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# Photoluminescence of silicon nanowires obtained by epitaxial chemical vapor deposition

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We have carried out photoluminescence measurements of silicon nanowires (SiNWs) obtained by the chemical vapor deposition method with a copper-catalyzed vapor-liquid-solid mechanism. The nanowires have a typical diameter of 200 nm. Spectrum of the as-grown SiNWs exhibits radiative states below the energy bandgap and a small contribution near the silicon gap energy at 1.08 eV. A thermal oxidation allows to decrease the intensity at low energy and to enhance the intensity of the 1.08 eV contribution. The behavior of this contribution as a function of the pump power is correlated to a free carrier recombination. Furthermore, the spatial confinement of the carriers in SiNWs could explain the difference of shape and recombination energy of this contribution compared to the recombination of free exciton in the bulk silicon. The electronic system seems to be in an electron-hole plasma (ehp), as it has already been shown in SOI structures [M. Tajima, et al., J. Appl. Phys. 84 (1998) 2224]. A simulation of the radiative emission of an ehp is performed and results are discussed.

## 1. Introduction

The silicon nanowires (SiNWs) obtained by the chemical vapor deposition (CVD) method [1–4] are really promising for electronics and opto-electronics thanks to their very interesting integration properties. They are compatible with the silicon technology and could be most elegantly grown directly at their final position in a device on a wafer. However, the nanowire epitaxial growth requires the use of a metallic catalyst. Gold is the one most used because the Si–Au eutectic temperature is relatively low. But, it is well known that gold creates deep-level defect in silicon, which is detrimental to good device operation. For the moment, the influence of catalyst on the nanowire properties is not well understood and other catalysts as TiSi<sub>2</sub> [5] or Cu [6] can catalyze the growth. Here, we report on photoluminescence (PL) measurements of copper-catalyzed SiNWs. As the nanowire diameters are hundreds of nanometers, there is no quantum confinement on electronic carriers.

## 2. Experimental

### 2.1. Sample preparation

The SiNWs are obtained by the CVD method using a vapor-liquid-solid mechanism. A thin copper layer (typically 5 nm)

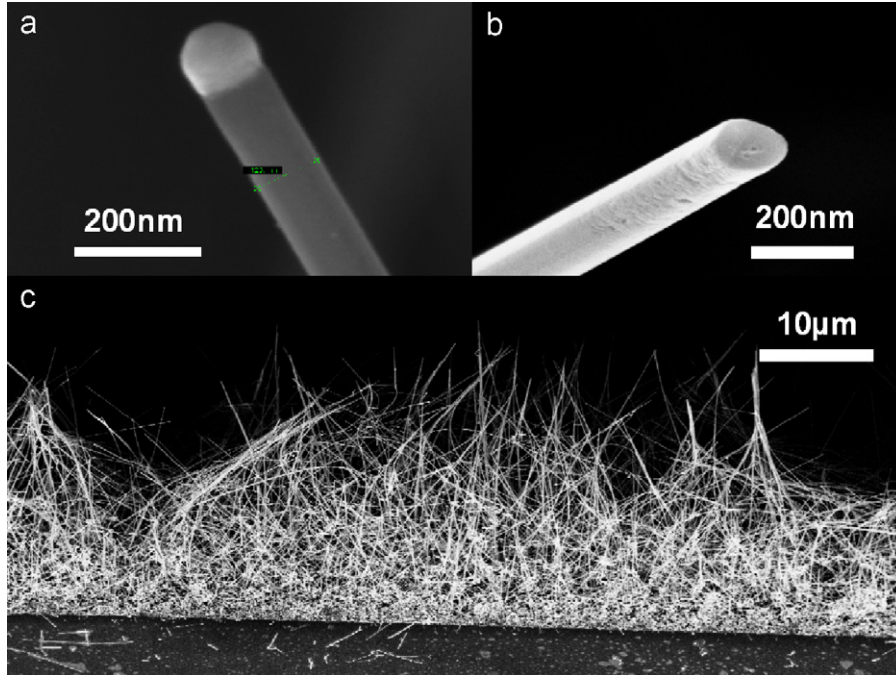
is evaporated on a silicon substrate. This layer is then heated at 850 °C under a hydrogen atmosphere to allow the formation of copper droplets with diameters of 100–300 nm. A silane-hydrogen-hydrogen chloride mixture flow allows the SiNWs growth (temperature ~800 °C during 40 min). Fig. 1a shows that the NW diameters are given by the catalyst size. Thus, in our experimental conditions, we obtained a high density of 80- $\mu$ m-long SiNWs with diameters of 200 nm (Fig 1c). A catalyst removal followed by a thermal oxidation is performed on SiNWs (Fig. 1b). To remove the copper droplets, the sample is deoxidized in a 49% HF solution during 1 min and then dipped for 2 min in an aqua regia bath (HCl(37%):HNO<sub>3</sub>(70%), 2:1). The thermal oxidation is performed in a furnace at 960 °C under a 10 mbar O<sub>2</sub> flow during 1 h. The samples cool down to room temperature in the furnace under a 10 mbar forming gas (H<sub>2</sub>:N<sub>2</sub>, 5:95) flow. The thermal oxide thickness is estimated to be 5–10 nm.

### 2.2. Photoluminescence

The optical pump of the PL experiment is a pulsed triple Nd:YAG laser. The pulses are 10 ns long and the repetition rate is 4 kHz and the excitation wavelength is 355 nm. The excitation beam is focused on a spot of 500  $\mu$ m diameter. Thus, the pump power density can be modulated from 5 kW/cm<sup>2</sup> up to 300 kW/cm<sup>2</sup> during the pulses. Samples are cooled down in a liquid helium circulation cryostat allowing a temperature control from 4.2 up to 300 K. The SiNWs' luminescence is analyzed in the

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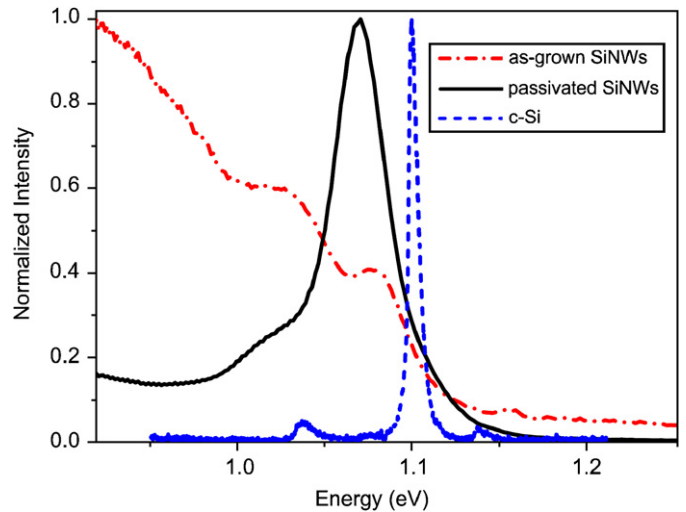


**Fig. 1.** MEB images of the nanowires obtained by a CVD method. The nanowires are copper catalyzed. (a) As-grown nanowire with its catalyst droplet. Its diameter is 120 nm. (b) Image of a SiNW obtained after the passivation step. (c) Side view of the sample shows the length (close to 80  $\mu\text{m}$ ) and the density of the sample studied here.

IR range (0.9–1.3 eV) with an InGaAs CCD, where indirect bandgap luminescence is expected.

### 3. Results and discussion

Fig. 2 compares the normalized PL spectra for the as-grown copper catalyzed SiNWs (red dash-dot curve), for the oxidized SiNWs (black solid curve) and for the crystalline silicon substrate (blue dash curve). All spectra are obtained at 10 K with a pump power density of 174  $\text{kW}/\text{cm}^2$ . One can clearly differentiate the substrate response from the PL spectrum of as-grown or oxidized SiNWs. The density of SiNWs is high enough to avoid substrate excitation and to ensure that the luminescence is directly coming from the NWs. The PL of the as-grown sample exhibits a low energy band whose origin is not well understood at this moment but could be attributed to dislocations [7]. In contrast, the small contribution at 1.08 eV could be attributed to the recombination of free carriers in the conduction and valence bands. However, the presence of the broad band does not allow us to conclude clearly on the electronic system which emits at this energy. The spectrum of oxidized SiNWs (black solid curve) is dominated by this 1.08 eV contribution. As thermal oxidation is known to passivate the silicon surface states, low-energy states (below 1.04 eV) can be attributed to surface states. The thermal oxidation is an essential step to exhibit a near gap contribution, thanks to its passivating role. We then study the dependence of the passivated SiNWs PL as a function of pump power. When pump power increases, the 1.08 eV contribution progressively dominates the spectrum (Fig 3a). And the plot (Fig 3b) of the maximum of intensity of this contribution (squares) as a function of the pump power density highlights a linear reliance on pump power. These behaviors are in agreement with a progressive filling of the conduction and valence bands and the recombination of free carriers in SiNWs. In contrast, the 0.95 eV intensity (circles) is saturating. Spatial confinement of carriers could explain the energy shift and the change in the spectrum shape compared to the bulk silicon (free



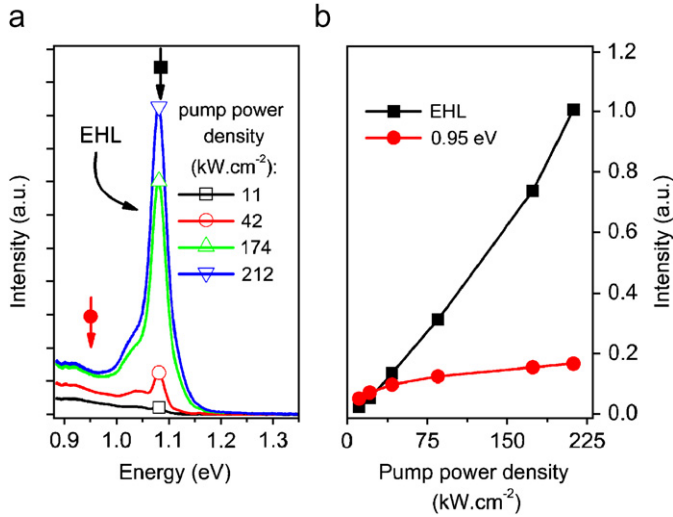
**Fig. 2.** Normalized intensity of the PL measurements of the as-grown (red dash-dot curve) and passivated (black solid curve) SiNWs. We compare them to the substrate (blue dash curve) PL. These spectra are obtained under an excitation power density of 174  $\text{kW}/\text{cm}^2$  and the temperature of consign of the cryostat is 10 K.

excitons). The many-body interactions could explain a broader lineshape and a smaller recombination energy. The interacting electron-hole system, also called an electron-hole plasma (ehp) [14,15], has already been observed in 200-nm-thick silicon on insulator thin films [8–10].

Simulation of the emission spectrum of an ehp by a convolution product of the density of states of the carriers affected by the Fermi-Dirac distribution is performed:

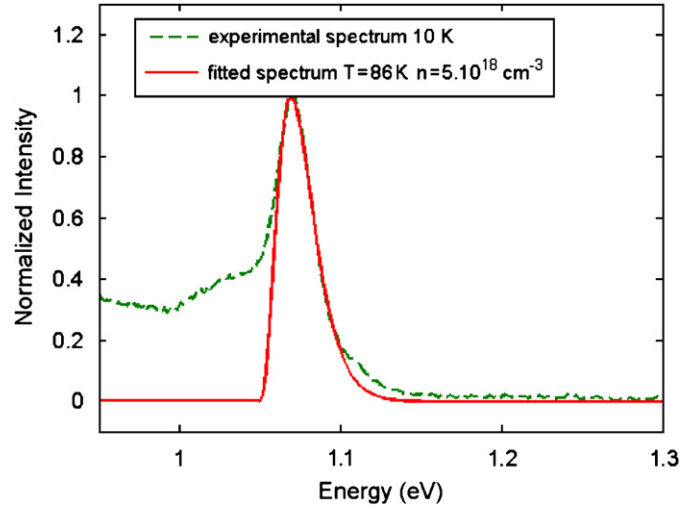
$$I(h\nu) = \int_{-\infty}^{\infty} \rho_e(\epsilon) \rho_h(\epsilon - h\nu) f_e^{\text{FD}}(\epsilon) f_h^{\text{FD}}(\epsilon - h\nu) d\epsilon$$

The densities of states are calculated for a three-dimensional system. The temperature-dependent expression of the gap energy



**Fig. 3.** (a) Pump power dependency of the PL spectra of the passivated SiNWs obtained for a cryostat temperature of 10 K. The ehp contribution is clearly exhibited. (b) Intensity at 0.95 eV (red circles) and at 1.08 eV (black squares). The graph shows clearly the linear dependency of the maximum intensity of the ehp contribution versus the pump power density. In contrast, the trap states are clearly saturating with the pump power. These behaviors are in agreement with two different electronic systems. The first one is a band-to-band recombination, and the other one is a trap-assisted electron-hole recombination.

in bulk Si [11] and the Vashishta [12] expression for the gap renormalization (due to the coulombian electron-hole interactions), which depends essentially on the ehp density, are used. We assume that coulombian interactions only affect the gap energy and not the electron/hole effective masses. Thus, the computation of the ehp emission spectrum depends on electronic temperature and ehp density. Fig. 4 shows the comparison of the experimental spectrum obtained at 10 K for a pump power density of 84 kW/cm<sup>2</sup> and the fitted emission spectrum of an ehp with a temperature of 86 K and a density close to  $5 \times 10^{18} \text{ cm}^{-3}$ . However, the theoretical value of the electron-hole liquid at thermodynamical equilibrium in bulk silicon and SOI layer is close to  $3 \times 10^{18} \text{ cm}^{-3}$  [13]. This latter value corresponds to the incompressible electron-hole phase, the so-called e-h liquid. Results are different from a SOI layer, but as the excitation is pulsed the electronic system is not at equilibrium during our experiment. The computation did not take into account the dynamics of the system, and gives mean values of the density and the temperature ( $\langle n \rangle \sim 5.10^{18} \text{ cm}^{-3}$ ,  $\langle T \rangle \sim 86 \text{ K}$ ) of the system. In any case, the shape of the simulation is in good agreement with experimental spectrum and that could confirm the presence of a plasma phase. But at this step of the study we cannot conclude on the phase diagram. To evaluate the density and temperature at equilibrium either a continuous PL experiment or a time-resolved PL experiment must be made.



**Fig. 4.** Comparison of the experimental spectrum (green dash curve) with simulated emission of an ehp (red solid curve). The experimental curve is the luminescence of passivated SiNWs obtained at 10 K and for a pump power of 84 kW/cm<sup>2</sup>. The fitted curve corresponds to an electronic temperature close to 86 K, an ehp density close to  $5 \times 10^{18} \text{ cm}^{-3}$ .

#### 4. Conclusions

We have shown evidence of a band to band electron-hole recombination in the SiNWs obtained by a CVD method. The passivation of the SiNW surfaces is essential to reduce the deep trap density and allow the observation of the radiative recombination of a free electron-hole system. This system differs from the bulk silicon, and we attribute the 1.08 eV contribution to the recombination of an electron-hole plasma.

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