

Ternary Self-Catalyzed GaAsP Nanowire Grown by Molecular Beam Epitaxy

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Abstract. III-V nanowires demonstrate controlled dimensions, high aspect ratio, high carrier mobility and light trapping ability, making them promising blocks for next generation electronic and photonic devices. GaAsP nanowire has been widely investigated for light-emitting diodes, solar cells due to its tunable bandgap. However, it is a very immature field and significant growth development need to be made for optimising their properties and further for a range of applications. In this paper, self-catalyzed GaAsP nanowires were grown on Si substrate without introducing contamination from metallic nanoparticles. Surface passivation technology was applied on nanowires to boost their optical performance.

1. Introduction

III-V epitaxial grown semiconductor nanowires have attracted extensive research due to their excellent performances on light-emitting diodes [1, 2], high-efficiency solar cell [3, 4], ultralow threshold lasers [5, 6] and memory devices [7]. Although, binary nanowires have been widely studied [8], ternary nanowires have advantage with tunable bandgap by altering their element composition. With tunable bandgap, these nanowires are ideal candidates for highly efficient optoelectronic devices, which are pursued for more than decades [9, 10]. InGaAs, InGaN, AlGaAs and AlGaN have been focused for extensive studies [11]. However, only a few publications reported GaAsP nanowires [3, 4, 10, 12, 13]. Ternary GaAsP nanowires are critical for light emission and photovoltaic due to their structure-induced novel properties and engineered band gap that can cover from green to infrared. For example, GaAsP is an ideal candidate for photovoltaics due to their engineered bandgap ranging from green to near infrared at room temperature. It covers the wavelength ranging from green (548 nm) to near-infrared (864 nm) at room temperature. It was predicted that a tandem solar cell with two junctions, consisting of a 1.7 eV GaAsP nanowire and Si junction, has efficiency as high as 33.8% under 1-sun and 42.3% under 500-sun [14]. Recently, a single nanowire solar cell achieved world record efficiency of 10.2% by fabricating p-i-n core-shell GaAsP nanowires [4].

Growth methods of nanowires are typically based on top-down and bottom-up method [8]. Top-down method is a complex process while bottom-up vapor-liquid-solid (VLS) is a facile method to grow nanowires [8, 15]. However, shortcoming of nanowire grown by VLS hinder their applications. Metal catalysts in VLS process, which are considered as deep level trap state, degrade optical and electronic properties of nanowires [16]. To avoid contamination from metal nanoparticles, catalyst-free growth was proposed [17]. Selective area epitaxy method is proposed but it is ill-suited for



largescale fabrication and it involves time-consuming electron beam lithography [18]. Oxide assisted growth is an alternative to grow metal-free nanowires but it lacks size control [19]. Self-catalyzed growth of III-V nanowires avoids any foreign metallic nanoparticles—it utilizes a droplet of the native group-III liquid to facilitate nanowire growth. As a result, it avoids any contamination issues and thus has become the focus for nanowire based optoelectronic devices in recent years [10, 12, 20, 21]. Besides, nanowires integrated with mainstream Si platform offer a possibility to revolutionize present optoelectronic devices. The lattice mismatch curbs the bandgap combination for tandem solar cells and monolithic integration with Si platform for high efficiency III-V material on low cost Si substrate. In tandem solar cells structure, lattice-mismatch can be overcome by using nanowires because the nanowire diameter is too small to form dislocations.

In this work, we developed self-catalyzed grown GaAsP nanowires on Si substrate. Ga-assisted GaAsP nanowires were grown by molecular beam epitaxy (MBE) followed by optical characterization. After that, they were passivated by $(\text{NH}_4)_2\text{S}$ to enhance its optical properties. Our experimental results may pave the way to achieve high performance ternary nanowire devices integrated on Si substrates.

2. Experimental method

GaAsP nanowires were grown in Si (111) substrate using a solid Ga source and As_4 and P_2 cracker cells in a solid-sourced MBE. Before growth, the Si substrate were annealed at 600 °C for 1 hour. The nanowire growth started with the assistance of Ga droplets for 1 hour at 630 °C. The beam equivalent pressures of As_4 and P_2 molecular beams were $3.53\text{e-}6$ and $4.8\text{e-}6$ for, respectively. The structure of the GaAsP nanowire was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). TEM measurements were performed under liquid nitrogen and the nanowires were mechanically transferred on copper grid. During optical characterization, nanowires were mechanically transferred to Si substrates covered with a 250 nm SiO_2 . A 522 nm laser was used to pump the nanowires. $(\text{NH}_4)_2\text{S}$ was used to passivate GaAsP nanowires.

3. Results and discussion

3.1. Structural characterization

The structure of GaAsP nanowire is illustrated in figure 1(a). Figure 1(b) and (c) show the SEM image of GaAsP nanowires. The diameters of nanowires are ~30-60 nm while the length of nanowires are ranging from ~2-4 μm . On the whole Si water, different size distribution can be attributed to thermal gradient. No kinking is observed in SEM, indicating the interfacial energetics maintained well during the growth of GaAsP nanowire.

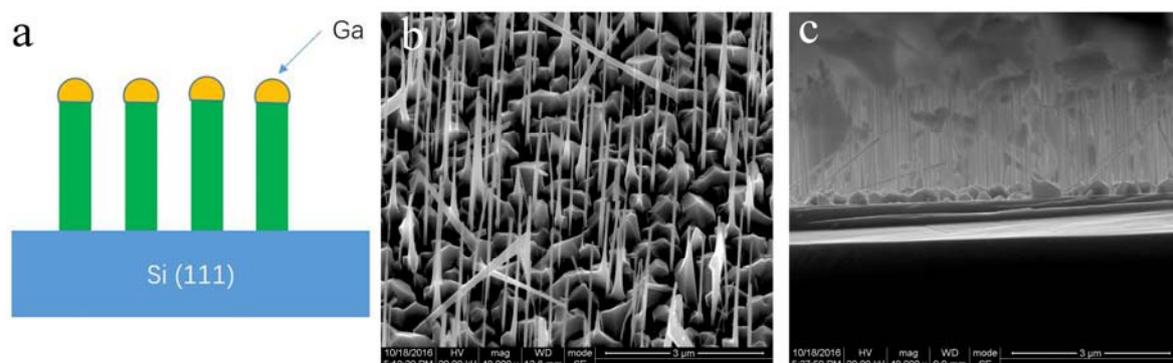


Figure 1. Structure of the GaAsP nanowire. (a) Illustration of GaAsP nanowire grown on Si (111) substrate; (b) SEM image of GaAsP nanowire with tilt angle of 40°. (c) Cross section view of GaAsP nanowire grown on Si (111) substrate.

TEM is used to evaluate the material composition of GaAsP nanowire, as shown in figure 2(a). Figure 2(b) shows the longitudinal scanning of GaAsP elements by energy-dispersive X-ray (EDX) analysis. The atomic percentage profile demonstrates that the GaAsP nanowire have a 50% percentage Ga element, 40% As and 10% P, respectively. This elements composition is an ideal candidate for solar cells achieving 33% efficiency under 1-sun illumination, as predicted by R. LaPierre [4, 14].

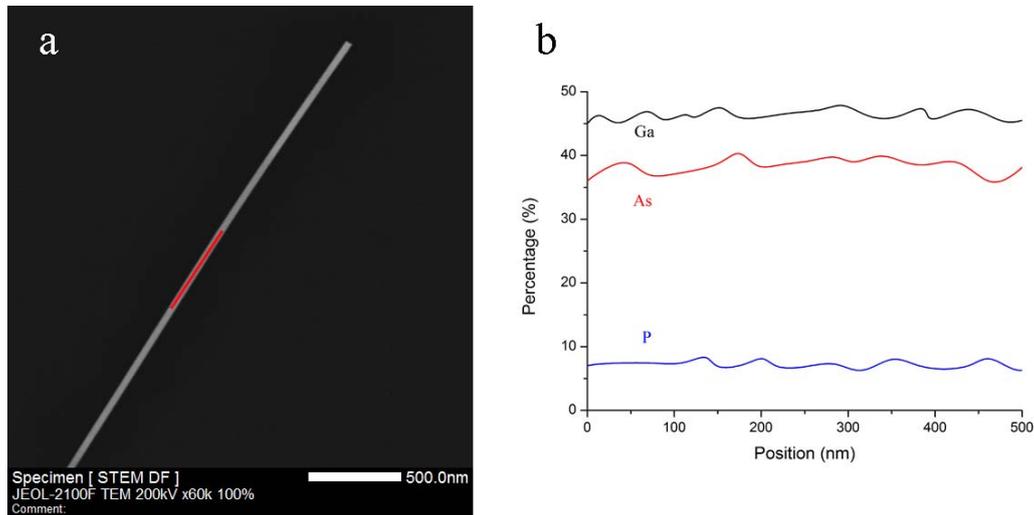


Figure 2. (a) TEM of GaAsP nanowire; (b) Element atomic percentage line scanning along the nanowire. The red line in (a) indicates where the EDX measurement takes.

3.2. Optical measurement

Figure 3(a) and (b) show the photoluminescence (PL) spectra of an ensemble of GaAsP nanowires as a function of temperature and excitation power, respectively. The laser is defocused to collection emitted light from nanowires as much as possible. As temperature increases, the PL intensity decreases and shift to blue region. The emission wavelength center shift can be explained by temperature-dependent bandgap and the temperature-dependent PL intensity can be well understood by using the Arrhenius formula [22]. The power-dependent PL was shown in figure 3(b) with power changing from 0.5 mW to 4 mW. Due to presence of surface state and defects, broadband emissions are observed.

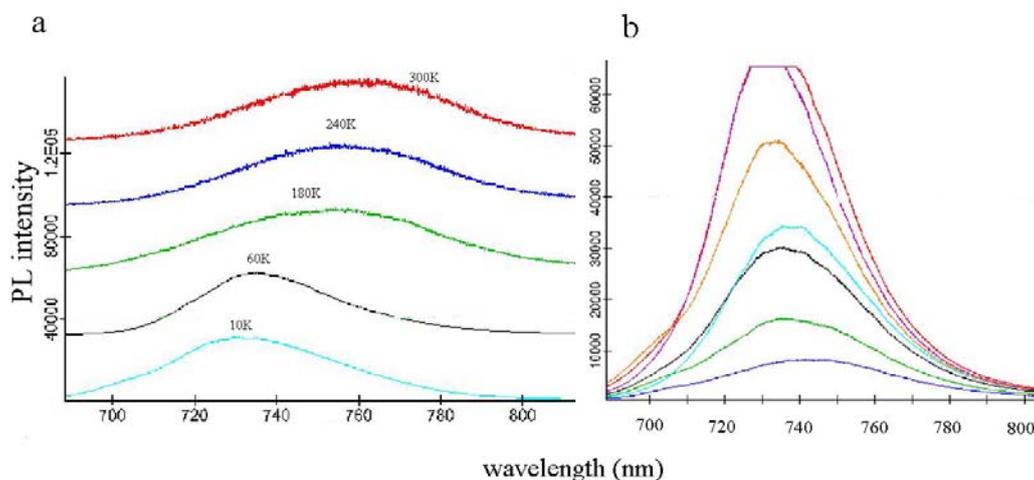


Figure 3. (a) Temperature-dependent PL under 2 mW excitation; (b) Power-dependent PL under 10K.

3.3. Passivation

Because nanowire have a high surface to volume ratio compared with their planar counterparts, surface states in nanowires is more serious. It is well-known that surface states can act as recombination centers in the band gap, which are detrimental to device performances. Therefore, it is critical to passivate the surface of the wires. The role of the passivation layer is stopping charge carriers from reaching the surface and recombining at surface states. We use ammonium sulphide to passivate the GaAsP nanowire. Before passivation, the transferred nanowires were soaked in 30% $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution to remove native oxide layer. PL intensity can be significantly influenced by oxide layer on nanowires [10]. As compared in figure 4, PL intensity of passivated nanowire is significantly enhanced by a factor of ~ 6 with respect to an untreated one. This means that it is attractive for solar cell, light emitting diode and laser. The PL enhancement is a result of the passivation of the semiconductor which originates from surface chemical interaction of sulfur ions in solution with semiconductor surface [23].

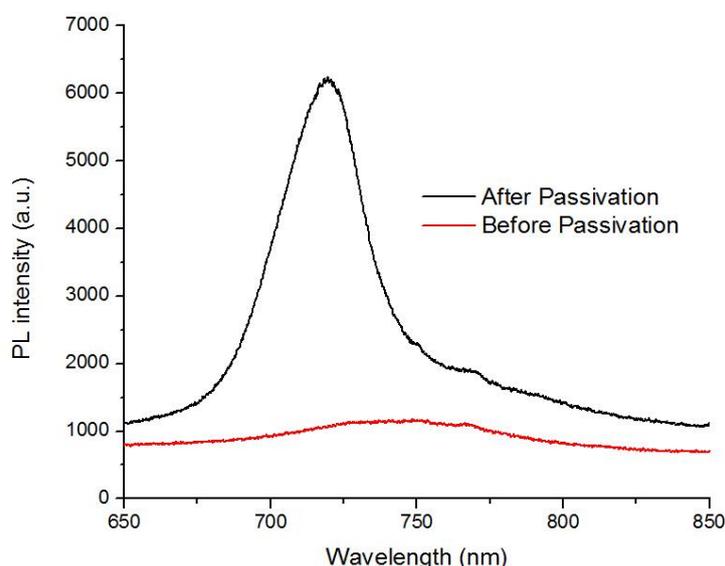


Figure 4. PL intensity of GaAsP nanowire before (red) and after (black) passivation.

4. Conclusion

In this paper, we demonstrate GaAsP nanowires grown by MBE on Si substrate. The self-catalyzed nanowire are different from foreign nanoparticle assisted growth, which is free of contamination, promising for high quality optoelectronic devices. SEM and TEM are used to confirm success growth of nanowires and elements. The element composition suggests that it is an ideal candidate for solar cells. Optical PL measurements are performed to investigate their optical properties. Temperature-dependent PL and power-dependent PL spectra suggest that the self-catalyzed GaAsP nanowires are best candidates for light emission devices. In order to boost their optical performance, $(\text{NH}_4)_2\text{S}$ is used to passivate GaAsP nanowires. The passivated nanowire demonstrates 6 orders of PL intensity enhancement. The self-catalyzed GaAsP nanowire and surface passivation technology will pave the way to achieving high performance III-V optoelectronic devices.

Acknowledgments

The authors declare no competing financial interests.

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