Size controlled nc-Si synthesis by SiO/SiO₂ superlattices

J. Heitmann a,1, R. Scholz a, M. Schmidt b, M. Zacharias a, b

a Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
b Otto-von-Guericke Universität Magdeburg, Inst. für Experimentelle Physik, PF, 4120, D-39016 Magdeburg, Germany

Abstract

The synthesis of nc-Si by reactive evaporation of SiO and subsequent thermal induced phase separation is reported. The size control of nc-Si is realized by evaporation of SiO/SiO₂ superlattices. By this method a separate control of crystal size and density is possible. A strong blueshift of the photoluminescence signal from 850 to 750 nm with decreasing crystal size without significant intensity degradation is observed. Temperature dependent investigations of the photoluminescence are included. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

After investigations on porous Si [1] showed a photoluminescence (PL) signal in the red region of the spectrum at room temperature, interest in the optical properties of semiconductor nanoparticles, especially porous Si and Si nanoparticles, has grown over the last decade [2–4]. Their compatibility with common microelectronic device fabrication materials and techniques make them attractive for potential applications in integrated optoelectronic devices. Recently, even light amplification has been demonstrated on Si nanoparticles in an SiO₂ matrix [5]. A debate as to whether the Si luminescence is caused by quantum confinement [6], defects at the nanocluster surface [7], by excitation over the nanocluster–nanocluster interface [3], by Si–Si bonds within the nanocluster itself [8] or by oxide related defect states [9] is still on-going. The influence of the strong variation in the synthesis processes might be one reason for the different explanations of the origin for the red luminescence of nc-Si systems. Different processes for the nc-Si synthesis like Si ion implantation into high quality oxides [3], sputtering of Si rich oxides [10] or reactive evaporation of Si rich oxides [11] are known. Using these methods the Si crystal size is controlled by the Si content in the SiO₂ matrix. This means crystal size and number cannot be controlled independently. Independent control of these properties should be possible based on SiO/SiO₂ superlattices.

2. Experimental

The investigated samples were prepared by alternating evaporation of SiO powder in vacuum
under a pressure below $10^{-7}$ mbar or oxygen atmosphere under a oxygen partial pressure of $10^{-4}$ mbar. This changes the stoichiometry $x$ of SiO$_x$ alternatively between 1 and 2 [11]. The thickness of the SiO layers varied between less than 1 and 3 nm. The SiO$_2$ layers had a thickness between 2 and 3 nm. The number of periods varied between 45 and 90. The evaporated samples were annealed at 1100 °C under N$_2$ atmosphere.

Transmission electron microscopy (TEM) investigations were performed using a CM20T or a JEM-4010 electron microscope. The cross-section samples were prepared in the usual way including final Ar ion milling. Imaging the superlattice structures as deposited and after annealing was realized applying the Fresnel defocus method at medium magnifications. The photoluminescence measurements were performed using an Acton Research 500L spectrometer with an attached LN cooled CCD camera. For the X-ray diffraction (XRD) investigations an URD6, Seifert/FPM with a Cu K$_\alpha$ source in the thin film diffraction mode was used.

3. Results

Fig. 1 shows TEM images of the sample with 3 nm thick SiO layers between 3 nm SiO$_2$ buffer layers (a) as prepared and (b) after annealing. The phase separation of the SiO layers after annealing into nc-Si and SiO$_2$ is clearly visible. The nanocrystal structure and their arrangement in layers parallel to the substrate surface becomes visible in the high resolution image (see Fig. 2). The mean radius of the nanocrystals extracted for this sample is $3.5 \pm 0.5$ nm. Please note, only crystals having the right orientation to the incident electron beam can be seen by their lattice image. By XRD the average nanocrystals size was estimated using the Scherrer equation to be $3.4 \pm 0.5$ nm for the same sample.
Fig. 3 shows the PL signals for samples with SiO layer thicknesses between less than 1 and 3 nm after annealing. The PL signal shows a blue shift from 843 nm for the sample with an SiO layer thickness of 3 nm to 754 nm for the sample with a layer thickness of less than 1 nm. For both samples the number of layer periods is 45. The spectra are calibrated for spectral response of the measurement system.

Fig. 4 demonstrates the energy shift of the temperature-dependent PL signal of the samples with SiO layers of 3, 2 and 1 nm. The PL peak energy shifts by 40 meV for the sample with 3 nm thick SiO layers, by 55 meV for the sample with 2 nm thick SiO layers and 70 meV for the 1 nm thick SiO layers in a temperature range from 300 to 4 K.

4. Discussion

Kahler et al. [11] suggested the quantum confinement model as origin of the strong room temperature luminescence of evaporated and phase separated thick SiO films and showed phonon replica in the resonant excited PL signal. The quantum confinement model predicts a shift of the PL signal towards higher energies (blue shift) and a higher recombination probability for the electron–hole pairs [12] for decreasing crystal size. Therefore, the observed blue shift of the PL signal with decreasing SiO layer thickness (see Fig. 3) demonstrates the correlation between crystal size
and SiO layer thickness under the assumption that the quantum confinement is the origin of the observed PL signal. The peak position of the PL signal for different SiO layer thicknesses is in agreement with calculated band gap energies for nc-Si with the corresponding crystal size [13]. The good agreement of the XRD and TEM results for the sample with the biggest SiO layer thickness supports this assumption, but has to be proven for thinner SiO layers in the future. Increasing recombination probability for decreasing crystal size could not be seen in decomposed thick SiO films or in implanted samples so far, because in comparable samples crystal size and number are coupled and so the PL intensity for samples containing smaller crystals decreases strongly. In addition, several size dependent effects, like the crystallization process itself, the critical crystallization radius [14] or the absorption cross-section [12] play an important role. The nearly size-independent PL intensity observed in our SiO/SiO$_2$ superlattices indicates the accomplishment of separate control of crystal size and number, although we did not observe the expected increasing PL intensity for samples with decreasing crystal size.

The temperature dependent PL energy shift between 40 and 70 meV underlines the quantum confinement as possible origin of the reported PL signal. For comparison: the band gap variation with temperature for bulk Si is 50 meV over a temperature range from 10 to 300 K. Si nanocrystals synthesized by ion implantation show a temperature dependent PL shift of 60 meV in the same temperature range [15].

5. Conclusions

Clearly separated Si nanocrystals layered arrangements in SiO$_2$ matrix were prepared. The SiO/SiO$_2$ superlattice arrangement gives a separate control of the number and size of the Si nanocrystals. The blue shift of the PL signal with decreasing SiO layer thickness and its temperature dependence is in agreement with the quantum confinement model.

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References