

# Absence of quantum confinement effects in the photoluminescence of Si<sub>3</sub>N<sub>4</sub>–embedded Si nanocrystals

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Superlattices of Si-rich silicon nitride and  $Si_3N_4$  are prepared by plasma-enhanced chemical vapor deposition and, subsequently, annealed at 1150 °C to form size-controlled Si nanocrystals (Si NCs) embedded in amorphous Si<sub>3</sub>N<sub>4</sub>. Despite well defined structural properties, photoluminescence spectroscopy (PL) reveals inconsistencies with the typically applied model of quantum confined excitons in nitride-embedded Si NCs. Time-resolved PL measurements demonstrate 10<sup>5</sup> times faster time-constants than typical for the indirect band structure of Si NCs. Furthermore, a pure Si<sub>3</sub>N<sub>4</sub> reference sample exhibits a similar PL peak as the Si NC samples. The origin of this luminescence is discussed in detail on the basis of radiative defects and  $Si_3N_4$  band tail states in combination with optical absorption measurements. The apparent absence of PL from the Si NCs is explained conclusively using electron spin resonance data from the Si/Si<sub>3</sub>N<sub>4</sub> interface defect literature. In addition, the role of  $Si_3N_4$  valence band tail states as potential hole traps is discussed. Most strikingly, the PL peak blueshift with decreasing NC size, which is often observed in literature and typically attributed to quantum confinement (QC), is identified as optical artifact by transfer matrix method simulations of the PL spectra. Finally, criteria for a critical examination of a potential QC-related origin of the PL from Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs are suggested. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4878699]

## I. INTRODUCTION

Silicon nanocrystals (Si NCs) were suggested for third generation "all-silicon" tandem solar cells.<sup>1,2</sup> Due to the high band offsets, Si NCs in SiO<sub>2</sub> are expected to have rather low carrier mobilities,<sup>3</sup> although first photovoltaic devices were demonstrated.<sup>4</sup> A lower band gap matrix like Si<sub>3</sub>N<sub>4</sub> with smaller band offsets is expected to allow for better electrical transport, e.g., via minibands,<sup>5</sup> although many other factors also influence the QD-QD coupling.<sup>6</sup> In addition, Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs were suggested for Si-based electroluminescent devices<sup>7</sup> and for the investigation of modulation doping mechanisms in nanoscale silicon.<sup>8</sup> Despite expected advantages from Si<sub>3</sub>N<sub>4</sub> as a matrix material for Si NCs, the fundamental origin of the luminescence from Si NC/Si<sub>3</sub>N<sub>4</sub> samples is still under debate. Many groups attributed the photoluminescence (PL) peak blueshift with decreasing NC size to quantum confined excitons in the nitride-embedded Si NCs amorphous silicon quantum dots (Si QDs).<sup>9-14</sup> or

Alternatively, radiative defects<sup>15–18</sup> or band tail luminescence<sup>11,16,19</sup> was suggested to explain the PL. In this work, we present evidence that PL emission from quantum confined excitons in nitride-embedded Si NCs is very unlikely due to the quenching effect of abundant non-radiative defects and a possible loss of confinement potential due to extensive tail states in Si<sub>3</sub>N<sub>4</sub>. Furthermore, the observed PL peak shifts with NC size are identified as an optical interference artifact.

#### **II. EXPERIMENTAL DETAILS**

A precise control of the Si NC size is required since the band gap of a QD is mainly determined by its dimensions. In order to control the NC size and density independently, as well as to avoid highly non-spherical or agglomerated NCs,<sup>20</sup> we use the superlattice (SL) fabrication method.<sup>21</sup> Silicon rich nitride (SRN) and stoichiometric silicon nitride (Si<sub>3</sub>N<sub>4</sub>) were deposited on wet chemically cleaned (100)-Si and quartz glass substrates using an Oxford Instruments "Plasmalab 100" plasma-enhanced chemical vapor deposition (PECVD) system (13.56 MHz) and SiH<sub>4</sub>/NH<sub>3</sub>/N<sub>2</sub>-based plasma chemistry. The process parameters (adjusted to allow for a sufficiently low

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deposition rate of  $\sim 2$  Å/s to enable a precise SL growth) were: substrate temperature 375 °C, pressure 600 mTorr, and RF-power 15 W. The stoichiometry of the SiN<sub>x</sub> films was varied by changing the  $\Gamma$ -ratio, defined as  $\Gamma = [SiH_4]/[NH_3]$ , as well as the  $N_2$  flow. The composition of the SiN<sub>x</sub> films was measured by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). In this study, we chose, for the SRN films, a  $\Gamma$ -ratio of 1.5 and 185 sccm N<sub>2</sub>, corresponding to a Si/N ratio of 1.25 (~22 at. % excess Si). Stoichiometric Si<sub>3</sub>N<sub>4</sub> for the barrier layers in the SL was achieved by  $\Gamma = 1$  and a N<sub>2</sub> flow of 980 sccm, corresponding to a Si/N ratio of 0.77. The refractive indices (at 633 nm) of the two silicon nitride materials used in the following were measured to be  $n_{SRN} = 2.35$  and  $n_{Si3N4} = 1.96$ . Further details of the structural and compositional material investigations can be found elsewhere.<sup>22</sup> After deposition, the samples were annealed in a quartz tube furnace at 1150 °C for 1 h in high purity N<sub>2</sub> ambient. Some samples were additionally annealed in pure H<sub>2</sub> ambient for 1 h at 500 °C and 700 °C.

The amount of SRN/Si<sub>3</sub>N<sub>4</sub> bilayers of the samples fabricated for this study was 20 (for PL and transfer matrix method (TMM) simulations) and 30 (for time-resolved PL and absorption measurements). Each deposition started with an initial 10 nm SiO<sub>2</sub> buffer layer (for stress compensation between Si and Si<sub>3</sub>N<sub>4</sub>) and was finalized by a 6nm Si<sub>3</sub>N<sub>4</sub> capping layer. The thickness of the SRN layers was varied between 2 and 5 nm in steps of 1 nm to achieve different NC sizes. The Si<sub>3</sub>N<sub>4</sub> barrier layers were chosen to be 6 nm for all samples, except for the samples made on quartz glass for optical absorption measurements, where the barrier thickness was intentionally reduced to 3 nm. In contrast to Si substrates, a severe deformation of the quartz glass was observed for layer stacks exceeding ~250 nm, which constrained the analysis of the absorption measurements. The bending of the quartz glass substrates occurred after annealing; no deformation was visible after deposition. Therefore, it is not attributed to the well known nitride inherent high uniaxial stress but to the  $\sim 6$  times smaller thermal expansion coefficient of quartz glass compared to Si<sub>3</sub>N<sub>4</sub>. Since the thermal expansion coefficients of Si<sub>3</sub>N<sub>4</sub> and Si differ by only  $\sim 20\%$ , no deleterious deformation was observed for samples on Si wafers.

Throughout this work, the superlattice samples are labeled in the following way: "bilayer number SL SRN thickness/Si<sub>3</sub>N<sub>4</sub> thickness," so that, e.g., 20SL4/6 denotes a superlattice consisting of 20 bilayers of 4 nm SRN and 6 nm Si<sub>3</sub>N<sub>4</sub>.

The SL cross-section as well as the NC sizes were investigated by energy-filtered transmission electron microscopy (EFTEM) using a JEOL 2010F equipped with a Gatan Imaging Filter. The images were obtained by filtering around the Si plasmon loss peak ( $\sim$ 17 eV). Specimens were prepared by mechanical polishing and Ar<sup>+</sup> ion milling. The Si NC size analysis was carried out for more than 50 nanocrystals of each sample and the standard deviation was determined by a Gaussian fit of the size distribution. Spectral PL measurements were performed between 350 and 1100 nm at room temperature with a LN<sub>2</sub>-cooled CCD detector coupled to a grating monochromator (f = 50 cm) and a HeCd laser  $(325 \text{ nm}, \text{ power density } \sim 400 \text{ mW/cm}^2)$  as excitation source. Time-resolved PL was measured using a Hamamatsu streak camera with a spectral window of  $\pm 100 \,\mathrm{nm}$  around the observed peak and a Ti-sapphire laser with a regenerative amplifier (400 nm, 100 fs, laser fluence  $\sim 1 \text{ mJ/cm}^2$ ) as excitation source. The excitation power density dependence of the PL intensity was measured using a sensitive micro-spectroscopy setup, which enables precise control of the excitation spot size and power. PL was excited by a 405 nm diode laser through an objective lens  $100 \times /0.8$  and collected by the same lens and detected by a LN2-cooled back-illuminated CCD camera attached to a grating monochromator (f = 30 cm). PL excitation (PLE) measurements were carried out by an Acton Research spectrometer with excitation by a Xe lamp (150 W) connected to a single-grating monochromator (f = 15 cm) and detected by a photomultiplier attached to a monochromator (f = 15 cm). Reference signal was detected by a Si diode. All signals were corrected for the spectral response. Light absorption was determined in a spectral range of 250-2000 nm via reflection-transmission measurements using a Varian Cary-500i spectrophotometer equipped with an integrating sphere.

# **III. RESULTS**

#### A. Structural properties of Si NC/Si<sub>3</sub>N<sub>4</sub> superlattices

Figures 1(a) and 1(b) show the EFTEM images of the 30SL3/6 and 30SL5/6 annealed at 1150 °C. Since the image contrast is generated by energy filtering around the Si plasmon loss peak, white to light gray areas are attributed to silicon, whereas the dark gray areas correspond to Si<sub>3</sub>N<sub>4</sub>. The multilayer structure is well maintained and the formation of silicon nanoclusters is clearly observed. These principal features are also reproduced in the EFTEM images of the samples 30SL2/6 and 30SL4/6 (not shown here). The mean Si NC sizes ( $\mu$ ) and standard deviations ( $\pm \sigma$ ) from the EFTEM analysis of 30SL2/6, 30SL3/6, 30SL4/6, and 30SL5/6 are  $2.6 \pm 1.1$  nm,  $3.4 \pm 1.2$  nm,  $3.7 \pm 1.3$  nm, and  $5.2 \pm 3.1$  nm, respectively. Similar to previous observations,<sup>23</sup> we find an upper limit for the Si NC size control at around 5 nm SRN thickness, which is indicated by the significantly increased size distribution. According to X-ray diffraction (XRD) analysis,<sup>22</sup> we observe after annealing at 1150 °C c-Si signals of the Si NCs but no evidence for a crystallized Si<sub>3</sub>N<sub>4</sub> matrix—in contrast to previous reports.<sup>24,25</sup> Considering



FIG. 1. EFTEM images of the SRN/Si\_3N\_4 SLs annealed at 1150  $^\circ\text{C}$ : (a) 30SL3/6 and (b) 30SL5/6.

additional defects in the vicinity of the Si NCs caused by a crystalline matrix (grain boundaries, dislocations, etc.) and the lattice mismatch between c-Si and c-Si<sub>3</sub>N<sub>4</sub>, an amorphous matrix surrounding the Si NCs is beneficial.

#### **B. Light emission**

The PL spectra of the samples 20SL2/6 to 20SL5/6 and a Si<sub>3</sub>N<sub>4</sub> reference sample (annealed 70 nm thick Si<sub>3</sub>N<sub>4</sub> film) are shown in Fig. 2. The peaks have an asymmetric Gaussian shape with a slightly broader half width half maximum (HWHM) on the low energy side of the peak. Whereas this asymmetry is pronounced for the samples with smaller NCs, it diminishes for the larger NC samples and the Si<sub>3</sub>N<sub>4</sub> reference. The peaks are located between 2.25 and 2.05 eV (550-600 nm). The full WHM (FWHM) values are around 700 meV for all samples except of 20SL2/6, which has a much broader peak (1050 meV). Typically, size controlled Si NCs made from SRON/SiO<sub>2</sub> SLs have peak widths of only 250–300 meV.<sup>26</sup> Also, it has to be noted that the overall PL intensity of the nitride samples is about 2 orders of magnitude weaker than typically observed for our Si NCs in oxynitride<sup>23</sup> and oxide matrix.<sup>27</sup> At first sight, a PL peak blueshift can be observed for samples 20SL5/6 to 20SL3/6 with decreasing NC size, i.e., following the trend expected from quantum confinement (Fig. 2; gray dashed arrow). However, the PL peak of 20SL2/6 does not follow this trend. Furthermore, the reference sample exhibits a PL peak located at 2.15 eV (575 nm) with a shape very similar to that of the superlattices. In other words, we can hardly distinguish between luminescence from the Si NC samples and the Si<sub>3</sub>N<sub>4</sub> reference sample. Regarding the PL peak shift as function of NC size, we observe approximately 100 meV blueshift per 1 nm reduction of the nominal NC diameter. Though a very similar value is observed for Si NCs embedded in silicon dioxide and oxynitride matrix,<sup>23,27</sup> this circumstance alone cannot be regarded as evidence for the quantum



FIG. 2. Normalized PL spectra of samples 20SL2/6–20SL5/6 and a  $\rm Si_3N_4$  bulk film for reference.

confinement origin of the PL. The actual origin of the PL peak shift will be explained in Sec. IV.

In the first place, no PL emission is expected from an ideal high band gap material like Si<sub>3</sub>N<sub>4</sub> under HeCd laser excitation at 3.8 eV. Therefore, the observation of luminescence casts doubts on the ideality of the Si<sub>3</sub>N<sub>4</sub> material. PL peaks around 2.1 eV from samples with Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs, i.e., from high temperature annealed and truly phase separated SRN films, were observed by several groups.<sup>13,14,28</sup> However, others reported PL peaks of nitride-embedded NCs in the range of 1.5 to 1.8 eV, <sup>11,12,24,28,29</sup> i.e., in the same range as oxide-embedded Si NCs. On the other hand, PL peaks up to 3.0 eV were also reported.<sup>10,30</sup> Hence, there is no universally accepted PL peak energy range for nitride-embedded Si NCs. Indeed, light emission at slightly higher energies from nitride-embedded Si NCs compared to oxide-embedded Si NCs would be consistent with density functional theory (DFT) calculations, which revealed larger HOMO-LUMO gaps for surface terminating groups with lower polarity (i.e., N- vs. O-termination).<sup>31</sup> Experimental evidence for this theory was demonstrated by a PL peak blueshift of ~30 meV caused by the incorporation of a sub-monolayer of N-atoms on the interface of SiO<sub>2</sub>-embedded Si NCs.<sup>27</sup> However, a detailed calculation of the recombination energy of fully N-coordinated Si NCs is not available up to now.

In order to study the origin of the luminescence, its decay was measured via time-resolved PL spectroscopy. The decay curves of the samples 30SL2/6-30SL5/6 are shown in Fig. 3 and they all exhibit the same decay behavior despite different NC sizes. Furthermore, the 1/e value of the PL decay time is around 300 ps for all samples, while the typical PL decay time of oxide- or oxynitride-embedded nanocrystalline silicon is in the range of 20 to 80  $\mu$ s at room temperature and a function of NC size.<sup>27,32</sup> Hence, the decay time measured here is  $10^5$  times faster and can hardly be attributed to the recombination of quantum confined excitons in the indirect band gap configuration of Si NCs. The function of the PL decay shown in Fig. 3 is clearly not single-exponential but the stretched exponential function typically used for Si NCs<sup>33</sup> is not applicable



FIG. 3. Normalized PL decays for 2/6, 3/6, 4/6, and 5/6 SiN<sub>x</sub>/Si<sub>3</sub>N<sub>4</sub> superlattices detected at (580  $\pm$  100) nm. The decay times were fitted to  $\tau_1 = 1.7$  ns and  $\tau_2 = 0.25$  ns. As shown in the inset, the PL peak intensity is linear over a broad excitation (cw) power density range.

either. However, a double-exponential decay function can be fitted and the two time constants of all four samples are:  $\tau_1 = 1.7 \pm 0.2$  ns and  $\tau_2 = 0.25 \pm 0.02$  ns. These decay constants are well in accordance with the literature, <sup>15,30,34</sup> though compared to Refs. 15 and 34, our slower component is slightly shorter than reported there. The amplitude ratio A<sub>2</sub>/A<sub>1</sub> from the double-exponential fits is on average ~12. Hence, the fast component ( $\tau_2$ ) is clearly dominating the PL decay.

In the inset, we show the PL peak intensity of sample 20SL4/6 as function of excitation power density (continuous wave). Over the whole range (up to 690 W/cm<sup>2</sup>), the dependence is well linear in contradiction to the typical behavior of Si NCs, where saturation at around  $\sim 1$  W/cm<sup>2</sup> is observed.<sup>35</sup> This saturation is commonly explained within the concept of quantum confined excitons in Si NCs: When the generation rate of excitons by incident photons exceeds the recombination rate, multiple excitons occur, which are subject to fast, non-radiative Auger recombination. In accordance with the very high recombination rates derived from time-resolved PL, no saturation can be observed even at excitation power densities that exceed the usual threshold by almost 3 orders of magnitude. Conversely, this represents another argument against the QC-origin of the PL from Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs.

## C. Light absorption

Absorption was measured using the sample set 30SL2/3-30SL5/3 on quartz glass substrates together with an annealed bulk  $Si_3N_4$  film of 200 nm thickness. In Fig. 4, the absorption coefficient  $\alpha$  of the SLs is calculated from the transmittance and reflectance data using only the total SRN thickness of the stacks (due to the absence of SRN  $\alpha_{Si3N4}$  of the reference sample is calculated with 200 nm thickness). This procedure is well justified considering the very low absorption of  $Si_3N_4$  in the near infrared and visible range, i.e., where the absorption edge of the Si NCs is expected. The  $E_{04}$  value (energy of  $\alpha = 10^4 \text{ cm}^{-1}$ ) is often used to quantify the optical band gap. Here,  $E_{04}$  is 2.30 eV and has no trend with the NC size. However, the absorption coefficient curves do not show any change or transition at  $E_{04}$ 



(e.g., from band-to-band to sub-gap absorption), making the significance of this energy questionable for these samples. Over the whole visible light range, the shape of the absorption coefficient curves of the SLs shows a comparable trend as c-Si (gray curve in Fig. 4). Starting from around 2 eV towards the near infrared range, the absorption curves start to differ slightly from each other in a way that could be attributed to quantum confinement. A small blueshift of the absorption can be observed for the SLs, though 30SL5/3 does not follow the NC size dependent trend over the full energy range under discussion (1.5-2.0 eV). Unfortunately, a deeper analysis of the absorption edge and potential sub-band gap absorption of Si tails states, as described by the Urbach energy parameter (i.e.,  $\alpha \sim \exp(E/E_U)$ ), becomes difficult since the resolution limit of the spectrophotometer is approached. The application of the Tauc formalism (i.e.,  $(\alpha h v)^{0.5}$  vs. hv plot) is not successful for the SL samples since no meaningful linear regions can be found. This is most likely attributed to significant absorption of defects over the whole energy range, in accordance with Ref. 36. The  $Si_3N_4$ sample shows two distinct absorption regions with a transition at around 3 eV (Fig. 4). For higher energies,  $\alpha_{Si3N4}$  is an exponential growth function with a slope of  $\sim$ 700 meV, i.e., within the concept of the Urbach energy parameter, a value of  $E_{U,Si3N4} \sim 700 \text{ meV}$  could be derived, although this interpretation is not unambiguous. Anyhow, we observe substantial subgap absorption in the UV, presumably from transitions between valence band (VB) tail states and conduction band (CB) tail states. For energies <3 eV, the reference sample transmits light quite well ( $\alpha_{Si3N4} \sim 10^2 \text{ cm}^{-1}$ ) and the absorption coefficient is a rather featureless function of energy. Since the absorption coefficient mirrors the joint density of states (JDOS) of VB and CB, it is obvious from the transitions at 3 eV that tail states extend significantly into the band gap.

PLE spectroscopy allows for an absorption analysis that correlates the excitation photon energy with the PL emission intensity. From the PLE spectra depicted in Fig. 5, three energetically similar regions are revealed for the Si NC



FIG. 5. PLE spectra of samples 20SL2/6, 20SL5/6, and a  $Si_3N_4$  bulk film for reference. The gray arrows indicate the approximated onsets of the exponential slopes at 2.8 and 3.7 eV.

samples and the Si<sub>3</sub>N<sub>4</sub> reference. Initially, the PL intensity is rising exponentially from ~2.8 eV (first gray arrow) up to ~3.1 eV and remains, then, rather constant for around 600 meV up to ~3.7 eV (second gray arrow). For higher excitation energies, the intensity increases exponentially with a slope of ~100 meV. Although the absorption measured by spectrophotometry is continuously increasing with photon energy (Fig. 4), PL efficiency seems to be limited in the excitation range from 3.1 to 3.7 eV so that the PLE signal appears to be constant with energy. With that information, it is unfortunately not possible to attribute absorption and emission to specific energy levels; however, the similarities between all PLE spectra prove that the excitation mechanism of Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs and pure Si<sub>3</sub>N<sub>4</sub> is identical.

#### IV. DISCUSSION

#### A. Band tail luminescence vs. radiative Si<sub>3</sub>N<sub>4</sub> defects

Taking into account, the Si<sub>3</sub>N<sub>4</sub> band gap of 5.3 eV (Ref. 37) and considering the measured lower energetic PL tails down to ~1.6 eV (cf. Fig. 2), the band tail states from VB to CB would have to protrude up to 1.85 eV from both sides into the band gap. Hence, only less than one third of the actual Si<sub>3</sub>N<sub>4</sub> band gap would be left as tail state free quasi-gap. This simple estimation assumes a symmetrical tail state distribution; however, using electron spectroscopy measurements, Iqbal *et al.* suggested that the VB-tail is significantly broader than the CB-tail.<sup>38</sup> Considering the values observed for a-Si:H, where the band tail states protrude only  $\leq$ 200 meV into the quasi-gap and whose PL at around 1.4 eV is indeed attributed to band tail luminescence,<sup>39</sup> the band tail PL model for Si<sub>3</sub>N<sub>4</sub> would require an enormous tailing.

An argument that casts doubts on the band tail model comes from the consideration of the DOS, which is an exponentially decaying function of energy for the tail states. Hence, if the PL originates from radiative recombination between the highest VB- and the lowest CB-tail states, the absorption would also have to increase exponentially starting from around 1.6 eV (lower energetic PL tail). However, the exponential onset of absorption of  $Si_3N_4$  was found at  $\sim 3 \text{ eV}$ (see Fig. 4) or, respectively, at  $\sim 2.8 \text{ eV}$  and  $\sim 3.7 \text{ eV}$  and (see Fig. 5). As indicated by  $(\alpha_{Si3N4 onset})$  in the schematic DOS(E) plot shown in Fig. 6(a), it could be argued that the CB tailing is insufficient for measureable absorption so that the exponential absorption onset takes place between the VB tail states and the fundamental CB states of Si<sub>3</sub>N<sub>4</sub>. Of course, this is purely speculative but, apparently, the optical properties of our samples cannot unambiguously be explained via the band tail model. It has to be noted that this model is well suited to describe the situation in homogeneous, i.e., not annealed, a-SiN<sub>x</sub>:H films as demonstrated recently by Kistner et al.<sup>19</sup> However, as soon as a high temperature treatment is applied and phase separation is completed, only H-free Si<sub>3</sub>N<sub>4</sub> and Si are present. Whereas, the Si NCs are obviously not responsible for the PL (cf. PL peak of the Si<sub>3</sub>N<sub>4</sub> reference sample), a high band gap material like Si<sub>3</sub>N<sub>4</sub> would require band tails reaching as deep as 3.7 eV into the



FIG. 6. Schematic DOS(E) plots of  $Si_3N_4$ . (a) The situation assuming tail states, which protrude extremely deep into the band gap as origin of the PL. In this case, the exponential absorption onset in the range of 3 eV from spectrophotometry or PLE is ambiguous. (b) The situation assuming a narrower tail state distribution and the presence of K-center defects. Transitions between the VB edge or its tails and the K-center are considered as PL origin and PLE onset. The absorption onset from spectrophotometry could also originate from tail-to-tail transitions.

band gap, making it ineffective as potential energy barrier for excitons in the QDs.

Since the energetic position of the measured PL peak is quite far away from the Si<sub>3</sub>N<sub>4</sub> band edges a defect related origin seems to be a better explanation. Initially, the two major paramagnetic Si<sub>3</sub>N<sub>4</sub>-based dangling bond (DB) defects, the K-center and the N-center, will be discussed, since both were suggested as luminescence centers; cf. Refs. 15-18, respectively. The K-center is configured as  $N_3 \equiv Si \cdot$  (where • denotes the dangling bond),<sup>40,41</sup> i.e., the DB is localized on a Si-atom, which is coordinated to three N-atoms. In the N-center, the DB is localized on the N-atom, which is backbonded to two Si-atoms: •N=Si<sub>2</sub>.<sup>42,43</sup> However, considering the energy band diagram developed by Warren et al.,<sup>44</sup> the N-center is unlikely to represent a radiative recombination center since its energy level in Si<sub>3</sub>N<sub>4</sub> is located only  $\sim 0.5 \text{ eV}$ above the VB maximum. For homogenous SRN films, the N-DB defect level even falls below the VB edge<sup>44</sup> and is hence inactivated as a recombination center. In contrast, the K-center is a midgap state in Si<sub>3</sub>N<sub>4</sub> that is separated by  $\sim$ 2.6 eV from the VB edge.<sup>15,44</sup> Taking into account the significant VB-tailing, as discussed above, and a possible Stokes shift between absorption and emission, then, the 700 meV broad PL peak centered at around 2.15 eV might be explained by a radiative recombination via the K-center (see Fig. 6(b)). Due to the amphoteric nature of the K-center, <sup>15,45</sup> transitions between the K-center and the CB are also possible. This explanation is further supported by the PLE onset at 2.8 eV (Fig. 5), which matches well with the midgap energy of Si<sub>3</sub>N<sub>4</sub> and it is likely to be caused by transitions between the VB and the K-center (or K-center and CB).

The similar PL intensities of the SLs and the reference sample prove that the origin of the PL is located in the Si<sub>3</sub>N<sub>4</sub> matrix. Even in the SRN films of our composition (22 at. % excess Si, corresponding to only ~10 vol. % excess Si due to the high atomic density of Si<sub>3</sub>N<sub>4</sub> of  $1.04 \times 10^{23}$  cm<sup>-3</sup>),

sufficient PL active Si<sub>3</sub>N<sub>4</sub> matrix material is available after phase separation. Typical K-center densities derived from electron spin resonance (ESR) measurements were reported<sup>46,47</sup> as  $(2-5) \times 10^{17}$  cm<sup>-3</sup>, however, for high temperature annealed (and therefore virtually H-free samples), even  $2 \times 10^{18}$  cm<sup>-3</sup> were observed.<sup>16</sup> Hence, we can estimate between  $4 \times 10^{12}$  and  $3 \times 10^{13}$  K-centers per cm<sup>2</sup> in our SLs, which is of the same order of magnitude as the estimated amount of Si NCs ( $\sim 1 \times 10^{12}$  Si NCs cm<sup>-2</sup> times 20 layers, i.e.,  $\sim 2 \times 10^{13}$  NCs cm<sup>-2</sup>).

In order to scrutinize the assumption of the K-center as origin of the PL, all samples were subjected to 1 h annealings in H<sub>2</sub> ambient at 500 °C and 700 °C. Typical DB passivation annealings in the Si/SiO2 system are carried out at 400-500°C.<sup>48,49</sup> Since the K-center dangling bond is easily passivated by hydrogen,<sup>46</sup> this treatment should efficiently quench any defect-related luminescence. However, the PL spectra and the absorption coefficients do not change at all after H<sub>2</sub> annealing at both temperatures, neither for the SLs nor for the Si<sub>3</sub>N<sub>4</sub> reference sample. The stability of the PL upon H<sub>2</sub> annealing might be considered as rebuttal of the defect-related PL origin. However, the diffusion coefficient of H<sub>2</sub> in Si<sub>3</sub>N<sub>4</sub> at 700 °C was reported<sup>50</sup> to be only  $\sim 10^{-17} \text{ cm}^2 \text{s}^{-1}$ , which is equivalent to a diffusion length of only 4 nm. Efficient H<sub>2</sub> diffusion through Si<sub>3</sub>N<sub>4</sub> requires temperatures in excess of 900 °C.<sup>51</sup> Given the equilibrium nature of thermal  $H_2$  passivation, it is unlikely that at this high temperature, the DB-H reaction still dominates over the opposing dissociation reaction.<sup>48,49</sup> Also, potential structural changes due to hydrogen acting as reducing agent are of concern. Nevertheless, in Ref. 29, a slightly increased PL intensity upon  $H_2$  annealing at 900 °C was reported, although that observation alone cannot reveal the origin of the luminescence.

#### B. The role of non-radiative defects

Apparently, the nitride-embedded Si NCs do not emit any additional PL since the PL peaks of Si<sub>3</sub>N<sub>4</sub> and the SLs were demonstrated to be similar. It is well established that Si dangling bond defects represent ultimate luminescence quenching centers.<sup>52</sup> Whereas, the Si/SiO<sub>2</sub> interface has been studied extensively for the bulk-interface<sup>53,54</sup> and, for the nanoscaleinterface,<sup>55,56</sup> the Si/Si<sub>3</sub>N<sub>4</sub> interface has been studied for the bulk-interface only.46,47,57,58 It turns out that the structure and atomic surrounding of the so-called PbN center<sup>57</sup> is very similar to the well known  $P_{b}$ - and  $P_{b0}$ -centers at the (111)- and (100)-Si/SiO<sub>2</sub> interfaces, respectively.<sup>47</sup> Concerning the occurrence and density of the P<sub>bN</sub> center, two major conclusions can be drawn from the literature: In case of the (100)-Si/Si<sub>3</sub>N<sub>4</sub> interface, a remarkably good interface quality with  $[P_{bN(100)}] = (5-7) \times 10^{11} \text{ cm}^{-2}$  was observed.<sup>47</sup> In contrast, the (111)-Si/Si<sub>3</sub>N<sub>4</sub> interface exhibits significantly higher defect density of  $[P_{bN(111)}] = (7-32) \times 10^{12} \text{ cm}^{-2}$ . Thermally nitrided (111)-Si wafers were shown to have the highest P<sub>bN</sub> densities after prolonged inert gas annealings that cause the total effusion of hydrogen from the films.<sup>57</sup> Considering our annealed SL samples, all the hydrogen from the deposition is expected to be effused (this assumption has also been corroborated by FTIR measurements) and hence the upper range of the P<sub>bN(111)</sub> defect density seems applicable. Further support for the expectation of a very high defect density comes from the argumentation of Stesmans et al. concerning the rigid structure of Si<sub>3</sub>N<sub>4</sub>: Whereas, the Si-O bond angle is quite flexible and capable to compensate interfacial stress, the Si-N bond angle is virtually invariant causing high dangling bond densities as a result of interfacial stress relief.<sup>57,58</sup> Recently, we have shown that the intrinsic  $P_{b(0)}$  defect density of the bulk-Si/thermal SiO2 interface is identical to the nanocrystalline interface even down to 2 nm NC size, which is evidently owing to the Si–O bond angle flexibility.<sup>56</sup> Hence, we expect for the nanocrystalline-Si/Si<sub>3</sub>N<sub>4</sub> interface even higher P<sub>bN</sub> defect densities than reported for the bulk Si interface. Irrespective of this speculation, the defect densities for the following considerations are taken directly from the bulk Si/Si<sub>3</sub>N<sub>4</sub> literature as  $[P_{bN(100)}] = 7 \times 10^{11} \text{ cm}^{-2}$  and  $[P_{bN(111)}] = 3 \times 10^{13} \text{ cm}^{-2}$ . Obviously, the actual surface faceting of the Si NC is of utmost importance. In analogy to the oxide-embedded Si NCs, the morphology of a (100)-truncated (111)-octahedron is assumed.<sup>55</sup> In this Archimedean solid, 22.4% of the total surface area  $A_S$  is (100)-oriented and 77.6% is (111)-oriented. We propose a Poissonian distribution of the defects over the NCs

$$P_{PbN}(k) = \frac{e^{-n_{PbN}} \cdot n_{PbN}{}^{k}}{k!},$$
(1)

where  $P_{PbN}(k)$  denotes the probability to have k defects on a Si NC and  $n_{PbN}$  is the average number (expected value) of the  $P_{bN}$  defects per NC.<sup>59</sup> Since only defect-free NCs can efficiently emit PL, the probability to have no defect (k = 0) on a NC is directly related to the PL intensity  $I_{PL}$ 

$$I_{PL} \propto P_{PbN}(k=0) = e^{-n_{PbN}}.$$
(2)

Taking the average NC diameters from EFTEM and identifying them with the midsphere diameter of the truncated octahedron, the average number of defects  $n_{PbN(hkl)}$  for both facets can be calculated (see Table I). The respective probabilities to find no  $P_{bN}$  defect on one of the two facets  $P_{PbN(hkl)}(0)$ , as well as the probability to find no  $P_{bN}$  defect on the whole truncated octahedron  $P_{PbN}(0)$  and hence a potentially luminescent Si NC is also given in Table I. Clearly, the defect-rich (111)-surface facets dominate the statistics of non-radiative defects of  $Si_3N_4$ -embedded Si

TABLE I. Estimation of the average number of defects  $n_{PbN(100)}$  and  $n_{PbN(111)}$  per (100)- and (111)-facet of a Si NC and the probabilities  $P_{PbN(100)}(0), P_{PbN(111)}(0)$  to find no  $P_{bN}$  defect on the respective (100)- and (111)-facets.  $P_{PbN}(0)$  denotes the probability for an overall  $P_{bN}$  defect-free Si NC;  $d_{NC}$  and  $A_S$  denote the NC diameter from EFTEM and the total surface area of the (100)-truncated (111)-octahedron.

d <sub>NC</sub> (nm)	2.6	3.4	3.7	5.2
$A_{S} (nm^{2})$	20.1	34.4	40.7	80.5
n <sub>PbN(100)</sub>	0.03	0.05	0.06	0.13
n <sub>PbN(111)</sub>	4.68	8.01	9.48	18.73
P <sub>PbN(100)</sub> (0)	0.97	0.95	0.94	0.88
P <sub>PbN(111)</sub> (0)	$9.3  imes 10^{-3}$	$3.3  imes 10^{-4}$	$7.6  imes 10^{-5}$	$7.3  imes 10^{-9}$
$P_{PbN}(0)$	$9.0  imes 10^{-3}$	$3.1\times10^{-4}$	$7.1  imes 10^{-5}$	$6.4 \times 10^{-9}$

NCs. The frequency of P<sub>bN</sub> defect-free NCs is even in the best case (smallest NCs with 2.6 nm) less than 1% and decreases down to the  $10^{-9}$  range for NCs larger than 5 nm. For comparison, we can derive for oxide-embedded Si NCs  $P_{Pb}(0)$  values of 30% to 50% for unpassivated and up to 95% for H<sub>2</sub>-passivated samples.<sup>56</sup> Please note, the defect values for nitride-embedded NCs do not account for any potential stress increase at the nanoscale interface and, moreover, consider only the paramagnetic (i.e., ESR-active and hence detectable) P<sub>bN</sub> defects. Once again in analogy to the Si NC/SiO<sub>2</sub> interface, the presence of non-paramagnetic PL quenching centers such as charged defects<sup>60</sup> or distorted bonds<sup>35</sup> should also be taken into account. Furthermore, the non-radiative decay of an exciton in a basically PbN-free NC via N- or K-centers in the adjacent Si<sub>3</sub>N<sub>4</sub> matrix might also contribute to the absence of measureable Si NC PL. Irrespective of such continuative considerations, the bare and well justified numbers given in Table I explain coherently why PL from quantum confined excitons in Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs is very unlikely.

The PL intensity of oxide-embedded Si NCs is well known to increase upon DB passivation with H2,56,61 which is related to the  $\sim 1.5$  orders of magnitude lower defect concentration after  $H_2$  annealing.<sup>27,62</sup> As explained above, the diffusion of H<sub>2</sub> in Si<sub>3</sub>N<sub>4</sub> at medium temperatures is insufficient for efficient passivation of PbN centers. Otherwise, at least the smallest Si NCs in Si<sub>3</sub>N<sub>4</sub> should reach sufficiently high P<sub>PbN</sub>(0) values to exhibit measureable NC-related PL. However, interface defects are not the only reason for the apparent absence of Si NC PL. Taking into account, the significant extension of the tail states into the Si<sub>3</sub>N<sub>4</sub> band gap (as discussed above), it can be argued that an exciton created in the Si QD is simply not efficiently confined by high potential energy barriers since the matrix material is interspersed with tail states especially from the VB (see schematic in Fig. 7). In other words, the quantum mechanical particle-in-a-box model cannot be considered to be comprised of quantum confined Si embedded in a matrix with 5.3 eV band gap, but rather in a material, whose effective tail state free quasi-gap is substantially smaller. Any radiative exciton recombination in DB-free NCs becomes impossible if, as shown schematically in Fig. 7, the hole can escape from the QD into VB tail states during the very long ( $\mu$ s) exciton lifetime. Furthermore, the electron might then be left behind in the QD without a fast and efficient recombination path, which represents a charge-separated state known from Auger ionization (cf. schematic in Ref. 63). The situation then resembles the one that was identified to be the origin of PL intermittency in Si QDs, i.e., the blinking between an ONand an OFF-state.<sup>63,64</sup> In other words, the presence of VB tails in the energetic vicinity of the Si QD VB edge can also explain the absence of PL from Si<sub>3</sub>N<sub>4</sub>-embedded Si NCs.

## C. Origin of the peak shift

The important question that remains to be answered is why a PL peak shift is observed for samples with different Si NC sizes. The intrinsic emission energy of tail state or defect-related luminescence is not altered by different SL



FIG. 7. Schematic band diagram for a DB-free Si NC in Si<sub>3</sub>N<sub>4</sub>. If the tail states, especially from the Si<sub>3</sub>N<sub>4</sub>-VB, approach the Si-VB, the exciton is likely to lose its hole (as indicated by the dotted arrow) into VB tail states. The electron left behind in the NC would cause Auger recombination for every new exciton generated in that NC, similar to the blinking effect. This energetic situation could explain the absence of Si NC PL, irrespective of non-radiative defects.

configurations; hence the peak shift has to be explained in an alternative way. Recently, it was shown that the PL intensity of a Si NC layer is strongly influenced by the thickness of adjacent SiO<sub>2</sub> capping and buffer layers.<sup>65</sup> It was found that Fabry-Pérot resonances of excitation and emission light at the layer interfaces lead to an oscillating function of PL intensity over SiO<sub>2</sub> layer thickness. In a recent study of parasitic oxidation of Si NCs due to undesired O–H groups in PECVD-SRON/SiO<sub>2</sub> superlattices, it was also demonstrated that the peak position of Si NC PL can be shifted by changing the SiO<sub>2</sub> capping and buffer layer thickness.<sup>66</sup> Hence, optical effects that depend on the thickness and refractive indices of the layer stack could provide a reasonable explanation for the observed PL peak shift in the Si NC/Si<sub>3</sub>N<sub>4</sub> samples.

In order to investigate the issue in detail, the PL emission was simulated using the TMM, considering light emission from chaotically oriented oscillating electrical dipoles.<sup>65</sup> The PL intensity is approximated by the intensity of out-coupled emission and the emitting dipoles are simulated to be located on the planes, which are uniformly distributed over the emitting layer. The number of planes is chosen to be proportional to the thickness of the emitting layer. Each layer within the model structure is assumed to have smooth, parallel interfaces; thicknesses and effective dielectric permittivities were obtained from ellipsometry.<sup>22</sup> Since the PL emission originates from the Si<sub>3</sub>N<sub>4</sub> matrix, the light emitters were distributed over the layer stack: 85% of the dipoles in the  $Si_3N_4$  barrier layers and 15% in the Si NC layers to account for the Si<sub>3</sub>N<sub>4</sub> material laterally between the Si NCs. Figure 8 shows the comparison of the measured PL



FIG. 8. TMM-simulations of light emitting dipoles located in the  $Si_3N_4$  matrix (dotted lines) compared to the measured PL spectra (solid lines) of samples 20SL2/6 to 20SL5/6.

spectra and the TMM simulations. Remarkably, the simulations are able to reproduce the redshift of the PL peak with increasing NC size by the increase of the SRN layer thickness: The total optical thickness of the sandwich structure increases and, consequently, the frequency of the Fabry-Pérot resonance of the PL light changes. Hence, the PL peak shift of samples 20SL2/6 to 20SL5/6 can be entirely explained by interference effects without taking quantum confinement into account. In other words, at least for the samples presented here, the observed NC size dependence of the PL emission energy is an artifact and cannot be related to the QC model.

# **V. CONCLUSIONS**

Size-controlled silicon nanocrystals in amorphous Si<sub>3</sub>N<sub>4</sub> matrix with sizes between 2.6 and 5.2 nm were fabricated and their spectral and time-resolved PL as well as their absorption were analyzed. Compared to oxide/oxynitrideembedded Si NCs, the PL of Si<sub>3</sub>N<sub>4</sub>-embedded Si NC samples is: (i) about 2 orders of magnitude weaker, (ii) 2-3 times broader (FWHM), (iii) at peak energies that are on average  $\sim 650 \,\mathrm{meV}$  more blueshifted, (iv)  $10^5$  times faster decaying, and (v) has identical lifetimes for all NC sizes. Moreover, the bare Si<sub>3</sub>N<sub>4</sub> reference sample exhibits a quite similar PL peak. The combined analysis of PL and absorption results provides arguments for both, radiative recombination via Si<sub>3</sub>N<sub>4</sub> band tails and a recombination mechanism between the Si<sub>3</sub>N<sub>4</sub>-VB and its tail states to the midgap K-defect center. Hydrogen passivation annealings at medium temperatures are ineffective due to the low diffusion coefficient of H<sub>2</sub> in Si<sub>3</sub>N<sub>4</sub>. Therefore, neither the Si<sub>3</sub>N<sub>4</sub>-based DBs (K-center) nor the Si/Si<sub>3</sub>N<sub>4</sub>-DBs (P<sub>bN</sub> center) can be passivated by standard passivation annealings to explore the impact on the PL. Though the ultimate identification of the actual luminescence origin is beyond the scope of this paper, we provide comprehensive evidence that the nitride-embedded Si NCs are not the origin of the PL. Taking into account, the inherently high Si/Si<sub>3</sub>N<sub>4</sub>-interface defect densities, we derive (especially for larger NCs) infinitesimal probabilities for the occurrence of P<sub>bN</sub>-defect free and hence potentially radiative Si NCs. Furthermore, the apparent abundance of tail states in the Si<sub>3</sub>N<sub>4</sub> band gap casts doubts on the general ability of silicon nitride to confine excitons in Si NCs. The observed PL peak shifts for different NC sizes were analyzed by optical simulations using the transfer matrix method: All peaks can be reproduced solely by considering interference effects and emission from PL centers in the Si<sub>3</sub>N<sub>4</sub> matrix, i.e., without the quantum confinement model. Whereas our results are well in accordance with theoretical predictions of the adverse effects of Si<sub>3</sub>N<sub>4</sub> on the optical performance of the Si NCs,<sup>67</sup> we can of course not generalize the absence of QC for all the PL studies presented in literature so far, especially since peak energies in the broad range of 1.5 to 3.0 eV were reported. However, the following criteria should be established to critically check the PL properties of nitride-embedded Si NCs before attributing it to QC: (a) Si<sub>3</sub>N<sub>4</sub> reference samples must not exhibit the same PL spectra as the Si NC/Si<sub>3</sub>N<sub>4</sub> samples, (b) TMM simulations should be carried out to identify potential PL peak shifts as optical artifacts or, alternatively, the total layer thickness has to be reduced to less than  $\sim$ 50 nm so that the interference artifacts do not play a dominating role,<sup>22</sup> (c) time-resolved PL has to show the typical  $\mu$ s-slow PL decay of excitons confined in the indirect band gap configuration of silicon, and (d) PL lifetimes have to be a decreasing function with decreasing NC-size. In addition, low temperature PL measurements<sup>26,32</sup> could help to distinguish between fundamental semiconductor and defect behavior. Finally, it would be desirable if theoretical simulations, e.g., using density functional theory calculations, could identify the actual energy range, where QC-related PL from nitride-embedded Si NCs is expected.

The absorption measurements presented here revealed a slight blueshift of the absorption edge with decreasing NC size, however, the limitations of spectrophotometry for the investigation of near- and subgap absorption prevents any further analysis. Besides this faint indication of QC-behavior of nitride-embedded Si NCs, So *et al.* also presented evidence of QC from modeling spectroscopic ellipsometry data.<sup>12</sup> Hence, QC-effects seem to be measureable in the Si NC/Si<sub>3</sub>N<sub>4</sub> system but PL spectroscopy is evidently not the optimum method to find trivial proof of it.

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