Si rings, Si clusters, and Si nanocrystals—different states of ultrathin SiO$_x$ layers

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Amorphous SiO/SiO$_2$ superlattices were prepared by reactive evaporation of SiO powder in an oxygen atmosphere. Infrared absorption and photoluminescence spectra were measured as a function of annealing temperature. Three photoluminescence emission bands were observed. A band centered at 560 nm is present in as-prepared samples and vanishes for annealing above 700 °C. The second band around 760 nm to 890 nm is detected for annealing temperatures above 500 °C. A strong red luminescence is observed for annealing temperatures above 900 °C. The origin of the different photoluminescence bands and different states of the phase separation of ultrathin SiO$_x$ layers is discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1525051]

Today’s silicon nanocrystal research is focused on the preparation of nanocrystals embedded in an oxide host. A new method was established based recently on the preparation of SiO/SiO$_2$ superlattices which enables independent control of size, size distribution, position and density of the crystals.\(^1\) Diffusion and phase separation processes in such confined geometries and in the presence of SiO$_2$ nearby interfaces have not yet been investigated in any detail. In addition, except for the crystallization of amorphous Si/SiO$_2$ superlattices,\(^2\) there is no theoretical work available to our knowledge which describes both phase separation and crystallization processes in the limit of ultrathin layers. In this letter, the different states of phase separation of thin SiO layers in SiO/SiO$_2$ superlattice after various annealing steps will be investigated based on infrared absorption, photoluminescence (PL), and structural characterization of the films.

A process that allows the preparation of size-controlled silicon (Si) nanocrystals was developed previously.\(^1\) For the samples investigated here, the thickness of the SiO layer was 2 nm (sample A) and 4 nm (sample B). The SiO$_2$ layers had a thickness of 3 nm. The number of periods was 45. For comparison, a bulk SiO and SiO$_2$ layer were prepared under the same conditions. Pieces of the different samples were annealed at selected temperatures between 300 and 1100 °C for 1 h under nitrogen atmosphere. Infrared (IR) spectroscopy was done using a Fourier transform infrared (FTIR) spectrometer in the range of 600 to 1500 cm$^{-1}$. The PL was excited by the 325 nm line of a HeCd laser and detected by a nitrogen-cooled charge-coupled device camera. Selected samples were prepared for cross section TEM investigations. Imaging the superlattice structures was realized by applying the Fresnel defocus method at medium magnifications.

The infrared spectra of the annealing states of sample A are presented in Fig. 1. In the range of 700 to 1500 cm$^{-1}$, various silicon–oxygen related absorption bands can be seen. The band around 810 cm$^{-1}$ is assigned to Si—O—Si bond bending motion in SiO$_2$.\(^3\) With higher annealing, a new band at 880 cm$^{-1}$ appears and increases in intensity up to 400–500 °C. For higher temperatures, this absorption band looses intensity and vanishes at 800 °C. This band is assigned to silicon ring configurations isolated by oxygen atoms.\(^4\) The band above 1000 cm$^{-1}$ is assigned to the asymmetric stretching of the Si—O—Si mode. The peak position can be used for reasonable stoichiometry estimation in case of a homogeneous SiO$_x$ alloy. For the as-prepared film (100 °C) a position of 1039 cm$^{-1}$ was found. The as-prepared position for the bulk SiO was measured to be at 980 cm$^{-1}$ and that of the as-prepared bulk SiO$_2$ to be at 1060 cm$^{-1}$. Please note, that samples A and B consist of a superlattice structure of SiO and SiO$_2$ layers which both contribute to the absorption shifting the overall mode to higher wave numbers compared to a bulk SiO film. The observed IR band shifts from 1039 to 1052 cm$^{-1}$ with annealing in the range of 100 to 600 °C. Between 700 and 900 °C, a more pronounced shift is observed which ends at 1080 cm$^{-1}$ representing the position of SiO$_2$. Annealing at higher tempera-

\[\text{FIG. 1. Infrared spectra of a SiO/SiO$_2$ superlattice. Each curve represents a piece of sample A annealed only once at the assigned temperature.}\]

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tures does not result in any further change of the Si—O related bands. The FTIR spectra of sample B and the bulk SiO film show a similar temperature dependence as sample A.

Figure 2 shows the temperature dependence of the PL signal of sample B. Three different luminescence bands are found. A band at 560 nm is observed which first increases in PL intensity before decreasing again for higher temperatures without changing the PL maximum position. This band vanishes for an annealing temperature of 800 °C. At 500 °C, a second luminescence band appears which gradually shifts from 750 nm to 880 nm as the temperature increases from 600 °C to 900 °C. The PL intensity of this band is weaker than that of the first PL band. Finally, a strong PL is observed above 900 °C with a peak position clearly dependent on the SiO layer thickness, i.e., 800 nm for sample A and 920 nm for sample B. A significantly broader peak centered around 940 nm is observed for the bulk SiO film reflecting the broader and asymmetric size distribution of the Si nanocrystals. Figure 3 compares the TEM images of sample A of the as-prepared amorphous and the annealed SiO/SiO₂ superlattices. The phase separation of the SiO layers (darker layers) after step-by-step annealing is clearly visible from Figs. 3(a)–(d). The evidence of the Si nanocrystals was proven for the 1100 °C annealed sample by high-resolution TEM.

The phase separation process of the annealed SiO/SiO₂ superlattice can be divided into three states: Stage 1, for 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 temperatures between 600 °C and 900 °C and still representing an amorphous state of the superlattice, is characterized by a more pronounced shift of the Si—O—Si stretching mode, the vanishing of the PL at 560 nm, and a development of a second PL band which gradually shifts its position with temperature. The third stage, observed for temperatures above 900 °C, shows a strong red PL with constant peak position, no further changes in the Si—O related absorption, and Si nanocrystals in the former SiO layer.

The deconvolution of the Si—O—Si stretching mode of the as-prepared superlattices cannot be done in a simple way. Effective medium or Bruggeman theory are often used for modeling inhomogeneous materials containing clusters of a different dielectric constant randomly distributed in material. These theories are not valid for our superlattices with nanometer thicknesses. The amount of material influenced by the interface increases with decreasing layer thickness which reflects the bonding too. Hence, only the peak shift, not the peak position, was used as a signature for the phase separation for discussion of the annealing behavior.

Considering the change of the 880 cm⁻¹ IR mode (Fig. 1), in stage 1 a transition occurs of the unordered intermixing of Si rings isolated by oxide and Si chain structures into a more ordered structure of oxide isolated Si rings. Such isolated Si rings represent the basic cells of the future Si clusters and nanocrystals. During the annealing, a bond rea-
rangement in the matrix might form different types of defects as intermediate states. An increase of defects can be seen by the increasing PL intensity of the defect related band at 560 nm which has found various explanations in literature. Ghislotti\textsuperscript{3} and Rinnert\textsuperscript{6} \textit{et al.} reported the increasing number of radiative defects produced by the ion implantation. According to Liao \textit{et al.}\textsuperscript{7} the defect is the E' center (O\textsubscript{3} \textasciitilde\textsubscript{Si}*) and it is reported that the defect density decreases with thermal annealing and is almost undetectable at 1000 °C. Jeong \textit{et al.}\textsuperscript{8} assumed that the E' center does not contribute to radiative recombination and suggested the non-bridging oxygen hole center (O\textsubscript{3} \textasciitilde\textsubscript{Si}–O*).\textsuperscript{9} Also in this case, a decrease in the 560 nm PL and a corresponding decrease in the 880 cm\textsuperscript{-1} IR absorption occur above 500 °C. In our model, we expect a growth of the Si rings into threedimensional amorphous Si clusters for higher annealing temperatures. At the cluster surface, different bond defects will remain. The nature of such defects in our films is currently under investigation. Although similar IR and PL bands have been reported for siloxen,\textsuperscript{10} we exclude siloxen as the origin because our superlattice did not contain any hydrogen due to the processes used.

The formation of the amorphous Si nanoclusters corresponds with the appearance of the second PL band in stage 2. The Si cluster formation in SiO\textsubscript{2} films for annealing at 750–950 °C was also observed by Furukawa \textit{et al.}\textsuperscript{11} and was well supported by the results of Kanzawa \textit{et al.}\textsuperscript{12} Their samples exhibited a broad PL band in the visible (1.6–1.9 eV). The PL peak shows a redshift with increasing temperature and increasing Si concentration. In our samples, we clearly see the development of amorphous clusters and an increase of the amorphous clusters size in the TEM images (Fig. 3) between 600 °C and 900 °C which agrees perfectly with the observed redshift of the PL.

At 900 °C, the phase separation of the amorphous Si and the amorphous SiO\textsubscript{2} phase is finished as evident from the 1080 cm\textsuperscript{-1} position of the IR absorption for higher temperatures. Above 900 °C, the crystallization of amorphous clusters into Si nanocrystals takes place, which can clearly be seen by dark-field TEM. The positions of the PL above 900 °C reflects the size of the Si nanocrystals. The quantum confinement origin for this strong room-temperature luminescence has been discussed elsewhere.\textsuperscript{1} Using our three-stage model, a more comprehensive understanding of the phase separation and crystallization process was developed showing that the different and seemingly contradicting observations in literature can be understood as different states of network reorganization during phase separation and crystallization processes.

In conclusion, phase separation of ultrathin SiO\textsubscript{2} layers in an amorphous SiO/SiO\textsubscript{2} superlattice was studied by combination of PL, FTIR, and TEM investigations. Three stages could be distinguished during the phase separation process: The transformation of a mixture of Si rings and Si chain structures isolated by oxide atoms into Si rings between 100 °C and 600 °C, the formation of amorphous Si clusters between 600 °C and 900 °C, and the crystallization of this amorphous Si clusters above 900 °C. The size of the resulting Si nanocrystals is predetermined by the SiO layer thickness. Si rings, amorphous Si clusters, and Si nanocrystals are different states of a nonstoichiometric SiO\textsubscript{2} matrix having typical signatures in IR absorption and photoluminescence.

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