Si nanocrystals embedded in SiO₂: Optical studies in the vacuum ultraviolet rangeV. Pankratov,^{1,4,*} V. Osinniy,² A. Kotlov,³ A. Nylandsted Larsen,^{1,2} and B. Bech Nielsen^{1,2}¹*Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Ny Munkegade, Bld. 1521, DK-8000 C Aarhus, Denmark*²*Department of Physics and Astronomy, Aarhus University, Ny Munkegade, Bld. 1520, DK-8000 C Aarhus, Denmark*³*HASYLAB at DESY, Notkestrasse 85, D-22607 Hamburg, Germany*⁴*Institute of Solid State Physics, University of Latvia, 8 Kengaraga, LV-1063 Riga, Latvia*

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Photoluminescence excitation and transmission spectra of Si nanocrystals of different diameters embedded in a SiO₂ matrix have been investigated in the broad visible-vacuum ultraviolet spectral range using synchrotron radiation. The dependence of the photoluminescence excitation spectra on the nanocrystals size was experimentally established. It is shown that the photoluminescence excitation and absorption spectra are significantly blueshifted with decreasing Si nanocrystal size. A detailed comparison of photoluminescence excitation and absorption spectra with data from theoretical modeling has been done. It is demonstrated that the experimentally determined blueshift of the photoluminescence excitation and absorption spectra is larger than the theoretical predictions. The influence of point defects in the SiO₂ matrix on the optical and luminescence properties of the embedded Si nanocrystals is discussed. Moreover, it is demonstrated that no energy transfer takes place between the SiO₂ and Si nanocrystals when the excitation energy is higher than the band-to-band transition energy in SiO₂.

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I. INTRODUCTION

The huge interest in silicon nanocrystals (Si NC's) for the past almost two decades has been caused by their unique fundamental physical properties and their promising applications. Si NC's have, for instance, superior optical properties as compared to bulk silicon due to quantum confinement effects. Novel properties of devices containing Si NC's have been demonstrated in new generations of optoelectronic devices^{1,2} as well as in third-generation photovoltaic solar cells.³ One of the biggest advantages of Si NC's compared to bulk Si is their intensive visible photoluminescence (PL). The origin of the PL from Si NC's embedded in SiO₂ has been the subject of intense dispute for a long time. The debate has mainly focused on whether interface defects or modifications of the electronic structure of Si NC's due to quantum confinement are responsible for the light emission (Ref. 4 and references therein). The study of luminescent and optical properties in the ultraviolet (UV) and vacuum ultraviolet (VUV) spectral ranges might highlight the origin of the PL in Si NC's. On the other hand, excitations in UV/VUV allow the creation of hot carriers. Therefore, processes where several electron-hole pairs or excitons are formed after absorption of one photon could potentially be observed and studied. It was recently demonstrated that space-separated quantum cutting processes⁵ and multiple exciton generation processes⁶ can be realized in Si NC's when the excitation energy exceeds $2E_g$ (E_g is the band gap of Si NC's). Such processes have the potential of drastically increasing the efficiency of solar cells.^{7,8}

Electronic and optical properties of Si NC's embedded in SiO₂ in the UV/VUV spectral range have been intensively studied theoretically^{9–16} using density-functional theory (DFT), time-dependent DFT, and fully quantum-mechanical DFT treatment. It was demonstrated that electronic and optical properties of Si NC's are strongly dependent on Si NC size and the surrounding interfaces. However, to the best of our knowledge, no experimental data from this spectral range have

been reported so far. The present study aims to remedy this shortcoming.

II. EXPERIMENTAL

The measurements were carried out using synchrotron radiation, which, due to its broad and continuous spectrum, is a very useful tool for the investigation of optical and luminescence properties of wide-band-gap materials^{17–20} where UV and VUV excitations are dominant. However, it is less useful for many bulk semiconductors where band-gap transitions can be excited by visible light from standard commercial spectrometers. On the other hand, band gaps of nanocrystalline semiconductors drastically increase due to quantum confinement effects, and excitations in the UV and VUV range become important. Furthermore, well-known intrinsic defects in SiO₂ have absorption energies in the UV/VUV spectral range²¹ and, therefore, possible energy transfers from defects to embedded Si NC's, and their influence on optical and luminescence properties of embedded Si NC's might be identified.

In the present study, optical and luminescence properties of Si NC's in the UV-VUV spectral range were studied with pulsed synchrotron radiation from the DORIS III storage ring of the Deutsches Elektronen-Synchrotron DESY (Hamburg, Germany). The Superlumi experimental station of HASYLAB was used for the measurements of emission, excitation, and transmission spectra.^{22,23} The excitation spectra were recorded in the 330–60 nm (3.7–20 eV) spectral range with a spectral resolution of 0.3 nm. Excitation spectra of sodium salicylate were normalized to equal synchrotron radiation intensities impinging on the sample. Luminescence spectra in the UV and visible-infrared range were recorded with a monochromator (SpectraPro-308i, Acton Research Corp.) equipped with a liquid-nitrogen-cooled charge-coupled-device (CCD) detector (Princeton Instruments) and a photomultiplier (HAMAMATSU R6358P). The spectral resolution of the

analyzing monochromator was typically 11 nm. Emission spectra were corrected for the spectral response of the detection system. A silicon photodiode (AXUV-100G, IRD Inc.) was employed for transmission (absorption) measurements. All the optical and luminescent measurements were carried out at 8 K. Low-temperature measurements are important as they allow the suppression of nonradiative relaxation channels as the thermal quenching of PL from Si NC's starts at temperatures higher than 150 K.²⁴

Randomly distributed Si NC's embedded into a SiO₂ amorphous matrix were produced on high-purity quartz substrates by means of radio-frequency magnetron sputtering with a subsequent thermal annealing in an N₂ atmosphere at 1100 °C for 1 h. The applied growth procedure has been described in details elsewhere.^{24,25} In the present paper, we report results for three samples that only differ from each other by the Si NC mean diameters, determined by transmission electron microscopy to be 2.5, 3, and 4.5 nm with size distributions of about 15%. A SiO₂ film on a quartz substrate produced in the same conditions was used as a reference for the absorption measurements.

III. RESULTS AND DISCUSSION

Emission spectra for the three samples with different Si NC average size are shown in Fig. 1. It should be noted that similar shapes and positions of the PL spectra are observed for varying excitation energies in the 3.7–8.5 eV range, indicating that the same PL centers are excited independently on the excitation energy. From Fig. 1, it is clearly seen that the peak positions depend on the Si NC size. According to literature data,^{26–28} the band gap of a Si NC increases when its size decreases due to quantum confinement effects. On the other hand, if the PL peak position is known, one can determine the mean size of a NC from a comparison to theory. According to theory,^{29–31} PL peaks at 1.4, 1.6, and 1.65 eV as in Fig. 1 correspond to ~5, ~3, and ~2.5 nm NC diameters, respectively. These values are in very good agreement with the values obtained by transmission electron microscopy. Besides the main peaks,

FIG. 1. PL spectra for Si NC's with different diameter under 150 nm (8.27 eV) excitation at 8 K.

FIG. 2. PL excitation spectra for Si NC's with different diameters. Each spectrum was measured at the maximum of the corresponding PL spectra. Black arrows show the threshold of multiplication of electronic excitation processes (see details in the text) for 2.8 and 2.4 nm Si NC's.

additional shoulders are resolved in the PL spectra. It was recently demonstrated that such shoulders in PL spectra can appear due to a Si NC's size distribution.²⁴

Photoluminescence excitation spectra for each sample measured at the maxima of the PL peaks are shown in Fig. 2, and a comparison of absorption and excitation spectra for each sample is shown in Fig. 3. It is clearly seen in Fig. 2 that the PL excitation spectra are different for the different samples in the 3.7–9 eV spectral range. We will discuss these differences shortly; before we do that, however, we will point out some peculiarities that are similar for all the PL excitation spectra shown in Fig. 2. For all samples studied, a strong suppression of the PL intensity is observed when the excitation energy exceeds 9 eV. Moreover, no Si NC emission under excitation in the 9–20 eV spectral range was observed. Taking into account that the band gap of SiO₂ is about 8.5–9 eV, this PL intensity suppression is most likely due to absorption in the surrounding oxide. It also demonstrates that energy transfer from the surrounding SiO₂ matrix to Si NC's is not efficient, and that charge carriers from the surrounding oxides (after band-to-band transition in SiO₂) do not form PL centers in the Si NC's. Such charge carriers could be either trapped on some imperfections (intrinsic or extrinsic point defects in the surrounding oxide) with a subsequent nonradiative relaxation, or form intrinsic PL centers in SiO₂. Our results show that, most likely, the formation of competing nonradiative relaxation channels is more efficient than the energy transfer to Si NC's.

The PL excitation spectra in the 3.7–9 eV spectral range have broad shapes, and at least three peaks can be resolved. These peaks are well defined in the spectrum of the largest NC's but less well defined for the smaller NC's; the peak positions are summarized in Table I. It is clearly seen that the excitation spectra (Fig. 2) as well as the absorption spectra (Fig. 3) are shifted to higher energies for the samples with the smaller Si NC diameters. It seems obvious that an explanation

FIG. 3. Comparisons of PL excitation (symbols) and absorption (solid lines) spectra for Si NC's with 2.4 nm (a), 2.8 nm (b), and 4.5 nm (c) diameter. The absorption of the reference SiO₂ film was subtracted from the total absorption for each spectrum to suppress the influence of absorption centers caused by the substrate and surrounding oxide. The black dashed line (c) is the theoretically calculated absorption for 1.5 nm Si NC's embedded in SiO₂ taken from Ref. 9.

of this behavior is related to the influence of the NC's size on the energies of the optical transitions. Indeed, due to quantum confinement effects, the band gap of the Si NC's increases and this band-gap change should be seen not only in the PL emission spectra (Fig. 1) but also in the PL excitation spectra. The energy position of the maximum of the individual PL excitation spectrum, however, is much higher than the effective band gap of the Si NC's. In fact, the main PL excitation peaks appear at 4.9, 6.0, and 6.3 eV (Fig. 2 and Table I), and these values are significantly higher than the effective band-gap values of 1.4, 1.6, and 1.65 eV, respectively, estimated from the PL spectra of Fig. 1. Therefore, first of all, we have to consider that the strong rise in PL excitation spectra for Si NC at energies higher than 4.5 eV could be due to direct transition. It is well established that direct transitions in bulk Si take place if the excitation energy exceeds 3.4 eV. Thus, it could be suggested that direct high-energy transitions in Si NC's are responsible for the main peaks (4.9, 6.0, and 6.3 eV) in the PL excitation spectra. It can be seen from Fig. 2 that the steep increase of the main excitation peaks for Si NC's of 2.5 and 2.8 nm diameter starts at about 4.5 eV. This would mean a blueshift of the direct transitions for these Si NC's of more than 1 eV when compared with bulk Si, where the threshold for direct transitions is about 3.4 eV. According to the PL spectra of Fig. 1, however, the indirect band gap increases by only 0.3, 0.5, and 0.55 eV for Si NC's with 4.5, 2.8, and 2.5 nm diameter, respectively, assuming an indirect band gap of bulk Si of 1.1 eV. Hence, if direct transitions are responsible for the observed excitation spectra, the blueshift of the direct high-energy transitions should be much bigger than that of the indirect transition. This is not the case, however, as will be shown in the following with reference to other high-energy PL excitation peaks. Indeed, the NC size seems to influence more strongly the low-energy PL excitation peaks. For example, the three resolved PL excitation peaks of the sample with the biggest Si NC's are located at 4.9, 5.8, and 7.7 eV, and at 6.3, 7.0, and 8.0 eV in the sample with the smallest NC's. Thus, due to the Si NC size reduction, the PL excitation peaks are shifted to higher energies by 1.4, 1.1, and 0.2 eV, respectively. A similar behavior is seen for the sample with a 2.8 nm Si NC diameter (Fig. 4). In fact, the data of Fig. 4 clearly demonstrate blueshifts of the PL excitation peaks of the small NC compared to the sample with the largest NC (4.5 nm). It can also be seen that the blueshifts are larger for the low-energy PL excitation peaks. The reason for choosing the 4.5 nm NC as a reference in this comparison is that we expect the PL excitation spectrum for the 4.5 nm NC to be less perturbed by quantum confinement effects than the smaller NC, where quantum size effects are expected to be much stronger.

Thus, the high-energy PL excitation peaks are less affected by the Si NC size. A similar behavior has been demonstrated theoretically in Refs. 9 and 11, where the optical properties of Si NC's embedded in SiO₂ were studied by means of *ab initio* DFT methods. In particular, these calculations demonstrate that the low-energy part of the absorption spectra is drastically changed when the Si NC size decreases, whereas the high-energy part is only slightly size-dependent.

Generally, the Si NC energy levels or "bands" are quite different from those of bulk Si. Taking into account that the

TABLE I. The dependence of PL and PL excitation peak positions on Si NC size. Diameters of NC's are shown in the first column based on transmission electron microscopy (TEM) data, whereas Si NC's estimated from PL spectra diameters are in the third column.

Diameter (nm) (TEM)	PL peak position (E_g) (eV)	Diameter (nm) (PL)	PL excitation peaks (eV)
4.5	1.4	5	4.9; 5.8; 7.7
2.8	1.6	3	6.0; 6.7; 7.8
2.4	1.65	2.5	6.3; 7.0; 8.0

indirect band gap in bulk Si becomes quasidirect in small Si NC's, it will be difficult to distinguish between direct and indirect transitions in Si NC's (in contrast to bulk Si). Therefore, we suggest another explanation of the large blueshift of the PL excitation spectra. Theoretical modeling indicates¹⁶ that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Si NC's embedded in SiO₂ are spatially separated, that is, the HOMO is localized at the interface between the Si NC and the oxide, whereas the LUMO is localized at the center of the Si NC. Therefore, the transition between these states has a very small oscillator strength.^{9,16} Additionally, it was demonstrated theoretically^{9,11,16} that the absorption spectra tend to be shifted toward higher energies with decreasing Si NC size. These results were explained by a strong influence of the nanocrystals size on the oscillator strengths of the transitions. We suggest, therefore, that the measured PL excitation spectra (Fig. 2) and absorption spectra (Fig. 3) demonstrate a dependence of the oscillator strength on the size of the Si NC's.

According to theory,^{9,11,16} a significant blueshift of the absorption spectra due to the influence of the nanocrystal's size on the oscillator strength should be expected for Si NC's smaller than 1.5 nm. The theoretically calculated absorption spectrum for 1.5 nm diameter Si NC (from Ref. 9) peaking at 4.2 eV is demonstrated for comparison in Fig. 3 (black dashed line). To the best of our knowledge, there are no reliable

theoretical data for larger Si NC's. Taking into account that the Si NC's in our study have diameters larger than 1.5 nm, it should be expected that the PL excitation spectra are redshifted with respect to those from Si NC's with 1.5 nm diameter. However, the PL excitation spectra [and the absorption spectra (Fig. 3)] from our study (Fig. 2) are strongly blueshifted already for Si NC's with diameter less than 5 nm.

There is one effect that could affect the PL excitation spectra, and that could explain the discrepancy between our experimental PL excitation spectra and the theoretical predictions. It is well established that the PL intensity increases if two or more electron-hole pairs or excitons are created per one absorbed photon, that is, if a so-called multiplication of electronic excitations (carrier multiplications) process occurs.³² In particular, multiple exciton generation (MEG)⁶ and space-separated quantum cutting (SSQC) processes⁵ are known in Si NC's. For a successful realization of these processes, the excitation energy of the photon must exceed a threshold energy $E_{th} = 2E_g$, where E_g is the effective band gap of the Si NC. Strictly speaking, to settle the issue of whether multiplications of electronic excitations are present, the quantum efficiency of the PL must be measured. However, even without such measurements some qualitative analysis can be made. For instance, it is seen from Fig. 2 that the rise of the PL excitation intensity for the sample with the smallest Si NC starts at about 4.5 eV. The effective band gap for a 2.4 nm Si NC is about 1.65 eV and the observed threshold of 4.5 eV is thus equal to about $2.7E_g$. The same value was also obtained for the Si NC's 2.8 nm in diameter. These values are close to the threshold energy for MEG in Si NC's ($E_{th} = 2.4 \pm 0.1E_g$) reported in Ref. 6. In Ref. 7 it was shown that the threshold energy for the multiplication process depends on the ratio of the effective masses of the electron and the hole, and, therefore, the threshold energy can vary between $2E_g$ and $3E_g$. Thus, we suggest that one or several multiplications of electronic excitation processes (MEG and/or SSQC) take place under the VUV excitation, and that it influences the PL excitation spectra of the Si NC's.

A comparison of the PL excitation spectra to the corresponding absorption spectra as done in Fig. 3 shows that the PL excitation and absorption spectra do not match each other. This experimental observation could indicate that some other centers (intrinsic and/or extrinsic defects in SiO₂, having strong absorption in the 6–8 eV range²¹) contribute to the absorption spectra but not to the PL excitation spectra, which essentially describe the absorption of the centers responsible for the PL, that is, the Si NC's. It is already known^{33–36} that there are so-called substoichiometric layers around embedded Si NC's in SiO₂. In fact, this is a region surrounding SiO₂

FIG. 4. Dependence of PL excitation peaks on Si NC diameter. The positions of the PL excitation peaks for 4.5 nm diameter Si NC's were chosen as reference points, that is, having zero shifts. The shifts for 2.4 and 2.8 nm Si NC's were all determined with respect to the positions of PL excitation peaks of 4.5 nm Si NC's.

with a high oxygen deficit, or, in other words, a region with high concentrations of intrinsic defects. If defects from the surrounding oxide (mainly from these substoichiometric layers around Si NC's) are responsible for absorption in the 6–8 eV range, the decrease of the PL intensity in this range could also originate from a weak energy transfer from defects to Si NC's. In other words, defects in the surrounding oxide can be considered to be competing relaxation channels that can absorb partially the excitation intended for PL centers (Si NC's). This leads to a gradual decrease of the PL excitation at energies higher than 6 eV, that is, at energies where defects absorb most intensively. It is important to note that such a decrease of the PL excitation is stronger for the Si NC with larger diameter. This means that the concentration of defects is higher in the sample with the largest Si NC because of the bigger interface layer around the NC. A similar dependence of the density of the interfacial defects on Si NC size was shown in Ref. 37.

The multiplication of the electronic excitation processes considered earlier can also explain the difference between the PL excitation and absorption spectra. Indeed, there are spectral regions (e.g., 4–5.5 eV) where the intensity of the PL excitation is high whereas the absorption is small, that is, one absorbed photon creates intensive PL. However, it is quite possible that a superposition of the processes described earlier occurs.

IV. CONCLUSIONS

In conclusion, absorption and luminescence properties of Si NC's embedded in SiO₂ have been studied in the VUV

spectral range at low temperatures. The dependence of the PL excitation spectra on the Si NC size was experimentally established. The general trend of the PL excitation spectra dependence on nanocrystal size agrees qualitatively with theoretical models that assume that nanocrystal size strongly influences the transitions oscillator strength. On the other hand, it is demonstrated that experimentally determined blueshifts of the PL excitation spectra are larger than the theoretical predictions. This discrepancy is explained by the possible presence of the multiplication of electronic excitations in Si NC's. A difference between PL excitation and absorption spectra for Si NC's embedded in SiO₂ is also observed. This difference is explained as a contribution from strong point-defect absorption in the surrounding oxide in the VUV range. Last but not least it was demonstrated that no energy transfer takes place between SiO₂ and the Si nanocrystals if the excitation energy is higher than the band-to-band transition energy in SiO₂.

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¹L. Pavessi *et al.*, *Nature (London)* **80**, 440 (2000).

²P. Ball, *Nature (London)* **409**, 974 (2001).

³M. A. Green, *Third Generation Photovoltaics* (Springer, Berlin, 2003).

⁴S. Godefroo *et al.*, *Nature Nanotech.* **3**, 174 (2008).

⁵D. Timmerman *et al.*, *Nature Photon.* **2**, 105 (2008).

⁶M. C. Beard *et al.*, *Nano Lett.* **7**, 2506 (2007).

⁷R. D. Schaller, M. A. Petruska, and V. I. Klimov, *Appl. Phys. Lett.* **87**, 253102 (2005).

⁸M. A. Green, *Physica E* **14**, 65 (2002).

⁹H.-Ch. Weissker, J. Furthmüller, and F. Bechstedt, *Phys. Rev B* **65**, 155328 (2002).

¹⁰N. Daldosso *et al.*, *Phys. Rev. B* **68**, 085327 (2003).

¹¹L. E. Ramos *et al.*, *Phys. Status Solidi B* **242**, 3053 (2005).

¹²M. Luppi and S. Ossicini, *Phys. Rev. B* **71**, 035340 (2005).

¹³P. Kroll and H. J. Schulte, *Phys. Status Solidi* **243**, R47 (2006).

¹⁴A. Gali *et al.*, *Nano Lett.* **9**, 3780 (2009).

¹⁵K. Seino, F. Bechstedt, and P. Kroll, *Nanotech.* **20**, 135702 (2009).

¹⁶L. Koponen, L. O. Tunturivuori, M. J. Puska, and R. M. Nieminen, *Phys. Rev. B* **79**, 235332 (2009).

¹⁷H. H. Rüter, H. v. Seggern, R. Reininger, and V. Saile, *Phys. Rev. Lett.* **65**, 2438 (1990).

¹⁸M. Kirm, G. Zimmerer, E. Feldbach, A. Lushchik, C. Lushchik, and F. Savikhin, *Phys. Rev. B* **60**, 502 (1999).

¹⁹V. Pankratov, M. Kirm, and H. von Seggern, *J. Lumin.* **113**, 143 (2005).

²⁰V. Pankratov *et al.*, *IEEE Trans. Nucl. Sci.* **55**, 1509 (2008).

²¹L. Skuja, *J. Non-Cryst. Solids* **239**, 16 (1998).

²²G. Zimmerer, *Nucl. Instrum. Methods Phys. Res. Sect. A* **308**, 178 (1991).

²³G. Zimmerer, *Rad. Meas.* **42**, 859 (2007).

²⁴V. Osinniy *et al.*, *Nanotechnology* **20**, 195201 (2009).

²⁵J. S. Jensen *et al.*, *J. Appl. Phys.* **101**, 056108 (2007).

²⁶N. A. Hill and K. B. Whaley, *Phys. Rev. Lett.* **75**, 1130 (1995).

²⁷S. Ögüt, J. R. Chelikowsky, and S. G. Louie, *Phys. Rev. Lett.* **79**, 1770 (1997).

²⁸T. van Buuren, L. N. Dinh, L. L. Chase, W. J. Siekaus, and L. J. Terminello, *Phys. Rev. Lett.* **80**, 3803 (1998).

²⁹F. A. Reboredo, A. Franceschetti, and A. Zunger, *Appl. Phys. Lett.* **75**, 2972 (1999).

³⁰C. Delerue, G. Allan, and M. Lannoo, *J. Lumin* **80**, 65 (1999).

³¹G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, F. Huisken, B. Kohn, and V. Paillard, *Phys. Rev. B* **62**, 15942 (2000).

³²J.-W. Luo, A. Franceschetti, and A. Zunger, *Nano Lett.* **8**, 3174 (2008).

³³Y. Kanemitsu, T. Ogawa, K. Shiraishi, and K. Takeda, *Phys. Rev. B* **48**, 4883 (1993).

³⁴G. Hadjisavvas and P. C. Kelires, *Phys. Rev. Lett.* **93**, 226104 (2004).

³⁵G. Faraci, S. Gibilisco, A. R. Pennisi, G. Franzo, S. LaRosa, and L. Lozzi, *Phys. Rev. B* **78**, 245425 (2008).

³⁶O. Jambois *et al.*, *J. Appl. Phys.* **100**, 123504 (2006).

³⁷X. X. Wang, J. G. Zhang, L. Ding, B. W. Cheng, W. K. Ge, J. Z. Yu, and Q. M. Wang, *Phys. Rev. B* **72**, 195313 (2005).