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MICRO-PHOTOLUMINESCENCE IN SILICON NANO-WIRES

Abstract. Silicon nano-wires are a new material with a very attractive for many different application optical properties. The main aim of the presented study is to investigate photoluminescence (PL) properties of silicon nanowires in as a function of temperature and excitation power. In this work silicon nano-wires (SiNWs) were prepared by wet chemical metal-assisted method. Monocrystalline silicon plates with p and n-type conductivity served as a substrate. Micro-photoluminescence spectra of obtained SiNWs samples measured by confocal microscopy setup. It is shown that strong PL signal centered at about 700 nm is observed only from SiNWs. Temperature-dependent PL measurements acquired for a range of temperatures 4K - 300K. It was shown that above 40K, PL signal decrease in intensity due to the increasing effect of non-radiative processes taking place causing carrier thermalization. It is also observed pronounced spectral redshift of PL spectra with increasing temperature, which is probably related with thermal de-trapping and possible migration of excitons from trapped states to lower available ones. From analysis of the PL dependence on excitation power we found that above 4 μW of input power, quenching of PL from carrier recombination in the region >750 nm is observed (slope changes from 1.23 to 0.22). The almost linear power dependence of the emission becomes sub-linear above 4 μW which could be an indication of saturation of Si-NC states (inherently low density of states). At the intermediate to high pump power regime, Auger recombination for example is possible in Si-NC structures as the Auger lifetime is shorter than the single exciton radiative lifetime.

Keywords: silicon nanowires, photoluminescence, temperature dependent photoluminescence, optical properties.

Introduction. Silicon nano-wiser with low light reflectance and high light absorbance values attract a huge interest of researchers during last 10 years because of their great application potential for microelectronics, optoelectronics, photonics, photovoltaics, bio- and chemical sensing [1-6]. One of the wide spread ways to form SiNWs that allows to control growth and structure of nanostructures is a metal-assisted chemical etching (MACE) [7-9]. There are many papers devoted to investigations of SiNWs optical properties [10-14] but only a small part reports photoluminescence studies [15-18]. We have therefore investigated temperature dependence of photoluminescence of SINWs. Here we report on our recent results on the characterization of SiNWs micro-photoluminescence spectra.

Experimental. SiNWs samples obtained by MACE, which performed in a few steps. First silicon surfaces dipped into 2% hydrofluoric acid (HF) aqua solution to remove the thin native silicon oxide layer and dried by argon blow, then silicon they were immersed into the first solution (thermostateted by 20°C) containing 5M HF and 0.01 M $AgNO_3$. After a uniform layer of Ag nanoparticles was coated, the wafers were then immersed in the etchant solution composed of HF, H_2O_2, and H_2O (the volume ratios HF/H_2O_2: 1:10) at room temperature in a sealed Teflon vessel. In the last step Si wafers were immersed in a solution of concentrated nitric acid solution in order to remove the excess Ag nanoparticles and rinsed with deionized water, and then dried in vacuum at 60°C. As substrates, we have used heavy doped n-type, monocrystalline silicon plates

Micro-photoluminescence (micro-PL) measurements were conducted using a confocal microscopy setup. The sample mounted on a continuous-flow liquid-helium microscope cryostat, which enabled cooling from 300K down to 4K. A microscope objective lens, which was mounted on a piezoelectric XYZ stage, was used to focus and collect the excitation laser light (405 nm) and the emitted PL, respectively. The laser spot size on the sample was about 2 micron in diameter. Power- dependent PL data were recorded whereby the laser power was measured before the microscope objective (actual light power on the sample is about 2.6 times less than measured). A broadband polarizing beam splitter was used to transmit the laser light into the objective lens axis and to reflect the emitted PL light into a 0.3m spectrometer where it was dispersed by a 300 line/mm grating. The entrance slit of the spectrometer was kept at 50 microns. The PL was detected by a Peltier-cooled Si charge couple device (CCD) [19].

Results and discussion.

Micro-PL spectra at room temperature. Figure 1 depicts room temperature spectra from three different samples: heavily n-doped SiNWs on Si substrate (A), weakly p-doped SiNWs on Si substrate (B) and weakly p-doped Si-NWs (C) on glass substrate transferred in solution. The spectra recorded at room temperature under similar experimental conditions within an excitation power range of 215-245 W/cm^2. The spectrum from the SiNWs on glass is presented for qualitative comparison as a different CCD was used for its detection. Overall, strong orange-coloured PL signal centred at about 715 nm was observed, which was visible by naked eye particularly for Sample A. Furthermore, the PL peak from all samples was broad with a FWHM of the order of 200 nm. The spectra exhibited periodic fringes, which were not due to a filter or detector etalon effect confirmed by using a front-illuminated detector. We suggested that the fringes originated from light interference effects possibly due to the difference in refractive index between air, etched region and substrate. It should be mentioned that the PL recorded from different positions on the same sample presented small variations, which confirmed a degree of structural inhomogeneity in the samples.

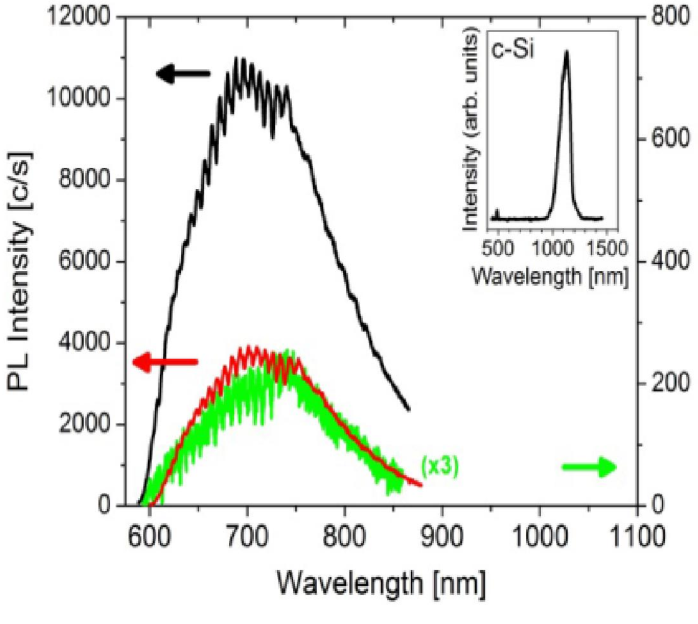

Figure 1 - PL measurements recorded at 300K from 3 different type samples: Sample A (black), Sample B (red) and Sample C (green). The input power density was 215-245W/cm^2. Inset: luminescence spectrum from initial bulk c-Si wafer

The spectrum from the SiNW solution on glass exhibited similar spectral features to the spectra from the other two etched Si wafers, albeit a less intense shoulder at about 700 nm. This suggests that the observed signal from Samples A and B (black and red) in the resulting etched structures. The origin of these luminescent quantum confined states is most likely multi-fold. According to the diameters of the SiNWs (>10nm), from quantum confinement theory no shift in PL peak energy compared to the bandgap of c-Si is expected. Tests have been conducted on similar structures which showed no influence of residual (if any) Ag atoms on the PL observed. The effect of native oxide on the PL (SiOx-related states, Si/SiO$_2$ interface states) was confirmed by HF post processing which resulted in a part of the higher energy tail of the spectra (>1.5 eV) to be quenched. Based on previous structural studies [20] and consistent etching test series, the charge carrier confinement is attributed to arise in Si nano-crystals (Si-NCs), in particular core-shell Si-NCs/SiO$_2$ resulting from nanowire sidewall roughness (of the order of 1-5nm) and within the porous structure of the samples, (particularly the heavily n-doped sample).

Temperature-dependent PL emission. Temperature-dependent PL measurements were acquired from Sample A for a range of temperatures 4K - 300K. Figure 2 shows two typical PL spectra at 4K and room temperatures. For analysis purposes and easier comparison, the data was smoothed using Fast Fourier Transform filter (30 points) and normalized.

The data was de-convoluted into 3 peaks (at 640 nm, 716 nm, 822 nm) using multi-Gaussian peak fitting as shown in the inset. The 4K spectrum exhibits a broader FWHM compared to the room temperature spectrum which shows a pronounced narrowing in intensity from 750-900nm. As previously mentioned, the low energy tail of the spectra is linked to quantum confined Si-NC states whereas emission from the higher energies is attributed to a range of oxide-related states. The broadness of the 4K spectra reflects the size distribution of the Si-NCs. At such temperatures, carriers are expected to be localized in traps, defects and NCs in the form of excitons (electron-hole pairs) as their binding energy exceeds the thermal energy of the system.

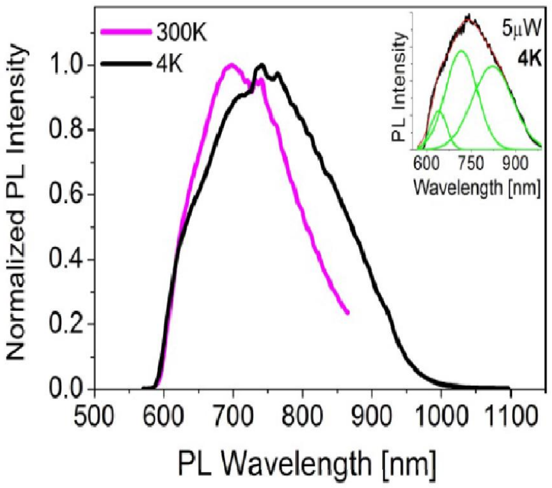

Figure 2 - Normalized PL measurements from etched Si-NWs in Sample A recorded at 300K and 4K. The input power was 4-5 µW and laser spot size was about 2 µm in diameter. Inset: The 4K spectrum is de-convoluted into 3 Gaussian peaks

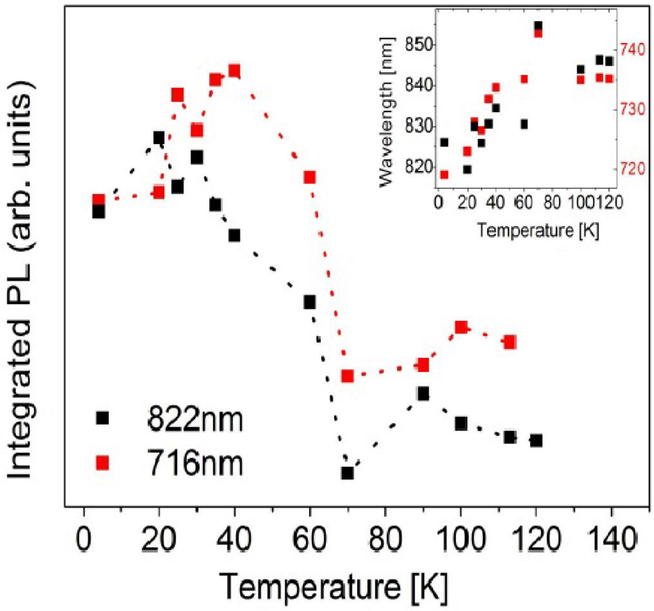

Figure 3 - Integrated PL from the de-convoluted peaks centred at 716 nm and 822 nm as a function of temperature (Sample A). Inset: Temperature-dependence of the emission wavelength of the two peaks.

Figure 3 shows the integrated PL intensity of the de-convoluted peaks 716 nm and 822 nm as a function of temperature from 4-120K. With increasing temperature a gradual quenching of the radiative contribution from the Si-NC complexes (peak 822 nm) is observed. An anti-correlated behaviour between the two peaks observed between temperatures 20-40K, whereby peak 716 nm shows an increase in intensity. Above 40K, both peaks decrease in intensity due to the increasing effect of non-radiative processes taking place causing carrier thermalization.

According to the inset of Figure 4, both peaks exhibit pronounced spectral redshift with increasing temperature. This differs from the expected temperature dependence of the bandgap of bulk Si which exhibits minimal redshift below 100K. The quenching of intensity, the spectral redshift and the reduction of FWHM for peak 822 nm suggest that thermal de-trapping and possible migration of excitons from trapped states to lower available energy states occurs. Also, the anti-correlated increase in PL intensity for peak 716 nm may suggest carrier transfer between Si-NCs and oxide/interface states.

PL emission as a function of excitation power. Figure 4 depicts normalized power dependent spectra from Sample B at room temperature. Sample A exhibited similar power-dependent PL behaviour. The main feature of the room temperature spectra is the spectral blue-shift accompanied by the relative intensity drop observed mainly for wavelengths > 750 nm. At 4.4K, a similar behaviour is observed in both samples with a more prominent drop in relative intensity in the long wavelength tail with increasing excitation power.

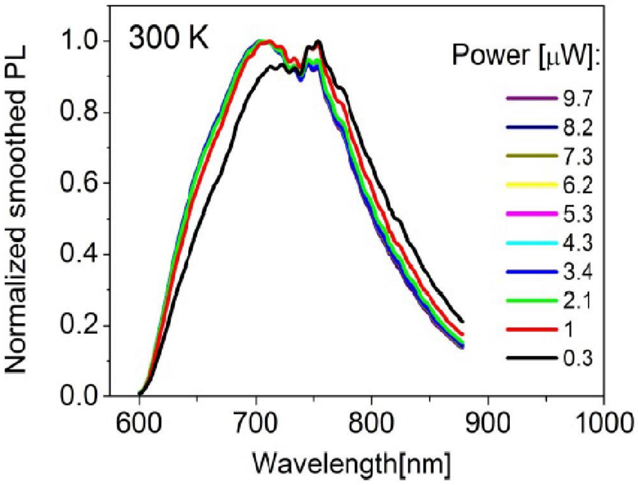

Figure 4 - Normalized power-dependent PL emission measurements from etched Si-NWs (weakly-doped p-type Si wafer) recorded at 300K. Spot diameter: 2 μm.

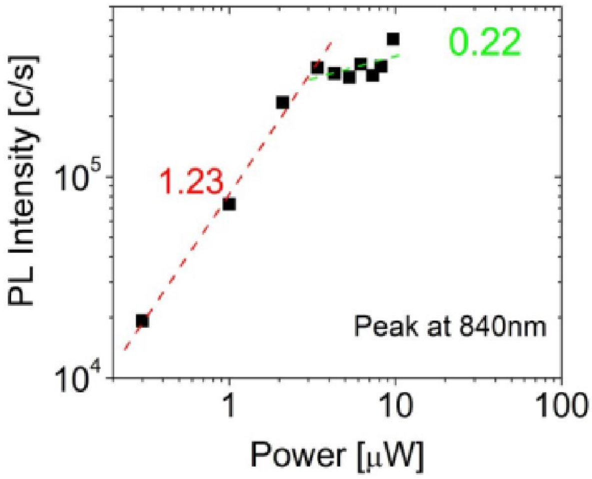

Figure 5 - The intensity of the de-convoluted peak at 840 nm (data shown in Fig. 4) is plotted as a function of excitation laser power.

Figure 5 shows the log-log plot of PL intensity of the low energy de-convoluted PL peak from the data presented in Figure 4 as a function of power. Above 4 μW of input power, quenching of PL from carrier recombination in the region >750 nm is observed (slope changes from 1.23 to 0.22). The almost linear power dependence of the emission becomes sub-linear above 4 μW which could be an indication of saturation of Si-NC states (inherently low density of states). At the intermediate to high pump power regime, Auger recombination for example is possible in Si-NC structures as the Auger lifetime is shorter than the single exciton radiative lifetime.

The samples produced by varied etching times using the two step WCE process are composed of differently shaped SiNWs that all show strong visible PL in the red-orange wavelength regime (1.5 . . . 1.6 eV). The measured and normalized spectra of photon flux distribution vs. photon energy are shown in Fig. 6. Measured spectra corrected by taking into account the transfer function of the calibrated setup. It is visible that PL peak energies increase monotonically with increasing of etching time in the second step.

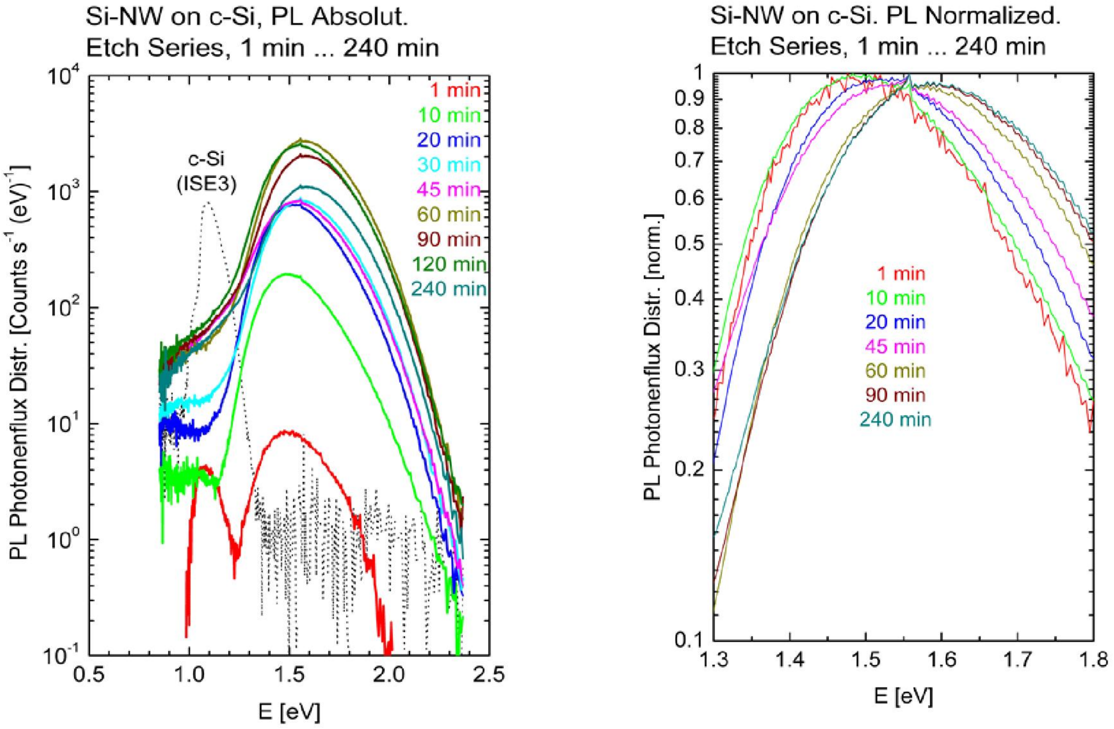

Figure 6 - Measured (left) and normalized(right) PL spectra of Si-NW samples produced by varying etching time during second etch step 2

Conclusions. We have performed detailed studies of photoluminescence properties of SiNWs grown by MACE on n- and p-type silicon wafers at room and low temperature. We have shown that strong PL signal centered at about 700 nm observed only from SiNWs. Temperature-dependent PL measurements acquired for a range of temperatures 4K - 300K. It was shown that above 40K, PL signal decrease in intensity due to the increasing effect of non-radiative processes taking place causing carrier thermalization. It is also observed pronounced spectral redshift of PL spectra with increasing temperature, which is probably related with thermal de-trapping and possible migration of excitons from trapped states to lower available ones. From analysis of the PL dependence on excitation power we found that above 4 μW of input power, quenching of PL from carrier recombination in the region >750 nm is observed (slope changes from 1.23 to 0.22). The almost linear power dependence of the emission becomes sub-linear above 4 μW which could be an indication of saturation of Si-NC states (inherently low density of states).

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МИКРО-ФОТОЛЮМИНЕСЦЕНЦИЯ КРЕМНИЕВЫХ НАНОНИТЕЙ

Аннотация. Кремниевые нанонити представляют собой новый материал с очень привлекательными оптическими свойствами для множества различных приложений. Основной целью представленной работы является исследование фотолюминесцентных свойств (ФЛ) кремниевых нанонитей в зависимости от температуры окружающей среды и и мощности возбуждающего излучения. В данной работе кремниевые нанонити (КНН) были получены методом мокрого химического металл-стимулированного травления. Монокристаллические кремниевые пластины с p- и n-типа проводимости служили в качестве подложек для выращивания наноструктур. Микро-спектры фотолюминесценции полученных образцов КНН, измерялись с помощью установки с конфокальным микроскопом. Показано, что интенсивный сигнал ФЛ с максимумом при длине волны 700 нм наблюдается только от КНН. Измерения спектров ФЛ в зависимости от температуры производились в диапазоне температур 4K-300K. Было показано, что при температурах выше 40K, наблюдается уменьшение интенсивности сигнала ФЛ в связи с усилением влияния нерадиационных процессов, в результате приводящих к термализации носителей. Кроме того, с ростом температуры отмечается выраженный сдвиг спектров ФЛ в красную область спектра, что, вероятно, связано с термическим захватом и возможной миграцией экситонов из локализованных состояний к более низким. Из анализа зависимости ФЛ от мощности возбуждения мы обнаружили, что при мощности возбуждающего излучения более 4 мкВт, в области с длинами волн > 750 нм наблюдается угасание ФЛ, связанное с рекомбинацией носителей. Почти линейная зависимость мощности излучения становится суб-линейной при мощностях выше 4 мкВт, что может быть признаком насыщения состояний Si-NC (низкой плотности состояний).

Ключевые слова: кремниевые нанонити, фотолюминесценция, температурная зависимость фотолюминесценции, оптические свойства.

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КРЕМНИЙ НАНОТАЛШЫҚТАРЫНЫҢ МИКРО-ФОТОЛЮМИНЕСЦЕНЦИЯСЫ

Андатпа. Кремний наноталшықтары алуан түрлі қолданулар үшін өте қажетті оптикалық қасиеттерге ие жаңа материал болып табылады. Берілген жұмыстың негізгі мақсаты болып қоршаған орта температурасы мен қоздырылатын сәулелену қуатына тәуелді болатын кремний наноталшықтарының фотолюминесценциялық қасиеттерін (ФЛ) зерттеу табылады. Аталған жұмыста кремний наноталшықтары (КНТ) сұйық химиялық метал-енгізілген жеміру әдісімен алынды. p- және n-типті өткізгіштігі бар монокристаллдық кремний пластиналары наноқұрылымдарды өсіруге арналған төсеніштер ретінде пайдаланылды. Алынған КНТ үлгілерінің фотолюминесценциясының микро-спектрлері конфокальді микроскопы бар қондырғының көмегімен өлшенді. Максимумы 700 нм толқын ұзындығында болатын ФЛ-дың интенсивті сигналы КНТ-нан ғана байқалатыны көрсетілді. Температураға тәуелді ФЛ спектрлерін өлшеу 4K-300K температуралар диапазонында жүргізіліді. 40K-нен жоғары температураларда радиациялық емес процесстердің күшеюімен байланысты нәтижесінде тасымалдағыштардың термализациясына әкелетін ФЛ сигналы интенсивтілігінің азаюы байқалатындығы көрсетілді. Сонымен қатар температура жоғарылаған сайын ФЛ спектрлерінің спектрдің қызыл облысына айқындалған жылжуы аталып өтеді, бұл термиялық қармаумен және экситондардың локализацияланған күйлерден төменірек күйлерге мүмкін болатын миграциясымен байланысты. Қоздыратын сәуленің қуатына байланысты ФЛ-ны талдаудан біз > 750 нм толқын ұзындықтары облысында қоздыратын сәулелену қуаты 4 мкВт-тан жоғары болған кезде тасымалдағыштардың рекомбинациясымен байланысты ФЛ-ның өшуі байқалатындығын таптық. 4 мкВт-тан жоғары қуаттарда сәулелену қуатының сызықтық тәуелділігі суб-сызықтық болады, бұл Si-NC (күйдің төмен тығыздығы) күйлерінің қанығуының белгісі болуы мүмкін.

Тірек сөздер: кремний наноталшықтары, фотолюминесценция, фотолюминесценцияның температуралық тәуелділігі, оптикалық қасиеттер.