

Alteration of band structure in Si nanocrystals

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Abstract

The photoluminescence of Si nanocrystals with dimensions ranging from 70 to 250 nm was investigated. Grains were prepared by mechanical ball-milling and subsequent sedimentation steps in order to segregate them in size. This was followed by heat treatment in argon atmosphere at 1000°C to reduce the density of dislocations introduced during milling. At the same temperature, an oxidation process in air was carried out in order to create a stable SiO₂/Si interface and reduce the dimensions of the grains. Crystallinity of the samples was checked by X-ray diffraction and transmission electron microscopy-related techniques. Two emission bands have been determined. One was identified with the D1 center usually assigned to dislocations. The second one is identified as being due to an excitonic recombination and shows phonon replicas characteristic for bulk silicon. This band is reported here for the first time. In the fraction of the smallest silicon grains, a gradual upshift of the excitonic line was observed with diminishing average grain diameter. This was associated with band structure perturbation due to size-confinement. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The visible photoluminescence of silicon nanostructures is a subject of extensive scientific interest, but also controversy [1] related to the origin of the observed emission. Discovery of visible light emission from nanocrystallites is especially attractive for the electronics industry. The development of silicon-based opto-electronics is a challenging task for present-day Si technology. However, the results of investigations of the optical properties of nanocrystalline silicon are presently in a stage of characterization and demonstration rather than practical application. The crucial problem here is the origin of the visible photoluminescence. According to Canham [2], the photoluminescence is due to quantum-confinement-induced band structure changes in the silicon grain. Other authors explain it in terms of extended surface-related defects such as, e.g. siloxene derivatives [3–5]. In this study, we investigate the origin of photoluminescence from large silicon grains with sizes in the order of 100 nm. According to theoretical estimations [6], size-related effects should start to occur for such grains. Here, in contrast to a few-nanometer grains, the surface-to-volume ratio is small. This allows for a

more reliable interpretation of the origin of photoluminescence emission.

2. Sample preparation

The main goal of the sample preparation procedure was to produce silicon nanocrystals in such a way that they would satisfy the following requirements,

- (a) Nanocrystals are developed by a size-reduction of bulk materials in such a manner that the perfect crystallinity of the grains is preserved.
- (b) The average grain dimensions are in the range of 100 nm.
- (c) The entire silicon grain retains perfect crystalline diamond structure, and the surface is terminated by a Si/SiO₂ interface layer.

Following the above goals, mechanical milling of crystalline Si was chosen for sample preparation. To avoid contamination, a ZrO₂ crucible with ZrO₂ balls was used. The grains were divided into fractions by free and centrifuged sedimentation. From scanning electron micrographs, the average grain dimensions and size distributions have been estimated. Nanocrystals were further annealed in an ambient atmosphere at 1000°C for 24 h in order to reduce the density of dislocation-related defects. Following this procedure, the grains were annealed in air atmosphere, also at 1000°C, in order to create a SiO₂ layer around the

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silicon core. In this way, grain sizes were reduced and a stable Si/SiO₂ interface was formed. Crystallinity of samples was confirmed by X-ray diffraction for oxidized and non-oxidized grains. Also, detailed investigation by techniques related to transmission electron microscopy (selected area diffraction patterning and bright field/dark field imaging) have proven that the entire grain core remains crystalline at all stages of production. The surrounding layer of SiO₂ is found to be amorphous. Its growth has been monitored by transmission electron microscopy. It has been shown to satisfy the formula, $d_{\text{SiO}_2} = 10.78\sqrt{t}$, where t is the oxidation time expressed in minutes and d_{SiO_2} is the thickness of the silicon dioxide layer expressed in nanometers [7].

3. Experiment

Photoluminescence experiments were performed in helium-bath and helium-flow cryostats over a wide range of temperatures, between $T = 4.2$ K and $T = 150$ K. An argon laser operating at $\lambda = 514.5$ nm was used as the excitation source. The excitation chopping was performed by a mechanical shutter with a frequency of 25 Hz. A high-sensitivity germanium detector was used to detect the emerging photoluminescence.

As a natural consequence of the mechanical treatment of the silicon, the dislocation-related photoluminescence was observed. The longer the heat treatment time in an ambient atmosphere or in air, the weaker the dislocation-related photoluminescence. In cases where the silicon grains were annealed in argon atmosphere for 24 h at 1000°C, and were further oxidized in air, a new multi-structure spectrum appeared with components in the wavelength range 1100–1350 nm. In Fig. 1, the full spectrum of photoluminescence emission from silicon nanocrystals is presented. It consists of the dislocation-related band D1 around 1520 nm [8,9], and the new band with a clear multi-component structure. The short lifetime of this transition, the low activation energy, as derived from its temperature dependence and a phonon-replicated structure are the arguments in favor of an excitonic origin of this new PL band. As can be seen in Fig. 1, the no-phonon transition (NP) with the energy $E_{\text{NP}} = 1097$ meV is followed by transverse acoustic (TA) and optical phonon (TO) replicas. The energies of phonons responsible for the replicas are the same as measured in bulk Si: $E_{\text{TA}} = 18.5$ meV and $E_{\text{TO}} = 58$ meV [10]. There are some indications of band structure perturbation in the investigated silicon nanocrystals: (a) different relative intensities of phonon replicas (TA and TO) than in bulk, (b) strong electronic coupling to the lattice observed as intense 2nd- and 3rd-order TO-phonon replicas, (c) broad line width of the NP transition, and TA and TO phonon replicas, and (d) an upshift of the excitonic structure when diminishing grain size by oxidation. The PL intensity ratio between the NP

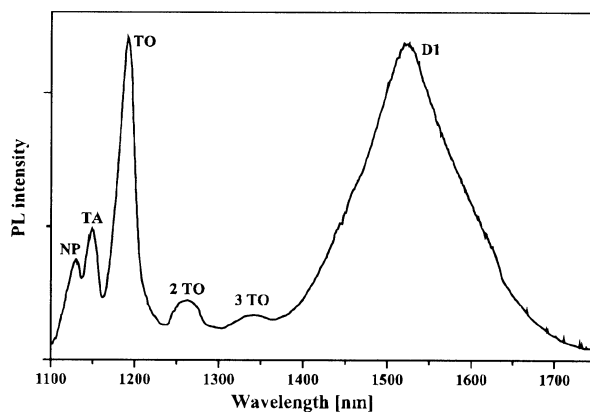


Fig. 1. Photoluminescence spectrum of ball-milled and sedimented silicon nanocrystals measured at $T = 4.2$ K under argon-laser excitation. The dislocation-related D1 band and a newly reported excitonic band can be seen. The average grain size of the crystals was $d = 200$ nm. Powder was annealed for 24 h in argon atmosphere at 1000°C, followed by heat treatment in air for 10 min.

transition and its replicas is $\text{NP/TA/TO} = 0.25:0.4:1$. This is significantly different from the ratios usually found for bulk material. The 2nd- and 3rd-order TO phonon replicas show line broadening with respect to the 1st-order TO replica. We derive the ratio between integrated photoluminescence intensities and determine it to be $1\text{st TO}/2\text{nd TO}/3\text{rd TO} = 1:0.13:0.09$. The estimated line width of the NP transition is 20 meV. The broad line width has been associated with a perturbed band structure in grains of various sizes. For the smallest powders, the excitonic structure has been observed to shift up in energy by 16 meV upon grain size reduction from $d = 115$ nm to $d = 75$ nm. The recombination energy E_{NP} of an exciton is expressed by the formula

$$E_{\text{exc}} = E_{\text{gap}} - E_{\text{e-h}} - E_{\text{b}}, \quad (1)$$

where $E_{\text{gap}} = 1170$ meV is the energy gap of bulk silicon at $T = 4.2$ K, $E_{\text{e-h}} = 14.3$ meV is the binding energy of electron and hole and E_{b} is the exciton localization energy. Since the small perturbation of silicon band structure should have only a secondary effect on $E_{\text{e-h}}$ electron-hole binding energy and $E_{\text{b}} = 59$ meV binding energy of the center, the upshift of the recombination energy can be associated with enlargement of the energy band gap due to a confined size of the nanocrystal. A similar shift has also been observed for the previously mentioned D1 line detected in the powders.

4. Conclusions

In the present studies, the dislocation-related photoluminescence and a new recombination of excitonic origin have been observed. The excitonic spectrum consists of a no-phonon transition, accompanied by phonon replicas. An upshift of the excitonic recombination with diminishing

average grain size has been associated with the size-related small band structure perturbations. These already occur for relatively large nanocrystals with dimensions in the order of 100 nm. Also, the different intensity ratios between the no-phonon transition and its transverse acoustical and transverse optical phonon replicas for bulk and nanocrystalline material indicate band structure perturbation.

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