Effect of Phosphorus Doping on Photoinduced Thermal Processes in Silicon Nanowires

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Abstract. We report on the effect of phosphorus doping of silicon nanowires (SiNWs) on the photoinduced heating processes. SiNWs samples were prepared by metal-assisted chemical etching of low boron-doped crystalline silicon (c-Si) wafers followed with thermo-diffusional doping with phosphorous (P) up to \(10^{20}\ \text{cm}^{-3}\). We establish that the P-doping (n-type) results in effective heat conduction along SiNWs toward the c-Si substrate during laser heating. Partial phase transition in P-doped SiNWs under intense photoheating was detected by means of Raman spectroscopy and photoluminescence. The observed doping effects were explained by a contribution of charge carriers (electrons) to the heat distribution along SiNWs and partial screening of the crystal lattice potential. The obtained results can be useful for the development of new photonic and optoelectronic devices based on SiNWs.

1. Introduction

There has been an active study of nanostructured semiconductor materials in recent decades where a variety of electrical, photoelectrical and optical properties is achieved due to quantum effects. Thus, one-dimensional silicon structures — silicon nanowires (SiNWs) are one of the widely studied promising materials [1, 2]. A wide range of potential applications of SiNWs has been demonstrated, the main of which are: anodes of lithium-ion batteries [3, 4], solar cells [5-7], biosensors [8], highly sensitive detectors of substances [9], etc.

Hexagonal allotropes of silicon (hex-Si) are of great interest for the purposes of optoelectronics and photonics. It is expected that some of hex-Si allotropes have a direct band gap and strong absorption in the visible region of the spectrum. [10] Earlier, the authors of [11] showed that the hex-Si phase in SiNWs can be reversibly formed under high-intensity laser radiation. In this case, hex-Si was detected both by the appearance of an additional line of Raman scattering of light (RS) and by the appearance of photoluminescence (PL) with a spectrum maximum significantly above the edge of the band gap of crystalline silicon (\(E_g = 1.124\ \text{eV}\) at \(T = 300\ \text{K}\)) with a cubic diamond-like crystal lattice (c-Si). However, the effect of doping impurities on photoinduced thermal effects and the c-Si–hex-Si transition has not been studied. On the one hand it can be assumed that high concentrations of charge carriers in heavily doped SiNWs may increase the probability of the structural phase transition due to the screening of the crystal lattice potential by charge carrier plasma. On the other hand, electrically active impurities can lead to barrier photovoltage during photoheating, changes in heat generation distribution, thermal gradients smoothing and averting hex-Si formation. In this work, the effect of phosphorus doping on the...
photoinduced thermal processes in SiNWs was experimentally investigated by means of Raman spectroscopy and photoluminescence.

2. Methods and Samples
Samples of SiNWs were prepared by etching of crystalline silicon wafers in an HF solution in the presence of a metal catalyst (Ag). We used the well-known preparation technique described previously [11]. We used lightly boron-doped c-Si wafers with a surface orientation (100) and a resistivity of $10^{-15}$ Ohm · cm as substrates. The formation of nanowires was performed by etching in a mixture of hydrofluoric acid and hydrogen peroxide for 90 minutes.

Some of the samples were doped with phosphorus impurity. Phosphoric dopant was a technological mixture of orthophosphoric acid. SiNWs were evenly coated with dopant solutions and dried for 30 minutes. Then annealing was carried out in a muffle furnace in an argon stream for 10 minutes at a temperature of 950 °C. Then the annealed samples were kept for 4 minutes in a furnace in an argon stream outside the heating zone and taken out to the atmosphere. Finally, by washing in HF solution, the residues of the dopant mixture and the probable oxide coating were removed.

The SiNWs samples that were not doped (hereinafter referred to as “initial SiNWs”) had been annealed like the doped samples, but without applying any dopant solutions on its surface.

The obtained samples were studied using a scanning electron microscope (SEM). Raman spectra were obtained using a compact confocal Raman microscope Confotec™ MR350 equipped with a 35 mW semiconductor laser at a wavelength of 633 nm. The laser beam spot diameter was about 2 μm.

3. Results and Discussion
Figure 1 shows SEM images of the prepared samples. The etching depth of the silicon wafer (filament length) was about 13 μm. Residues of the dopant mixture were not observed on the doped samples.

![Initial SiNWs](image1)

![SiNWs:P](image2)

**Figure 1.** Cross-sectional SEM images of the prepared SiNWs samples. The insets show top views of the samples. All fragments are on the same scale.

Firstly, the Raman spectra of unheated samples were obtained (the effect of heating on Raman spectrum was negligible). Figure 2 shows the Raman spectra of initial and P-doped SiNWs obtained under low laser intensity. “Low laser intensity” was determined as the intensity, which did not lead to the optical phonon line shift due to heating [12]. Asymmetrical shape of the observed P-doped SiNWs phonon line is due to the Fano effect [13] which takes place in heavily doped semiconductors.

Secondly, sets of Raman spectra under various laser powers were obtained for both initial and P-doped SiNWs. The laser powers applied were enough to cause significant changes in Raman Spectra (Figure 3).
Figure 2. Raman spectra of initial and P-doped SiNWs under low photoexcitation powers without photoinduced heating influence.

Figure 3. Raman spectra of initial SiNWs (a) and P-doped SiNWs (b) under various photoexcitation powers.
In both cases the duplication of the optical phonon peak was observed under 20 mW laser power (spot diameter is about 2 μm). It can be related to inhomogeneous photoheating. Since we observed samples from above, we saw the tips of the filaments and the substrate. The temperature of tips assumed to be higher than substrate temperature, so the temperature shift of Raman lines of filaments and a substrate is different [12].

Further increase in photoexcitation power showed different behavior of Raman line evolution for initial and P-doped SiNWs. Double peak system was observed for initial SiNWs under 30 and 35 mW. This can be explained by significant temperature gradient between filament tips and the substrate. P-doped SiNWs spectra observed under 30 and 35 mW have a complicated shape, however the absence of the initial “cold substrate”-related peak is obvious. This fact indicates that the substrate heating is not moderate now. The doping related free charge carriers facilitate the heat transport along nanowires in spite of the fact that the phosphorus can decrease the lattice thermal conductivity of c-Si [14, 15]. Also, it can be seen from figure 3 that the maximum of P-doped spectrum at the highest power is less shifted than the “hot” peak of initial SiNWs. Thus filament tips have lower temperature in case of doping. So the temperature gradient along filaments is greatly lower in case of P-doping.

Moreover, it was noticed that the P-doped sample spectrum at 35 mW seems to have a broad peak at about 480 cm$^{-1}$. It can be related to amorphous silicon (a-Si) or hex-Si phase formation [11].

Finally, the photoluminescence (PL) of initial and P-doped SiNWs was recorded at the same laser powers as for the Raman spectra.

![Figure 4. Photoluminescence spectra of initial SiNWs (a) and P-doped SiNWs (b) under various photoexcitation powers.](image_url)
The obtained PL spectra are shown on figure 4. It is worth noting that PL intensity significantly and irreversibly degraded during measurements under 30-35 mW exposure. Such degradation can be a consequence of silicon oxidization on air because of high temperatures.

PL intensity of initial SiNWs demonstrates strong dependence on temperature starting from the step of 20 mW excitation power, while PL intensity of P-doped SiNWs enhances sharply only from the next step (30 mW). This fact proves better cooling due the heat transport along nanowires in P-doped SiNWs.

However, the PL intensities of the samples under 35 mW are approximately equal. PL intensity of P-doped SiNWs enhances dramatically between 30 and 35 mW. It can be related with the new silicon phase formation (a-Si or hex-Si), which was noticed by the appearing of the Raman peak at about 480 cm\(^{-1}\). Moreover, it is clearly seen that the P-doped SiNWs PL under 35 mW is more redshifted in comparison with the PL of initial SiNWs under the same power.

Thus, the influence of P-doping on photothermal processes in SiNWs was investigated in this work. The observed Raman line transformations under various photoheating powers were explained using well known Raman dependence on temperature for SiNWs [12]. The formation of an additional Si phase in P-doped SiNWs was assumed from both Raman and PL spectra.

Further investigations of the heat transport along heavily doped Si nanowires are required to clarify the role of free charge carriers in photoinduced heating and phase transitions.

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