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To cite this article: L A Golovan et al 2012 Laser Phys. Lett. 9 145

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Abstract: In this letter, we, for the first time, report on coherent anti-Stokes Raman scattering (CARS) spectroscopy of an ensemble of silicon nanowires (SiNWs) formed by wet chemical etching of crystalline silicon with a mask of silver nanoparticles. The fabricated SiNWs have diameter ranged from 30 to 200 nm and demonstrate both visible and infrared photoluminescence (PL) and spontaneous Raman signal, with their intensities depending on presence of silver nanoparticles in SiNWs. The efficiency of CARS in SiNW ensembles is found to be significantly higher than that in crystalline silicon. The results of CARS and PL measurements are explained in terms of resonant excitation of the electron states attributed to silicon nanoparticles.

Coherent anti-Stokes Raman scattering in silicon nanowire ensembles

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Received: 23 August 2011, Revised: 25 August 2011, Accepted: 28 August 2011
Published online: 2 December 2011

Key words: silicon nanowires; Raman scattering; CARS; photoluminescence

1. Introduction

Silicon (Si) photonics is a fast-advancing area of the modern optical engineering [1–4], whose success is based on a powerful blend of well-established methods for silicon nanostructuring and advanced optical technologies. Among various prospective Si-based systems for photonics and optoelectronics, a special attention is paid to Si nanostructures, for which their optical properties can be controllably varied with respect to crystalline Si (c-Si). In particular, silicon nanowire (SiNW) ensemble presents an intriguing system, for which optical properties are relatively unexplored. These structures are often formed by molecular-beam or electron-beam evaporation combined with vapor-liquid-solid (VLS) growth with a help of Au droplets deposited on silicon surface [5, 6] or by wet etching [7, 8]. In the latter case, silver nanoparticles deposited on the Si surface play a role of catalyst and initiate the etching of pores at the places of particles’ deposition. SiNWs are typically characterized by ordered straight or zigzag columns of c-Si of about 100 nm in diameter, with Si nanocrystals of much smaller size covering the column’s sidewalls. These nanocrystals are believed to result in the visible photoluminescence (PL) through the quantum confinement mechanism [8]. The SiNWs grown by VLS methods have Au nanoparticles covering the top sur-
face of nanowires, giving rise to a possibility of a locally enhanced Raman signal due to a well-known effect of surface enhancement [5, 6]. An order of magnitude Raman signal enhancement in comparison with the initial c-Si was also found in SiNW ensembles formed by a wet-etching processing. This observation can be attributed to the multiple scattering effects of light in the sample resulting in the increase of the optical path and, therefore, the rise of the total Raman scattering efficiency in the sample [9].

The same effect of multiple light scattering is responsible for a significant (one or two orders of magnitude) increase of the nonlinear-optical interaction efficiency in nanostructured semiconductors, such as mesoporous Si and macroporous GaP in comparison with bulk ones. In particular, a substantial improvement of the efficiencies of several nonlinear optical processes, i.e. the second- and third harmonics generation, sum-frequency generation and self-action, has been observed [10–15]. However, our previous results on coherent anti-Stokes Raman scattering (CARS) in macroporous GaP indicate that this particular nonlinear-optical process does not follow the general trend, most probably, due to a short coherence length, which is less than the size of nanocrystals [14].

CARS is a nonlinear optical process of parametric interaction of three waves with frequencies $\omega_1$, $\omega_2$, and $\omega_3$ resulting in generating a wave at the frequency $\omega_{CARS} = \omega_3 + (\omega_1 - \omega_2)$. For the sake of simplicity of experimental set up, a degenerative optical interaction, in which the same laser is used for $\omega_1$ and $\omega_3$, is often employed. Given the parametric nature of the CARS signal, it occurs at any combination of frequencies $\omega_1$ and $\omega_2$, leading to a so-called “non-resonant” background. When the difference frequency, $\omega_1 - \omega_2$, is at or near the resonance with some vibrational or electronic transition, it results in a significant rise of the signal at $\omega_{CARS}$. Being a coherent nonlinear-optical process, the CARS efficiency is sensitive to the phase matching of interacting waves. Among variety of modern nonlinear-optical research techniques [16–18], CARS is recognized to be an invaluable tool for studying microobjects and their molecular environment [19–21], chemical and biological object [22–25], and for frequency conversion in various media, including Si-based ones [26].

In this letter, we report on the CARS spectroscopy of SiNW ensembles and compare those results with the photoluminescence and spontaneous Raman scattering data.

2. Experimental

2.1. Samples

The SiNW samples were prepared by the wet etching process of low boron-doped (100) c-Si (1–10 $\Omega$ cm) wafer. We followed the two-step procedure of SiNW formation [7]. In the first step, silver nanoparticles were deposited on the c-Si surface during the immersion of c-Si wafer in the aqueous solution of 0.02 M AgNO$_3$ and 5 M HF in the volume ratio 1:1 for 1 minute. The second step was the etching of c-Si wafer covered by Ag nanoparticles in solution of 5 M HF and 30% H$_2$O$_2$ in the volume ratio 10:1 for 30 minutes. As a result, SiNWs were formed (see Fig. 1). The thickness of the SiNW layer was 24 $\mu$m, the diameter of wires ranged from 30 to 200 nm. The SiNWs are well-ordered, as it is clearly seen from the scanning electron

Figure 1 SEM image of SiNWs illustrating the whole structure (a) and TEM image of a single SiNW with Ag nanoparticles (b). The scale bars are shown on the bottom of each image.
microscope (SEM) images (Fig. 1a). The fabricated samples contained residual Ag nanoparticles (Fig. 1b), with fraction being of about 1% according to the X-ray microanalysis data. To remove those nanoparticles from the surface, some samples were washed in HNO$_3$ for about 15 minutes.

2.2. Optical characterization of the samples and CARS measurements

Due to the size of SiNWs, which are comparable with the optical wavelength, all the samples exhibited substantial scattering. To characterize electronic and vibrational properties of the formed SiNW samples we employed techniques of PL and spontaneous Raman scattering. PL was excited by the ultraviolet (UV) line of an Ar-ion laser (364 nm) and detected by a spectrometer (MS750, SOLAR TII) equipped with detectors both for the visible and the infrared (IR) spectral regions. A Fourier-transform IR spectrometer (IFS 66 v/S, Bruker) with a Raman unit (FRA106 FT, Bruker) allowed us detecting the PL and Raman spectra excited by a CW Nd:YAG laser (1064 nm). In the latter case, even though absorption length for used wavelength is of order of 100 µm, the strong light scattering prevented incident radiation from penetrating deep into the sample, thus, generating the measured signals predominantly in SiNW ensembles [9].

For the CARS experiments, we used the home-build broadband system, described elsewhere [27–30]. In brief, the laser system was based on a diode-pumped, extended cavity Nd:YVO$_4$ oscillator with “nonlinear mirror” modelocking (master oscillator) and a multipass Nd:YVO$_4$ amplifier, which provided 8-ps laser pulses of 2 µJ at wavelength 1064 nm at the repetition rate of about 1 MHz. Some part of the fundamental radiation was split with a help of the half-wave plate and polarizing beam-splitter and used for broadband, red-shifted continuum generation in a single-mode GeO$_2$-doped optical fiber. The broadband continuum radiation from the output of the fiber was collimated and combined together through a dichroic beamsplitter with a time-delayed residual 1064 nm radiation. Both pulses were then focused onto the sample with an aspheric lens ($FL = 16$ mm). In the employed experimental setting, the broadband CARS signal was generated at the frequency $2\omega - \omega_{cont}$, where $\omega$ was the frequency of the Nd:YVO$_4$ laser radiation and $\omega_{cont}$ was the frequency of the continuum radiation. The CARS signal in the spectral region from 800 to 1030 nm was collected in the backscattering geometry by the same lens, spectrally separated from the incident radiation with a help of a dichroic filter (1050 nm long pass; Semrock, Inc.) and directed to a spectrometer (TRIAX-550; Horiba Jobin-Yvon), where it was detected by a multichannel CCD detector (iDus; An-

![Figure 2](www.lphys.org) PL spectra of SiNW with (solid line) Ag nanoparticles and after their removal (dashed line). Spectra were excited by the Ar-ion laser radiation at 364 nm.

![Figure 3](www.lphys.org) PL and spontaneous Raman spectra of c-Si and SiNWs excited by the 1064-nm radiation. A dip at around 0 cm$^{-1}$ is attributed to the transmission properties of the employed notch filter.
In order to shed more light on the properties of SiNWs and c-Si, we collected PL and Raman spectra excited by the near-IR excitation at 1064 nm (Fig. 3). Those spectra consist of a broad PL band and a relatively narrow Raman peak at 520 cm$^{-1}$. The Raman signal from SiNW ensembles with Ag nanoparticles on columns’ surface exceeds by four times the Raman signal from the c-Si sample collected in the same experimental conditions. The removal of Ag nanoparticles further increased the Raman signal making it 5 times stronger the one from the c-Si sample. The PL signal from the SiNWs ensembles without Ag nanoparticles on its surface is 1.4 times stronger than the one from the c-Si samples, while the SiNWs with Ag nanoparticles demonstrate a slightly weaker PL signal than the original c-Si wafer. For all the samples, the PL signal possessed square dependence on the incident light intensity $I_{\text{exc}}$ (Fig. 4), which is typical for the interband electronic transition, however, at $I_{\text{exc}} > 4$ W/cm$^2$ the PL signal showed the tendency to saturation with the increase of $I_{\text{exc}}$. In the same time, the Raman signal linearly depends on $I_{\text{exc}}$, which is typical for the spontaneous Raman scattering process, where no structural changes or substantial temperature heating of the sample are present. Note that the PL spectra presented in Fig. 2 and Fig. 3 were obtained using substantially different excitation wavelengths (UV and IR), which results in a drastic difference in the thicknesses of the light-absorbing layer (for the c-Si, for example, those absorption depths are 10 nm in the UV and 100 µm in the near-IR). This fact can explain why the near-IR PL was sensitive to the presence of Ag nanoparticles, whereas PL excited by the UV radiation was not.

The Raman and PL spectra were complemented by the CARS spectra. Fig. 5 shows the CARS spectra for c-Si and SiNWs with and without Ag nanoparticles. The CARS spectrum collected from the c-Si sample consists of the background and a peak at 1008 nm, corresponding to the resonance with the phonon frequency of Si lattice. The amplitude of the CARS signal increases with the increasing CARS wavelength. The resonant signal showed the tendency to saturation with the increase of $I_{\text{exc}}$.

3. Results and discussion

The PL spectra of SiNW samples both with and without Ag nanoparticles on the surface are shown in Fig. 2. The PL spectra exhibit broad band ranging from 600 to 1100 nm. This fact indicates the presence of Si nanoparticles, in which the quantum-confinement effect results in the rather efficient visible PL. The presence of Ag nanoparticles on the top surface of SiNWs does not significantly affect the shape of PL spectra.
The resonant CARS peak corresponding to the Si lattice vibration was found to be 4 times stronger in the SiNWs ensembles without Ag nanoparticles as compared to the one from the c-Si and the SiNWs ensembles with Ag nanoparticles. The non-resonant CARS signal in the SiNWs ensembles was found to be substantially stronger than that in c-Si for the CARS wavelengths less than 1000 nm. These results could be explained by taking into account both the effects of light scattering in the SiNWs ensembles and the electron and hole states, whose transition frequencies are resonant to the CARS frequencies.

4. Conclusion

In conclusion, we fabricated SiNWs by means of the wet electroless process and investigated their optical properties using a battery of tools, which included photoluminescence, spontaneous Raman and nonlinear Raman spectroscopy. The resonant CARS peak corresponding to the Si lattice vibration was found to be 4 times stronger in the SiNWs ensembles without Ag nanoparticles as compared to the one from the c-Si and the SiNWs ensembles with Ag nanoparticles. The non-resonant CARS signal in the SiNWs ensembles was found to be substantially stronger than that in c-Si for the CARS wavelengths less than 1000 nm. These results could be explained by taking into account both the effects of light scattering in the SiNWs ensembles and the electron and hole states, whose transition frequencies are resonant to the CARS frequencies.

Acknowledgements This work was supported by the Russian Foundation for Basic Research (grants No.11-02-01087 and...
No. 11-02-90506), the Ministry of Education and Science of the Russian Federation (project No. 16.513.12.3010), the National Institutes of Health (USA) (grants No. R15EY020805 and No. R21EB011703), and the National Science Foundation (USA) (grants No. ECS-0925950 and No. DBI-0964225). Authors are indebted to V.A. Sivakov and P.K. Kashkarov for extremely fruitful discussions, S.S. Abramchuk and D.V. Petrov for the electron microscopy measurements, and A.V. Neskoromnaya for the assistance in the sample preparation.

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