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# Morphology and photoluminescence properties of silicon nanoparticles deposited in helium-nitrogen mixtures maintained at low residual pressures

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**Abstract.** We elaborated a technique of pulsed laser ablation in gas mixtures (He-N<sub>2</sub>), maintained under residual pressures of 0.5–5 Torr to deposit silicon (Si)-based nanostructured films on a substrate. We show that the deposited films can exhibit strong photoluminescence (PL) emission with the position of peaks depending on the pressure of ambient gas and the ratio of gases in the mixture. Nanostructured films prepared in pure He gas exhibited a strong band in the infrared range (around 760 nm) and a weak band in the green range (550 nm), which were attributed to quantum-confined excitonic states in small Si nanocrystals and radiative transitions via the localized electronic states in silicon suboxide coating, respectively. In contrast, nanostructured films prepared in He-N<sub>2</sub> mixtures exhibited more intense “green-yellow” PL band centered at 580 nm, which was attributed to a radiative recombination in amorphous oxynitride (a-SiN<sub>x</sub>O<sub>y</sub>) coating of Si nanocrystals. We also present a detailed analysis of morphology of nanostructures Si-based films prepared by laser ablation. Finally, we show that the nanocrystals can be removed from the substrate and milled by ultrasound to form aqueous solutions of colloidal Si nanoparticles. The fabricated Si-based nanocrystals present a promising object for theranostics, combining imaging functionality based on PL emission and a series of therapy functionalities (photo and radiofrequency hyperthermia, photodynamic therapy).

## 1. Introduction

Nanostructured silicon (nanosilicon) is in the focus of interest for last couple of decades due to its unique optical properties, particularly a strong luminescence emission the visible-infrared range [1], promising attractive applications in optoelectronics, photovoltaics, etc. [2,3]. Biomedical applications look like



main beneficiaries of this nanomaterial as Si nanoparticles can be used as markers in biological imaging [4-6], or sensitizers of various therapies, including Photodynamic therapy [8], photothermal therapy [9,10], radiofrequency radiation-induced hyperthermia [11], ultrasound-induced hyperthermia [12], as well as vectors of drugs such as radionuclides in nuclear medicine [13]. Such applications are further justified by the fact that silicon has excellent biocompatibility, while silicon nanostructures are biodegradable as in biological environment they decay into orthosilicic acid and then excrete from the organism [14-16]. However, the fabrication of nanosilicon structures for biomedical applications is not easy as these applications require the material in ultrapure, uncontaminated state. Indeed, nanosilicon prepared by wet chemistry methods are typically contaminated by hazardous by-products of synthesis [17], while porous silicon prepared via anodical etching in HF/ethanol solutions [1,2] is typically contaminated by hydro fluoric acid derivatives, which can lead to toxicity problems [18].

Pulsed laser ablation in gases presents one of promising dry methods to fabricate Si-based nanostructured films, which can provide interesting optical properties under exceptional purity of deposits [19]. This method is based on a natural production of nanoclusters during the action of pulsed laser radiation on a solid target [20,21]. Being ablated in the presence of a buffer gas, the nanoclusters experience collisions with gas atoms/molecules and cool down, which leads to their coalescence and crystallization in the vapour phase. When ablated in a high (e.g., atmospheric) gas pressure, the nanoclusters typically return to the target forming a thin nanocrystal layer inside and around the laser crater [22,23]. If the nanoclusters are ablated in a light neutral gas such as helium at a reduced gas pressure (typically between 0.1 and 10 Torr), their condensation and growth become controllable and they can be deposited on a substrate placed at some distance from the target. In this case, one can obtain appropriate size, crystallinity state and porosity by varying laser fluence, target-to-substrate distance and the ambient gas pressure [24-28]. In particular, we previously developed a pulsed laser ablation methodology to fabricate crystalline Si-based films under pulsed laser ablation in residual He gas and showed that PL bands from these films strongly depend on their porosity, which can be varied by changing the pressure of He during the deposition [27,28]. We then identified that the origin of red-infrared band is due to quantum-confined excitonic states in small Si nanocrystals [6]. After milling of such laser-synthesized Si crystals and dispersing in water, we demonstrated their use as markers in biological imaging [6], as well as sensitizers of various therapies [29,30]. Recently, we modified the technique of pulsed laser ablation in He-N<sub>2</sub> mixtures to achieve the tuning of PL emission [31], which is important for bioimaging tasks.

In this paper, we present additional data on structural and optical properties of Si-based nanostructured films prepared by pulsed laser ablation of Si target in He gas and He-N<sub>2</sub> mixtures maintained at low residual pressures, and describe a procedure to mill the films and disperse the formed nanocrystals in aqueous solutions.

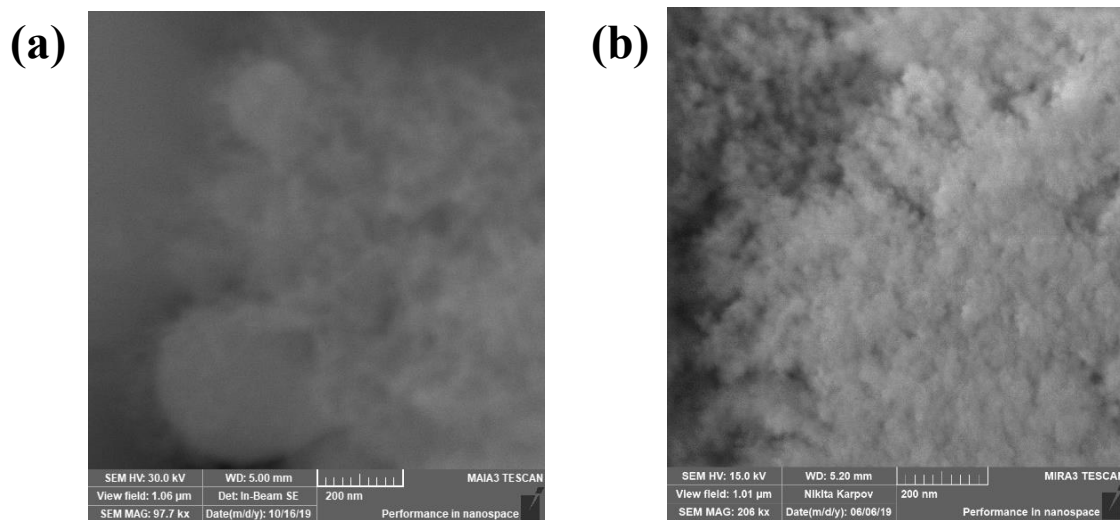
## 2. Sample fabrication

Si films deposition experiments were made using the PLD/MBE-2000 laser and the Coherent/Lambda Physik COMPex PRO 110 laser. UV KrF laser (wavelength 248 nm) was used as a source of radiation in pulsed laser deposition (PLD). The laser system operates at a frequency of 15 - 105 Hz at 100 - 250 mJ in pulse with an average power output of 3 - 25 W. A focused beam from the laser was used to irradiate a c-Si target at the angle of 45 deg. in the presence of He or He-N<sub>2</sub> gas mixtures maintained at reduced pressures of 1-5 Torr. The target was constantly rotated in order to minimize the ablation of material from the same place on the target surface. The range of pressures of He or He + N<sub>2</sub> mixtures was between 0.1 and 10 Torr. A laser-initiated plasma plume expanded perpendicularly to the target surface [19]. The ablated material was then collected on a substrate (c-Si wafer or glass slide) placed 2 cm from the target. A thin film of deposited material was visible on the substrate after several thousands of laser shots. The obtained films were studied by means of Raman scattering, the scanning electron microscopy (SEM), and photoluminescence (PL) spectroscopy. Parameters of setups related to these experiments were described in our previous work [31].

### 3. Structure of Si films

Size and shape of Si nanoparticles in films were studied by scanning electron microscopy (SEM). As shown in Fig. 1, the films deposited in pure He gas and in the mixture of He and N<sub>2</sub> had a similar porous texture, while the films deposited in the gas mixture seemed to have a larger porosity. As we showed in previous studies [28], the porosity of nanocrystalline Si-based films strongly depends on pressure of ambient gas during the deposition. Nanoclusters ablated under low gas pressures do not have a lot of collisions with gas atoms/molecules before reaching the substrate and cool down and crystallize directly on its surface forming a dense and partially amorphous film. In contrast, nanoclusters ablated under high pressures experience an excessive number of collisions in the laser plume and condense and crystallize before reaching the substrate forming a fully nanocrystalline porous films with the porosity rate proportional to the pressure of ambient gas during the deposition. At high pressures (> 10 Torr), the porosity exceeds 90% and the deposit presents a powder-like structure [28]. The porosity rate should be also dependent on the atomic mass of gases as heavier gas atoms induce the more collisions in the laser plume, which leads to a higher probability of condensation and crystallization before reaching the substrate. Indeed, as follows from the analysis of SEM images, the films deposited in the mixture of light He and heavy N<sub>2</sub> have a higher porosity that the films deposited uniquely in light helium gas.

In our tests, we also studied volt-ampere characteristics (VAC) of the films. In our case, the tunnel contact consisted of tungsten probe (metal) and a Si nanocrystal-based film. The observed VAC dependences (not shown) were fully consistent with the typical volt-ampere characteristics of the tunnel contact between a metal and a semiconductor. Therefore, it was concluded that the prepared films had semiconductor properties and nanocrystalline structure, while the amorphous fraction was negligible. The phase composition of the obtained samples was also studied by Raman spectroscopy and results of these tests confirmed the presence of nanocrystalline silicon phase.

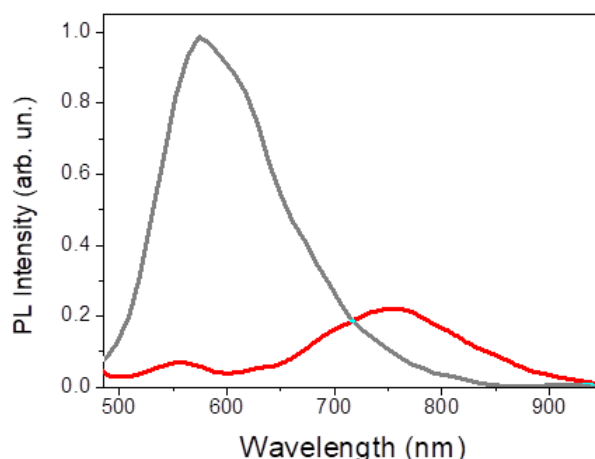


**Figure 1.** Typical SEM images nanostructured Si-based films deposited in pure He (a) and in 1:1 mixture of He and N<sub>2</sub> under the gas pressure of 5 Torr.

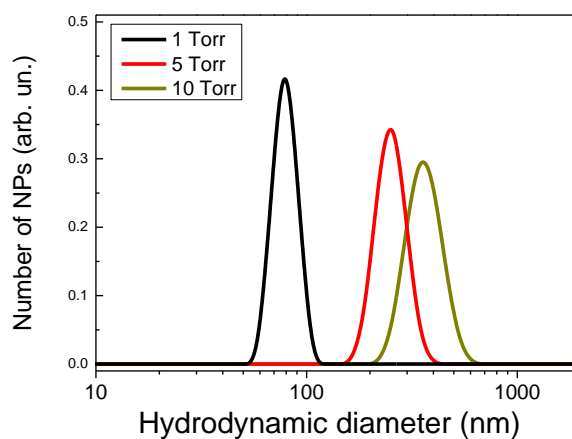
### 4. Luminescent properties of Si films

The luminescence was excited using 350 nm or 450 nm pumping wavelengths, while the system made possible the analysis of spectra until 1200 nm. As shown in Fig. 2, the films fabricated by pulsed laser ablation in gas ambient exhibited strong PL signals just after their exposition to ambient air. The spectrum of luminescence for the films deposited in pure He (red curve) consisted of two PL bands centered around 760 nm and 550 nm, respectively, which is consistent with our previous data [6,28,31]. The first red band was earlier shown to be due to the radiative exciton transitions in Si nanocrystals [6], while the second blue-shifted band can be explained by the radiative transitions via the localized electronic states in silicon suboxide (SiO<sub>x</sub>) coating of Si nanocrystals under the aging of laser-ablated

films in ambient air [28,6]. As shown in Fig. 2, films prepared in He-N<sub>2</sub> mixtures had quite different PL properties. One can see that the addition of N<sub>2</sub> led to a complete disappearance of near-infrared peak associated with radiative exciton transitions in Si nanocrystals, while the second band in the green band evolved into at least 10-times more intense band in the yellow range (center at 570-580 nm). The generation of this green-yellow band can be unambiguously related to nitrogen-based passivation of Si nanocrystals and attributed to radiative transitions between electronic states in a-SiN<sub>x</sub>O<sub>y</sub> coating on the surface of Si nanocrystals [31].



**Figure 2** PL spectra of laser-ablated Si films prepared in different gas mixtures: 100% He, pressure 5 Torr (red), 50% He, 50% N<sub>2</sub>, 5 Torr (grey).



**Figure 3.** Hydrodynamic size distributions of Si NPs prepared from laser-ablated films deposited in 1:1 mixture of He and N<sub>2</sub> under different residual gas pressure.

The projected biomedical applications require the milling of nanocrystals and their dispersion in aqueous solutions. To explore if such a dispersion is possible, we carried out ultrasound-assisted breakage (sonification) of the laser-deposited films. The processing was performed in deionized water or saline (0.9% NaCl in H<sub>2</sub>O) for 1 h. The power density and frequency of ultrasound were 5 W/cm<sup>2</sup> and 44 kHz, respectively. The nanocrystalline porous films were detached from the substrate as a result of this sonification and dispersed in the solution forming a colloidal suspension of Si nanoparticles. As shown in Fig. 3, the hydrodynamic size increased with the increase of total gas pressure during the deposition, which was in agreement with results of scanning electron microscopy measurements. It should be noted that we managed to mill substrate-supported nanocrystalline films and disperse so-

formed nanoparticles in aqueous solutions for the films deposited under different gas pressures. We earlier showed that the dispersed nanoparticles present quantum dots and can serve as efficient markers for bioimaging [6].

Thus, the proposed procedure based on pulsed laser ablation from a Si target in helium/nitrogen mixtures, followed by ultrasound-based milling and water-dispersion of nanocrystals, presents a promising pathway for the synthesis of non-toxic quantum dots for bioimaging. In the absence of hazardous chemicals during the fabrication process the Si quantum dots are exposed only to clean ambients (residual gases, air, physiological solutions) and should have ultraclean surface. Combined with a possibility of initiating therapeutic functionalities [8-12], the synthesized nanostructures present a novel promising theranostic agent. On the other hand, the proposed approach enables one to deposit nanostructured porous Si films on virtually any substrate (glass, gold film, etc.), which opens up avenues for novel applications. In particular, as we showed in earlier studies [32], such nanostructured porous films can be deposited on gold and be used as matrices for bioimmobilizations in surface plasmon resonance biosensors using a prism-based coupling geometry [33-36]. However, to excite surface plasmons over such a matrix, silicon-based prism having high refractive index ( $> 3$ ) is typically required [37,38].

## 5. Conclusion

Using methods of pulsed laser ablation in residual gases (pure He and He-N<sub>2</sub> mixtures), we deposited Si-based films on a substrate. We found that the films are composed of Si nanocrystals arranged in a porous matrix, while the porosity rate is proportional to the pressure of ambient gases during the deposition. The data on crystallinity of formed films were confirmed by Raman spectroscopy studies and electric measurements. We showed that the fabricated films exhibited strong PL signals: the films deposited in pure He exhibited two bands around 760 and 550 nm, while the films deposited in He-N<sub>2</sub> mixtures exhibited a single band centered around 570-580 nm. We finally demonstrated the possibility for ultrasound-based milling of the films and the formation of aqueous solutions of colloidal Si nanocrystals. The fabricated nanostructures are important for theranostic applications.

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