06

Multiphoton microscopy as a way to control the purification efficiency of silicon filamental nanocrystals

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Multiphoton microscopy is a promising method for controlling the degree of contamination and purification efficiency in solid-state structures and microstructures. It has been demonstrated that, unlike conventional scanning laser microscopy techniques, multiphoton microscopy provides information about the localization of contaminants on silicon filamentary nanocrystal structures and enables qualitative evaluation of their purification level after cleaning procedures.

Keywords: Two-photon microscopy, two-photon photoluminescence, filamentary nanocrystals, silicon.

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There exist numerous methods for producing structures and microstructures, after which the obtained structures require cleaning from contaminants. Such contaminants may be byproducts of side reactions, impurities deposited from the environment, residual precursors, impurities contained in precursors, and raw material contamination. Additionally, preliminary cleaning of raw materials is often required. Purification of structures and raw materials is frequently mandatory, and its quality must be controlled at every production stage.

The monitoring of material purity levels and cleaning quality can be performed using various methods, among which microscopic techniques are the most prevalent. The fastest, most convenient, simplest, and most universal approaches are those of optical microscopy.

This work proposes the application of multiphoton microscopy (MPM) for investigating contamination levels and purification efficacy in solid-state microstructures. The method is based on the nonlinear optical effect of multiphoton absorption and consequently possesses several significant advantages over other optical microscopy techniques [1,2]. Multiphoton absorption involves the nearly simultaneous absorption of two or more photons, with such low-energy photons typically belonging to the near-IR range. To observe multiphoton absorption phenomena, extremely high light intensity must be achieved, for which MPM employs a femtosecond laser. This laser generates ultrashort pulses with durations of several tens of femtoseconds, reaching power levels of several MW. The radiation is focused in the sample region, which further enhances the radiation intensity at the focal point. Meanwhile, the average laser power remains low, on the order of tens of mW.

The low average power and IR radiation range make MPM ideal for studying biological objects [3,4]. Living tissues are transparent to IR radiation, while its low power prevents phototoxicity and photobleaching of biological specimens. Furthermore, the use of IR radiation enables investigation of numerous solid-state materials in bulk, which is impossible for most other optical microscopy methods, since such materials absorb visible radiation but transmit IR [5,6].

An additional advantage of MPM is that multiphoton absorption removes the constraints imposed by dipole selection rules for optical transitions [7]. Consequently, the photoluminescence (PL) property becomes observable in numerous materials that do not exhibit it under single-photon absorption.

The aim of this work is to demonstrate that MPM represents the most preferable method for monitoring contamination levels in solid-state structures among optical techniques.

Silicon filamentary nanocrystals (FNCs) were synthesized via plasma-chemical etching. A KDB-12 monocrystalline silicon wafer with (001) crystallographic orientation was placed in an autoclave and exposed to chemically active radicals generated through SF_6 gas molecule ionization by inductively coupled plasma [8]. Such silicon-based structures, along with those of other materials, are extensively utilized for developing sensor and photonic components [9,10], whose properties are critically dependent on surface conditions, including contamination levels.

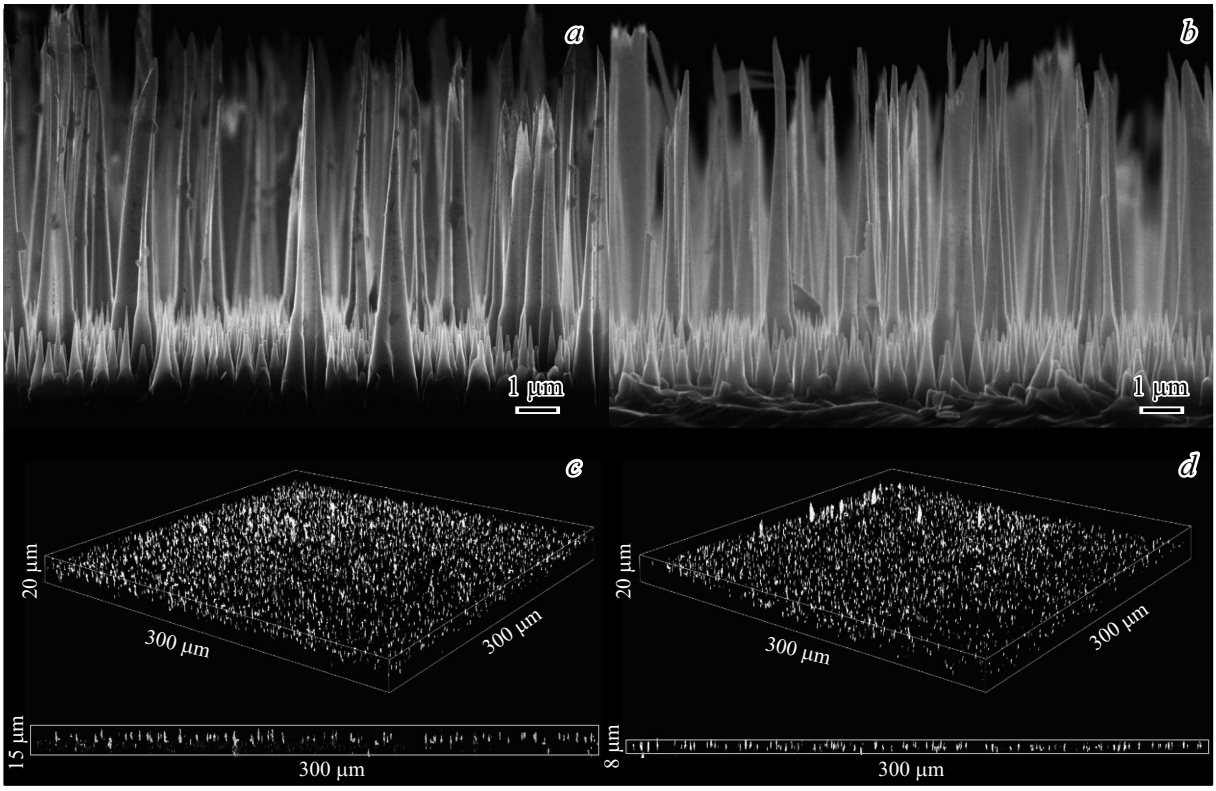

Figure 1. SEM images of filamentary nanocrystals before (*a*) and after (*b*) cleaning and MPM images of filamentary nanocrystals before (*c*) and after (*d*) cleaning.

Scanning electron microscopy (SEM) images were acquired using a Zeiss Supra 25 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) operating at an accelerating voltage of 18 kV.

MPM images were acquired using a Bergamo II multiphoton microscope (Thorlabs, Newton, USA) equipped with a Ti:sapphire femtosecond laser, Tibetius (Thorlabs). The laser parameters were as follows: wavelength 800 nm, pulse duration 140 fs, pulse repetition rate 77 MHz, average power 150 mW. PL was detected within the 300–705 nm spectral range.

Fig. 1, *a* shows FNCs that have not undergo the purification procedure. The image reveals particles deposited on the FNC walls, resulting from secondary deposition of silicon, silicon and sulfur oxides, silicon fluoride, and other reaction byproducts [8,11]. The structural imperfections and complex composition of these particles cause them to exhibit PL properties under two-photon excitation, whereas no PL was detected under single-photon excitation. As shown in Fig. 1, the PL from these particles, which are essentially contaminants, replicates the FNC morphology. The PL distribution extends approximately 15 μm in height, matching the FNC dimensions.

Following the cleaning procedure, which involved soaking the sample in a 30 % nitric acid solution for 5 minutes, most particles on the FNC surface were removed (Fig. 1, *b*). The PL distribution map (Fig. 1, *d*) shows reduced PL intensity, with a height distribution of approximately 8 μm. These results indicate that the cleaning procedure effectively purified only the upper layers of the FNC structure, while leaving near-substrate regions largely unaffected. These areas contain numerous small silicon peaks and exhibit smaller inter-FNC distances. A comparison of the initial PL distribution histograms before and after cleaning is presented in Fig. 2. The ratio of average brightness levels in the PL distribution maps is 1.42, demonstrating a significant decrease in average PL intensity after cleaning.

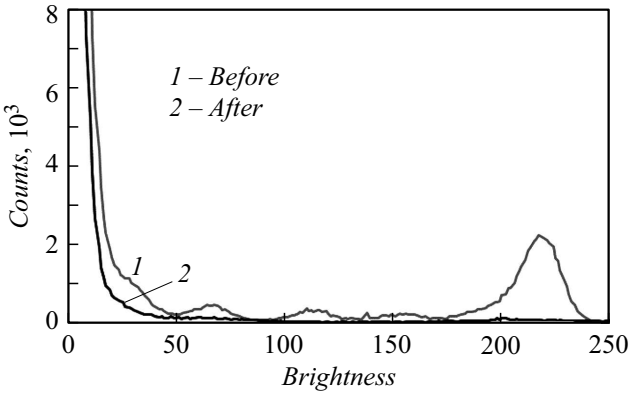

Figure 2. Histograms (depending on brightness) of the FNC PL distribution patterns before (*1*) and after (*2*) cleaning.

The MPM method enabled rapid and efficient acquisition of PL distribution maps for the structures both before and after sample cleaning, allowing for determination of contaminant localization and purification quality assessment. Notably, conventional laser scanning microscopy methods failed to detect any PL signal in the studied samples. Through more detailed structural analysis and establishment of definitive correlations between quantitative contamination parameters (such as contaminant distribution density) and the observed PL distribution patterns, comparative analysis of PL maps could serve as a rapid and convenient approach for monitoring structure purification levels. The MPM technique may potentially replace more labor-intensive and costly control methods and could be implemented in industrial production processes.

Conflict of interests

The authors declare no conflict of interests.

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