Nearly intrinsic exciton lifetimes in single twin-free GaAs/AlGaAs core-shell nanowire heterostructures

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CW and time-resolved photoluminescence measurements are used to investigate exciton recombination dynamics in GaAs/AlGaAs heterostructure nanowires grown with a recently developed technique which minimizes twinning. A thin capping layer is deposited to eliminate the possibility of oxidation of the AlGaAs shell as a source of oxygen defects in the GaAs core. We observe exciton lifetimes of ~1 ns, comparable to high quality two-dimensional double heterostructures. These GaAs nanowires allow one to observe state filling and many-body effects resulting from the increased carrier densities accessible with pulsed laser excitation. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2967877]

Because semiconductor nanowire (NW) heterostructures are increasingly important for use in ultrasensitive miniaturized electronic and optoelectronic devices, improvements in the quality of these structures is of great importance. Exciton recombination times are extremely sensitive to nonradiative recombination at surface, interface, and bulk defects. Surface and interface processes become increasingly dominant as the surface to volume ratio increases for semiconductor NWs. Recently, Reitzenstein *et al.*[1] and Titova *et al.*[2] showed that bare InP NWs can achieve nearly intrinsic lifetimes (~1 ns) equivalent to thick epilayers, an achievement attesting to the high quality of the NWs and also reflecting the relatively low surface recombination velocities in InP. This achievement is remarkable considering that the diffusion length ($\sqrt{D\tau}$) in InP for holes at low temperatures is 1 μm; photoexcited carriers interact with the surface and sample a significant fraction of the InP surface and volume during their lifetimes.

The situation for GaAs NWs is significantly more challenging. First, the sensitivity of photoexcited carriers to surface states is much higher in GaAs than in InP. The surface recombination velocity, S, which is 1000 cm/s in InP,[3,4] is three orders of magnitude larger (10^6 cm/s) for GaAs.[5,6] Recent time-resolved pump-probe terahertz spectroscopy showed that the carrier lifetime in bare GaAs wires is approximately 1 ps, consistent with the expected nonradiative lifetime of $\tau_{NR} \approx d/2S \approx 1.5$ ps for a NW diameter of 30 nm and $S=10^6$ cm/s.[7] In addition, the low temperature hole mobility in GaAs is an order of magnitude larger than for InP, which results in a diffusion length which is three times larger than for InP; this increases the sensitivity of carriers to defects within the bulk of the NW core. The recombination lifetime in GaAs is also particularly sensitive to bulk defects such as vacancies and arsenic-antisite defects.[8,9]

Previously, Hoang *et al.* showed that the addition of an AlGaAs shell around the GaAs core increases the intensity of the emission from the NWs by a factor of 20, but that the measured lifetime was nonetheless found to be shorter than the system response of 50 ps.[10,11] However, these NWs contained bulk defects (twins) and oxygen deep levels within the GaAs core from oxidation of the AlGaAs shell. In this letter we show that addressing these two problems can dramatically increase the observed recombination lifetime for single NWs.

Gold nanospheres serve as the catalysts for the III-V NWs which grow along the $\langle 111 \rangle B$ crystallographic direction of the substrate. Twin planes can form normal to the growth direction through 60 deg rotations around the growth axis. These have been reported in NWs fabricated from a wide variety of materials.[12] The density of defects in zincblende (cubic) NW can be quite ahigh with twins observed with a spacing comparable to or less than the diameter of the NW.[12,13] Twinning defects may seriously compromise the performance of optoelectronic devices, as they specifically reduce the recombination lifetime. Very recently, Joyce *et al.* showed an efficient and effective way to produce nearly twin-free GaAs NWs using a modified two-temperature growth technique.[14]

In the previous experiments by Hoang *et al.* on GaAs/AlGaAs core-shell NWs which showed short lifetimes, the protective AlGaAs shell was grown around the GaAs core with the outer surface of the shell exposed to air.[10,11] Ryan *et al.* and Orton *et al.* have shown in 2D heterostructures that AlGaAs rapidly oxidizes, providing a route for oxygen incorporation into the GaAs well. Oxygen acts as a deep level in GaAs, which can reduce the recombination lifetime and quantum efficiency of the structure by an order of magnitude.[15,16] Thus, even though a AlGaAs shell reduces nonradiative surface recombination in the GaAs core of the NW, it introduces the difficulty of oxygen absorption. In 2D structures, capping the AlGaAs confinement barrier with a very thin (~5 nm) GaAs layer ameliorates this problem. This outer layer added to the core-shell NWs does not con-

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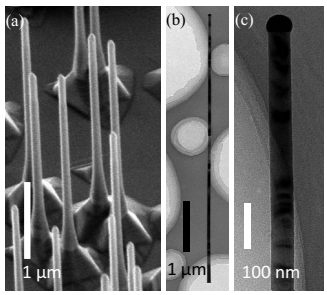

FIG. 1. (a) A FESEM micrograph of the GaAs/AlGaAs core-shell NWs studied. (b) A TEM micrograph of a GaAs NW core without AlGaAs shell layer. This shows the minimal tapering and straight sidewalls of the GaAs cores. (c) A magnified TEM micrograph of the same GaAs NW which shows the absence of twin defects.

tribute to the emission from the structures because any carriers rapidly recombine nonradiatively at the surface.

Following the method described by Joyce *et al.*,[14] the NWs studied here are first nucleated from gold catalyst at a temperature of 450 °C at a V/III ratio of 45 for 1 min, followed by an extended growth of the GaAs NW core at 375 °C.[14] Such a method results in smooth parallel sidewalls and long NW cores which are nearly free of twin defects. Following growth of the core, the temperature is raised back to 650 °C and a nominally 24% AlGaAs shell ~20 nm thick is grown; this is followed by an ~5 nm GaAs capping shell. Figure 1(a) shows a field emission scanning electron microscopy (FESEM) micrograph of the particular GaAs/AlGaAs core-shell NWs (including the GaAs cap) studied here. Figure 1(b) showed a transmission electron microscopy (TEM) image of a GaAs core, grown under identical conditions, which displays a NW core with straight sidewalls and minimal tapering. Figure 1(c) shows a magnified image of the same GaAs core free of twin defects. From this we conclude that the core of the wires in Fig. 1(a) should be free of twins and be of uniform diameter. The small amount of tapering seen above the pedestal is due to tapering of the AlGaAs shell and GaAs cap. These core-shell capped NWs were removed for single NW spectroscopy onto a Si substrate.

Photoluminescence (PL) measurements were carried out at 10 K using both cw and pulsed excitation. Single NWs were excited using the 780 line (~1.59 eV) from a Ti:sapphire laser operating cw or mode locked (200 fs pulses every 13 ns). A 50× objective with NA=0.5 was used to focus the laser to a 1.5 μm spot onto a single NW and to collect the emitted PL. The emitted PL was imaged onto the entrance slit of a spectrometer. cw spectra were acquired using a cooled charge coupled device camera, while time-resolved spectra and time decays were obtained using a silicon avalanche photodiode and time-correlated single photon counting. Figure 2 shows typical cw spectra from a single GaAs/AlGaAs core-shell capped NW (wire 1) grown using the new technique. The excitation power of the 780 nm cw laser was varied over an order of magnitude, from ~30 to ~450 μW. Low-power PL spectra display a 10 meV full width at half maximum emission line which is centered at the free exciton energy of 1.51 eV. We estimate that the emission intensity of these NWs is an order of magnitude brighter than those in the two studies reported by Hoang *et al.*[10,11] As the excitation power increases, the PL emission line exhibits asymmetric broadening on both the high energy and low energy sides, but the peak intensity remains near

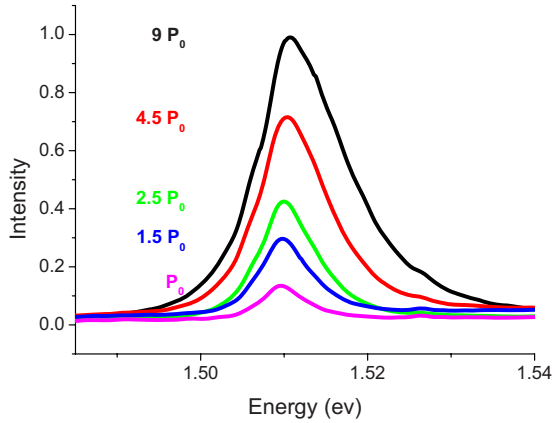

FIG. 2. (Color online) cw PL spectra as a function of power from single GaAs/AlGaAs NW (wire 2). $P_0 \sim 30$ μW.

1.51 eV. This is consistent with a significant increase in the photoexcited carrier density without heating of the NW.

In Fig. 3 we show time decays of PL from several single NWs photoexcited by 200 fs pulses at 780 nm at very low average powers. The time decays are extracted from PL data collected at the free exciton emission energy of 1.51 eV. The decays are single exponential with a lifetime for wire 1 that exceeds 1 ns. This lifetime is comparable to very high quality 2D GaAs/AlGaAs wide double heterostructures and is consistent with an intrinsic exciton radiative recombination.[17] Over half of the NWs we have studied which were grown using the new technique exhibit comparable lifetimes. Approximately a third of the NWs exhibit shorter lifetimes, suggesting recombination which is dominated by nonradiative recombination either at isolated occurrences of twin defects or at the AlGaAs/GaAs interface. In every case, the emission lifetime from these NWs is significantly longer than measured previously for GaAs NWs.[10,11]

Photoexcitation with 200 fs pulses results in average carrier densities several orders of magnitude larger than can be achieved with CW laser excitation. At high carrier densities, emissions both on the low and high energy sides of the exciton energy exhibit strikingly nonlinear decays consistent with nonexcitonic emission. We have acquired time-resolved spectra by accumulating time decays as a function of energy. We have assembled the data into a 2D map as shown in Fig. 4(a) where the vertical axis shows time after arrival of the

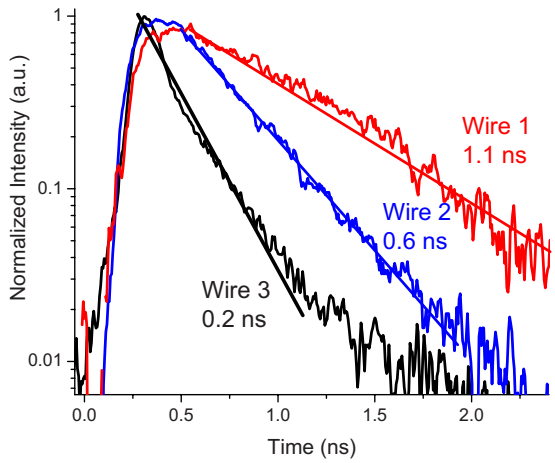

FIG. 3. (Color online) Low-power time decays accumulated at the peak emission energy (1.515 eV) from three single GaAs/AlGaAs core-shell NWs grown using the two-temperature technique.

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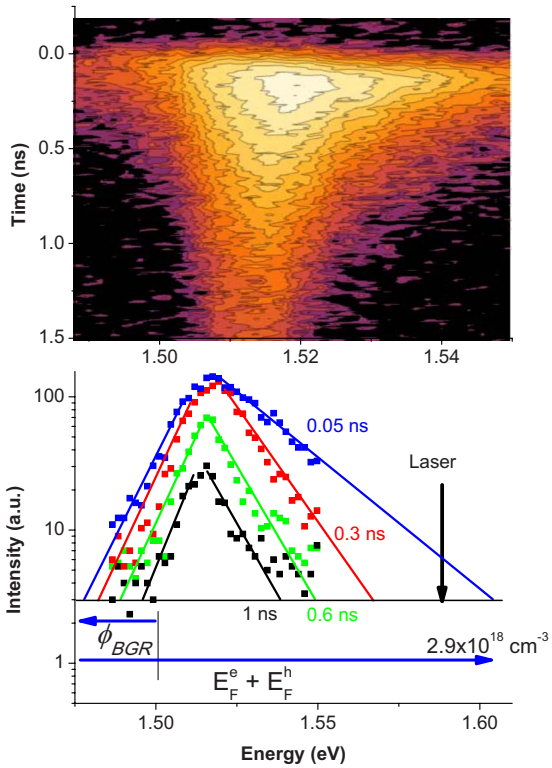

FIG. 4. (Color online) Time-resolved spectra from a GaAs/AlGaAs NW (wire 4) which exhibits a recombination lifetime of 1 ns. (a) An emission energy vs time 2D map. Lighter colors represent higher intensities than darker colors. (b) Spectra extracted from the time-resolved spectrum at 50, 300, 600, and 1000 ps after the laser pulse and plotted on an enlarged energy scale. Arrows (blue) show the calculated band gap renormalization (ϕ_{BGR}) and the sum of the electron and hole Fermi energies for an electron-hole pair density of 2.9×10^{18} cm^{-3} at zero temperature.

excitation pulse, while the horizontal axis shows the emission energy. In such spectra one can follow the evolution of carriers from extremely high densities just after the laser pulse, to much lower carrier densities as the electron-hole pairs recombine. At late times (>2 ns) one can see emission from excitons centered at 1.51 eV, but at earlier times (and higher densities) the emission line broadens dramatically on both the high and low energy sides. Similar effects have been recently reported in InP NWs by Titova *et al.*[2] and are consistent with the emission from an electron-hole plasma. Several individual spectra are extracted from the time-resolved spectrum and plotted on a log intensity scale in Fig. 4(b) at times ranging from 0.05 to 1.0 ns after the laser pulse. The movement to lower energies results from many-body effects which produce an effective renormalization of the band gap, while the high energy side results from degenerate filling of the electron and hole bands.[2] Using the procedure explained in detail in Ref. 2, we can self-consistently determine the carrier density by adjusting the band gap renormalization using the universal form of Vashishta and Kalia,[18] and calculating the zero-temperature Fermi energy. The band gap renormalization and zero temperature Fermi energies for the 0.05 ns spectrum in Fig. 4(b) are shown by the horizontal arrows. We find that the 15 meV band gap renormalization determines an electron-hole pair density of 2.9×10^{18} cm^{-3}, so that the sum of the electron and hole Fermi energies is 120 meV. At later times the carrier density decreases rapidly due to direct electron-hole recombination, until the average carrier density falls below the Mott density ($\sim3\times10^{15}$ cm^{-3} at 10 K) where excitons become stable resulting in the symmetric emission at 1.51 eV at late times (>1ns).

Using PL and time-resolved PL measurements of single GaAs/AlGaAs capped core-shell NW heterostructures, we have shown that high optical quality NWs with unusually long lifetimes are possible when growth parameters are well controlled. Combining twin-free growth of the GaAs core along with a confining AlGaAs shell which is protected from oxidation through an additional ~5 nm GaAs cap makes it possible to achieve NWs with excellent optical properties and nearly intrinsic exciton recombination lifetimes. At high photoexcited carrier concentrations these GaAs/AlGaAs NWs exhibit significant bandgap renormalization and state filling. These results show that it is possible to achieve NW optical qualities which approach that of the best 2D heterostructures, so that fabrication of highly efficient one-dimensional devices may soon become a reality.

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[1] S. Reitzenstein, S. Munch, C. Hofmann, A. Forchel, S. Crankshaw, L. C. Chuang, M. Moewe, and C. Chang-Hasnain, Appl. Phys. Lett. **91**, 091103 (2007).
[2] L. V. Titova, T. B. Hoang, J. M. Yarrison-Rice, H. E. Jackson, Y. Kim, H. J. Joyce, Q. Gao, H. H. Tan, C. Jagadish, X. Zhang, J. Zou, and L. M. Smith, Nano Lett. **7**, 3383 (2007).
[3] Y. Rosenwaks, Y. Shapira, and D. Huppert, Phys. Rev. B **45**, 9108 (1992).
[4] H. C. Casey, Jr. and E. Buehler, Appl. Phys. Lett. **30**, 247 (1977).
[5] J. Lloyd-Hughes, S. K. E. Merchant, L. Fu, H. H. Tan, C. Jagadish, E. Castro-Camus, and M. B. Johnston, Appl. Phys. Lett. **89**, 232102 (2006).
[6] R. J. Nelson and R. G. Sobers, J. Appl. Phys. **49**, 6103 (1978).
[7] P. Parkinson, J. Lloyd-Hughes, Q. Gao, H. H. Tan, C. Jagadish, M. B. Johnston, and L. M. Herz, Nano Lett. **7**, 2162 (2007).
[8] F. Ganikhanov, G. R. Lin, W. C. Chen, C. S. Chang, and C. L. Pan, Appl. Phys. Lett. **67**, 3465 (1995).
[9] I. S. Gregory, C. M. Tey, A. G. Cullis, M. J. Evans, H. E. Beere, and I. Farrer, Phys. Rev. B **73**, 195201 (2006).
[10] L. V. Titova, T. B. Hoang, H. E. Jackson, L. M. Smith, J. M. Yarrison-Rice, H. J. Joyce, H. H. Tan, and C. Jagadish, Appl. Phys. Lett. **89**, 173126 (2006).
[11] T. B. Hoang, L. V. Titova, J. M. Yarrison-Rice, H. E. Jackson, A. O. Govorov, Y. Kim, H. J. Joyce, H. H. Tan, C. Jagadish, and L. M. Smith, Nano Lett. **7**, 588 (2007).
[12] J. Johansson, L. S. Karlsson, C. P. T. Svensson, T. Martensson, B. A. Wacaser, K. Deppert, L. Samuelson, and W. Seifert, Nat. Mater. **5**, 574 (2006).
[13] J. Bao, D. C. Bell, F. Capasso, J. B. Wagner, T. Mårtensson, J. Trägårdh, and L. Samuelson, Nano Lett. **8**, 836 (2008).
[14] H. J. Joyce, Q. Gao, H. H. Tan, C. Jagadish, Y. Kim, X. Zhang, Y. N. Guo, and J. Zou, Nano Lett. **7**, 921 (2007).
[15] J. M. Ryan, J. W. Huang, T. F. Kuech, and K. L. Bray, J. Appl. Phys. **76**, 1175 (1994).
[16] J. W. Orton, P. Dawson, D. E. Lacklison, T. S. Cheng, and C. T. Foxon, Semicond. Sci. Technol. **9**, 1616 (1994).
[17] D. J. Wolford, G. D. Gilliland, T. F. Kuech, L. M. Smith, J. Martinsen, J. A. Bradley, C. F. Tsang, R. Venkatasubramanian, S. K. Ghandi, and H. P. Hjalmarson, J. Vac. Sci. Technol. B **9**, 2369 (1991).
[18] P. Vashishta and R. K. Kalia, Phys. Rev. B **25**, 6492 (1982).

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