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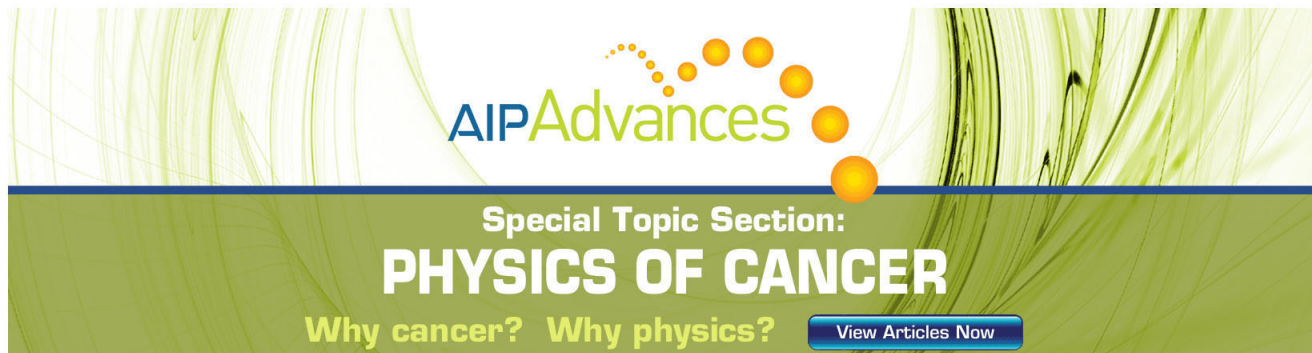
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Long minority carrier lifetime in Au-catalyzed GaAs/Al_xGa_{1-x}As core-shell nanowires

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GaAs/Al_xGa_{1-x}As core-shell nanowires were grown by metal organic chemical vapor deposition with optimized Al_xGa_{1-x}As shell and twin-free Au-catalyzed GaAs cores. Time-resolved photoluminescence measurements were carried out on single nanowires at room temperature, revealing minority carrier lifetimes of 1.02 ± 0.43 ns, comparable to self-assisted nanowires grown by molecular beam epitaxy. The long minority carrier lifetimes are mainly attributed to improvement of the GaAs/Al_xGa_{1-x}As interface quality. The upper limit of surface recombination velocity of the structure is calculated to be 1300 cm/s with the Al_xGa_{1-x}As shell grown at 750 °C, which is comparable with planar double heterostructures. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4735002>]

Semiconductors nanowires (NWs) are promising for applications in future photonic and electronic devices.¹⁻³ Thus, it is of great importance to develop optimized growth procedures for producing high quality NWs. With their direct band gap and high electron mobility, GaAs NWs are considered to be a prime candidate for advanced optoelectronic devices. However, the electronic performance—i.e., carrier lifetime and mobility—of GaAs NWs has yet to match that of state-of-the-art planar GaAs devices.^{2,4} The present deficiency is typically attributed to the large surface-to-volume ratio inherent to NWs,⁵ and the tendency for non-radiative recombination centers to form at the surface or interface. The minority carrier lifetime (τ_{mc}) and surface/interface recombination velocity (S), which in part determine the optoelectronic device performance, have been well studied in GaAs epilayers. When high quality epitaxial passivation layers were used, τ_{mc} as long as micro-seconds have been observed and virtually “surface-effect-free” GaAs epilayers have been reported.⁶⁻⁸ In comparison, there are few published reports of the τ_{mc} and S in GaAs NWs. Long τ_{mc} (~ 2 ns) were observed in self-assisted GaAs NWs grown by molecular beam epitaxy (MBE),^{9,10} however, only ~ 30 ps τ_{mc} have so far been reported in Au-catalyzed NWs grown by metal organic chemical vapor deposition (MOCVD)¹¹ despite the industrial importance of this growth technique.

Many non-radiative recombination pathways are known for carriers in GaAs; for instance, bulk defects and surface states are known to play varying roles for materials with low-temperature growth¹² and large surface-to-volume ratio.⁷ NWs are known to suffer from both of these effects. It is well established that covering the GaAs surface with an Al_xGa_{1-x}As layer is an effective method to reduce non-radiative carrier recombination at the surface.^{6,13} The Al_xGa_{1-x}As layer, with a wider band gap and negligible lattice mismatch, reduces the electronic surface states of GaAs. The effect of bulk defects is also evident for NWs with planar defects, where the temperature dependence of photolumi-

nescence (PL) measurements from single core-shell GaAs/Al_xGa_{1-x}As NWs with GaAs core grown at 450 °C shows rapid PL quenching above 120 K.¹⁴ This has been markedly improved by optimizing the quality of GaAs core with significant reduction in the number of twin defects and by adding a thin outer “capping” shell of GaAs to prevent oxidation of the Al_xGa_{1-x}As shell.^{11,15} At low temperature, nearly intrinsic exciton lifetimes have been observed for such NWs.¹⁵ However, the same NWs showed rather poor carrier lifetimes at room temperature.¹¹ To improve the room temperature carrier lifetime, we have optimized the structure by changing the Al_xGa_{1-x}As shell growth conditions. In this study, we demonstrate that nanosecond τ_{mc} can be achieved in GaAs/Al_xGa_{1-x}As/GaAs core-shell-cap NWs with the shells deposited at a high temperature (750 °C).

GaAs core NWs were grown using MOCVD following the two-temperature procedure developed by Joyce *et al.*¹⁶ Trimethylgallium (TMGa), trimethylaluminum (TMAI), and arsine (AsH₃) were used as the Ga, Al, and As source materials, respectively. Au particles of 50 nm diameter were dispersed on GaAs (111) B substrate, and GaAs NW cores were first nucleated at 450 °C for 1 min followed by 45 min growth at 375 °C. Figure 1(a) shows a field emission scanning electron microscopy (FESEM) image of such GaAs NWs. All NWs grew vertically on the substrate in the [111] direction with uniform diameters of 53 ± 5 nm. The two temperature growth has significant advantages in minimizing undesirable radial growth and eliminating twin defects to provide a high quality GaAs core.¹⁶ An Al_xGa_{1-x}As shell was grown at 750 °C for 3 min with an Al mole fraction in the vapor phase, x_v [TMAI]/([TMGa] + [TMAI]), of 0.5. The Al_xGa_{1-x}As shell grew uniformly surrounding the core NWs, resulting in smooth parallel sidewalls with minimum tapering except at the base (Figure 1(b)). The diameter of the NWs after shell growth was determined to be 91 ± 5 nm and from this, a 19-nm-thick Al_xGa_{1-x}As layer was deduced. Finally, an outer GaAs shell was deposited around the NWs to act as a cap layer to prevent oxidation of Al_xGa_{1-x}As. The total diameter of the core-shell-cap NWs was measured to be 108 ± 10 nm (Figure 1(c)).

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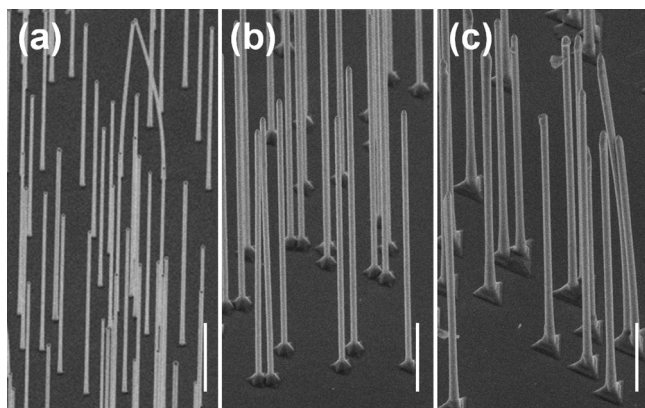


FIG. 1. FESEM images of (a) bare GaAs NWs, (b) GaAs/Al_xGa_{1-x}As core-shell NWs, and (c) GaAs/Al_xGa_{1-x}As/GaAs ($x_v=0.5$) core-shell-cap NWs. Scale bars are 1 μm .

Single NW PL measurements were carried out at room temperature in air. A 522 nm solid state pulsed laser was used, providing 0.5–2.0 μW (<0.1 pJ/pulse) within a 1.5 μm diameter focal spot through a 100 \times objective lens. The excitation power was reduced until all band gap renormalization and band filling effects were eliminated.¹⁷ The emitted PL was detected using a monochromator and a cooled CCD (for spectral information) or a single photon avalanche photodiode and a time-correlated single photon counting system (for lifetime data) with an instrument response of ~ 50 ps at full-width-at-half-maximum. Ten NWs were chosen for both PL and time-resolved PL measurements. A typical PL spectrum of a single NW is shown in Figure 2(a). An emission peak at 1.425 eV is observed, corresponding to zinc-blende GaAs band edge emission at room temperature.¹⁸ All the measured NWs showed very strong PL emission, while no PL signal could be detected for bare GaAs NWs, indicating the efficient reduction of non-radiative recombination at the GaAs/Al_xGa_{1-x}As interface of the NWs.

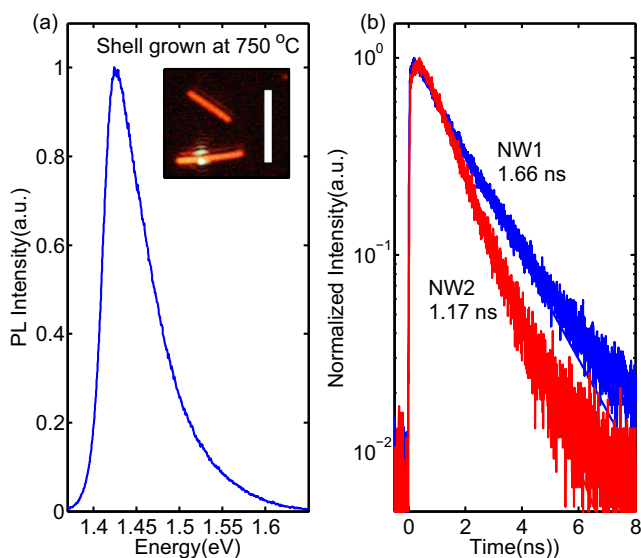


FIG. 2. (a) Typical room temperature PL spectrum from single GaAs/Al_xGa_{1-x}As ($x_v=0.5$) NWs showing a peak emission at 1.425 eV. The inset shows an optical microscope image of the excited NW. The scale bar is 6 μm . (b) Low power time-resolved PL at the peak emission energy of 1.425 eV from two single GaAs/Al_xGa_{1-x}As ($x_v=0.5$) NWs. Mono-exponential fits are shown for each decay, with τ_{mc} as shown.

Time-resolved PL from single NWs was measured at the peak emission energy of (1.425 ± 0.002) eV. As room temperature emission is measured, it is expected that the PL lifetime is equivalent to the τ_{mc} .¹³ Figure 2(b) displays two typical time-resolved PL decays with mono-exponential fits. The average carrier lifetime is 1.02 ns with a wire-to-wire standard deviation of 0.43 ns. The longest observed τ_{mc} is 1.66 ns for NW1 (Figure 2(b)). The lifetime obtained here is almost two orders of magnitude longer than the lifetime of NWs grown with the same core growth parameters reported using transient terahertz photoconductivity measurements,¹¹ and comparable to that observed for self-assisted NWs grown by MBE.^{9,10}

The temperature dependence (10 K–300 K) of the PL lifetimes of the NWs with Al_xGa_{1-x}As ($x_v=0.5$) grown at 750 °C from 10 K to 300 K is shown in Figure 3. The PL lifetimes are distributed in the vicinity of 1 ns without obvious variation with temperature. While at low temperature, the recombination can be considered to be dominated by the radiative decay of excitons,¹³ the purely radiative lifetime is known to increase with $T^{3/2}$ as the excitons split into free electron-hole pairs above ~ 50 K.^{13,19} Since this trend cannot be observed in Figure 3, an additional non-radiative recombination path must be present and dominates at higher temperature. The microscopic nature of this non-radiative recombination pathway cannot easily be determined. Nevertheless, inferences can be drawn from a comparison of these NWs with similar GaAs/Al_xGa_{1-x}As NWs which were grown under different conditions.

Both the NWs in this study and those in Ref. 11 were grown with the GaAs core using the same two-temperature procedure. The differences between them are the growth temperature (750 °C and 650 °C, respectively) and nominal Al vapor mole fraction ($x_v=0.5$ and 0.26, respectively) in the Al_xGa_{1-x}As shell.¹¹ Considering the near intrinsic exciton lifetimes of GaAs/Al_xGa_{1-x}As ($x_v=0.26$) NWs at low temperature,¹⁵ the poor τ_{mc} at room temperature is unexpected and may be explained by an insufficient barrier height

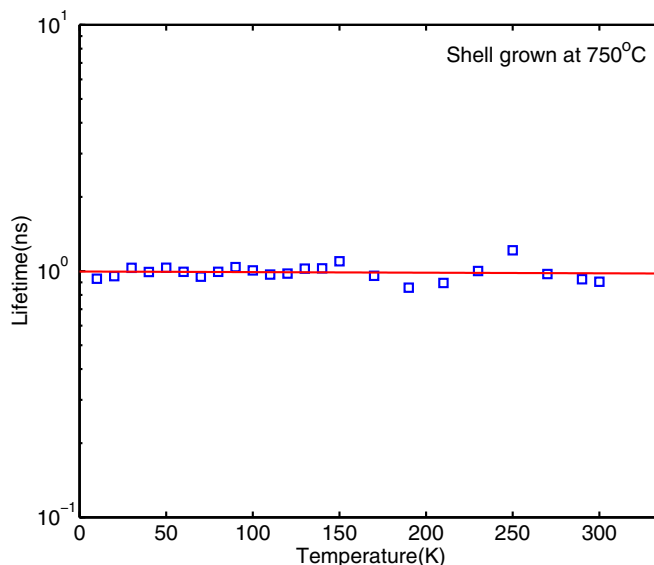


FIG. 3. Temperature dependence of the carrier lifetimes of GaAs/Al_xGa_{1-x}As ($x_v=0.5$) NWs. Lifetimes are scattered around 1 ns and do not show obvious temperature dependency.

in the shell. X-ray diffraction measurements (not shown) were carried out on the NWs with the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x_v = 0.5$) shell grown at 750°C , revealing only about 20% Al in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell (i.e., $x = 0.2$). This could be due to the different sticking coefficients and surface diffusion lengths of Ga and Al species on (110) facets.²⁰ In addition, compositional non-uniformity of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers in non-planar epitaxial growth has also been reported.^{20–22} Thus, it is possible that lower Al concentration within the GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x_v = 0.26$) NWs grown at 650°C combined with local variations may have given rise to regions of insufficient confinement such that some carriers might have diffused from the GaAs core through the shell to the free NW surface. This would explain the relatively short τ_{mc} in Ref. 11 at room temperature. Measurements were also carried out for NWs with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell grown at the same temperature (650°C) but with $x_v = 0.5$ (not shown). Indeed, these results show that the τ_{mc} are increased 7-fold to 200 ps, indicating better confinement within the GaAs core. However, this is still significantly shorter than that observed in Figure 2, with an $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x_v = 0.5$) shell grown at 750°C . Therefore, enhanced confinement cannot be the only factor for the observed improvement in τ_{mc} .

In order to show that the shell growth temperature itself plays a central role in determining τ_{mc} , similar PL measurements were carried out on NWs with identical core-shell structures ($x_v = 0.5$) but a slightly lower shell growth temperature of 700°C . The results are shown in Figure 4. The emission spectra display a shape similar to that in Figure 2(a) for identical excitation power, but the PL peak intensity is much lower than that of the NWs with shell grown at 750°C . Time-resolved PL measurements were taken for a few NWs at 1.425 eV and typical decays of two single NWs are displayed in Figure 4(b). All the NWs exhibited shorter lifetimes with 360 ps being the longest observed. Thus, the increase of shell growth temperature from 700°C to 750°C leads to a 4-fold increase in τ_{mc} . A similarly strong effect of

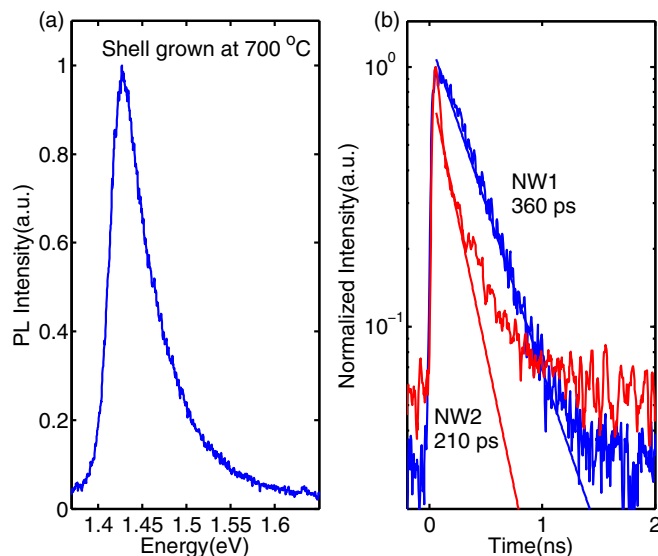


FIG. 4. Typical room temperature (a) single NW PL spectrum and (b) time-resolved PL from two single GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ NWs with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x_v = 0.5$) shell grown at 700°C . Mono-exponential fits are shown for each decay, with τ_{mc} as shown.

growth temperature on τ_{mc} has been reported for planar GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ double heterostructures.^{13,23} This result clearly shows the positive correlation between increased shell growth temperature and τ_{mc} of the NWs.

A careful comparison with planar GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ double heterostructures can assist in the identification of the dominant non-radiative recombination path. To this end, it is very instructive to consider the surface recombination velocity, S , which can be thought of as a measure of surface/interface quality independent of the sample surface-to-volume ratio. By attributing all the non-radiative losses to surface/interface recombination in our NWs, an upper limit to the surface recombination velocity (S_{max}) can be calculated by $1/\tau = 4S_{max}/d$,⁹ resulting in $S_{max} = 1300\text{ cm/s}$, where τ is the measured lifetime and d is the NW core diameter. To put this into perspective, established values for S range from around 1000 cm/s for decent GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heterointerfaces grown by MOCVD at 750°C ,^{13,24} to 5500 cm/s as well as 34 000 cm/s for NaS_2 -passivated and bare GaAs surfaces, respectively.⁶ Thus, the GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ core-shell heterointerface in our nanowires grown at 750°C can be considered to be almost as good as in comparable planar double heterostructures and additional non-radiative recombination centres need not necessarily be significant.

Recently, Breuer *et al.* questioned the suitability of GaAs NWs grown using Au for high efficiency optoelectronic applications because they found considerably shorter τ_{mc} in GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ core-shell NWs for Au-assisted (5 ps) compared to self-assisted NWs (2.5 ns) using MBE growth.⁹ By comparing the τ_{mc} of Au-assisted GaAs core-shell NWs with the self-assisted GaAs NWs, they suggested an attribution of the drastic difference of τ_{mc} to Au related deep traps.⁹ Although Au atoms have been observed in Au-assisted GaAs NWs grown by MBE recently,²⁵ it is still not confirmed whether Au atoms are incorporated into NWs under our MOCVD growth conditions. At any rate, despite the possibility of Au incorporation during GaAs NW core growth, the NWs with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell grown at 750°C presented in this study exhibit carrier lifetimes that are very comparable with that of the self-assisted NWs of Ref. 9. The long carrier lifetimes of our NWs indicate that: either (1) no Au incorporation occurred during the low temperature (375°C) growth of the GaAs NW core or (2) any traces of incorporated Au atoms are not acting as non-radiative centers.

In summary, high quality GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ NWs have been grown with Au seeding particles by MOCVD. Their minority carrier lifetimes at room temperature of $1.02 \pm 0.43\text{ ns}$ are almost two orders of magnitude longer than that of similar Au-catalyzed NWs reported earlier and comparable with those achieved by self-assisted growth. A minimum Al vapor mole fraction appears to be critical to obtain sufficient confinement of carriers in the core at room temperature. Moreover, a high $\text{Al}_x\text{Ga}_{1-x}\text{As}$ shell growth temperature has been demonstrated to lead to a significant increase of the minority carrier lifetimes, which we suggest is mainly the result of an improvement of the GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ interface quality. These results show that it is possible to grow high quality NWs with excellent minority carrier lifetimes by MOCVD using Au particle seeds, which are essential for efficient NW devices.

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