



Formation of size-controlled silicon nanocrystals in plasma enhanced chemical vapor deposition grown $\text{SiO}_x\text{N}_y/\text{SiO}_2$ superlattices

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ABSTRACT

Size controlled silicon nanocrystals (SiNC) in silicon oxynitride matrix were prepared using plasma enhanced chemical vapor deposition. The as-deposited superlattices (SLs) and the corresponding bulk films were treated by thermal annealing. Hydrogen effusion was performed during the heating up by choosing a sufficiently low heating ramp. The phase separation of the layers into SiNCs and surrounding oxynitride matrix was studied at temperatures of up to 1150 °C. The influence of the annealing temperature on $\text{SiO}_x\text{N}_y/\text{SiO}_2$ -SLs with varying SiO_xN_y layer thickness was investigated by several analytical techniques including variable angle spectroscopic ellipsometry, photoluminescence (PL) spectroscopy, x-ray photoelectron spectroscopy, Fourier transform infrared spectrometry (FTIR) and transmission electron microscopy (TEM). Before annealing FTIR investigations show in addition to the expected Si-O bonds also the formation of nitrogen and hydrogen related bonds. The shift of the Si-O-Si stretching vibration to higher wave numbers after annealing indicates phase separation. The disappearance of the hydrogen related bonds indicates the hydrogen effusion. The PL signal is rising significantly with increasing annealing temperature and the PL peak position is strongly related to the thickness of the SiO_xN_y sublayers due to quantum confinement effects. TEM investigations confirm the size-controlled growth of SiNCs within the oxynitride matrix. The role of incorporated nitrogen and hydrogen is discussed.

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1. Introduction

In times of the global warming the demand to develop highly efficient renewable energy sources is drastically increasing. Photovoltaic devices are playing a major role among the various directions for such renewable energy sources. However, the efficiency of single junction Si based solar cells is limited and this limit can only be overcome by using new concepts. One of the possible solutions could be the applications of Si nanocrystals (SiNC) for high efficiency photovoltaic (PV) devices by including the nanocrystals into a Si tandem cell [1]. Based on the quantum confinement effect the absorption edge of the SiNCs can be shifted into the visible range of the sun spectrum. However, for best results, the absorption and hence the size of the nanocrystals should be controlled in an effective way. Many different fabrication techniques to produce SiNC have been employed since the discovery of quantum confinement in porous Si in 1990 [2,3], but most of them suffer from a limited size control. In

addition, the fabrication of such size-controlled SiNCs should be reliable at least on wafer scale. In 2002, the control of the NCs sizes was demonstrated using the growth and subsequent annealing of SiO/SiO_2 superlattices obtained from reactive evaporation [4,5] or later by co-sputtering [6]. However, reactive evaporation as well as co-sputtering does not represent the optimum choice from the economic point of view (large area scalability). Most of the nowadays used deposition processes in microelectronics are based on plasma enhanced chemical vapor deposition (PECVD) because this technology is easily up-scalable and large PECVD deposition systems already facilitate thin film PV devices such as a-Si solar cells [7]. These CVD processes are using silane (SiH_4) and, in contrast to the above mentioned reactive evaporation process, oxygen gas is replaced by N_2O due to safety reasons. Hence, if trying to prepare SiO/SiO_2 superlattices by PECVD, the incorporation of nitrogen as well as hydrogen into the growing films cannot be avoided. Whether this is an advantage or disadvantage and how it will influence the growth of the SiNCs during the thermally controlled phase separation will be analyzed as a major focus of the paper. In principle the use of the $\text{SiH}_4/\text{N}_2\text{O}$ combination offers the advantage of a reliable control of the SiO_x stoichiometry between $0 < x \leq 2$, hence a larger density of the nanocrystals within the former SiO_x layers, as suggested already in

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our original paper from 2002. This fact might be very important for the extraction of carriers in future solar devices based on SiNCs.

Up to now, the majority of research has been devoted to SiNCs in SiO₂ matrix and the growth of the SiNCs by phase separation of the respective SiO layers is well understood [8]. Owing to the chemical nature of PECVD, the choice of precursor gases introduces a new degree of freedom by choosing various kinds of matrix materials such as silicon oxynitride or silicon nitride. As a drawback, the whole SiNCs formation process has to be reinvestigated for the nitrogen (and hydrogen) containing Si rich oxide (SRO) layers to understand the influence of hydrogen and nitrogen on the formation process. It was already reported that nitrogen influences the phase separation as well as increases the crystallization temperature [9,10]. But still, a comprehensive understanding is missing. In this study, optimized size-controlled SiNC superlattices in oxynitride matrix (by using SiH₄ and N₂O) will be demonstrated. Two PECVD inherent problems will be discussed: The effusion of the hydrogen during annealing and the role of the inevitably present nitrogen in the phase separation that forms the Si nanocrystals.

The stoichiometry of the respective thin films and the phase separation within the nonstoichiometric oxide induced by thermal annealing were investigated combining x-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (FTIR). After crystallization the superlattices were analyzed by photoluminescence spectroscopy (PL) as well as transmission electron microscopy (TEM). The substantial differences in the luminescence of size-controlled SiNCs in oxynitride matrix compared to a nitrogen (and hydrogen) free oxide matrix will be discussed.

2. Experimental details

Alternating layers of silicon rich silicon oxynitride (SRON) and stoichiometric silicon dioxide (SiO₂) were deposited on piranha cleaned (H₂SO₄ and H₂O₂, 70 °C, 10 min) n-type (100)-Si substrates using an Oxford Instruments “Plasmalab 100” PECVD system with a 13.56 MHz driven parallel plate reactor. SiH₄ diluted by high purity Ar (5% SiH₄ in Ar) and N₂O were used as precursor gases. The use of diluted gases enables a better control of the growth rate for the thin films. The stoichiometry of the thin films was controlled by varying the flow ratio $\Gamma = [\text{N}_2\text{O}]/[\text{SiH}_4]$. Chamber pressure, total flow rate and flow ratio were kept at 667×10^{-3} mbar (500 mTorr), 730 sccm and $\Gamma = 660$ for the stoichiometric SiO₂ layers and at 800×10^{-3} mbar (600 mTorr), 1080 sccm and $\Gamma = 5$ for the SRON layers, respectively. All depositions were carried out at a substrate temperature of 375 °C and a RF-power of 13 W (corresponding to a power density of 40 mW/cm²). Thereby, a deposition rate in the range of only 1.5–2.5 Å/s was achieved as confirmed by systematic ex-situ spectral ellipsometry measurements. The respective layer thickness was then controlled by varying the deposition time. It should be noted, that a deposition rate in the lower Å/s range is mandatory for precise superlattice depositions. Furthermore, we confirmed by extensive ellipsometry wafer mappings that the essential layer homogeneity in the sub-percent range can be achieved over the whole 4 in. wafer for the above deposition parameters. Multilayers consisting of 20 SiO_xN_y/SiO₂ bilayer sequences were fabricated. Below and on top of the multilayer structure, a 10 nm film of SiO₂ was deposited as buffer and capping layer, respectively. The thickness of the SRON was varied from 2.5 nm to 7 nm in steps of 1.5 nm. The thickness of the SiO₂ barrier layers was fixed to 4 nm. An overview of all samples and their respective parameters are given in Table 1.

Subsequently, the samples were annealed for 1 h in N₂ ambient using temperatures ranging from 550 to 1150 °C. The annealing was carried out in a quartz tube furnace equipped with a turbomolecular pump and an electronically controlled pressure regulation. The furnace tube was first evacuated to 1×10^{-6} mbar in order to avoid any SiNC oxidation by residual oxygen in the annealing atmosphere.

Table 1
Parameters of the investigated samples.

Sample name	Number of periods	SiO ₂ buffer/capping thickness (nm)	SiO ₂ barrier thickness (nm)	SiO _{1.1} N _{0.25} thickness (nm)	Total thickness (nm)
SL_2.5/4	20	10	4	2.5	152.5
SL_4/4	20	10	4	4	184
SL_5.5/4	20	10	4	5.5	215.5
SL_7/4	20	10	4	7	247
TF_184	–	0	0	184	184

Then, a N₂ gas flow of 50 sccm was established at a constant pressure of 1050 mbar using high purity N₂ (99.9999%). The heating rate for all experiments was fixed to 10 K/min enabling a slow hydrogen effusion during the heating up which is mandatory to avoid cracks in the films. One piece of each annealed sample was subjected to an additional forming gas (5% H₂ in N₂) annealing (450 °C, 1 h) in the same furnace to passivate defects at the SiNC/SiO₂ interface [11]. Additional experiments were carried out to study the hydrogen effusion during the crystallization process using the combination of a second heated quartz tube furnace equipped with a mass spectrometer.

Thickness and refractive index of the films were measured using variable angle spectroscopic ellipsometry in an energy range of 1.1–4 eV at room temperature. Refractive indices given below correspond to values obtained at 1.96 eV (633 nm). The composition of the layers was determined by x-ray photoelectron spectroscopy (XPS) with a PHI Quantum 2000 (Physical Electronics) XPS spectrometer using monochromatic Al-K_α radiation (1486.6 eV). The spectra were taken after 1 min sputter etching with Ar⁺-ions to remove surface contamination with an ion energy of 4 keV and a corresponding sputter rate of 12 nm/min. Uniform depth profiles of some reference samples (not shown here) exclude any preferential sputtering effects. Single layers of 100 nm thickness were deposited for the respective SiO₂ or SRON layers to investigate the composition.

Photoluminescence (PL) was measured at room temperature with a LN₂-cooled CCD camera attached to a single grating monochromator using a HeCd laser (3.8 eV line) as excitation source. All spectra were corrected for the spectral response of the setup. To obtain structural information of the samples transmission electron microscopy (TEM) was performed with a JEOL J2010F (S)TEM microscope operating at 200 keV. The energy filtered images (EFTEM) were obtained in the low loss region of the EELS spectrum using a Gatan Imaging Filter (GIF 2000) spectrometer. Energy slits of 5 eV were used in order to select energies close to the plasmon peak of crystalline silicon, corresponding to 17 eV, and to differentiate from the SiO₂ plasmon peak located at 23 eV. Cross sectional TEM specimens were prepared by conventional mechanical polishing and final Ar ion beam thinning in a PIPS-Gatan equipment. To investigate the qualitative change in bond structures FTIR absorption measurements were carried out with a Bruker IFS113V spectrometer in the spectral range between 400 and 4000 cm^{−1} with a resolution of 6 cm^{−1}. All spectra are baseline corrected and corrected by the background signal and the signal of an uncoated Si reference substrate.

3. Results and discussion

In a first step, various samples with gas flow ratios ranging from $\Gamma = 3$ to $\Gamma = 660$ were deposited to find suitable compositions for the substoichiometric (crystallization) layers and the stoichiometric barrier layers. A strong PL from the SRON layers can be observed after annealing for samples deposited with gas flow ratios ranging from $\Gamma = 3$ to $\Gamma = 7$. Hence, for the investigations in this work a gas flow ratio of $\Gamma = 5$ was used for the SRON layers. For the stoichiometric SiO₂ barrier layers a gas flow ratio of $\Gamma = 660$ was used. XPS investigations of the SiO_xN_y films revealed for the as-prepared SRON layer ($\Gamma = 5$) (42.8 ± 1)at% (Si), (46.5 ± 1)at% (O) and (10.7 ± 1)at% (N),

respectively, corresponding to a stoichiometry of $\text{SiO}_{1.1}\text{N}_{0.25}$ with a refractive index of 1.74. For the SiO_2 film ($\Gamma=660$) a composition of $(33.3 \pm 1)\text{at\% (Si)}$, $(66.7 \pm 1)\text{at\% (O)}$ and a nitrogen content below the detection limit of the XPS (atom per mille range) was measured, corresponding to stoichiometric SiO_2 with a refractive index of 1.45. Hydrogen is automatically incorporated in the layers because of the SiH_4 precursor gas, but cannot be measured by XPS. Hence, to estimate the hydrogen content, the hydrogen related bonds in the FTIR spectra (Fig. 1) were analyzed using the method of Lanford and Rand [12]. It was found that the as-prepared films contain hydrogen in a range of 10–20 at.%. Additional hydrogen effusion measurements were done to monitor the hydrogen effusion during the annealing. It could be shown that the hydrogen effuses mainly at temperatures of around 550 °C. The same behavior can be monitored by FTIR spectroscopy. Previous annealing experiments using SiO_x films prepared by evaporation reported that the phase separation and rearrangement of oxygen starts even at temperatures as low as 400 °C [8]. We expect that hydrogen inside of the films can interfere with the rearrangement of oxygen and might hinder the Si clustering. However, we found from effusion experiments that the hydrogen effuses quite quickly. Hence, a rather low heating rate of 10 K/min was chosen to allow the hydrogen to escape during the heating up but without destruction of the layer due to H_2 bubbles as used in the so called smart-cut process [13].

Fig. 1 shows the FTIR measurements of the $\text{SiO}_{1.1}\text{N}_{0.25}$ bulk film for various annealing temperatures. A number of IR bands can be seen, with some of them showing a characteristic change with increasing annealing temperature. The very intense absorption band around 1000 cm^{-1} corresponds to the asymmetric stretching vibration of the oxygen atom in its twofold coordinated bridging bonding site [14,15]. As can be seen, the peak position moves slightly from 1017 to 1070 cm^{-1} with increasing annealing temperature as expected for an increased separation of the two phases (Si and SiO_2) representing the higher x in the remaining matrix material. It indicates that the chemical composition of silicon oxynitride matrix becomes close to nitrogen-free stoichiometric SiO_2 for which a peak position of 1080 cm^{-1} was reported [8]. The absorption band observed around 2200 cm^{-1} corresponds to the Si-H stretching modes with back-bonded oxygen [14,15] due to the presence of different structural units of $\text{HSi}-(\text{Si}_3-\text{O})_n$ [14]. It consists of three main components at 2145, 2200, 2238 cm^{-1} . The absorption band around 3400 cm^{-1} corresponds to the stretching vibration mode of N-H [16,17]. Some hydrogen related vibrations can still be seen for temperatures up to 550 °C; however, they are undetectable for temperatures of 700 °C or higher. The peak at 880 cm^{-1} represents the Si-O-Si mode of a $(\text{SiO})_n$ ring configuration reported before [8] overlaid by additional hydrogen related modes (for instance the bending mode of H-SiO_3 , or the

doublet wagging/bending for SiH_2) and the Si-N stretching mode [18] at 830 cm^{-1} . For higher temperatures, all the hydrogen is effused and the related modes are gone, too. In addition, at 900 °C, the phase separation of the SiO_xN_y is completed resulting in a vanishing of the $(\text{SiO})_n$ ring mode. However, the nitrogen related band at 830 cm^{-1} is obviously preserved even for annealing temperatures of 900 to 1150 °C. For more details, see the Table of IR modes in ref. [15] and reference therein. For annealing temperatures higher than 700 °C, an additional band at 800 cm^{-1} can be observed which should be related to the Si-O bending mode. The absorption mode at around 450 cm^{-1} is associated with the out-of-plane Si-O rocking mode in SiO_2 [19]. It increases with increasing annealing temperature and is a further hint for the establishing of a SiO_2 matrix for higher annealing temperatures. Please note that FTIR spectra of the SiO_2 bulk films deposited with $\Gamma=660$ (not shown here) exhibit no nitrogen related absorption bands. This is in good agreement to our XPS measurements where no nitrogen was detected. Hydrogen related absorption bands were only observed in the as-deposited SiO_2 films. All hydrogen was effused for annealing temperatures of 550 °C in agreement with our effusion experiments. For reasons of clarity all the discussed infrared modes are summarized in Table 2.

Fig. 2 shows TEM images of a selected superlattice (SL_{4/4}) after crystallization at 1100 °C. The shown sample was deposited with a regular stacking of 4 nm SiO_xN_y and 4 nm SiO_2 sublayers. The TEM images are obtained in the centre of the sample structure. The Si nanoparticles are arranged within the ~4 nm thick layers of the former SiO_xN_y sublayers. The dark regions in Fig. 2 (a) correspond to the crystallized layers and have an average thickness of 3.9–4.1 nm which is close to the nominal deposited values of the SiO_xN_y measured by ellipsometry. Using higher magnification EFTEM images the nanoparticle mean size (averaged over 20 nanoparticles) was found to be $3.9 \pm 0.7\text{ nm}$ (Fig. 2b). The size estimation of the whole samples set investigated in this study is shown in Fig. 3. As can be seen, the control of the Si NC size with the former SiO_xN_y layer thickness works for a nominal layer thicknesses of up to 5.5 nm. An upper size limit for the NCs size deviating from the prepared sublayer thicknesses was observed for thicknesses larger than 5.5 nm. There are two effects which can contribute here. First, for thicker layers, the same situation is expected as in case of bulk layers: based on the random process of nucleation the Si cluster formation and growth proceeds by diffusion processes and Ostwald ripening [20,21]. The average distance of the starting nuclei in the layer thickness will influence the growth process because they are competing for the limited Si atoms. For layer thickness in the range of 7 nm we observed in the past more than one nucleus over the layer thickness. The second effect has its origin in the presence of nitrogen in the SiO_xN_y based crystallization layers: due to the lower mobility of silicon in nitrogen containing oxides [9,10] the diffusion based phase separation might be slower. Hence, higher annealing temperatures for nitrogen containing superlattices are

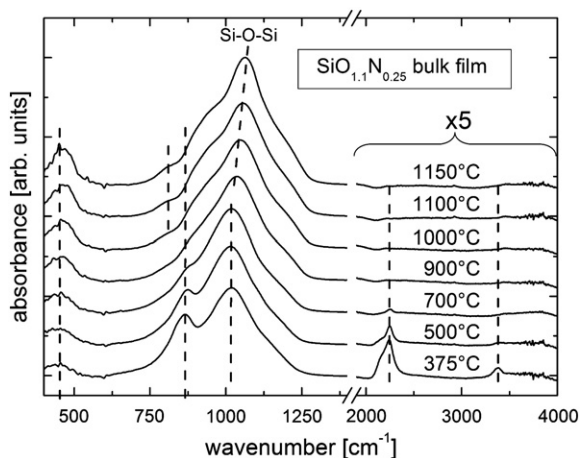


Fig. 1. FTIR measurements of the as-prepared $\text{SiO}_{1.1}\text{N}_{0.25}$ bulk film for various annealing temperatures.

Table 2
Assignments of the infrared absorption modes.

$\omega\text{ (cm}^{-1}\text{)}$	Assignment of the infrared mode	Ref.
450	Out-of-plane Si-O rocking mode in SiO_2	[19]
800	Si-O bending mode	[14,15]
830	Si-N stretching mode	[18]
880	Si-O-Si mode of a $(\text{SiO})_n$ ring configuration overlaid by additional hydrogen related modes (for instance the bending mode of H-SiO_3 , or the doublet wagging/bending for SiH_2)	[8]
1000	Asymmetric stretching vibration of the oxygen atom in its twofold coordinated bridging bonding site	[14,15]
1080	Si-O stretching for thermally grown SiO_2	[8]
2200	Si-H stretching modes with back-bonded oxygen	[14,15]
2145, 2195, 2265	Si-H stretching in $\text{HSi-Si}_3-\text{O}_n$ for $n=1, 2$ and 3	[14]
3400	N-H stretching vibration mode	[16,17]

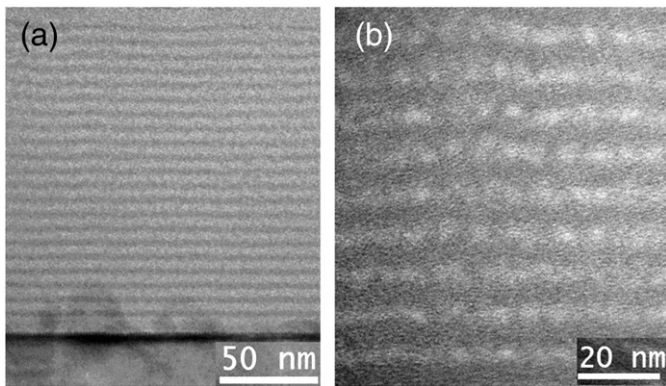


Fig. 2. (a) Bright-field TEM image of sample SL_4/4 annealed at 1100 °C. The regions in dark grey correspond to 4.1 nm of the SRON layers. (b) EFTEM image at higher magnification in a thinner region of the specimen. The Si nanoparticles are embedded in 4 nm thick bands.

normally required for a completed crystallization compared to nitrogen-free superlattices obtained from reactive evaporation [4]. A rather dense network of starting nuclei over the cross-section of the thicker sublayers (and their competition for the Si) and the slower Si diffusion can be used to explain the size limit of around 5 nm observed for our 1 h standard annealing time.

In addition to the above study of the phase separation by IR spectroscopy the involvement and signature of defects, amorphous clusters, and Si nanocrystals can be studied using PL spectroscopy. Fig. 4 represents the PL spectra of sample SL_4/4 (Table 1) as a function of the varied annealing temperature. For the as-deposited superlattice a PL peak at around 600 nm was observed. With increasing annealing temperature the PL peak position shifted slowly to higher wavelength (750 nm). For annealing temperatures of 900 and 1000 °C a further redshift to 795 nm was observed. The slight increase in PL intensity indicates the phase separation in the layers. Annealing at 1100 °C results in crystallization of Si NCs within the sublayers which enhances the PL intensity by a factor of 20 or more. Further increasing the temperature from 1100 to 1150 °C increases the PL intensity only slightly, but the PL peak position still shifts slightly to the red. This indicates that the crystallization is not yet completely finished at 1100 °C. The incorporated nitrogen in the layers hinders the crystallization at these “low” annealing temperatures due to the reduced mobility of Si in nitrogen containing oxides which slows down the crystallization rate of Si clusters. Hence, in average, higher annealing temperatures are required to achieve a complete crystallization of the silicon nanoparticles [9,10].

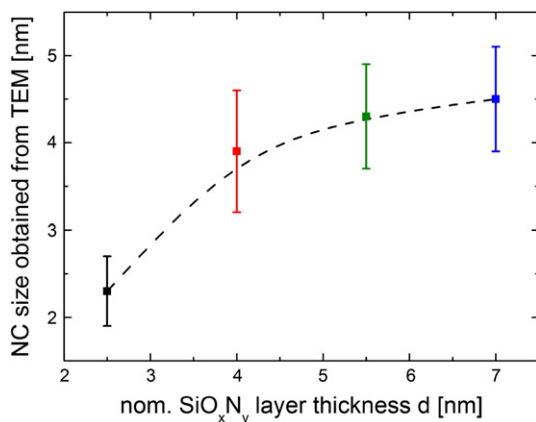


Fig. 3. Nominal $\text{SiO}_{1.1}\text{N}_{0.25}$ crystallization layer thickness versus NC size obtained from TEM measurements (the dotted line is just a guide to the eye).

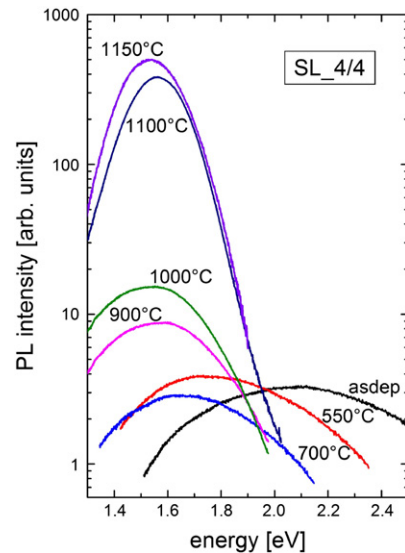


Fig. 4. Behavior of the PL signal of an exemplary sample with a regular stacking of 4 nm thick $\text{SiO}_{1.1}\text{N}_{0.25}$ and 4 nm thick SiO_2 sublayers for various annealing temperatures.

The high temperature annealing results in hydrogen effusion as can be seen in Fig. 1. However, as was shown previously, dangling bond (DB) defects will quench the luminescence of Si NCs [22,23]. The probability that a nanocrystal has a P_b -type defect is larger for the larger nanocrystals. In case of Si NCs prepared by thermal evaporation we showed previously that the paramagnetic defect density strongly depends on the H_2 post-annealing and correlates directly with the PL intensity [24]. It was found that the paramagnetic defect density prior to H_2 passivation is similar to standard thermal oxide quality and that a significant reduction by one to two orders of magnitude can be achieved by H_2 post-annealing [24,25]. Since the H_2 treatment reactivates the formerly “dark” nanocrystals they contribute now to the luminescence, resulting in an up to one order of magnitude enhancement in PL intensity. Hence, H_2 passivation experiments subsequent to the crystallization process in combination with PL can give additional information about the interface defect states. The comparison of the PL intensity ratio before and after H_2 passivation of the samples annealed at 1100 °C and the samples annealed at 1150 °C exhibits no unequivocal trend. Hence the initial defect density seems to be independent from annealing temperature for temperatures of 1100 °C and higher.

For comparison an additional SiO_xN_y single layer thin film (TF_184) was deposited having the same total thickness (184 nm) as in case of the SL_4/4 superlattice (Table 1). Annealing such a thin film results in a reduced NC number and in a lognormal size distribution (due to Ostwald ripening) with a tail on the large size part. The superlattice structure has a much higher area density of the size-controlled Si NCs compared to the annealed substoichiometric thin film single layer. PL investigations (not shown here) reveal that PL intensity of TF_184 after annealing at 1100 °C is two times lower than that of the respective superlattice (SL_4/4) annealed at the same temperature. The PL peak of the bulk film sample (TF_184) is in addition redshifted and broadened compared to the respective superlattice (SL_4/4). This is caused by the reduced number of the crystals and the shift of the size distribution to larger sizes.

As a last experiment Fig. 5 shows the normalized PL spectra for the whole set of $\text{SiO}_x\text{N}_y/\text{SiO}_2$ superlattices after crystallization at 1100 °C with varying SiO_xN_y sublayer thickness from 2.5 to 7 nm in steps of 1.5 nm and in addition the spectrum of the respective bulk film. All superlattices consist of 20 periods. A clear blueshift of the PL peak position can be observed from 1.4 to 1.7 eV as a function of decreasing SiO_xN_y layer thickness. The observed PL signal of the crystallized samples can clearly be assigned to quantum confinement effects [26].

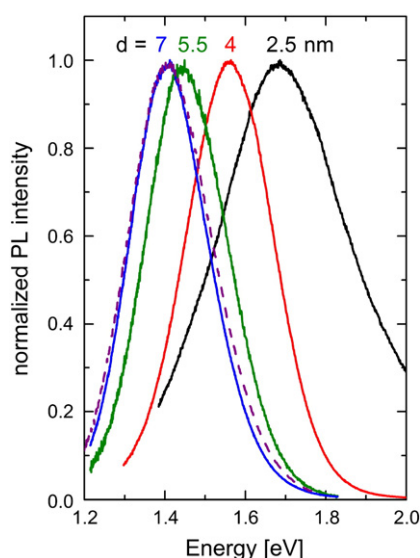


Fig. 5. Normalized PL spectra of the $\text{SiO}_{1.1}\text{N}_{0.25}/\text{SiO}_2$ superlattices with different SiNC sizes after crystallization at 1100 °C. The dotted line represents the PL spectrum of the corresponding $\text{SiO}_{1.1}\text{N}_{0.25}$ bulk film (TF_184).

The PL peak maximum of the bulk film (dotted line) is nearly at the same position as for sample SL_7/4 but slightly broader. That indicates that the size distribution of the crystals in the SL_7/4 is smaller than in the bulk film, but as mentioned before, the same effects are expected for thicker SRON interlayers (>5.5 nm) as in case of bulk layers (diffusion; Ostwald ripening). Therefore the mean crystal size and thus the PL peak position are identical for SL_7/4 and the corresponding interlayer bulk film.

4. Conclusion

Size controlled Si nanocrystals in silicon oxynitride using the superlattice approach were prepared by PECVD and the thermally induced phase separation was investigated. A rather low heating rate of 10 K/min was chosen for the annealing to remove the incorporated hydrogen non-destructively during heating up. This is supposed to result in an undisturbed transformation of the SiO_xN_y into Si clusters embedded in an oxynitride matrix. The size control is confirmed by TEM measurements. After annealing at temperatures of 1100 °C the observed nanocrystals show a very intensive PL intensity. The fact that

the PL signal still increases and redshifts for 1150 °C indicates that the crystallization is not completely finished at 1100 °C due to the nitrogen incorporated in the layers that leads to a lower mobility of Si in the oxynitride matrix. However, the blueshift of the PL peak position with decreasing SiO_xN_y sublayer thickness indicates that the origin of the PL can clearly be assigned to quantum confinement effects.

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