Applied Surface Science 434 (2018) 674–680

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

# Enhanced red photoluminescence of quartz by silicon nanocrystals thin film deposition

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ARTICLE INFO

*Article history:*
Received 14 July 2017
Received in revised form 13 October 2017
Accepted 1 November 2017
Available online 2 November 2017

*Keywords:*
Silicon nanocrystals
Thin film
Quartz substrate
Photoluminescence
Interface defect states

ABSTRACT

The room-temperature photoluminescence properties of silicon nanocrystals (SiNCs) thin film on a quartz substrate were investigated, which presents the red emission enhancement of quartz. We show that the photoluminescence intensity of quartz, in the wavelength range of 640–700 nm, can be enhanced as much as 15-fold in the presence of the SiNCs thin film. Our results reveal that the defect states at the SiNCs/$SiO_2$ interface can be excited more efficiently by indirect excitation via the SiNCs, leading to the prominent red photoluminescence enhancement under the photo-excitation in the range of 440–470 nm. This work suggests a simple pathway to improve silicon-based light emitting devices for photonic applications.



## 1. Introduction

Silicon nanocrystals (SiNCs) are opening new routes for high quantum efficiency light emission due to observation of strong luminescence in the visible region at room temperature [1–4]. In recent years, nano-crystalline silicon films have attracted great interests as efficient Si-based light emitting devices for optoelectronics applications [5–8]. Many researches have been focused on development of the SiNCs film synthesis including purity, uniformity and crystallinity of silicon nanostructures to make a comprehensive understanding of its electronic and optical properties [9–11]. The films have been prepared by different methods such as plasma-enhanced chemical deposition [9], pulsed laser deposition [12], pulsed ion-beam evaporation [13] and etc. However, an effective and low-cost synthesis method which can provide the luminescent nano-crystalline silicon films with efficient emission properties is significant for many device fabrications.

In the last decade, synthesis and luminescence properties of silicon nanocrystals embedded in $SiO_2$ matrix have received considerable attention for low cost applications [14–19]. It has been shown that in the presence of SiNCs with size less than 5 nm, the crystalline features of $SiO_2$ matrix may change and different luminescence properties can be obtained [14–19]. The origin of the emissions is still controversial, but it has been ascribed either to the Quantum Confinement Effect (QCE) of the SiNCs or to the radiative recombination at the interfacial defect states of SiNCs/$SiO_2$ [14,20]. In particular, the SiNCs/$SiO_2$ interface defect states may play an important role in the origin of the luminescence process and result in emissions with energies close to those one expected from QCE in the SiNCs [14]. In this work, for the first time, we present an experimental analysis of the photoluminescence (PL) properties of SiNCs thin film on a quartz substrate by a new approach focusing on the change of quartz PL emissions in the presence of the nanocrystals film. We will show that deposition of a SiNCs thin film on the quartz substrate can improve its defect luminescence intensity in the wavelength range of 640–700 nm by a maximum factor of ~15. The results indicate that this prominent PL enhancement may originate from the effective excitation of the defect states of quartz by the nanocrystals at the SiNCs/$SiO_2$ interface.

This work is aimed to improve the emission properties of quartz by SiNCs thin film deposition. After fabrication of nano-crystalline silicon film on a quartz substrate by a simple method of centrifuge deposition of nanoparticles from a colloidal solution, the crystal structure and surface morphology of the film are characterized and reported. The luminescence properties of the film is investigated under the photo-excitation in the range of 440–470 nm and the corresponding schematic of the PL process is presented. The results show that the deposition of the film containing SiNCs with an appropriate size distribution of 2–6 nm can enhance the red PL intensity of quartz significantly.

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https://doi.org/10.1016/j.apsusc.2017.11.001
0169-4332/

## 2. Experimental details

### 2.1. Fabrication of SiNCs colloid

To prepare colloidal SiNCs, laser ablation of a crystalline silicon wafer (*n*-type) in water is carried out with fundamental harmonic beam (1064 nm) of a Q-switched Nd: YAG laser operating at 1 Hz with an 18 ns pulse width. The laser beam is focused onto the wafer surface by a lens having a focal length of 50 cm. The setup is described in our previous report [21]. The laser ablation process results in preparation of a yellowish colloidal solution of SiNCs with a volume fraction of about $7.5 \times 10^{-5}$. The nanostructure size and morphology are studied using a transmission electron microscope (TEM).

### 2.2. Preparation and characterization methods of SiNCs thin film

The centrifugation of colloidal nanoparticles has been introduced as a suitable method for depositing different types of nanoparticles on a variety of flexible or rough substrates [22]. This method offers a fast and simple procedure for nanoparticle deposition compared to other currently known techniques. Especially, it allows good coverage of a uniform nanoparticle film from the SiNC colloid with low concentration, compared to the spin coating which requires highly concentrated nanoparticle solutions [22]. To fabricate the nanocrystal film, the quartz substrate of 1 mm thickness with area of $9 \times 20\,mm^2$ is placed in a centrifuge tube filled with the SiNC colloid and is centrifuged. During centrifugation the nanoparticles accelerate toward the substrate and adhere to its surface. The adhesion mechanism may be described as a combination of van der Waals and capillary forces which strongly depend on the nanoparticles size and shape [23]. The film is fabricated by multiple coating of SiNCs on the substrate and after each stage the film is annealed at the temperature of 750 °C for two hours. The purpose of multiple coating of the nanocrystals on the substrate is to provide a uniform SiNCs thin film for studying the size-tunable optical properties of the film.

The crystal structure of the SiNCs film is investigated by a PANalytical X'Pert Pro MPD X-ray diffractometer with high intensity Cu Kα radiation (λ = 1.5406 Å). The surface morphology of the film is analyzed by a Veeco Autoprobe CP-Research atomic force microscopy (AFM) and the images are obtained at non-contact mode. The optical absorption spectra of the SiNCs film are measured using a UV–vis spectrometer (Perkin-Elmer, lamda 25). The photoluminescence measurements of the SiNCs thin film are performed at room temperature and ambient atmosphere on a fluorophotometer (Perkin-Elmer, LS 45). Fourier transform infrared (FTIR) spectroscopy (Bruker, IFS-66) is utilized to identify the surface composition of the SiNCs.

## 3. Results and discussion

The laser ablation of a silicon wafer in water resulted in the production of colloidal SiNCs with a size distribution of ∼2–6 nm (average size of ∼3.7 nm), as reported in our previous work [21]. The size and morphology of the freshly synthesized SiNCs were studied by using the TEM image of the colloid and the results are shown in Fig. 1. As this figure shows, the SiNCs have an almost spherical morphology with uniform size distribution of ∼2–6 nm. It should be noted that the TEM image reveals that the SiNCs agglomeration occurs, and therefore, some big particles were also observed. Laser ablation of silicon in water offers the possibility of production of well dispersed colloidal SiNCs with unique surface characteristics such as oxide and hydroxyl surface passivation [24,25]. Indeed, the process of laser ablation can result in formation of stable surface products on the nanocrystals because of intense plasma interaction with water environment. The surface characteristics of the SiNCs were evaluated by inspecting the FTIR spectra of the nanocrystals and the results are shown in Fig. 2. This figure shows that the main absorption bands are related to the vibration modes of Si—O—Si (in the range of 1000–1100 $cm^{-1}$) and Si—OH (wide band around 3400 $cm^{-1}$) [24]. These results indicate that the surface of SiNCs is oxidized.

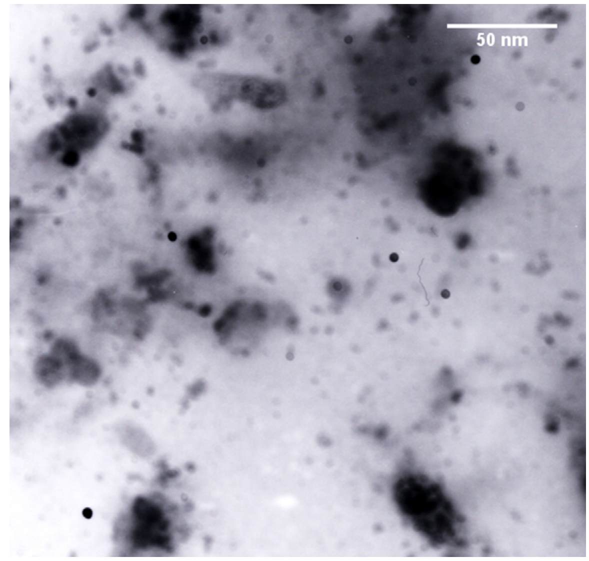


**Fig. 1.** TEM image of the SiNC colloid.

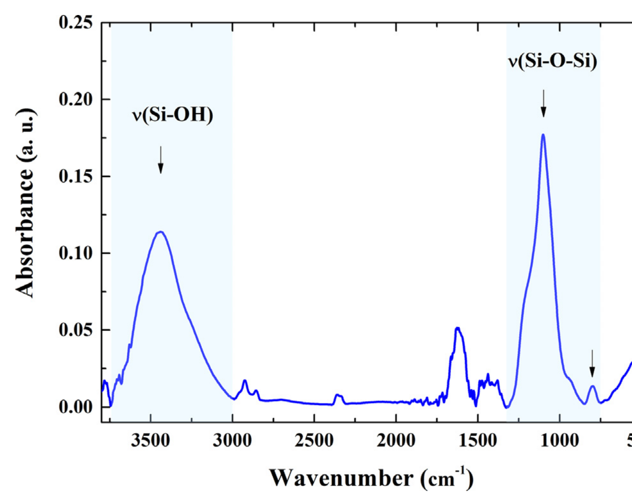


**Fig. 2.** FTIR spectrum of the SiNCs which shows the presence of the oxide layer on the surface of nanocrystals.

The X-ray diffraction pattern of the SiNCs film is shown in Fig. 3, which confirms the diamond crystalline nature with well-resolved three diffraction peaks for the silicon (111), (220) and (311) planes. This shows that the centrifuge deposition of nanoparticles from a colloidal solution is an effective technique for preparation of the nanocrystals thin film. Fig. 4 shows the AFM surface morphology of the film which indicates the formation of low density SiNCs on the quartz substrate. The bright field spots in this image correspond to the nanocrystals.

The UV–vis absorbance (optical density) of the SiNCs film at room temperature is presented in Fig. 5. According to this figure, a broad absorbance with visible onset and increasing absorption cross-section at higher energies is observed due to the QCE of the SiNCs [26]. In addition, observation of a rapid increase in the