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Electron beam induced current microscopy investigation of GaN nanowire arrays grown on Si substrates

Vladimir Neplokh [a,*], Ahmed Ali [a], François H. Julien [a], Martin Foldyna [b], Ivan Mukhin [c,d], George Cirlin [c,d,e], Jean-Christophe Harmand [f], Noëlle Gogneau [f], Maria Tchernycheva [a,*]

[a] Institut d'Electronique Fondamentale, UMR CNRS 8622, University Paris Sud, University Paris Saclay, Orsay 91405, France
[b] CNRS, Laboratoire de Physique des Interfaces et Couches Minces (LPICM), Ecole Polytechnique, 91128 Palaiseau, France
[c] ITMO University, St. Petersburg 197101, Russia
[d] St. Petersburg Academic University, Khlopina 8/3 A, St. Petersburg 194021, Russia
[e] Peter the Great Saint-Petersburg Polytechnic University, Polytechnicheskaya 29, St. Petersburg 195251, Russia
[f] Laboratoire de Photonique et de Nanostructures Route de Nozay, 91460 Marcoussis, France

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ABSTRACT

We report on the electron beam induced current (EBIC) investigation of GaN nanowires grown on n-doped Si (111) substrates. The objective of this study is to acquire information about the modifications of the substrate properties induced by the wire growth. We show that the growth procedure using deposition of an ultra-thin AlN layer prior to the nanowire growth step leads to the formation of a p-n junction in the Si substrate with a high surface conductivity. The induced p-n junction exhibits a photoresponse over the spectral range from 360 nm to 1100 nm. The properties of the induced p-n junction are investigated on the cross section and in a top view configuration with EBIC microscopy. For a localized contact of the GaN nanowires, the collection range in Si extends over a few millimeters. The treatment of the surface using reactive ion etching with a CHF_3 plasma leads to the inhibition of the surface conductivity and to the appearance of an S-shape in the current-voltage characteristics under illumination. The conversion efficiency of the plasma-treated sample under AM1.5G solar spectrum is estimated to be in the 2.1–2.7% range.

1. Introduction

Recently III-nitrides have been proposed as "new solar materials" for multi-junction devices thanks to the direct bandgap of InGaN alloy spanning from 0.65 to 3.42 eV. The commonly adopted approach for nitride photovoltaics (PV) uses InGaN/GaN quantum wells as the absorbing medium, which allows to achieve high external quantum efficiencies of 72% and 39% in the blue and green spectral range, respectively [1,2]. The integration of a III-nitride subcell with non-III-nitride solar cells has recently been proposed in order to improve the overall performance by the efficient conversion of high energy photons [3]. It should be noted that today there is no established technology for efficient conversion of the green and blue parts of the solar spectrum. III-Nitrides are among the few semiconductors that can provide bandgaps of 2.3 eV or larger to enhance the conversion of the green and blue parts of the solar spectrum in view of future ultra-high efficiency multi-junction solar cells (e.g. 4-junction cells for space applications). In addition, III-nitride semiconductors are characterized by (i) a high absorption coefficient (10^5 cm^{-1} at the band edge); (ii) a high thermal conductivity; (iii) a superior resistance to ionizing radiations and (iv) a superior thermal, mechanical and chemical stability. Moreover, there is a naturally obtained alignment between the conduction band of n-type $In_{0.46}Ga_{0.54}N$ and the valence band of p-type Si allowing for a direct low resistance connection between InGaN and Si cells in a tandem [4].

One key issue slowing down the development of nitride on Si PV devices consists in a poor material quality of the InGaN 2D layers. The lattice mismatch between the III-nitrides and Si induces a large density of threading dislocations (up to 10^{10} cm^{-2}) in the nitride epitaxial layers. This issue can be solved by replacing 2D films by nanowires (NWs). Indeed, the small NW footprint allows relaxing the strain by the free lateral surface [5] and if a misfit dislocation is created, it is naturally bent to the NW lateral surfaces. This allows to grow high crystalline quality NWs on any substrate and also to fabricate axial heterostructures using In-rich alloys with a relatively large lattice mismatch.

* Corresponding author.
E-mail addresses: vladimir.neplokh@u-psud.fr (V. Neplokh), maria.tchernycheva@u-psud.fr (M. Tchernycheva).

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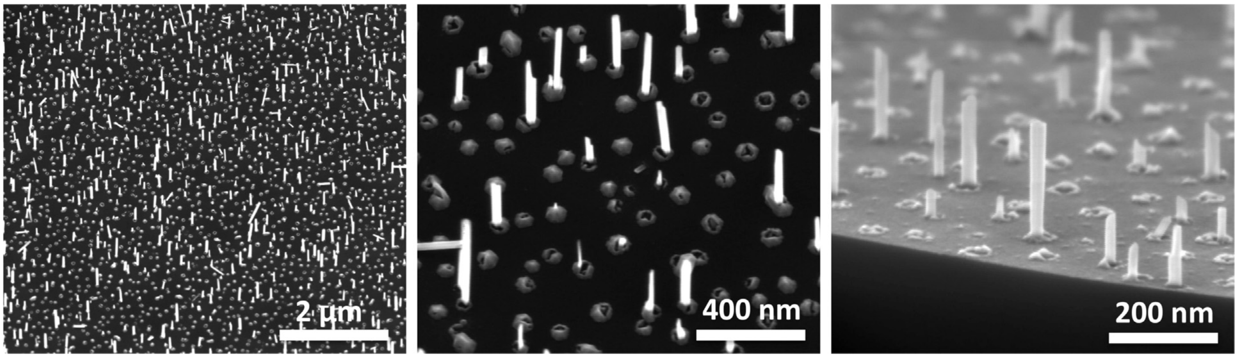

Fig. 1. Tilted SEM images of the surface of the as-grown sample at different magnifications. White contrast corresponds to GaN NWs, grey to residual 2D GaN and AlN islands and dark to the Si wafer surface.

The applications of nitride NWs cover different optoelectronic domains such as, for example, light emission [6,7] or photodetection [8–10]. For solar cells, the most promising fabrication approach uses molecular beam epitaxy (MBE) [11–14], characterized by a relatively low growth temperature in comparison to metal organic vapor phase epitaxy, allowing to achieve InGaN NWs with In-rich composition [15,16]. Several nitride NW solar cells on Si have been reported in the literature [11–14,17]. However, the thermal budget for the NW growth remains relatively high even for the MBE technique and the direct NW growth on a Si p-n junction, necessary to form a tandem device, can modify the Si underlying sub-cell properties.

In this context, it is interesting to explore processes taking place in the Si substrate during the nitride NW growth. Here we report on the electron beam induced current (EBIC) investigation of GaN NWs grown on n-doped Si (111) substrates to acquire information about the modifications of the substrate properties induced by the wire growth. We show that the growth procedure using the deposition of an ultra-thin AlN layer prior to the NW growth step leads to the formation of a p-n junction in the Si substrate with a high surface conductivity. The induced p-n junction exhibits a photoresponse over the spectral range from 360 nm to 1100 nm. The GaN NWs act as passive conductors and do not participate in the PV conversion. The properties of the induced p-n Si junction are investigated on the cross section and in a top view configuration with EBIC microscopy. For a localized contact of the GaN NWs, the collection range in Si extends over a few millimeters. The treatment of the surface for 20 min using reactive ion etching (RIE) with a CHF_3 plasma leads to the inhibition of the surface conductivity and to the appearance of an S-shape in the current-voltage characteristics under illumination. The short circuit photocurrent, the open circuit voltage and the fill factor under the AM1.5G solar spectrum were found to be 0.17 mA (25 µA), 0.37 V (0.36 V) and 27% (20%) for as-processed (plasma treated) devices, respectively. We estimate the energy conversion efficiency of the plasma-treated sample to be in the 2.1–2.7% range.

2. Materials and methods

GaN NWs were grown on degenerately n-type doped (resistivity 0.007 Ω cm) Si(111) 350 µm thick wafers by molecular beam epitaxy (MBE), active nitrogen being supplied by a radio-frequency plasma cell. After a standard chemical cleaning procedure of the substrate using a diluted H_2SO_4 solution for 15 min and oxide removal using diluted HF for 30 s, the substrates were introduced in the growth chamber and kept at a high temperature of 780 °C for 1 h and further heated to 805 °C for 5 min. Prior to the growth of GaN NWs, a 2.5 nm thick AlN layer was grown at 600 °C, by depositing Al on the Si(111) substrate followed by exposing the surface to nitrogen. This substrate preparation procedure was adapted to improve the NW verticality [18–20]. The growth of GaN NWs was performed at 800 °C under N-rich conditions with an N/Ga ratio of ~8.7 (Ga flux corresponding to an equivalent 2D-growth rate of 0.3 A/s). The NWs growth was stopped after 3 h and 30 min. Further details on the NW growth and properties can be found in Ref. [21].

The NW arrays were processed for electrical-optical characterization as follows. The processing started with hydrogen silsesquioxane (HSQ) spin-coating to electrically insulate the Si substrate. The HSQ was annealed for 1 h at 400 °C to transform it into SiOx [22]. Then the encapsulation coating was partially wet etched in HF: H_2O 1: 200 solution to release the GaN NWs, leaving a thin SiOx layer covering the substrate surface. Then square $300 \times 300\ \mu m^2$ and $700 \times 700\ \mu m^2$ pads were defined by optical lithography and 200 nm of transparent conductive indium tin oxide (ITO) was deposited by sputtering followed by a lift-off procedure. The sample was annealed in $Ar+H_2$ atmosphere at 400 °C for 10 min to improve the ITO conductivity. The top contact preparation was finalized by depositing a Ni/Au 10/200 nm frame and bonding pad defined by optical lithography. The bottom contact was taken from the backside of the Si substrate using silver paint.

After processing, the sample was cleaved into two pieces. The first piece was investigated directly after processing, while the second one was treated for 10 min by RIE using a CHF_3 plasma (pressure 30 mTorr, power 300 W) without any protective mask. CHF_3 plasma etches the HSQ encapsulation and can also attack the Si substrate, but it does not attack either the ITO or Au metallic frame, therefore the contacted pads are preserved. The purpose of the CHF_3 etching was to limit the photovoltaic conversion activity to ITO-contacted regions only in order to allow an accurate measurement of the conversion efficiency.

The electrical properties of the contacted NW arrays were measured at room temperature in the dark and under illumination using microprobes, a Keithley 2636 source meter and a commercial AAA grade solar simulator delivering 1 sun AM1.5G spectrum. The spectrum of the external quantum efficiency (EQE) of the device was probed using a tunable visible–UV light source consisting of a Xe lamp coupled with a Jobin Yvon Triax 180 spectrometer.

To understand the origin of the current generation, EBIC mapping was performed on the cross section and in a top view configuration. The EBIC microscopy is a type of charge collection microscopy in which electron–hole pairs are locally generated by the electron beam. In case of the presence of a built-in internal field, the electron–hole pairs can be separated and collected producing a measurable current [23]. The EBIC maps were measured at room temperature under zero external bias in a Hitachi SU8000