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Raman spectroscopy of silicon nanowires formed by metal-assisted chemical etching

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Abstract. Silicon nanowires obtained by metal-assisted chemical etching of crystalline silicon (Si) wafers are studied by Raman spectroscopy to reveal the effect of the formation time of nanowires and their additional doping with boron and phosphorus. The observed modification of the spectrum shape in the boron-doped samples due to the Fano effect made it possible to estimate the concentration of free holes in Si nanowires, which is of the order of 10^{19} - 10^{20} cm^3, depending on the preparation conditions. The obtained results indicate the potential of the Raman spectroscopy for contactless diagnostics of Si nanostructures.

1. Introduction

Nanostructured semiconductors attract research attention due to their unique physical properties and a wide range of applications in electronics, photonics, renewable energy and biomedicine [1]. Considerable effort has been made to study various types of silicon nanostructures, including porous silicon (Si) [2]. Also, Si nanowires (SiNWs) obtained by metal-assisted chemical etching (MACE) of crystalline silicon (c-Si) are promising for applications in microelectronics, thermoelectric energy converters and biosensorics due to new physical and bioactive properties [3,4].
In our work we use the Raman scattering spectroscopy to investigate the role of MACE duration and subsequent additional doping of SiNWs on their structural and electrical properties, respectively.

2. Experimental

Investigated samples were ensembles of SiNWs grown by MACE on lightly boron- and phosphorus doped c-Si substrates with specific resistivity 1-10 Ohm*cm and crystallographic surface orientation (100). The MACE process was performed using the standard two-steps approach, i.e. (i) chemical deposition of silver (Ag) nanoparticles (NPs) on the surface of c-Si wafers by reduction from the silver nitrate solution followed by (ii) anisotropic etching of the c-Si wafers catalyzed by Ag NPs [4]. The length of SiNWs (depth of the SiNW layer) was controlled by the duration of the second processing step. Residual Ag NPs were removed from the prepared SiNWs by etching in concentrated nitric acid (see for details [5,6]). A part of the samples was subjected to thermoactivated diffusion with boron or phosphorus impurities by impregnation with standard boron- or phosphorus-containing solutions, respectively, followed by rapid thermal annealing in inert gas atmosphere at temperature of 950^{o}C (see for details [7]). The structural properties of obtained samples were studied using scanning electron microscope (SEM) SUPRA 40-30-87.

Results of the SEM study of SiNWs formed in 30 min are shown in figure 1. As it can be seen from the figure, SiNWs are characterized by the lateral dimensions of about 100-200 nm. The length of SiNWs was about 2.5 microns for this sample and it could be varied from 1 to 30 microns by changing the MACE time. The doping of boron samples did not change the structural properties of SiNWs. The same conclusion was reached for the samples doped with phosphorus.

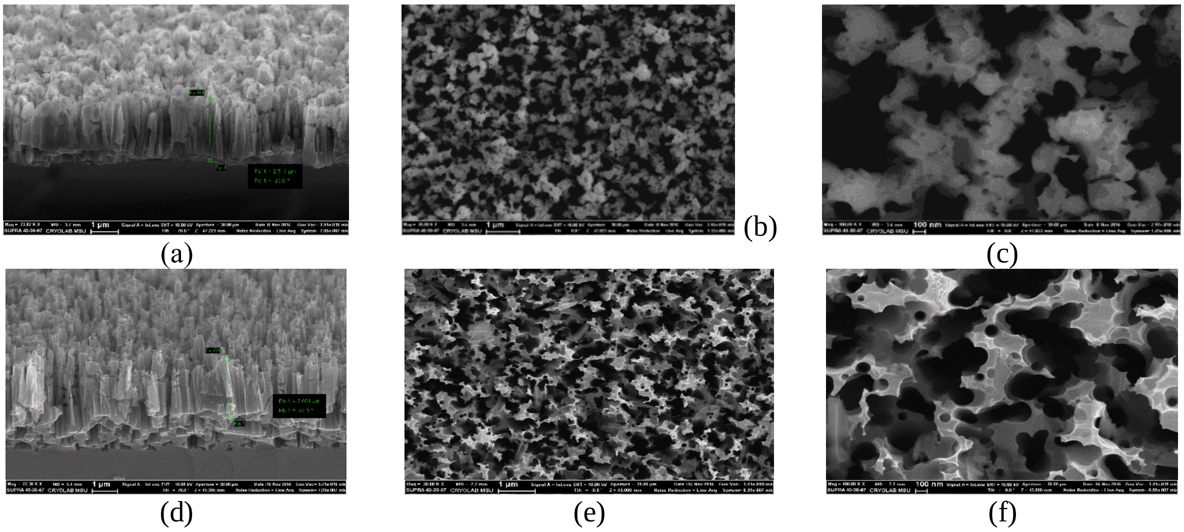

Figure 1. SEM images of SiNWs samples (MACE for 30 min) before (a), (b) and (c) and after (d), (e) and (f) doping with boron.

3. Results and discussion

Figure 2 shows typical Raman spectra of SiNWs with different duration of etching. The figure shows that the intensity of Raman scattering is much higher than that for c-Si substrate. The samples of SiNWs prepared for prolonged MACE time above 3 h are characterized by an increase in the intensity in the low-frequency region of the spectrum, which can be caused by both the contribution of nanometer surface roughness SiNWs and photo-induced heating, which, as shown by our and previous studies, is much stronger for SiNWs than for c-Si due to the low thermal conductivity of the former [6].

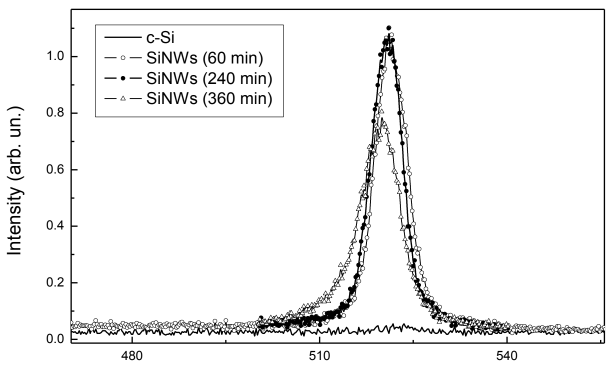

Figure 2. Raman spectra of c-Si substrate and SiNWs samples grown by MACE for different time.

Figure 3 shows dependence of the Raman intensity of as-prepared SiNWs on MACE duration. There is a sharp increase in the Raman intensity of about 50 times compared with the substrate c-Si and a very smooth decrease in long-term etching. SiNWs obtained by MACE from 1 to 3 h are characterized by highest Raman intensity. The significant increase of the Raman signal can be explained by the effect of partial localization of the exciting light due to multiple elastic scattering in SiNW array that leads to an increase in the efficiency of the interaction of light with matter [5]. The decrease in the Raman intensity for SiNWs during long-term MACE is probably due to the appearance of smaller Si nanostructures on the surface and tops of SiNWs [4], which reduces the scattering efficiency and shifts the scattering frequency to low frequency due to the phonon confinement effect (for example [2]).

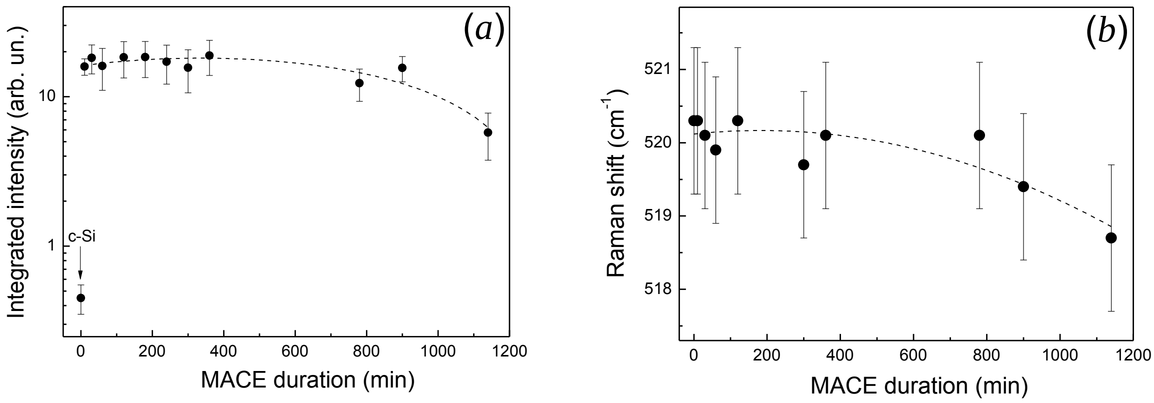

Figure 3. Dependences of the integrated intensity (a) and Raman shift (b) of SiNWs on MACE duration.

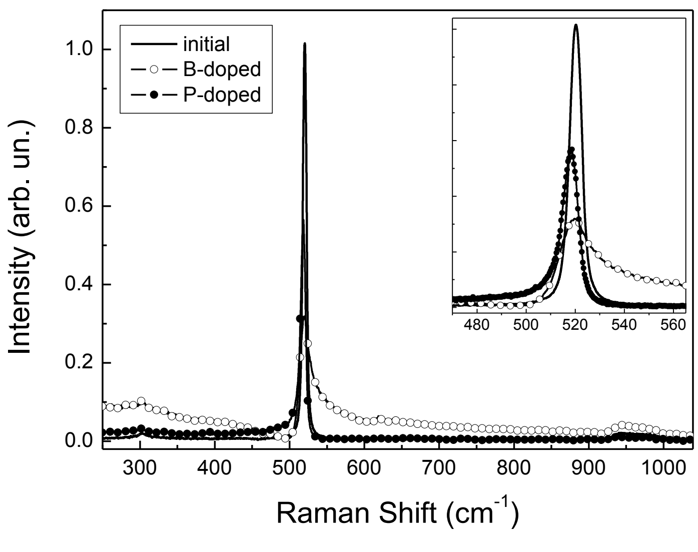

Figure 4. Raman spectra for initial and boron- and phosphorous-doped SiNWs.

Figure 4 shows Raman spectra of the phosphorous and boron doped SiNWs together with the undoped ones. It is evident that the Raman intensities of the doped samples decrease, and their line shapes become asymmetric, which indicates the Fano effect [8] due to the interaction of free charge carriers with phonons [9]. For the samples doped with boron, there is a shift in the maximum line in the high-frequency region and its significant broadening. At the same time, for the samples doped with phosphorus, there is a slight shift in the Raman line in the low-frequency region.

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The concentration of free charge carriers was investigated for the samples with high (sample NW_1) and moderate (sample NW_2) levels of doping with boron, which is determined by amount of incorporated boron impurities. Besides the boron-doped SiNW/c-Si structures we have also studied samples of nanowires with a moderate level of boron doping which were mechanically separated from the substrate (sample NW_2). The Raman spectra of these samples are shown in figure 5.
By analysing the line shape of the Raman spectra of doped SiNWs with regard to the Fano effect in p-type silicon [9], we can calculate the concentrations of free charge carriers (holes) in SiNWs, which are given in Table 1. The difference in the concentrations of holes for SiNWs on the substrate and powder of SiNWs, is apparently, due to the heterogeneity of the doping layer thickness SiNWs, in which the surface layer is more strongly doped than the region at the interface with the substrate.

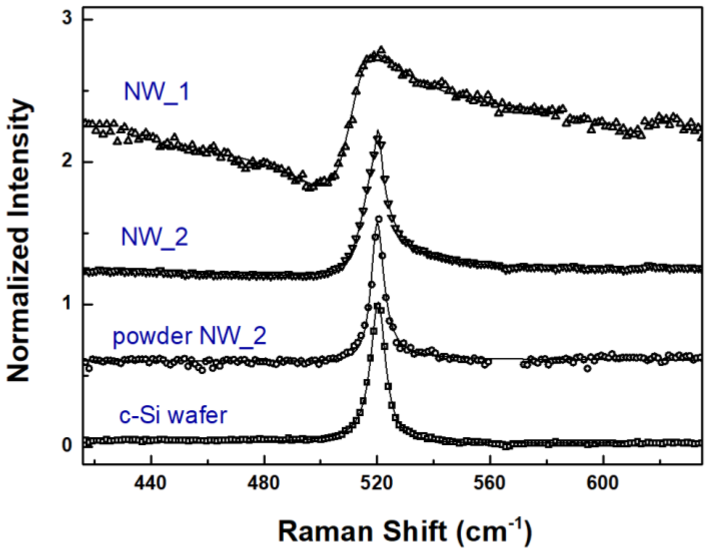

Figure 5. Raman spectra for different boron-doped SiNWs and c-Si substrate.

Table 1. Concentrations of free holes determined from the Raman spectra of SiNWs shown in Figure 5

Sample	Hole concentration (10^{19} см$^{-3}$)
NW_1	28±3
NW_2	7.8±0.9
NW_2	1.6±0.2

4. Conclusion
The obtained results show that the Raman spectroscopy allows us to monitor both the morphology and the electrical properties of silicon nanowires prepared by metal-assisted wet-chemical route. The Raman data reveal the possibility to achieve the free hole concentrations in silico nanowires of the order of 10^{19}-10^{20}см$^{-3}$, depending on the preparation conditions. It should be noted that the latter concentration of free charge carriers is important for the infrared photonic applications of Si-based nanostructures with form anisotropy [10]. The Raman spectroscopy can be used as a contactless method for the express-diagnostics of both the morphology of silicon nanostructures during their formation and the appearance of free charge carriers in them as a result of doping.

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