 mTorr, a total gas flow of 535 sccm and a ratio between N\textsubscript{2}O and SiH\textsubscript{4} of three are applied. Here the growth rate is 0.31 nm s\textsuperscript{−1}. Due to the low gas ratio, the content of nitrogen is increased to 17%–21%. This nitrogen content was validated experimentally using EDX. To assemble the silicon nanocrystals in the SiO\textsubscript{2} layers, a high-temperature treatment in a tube furnace at 1150 °C or 1200 °C for 60 min under nitrogen atmosphere is applied [31]. Due to the high temperature, the silicon in the silicon-rich SiO\textsubscript{2} layers can diffuse and cluster together to form small silicon crystals (figure 1(b)).

3. Size-dependence of the band gap

Effects due to electronic quantum confinement in silicon nanoparticles have been observed for particles with diameter \(d \leq 10\) nm [9, 34]. Obviously, it is possible to exploit this dependence in order to determine the particle size. However, for high-accuracy size determination, the size-dependence of the band gap has to be known as precisely and reliably as possible. In order to fit results from optical spectroscopy, an easy-to-handle empirical approximation for the band gap is required. Therefore, we conduct a thorough review of published experimental and theoretical results for the band gap of silicon nanoparticles.

Belyakov [12] and Delerue [35] proposed two different simple analytical equations for the size dependence of the optical band gap. Belyakov suggests the equation:

\[ E_{\text{gap}}(eV)(R) = \sqrt{\frac{\Delta \varepsilon_x(eV)^2 + 4.8}{R(nm)^2}}, \]  

where \(E_{\text{g}} = 1.24\) eV is the \(\Gamma - X\) energy difference of bulk silicon. Delerue suggests to use a simple power law dependence:

\[ E_{\text{gap}}(eV)(R) = E_{\text{g}}(eV) + \frac{3.73}{[2R(nm)]^{1.59}} \]

The size-dependence resulting from these two equations is shown as solid lines in figure 2 together with different results from experiment (lower part of the figure) and theory (upper part).
Figure 2. (a) Comparison between different analytical and numerical models to calculate the size dependent band gap of a silicon nanocrystal. (b) Comparison between different experimental data for the nanocrystal band gap and the calculation model from Delerue [35].

Firstly, we consider results from different numerical methods like density functional theory (DFT) [36, 37], pseudopotential method (PP) [38, 39] or tight-binding models (TB) [40, 41] to determine the band gap of the nanocrystals (figure 2(a)). From the figure, it can be seen that due to its computational effort, DFT results are limited to smaller particle sizes than pseudopotential or tight-binding methods. Weissker et al [36] use a Δ-self-consistent field DFT approach, which underestimates the excitation energies, especially for larger particles. In figure 2(b), experimental data from this work and other sources are shown [42–44], together with equations (1) and (2). The figure shows that for particles with diameters between 2 nm and 4 nm, the experimental values from all sources are very close and in excellent agreement with both empirical equations. Only for the smallest particle sizes a slight deviation from the suggested equations is found. Taking into account both the experimental and theoretical data in figure 2, it can be concluded that both Belyakov’s and Delerue’s empirical approach describe the size-dependence of the band gap with sufficient accuracy in the size regime under consideration. Due to the fact that the simple power law suggested by Delerue is easier to handle numerically, we will use this equation in the following for the optical band gap of Si nanocrystals.

Additionally, we have performed electronic state calculations for the valence band to estimate the influence of the surrounding matrix. The nanocrystals investigated here are located in a matrix that consists of non-stoichiometric SiON and can be described by a linear composition of about 80% SiO₂ and 20% Si₃N₄. From the calculations, we can conclude that the impact of the SiON matrix on the interband recombination of the Si nanocrystals is for the smallest particles (d ~ 2 nm) in the range of 20 meV to 40 meV when compared to isolated particles in vacuum. The impact decreases for increasing particle size. The effect is therefore considerably smaller than the energy spreading caused by the size distribution of the particles and the phonon broadening.

4. Transmission electron microscopy

The nanocrystals are studied by energy-filtered and high resolution transmission electron microscopy at 80 kV acceleration voltage on conventionally thinned cross-sectional TEM samples. Higher acceleration voltages of up to 200 kV cannot be used, because the NCs are not stable at that voltages. With HRTEM images, it is possible to achieve such a high resolution that the nanocrystals with sizes of 3 nm to 4 nm can be displayed. Two exemplary images in which nanocrystals can be found are shown in figure 3, where in (a) the original HRTEM data are shown and in (b) a Fourier-filter algorithm, background subtraction and contrast enhancement are used. In high-resolution transmission electron microscopy, only particles that are oriented with high-symmetry directions in parallel to the electron beam can be imaged.

Here, the signal from the volume plasmons of silicon bulk valence band [≈17.0(2.5) eV] is detected and used for image formation. This allows for the visualization of the distribution of silicon NCs in the sample and their distinction from the surrounding SiO2 which has a bulk plasmon of 25 eV. From the resulting images, the size of the silicon nanocrystals can be measured with an experimental uncertainty for the diameter of about ±0.3 nm. The crystal size is determined for a large number of different particles and displayed in the histogram in figure 4. The size distribution follows well the fitted log-normal distribution [45, 46], as described by equation (3).

\[ \frac{dn}{d\bar{d}} = \left(\frac{2\pi}{\bar{d}\ln\sigma}\right)^{-1} \cdot \exp\left\{ -\ln^2(d/d_0)/(2\ln^2\sigma) \right\}, \]

where \( d_0 \) is the mean crystal diameter and \( \sigma \) the standard deviation. From \( \sigma \), the upper and lower deviations \( \Delta d_u \) and \( \Delta d_l \) are calculated using \( \Delta d_u = d_0 \cdot (\sigma + 1) \) and \( \Delta d_l = -d_0 \cdot (1/\sigma - 1) \). The resulting mean crystal diameter is \( d_0 = (3.70 \pm 0.81)/(-0.67) \) nm.

In the size regime of ultra-small particles considered here, with mean particles \( d < 5 \) nm, a symmetric particle size distribution function like, e.g., the Gaussian distribution, fails to accurately describe the experiment. A symmetric distribution cannot account for small particles that nucleate and grow from individual atoms but instead results in particles with negative diameters [45].

5. Room temperature photoluminescence

Furthermore, the size of the nanocrystals is determined via photoluminescence measurements at room temperature. For excitation, a He-Cd Laser (λ = 325 nm, \( P_{\text{exc}} = 5 \) mW) is used in a confocal setup. Here, the same approach as in [9] is used, which is also based on a log-normal distribution of the crystal diameters. In addition, another part of the fit function is the oscillator strength \( f_{\text{osc}}(\omega) \) [47] that links Fermi’s golden rule and the recombination time \( \tau_R \), which is also taken from
The band gap of nanocrystals after Delerue [35], equation (2), the size dependence of the oscillator strength $f_{osc}(\bar{d})$ can be obtained. In addition, the broadened spectral shape of the PL emission of a particle ensemble is required. Here, we assume that each individual nanocrystal acts like an inhomogeneously broadened emitter with emission intensity $I_{NC}$, peak emission energy $E_\gamma$ and spectral width $\Delta E$:

$$I_{NC}(\hbar\omega, E_\gamma, \Delta E) \propto \frac{1}{\Delta E} \exp \left\{ \frac{(-\hbar\omega - E_\gamma)^2}{(2\Delta E)^2} \right\}$$  \hspace{1cm} (4)

By combining the oscillator strength, log-normal distribution and PL emission of a single nanocrystal, we obtain a formula for a PL emission spectrum of a nanocrystal ensemble [9]:

$$I(\hbar\omega) = \int_0^\infty f_{osc}(\bar{d}) \frac{dn(\bar{d}, d_0, \sigma)}{d\bar{d}} I_{NC}(\hbar\omega, E_\gamma, \Delta E(\bar{d})) d\bar{d}$$  \hspace{1cm} (5)

This equation is used to fit the experimental PL data shown in figure 5(a) from the same sample as analyzed before by EFTEM. Also note that the broad PL emission is modulated by Fabry–Perot oscillations due to the overall high layer thickness of 435 nm.

The fit function is in good agreement with the experimental data. The mean crystal diameter, which is determined from the PL measurement is $(d_0 = 3.90 \pm 0.43/ -0.39)$ nm and the mean diameter obtained from the EFTEM measurement is $(d_0 = 3.70 \pm 0.81/ -0.67)$ nm. Both results agree with each other within the measurement accuracy. In the EFTEM measurement, the deviations from the mean size appear larger than in the PL measurement, due to possibly overlapping nanocrystal cross sections in the projection of EFTEM images. This overlap is due to the fact that the TEM specimen was between 17 and 34 nm thick and the center-to-center distance of Si NCs is in the order of 5 nm to 8 nm.

These results prove that the method suggested in [9]—together with the size-dependence of the oscillator strength—is valid not only for discrete particles formed heterogeneously from the gas phase but also for silicon particles formed by thermal precipitation in SiON films.

6. Temperature dependence of excitonic properties

The electronic and excitonic properties are examined via temperature-dependent photoluminescence spectroscopy. These measurements allow the determination of the ratio of the dark and bright excitonic radiative constants and the energy splitting between the excitonic states. While cooling down silicon nanocrystals, the intensity of the PL emission increases slightly down to a certain temperature, where the intensity reaches its maximum. When the cooling is continued, the intensity of the emission rapidly starts to decrease, almost showing no PL emission at all for 10 K [21, 50]. This behaviour is entirely different than for most other nanoparticle/quantum dot systems like CdSe [51] or InAs [52], where a monotonous increase in intensity is observed with decreasing temperature. The behaviour of the PL emission intensity can be explained by the excitonic fine structure [50]. The highest state of the valence band is the heavy hole...
Figure 5. (a) Layer deposition in a PECVD process at 375 °C and subsequent high-temperature treatment in a tube furnace. (b), (c) Experimental PL spectra and fit function of two samples with different SiON layer thicknesses. In (b) the spectrum is obtained after a high-temperature treatment at 1200 °C. The size of the nanocrystals is \( d = (3.9 + 0.43/–0.39) \) nm with \( \sigma = 1.1 \) and \( \Delta E = 0.017 \) eV. In (c) the smaller nanocrystals are formed in a temperature treatment at 1150 °C with \( d = (2.6 + 0.42/–0.36) \) nm with \( \sigma = 1.16 \) and \( \Delta E = 0.05 \) eV and the spectrum from bigger nanocrystals is recorded after an annealing at 1200 °C with \( d = (3.6 + 0.43/–0.39) \) nm with \( \sigma = 1.12 \) and \( \Delta E = 0.012 \) eV.

Figure 6. (a) Electronic band structure of nanocrystalline silicon. (b) Excitonic fine structure, where the upper excitonic state is called ‘bright’ and the lower one is called ‘dark’.

(figure 6(a)), with a total angular momentum of \( J_z^{hh} = \pm 3/2 \). The conduction band electron state has a total angular momentum of \( J_z^e = \pm 1/2 \). The resulting excitonic states can have total angular momentums of \( J_z^{exc} = \pm 2 \) (parallel) and \( J_z^{exc} = \pm 1 \) (anti-parallel). The latter states have a higher energy and are called bright states, due to their high radiative recombination rate. The energy separation is marked as \( \Delta \) and is caused by the short-range exchange interaction between electron and hole. The lower state is called dark state, because the radiative recombingation is prohibited. Both states can be described by different radiative constants \( R_1 \) (bright) and \( R_2 \) (dark). Due to the selection rules for the orbital angular momentum, the dark exciton should show no luminescence, thus \( R_1 \gg R_2 \) is expected. Because of the spin–orbit coupling, however, states are slightly mixed, consequently radiative recombination from the dark exciton is possible. At temperatures above the crossover point of 35 K [50], the PL emission is dominated by the bright excitonic transition with higher energy. With decreasing temperature, the relative occupation of the dark exciton states increases and dominates the PL emission. Thus, more photons are emitted by the dark exciton, but since the radiative constant \( R_2 \) is fairly low, the overall PL intensity decreases. The decrease in PL intensity can thus be explained by freezing out of the recombination of the bright exciton. In figure 7 experimental PL data are shown for different temperatures. As expected for silicon nanocrystals from 300 K down to 150 K the PL intensity increases, while a clear decrease of the intensity can be observed for lower temperatures.

Here the maximum intensity is achieved at 150 K, while other papers report a maximum at lower temperatures between 80 and 100 K [50, 53]. Possible reasons are stress caused by the SiON matrix surrounding the nanocrystals that affects the crystal symmetry and therefore acts on the electronic band structure. From the overall intensity of the temperature-dependent PL spectra \( I_{PL} \), the ratio of the radiative constants \( R_1/R_2 \) and the energy separation \( \Delta \) can be determined. We follow the approach of Brongersma et al [53], so the radiative recombination rate \( R_R \) is given by the PL intensity \( I_{PL} \) and the effective recombination rate \( R_{PL} : R_R = R_{PL} \cdot I_{PL} \). Besides, addition of the radiative recombination rate \( R_R \) and non-radiative rate \( R_{NR} \) gives the total recombination rate \( R_{PL} : R_{PL} = R_R + R_{NR} \) [53]. Thus, we obtain:

\[
I_{PL} = \frac{R_R}{R_R + R_{NR}} \tag{6}
\]

with the radiative recombination rate

\[
R_R = \frac{2R_2 + 2R_1 \cdot \exp(-\frac{\Delta}{kT})}{2 + 2 \cdot \exp(-\frac{\Delta}{kT})} \tag{7}
\]

The measured PL data are fitted with equation (6), with the assumption that \( R_{NR} \) depends linearly on the temperature [53]. The ratio of the radiative constants is \( R_1/R_2 = 158 \). A finite ratio is determined because the dark and bright excitonic states get slightly mixed, so the radiative recombination is
The ratio was determined to be $R_1/R_2 = 8$, which deviates stronger from the selection rule argument. This low ratio of the radiative recombination rates is explained by the fact that both the transition of the dark exciton and the transition of the bright exciton require a phonon to ensure momentum conservation, since silicon is an indirect semiconductor. However, the nanocrystals investigated in this work are significantly smaller than the nanocrystals studied in the work by Lüttjohann et al [50], suggesting that the nanocrystals have a quasidirect recombination channel, thus the radiative recombination of the bright exciton can take place without involvement of a phonon, as suggested as well by Kovalev [21]. This significantly increases the probability for radiative recombination compared to the dark exciton. Due to the different ratios of $R_1/R_2$ it can be explained that the splitting between the excitonic states is larger in this work, namely $\Delta = 13.6$ meV as compared to $\Delta = 5.8$ meV in [50]. Thus, a larger energy separation between the excitonic states causes a shifting of the intensity maximum to higher temperatures. The energy splitting $\Delta$ determined in this work is consistent with the experimental data and the theoretical considerations of Cullrott [19]. The experimental data are examined from a fit to the temperature dependence of the lifetime of the slow band and the calculations were done with an effective-mass approximation. With help of the diagram of these methods the energy splitting can be used to determine the photon energy ($E = 1.78$ eV with the experimental approach and $E = 1.71$ eV with the experimental data). By utilizing the equation of Delerue [35], the mean size of the nanocrystals can be obtained to $d_0 = 3.49$ nm and $d_0 = 3.75$ nm. The values obtained from the fine structure energy splitting deviate only little from the PL data ($d_0 = 3.6$ nm) by 3.1% to 4.2%. Consequently, the result obtained by energy splitting is consistent to other works and can also be used as a reliable size determination.

7. Nonlinear response

For the nonlinear PL measurements an optical parametric oscillator (OPO) pumped by a Ti:sapphire laser is used to excite the samples with an excitation wavelength of 1200 nm. The samples are examined with a power-dependent measurement in transmission geometry, where the laser radiation enters the sample the substrate side. A bare silicon substrate and two layer stacks after high temperature treatment at 1150 °C and 1200 °C are studied (PL data in figure 5(b)). Figure 8 shows the overall intensity of the second and third harmonic generation (SHG and THG) peaks.

The THG intensity is expected to be in the same order of magnitude for all the analyzed samples, since it is generated from almost any material and shows a cubic dependence on the excitation intensity, because it is a third order nonlinear process. Deviations in the intensities can occur due to variations of the focus point on the sample. It can thus be demonstrated that all studied samples produce THG and the intensities are of the same order of magnitude. In contrast to THG, SHG light is solely generated in non-centrosymmetric crystals and at surfaces or interfaces due to the reduced symmetry. Since silicon is a centrosymmetric crystal, the SHG in the substrate can only be generated due to the symmetry-breaking at the interface. In the studied nanocrystal samples, the additional interfaces caused by the silicon particles cause an enhancement of the intensity of the SHG signal. It is an unexpected behaviour that the intensities of samples annealed for 60 min at 1150 °C and 1200 °C show an SHG signal in the same order of magnitude, because the nanocrystals should be larger after the treatment at 1200 °C. So, there are more interfaces and symmetry-breaking effects that create the SHG signal. Overall the specific surface/interface area is 12.3 (with a density of $\rho = 1.2 \times 10^{18}$ NCs cm$^{-3}$) times bigger than in the silicon substrate without layer stack. In the sample with 2.6 nm diameter nanocrystals (annealing at 1150 °C) the surface is 6.4 times larger compared to the bare substrate. A possible reason for the similar results of the SHG intensities could be that the surfaces of the nanocrystals are not clearly demarcated, but slightly smudged. Overall, the SHG signal can be increased by a factor of $3.2 \pm 0.8$ for the high-temperature treatment at 1200 °C and $3.3 \pm 0.8$ for the treatment at 1150 °C by the influence of nanocrystals.

Although these results clearly show that the second order nonlinear response is enhanced by the silicon nanoparticles, these data are not usable for a valid determination of particle size. The main uncertainty remains in the strong dependence on the excitation conditions (e.g. focus position, etc.), but also intermixing at the interfaces between nanocrystals and matrix obviously plays a significant role. This might be different, however, for e.g., pellets of isolated nanoparticles with a clear demarcation between particle core and surroundings.

Figure 8. Double logarithmic plot of THG and SHG intensities of silicon substrate and samples after high temperature treatments by 1150 °C and 1200 °C.
8. Conclusion

We have evaluated different approaches for size determination of ultra-small Si particles embedded in SiON matrices, where conventional methods for size determination fail. While TEM measurements provide a wealth of structural and morphological information, the required experimental effort makes it often unpractical. From all the investigated techniques, the most easy and straightforward technique is the measurement of room temperature PL. When carried out thoroughly, it can deliver excellent results on both particle size and width of the distribution. The results are in excellent agreement with EFTEM valence band imaging technique as well as temperature-dependent PL spectroscopy, where the excitonic fine structure is determined.

Nonlinear optical spectroscopy should in principle also be a tool that is sensitive to the particle size distribution. However, it was found that the intrinsic strong dependence on the excitation conditions along with the fact that rigorous assumptions on the interfaces are required makes nonlinear spectroscopy too unreliable in comparison with the other techniques.

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