Photoluminescence Evolution in GaAs/AlGaAs Core/Shell Nanowires Grown by MOCVD: Effects of Core Growth Temperature and Substrate Orientation

Yi-Hsin Chiu^a, Nicholas G. Minutillo^a, Robert E. A. Williams^b, Greg J. Smith^a, David W. McComb^b, John A. Carlin^c, Ezekiel Johnston-Halperin^{a,*}, Fengyuan Yang^{a,*}

^aDepartment of Physics, The Ohio State University, Columbus, Ohio 43210-1117, USA

^bCenter for Electron Microscopy and Analysis, The Ohio State University, Columbus, Ohio 43212-1157, USA

^cInstitute for Materials Research, The Ohio State University, Columbus, Ohio 43210-1117, USA
43210-1117, USA

*Corresponding authors: Ezekiel Johnston-Halperin: Email: ejh@physics.osu.edu Address: 191 West Woodruff Ave, Columbus, Ohio 43210-117, USA. Fengyuan Yang: Email: fyyang@physics.osu.edu Address: 191 West Woodruff Ave, Columbus, Ohio 43210-117, USA

Abstract

We explore the growth temperature dependence of GaAs/AlGaAs core/shell nanowires (NW) grown by metal-organic chemical-vapor deposition (MOCVD) on (100) and (111)B GaAs substrates. *In-situ* calibration of the growth temperature allows for a systematic variation with unprecedented resolution. Characterization by photoluminescence (PL) indicates that, at low growth temperatures, nanowires grown on (111)B substrates incorporate higher density of defects than wires on (100). On either substrate, nanowire core growth temperatures above 450°C result in rising defect luminescence in the PL spectra concomitant with the increased epitaxial growth on the nanowire sidewalls at these higher temperatures. This work presents a systematic study of nanowire growth conditions that reveals the correlation between the growth temperature of the GaAs core, the chosen substrate surface orientation, and the resulting optical properties of GaAs/AlGaAs nanowires.

Keywords

B2. Semiconducting gallium arsenide; A3. Metalorganic chemical vapor deposition; A1. Photoluminescence; A1. Defects

1. Introduction

Metal-organic chemical-vapor deposition (MOCVD) is a proven technique for semiconductor nanowire growth via the vapor-liquid-solid (VLS) mechanism [1–8] which has been used to grow III-V nanowire heterostructures for electronic [9] and optoelectronic applications [10]. As with all semiconductor nanostructures, fabrication of high quality materials is the first step toward realizing the full potential of these structures. In particular, for III-V nanowires with high surface-to-volume ratio, minimizing surface defect states is essential [11]. Furthermore, understanding of the VLS mechanism itself has advanced since it first emerged [3,4,6,12–14]. Here we report the study of Photoluminescence (PL) spectra of Au-catalyzed GaAs/AlGaAs core/shell nanowires grown on both GaAs (100) and (111)B substrates at varying growth temperatures. Growth temperatures are calibrated *in-situ* to avoid possible drift in the chamber condition, allowing for a systematic, high resolution, variation of the growth temperature. The optical quality is quantified by measuring the PL intensity ratio between band-edge and defect-mediated photoluminescence. It is found that defect incorporation as a function of the growth temperature is dependent on the substrate orientation, despite the fact that the direction of the nanowire growth is the same for both substrates (along $\langle 111 \rangle$). Finally, a window in core growth temperature where defects that degrade optical quality may be minimized is identified.

2. Experimental Methods

To prepare substrates for growth, GaAs (100) and (111)B wafers are cut into pieces and placed in an ultraviolet (UV) ozone cleaner to remove any organics absorbed on the surface. This also produces a hydrophilic surface desired for subsequent dispersion of Au nanoparticles. The surfaces are then functionalized with 0.1% Poly-L-Lysine solution (Ted Pella Inc.), rinsed with

deionized water (resistivity $> 18 \text{ M}\Omega$), and dried with N_2 . Next, tannic acid capped 40-nm Au colloid suspension (Ted Pella Inc., 7.72×10^{10} particles/mL) is dropped on the surface and allowed to sit for 15 minutes. Excess suspension is removed by blowing the surface dry with a N_2 gun. The substrates with Au nanoparticles are then placed in an Aixtron 3 $\times$ 2" Close Coupled Showerhead (CCS) MOCVD reactor for nanowire growth.

As reported in the literature [1–6,15–17], III-V nanowire growth requires a balance between the pyrolysis of the organometallic precursors, the solubility of the group III and group V atoms in the Au colloid, and the diffusion of atomic species on the substrate and nanowire surface. As a result, particular care for accurate and reproducible measurements of the substrate temperature during growth is essential. Although pyrometers have been widely used for in-situ measurement of the actual substrate temperature, it is challenging to use pyrometers to monitor GaAs nanowire growth because the typical temperature window for VLS growth of GaAs nanowires is below the range of pyrometers available for MOCVD systems. In our MOCVD reactor, the surface temperature is directly observed in real time with an emissivity-corrected pyrometer that has a lower temperature limit of 480°C while the temperature range for nanowire growth spans from 400°C to 470°C (indicated by the hatched region in Fig. 1). This limitation requires a calibration of the actual substrate temperature above 480°C based on a linear relationship between the pyrometer and thermocouple (TC) readings and a linear extrapolation to lower temperatures. The overall linearity of the temperature response of the system is confirmed by using a pyrometer to measure the temperature of the bare susceptor (triangles in Fig. 1). The estimated error for a given surface temperature generated by this extrapolation is around $\pm 1^\circ\text{C}$. Substrate temperatures of nominally identical growth conditions are reproducible to within $\pm 3^\circ\text{C}$.

Fig. 1. Temperature readings of the thermocouple (TC) in the MOCVD susceptor calibrated by a pyrometer on a bare susceptor (triangles) and a susceptor loaded with GaAs wafers before nanowire growth (squares). The pyrometer has a minimum operational temperature of $T_{min} = 480^{\circ}\text{C}$. The hatched box represents the nanowire growth temperatures (below T_{min}). The actual surface temperatures of GaAs wafers for NW growth are obtained from linear extrapolation.

To desorb surface oxides before nanowire growth, the prepared substrates are baked at 590°C (all temperatures given are actual substrate temperatures) for 15 minutes under an arsine flow of $1040 \mu\text{mol}/\text{min}$ at a pressure of 150 mbar that is maintained for the entire growth. The temperature is then lowered to 500°C and stabilized to monitor the system temperature and extrapolate a growth temperature as shown in Fig. 1. Next, the temperature is lowered to the growth temperature between 410 and 472°C and allowed to stabilize. The arsine flow is adjusted to $223.2 \mu\text{mol}/\text{minute}$ and a trimethylgallium (TMGa) flow of $8.6 \mu\text{mol}/\text{minute}$ is introduced into the reactor to begin the GaAs core nanowire growth. After 15 minutes of nanowire growth, the substrate is heated to 650°C under arsine and a shell of $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ is deposited on the core

GaAs nanowires for 3 minutes. For the shell deposition, the TMGa and AsH₃ flows are adjusted to 26 $\mu\text{mol/minute}$ and 1786 $\mu\text{mol/minute}$ respectively, with an additional flow of trimethylaluminum (TMAI) at 10.3 $\mu\text{mol/minute}$. These AlGaAs shell growth conditions are identical across the entire sample set. The quoted Al composition is nominal and is based on the characterization of previous thin film growths using the same reactor conditions. The role of the Al_{0.35}Ga_{0.65}As shell is to passivate the surface of the GaAs core, protecting it from the formation of surface defect states [8,11]. While there may be a deviation from the targeted 35% Al, the Al composition should be consistent for all samples.

PL spectra are excited with a Nd:YVO₄ continuous-wave laser with wavelength $\lambda = 532$ nm, power of 8.1 mW, and spot size of 100 μm . They are measured at 5 K using a 0.3 m spectrometer with a LN₂-cooled back illuminated CCD detector. In order to avoid parasitic luminescence from the GaAs substrate, the nanowires are transferred onto a silicon wafer by gently rubbing the sample across the surface. Measurement of multiple nanowire ensembles provides insight into the collective spectral quality of the $\sim 10^8$ wires grown per substrate per core growth temperature. To avoid oxidation of the AlGaAs shell, all spectra were collected within 24 hours of growth and samples were stored in a nitrogen environment between growth and measurement. Our PL measurements indicate that aging does not impact the PL within one month of growth under our storage conditions.

Scanning Electronic Microscopy (SEM) imaging was performed using an FEI Helios Nanolab 600 SEM. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive x-ray spectroscopy (EDS) maps were acquired using an FEI Image-Corrected TitanTM 60-800 scanning transmission electron microscope (STEM) equipped with Super EDXTM as well as an FEI Probe-Corrected TitanTM 80-300.

Nanowire growth rate was estimated by measuring 30 or more nanowires from each SEM image to obtain an average length. We note that the reported growth rates were deduced from the wire length and are without the correction for nucleation time, which can be different for wires grown on different substrates.

3. Results and Discussion

Fig. 2(a) shows a HAADF-STEM image of a few GaAs/AlGaAs nanowires, where the bright dots at the tapered end of nanowires are Au catalysts. A closer look at the region just under the Au catalysts [Fig. 2(b)] reveals a high density of stacking-fault type defects near the tip. EDS mapping of the GaAs/Al_{0.35}Ga_{0.65}As nanowires in Figs. 2(c) – 2(f) shows the following: 1) As is uniformly distributed in the whole core/shell nanowires; 2) Ga has a higher concentration in the core region starting at ~100 nm below the Au; 3) Al is concentrated in the ~100-nm section below the Au and in the thin 15-nm shell, as expected; 4) Au is only found at the end of the nanowires. First, the EDS mapping confirms the designed composition distribution of the core/shell structure. Second, it demonstrates that during the epitaxial growth of the 15 nm AlGaAs shell on the side wall of the core GaAs nanowires, AlGaAs also grows through the Au, yielding high stacking fault density and the tapered shape near the Au particle. Fig. 2(g) shows a probe corrected HAADF-STEM image projected down a $\{1\bar{1}0\}$ plane of a GaAs nanowire inside a thin AlGaAs shell where the GaAs dimer structure is clearly resolved. The nanowire exhibits zinc-blende crystal structure with a clear stacking fault. The inset to Fig. 2(g) highlights the zinc-blend ABCABC stacking sequence at both sides of the stacking fault, while the two sides are mirror image of each other about the fault line.

Fig. 2. (a) Image corrected HAADF-STEM image of four GaAs/AlGaAs core/shell nanowires. (b) zoom-in view near the Au catalysts, and the corresponding EDS maps of (c) As, (d) Ga, (e) Al, and (f) Au highlighting the distribution of each element. (g) Probe corrected HAADF-STEM image of the core GaAs nanowire shows the zinc-blende crystal structure with the ABCABC sequence of atomic planes along the nanowire axial axis $\langle 111 \rangle$, where the plane sequence forms a mirror image about a stacking fault (green dashed line).

Photoluminescence is an effective way to characterize the optical quality of semiconductor nanowires grown at various temperatures. Fig. 3 shows the PL spectra of GaAs(40 nm)/AlGaAs(15 nm) core-shell nanowires grown on GaAs (100) and (111)B substrates with the growth temperature of GaAs core wires varied between 410°C and 472°C. While a sharp band edge emission centered at 819 nm⁸ is observed at growth temperatures between

410°C and 430°C for wires grown on (100) substrates, 430°C is the optimal temperature for band edge emission for wires on the (111)B substrate. This dominance of band edge emission in PL is an indication of high optical quality and low defect density, i.e., the dominant recombination mechanism is band edge luminescence rather than defect mediated or non-radiative recombination. As the growth temperature deviates from that of optimal band edge luminescence, wires on both substrates show a red shift in the spectral weight from the band edge emission at 819 nm. A broad peak centered at 830 nm is commonly associated with carbon impurities in GaAs thin films and nanowires grown by MOCVD [5,7,18]. Such a peak is found here in nanowires grown at higher temperatures.

Fig. 3. PL spectra measured at 5 K for 40-nm GaAs NWs with a 15-nm AlGaAs shell at NW growth temperature of (a) (b) 410°C, (c) (d) 422°C, (e) (f) 430°C, (g) (h) 454°C, and (i) (j) 472°C on GaAs (100) (left column) and (111)B (right column) substrates. While a sharp band edge emission centered at 819 nm is observed at growth temperatures between 410°C and 430°C for wires grown on (100) substrates, 430°C is the optimal temperature for band edge emission for wires on the (111)B substrate.

The observation of enhanced defect luminescence at the high temperature end of our growth window (450 °C – 472 °C) is likely a result of an increase in sidewall growth with increasing growth temperature. When the growth temperature increases, a shift from VLS to a thin film growth mode induces sidewall growth, leading to a decrease in the axial nanowire growth rate [1,7,20]. Furthermore, in a related case where the growth rate is controlled by V/III ratio rather than growth temperature, Joyce *et al*⁶ showed that higher sidewall growth rates of GaAs/AlGaAs NWs are correlated with higher defect incorporation. Figs. 4(a) and 4(b) show the axial growth rates of the GaAs/AlGaAs nanowires. The overall trend in growth temperature is in general agreement with those reported in the literature [1,19]. The temperature regime where increased sidewall growth reduces the axial growth rate agrees well with that of the enhanced defect luminescence, both occurring at the regime of 450 – 472°C, suggesting the the sidewall growth as a potential origin of defect luminescence. We note that the temperatures of maximum growth rate, 440°C to 450°C for both substrates, are 10°C to 20°C lower than those reported by both Borgström *et al.* and Fortuna *et al* [1,19]. This difference may be due to an offset among different pyrometry systems.

Fig. 4. Growth rate as a function of the substrate temperature for nanowires grown on (a) GaAs (100) (left column) and (b) GaAs (111)B (right column) substrates. The error bars are one standard deviation from 30 or more nanowires. (c) (d) Ratio of integrated intensities of the 819 nm band edge peak ($I_{819\text{nm}}$) to the 830 nm defect peak ($I_{830\text{nm}}$) with a bandwidth of 4 nm. (e) (f) Normalized PL intensity of both the band edge (solid diamonds) and the 830-nm defect peaks (open circles) as a function of the growth temperature.

The PL intensity ratio, $I_{819\text{nm}}/I_{830\text{nm}}$, is calculated by integrating the photoluminescence at 819 nm and 830 nm with a bandwidth of 4 nm (grey areas in Fig. 3), as shown in Figs. 4 (c) and 4 (d). Since PL is measured on transferred nanowires to eliminate the substrate signal, the

nanowire density varies and relative intensities cannot be immediately compared. This relative strength of the 819 nm band edge peak compared to the 830 nm defect peak provides a density independent measure of nanowire optical quality. On both substrates, the peak ratios exhibit sensitive dependence on the growth temperature. In the high temperature regime, decreasing the growth temperature decreases the defect peak around 830 nm hence increasing the peak ratio on both substrates. This observation is consistent with the prior discussion and are attributed to the dominance of the VLS growth mode over sidewall growth, leading to reduced defect states in GaAs. In contrast, the peak ratios at temperatures below the maximum growth rate exhibit opposite trends on the different substrates. The 830 nm intensity in this region can still be understood as a benchmark for defect intensity, but does not necessarily correspond to the same defects found in the high growth temperature case.

To further understand these different trends at lower growth temperatures, an estimate of the average sample density was made and used as an approximate weighting factor for comparison across transferred samples. The resulting normalized PL is shown in Figs. 4(e) and (f). Fig. 4(e) shows the band edge PL for the (100) grown wires improves with decreasing growth temperature from 450°C to ultimately level off in the 410 – 430°C range. The intensity of the defect peak largely remains constant from 450°C down to 410°C. Hence, those wires grown between 410°C and 420°C exhibit the most band edge dominant PL spectra [Fig. 4(c)]. Fig. 4(f) shows the band edge intensity of the (111)B grown wires also grows with decreasing growth temperature from 450°C. In this case, however, the defect intensity becomes stronger from 440°C down to 410°C. As a result, the PL spectra of wires grown at 430°C are the most band edge dominant while those grown at lower temperatures show increasing defect emission [Fig. 4(d)]. For further comparison, the (100) wires at 410°C as well as the (111)B wires at

430°C both have a full-width-at-half-maximum (FWHM) of $\lambda_{\text{FWHM}} \approx 7$ nm corresponding to FWHM of energy, $E_{\text{FWHM}} \approx 13$ meV.

These results identify a substrate-dependent window in the core growth temperature where defects that degrade optical quality may be minimized. In particular, the sensitive dependence of optical characteristics on the growth temperature indicates the importance of optimizing growth temperature in order to prepare high quality GaAs/AlGaAs NWs, as a difference of 10 °C could have considerable impact. Additionally, the substrate dependence originating from defect incorporation suggests that the growth dynamics are not independent of the starting substrate. Although the nanowires grow in the $\langle 111 \rangle$ direction on both substrates, the starting substrate and NW geometry play a critical role on the precursor diffusion and subsequent defect density. These results provide insights and directions for future studies on VLS growth dynamics of III-V NWs.

4. Conclusion

We have studied the effect of growth temperature on the optical characteristics of GaAs/AlGaAs core/shell nanowires grown on (100) and (111)B GaAs surfaces. PL analysis reveals increased defect density in growth temperatures of 450 °C - 470 °C, where the GaAs sidewall growth on the core begins to increase. Below this, defect incorporation differs depending on the orientation of the GaAs substrate. At lower growth temperatures, wires grown on a (111)B GaAs substrate exhibit stronger defect emission in their PL spectra than do those grown on a (100) substrate. This work presents a systematic study that reveals the correlation between the growth temperature of the GaAs core, the chosen substrate surface orientation, and the resulting optical properties of GaAs/AlGaAs NWs. A substrate-dependent window in the core growth temperature can be identified that minimizes defects that degrade optical quality.

Future studies of microscopically-resolved PL will allow direct comparison of individual nanowire PL intensities as a function of growth conditions. In conjunction with STEM, imaging of a single nanowire will facilitate highly spatially resolved PL data that would yield correlations between specific crystallographic defects and a particular spectral feature.

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