Growth, Structural and Optical Properties of High Quality GaAs Nanowires for Optoelectronics

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Abstract-We investigate how growth parameters may be chosen to obtain high quality GaAs nanowires suitable for optoelectronic device applications. Growth temperature and precursor flows have a significant effect on the morphology, crystallographic quality, intrinsic doping and optical properties of the resulting nanowires. Significantly, we find that low growth temperature and high arsine flow rate improve nanowire optical properties, reduce carbon impurity incorporation and drastically reduce planar crystallographic defects. Additionally, cladding the GaAs nanowire cores in an AlGaAs shell enhances emission efficiency. These high quality nanowires should create new opportunities for optoelectronic devices.

Keywords-nanowire; GaAs; MOCVD; photoluminescence.

I. INTRODUCTION

Semiconductor nanowires have attracted considerable research attention as nanocomponents of future electronic and optoelectronic devices [1, 2]. In the past decade, nanowire based devices ranging from photodetectors to biochemical sensors have been demonstrated [3, 4]. GaAs nanowires are particularly promising candidates for future optoelectronic devices, owing to the direct band gap and high carrier mobility of the GaAs material system [5, 6]. Metalorganic chemical vapour deposition (MOCVD), using Au nanoparticles as catalysts, is a potentially scalable, flexible and well-controlled means of growing epitaxial GaAs nanowires. In this process, GaAs deposition takes place preferentially at the Au nanoparticle–GaAs interface. Highly anisotropic growth takes place with a nanoparticle at the growing tip of each nanowire.

Electronic and optoelectonic device applications demand straight, uniformly aligned nanowires with uniform diameters and excellent crystallographic, electronic and optical properties. Currently, the usefulness of GaAs nanowires in these devices is limited by certain defects: crystallographic twin defects [7], nanowire kinking [8], intrinsic doping and surface states [9]. We find that by tailoring growth parameters such as temperature and precursor flow, these issues can be overcome to produce defect free nanowires suitable for device applications [8].

II. EXPERIMENTS

Nanowires were grown on semi-insulating GaAs(111)B substrates. These substrates were first functionalised with poly-L-lysine solution and then treated with Au colloid solution containing Au nanoparticles. We tested a range of Au colloid diameters ranging from 2 nm to 50 nm. Nanowires, catalysed by these nanoparticles, were grown by low pressure horizontal flow MOCVD using trimethylgallium (TMG) and arsine (AsH$_3$) precursors at temperatures between 330 ºC and 500 ºC. Growth times were between 1 and 60 minutes.

Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and photoluminescence (PL) were employed to study the structural, crystallographic and optical properties of these nanowires. For GaAs/AlGaAs core-shell nanowires, GaAs nanowire cores were grown as described above, then AlGaAs shell growth was performed for 20 minutes at 650 ºC using trimethylaluminium, TMG and AsH$_3$.

III. RESULTS AND DISCUSSION

A. Influence of surface states

GaAs is highly sensitive to surface states. These act as non-radiative recombination centres which can limit the performance of GaAs-based optoelectronic devices. With their high surface to volume ratio, GaAs nanowires are particularly sensitive to these surface states.

The first step towards improving the optical properties of GaAs nanowires was passivation of the nanowire core, by coating the core with an AlGaAs shell. Figure 1a illustrates a schematic of the structure. Figures 1b and c illustrate bare GaAs core nanowires, and GaAs/AlGaAs core/shell nanowires, respectively. The emission efficiency of AlGaAs clad

nanowires was over an order of magnitude higher than that of unclad nanowires [9]. A representative PL spectrum is shown in Figure 1d. All PL measurements presented in this paper were obtained from AlGaAs clad nanowires.
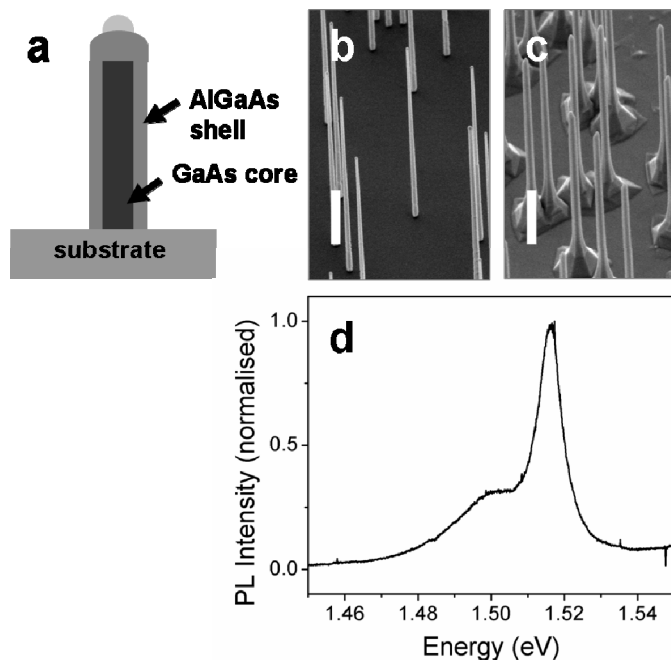

Figure 1. (a) Schematic of a GaAs/AlGaAs core-shell nanowire. FESEM images of (b) unclad GaAs core nanowires and (c) GaAs/AlGaAs core-shell nanowires. Samples are tilted at 40º. Scale bars are 1 μm. (d) 18 ºK PL spectrum from an ensemble of GaAs/AlGaAs core-shell nanowires.

The spectrum of Figure 1d features a peak at approximately 1.517 eV attributed to the recombination of excitons in the GaAs core. The broad low energy peak between 1.49 and 1.50 eV is attributed to neutral donor to carbon acceptor (D_0, C_{As}) recombination. The intensity of this peak, relative to the exciton peak, is a measure of the carbon impurity content of these nanowires [10, 11].

B. Influence of growth temperature

High growth temperatures (> 400 ºC) tend to increase the degree of nanowire tapering and the degree of carbon impurity incorporation [12]. At lower growth temperatures (< 400 ºC), however, nanowires tend to kink during growth and have irregular growth orientations. We developed a two-temperature procedure consisting of a brief high temperature nucleation step (~450 ºC), followed by prolonged growth at a low temperature (~390 ºC) [8]. We obtain minimally tapered, straight nanowires (Figure 2a). These nanowires are free of twin defects (Figure 2b), exhibit minimal carbon impurity incorporation and exhibit strong photoluminescence (Figure 2c) with a long exciton lifetime approaching 1 ns.
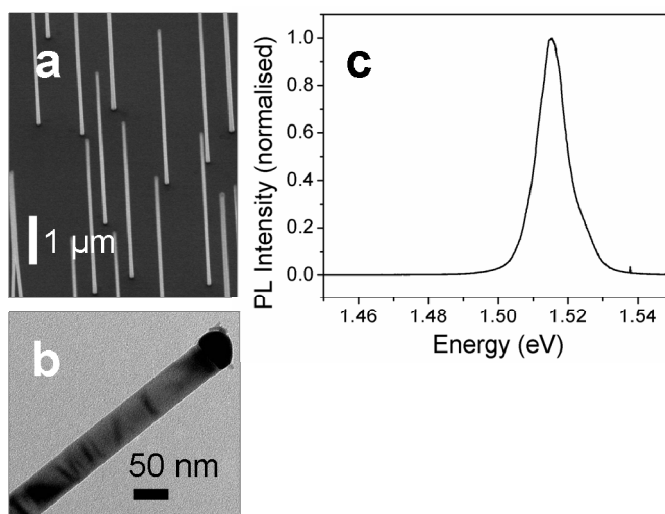

Figure 2. (a) FESEM image (b) TEM image and (c) 18 K PL spectrum of twin-free nanowires grown via the two-temperature procedure.

C. Influence of arsine flow

Study of arsine flow is equivalent to study of V/III ratio, that is, the ratio of group V to group III precursor flows. This key growth parameter has a profound influence on nanowire properties. FESEM images of nanowires grown with various V/III ratios are illustrated in Figure 3. TEM and PL studies (Figure 4) revealed that a high V/III ratio reduces crystallographic twin defects and minimizes carbon impurity incorporation, resulting in nanowires with excellent optical properties. The exciton linewidth is approximately 5 meV (Figure 4b).
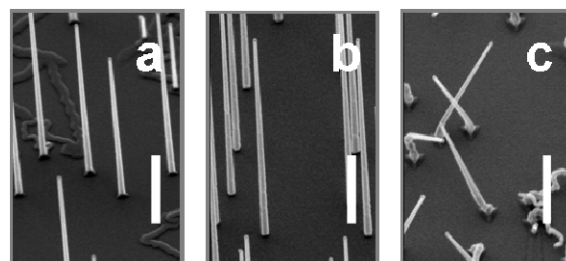

Figure 3. FESEM images of nanowires grown with V/III ratio of (a) 12 (b) 46 and (c) 190. Scale bars are 1 μm.

At the highest V/III ratios, however, nanowires tend to kink to non-[111]B orientations, as in Figure 3c. If straight, vertically oriented nanowires are desired, this places an upper limit on the useful V/III ratio. The upper limit depends on the diameter of the Au nanoparticle, and is lower for smaller diameters.
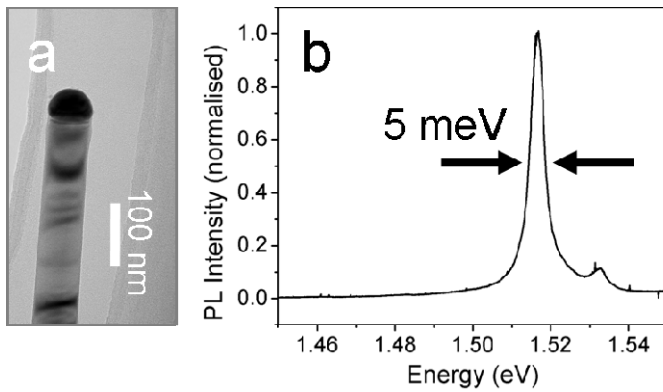
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Figure 4. (a) TEM image of nanowire grown with high V/III ratio of 93. (b) 18 K PL spectrum of nanowires grown with high V./III ratio of 93.

Figure 5. SEM images of nanowires grown with a V/III ratio of 46 and group III flows of (a) 2.9×10^{-6} mol/min ,(b) 1.2×10^{-5} mol/min and (c) 4.6×10^{-5} mol/min grown for (a) 60 min, (b) 15 min and (c) 3 min 45 s. Scale bars are 1 μm.

D. Influence of growth rate

Increasing the flow rates of group III precursors (whilst keeping V/III ratio constant) increases the axial nanowire growth rate. Figure 5 illustrates nanowires grown with increasing group III flow rate and growth time scaled inversely with group III flow rate. Because the axial growth rate increases with increasing precursor flow, shorter growth times may be used to achieve nanowires of a given length.

Increasing group III precursor flows has a significant effect on nanowire tapering. We define nanowire tapering as the increase in nanowire radius (r) per unit of nanowire length (L), which is equivalent to the radial growth rate divided by the axial growth rate:

$$\text{Tapering parameter} = \frac{\Delta r}{\Delta L} = \frac{dr/dt}{dL/dt}$$

Figure 5c illustrates minimally tapered nanowires which were achieved with high group III precursor flows. We believe the decrease in tapering, observed with increasing precursor flow, is because of the differences between axial and radial growth mechanisms. Axial growth is mass-transport limited, that is, limited by the arrival of reaction species. Radial growth, which is responsible for tapered nanowire morphologies, is kinetically limited. As a result, increasing the group III and V precursor flow rates causes a significant increase in axial growth rate, but only a minor increase in radial growth rate. This differential between axial and radial growth means that minimally tapered nanowires can be achieved by increasing precursor flow, and accordingly using a shorter growth time to achieve a given nanowire length.

Furthermore, in conventional planar growth, a rapid growth rate is associated with material of lower electrical and optical quality. In marked contrast, for GaAs nanowires, we find that increasing growth rate reduces crystallographic twin defects and reduces carbon impurity incorporation. The reasons behind this anomaly are currently under investigation.
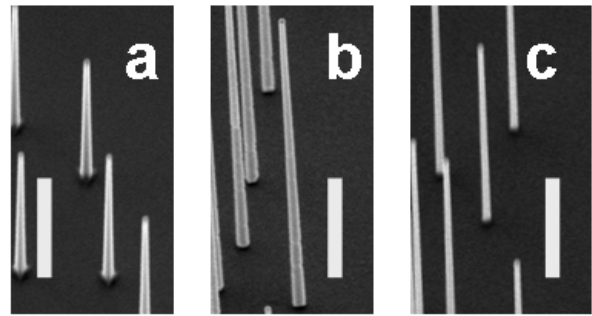
IV. CONCLUSION

The structural, crystallographic and optical properties of GaAs nanowires may be tailored by choosing appropriate growth parameters. High quality nanowires should create new opportunities for optoelectronic devices. In future, by adjusting growth parameters we aim to achieve high quality nanowires of diameters less than 10 nm. These should enter the quantum confined regime and permit novel devices utilising quantum confinement.

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