Photoluminescence of confined electron-hole plasma in core-shell silicon/silicon oxide nanowires

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We study by low temperature photoluminescence measurements the electronic states of silicon nanowires obtained by copper catalyzed chemical vapor deposition and compare them with those of wires made by etching silicon on the insulator structure. Thermal oxidation of nanowires appears to be absolutely necessary to passivate surface states and to enhance radiative recombinations at the silicon band gap. The study of the behavior of this transition as a function of temperature and pump power demonstrates that it involves the phonon assisted recombination of free carriers. The recombination energy appears at the silicon band gap, renormalized by exchange and correlation interactions favored by spatial confinement. © *2008 American Institute of Physics*.
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Nanowires (NWs) are the present topic of intense research for their extremely promising properties. Indeed, as NWs are one-dimensional systems, their high surface/volume ratio allows them to be very efficient nanosensors; their small dimensions could also make them useful as nanotransistors. Furthermore, they are also unique objects in the study of one-dimensional electronic system properties. The most used silicon NW (SiNW) growth process is chemical vapor deposition (CVD),[1–5] which needs metal catalysts (Au, Cu, etc.). These metals, if incorporated in silicon, generate electronic deep levels that drastically reduce the carrier lifetime and strongly affect the electronic and optical properties of CVD SiNWs. Some studies have already been reported on photoluminescence (PL) measurements from SiNWs in the visible range[6–8] and visible contributions are explained by quantum confinement effects. However, the silicon/silicon oxide interface emits also in the visible range and it is always difficult to conclude on the origin of the luminescence. Jia *et al.*[8] reported some PL of SiNWs with an average diameter of about 20 nm in the infrared region below the silicon gap energy related to dislocation states. Furthermore transport studies generally show transient phenomena on SiNWs, which could be attributed to the presence of structural defects as well as interface trap states.[9–11] But nobody has yet clearly identified band-to-band recombination in any CVD SiNW.

In this letter, we report on the observation of radiative recombination within a system of free carriers in CVD SiNWs whose diameter is greater than 50 nm in order to avoid any quantum confinement. We demonstrate the importance of the passivation process to drastically decrease the defect and trap densities and to observe a luminescent transition at the silicon band gap. The temperature and pump power behavior of this PL line is studied and is in agreement with a band-to-band recombination of free carriers. The same kind of transition is also observed in the PL spectra of etched-SiNWs (E-SiNWs). The analyses of shape and spectral position of the PL line lead us to attribute this transition to the existence of an electron-hole plasma (ehp) confined in the NWs.

NWs are synthesized by the vapor-liquid-solid method using low pressure CVD.[1–5] A 5 nm thick copper layer is deposited on a ⟨100⟩ silicon substrate surface and heated up to 850 °C to form copper nanodroplets that will act as NW growth catalysts. Introduction of silane-hydrogen-HCl gas mixture leads to the epitaxial growth of NWs at a temperature of 850 °C. The NWs are 80 μm long and have a diameter in the 50–300 nm range without any tapering (see Fig. 1), and high-resolution transmission electron microscopy measurements exhibit three different growth directions: ⟨111⟩, ⟨112⟩, and ⟨110⟩. We also study NWs obtained by combination of electron beam lithography and reactive ion etching (RIE) of a silicon-on-insulator wafer. The initial structure is a stack of a 200 nm silicon layer on a 400 nm oxide layer. The NWs are 40 μm long and have rectangular cross sections from 75×200 nm^2 to 500×200 nm^2. The crystallographic axis along the large dimension is ⟨110⟩. Before the process of oxidation, the catalyst droplets are carefully removed from the top of NWs with an aqua regia solution for a few minutes. The oxidation is performed in a furnace with a 10 mbar O_2 pressure at a temperature of 960 °C for 1 h. This process leads to a core-shell structure with a silicon core and a thermal silicon oxide shell (see inset

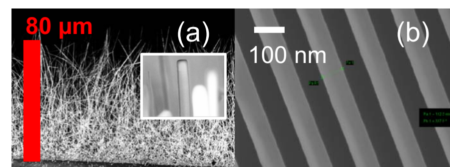

FIG. 1. (Color online) (a) SEM images of low pressure chemical vapor deposition copper catalyzed SiNWs. We can estimate the NWs length to 60–70 μm. The inset is a SEM image of a passivated NW. (b) SEM image of the 40 μm$\times$200 nm$\times$75 nm etched NWs.

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of Fig. 1(a)). In these conditions the oxide thickness on ⟨100⟩ bulk silicon is typically of 10 nm. The sample cooling down is made under 400 mbar of forming gas.

Micro- and macro-PL experiments are performed between liquid He and room temperature. In the macro-PL experiment, the sample is cooled down by a He gas flow. In this setup, we optically pump the NWs with the 355 nm line of a pulsed tripled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser focused on a 300 μm spot. The pulses are 10 ns long and the repetition rate goes from 500 Hz to 10 kHz. The excitation wavelength is situated just above the direct band gap of silicon, is totally absorbed by the NWs on a depth of 30 nm, and avoids the excitation of the substrate. To study E-SiNWs, a micro-PL setup is used to decrease the spectral contribution of the substrate. In this setup, the sample is in vacuum and is cooled down on a cold finger. The pump excitation is a 364 nm argon laser line focalized on a 5 μm diameter spot with a Cassegrain objective, which is also used for collection. Most of the infrared luminescence spectra from 0.9 to 1.3 eV are analyzed by a monochromator with a 75 tr/mm or a 900 tr/mm grating and detected continuously by an InGaAs charge coupled device (CCD) camera. A cooled photomultiplier tube with an InGaAs photocathode and photon counting electronics is used to record the time delayed spectra after pulsed excitation.

In Fig. 2(a), we report the PL spectra of NWs obtained with the macro-PL setup for a peak pump density of 150 kW cm^{-2} at a cryostat temperature of 10 K. The right part compares the normalized spectra of the as-grown and oxidized SiNWs with the substrate. First, we notice that the NW luminescence is clearly different from that from the substrate, which is dominated by the longitudinal optical (LO) phonon assisted recombination of free exciton (FE) at 1.10 eV. In fact, the NW density ($\sim$10 μm^{-2}) and length (80 μm) are so high that the laser beam cannot directly pump the substrate. The PL spectrum of the as-grown SiNWs is dominated by below band gap recombination (1.05 to 0.85 eV limited by the CCD cutoff), with a weak contribution near the energy band gap of the diamond phase of silicon (close to 1.10 eV). These low energy bands are associated with the presence of trap states that are not yet clearly identified, but Jia *et al.*[8] already observed this kind of band and attributed it to the presence of dislocations in NWs. After thermal oxidation the PL spectra of SiNWs are strongly modified. First, the formation of a SiO_2 shell by thermal oxidation induces an emission yield ten times higher than the as-grown NWs and drastically decreases the relative importance of the trap contribution compared to the near gap contribution. The spectrum of the core-shell NWs is now dominated by an asymmetric band peaking near 1.08 eV. Such a band is commonly observed in ultrapure bulk silicon[12,13] and in two-dimensional $SiO_2/Si/SiO_2$ quantum wells,[14–16] and results from the LO phonon assisted recombination of electron-hole pair inside a dense plasma, which can be either in a liquid or a gas phase depending on temperature, excitation density, and spatial confinement.

Figure 2(b) shows the evolution of the PL spectra of the core-shell NWs as a function of the pump power. The inset of Fig. 2(b) compares the variation in the integrated intensity from 1.058 to 1.4 eV (black squares) and from 0.85 to 0.95 eV (circle red curve) as a function of the pump power density. The low energy contribution saturates quickly as a result

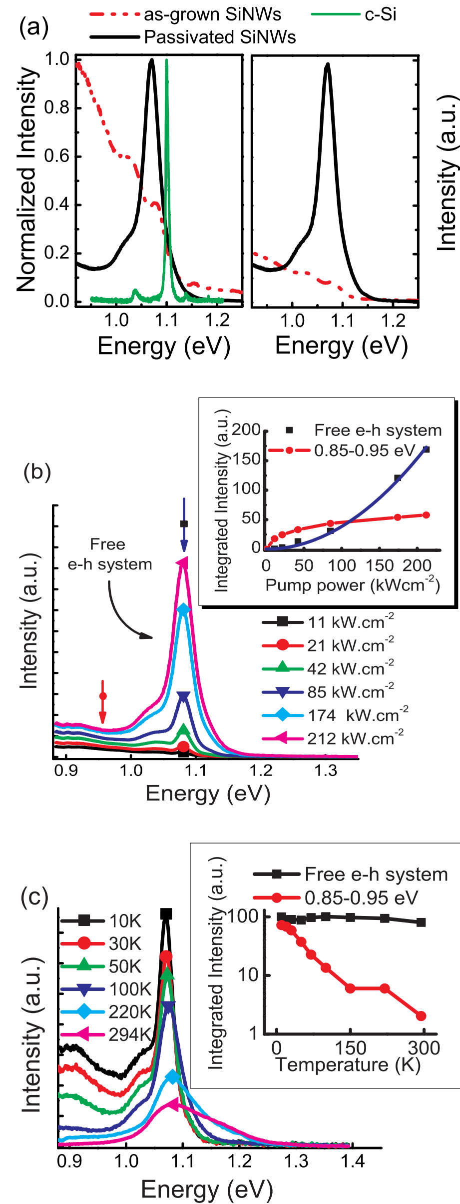

FIG. 2. (Color online) PL spectrum obtained with a 4 kHz rate Nd:YAG focalized on a spot of 0.3 mm in diameter at cryostat temperature of 10 K. (a) Left: comparison of normalized spectral response of as-grown NWs, passivated NWs, and bulk silicon. Right: absolute spectrum of as-grown and oxidized SiNWs. (b) [and (c)] Pump power (and temperature) dependence of passivated NWs.

of a finite density of states expected for defect related traps. In contrast, the integrated intensity of the band centered at 1.08 eV increases monotonously with a quadratic dependence on the pump power. This is interpreted as a progressive filling up of the conduction and valence bands when the pump power increases with a broadening, reflecting both the increase in the lattice and electronic temperatures of free carriers forming a dense plasma.

Figure 2(c) shows the dependence of the PL emission of core-shell SiNWs with cryostat temperature between 10 and 300 K and allows to distinguish the thermal dependence of the trap states and the 1.08 eV contribution. The intensity at low energy decreases by two orders of magnitude when the temperature goes from 10 K up to room temperature, while the 1.08 eV band intensity is slightly affected. The inset shows the intensity of the near gap contribution (black square curve) integrated from 1.04 to 1.40 eV and of the trap

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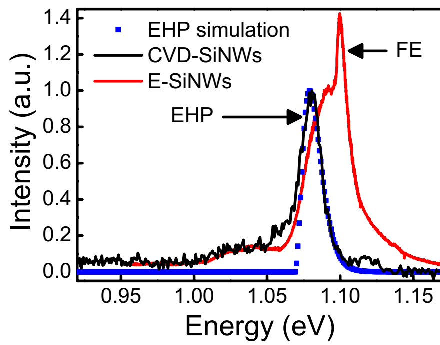

FIG. 3. (Color online) Comparison of the PL of E-SiNWs [with a cross section of 500×200 nm^2 (red curve)] and time resolved PL of CVD-SiNWs (black curve) at 10 K. The spectrum is taken 100 ns after the pulse and the temporal windows are of 10 ns. The blue curve is the computation of the emission spectrum of an ehp with a density of 3.3×10^{18} cm^{-3} and a temperature of 46 K.

states (red circle curve) integrated from 0.85 to 0.95 eV. The decrease in integrated intensity between 0.85 and 0.95 eV with the temperature corresponds to an ionization of the trap states. In contrast, the 1.08 eV transition just broadens toward higher energy and the integrated intensity is practically independent of the temperature. That ensures that the number of carriers, which recombine in this transition, is not affected by thermal energy as a result of spatial confinement. The broadening reflects the thermal dependence of the Fermi–Dirac distribution of the carriers in the bands. All these results clearly indicate that the 1.08 eV transition observed in core-shell CVD SiNWs is associated with an intrinsic recombination of electrons and holes free to move inside the wires. Another proof is given by comparing the PL spectra of core-shell SiNWs made by CVD to those made by etching, where we expect much better crystallinity and purity without any Cu contamination, but in counterpart some surface damages were created by the RIE process. Figure 3 shows the PL spectrum of E-SiNWs with a 200×500 nm^2 cross section (red solid curve). Except the emission of FEs created in the substrate, which is directly excited by the laser in this particular horizontal geometry, the spectrum is very similar to that of CVD SiNWs, with a band centered at 1.09 eV and a low energy (<1.00 eV) contribution. Time resolved PL of CVD NWs is performed and allows to demonstrate that the time delayed spectra after the laser pulse are stable during hundreds of nanoseconds. This means that the electronic system is in quasiequilibrium and its spectral response 100 ns after the excitation is given in Fig. 3 by the black curve (which is different from curves in Fig. 2(c) because the spectral response is on a short temporal window) and exhibits the 1.08 eV transition attributed to an ehp recombination,[13–17] whose line shape is given by a convolution product of the carrier density of states affected by the Fermi–Dirac distribution, $I(h\upsilon)=\int_{-\infty}^{\infty}\rho_e(\varepsilon)\rho_h(\varepsilon-h\upsilon)f_e^{\mathrm{FD}}(\varepsilon)f_h^{\mathrm{FD}}(\varepsilon-h\upsilon)d\varepsilon$,[18–23] which depends on the density and the temperature of the ehp. The strong carrier correlations induce a gap renormalization, which depends essentially on the density.[18] The computation for an ehp with a density of 3.3×10^{18} cm^{-3} (3.1×10^{18} cm^{-3}) and a temperature of 46 K (resp. 100 K) has a good overlap with the spectrum of the CVD (etched) SiNWs obtained at 10 K, which proves a weak thermalization of the NWs. These latter values of the density are close to the theoretical and experimental values of the liquid phase of the ehp at equilibrium in bulk silicon and in quantum wells.[13–17]

The liquid-plasma transition is usually observed in bulk for temperatures close to 30 K,[14] which suggests that the phase diagram could be modified in SiNWs. Concerning the low energy contribution below the silicon band gap, several contributions could be advanced to explain the origin of this broad band. As the spectra of E-SiNWs exhibit a low energy contribution whose intensity increases with the surface/volume ratio, this contribution could be attributed to luminescent surface states. Moreover, it is well known[24,25] that copper is a luminescent center in silicon and Weber *et al.*[12] showed that this luminescent center emits in the 1.014–0.89 eV energy range, which corresponds to the energy range of the contribution. Also, as we already mentioned, Jia *et al.*[8] observed a contribution below the silicon band gap energy in NW spectra and attributed it to dislocations. At this point of our study the demonstration of the origin of the PL line is still an open question.

To conclude, we reported here the observation of a near silicon gap transition in CVD SiNWs by PL experiments. Thermal oxidation is very efficient and necessary to enhance the emission intensity of this transition. Its evolution as a function of either temperature or optical pump power is strongly correlated with a band-to-band recombination of free carriers. The comparison with E-SiNWs allows to attribute this transition to the existence of an ehp in CVD SiNWs.

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