Temperature dependence of photoluminescence from single core-shell GaAs–AlGaAs nanowires

L. V. Titova,[a] Thang B. Hoang, H. E. Jackson, and L. M. Smith
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221

J. M. Yarrison-Rice
Department of Physics, Miami University, Oxford, Ohio 45056

Y. Kim
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australian Captial Territory 0200, Australia and Department of Physics, College of Natural Science, Dong-A University, Hadan 840, Sahagu, Busan 604-714, Korea

H. J. Joyce, H. H. Tan, and C. Jagadish
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australian Captial Territory 0200, Australia

(Received 4 August 2006; accepted 14 September 2006; published online 26 October 2006)

Temperature-dependent polarized microphotoluminescence measurements of single GaAs/AlGaAs core-shell nanowires are used to probe their electronic states. The low-temperature emission from these wires is strongly enhanced compared with that observed in bare GaAs nanowires and is strongly polarized, reflecting the dielectric mismatch between the nanowire and the surrounding air. The temperature-dependent band gap of the nanowires is seen to be somewhat different from that observed in bulk GaAs, and the PL rapidly quenches above 120 K, with an activation energy of 17 meV reflecting the presence of nonradiative defects. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2364885]

Recently, semiconductor nanowires have attracted considerable attention as candidates for bottom-up construction of numerous nanoscale photonic devices such as nano-light-emitting-diodes, lasers, waveguides, and photodetectors.[1–5] The large surface-to-volume ratio inherent in nanowires leads to increased sensitivity to surface states, which act as nonradiative carrier traps and as a source of potential fluctuations associated with surface-trapped charges; these surface states adversely affect optoelectronic device performance.[6] The recent demonstration of custom-designed radial nanowire structures[7,8] has pointed to a successful route to overcoming these limitations. Deposition of a larger band gap material on the surface of a nanowire results in core-shell nanowires.[8,9] The shell acts as a barrier and spatially separates the nanowire core electronic states from the surface, thus effectively reducing the influence of the surface states. However, despite the success in fabrication, little is known about the electronic structure and optical properties of individual core-shell nanowires.

In this letter, we examine the low-temperature optical emission properties of single GaAs–AlGaAs core-shell nanowires from 5 to 150 K. We observe a dramatic increase in the luminescence efficiency of AlGaAs/GaAs core-shell nanowires compared to the bare GaAs nanowires. The emission and excitation of GaAs–AlGaAs nanowires are shown to be strongly polarized in direction along the nanowire axis but with a degree which appears to vary from wire to wire probably reflecting nonuniformities in nanowire morphology. In addition, we study the temperature dependence of the photoluminescence (PL) emission energy and find that the temperature-dependent gap for core-shell nanowires is different than that observed in the bulk. The PL from single core-shell nanowires is observed to quench rapidly above 120 K with an activation energy of ~17 meV reflecting the presence of nonradiative defects.

Bare GaAs nanowires and GaAs/AlGaAs core-shell nanowires are prepared according to the vapor-liquid-solid mechanism and employing gold nanoparticles as catalyst. Gold nanoparticles of 30 nm in diameter were deposited on a GaAs (111)*B* wafer functionalized in 0.1% poly-L-lysine (PLL) solution. GaAs nanowires with an estimated average diameter of 40 nm were grown along the (111)*B* axis by horizontal flow metal organic chemical vapor deposition at 450 °C. For core-shell structures, AlGaAs shells (with vapor composition of 26% Al) were grown at 650 °C following the growth of the GaAs core. The resulting core-shell nanowires have a pronounced tapered shape with an average diameter of 80 nm and a length of 6–8 μm, as can be seen in the 45° tilted field-emission scanning electron microscopy FESEM image of the nanowires on the growth substrate, as displayed in Fig. 1. Since the diameter of the GaAs core is larger than exciton Bohr radius in GaAs (12 nm), we expect only very weak quantum confinement effects in these nanowires.

For single nanowire optical measurements, the nanowires were ultrasonically removed from the growth substrate into a methanol solution, dispersed onto a silicon substrate, and placed into a continuous flow helium cryostat, where the temperature can be varied from 4 to 300 K. Single nanowire PL measurements were performed in the slit-confocal configuration as detailed in Ref. 10 Nanowires were excited by 20 mW of 750 nm emission from a cw Ti:sapphire laser. The laser beam was defocused to a 20 μm spot in order to illuminate uniformly the entire nanowire of interest. We estimate that at this laser power and wavelength fewer than 100 excitons are present within the nanowire at any given time, so

[a]Electronic mail: ltitova@physics.uc.edu

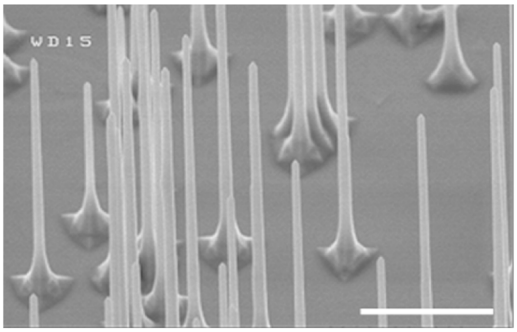

FIG. 1. FESEM image of GaAs–AlGaAs nanowires on a GaAs substrate. The scale bar is 2 μm.

they can be considered to be noninteracting. A 50×/0.5 numerical aperture long working length microscope objective was used to collect the PL emission with the nanowire image oriented along the entrance slit of the spectrometer.

We have studied eight different GaAs–AlGaAs nanowires with an average diameter of 80 nm. Their PL spectra measured at 10 K are displayed in Fig. 2(a). The spectra of all nanowires consist of a single broad peak (full width at half maximum of 23±3 meV) at 1.518±0.003 eV, which corresponds closely to the free exciton emission in bulk GaAs. The large peak width and the variability in the peak position may be related to the variations (albeit small) in the blueshift of the exciton emission energy due to strain and compositional nonuniformities.

The emission efficiency of the core-shell nanowires is over an order of magnitude higher compared to the emission efficiency of bare GaAs nanowires. Representative PL spectra of the most intense core shell and of the most intense bare nanowire recorded at identical excitation conditions are compared in Fig. 2(b). The enhancement of the low-temperature PL efficiency by passivating the GaAs surface with AlGaAs is comparable to that previously reported in room temperature PL measurements on similar core-shell structures grown by selective-area metal organic vapor phase epitaxy.[9] On the other hand, time-resolved measurements (not shown here) have indicated that the recombination lifetime of excitons in both the bare and core-shell GaAs nanowires at 5 K is less than 80 ps, which is the system response time of our time-correlated photon counting system. Even in the core-shell GaAs structures such a lifetime is more than an order of magnitude less than the lifetime observed in high quality GaAs double heterostructures.[11] This reduced lifetime may result from defects within the GaAs nanowire core, or at the GaAs–AlGaAs interface. Transmission electron microscopy studies (not shown here) of bare GaAs nanowire have shown the existence of twinning defects, which are known to adversely affect the optical and electronic properties of semiconductors.[12,13] This suggests that there is still significant room for improvement in optimizing the luminescence efficiency of these core-shell nanowires.

The core-shell GaAs–AlGaAs nanowires exhibit strong linear polarization anisotropy for both emission and excitation with the preferential polarization along the nanowire axis. In Fig. 2(c) we show PL emission from nanowire A, excited by the laser polarized parallel and perpendicular to the nanowire. We find that the PL intensity is ~70 times stronger for the 780 nm laser polarized along the nanowire than for the laser polarized perpendicular to it. The degree of excitation polarization, defined as $P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$, is

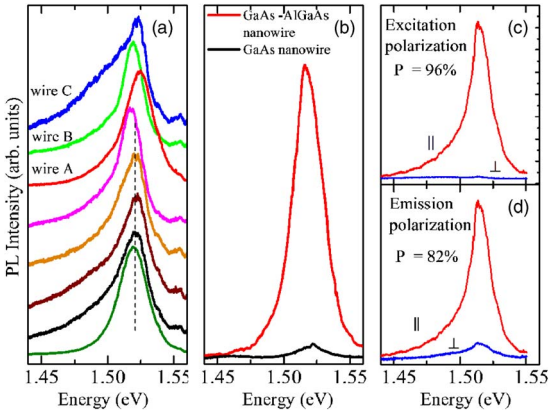

FIG. 2. (Color online) (a) Normalized PL spectra of seven GaAs–AlGaAs nanowires, (b) PL spectra of the most intense bare GaAs and core-shell GaAs–AlGaAs nanowires, (c) PL spectra of wire A with excitation laser polarized parallel and normal to the wire, and (d) polarized PL spectra of wire A analyzed parallel and normal to the nanowire with excitation linearly polarized along nanowire direction.

96% for wire A. Similar degrees of excitation polarization were observed in other nanowires. Figure 2(d) shows the linear polarization of the PL emission from wire A. For this measurement, the 780 nm laser was linearly polarized along the nanowire axis, and the components of the resultant PL were analyzed parallel and perpendicular to the nanowire. The observed degree of wire A emission polarization is 82%. This strong polarization anisotropy is similar to the one observed in InP nanowires[14] and is caused primarily by the dielectric mismatch between the nanowire and its surroundings, which causes strong suppression of the component of the electric field inside and perpendicular to the nanowire.[15] Quantum confinement effects are unlikely to be a significant contributing factor to the polarization anisotropy since the exciton Bohr radius is smaller than the size of the GaAs core. Interestingly, Ruda and Shik[15] calculated that the emission from GaAs nanowires should have a degree of polarization of approximately 92%, which is somewhat higher than that

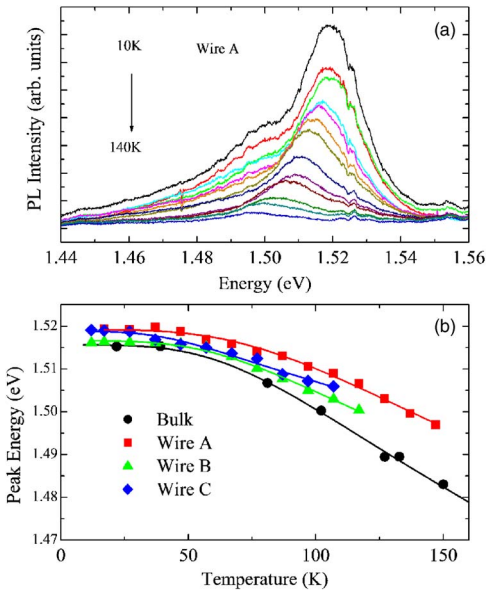

FIG. 3. (Color online) (a) PL spectra from nanowire A at different temperatures from 10 to 140 K. (b) The symbols show temperature dependence of the emission energy of several nanowires as well as bulk GaAs band gap temperature dependence from Ref. 16. The solid lines show fits to these data using the modified Varshni equation (Ref. 17).

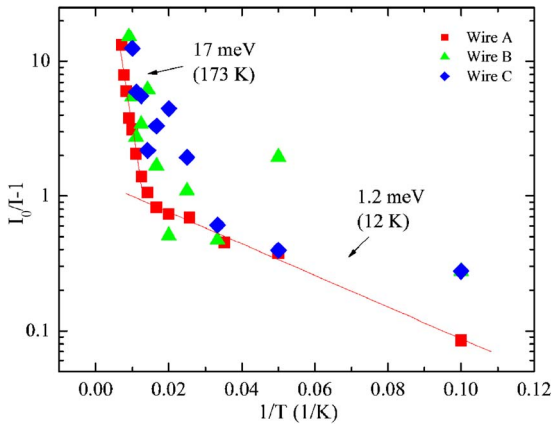

FIG. 4. (Color online) Temperature-dependent quenching of nanowire PL; I_0 is a fitting parameter of the PL intensity at $T=0$, while I is the PL intensity at temperature T. The symbols show experimental data from wires A, B, and C, while the lines are linear fits in the low- and high-temperature regions showing activation energies.

observed in nanowire A [Fig. 2(d)]. This perhaps reflects inhomogenieties or deviations of nanowire A from cylindrical symmetry. This conclusion is supported by the fact that other nanowires we have studied display similar behavior with the degree of polarization varying from 75% to 85%. More detailed studies to connect PL polarization with the detailed structure of the nanowires are needed.

A series of PL spectra for one of the GaAs–AlGaAs nanowires as a function of temperature from 10 to 120 K is shown in Fig. 3(a). As the temperature increases, the nanowire emission broadens and redshifts and is strongly quenched at temperatures above 120 K. The temperature dependence of the emission energy is shown in Fig. 3(b) along with the bulk GaAs epilayer temperature-dependent band gap.[16] Fits to these data were carried out using a modified form of the Varshni equation, which varies as E^4 at low temperatures and becomes linear at higher temperatures. Cardona *et al.*[17] have argued that this is a thermodynamically correct form for the variation of the energy gap as a function of temperature in contrast to the phenomenological form used by Varshni, which varies quadratically at low temperatures. While the GaAs/AlGaAs nanowires emit approximately at the same energy as bulk GaAs, the fits to the modified Varshni equation are significantly different from that for the bulk semiconductor. In particular, the linear slope of the curve at low temperatures is significantly shallower than observed in the bulk. The reasons for this behavior are not clear at this moment, but may be due to different phonon responses for nanowires or the appearance of strain as the temperature is raised.

The PL of the nanowires quenches above 120 K. In order to observe the activation energies associated with this behavior, we plot the I/I_0-1, where I_0 is a parameter which reflects the intensity of the PL line at zero temperature and I is the intensity of the PL line at a temperature T. If one plots this expression as a function of $1/T$, the activation energy is given by the slope of the lines fit to the data.[18] As displayed in Fig. 4, we find that while the intensity of the PL changes dramatically around 50 K, it is not possible to observe a change in slope and thus the ~4 meV activation energy expected for ionization of excitons in GaAs. This is probably because the emission lines are wide enough that we are not able to distinguish spectrally the transition from exciton emission to emission from an electron-hole plasma which should occur at temperatures above 50 K. Moreover, the nanowire PL strongly quenches with an activation energy of 17 meV, which is probably associated with the presence of nonradiative centers, possibly at the uncovered end of the nanowire, which was originally in contact with the substrate before ultrasonication. In contrast, in high quality AlGaAs/GaAs double heterostructures where surface recombination is extremely small, PL emission can be observed all the way to room temperature.[11]

In summary, we have presented detailed studies of the optical properties of the single core-shell GaAs–AlGaAs nanowires. All of the nanowires studied exhibit a single PL peak in the energy range of the bulk free excitons. The nanowire emission has been found to be strongly polarized in the direction along the nanowire axis due to the dielectric mismatch between the nanowires and their surroundings. We have also observed that the temperature dependence of the nanowire emission energy deviates from the bulk GaAs band gap temperature dependence but quenches at ~120 K suggesting the presence of nonradiative centers. Nevertheless, we have observed a dramatic enhancement of the luminescence efficiency in these GaAs/AlGaAs core-shell nanowires compared to the bare GaAs nanowires. This suggests that additional efforts to optimize the structure and quality of core-shell nanowires would be worthwhile.

This work was supported by the University of Cincinnati. Australian authors gratefully acknowledge the financial support from the Australian Research Council.

[1] X. Duan, Y. Huang, R. Agarwal, and C. M. Lieber, Nature (London) **421**, 241 (2003).
[2] R. Agarwal, C. J. Barrelet, and C. M. Lieber, Nano Lett. **5**, 917 (2005).
[3] Y. Gu, E.-S. Kwak, J. L. Lensch, J. E. Allen, T. W. Odom, and L. J. Lauhon, Appl. Phys. Lett. **87**, 043111 (2005).
[4] C. J. Barrelet, A. B. Greytak, and C. M. Lieber, Nano Lett. **4**, 1981 (2004).
[5] A. Urbieta, P. Fernández, and J. Piqueras, Appl. Phys. Lett. **85**, 5968 (2004).
[6] G. W. Bryant and W. Jaskolski, J. Phys. Chem. B **109**, 19650 (2005).
[7] L. J. Lauhon, M. S. Gudiksen, and C. M. Lieber, Philos. Trans. R. Soc. London, Ser. A **362**, 1247 (2004).
[8] N. Sköld, L. S. Karlsson, M. W. Larsson, M. E. Pistol, W. Seifert, J. Trägårdh, and L. Samuelson, Nano Lett. **5**, 1943 (2005).
[9] J. Noborisaka, J. Motohisa, S. Hara, and T. Fukui, Appl. Phys. Lett. **87**, 093109 (2005).
[10] S. Mackowski, T. Gurung, H. E. Jackson, L. M. Smith, G. Karczewski, and J. Kossut, Appl. Phys. Lett. **87**, 072502 (2005).
[11] 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).
[12] A. Mikkelsen, N. Sköld, L. Ouattara, M. Borgström, J. N. Andersen, L. Samuelson, W. Seifert, and E. Lundgren, Nat. Mater. **3**, 519 (2004).
[13] B. A. Wacaser, K. Deppert, L. S. Karlsson, L. Samuelson, and W. Seifert, J. Cryst. Growth **287**, 504 (2006).
[14] J. Wang, M. S. Gudiksen, X. Duan, Y. Cui, and C. Lieber, Science **293**, 1455 (2001).
[15] H. E. Ruda and A. Shik, Phys. Rev. B **72**, 115308 (2005).
[16] P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **35**, 9174 (1987).
[17] M. Cardona, T. A. Meyer, and M. L. W. Thewalt, Phys. Rev. Lett. **92**, 196403 (2004).
[18] A. Chiari, M. Colocci, F. Fermi, Y. Li, R. Querzoli, A. Vinattieri, and W. Zhuang, Phys. Status Solidi B **147**, 421 (1988).