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# Sonosynthesis of microstructures array for semiconductor photovoltaics

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ABSTRACT

The properties of the silicon samples subjected to cavitation impacts have been studied. It was shown that high-intensity (15 W/cm$^2$) and high-frequency (1–6 MHz) sonication of silicon samples in the liquid nitrogen induces changes of the physical, chemical, and structural properties of semiconductor surface. Optical, atomic force and scanning electron microscopy techniques as well as energy dispersive X-ray spectroscopy, X-ray diffraction and photoresponse spectroscopy were used. The experimental study demonstrates the microstructure formation as well as a change of the chemical composition at the silicon surface. It was found that a significant rise in value and expansion of the spectral range of photosensitivity take place after cavitation treatment. The photoresponse of about 2.0 eV can be connected with the formation of Si-rich $SiN_x$ compound inside the ultrasonically structured region of Si. The obtained value of the refractive index confirms this assumption.



## 1. Introduction

Structuring of semiconductor surfaces is important in many branches of science and technology [1]. Such surface properties as roughness, light reflectivity, chemical activity, and biocompatibility have a potential use especially in electronics and medicine. For example, standard solar cell fabrication technique uses silicon wafers with textured surfaces, since the surface texturing is a well-established strategy for reducing reflection. Surface structuring is also applied in MEMS (micro-electromechanical systems) [2]. Thanks to the development of such booster technologies as reactive ion etching, isotropic etching, plasma ashing/cleaning the manufacturing of all silicon devices based on the scaling law became possible [3]. At the same time solid surfaces can develop a wide range of topological features upon bombardment with ions as well as under irradiation by laser pulses with femto- and picosecond duration. Nowadays, ultrasound is used extensively in mechanical engineering for bonding and manipulation in micro-machines, for cleaning in electronic engineering and medical/pharmaceutical industries, for nondestructive control and measurement, for health diagnosis, food treatment, etc. [4]. Extreme conditions of the ultrasonic cavitation such as local temperature and the pressure [5] are widely used in chemistry, as for example to synthesize nano-materials [6], to enhance the electrochemical reactions and to modify the surface properties of electrodes [7], as well as to generate the novel materials in a liquid medium [8].

In the previous work, we have shown that the exposure of semiconductor substrate to megasonic cavitation leads to the surface structuring [9,10]. It was revealed that the characteristic dimension of the peculiarities on the semiconductor surface depended on the exposure parameters

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and can be controlled (from micron- to nano-scale dimension) by the regulation of the acoustic frequency. In this investigation, we demonstrate that topological features induced by sonication on the semiconductor surface can be useful for the photovoltaic application.

## 2. Experimental section

### 2.1. Materials

Boron-doped *p*-type silicon (wafers grown by the liquid-encapsulated Czochralski method, with diameter about 76.2-mm, one-side polished), with a (100) surface crystallographic orientation, were used in this study. Samples were cut into 5 mm × 5 mm squares to fit the sample holder used for sonication experiments. Before the investigation all samples were cleaned for 10 min in ethanol and then in $ddH_2O$ (water for analytical laboratory use, ISO 3696:1987). The initial surface was found to be totally flat, devoid of defects, with a measured roughness lower than 1 nm. The roughness was determined by atomic force microscopy (AFM) on a few randomly chosen areas of $40 \times 40\ \mu m^2$. X-ray diffraction (XRD) patterns from the initial samples besides the Si 400 diffraction peak reveal higher intensity background in the range of $2\theta = 20–30^\circ$ that denotes the existence on the Si substrate surface of amorphous thin film, obviously from the amorphous native silicon oxides, as was observed in [10]. This layer was not removed as it is going to disappear during the process of sonication, since the modified region is entirely below the original surface.

### 2.2. Sonication and post-treatment annealing

In typical experiments, the Si samples were sonicated in cryogenic liquid such as liquid nitrogen (LN). For cavitation activation, a homemade megasonics (1–6 MHz) system with focused energy resonator described elsewhere [9] was used. Semiconductor target was placed inside the acoustically driven copper cell filled with technical liquid nitrogen, where the cavitation processing was initiated. The maximal value of the acoustic intensity was about $\sim 15\ W/cm^2$ in the focus of the acoustic system. Sonication were performed at constant temperature (80 K) using a cryostat system. Post thermal annealing was carried out in the atmospheric ambient at 980 °C for 1 h.

### 2.3. Characterization

All processed surfaces were examined after fixed cavitation intervals using optical and atomic force microscopy. Scanning electron microscopy (SEM) characterization was realized using JSM-6490 microscope supplemented by energy dispersive X-ray analysis (EDAX). Operating conditions for SEM and EDAX were the same. A standard procedure of photoresponse spectroscopy was employed before and after the sonication. The structural characterization of the silicon samples was carried out by XRD in the standard symmetric reflection geometry using CuKα radiation. XRD rocking curves measured using the $\omega$-$2\theta$ scan for the samples investigated before and after sonication were obtained by a Triple-axis X-ray PANalytical X'Pert Pro diffractometer. The CuKα1 radiation with a wavelength of 0.15418 nm was separated out using a four-bounce (440) Ge monochromator. The optical characteristics of the typical annealed sample were studied by ellipsometry. The measurements were performed using a laser ($\lambda = 632.8$ nm) photoelectric compensation null ellipsometer (LEF 3G-1). The ellipsometric parameters $\Delta$ and $\psi$ were determined from the results of multi-angle measurements in a range of incidence angle $\phi = 50–75^\circ$.

## 3. Results

It was found that the sonication of the silicon samples has resulted in the essential change of the physical and structural properties of semiconductor surface. First of all, the sonication has resulted in the silicon surface structuring as well as in a significant rise of the silicon photosensitivity.

### 3.1. Surface morphology and elemental composition

In the previous work we observed that the characteristic dimension of the structures on the semiconductor surface depends on the exposure parameters (duration, acoustic power) and can be controlled by the regulation of the acoustic frequency [9]. In particular, a dendrite-like micron-scale array formation inside the ultrasonically structured region was found. In this investigation, morphology of the structured surface was investigated using different techniques. Optical microscopy revealed the growth of dendritic crystal inside the structured region of Si sample during sonication at the maximum value of acoustic intensity in the LN at 1–3 MHz (Fig. 1a). The increase of processing time results in the appearance of the features with crystal symmetry as shown in Fig. 1b. Fig. 1c illustrates the changes in the silicon surface after the post-sonication annealing.

Fig. 2 illustrates SEM and AFM images of ultrasonically structured regions with the dendrite-like structures of silicon sample sonicated in the liquid nitrogen before annealing. The height of typical dendrite-like structures measured using AFM was about 160 – 200 nm (see Fig. 2b). SEM characterization supplemented with EDAX shows that both surface morphology and the elemental composition of the silicon surface undergo dramatic changes at a small scale under sonication. The chemical composition of the samples was studied on a numerous randomly chosen areas of $5 \times 5\ \mu m^2$ as shown in Fig. 2a. EDAX shows that together with the peaks corresponding to Si atoms appeared the peaks corresponding to the following elements: O, Na, K, Ca and Cl (see Table 1). In our previous investigation we found an inhomogeneous incorporation of the nitrogen atom into the GaAs substrate exposed to the acoustic cavitation in liquid nitrogen [9]. At the same time, the nitrogen atoms on the silicon surface have not been observed by EDAX. Ultrasonically structured regions with the dendrite-like structures have a silicon nature, contain a number of alkali metals (region 2, Fig. 2a, Table 1) and are surrounded with the oxidized surface (region 3, Fig. 2a, Table 1).