Size-Controlled Si Nanocrystals for Photonic and Electronic Applications

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Keywords: Si Nanocrystals, size control, photoluminescence, quantum confinement

Abstract. A new approach for the fabrication of ordered Si quantum dots fully compatible with normal Si technology is presented. The preparation of SiO/SiO₂ superlattices represents a simple and efficient method for fabricating highly luminescent Si nanocrystals and allows independent control of size, size distribution, and density. The Si nanocrystals can be arranged to a specific depth and for a specific number of layers with a nanometer adjustment. The density of the Si nanocrystals is in the range of 10¹⁹/cm³. TEM and XRD investigations confirm control of the upper limit of the nanocrystal size to an average size of below 2.5 nm with a full width at half maximum of 0.6 nm. We report on TEM images showing early states of phase separation in SiO/SiO₂ superlattices and combine these results with IR and PL investigations. Three different states of phase separation are distinguished and correlated to specific luminescence and infrared features. Photoluminescence experiments after crystallization show a size-dependent blue shift of the luminescence from 950 to 750 nm and a luminescence intensity comparable to porous Si. The nearly size-independent PL intensity observed in our SiO/SiO₂ superlattices indicates the achievement of independent control of crystal size and number. In addition, PECVD preparation of amorphous SiO/SiO₂ superlattices is reported which shows a similar size dependent luminescence after crystallization.

Introduction

Bulk crystalline silicon is the standard material for semiconductor processing and devices. Due to the indirect nature of the silicon band gap, light emission of bulk crystalline silicon is highly inefficient. Hence, today's light emitting devices are normally based on III-V semiconductors. The first reports on efficient visible light emission from a silicon based material [1, 2] established a period of intense research on the preparation and stabilization of porous silicon with deeper insight into the physics and chemistry of porous and nanocrystalline materials. In recent years, silicon nanocrystal research has shifted to the preparation of nanocrystals embedded in an oxide host. Methods applied for preparation are; Si ion implantation into high quality oxides, sputtering of Si rich oxides or reactive evaporation of Si rich oxides. With these methods the Si crystal size is controlled by the Si content in the SiO₂ matrix and the crystal density cannot be controlled independently. In addition, there is only limited control of size distribution using these methods. During recent years, methods have been developed, based on laser pyrolysis of silan, which lead to a molecular beam of freely propagating nanoparticles [3]. Size selection was achieved by using a simple molecular beam chopper and the deposition of nanoparticles on planar substrates [4]. We recently developed a new approach for the fabrication of ordered Si nanocrystals [5]. This approach is based on the preparation of amorphous SiO/SiO₂ superlattices and thermal annealing for phase separation and crystallization. The preparation of SiO/SiO₂ superlattices is an elegant and efficient method for the synthesis of size controlled Si nanocrystal. The resulting Si nanocrystals show a strong room temperature luminescence after crystallization. The process of phase separation and crystallization of such ultra thin SiO layers was investigated in detail. The thermally induced phase separation was studied using a combination of IR and photoluminescence (PL) spectroscopy, and TEM investigations at selected temperatures. In addition, preliminary results will be shown for preparing the superlattice structure by plasma enhanced chemical vapor deposition (PECVD).

Experimental Details

Amorphous $\text{SiO}_x/\text{SiO}_2$ superlattices were prepared by reactive evaporation of SiO powders in an oxygen atmosphere under vacuum. The films were deposited on 4" n-type Si wafers in a conventional evaporation system with two symmetrically arranged evaporators. Rotation of the substrate enables a homogeneity of around 10 % over the whole wafer. Before evaporation the chamber was pumped down to 1×10^{-7} mbar. The substrate temperature was held constant at 100°C . A stoichiometry of $x \sim 1$ was used for the ultra thin SiO_x layers. We prepared SiO layers with thicknesses in the range between 1 nm and 4 nm with 3 to 45 periods separated by SiO_2 layers of 3 or 4 nm. The superlattice structure forces the nanocrystals into a dense and layered arrangement. For comparison, bulk SiO and SiO_2 films were prepared under the same conditions. In addition, amorphous $\text{SiO}_x/\text{SiO}_2$ superlattices with 30 periods were deposited by plasma enhanced chemical vapor deposition (PECVD) at 350°C using N_2O as oxygen source and either a SiH_4/N_2 or a SiH_4/Ar plasma with a RF power of 40W. The PECVD process enables a cost effective production of such nanocrystalline structures. Pieces of the different samples were annealed at selected temperatures between 300 and 1100°C for 1 h in nitrogen (99.999% purity), each piece being annealed only once.

Infrared absorption (IR), photoluminescence (PL) spectroscopy and transmission electron microscopy (TEM) were used to study the phase separation and to monitor the different states of phase separation and crystallization. Infrared spectroscopy was performed using an FTIR Bruker IFS66v spectrometer equipped with a mercury cadmium telluride infrared detector in the range of 600 to 1500 cm^{-1} and using a plain piece of the same wafer as reference. The photoluminescence was excited by the 325 nm line of a HeCd laser with a power of 1.9 mW or 0.19 mW. The PL signal was focused into a single monochromator and detected by a nitrogen cooled CCD camera. All spectra were corrected for spectral response of the measurement system.

Selected samples were prepared for cross section transmission electron microscopy (TEM) investigations in the usual way including final ion milling. Imaging the superlattice structures as deposited and after annealing was realized applying the Fresnel defocus method at medium magnifications. In addition, we used dark field images for showing the presence, size and size distribution of the nanocrystals. Please note, that only nanocrystals having the right orientation to the incident electron beam can be seen in the dark field contrast images. Also, the images contain contributions from nanocrystals arranged up to a depth of 40 nm which superimpose their signals.

Experimental Results

Amorphous SiO is not a stable chemical compound and will easily decompose into Si and SiO_2 during high temperature annealing. Annealing the amorphous SiO/SiO_2 superlattice films at high temperatures (1100°C) results in phase separation of the ultra thin SiO layers and in nanometer sized Si clusters covered by amorphous SiO_2 . This process is schematically shown in Fig. 1. The SiO layer is thermally decomposed following equation (1):

Such a phase separation of the SiO automatically ensures that nucleated Si nanocrystals/nanoclusters are separated from each others by a SiO_2 shell. Based on the above equation the thickness of the oxide between the Si nanoclusters depends on the stoichiometry of the SiO_x as well. A cross sectional transmission microscopy (TEM) image of an actual sample after crystallization at 1100°C is shown in Fig. 2 and agrees well with our schematic model (Fig.1). The dark spots are the more dense Si material and represent the nanocrystals. However, the cross section

sample has a certain thickness and contains not only one row of nanocrystals. The crystals from different depth can not be separated which effects shape and density of crystals seen in the image.

Fig. 1: Fabrication of amorphous SiO/SiO₂ superlattice and thermal induced phase separation and crystallization. [6]

Fig. 2: Cross sectional TEM image of layer arranged Si crystals (~3nm) clearly separated by oxide.[6]

Fig. 3 (a): Dark field image of a crystallized SiO/SiO₂ superlattice with layer thickness of 2nm/3nm.

Fig. 3 (b): Dark field image of a crystallized SiO/SiO₂ superlattice with layer thickness of 4nm/3nm.

Fig. 3 (c): Dark field image of a “bulk” SiO film after crystallization.

Figure 3 shows the phase separation in the case of confined geometries in dark field contrast for a 2nm/3nm (a) and a 4nm/3nm crystallized SiO/SiO₂ superlattice (b). Please note, that the thicknesses given here for the as-prepared samples are nominal thicknesses estimated from the growth rate of a bulk 100 nm SiO layer and scaled down to thin layers. In contrast, a “bulk” thick SiO film is shown in Fig. 3 (c) in dark field. The bulk SiO film shows much larger sizes and a broader size distribution of the crystals than the superlattices. Analyzing the average size and the size distribution we estimated (4.5 ± 1.7) nm for the average size of the bulk SiO sample. In case of the superlattices, the thin oxide barrier separates the thin SiO layers and prevents interlayer diffusion during crystallization. This easily correlates the lateral size to the layer thickness for thickness below 5nm and the crystallization procedure used. We found (2.8 ± 0.3) nm and (3.3 ± 0.5) nm for the average size of the samples in Fig. 3 (a) and (b), respectively.

Annealing experiments using the superlattices prepared by reactive evaporation were performed to reveal the different states of phase separation by comparison of luminescence and infrared signature of different samples. The infrared spectra at temperatures ranging from 100°C (as-prepared) to 1100°C are shown in Fig. 4 for the sample with 4 nm thick SiO layers. The film with 2 nm SiO thickness shows similar IR spectra [7]. Various silicon-oxygen related absorption bands can be seen in the range from 700 to 1500 cm^{-1} . Due to the fact that our method is based on a totally hydrogen free process we can exclude all hydrogen related IR modes in the investigated range. The band around 810 cm^{-1} is assigned to Si-O-Si bond bending motion in SiO_2 [8]. With higher annealing, a band at 880 cm^{-1} appears and increases in intensity for temperatures of 400-500°C. The 880 cm^{-1} absorption loses intensity at higher temperatures and vanishes above 700°C. The IR vibration above 1000 cm^{-1} is the asymmetric stretching motion of oxygen in a Si-O-Si bridging configuration. The peak position can be used for a crude estimate of stoichiometry for homogeneous SiO_x [9]. For the bulk SiO_x film with $x \sim 1$ a position of 980 cm^{-1} was measured. For the as-prepared superlattice films (100°C) a position of 1039 cm^{-1} was found, which is the contribution of both the thin SiO and SiO_2 layers. However, a deconvolution of the modes into the SiO and SiO_2 parts can not be accomplished in a simple way. Due to the large number of SiO_2 interfaces and the very thin layers neither the effective medium nor the Bruggeman theory is valid for our system. Hence, we only monitor the shift of the mode as a measure for the phase separation. The observed IR vibration shifts from 1039 cm^{-1} to 1052 cm^{-1} for annealing from 100 to 600°C (2.6 $\text{cm}^{-1}/100\text{K}$). Annealing between 700 and 900°C results in a more pronounced shift (9.3 $\text{cm}^{-1}/100\text{K}$) with a final position at 1080 cm^{-1} representing the position found for the bulk amorphous SiO_2 film. Further annealing at higher temperatures does not shift the peak position of the vibration mode.

Fig. 4: IR absorption for the sample with a 4nm/3nm SiO/SiO₂ superlattice annealed at temperatures in the range between 100 and 1100°C

Fig. 5: Development of the PL spectra with increased annealing for the 2nm/3nm SiO/SiO₂ superlattice.

Fig. 5 gives the PL spectra at different annealing stages for the sample with 2 nm thick SiO layers. The spectra of the sample with 4 nm show similar developments as a function of temperature and has already been published in [7]. Three different luminescence bands may be distinguished. A band

at 560 nm is observed. The PL intensity increases first before decreasing again for higher annealing temperatures. At 800°C the PL band vanishes in the samples investigated so far. The PL maximum position of this band remains constant independent of the annealing temperature used.

Fig. 6: TEM images of the superlattice at various states of annealing: (a) as-prepared state.

(b) after 600°C annealing

(c) after 900°C annealing, and

(d) after 1100°C annealing

At 500°C a second luminescence band appears which gradually shifts from a position of 750 nm to 880 nm as the annealing temperature increases from 600°C to 900°C. The PL intensity of this band is weaker than that of the first luminescence band but varies from sample to sample. Finally a Gaussian shaped strong luminescence is observed for temperatures above 900°C with a peak position clearly depending on the SiO layer thickness, i.e. 800 nm for the sample in Fig. 5. For the sample with 4 nm SiO layers we found a peak position of 920 nm. The PL spectra of the whole set of samples with SiO layer thickness from around 4 nm to below 1 nm was shown before [5]. A size dependent blue shift from around 950 nm to 760 nm was observed with decreasing thickness without a significant drop in PL intensity. More results containing resonant excited PL spectra, lifetime and temperature dependent lifetime investigations will be presented soon [10]. As can be seen in Fig. 5, the intensity increases even more for the 1100°C annealing but the peak position remains constant. The PL peak intensity after crystallization is around 30 times stronger than any of the luminescence of the first and second stages. However, a significant broader non-Gaussian peak centered around 940 nm is observed for the bulk SiO film reflecting the larger size and the broader

and asymmetric size distribution of the Si nanocrystals. The PL intensity of the bulk SiO film is about one order of magnitude lower compared to our superlattices.

Selected phase separation stages of the 2/3 nm film are shown in the TEM bright field images of Fig. 6 (a-d). Due to the low element contrast between the SiO and SiO₂ layers the use of the defocus Fresnel contrast method is essential for imaging our samples. The film is amorphous for temperatures between 100°C (a) and 900°C (c), and clearly crystallized after 1100°C annealing (d). Especially in the case of the amorphous state of our samples, the images are strongly influenced by the Fresnel defocus contrast. In Fig. 7 we give the TEM images of an as-prepared (a) and annealed (b) PECVD sample. A phase separation similar to the evaporated superlattices is observed. The average size of the nanocrystals in Fig. 7 (b) was estimated as (3.25 ± 0.45) nm for an initial SiO layer thickness of 3.5 nm. Fig. 8 shows the comparison of the annealed samples with 3.5 and 3.8 nm layer thickness. Please note that our two PECVD prepared samples show a similar blue shift (from 958 to 894 nm corresponding to the used range of layer thickness) like the evaporated superlattices with comparable SiO layer thicknesses as can be seen in Fig. 8. The PL signal of the PECVD samples is around 20 times weaker compared to samples prepared by the evaporation technique.

Fig. 7 (a): As-prepared SiO_x/SiO₂ superlattice (3.5/3.8 nm) prepared by PECVD.

Fig. 7 (b): The same film after 1100°C annealing shows layered arranged Si nanocrystals in the dark field TEM image separated by SiO₂.

Fig. 8: PL spectra of two superlattices prepared by PECVD with SiO layers of 3.5 and 3.8 nm.

Discussion

As evident from Fig. 1 to 3, well arranged Si nanocrystals can be fabricated with a narrow size distribution. The thickness of the SiO layer limits the crystallization process and determines the size of the approximately spherical nanocrystals. Larger crystals can clearly be avoided by using our special superlattice structure. The density of crystals is increased in the superlattice approach as compared to the crystallized bulk SiO film and is in the range of 10^{19} cm^{-3} . This fact is very important for high PL intensities because the intensity scales directly with the number of excited nanocrystals. Larger crystals might contain defects, i.e. the carriers might preferably recombine using non-radiative channels. Also, the lifetime is longer and the recombination probability is lower for larger nanocrystals [10].

Our combined IR absorption and PL experiments were focused to demonstrate the evidence of early stages of phase separation and how, in principle, the phase separation takes place in the limit of ultra thin layers strained by SiO₂ interfaces. We conclude from our IR experiments that the phase separation process of the annealed SiO/SiO₂ superlattice can be divided into three stages:

- Stage 1 for annealing temperatures up to 600 °C is characterized by a PL signal at 560 nm and a corresponding 880 cm^{-1} IR absorption.
- Stage 2 for annealing temperatures between 600°C and 900°C still represents an amorphous state of the superlattice. Stage 2 is characterized by a more pronounced IR shift of the Si-O-Si bridging mode above 1000 cm^{-1} , the vanishing of the PL at 560 nm and the development of a new PL band which gradually shifts its position to 900 nm with increasing temperature.
- Stage 3 is observed for annealing temperatures above 900°C. It is associated with a very strong red or near infrared luminescence with the peak position depending on the SiO layer thickness, no further changes in the Si-O related absorption band, and Si nanocrystals are detected in the former SiO layer.

Stage 1 can be understood as a first rearranging and ordering of bond angles and bond length in the amorphous material without a significant phase separation. The 880 cm^{-1} absorption mode has been discussed in literature either as a mode related to oxide isolated Si rings [11, 12,13] or as a bending motion of pyramidal oxygen complex [14]. The mode is exclusively observed in the temperature range where reordering takes place and is obviously a signature of such processes. The reconstruction, ordering and phase separation is accompanied by diffusion of Si, O atoms or Si-O groups. Having no hydrogen at all in the films the 880 cm^{-1} band is clearly assigned to oxygen. The O₃ pyramidal configuration discussed in [14] with one oxygen bonded to three silicon atoms seems energetically rather unlikely even for oxygen at the surface of very small Si clusters. Oxide isolated Si rings represent a plane arrangement of the basic lattice cells for the developing Si clusters and Si nanocrystals. It is not clear to date if there are special groups favoured which mediate the phase separation and diffusion process in the amorphous SiO and show up in IR. Thus, additional experiments and calculations are needed for unambiguous assignment of the 880 cm^{-1} mode.

Bond structures occur in the matrix during the annealing which represent different types of defects as intermediate states. The increase and decrease of the defect related PL at 560 nm with temperature is at least a hint for such states. The 560 nm PL found various explanations in literature. Similar to our PL, Ghislotti [15] and Rinnert et al. [16] reported an increasing number of radiative defects produced by ion implantation. According to Liao et al.[17], the defect is the E' center (O₃≡Si•) and it is reported that the defect density decreases with thermal annealing and is almost undetectable at 1000°C. In contrast, Jeong et al. [18] assumed that the E' center does not contribute

to radiative recombination and suggested that the orange luminescence presumably originates from other defects such as the non-bridging oxygen hole center (NBOHC, $\text{O}_3\equiv\text{Si}-\text{O}\bullet$) [19]. Also, a decrease of the 560 nm PL intensity and a corresponding decrease of the 880 cm^{-1} IR absorption is observed in this report above annealing temperatures of 500°C .

In our three stage model, we expect a growth of the planar Si rings into 3 dimensional amorphous Si clusters for higher annealing temperatures. At the cluster surface, different bond defects will remain up to completing the phase separation. Although similar IR and PL bands have been reported for siloxen [20,21], we exclude siloxen structures in our superlattice. Our structures do not contain any hydrogen due to the high vacuum evaporation of SiO powder and inert gas (N_2) annealing process used. Using IR spectroscopy we did not see any hydrogen-related wagging or stretching modes.

The appearance of amorphous Si nanoclusters in the TEM image for annealing temperatures above 600°C corresponds to the appearance of the second PL band in stage 2. Similar PL spectra for amorphous Si/SiO₂ superlattices prepared by rf magnetron reactive sputtering from a silicon target in argon gas were reported by Liu et al. [22] Furukawa et al. [23] observed the process of Si cluster formation in SiO₂ films for annealing between 750 and 950°C . Kanzawa et al. [24] prepared samples by RF co-sputtering of Si and SiO₂ which showed a broad PL band in the visible region (1.6-1.9 eV) and a red shift with increasing annealing temperature and Si concentration. In our samples, we see the development of amorphous clusters and an increase of the amorphous cluster size in TEM (Fig. 6) between 600°C and 900°C which agrees with the observed red shift of the PL. For amorphous clusters the PL signal is expected to be very weak which is in agreement with our observations.

The phase separation of the amorphous Si and SiO₂ phase is completed at 900°C as evident from the now stable 1080 cm^{-1} IR absorption for the higher annealing temperature (Fig. 4). Above 900°C the crystallization of the amorphous Si clusters into Si nanocrystals takes place limited by the former SiO layer thickness. The Si nanocrystals then can be seen in the dark field TEM images as bright spots. The fixed position of the PL above 900°C shows that the size of the Si nanocrystals is determined by the former thickness of the SiO layer and the correlated cluster size. However, after 1000°C not all of the Si clusters are crystallized which results in a lower PL intensity. By using 1100°C , more and more clusters are crystallized. This can be explained by the exponential dependence of the crystallization temperature from cluster size [25]. Smaller crystals need a higher temperature for crystallization which is reflected by the strongly enhanced PL intensity for the 2nm SiO layer sample after 1100°C . The quantum confinement origin for the strong room temperature luminescence has been discussed in detail elsewhere [5, 10]

The superlattice approach was tested by using PECVD which is demonstrated in Fig. 7 (a,b) but needs further optimization. The as-prepared samples show a slightly wavy structure which is the result of an unoptimized process. Nevertheless, for such films, the size of the nanocrystals can be controlled as demonstrated by the PL blue shift for thinner SiO layer thicknesses. This opens the way for mass production of such structures in a very cost efficient way. All the samples show room temperature PL. However, in our first experiments, the PL intensity was significantly lower than with the evaporated samples. The lower PL intensity might be due to a lower number of Si nanocrystals in the films. Also, the films were deposited using a hydrogen and nitrogen containing gas. We expect a significant influence of hydrogen within the films on the phase separation process and the remaining defects in the films. It is known that hydrogen effuses at $\sim 500^\circ\text{C}$ for amorphous silicon. We expect a strong influence on the early states of phase separation because a large amount of hydrogen saturates the bonds necessary for an efficient rearrangement of the oxygen atoms during

the phase separation process. No further investigations and parameter optimization of the PECVD films and the annealing process have been performed so far. Nevertheless, the presented preliminary data demonstrate that PECVD has the potential to be used for preparing high-density size-controlled Si nanocrystals. Further investigations will be carried out in the near future.

Summary

We can arrange Si nanocrystals to a specific depth and for a specific number of layers and with a specific density. The thickness of the SiO layer controls the size of the crystals. The stoichiometry parameter x enables the control of the crystal density within the layers as well as the separation of the nanocrystals by a sufficiently thick oxide barrier. The density of the Si nanocrystals is in the range of $10^{19}/\text{cm}^3$. Using our three stage model we developed a more comprehensive understanding of phase separation and crystallization showing that the different and seemingly contradicting observations in the literature can be understood as different stages of network reorganization. The amorphous state of the SiO layer can be understood as a mixture of Si rings isolated by oxide as nucleation sites for small Si clusters in the temperature range between 100°C and 600°C. Amorphous Si clusters are growing between 600°C and 900°C and the crystallization of these amorphous Si clusters takes place above 900°C. The size of the resulting Si nanocrystals is predetermined by the SiO layer thickness and the corresponding cluster size. Si rings, amorphous Si clusters and Si nanocrystals are correlated to different states of a non-stoichiometric SiO_x matrix having typical signatures in IR absorption and photoluminescence. Photoluminescence experiments show a size-dependent blue shift of the luminescence due to quantum confinement. We demonstrated the possibility of PECVD for the preparation of size controlled Si nanocrystals.

Acknowledgement

The authors acknowledge Oxford Instruments for help in preparation of the PECVD samples. Financial support by the DFG are grateful acknowledged.

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