

Recombination Dynamics of Spatially Confined Electron–Hole System in Luminescent Gold Catalyzed Silicon Nanowires

O. Demichel,* V. Calvo, N. Pauc, A. Besson, P. Noé, F. Oehler, P. Gentile, and N. Magnea

Laboratoire Silicium Nanoélectronique Photonique et Structure, Service de Physique des Matériaux et Microstructures, Institut Nanosciences et Cryogénie, Commissariat à l'Energie Atomique, 17 rue des Martyrs, F-38054 Grenoble Cedex, France

Received March 9, 2009; Revised Manuscript Received May 20, 2009

ABSTRACT

We study by time-resolved low temperature photoluminescence (PL) experiments of the electronic states of silicon nanowires (SiNWs) grown by gold catalyzed chemical vapor deposition and passivated by thermal SiO₂. The typical recombination line of free carriers in gold-catalyzed SiNWs (Au-SiNWs) is identified and studied by time-resolved experiments. We demonstrate that intrinsic Auger recombination governs the recombination dynamic of the dense e-h plasma generated inside the NW. In a few tens of nanoseconds after the pulsed excitation, the density of the initial electronic system rapidly decreases down to reach that of a stable electron–hole liquid phase. The comparison of the PL intensity decay time of Au-SiNWs with high crystalline quality and purity silicon layer allows us to conclude that the Au-SiNW electronic properties are highly comparable to those of bulk silicon crystal.

Semiconductor nanowires (NWs) have promising electronic and optical properties. They are the present topic of intense research for fundamental understanding of one-dimensional systems as well as for next generations of nanoelectronic and photonic devices. Chemical vapor deposition (CVD) using vapor–liquid–solid (VLS) mechanism is the most developed NW growth process^{1–4} given its widespread use in industry. This growth mode proceeds via preferential precursor cracking at the catalyst site, resulting in highly contrasted material deposition rate between seeded and unseeded sample zones and thus columnar-like growth of nanowires below the catalyst. Up to now, gold is the most studied catalyst for the silicon nanowire (SiNW) growth due to the very low temperature of the gold–silicon eutectic and the simplicity of the Au–Si phase diagram. However, it is well known that gold when incorporated in silicon structures acts as a deep level for free carriers that are trapped and can recombine. Thus, both electronic and optical properties can be altered.^{5–7}

Because of its ability to produce state of the art silicon nanowires, gold as a catalyst has been raising great interest but also many ambiguous questions as far as it has been used

in VLS growth. Several groups are working on the still opened-question on the presence and distribution of gold particles (cluster or elemental) in gold-catalyzed SiNWs (Au-SiNWs)^{8,9} and its implications on the nanowire electronic properties. Strong efforts are also made by the community to develop SiNW growth process with other catalysts.^{10–12} Furthermore, observation of quantum-confined excitons has been claimed in TiSi₂-catalyzed SiNWs, but not in Au-SiNWs.^{13,14}

In this letter, we demonstrate that photogenerated carriers can freely recombine in Au-SiNWs without a noticeable effect of residual gold contamination. As gold is the most-used catalyst, the knowledge on the gold-catalyzed SiNWs growth is the most developed and controlled. It can thus be used to enhance fundamental understanding of one-dimensional systems and for the next generation of nanodevices based on nanowires.

In a previous paper, we demonstrated by photoluminescence (PL) experiments the crucial importance of the surface passivation to allow intrinsic carrier recombination in copper-catalyzed silicon nanowires (Cu-SiNWs).¹⁵ The same effect is also observed for well-passivated Au-SiNWs. Time-resolved PL experiments demonstrate that the main recombination mechanism is the Auger recombination as expected in silicon structures (for high carrier density) and that the

* To whom correspondence should be addressed. E-mail: olivier.demichel@cea.fr.

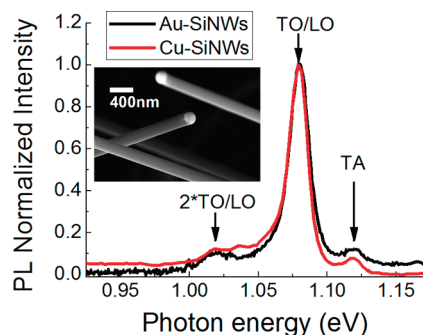


Figure 1. Time delayed PL spectra of Cu- and Au-SiNWs obtained at 10 K with a pump power of 1 μJ per laser pulse. Spectra are respectively acquired in the temporal windows 30–130 ns and 20–120 ns. The inset shows a SEM image of Au-SiNWs.

electronic system condenses in a stable phase at low temperature: the electron–hole liquid (ehl). In contrast, even if electron–hole plasma phases can be observed in direct band gap semiconductor nanowires^{16–18} in such materials the phase density never reaches a stable value and just decreases down to have no more many-body effects. Furthermore, the comparison of the Au-SiNWs and silicon-on-insulator (SOI) and crystalline silicon (c-Si) PL decay times gives an additional evidence of the high quality and chemical purity of Au-SiNWs.

The SiNWs are synthesized by the VLS method in a low pressure chemical vapor deposition (LPCVD) reactor.^{1–4} The Au-SiNW growth is catalyzed by colloids (200 nm in diameter) deposited on a silicon substrate (111) and heated at 650 °C for 10 min. The introduction of a silane-hydrogen-HCl gas mixture at a temperature of 650 °C during 15 min allows the epitaxial growth of 25 μm long nontapered Au-SiNWs with an uniform diameter close to 200 nm (see inset in Figure 1). After growth, the catalyst droplets are removed from the top of the NWs with an aqua regia solution (HCL (70%)/HNO₃ (37%), 1:2) prior to an oxidation process. The standard cleaning used in microelectronic (CARO, SC1, SC2) is employed to clean up the sample surface before the oxidation step. The oxidation is performed in a quartz tube furnace at 960 °C under an oxygen flow at 10 mbar for one hour. The oxide thickness obtained on a (111) silicon substrate is close to 7 nm. After the oxidation, the nanowires are annealed at 450 °C for one hour in an atmospheric pressure of forming gas (N_2/H_2 , 95%/5%).

The samples placed in a circulating He gas cryostat are optically pumped in a macro-PL setup with the 355 nm line of a pulsed tripled Nd:YAG laser. The PL decay curves and time-delayed spectra are recorded by a cooled photomultiplier tube with an InGaAs photocathode and a photon counting electronics.

Figure 1 presents the PL spectra of gold- and Cu-SiNWs passivated with the same oxidation process described above. As silicon is an indirect band gap semiconductor, radiative recombinations of free carriers need a third particle to conserve the momentum, and usually phonon-assisted recombinations are observed. Here, the three contributions of both spectra are attributed to the transverse acoustic (TA), transverse and longitudinal optical (TO/LO) and the 2 TO/

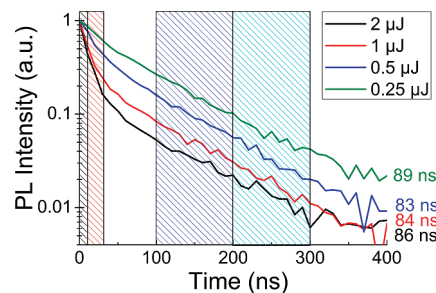


Figure 2. PL decay curves of Au-SiNWs for several optical pump powers at 10 K. The respective decay times after 100 ns and the temporal-windows used for the time-delayed spectra are indicated.

LO phonon-assisted recombinations of intrinsic carriers. The strong overlap of both spectra gives an evidence that the electronic band structures are similar in both kind of SiNWs. In this letter, we will focus our attention on the 1.08 eV PL line which is ascribed to the TO/LO phonon assisted radiative band-to-band recombination of free carriers as observed in bulk silicon.¹⁹ Despite the use of gold as catalyst, it is shown here that optically generated carriers in Au-SiNWs can remain in a free state before recombining rather than relaxing via gold-trap channels. In the following, we report on the PL decay curves and time-delayed spectra of Au-SiNWs.

Figure 2 shows the time decay of the 1.08 eV PL line of Au-SiNWs at a temperature of 10 K for several optical pump powers. The pump power clearly influences the system recombination dynamics during the first 50 ns; the more intense the pump power is, faster the decay time is. This behavior can be strongly linked to the Auger mechanism, which is known to be the main recombination mechanism in silicon structures at high e-h pair density because the nonradiative Auger recombination rate increases quadratically with the carrier density. Thus, as the initial carrier density is tuned by the pulse energy, the initial recombination rate depends tightly on the pump power. Furthermore, in Figure 2 after 50 ns the decays are single exponential and the lifetime is of 85 ns for all pulse energies. As Auger mechanism governs the recombination dynamics in those structures, the carrier density can be considered constant passed this delay. Beyond this stabilization time, the slopes of the PL decay curves are independent of the pump power, indicating that the equilibrium density of the electronic system does not depend on its initial density.

The recombination dynamics of the e-h pairs can be better understood with time-resolved spectra. In Figure 3, we present time-delayed PL spectra of Au-SiNWs obtained on several temporal-windows (defined in Figure 2) after the laser pulse. The 1.08 eV PL line width is very large at the end of the laser pulse and shrinks with time. After 100 ns, the PL spectrum does not evolve anymore; this behavior is strongly correlated to the constant density of the electronic system as deduced from our analysis of decay curves in Figure 2.

To analyze the line shape evolution of the 1.08 eV line in Au-SiNWs, we use the theory of the Fermi–Dirac condensation of excitons in semiconductors developed for bulk silicon,^{20–25} and checked in bulk and spatially confined

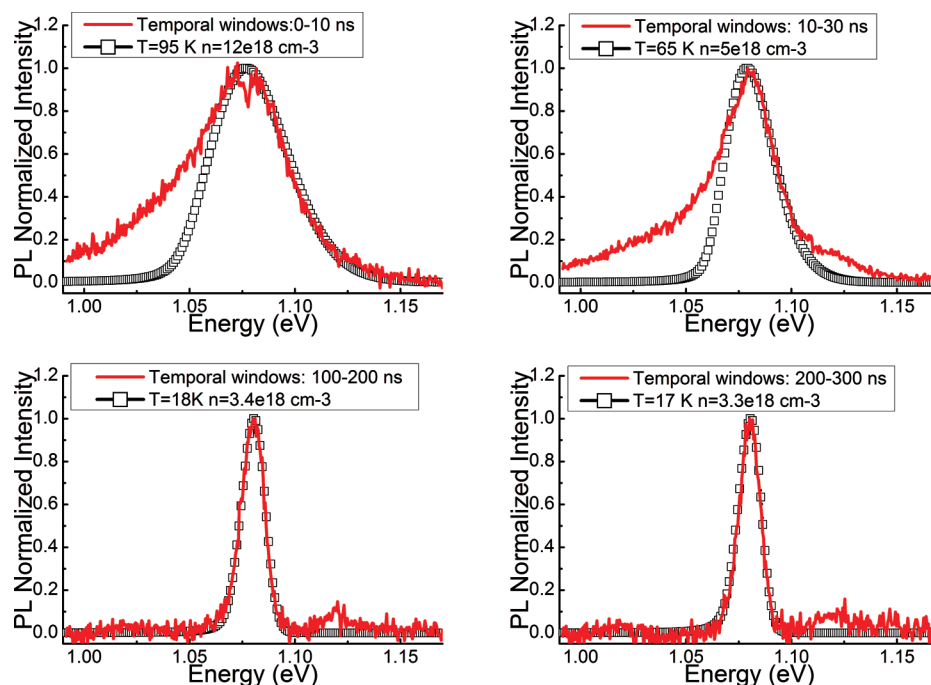


Figure 3. (In red) time-delayed spectra of Au-SiNWs obtained for four temporal windows at 10 K for a pump power of 1 μJ per pulse. (In black square) computed spectra of the electron–hole plasma are plotted. Computation parameters are indicated in the insets.

silicon and germanium structures.^{19,26–31} The shape and the energy position of the PL line of correlated e-h phases are strongly related to the density n and temperature T of the phase. Thus, temporal evolution of n and T can be directly extracted from time-dependence of the PL line shape. The line shape of an electron–hole plasma (ehp) recombination line can be described by the convolution product of the electron and hole distributions, $I(h\nu) = \int_{-\infty}^{\infty} \rho_e(\epsilon) \rho_h(\epsilon - h\nu) f_e^{\text{FD}}(\epsilon) f_h^{\text{FD}}(\epsilon - h\nu) d\epsilon$, where ρ_i and f_i^{FD} are, respectively, the density of states and the Fermi–Dirac distributions of carriers. Exchange and correlation interactions within this condensed phase induce a band gap renormalization (apparent decrease in the band gap energy) that essentially depends on the ehp density. In order to take into account the finite carrier lifetime, the density of states are calculated within the model of R. W. Martin and H. L. Störmer which explains the low energy tail of the recombination spectrum by the energy broadening of intermediate states created during Auger recombinations.³² Figure 3 compares experimental time-resolved PL spectra acquired on Au-SiNWs with their corresponding ehp spectra computed with the n and T parameters indicated in the insets. The overlap between both experimental time-delayed spectra of Au-SiNWs and corresponding computed spectra is excellent, especially for spectra obtained more than 100 ns after the excitation pulse. Using those comparisons, we extract reliable parameters of the electronic system for each time-windows. The low energy tail of the PL spectra acquired during the first 50 ns does not fit the theoretical curves. Indeed, at very short time the density and temperature are changing very quickly, so the plasma is too far from quasi equilibrium to be correctly described by the previous model for the whole energy scale. The density and temperature are then extracted from the high energy part and must be considered as time averaged values.

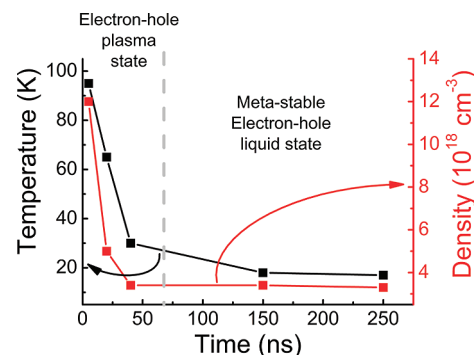


Figure 4. Time dependence of the electronic temperature and the density of the electron–hole plasma. The electronic system condenses in an electron–hole liquid after a few tenth of nano-seconds.

In Figure 4, the numerical computed values of n and T are plotted versus the time delay after the laser pulse. Both density and temperature rapidly decrease with time delay to reach their equilibrium value above 50 ns. In particular, very high density of $12 \times 10^{18} \text{ cm}^{-3}$ and temperature as high as 95 K are estimated near the laser pulse. This greatly differs from the monitored temperature in the cryostat (10 K) showing the difficulty to extract at this scale the thermal energy from a network of nanowires. After a rapid decrease, the density of the condensed phase reaches a constant value of $3.3 \times 10^{18} \text{ cm}^{-3}$. This latter value corresponds remarkably well to the density of the so-called ehl in silicon. At the same time, the electronic temperature progressively comes closer to the cryostat temperature as a result of the thermalization process to reach $\sim 17 \text{ K}$. This temperature is compatible with the temperature range where bulk ehl still condenses (condensation temperature $T_c < 28 \text{ K}$).

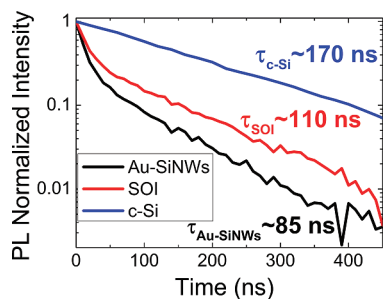


Figure 5. Comparison of the 1.08 eV PL intensity decay curves of c-Si, Au-SiNWs, and 100 nm silicon on insulator at 10 K and for a pump power of 1 μ J per pulse.

In these experimental conditions, the initial density is higher than the density of the stable phase (ehl), and internal Auger recombination added to a rapid expansion of the volume occupied by the ehp allows the fast decrease of the ehp density down to $3.3 \times 10^{18} \text{ cm}^{-3}$. Once this value is reached, the system can be seen as a liquid droplet with a constant density whose size decreases with time. That clearly explains the form of the PL decay curves of Figure 2.

Figure 5 compares the 1.08 eV PL intensity decay-curves of Au-SiNWs with those of crystalline bulk silicon (c-Si) and of a silicon layer of 100 nm obtained with SOI whose top surface has been passivated with the process described above. Silicon in this layer has a perfect crystalline quality and high chemical purity ($\text{Na-Nd} = 10 \times 15 \text{ cm}^{-3}$). The transient regime ($<50 \text{ ns}$) is less pronounced in the 2D layer because the e-h system can expand more easily into 2D than in the 1D nanowires to reduce its density, and this regime is not visible in c-Si where there is no spatial confinement of carriers. The decay times following the transient regime are decreasing from c-Si to SiNWs (c-Si, 170 ns; silicon layer, 110 ns; Au-SiNWs, 85 ns). Surface recombinations at the Si/SiO₂ interfaces can strongly modify the recombination rate and could explain the carrier lifetime differences between c-Si and nanostructures. Indeed, carrier lifetime in c-Si is close to 170 ns, and the surface recombinations of the SOI silicon layer induce a decrease of the lifetime down to 110 ns. In nanowires, surfaces are more important and the lifetime decreases again. In that sense, even if the existence of gold contamination in Au-SiNWs after the cleaning and thermal oxidation process is still an opened-question, these experiments indicate at this stage that residual gold atoms, if present, do not alter significantly the free recombinations of the well-passivated Au-SiNWs.

To conclude, we demonstrated the intrinsic nature of the luminescence of gold-catalyzed SiNWs at energy close to the silicon band gap energy. Comparison of the Au-SiNWs and Cu-SiNWs spectra, along with the characteristics of the decay time of the 1.08 eV PL line in Au-SiNWs and SOI,

allow one to attribute this 1.08 eV PL line to the TO/LO phonon assisted radiative recombination of free carriers condensed in an electron–hole liquid in gold-catalyzed nanowires. Pump power dependence of the PL decay curves is explained through Auger recombination. After a transient regime constituted of an out of equilibrium plasma phase, the density of the electronic system rapidly decreases toward the well-known density of the electron–hole liquid in silicon ($3.3 \times 10^{18} \text{ cm}^{-3}$). All these results show that passivated core–shell SiNWs/SiO₂ grown from gold colloids have behavior similar to classical Si/SiO₂ heterostructures in our experimental conditions.

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NL900739A