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Analysis of the core–shell interface between zinc-blende GaP and wurtzite ZnO

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ABSTRACT

Core–shell GaP/ZnO nanowires (NWs) were prepared in a two-step process: (1) GaP NWs were grown on GaP substrate by low-pressure metalorganic vapour phase epitaxy using 30 nm Au seeds as nucleation centres, (2) the GaP NWs were covered in a thin nanocrystalline Ga-doped ZnO layer by sputtering in a Perkin Elmer planar RF diode system. Electrical contacts were processed to individual GaP/ZnO NWs using electron beam lithography, evaporation and lift-off of metallic layers: Au/Zn (GaP core) and Au/Al (ZnO shell). Electrical and photocurrent measurement of the NWs confirmed that a radial pn heterojunction was formed between the GaP core and ZnO shell.

1. Introduction

Core–shell nanowire heterostructures are very promising for applications in electronic and photonic devices such as field-effect transistors, solar cells and sensors [1–4]. A core–shell nanowire usually consists of a low band gap core and a higher band gap shell. This leads to spatially direct transitions between electrons and holes. The shell protects the active core–shell interface [5]. The band offset of a core–shell NW heterostructure is adjusted to enhance the carrier confinement [6]. The band gap structure (for appropriate material combinations) is designed so as to extend the spectral sensitivity [7]. Such nanowires can be doped by modulation doping [8].

Core–shell nanowires (NWs) can also have a radial pn heterojunction with a p-type core and n-type shell or vice versa. The NW cores are usually prepared on a substrate of identical conductivity and the shells are deposited by various techniques. The NWs are contacted at one end through the conductive substrate. This is very convenient for large area solar cells. Large area Si solar cells covered with NWs were reported by Li et al. [9] and p-Si NWs with ZnO shells by Choi et al. [10]. The high conversion efficiency of NW-based solar cell was attributed to the extremely low reflectance of periodically aligned nanowire structure and the radial pn junction geometry.

In case of tandem III–V solar cell a typical AR coating consists of two thin dielectric layers (usually MgF2/ZnS). This AR coatings are not ideal solution due to limited wavelength range and narrow angular response. This deficiency can be compensated by employing of structures with graded refractive index behaviour. Here the material compatibility with the top tandem cell material InGaP plays a crucial role. We studied a preparation of thin ZnO layer with embedded GaP nanowires. In this case a compatibility with top InGaP is ensured by GaP NWs and an improvement of the optical properties (reflectance decrease) is caused by combination of two effects: size effect and ZnO optical properties. We believe that this is a promising alternative for photovoltaics.

GaP NWs can have shells from various materials. This includes (1) GaP/Ga_2O_3 NWs produced by Ga_2O_3 and red phosphorus powder synthesis in NH_3 and Ar [14], (2) GaP NW with amorphous gallium oxide shell synthesized from mixed Ga/GaP powder as a precursor [15], and (3) a double-heterostructure core–shell GaP/GaInP NWs with a radial junction [16].

ZnO is widely used in various optoelectronic devices due to its direct band gap (3.37 eV at room temperature), large exciton binding energy (60 meV), high transparency, and inherent n-type conduction behaviour. It is easy to prepare n-type ZnO, but it is quite difficult to make a stable p-type ZnO material due to the

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well-known dopant compensation effect [11]. Therefore, pn junctions for optoelectronic devices are often formed by combining n-type ZnO with another p-type material, such as p-type silicon [10] or Cu_2O [12].

This paper reports on core–shell p-GaP/n-ZnO NWs prepared by MOVPE and RF sputtering. We studied the NWs using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrical and photocurrent measurement. It is demonstrated herein that such NWs have a radial pn heterojunction.

2. Experimental

GaP NWs were grown by MOVPE on p-type Zn-doped ($p = 1 \times 10^{18}\,cm^{-3}$) GaP (1 1 1)B substrate in vapour–liquid–solid (VLS) mode using 30 nm colloidal gold particles. During growth the particles are expected to transform into nucleation centres (seeds) of a liquid alloy. The seeds then preferentially adsorb growth species from the vapour phase. Once they become supersaturated, GaP crystal begins to nucleate at their liquid–solid interface. We grew the NWs at a temperature of 500 °C and pressure of 100 mbar during four minutes and doped them with zinc to be p-type in an AIX 200 MOVPE low-pressure reactor [17]. Electrical properties of the individual GaP NWs were described previously [13].

To form core–shell GaP/ZnO NWs, GaP NWs were covered with an 80 nm thick nanocrystalline Ga-doped ZnO layer. It was deposited on the NWs and substrate by sputtering at room temperature at an 1.3 Pa Ar pressure and a power at 600 W from a ceramic $ZnO:Ga_2O_3$ (98 wt%:2 wt%) target (∅ = 100 mm) in a Perkin Elmer planar RF diode system. The core–shell NW structure is shown at longitudinal TEM view (Fig. 1).

The GaP/ZnO NWs were characterized also electrically. Electrical contacts were processed to individual NWs using electron beam lithography, evaporation and lift-off of different metallization systems. They were alloyed at different temperatures below the growth temperature of the GaP NWs. Processing of the electrical contacts was not trivial because the core and shell considerably differed in mechanical and chemical properties.

The ZnO shell was removed in a concentrated KOH solution at one NW end via a window in PMMA through which Au/Zn was deposited onto the GaP core. The metallic layer was annealed at 450 °C. The shell was electrically contacted with Al/Au annealed at 232 °C [18]. Fig. 2a shows side view on the group of GaP/ZnO nanowires and Fig. 2b shows a detailed view of a NW: the ZnO shell is partly removed from the NW; the GaP core resides in the Au/Zn metallization.

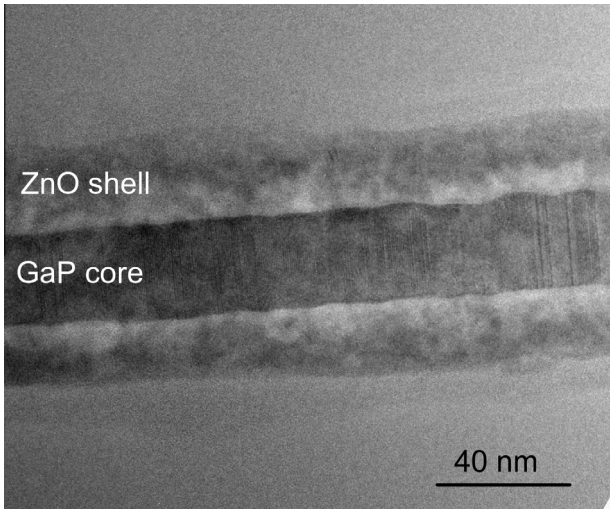

Fig. 1. Typical longitudinal TEM view on the core–shell structure of the GaP/ZnO nanowire.

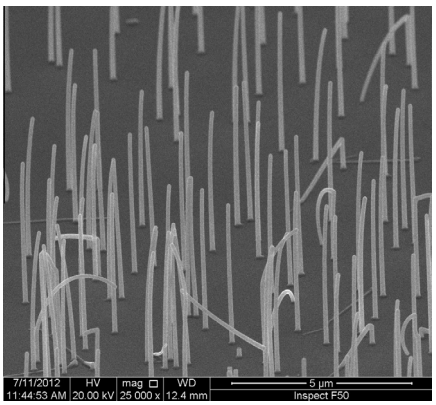

Fig. 2a. Scanning electron microscopy (SEM) view on GaP nanowires covered by ZnO shell with thickness of 35 nm.

3. Results and discussion

SEM analysis showed that the GaP cores were conic (∅ ~ 80 nm at the substrate and 30 nm under the seeds) but the core–shell NWs were cylindrical (∅ ~ 200 nm). The ZnO shell compensated for the initial conic shape of the GaP NWs. The core–shell NWs were 5 µm long on average and had a fine grain surface morphology [20].

The NW microstructure and crystallographic phases were analyzed using cross-sectional and longitudinal TEM micrographs (Jeol, 120 keV). The latter were used to precisely estimate the shell thickness along the NWs. For TEM analysis, the NWs were deposited on a standard copper grid covered by carbon and were oriented using electron diffraction patterns into $\langle \bar{1}10 \rangle$ or $\langle 11\bar{2} \rangle$ direction.

The ZnO shell consisted of nanocrystals with a wurtzite-like structure, similar to the structure of ZnO deposited on the substrate. TEM and XRD showed that size of the nanocrystals ranged between 13 and 20 nm [19]. The nanocrystals were arranged into nanocolumns at (1 1 1)B facets of the GaP cores. The crystallographic structure of GaP NWs can be zinc-blende or wurtzite depending on growth conditions. A detailed study of TEM diffraction patterns showed that our GaP NWs had a zinc-blende structure [19,20].

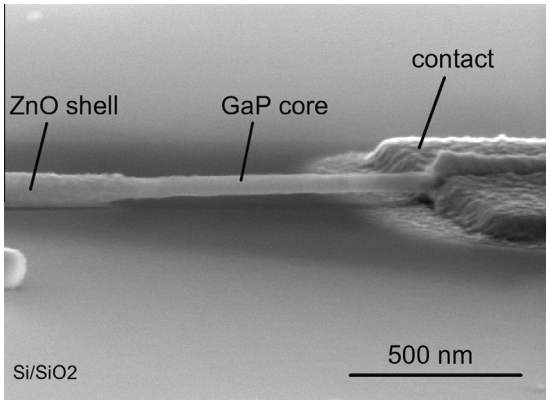

Fig. 2b. SEM micrograph of a partly removed ZnO shell from a GaP NW core. The GaP core is embedded in Au/Zn metallization.