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Original Research

Reducing Zn diffusion in single axial junction InP nanowire solar cells for improved performance

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ABSTRACT

In this work axial n-i-p junction InP nanowires were grown by selective-area metal organic vapor phase epitaxy (SA-MOVPE) technique with the growth sequence starting from n-segment. The optical properties and carrier lifetimes of the n-, i- and p-type segments were studied and compared using time-resolved photoluminescence (PL) and cathodoluminescence (CL) measurements. We demonstrate for the first time that CL is capable of resolving the electrical profile of the nanowires, namely the varied lengths of the n-, i- and p-segments, providing a simple and effective approach for nanowire growth calibration and optimization. The CL result was further confirmed by electron beam induced current (EBIC) and photocurrent mapping measurements performed from the fabricated single nanowire solar cell devices. It is revealed that despite a non-optimized device structure (very long n-region and short i-region), the n-i-p nanowire solar cells show improved power conversion efficiency (PCE) than the previously reported p-i-n (growth starts with p-segment) single nanowire solar cells due to reduced p-type dopant (Zn) diffusion during the growth of n-i-p solar cell structure.

1. Introduction

III-V semiconductor nanowires have been studied intensively in recent years as promising candidates for optoelectronic applications such as lasers [1,2], photodetectors [3,4], light-emitting diodes (LEDs) [5,6] and solar cells [7–9]. For solar cell applications, due to their suitable bandgaps, superior optical and electrical properties, and small footprints, III-V compound semiconductor based nanowire solar cells have shown great promise in achieving high power conversion efficiency (PCE) with much reduced material cost. To date InP and GaAs nanowire array solar cells fabricated by bottom-up approach have been reported with the record efficiencies of 13.8% and 15.3%, respectively [8,9]. Top-down approaches also lead to a record efficiency as high as 17.8% [10]. However, these experimentally reported solar cell efficiencies are far below theoretical predictions, for instance, ~ 32.5% for bandgap at ~ 1.34 eV under AM 1.5 solar spectrum [11,12]. This is mainly because nanowire synthesis, device fabrication and junction design are still far from ideal and require substantial optimization. To understand and further improve the nanowire solar cell device properties especially the electrical properties, while avoiding the complication from the average effect of large number of nanowires in array nanowire solar cells, characterization and understanding of single nanowire materials and devices are essential.

Several III-V single nanowire solar cells have been demonstrated including GaAs [13,14], InP [15,16], InGaP [17] and GaAsP [7]. Compared to other III-V nanowires, InP nanowires are favorable for solar cell applications due to their low surface recombination velocity (SRV) [1,16,18,19]. We have previously reported single axial p-i-n InP nanowire solar cells with an efficiency up to 6.5% without any surface passivation [16]. By using the electron beam induced current (EBIC) technique, the spatially-resolved electrical structure in the p-i-n nanowire was obtained and revealed that Zn (p-dopant) diffusion was significant causing degradation of the device performance. In this work, single axial n-i-p InP nanowires were grown with n-segment first followed by i- and p-segments. Since the p-segment was grown the last, it is expected that the effect of Zn diffusion may be reduced or eliminated. We also introduce cathodoluminescence (CL) spectroscopy to directly characterize p-n junction configuration, through which the electron beam acts as a highly localized excitation source [20] to offer nanoscale resolution that cannot be achieved by other optical methods such as

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micro-photoluminescence (PL). Although such technique has been widely used to detect heterostructures [21–23], we show for the first time that it can be used to profile the segment length of the n-i-p structure of the same material and crystal structure. More importantly this technique does not require a complex and time consuming electrode fabrication processes, providing a simple and convenient method for growth calibration and optimization. Finally horizontally lying single nanowire solar cell devices were fabricated and characterized, demonstrating an improved performance compared with p-i-n solar cells due to reduced Zn diffusion as confirmed by EBIC measurement.

2. Experimental

2.1. Nanowire growth

The axial n-i-p junction InP nanowires were synthesized by selective-area metal organic vapor phase epitaxy (SA-MOVPE) technique on a SiO_2-masked n^+-doped 111(A) InP substrate. The substrate was first prepared by electron beam lithography (EBL) and wet chemical etching with the designed pattern of a hexagonal array targeting at holes of 180 nm in diameter and 800 nm in spacing [1,16]. Then the nanowire growth was carried out in a horizontal flow MOVPE reactor (AIXTRON 200/4) at 100 mbar with H_2 as the carrier gas. Trimethylindium (TMIn) and phosphine (PH_3) were used as precursors for In and P, respectively. The growth temperature was 730 °C with a V/III ratio of 81 (flow rate of 6.07×10^{-6} mol/min for TMIn and 4.91×10^{-4} mol/min for PH_3). Silane (SiH_4) was used as n-type dopant with a flow rate of 1.01×10^{-6} mol/min, while diethylzinc (DEZn) was used as p-type dopant with a flow rate of 2.03×10^{-5} mol/min. The growth sequence was such that n-segment was firstly grown for 10 min followed by i-segment for 10 min and p-segment for 10 min.

2.2. Optical characterization

The nanowires were first mechanically transferred to a thermally oxidized p^+-Si substrate with a 300-nm SiO_2 layer and excited by a 522 nm (frequency doubled) pulsed laser with pulse width of 300 fs and repetition rate of 20.8 MHz. The laser beam was focused by a 100× (NA 0.9) focusing objective with a spot size of 0.305 μm in radius estimated by vector diffraction calculation [24]. The PL signal was first collected by a grating spectrometer and recorded by a charge-coupled device (CCD) [24]. A Si single photon avalanched diode (SPAD) and Picoharp 300 time-correlated single photon counting system (TCSPC) were used to detect PL intensity decay [24]. The time-resolved PL (TRPL) intensity decay at the peak wavelength was fitted by a single-exponential decay to extract the minority carrier lifetime [1]. In our measurements, the power was fixed at a low excitation power of 0.26 μW (1 mW average laser power equals an excitation pulse energy of 48 pJ). So the excitation power density is 4.27 $\mu J/cm^2$/pulse.

The nanowires were also mechanically transferred to a Si substrate for CL measurement in a FEI Verios 460 field emission scanning electron microscope (SEM), with a Gatan MonoCL4 Elite CL detection system that enables CL mapping and spectroscopic studies.

2.3. Single nanowire solar cell fabrication

To fabricate single horizontal nanowire solar cell devices, nanowires were first mechanically transferred to a thermally oxidized p^+-Si substrate with a 300-nm SiO_2 layer and then the electrodes were defined by EBL patterning followed by buffered HF etching to remove the surface native oxide. Finally 10 nm Ti and 220 nm Au were deposited by electron beam evaporation and Ti/Au electrodes were formed on two ends of nanowires after the lift-off process.

2.4. Single nanowire solar cell characterization

The 1 Sun @ AM1.5G current-voltage (*I-V*) measurements of the nanowire solar cells were performed using an Oriel Solar Simulator (Mode-92250A). EBIC measurements on the fabricated devices were carried out by a FEI Helios 600 NanoLab DualBeam focused ion beam (FIB) system that allows for high resolution SEM imaging (~ 0.9 nm). Then the devices were characterized by 2-dimensional (2D) reflection and photocurrent mappings using a WITec alpha300S scanning microscopy system. Light at 532 nm from a Fianium WhiteLase supercontinuum laser was focused using a 100×, NA0.9 objective lens and then scanned across the sample using a piezo-driven sample stage. The spot size was estimated to be 721 nm in diameter. The photocurrent was measured using the conventional amplitude modulation technique with an Agilent 33210A 10MHz function/arbitrary waveform generator with a frequency of 333 Hz, Stanford SR570 low-noise current pre-amplifier, and Stanford SR850 lock-in amplifier. The reflected light was simultaneously detected by a confocal microscope and a Si avalanche photo-diode (APD).

3. Results and discussion

The 10° tilted SEM image of the as-grown InP nanowire array is displayed in Fig. 1a, showing good surface morphology and relatively uniform lengths (~ 7-8 μm). However, some deviation from perfect hexagonal cross-section is observed in the top-view SEM image (inset of Fig. 1a) due to the relatively large nanowire spacing (800 nm) and consequent non-uniform lateral growth [1,16]. As confirmed by the *I-V* characteristics shown in Fig. 3b, the lateral growth is insignificant such that it does not lead to the formation of a conformal radial junction.

To investigate the optical properties of n-, i- and p-segments, we measured PL and TRPL from the n-i-p nanowires at room temperature. The PL intensity and TRPL decays with the fitting from three positions of the n-, i- and p-regions are displayed in Fig. 1b and c. The minority

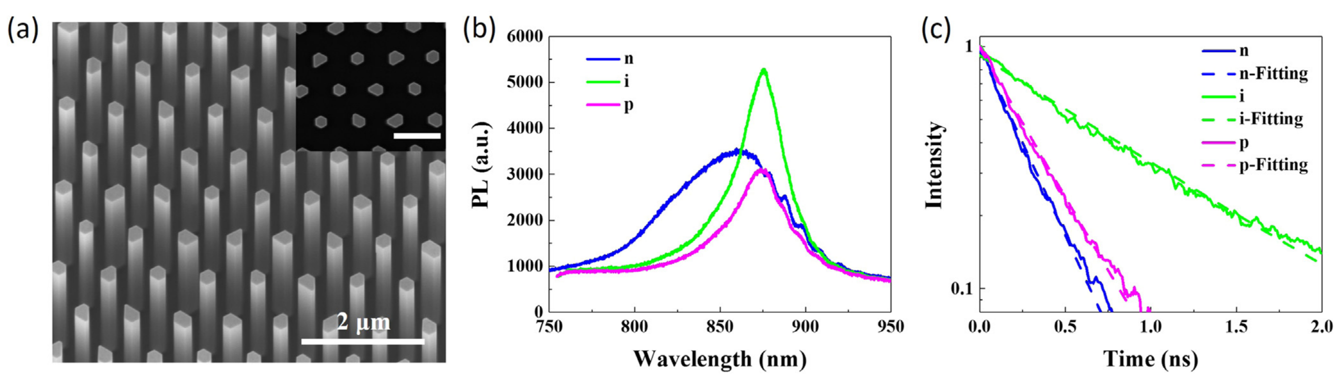

Fig. 1. (a) SEM image at 10° tilt view of the InP nanowire array grown for this work. Inset shows the top view SEM image. The scale bar of the inset is 1 μm. (b) PL and (c) TPRL decays with fittings of n-, i- and p-regions, respectively.