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Ramon M. Delos Santos
Jasher John Ibañes
Maria Herminia Balgos
Rafael Jaculbia
Jessica Pauline Afalla

See next page for additional authors

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Authors
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Dynamics of Optically-Generated Carriers in Si (100) and Si (111) Substrate-Grown GaAs/AlGaAs Core-Shell Nanowires

Ramon delos Santos1,2*, Jasher John Ibañes1, Maria Herminia Balgos1, Rafael Jaculbia1, Jessica Pauline Afalla1, Michelle Bailon-Somintac1, Elmer Estacio1, Arnel Salvador1, Armando Somintac1, Christopher Que3, Satoshi Tsuzuki4, Kohji Yamamoto4 and Masahiko Tani4

Abstract
GaAs/Al0.1Ga0.9As core-shell nanowires (CSNWs), with average lateral size of 125 nm, were grown on gold nanoparticle-activated Si (100) and Si (111) substrates via molecular beam epitaxy. Room temperature-photoluminescence (RT-PL) from the samples showed bulk-like GaAs and Al0.1Ga0.9As bandgap emission peaks at 1.43 and 1.56 eV, respectively. Higher PL emission intensity of the sample on Si (111) compared to that on Si (100) is attributed to uniform Al0.1Ga0.9As shell passivation of surface states on Si (111)-grown CSNWs. Carrier dynamics in two different temporal regimes were studied. In the sub-nanosecond time scale (300–500 ps), time-resolved radiative recombination efficiency of carriers was examined. In the 0–4 ps range, surface field-driven ballistic transport of carriers was probed in terms of the radiated terahertz (THz) waves. Time-resolved PL measurements at 300 K revealed that the carrier recombination lifetime of the GaAs core on Si (100)-grown CSNWs is 333 ps while that on Si (111)-grown sample is 500 ps. Ultrafast photoexcitation of GaAs core on the two samples generated a negligible difference in the intensity and bandwidth of emitted THz radiation. This result is ascribed to the fact that the deposited GaAs material on both substrates produced samples with comparable NW densities and similar GaAs core average diameter of about 75 nm. The samples’ difference in GaAs core’s carrier recombination lifetime did not influence THz emission since the two processes involve distinct mechanisms. The THz spectrum of CSNWs grown on Si (111) exhibited Fabry-Perot modes that originated from multiple reflections of THz waves within the Si substrate.

Keywords: Optical properties of nanowires; Time-resolved spectroscopy; Infrared and Raman spectra of III-V semiconductors; Molecular beam epitaxy; Semiconducting gallium arsenide; Optical properties of semiconductors

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Background
Semiconducting nanowire (NW)-based devices are considered to be versatile building blocks for optical and optoelectronic circuits at the nanoscale [1–7]. The compound semiconductor GaAs is one of the most viable choices for NW material due to the already existing technological platform. Epitaxial growth of GaAs NWs on Si substrate is of considerable interest because it has paved the way for the integration of III-V semiconductor nanoscale devices with well-established Si technology [8]. Nevertheless, the optical performance of bare GaAs NWs is relatively poor as a result of sensitivity to surface states that act as nonradiative carrier traps in the NWs [9, 10]. To surmount this problem, a higher bandgap material like AlGaAs can be grown as a passivation layer on the facets of GaAs NWs to form a structure called core-shell NWs (CSNWs). The higher bandgap material prevents interaction of the carriers in the GaAs core with the surface states [9, 10].

* Correspondence: rdelossantos@nip.upd.edu.ph
1National Institute of Physics, University of the Philippines, Diliman, Quezon City, Philippines
2Department of Physics, Ateneo de Manila University, Quezon City, Philippines
3Full list of author information is available at the end of the article

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In this paper, the dynamics of optically-generated carriers in GaAs/AlGaAs CSNWs grown on Si (100) and Si (111) substrates were investigated. Room temperature-photoluminescence (RT-PL) spectroscopy was utilized to determine material composition of CSNWs and the quality of AlGaAs shell. Carrier dynamics in the sub-nanosecond time scale was examined via time-resolved PL (TRPL) spectroscopy while that in the 0–4 picoseconds (ps) regime was probed using terahertz-time domain spectroscopy (THz-TDS). In particular, TRPL was employed to measure GaAs core’s carrier recombination lifetime. On the other hand, the main purpose of THz-TDS measurement is to shed light on the drift of photoexcited carriers by the strong surface depletion field. Ultrafast optical excitation of GaAs generates current surge, which is associated with the drift of photoexcited carriers and is manifested in terms of a transient THz wave emission \cite{11, 12}. The THz electric field amplitude is proportional to the time derivative of the surge current \cite{13, 14}. Using THz-TDS measurements, GaAs core’s THz emission from samples on Si (100) and Si (111) were compared to that of a semi-insulating (SI)-GaAs (100) substrate.

**Methods**

GaAs/AlGaAs CSNWs were synthesized using anodized aluminum oxide (AAO)-patterned gold (Au) nanoparticles on Si (100) and Si (111) substrates. A single nanoparticle array template was fabricated on these substrates to initiate the vapor-liquid-solid (VLS) growth of GaAs core. Samples were grown side-by-side in a Riber 32P molecular beam epitaxy (MBE) chamber to ensure similar growth conditions. The CSNW growth sequence started with the deposition of GaAs at 580 °C for 30 min to form the GaAs core, followed by AlGaAs deposition for 30 min on the surfaces of GaAs NWs to form the core-shell structure. A thin Si-doped GaAs cap layer was also grown over the core-shell to prevent oxidation of the AlGaAs shell. To approximate the core diameter of CSNW samples, uncoated GaAs NWs were grown using the same growth parameters.

For the investigation of surface morphology and steady-state optical properties of the as-grown CSNW samples, field emission scanning electron microscopy (FE-SEM) and PL spectroscopy analyses were performed, respectively. SEM images were obtained in a Philips XL 30 Field Emission Gun (FEG) system. PL measurements were done using a 488 nm continuous-wave Ar⁺ laser as an excitation source. The output signal was collected by a SPEX 500 M monochromator and detected by a Hamamatsu GaAs photomultiplier tube (PMT). TRPL experiments were carried out using a frequency doubled Ti/Sapphire femtosecond laser (400 nm) with 100 fs pulses at 80 MHz repetition rate. The resulting 800 nm excitation wavelength did not excite the AlGaAs shell. The GaAs PL signal was made available to a streak camera system consisting of Digikröm spectrometer with an Optronis streak camera attached to it.

THz emission of the CSNW samples and SI-GaAs (100) wafer was measured via a standard THz-TDS system in 45°-reflection excitation geometry mode. Ultrafast photoexcitation of GaAs material was performed using a mode-locked Ti/Sapphire laser as an excitation source, centered at 850 nm wavelength, emitting 100 fs pulses at a repetition rate of 80 MHz. The time domain plots of THz transients were detected by optically gated, low temperature-grown GaAs photoconductive antenna. The 850 nm excitation wavelength generated THz emission from the GaAs core only since the associated energy of the laser is not adequate to excite the AlGaAs shell.

**Results and Discussion**

Tilted view SEM micrographs of GaAs/AlGaAs CSNWs grown on Si (100) and Si (111) are shown in Fig. 1a,b, respectively. The CSNWs have an average lateral size of 125 nm. Most of the CSNWs on Si (100) are believed to have grown in the four equivalent <111> directions, as shown in Fig. 2, indicating bulk-like GaAs and AlGaAs components of the CSNWs have good optical and crystalline quality. Hence, CSNWs on Si (111) have a growth direction that is predominantly perpendicular to the substrate surface. The NW density on both samples is approximately 10⁸ NWs per square centimeter. In Au-assisted VLS growth of GaAs NWs, growth area is dictated by the lateral size of liquid Au-Ga alloy droplet and the diameter of NWs is approximately given by the size of Au nanoparticles \cite{16, 17}. Consequently, the two CSNW samples are expected to have similar GaAs core diameters since a single nanoparticle array template was fabricated on both substrates. Using the uncoated GaAs NW sample, the estimated core diameter is about 75 nm.

The RT-PL spectra of CSNWs on Si (111) and Si (100) are shown in Fig. 2, indicating bulk-like GaAs and Al₀·₁Ga₀·₉As bandgap emission peaks. Emissions with energies at 1.427 and 1.558 eV are attributed to GaAs and Al₀·₁Ga₀·₉As sections, respectively, of the CSNWs on Si (100). The emissions at 1.434 and 1.560 eV correspond to the GaAs and Al₀·₁Ga₀·₉As components of the CSNWs on Si (111). The well-defined PL spectra from the two samples at 300 K indicate that both GaAs and AlGaAs components of CSNWs have good optical and crystalline quality.

However, GaAs PL emission intensity of the sample grown on Si (111) is roughly three times higher than that of the sample on Si (100). This can be explained by better AlGaAs shell passivation on Si (111). When the NWs are perpendicular to the substrate surface and the
substrate is rotated during growth, AlGaAs deposition on the surfaces of GaAs NWs is uniform [18]. On the other hand, the inclined orientation of NWs from a substrate surface produces partial AlGaAs passivation due to selective deposition of well-directed molecular beams only on the exposed NW facet [18]. Surface states in some parts of NWs without passivation allow photoexcited carriers to recombine nonradiatively, thus decreasing the PL intensity [19]. Based on Fig. 2, the PL intensity of Al$_{0.1}$Ga$_{0.9}$As relative to GaAs is 30% better when CSNWs are grown on Si (111) compared to Si (100). This is consistent with the idea of uniform Al$_{0.1}$Ga$_{0.9}$As shell on Si (111)-grown CSNWs.

The samples were also characterized by TRPL spectroscopy at room temperature to analyze carrier dynamics within the GaAs core of CSNWs grown on Si (100) and Si (111). Generation of carriers is manifested as the TRPL rise while recombination of carriers is described by the TRPL decay in Fig. 3. The rise time constant is fixed at 10 ps, which is also the resolution of our TRPL setup. Although the GaAs TRPL data of Si (100)-grown CSNWs seems to be not entirely monoexponential, two time constants cannot be fitted with confidence in the said curve since the TRPL intensities from 808 up to 1798 ps have very low signal-to-noise ratio (SNR). This feature is a consequence of the fact that GaAs PL emission intensity of the sample grown on Si (100) is less than that of the sample on Si (111). On Si (111)-grown CSNW sample, the TRPL of GaAs core is characterized by a single exponential decay rate. Hence, it is more...
appropriate to use decay time fitting that has a single rate on both samples. GaAs core’s carrier recombination lifetime, $\tau$, in CSNWs grown on Si (100) is shorter than that on Si (111) as shown in Fig. 3. Since the two samples were grown side-by-side in an MBE chamber and had the same growth direction, crystalline quality and density of defects on GaAs core of the CSNWs are presumably identical. Thus, the longer recombination lifetime of carriers within the GaAs core of CSNWs grown on Si (111) is due to superior AlGaAs passivation of surface states [19].

THz-TDS measurements were performed to shed light on the drift of photoexcited carriers by the surface depletion field. The logarithmic THz emission spectra and the corresponding time domain data (inset) generated from ultrafast photoexcitation of GaAs core and Si-GaAs (100) substrate are shown in Fig. 4. Generation of THz took place in less than 5 ps based on the time domain data. THz emission from the GaAs component of CSNW samples was one order of magnitude higher than that of GaAs wafer. The morphology of the grown CSNWs, as dictated by the Si substrate orientation, does not affect their THz emission efficiency. Results indicate a negligible difference on the intensity and bandwidth of THz radiation emitted from the two samples. This supports the fact that the deposited GaAs material on both substrates produced samples with comparable NW densities and similar GaAs core diameters. The samples’ difference in GaAs core’s carrier recombination lifetime did not influence THz emission since the two processes involve distinct mechanisms.

The THz emission intensity profile shown in Fig. 5 reveals Fabry-Perot modes only on the spectrum of CSNWs grown on Si (111). The separation between any two adjacent Fabry-Perot peaks, $\Delta f$, in the graph matches with an optical cavity length $L$ that can be calculated using the equation:

$$\Delta f = \frac{c}{2Ln \cos \theta}$$

where $c$ is the speed of light and $n$ is the index of refraction [20]. The angle of incidence $\theta$ is equal to 45° because of the reflection excitation geometry setting of the THz-TDS setup. Using $n = 3.42$ for the index of refraction of Si at THz frequencies [21, 22], the cavity length is estimated to be 820 $\mu$m. It is interesting to note that the calculated value for $L$ is in the same order of magnitude as the thickness of the Si (111) substrate. The oscillatory modes that were observed on the Si (111)-grown sample are attributed to highly directional THz beam propagation, as dictated by the drift of carriers along the NW length. Vertical NWs, such as the Si (111)-grown sample shown in Fig. 1, the THz dipole radiation pattern is parallel to the substrate surface [23, 24]. This geometry ensures THz directional as it undergoes multiple reflections within the substrate. It has been observed that reflections at the internal interfaces of a Si substrate can manifest as Fabry-Perot modes in the THz intensity profile, when THz waves interact with the planar material [22].

In summary, TRPL alongside with THz emission measurements enabled us to look at carrier recombination dynamics vis-à-vis carrier transport at room temperature. Carrier dynamics in two different temporal regimes were studied. In the sub-nanosecond time scale (300–500 ps), time-resolved radiative recombination efficiency of carriers was examined. In the 0–4 ps range, surface field-driven ballistic transport of carriers was probed in terms
of the radiated THz waves. The samples’ difference in GaAs core’s carrier recombination lifetime did not influence THz emission since the two processes involve distinct mechanisms.

Conclusions

GaAs/Al\textsubscript{0.1}Ga\textsubscript{0.9}As CSNWs were grown using AAO-patterned gold nanoparticles on Si (100) and Si (111) substrates. The nanowire density on both samples is around 10⁸ NWs/cm². RT-PL from the samples showed bulk-like emission peaks close to GaAs and Al\textsubscript{0.1}Ga\textsubscript{0.9}As bandgaps. The Si (111)-grown CSNWs produced an enhanced luminescence due to uniform Al\textsubscript{0.1}Ga\textsubscript{0.9}As shell passivation. TRPL measurements at 300 K obtained shorter GaAs carrier recombination lifetime for CSNWs grown on Si (100) than that on Si (111) because of better passivation of surface states on the GaAs core of CSNWs grown on the latter. Ultrafast optical excitation of GaAs core on the two samples generated a negligible difference in the intensity and bandwidth of emitted THz radiation since the deposited GaAs material on both substrates formed samples with comparable NW densities and similar GaAs core diameters. The THz spectrum of CSNWs grown on Si (111) exhibited Fabry-Perot modes that originated from the multiple reflections of THz waves within the Si substrate. Our results on the carrier dynamics of Si (100) and Si (111) substrate-grown GaAs/AlGaAs CSNWs are believed to be valuable in designing functional NW-based photovoltaic and optoelectronic devices.

Abbreviations

AlGaAs: aluminum gallium arsenide; GaAs: gallium arsenide; Si: silicon.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

RDS and JJI were responsible for establishing the growth parameters to synthesize gold nanoparticles using e-beam evaporator and GaAs NWs in our in-house molecular beam epitaxy system. RDS also did data processing and analysis and worked on the draft of the manuscript. JJI carried out the core-shell nanowire growth and calculated optical cavity length from the THz data. MHJB, RJ, JPA, and MBS conducted the microscopy and spectroscopy measurements. EE, ASa, and ASco planned and designed the growth and spectroscopy experiments, supervised the project, and finalized the manuscript. EE, KQ, and MT designed the THz-TDS experiment. All authors read and approved the final manuscript.

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Author details

1National Institute of Physics, University of the Philippines, Diliman, Quezon City, Philippines. 2Department of Physics, Ateneo de Manila University, Quezon City, Philippines. 3Department of Physics, De La Salle University, Manila, Philippines. 4Research Center for Development of Far-Infrared Region, University of Fukui, Fukui, Japan.