Modeling, synthesis and study of highly efficient solar cells based on III-nitride nanowire arrays grown on Si substrates

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Abstract. In this letter we investigate photovoltaic properties of GaN nanowires (NWs) – Si substrate heterostructure obtained by molecular beam epitaxy (MBE). Antireflection properties of the NW array were studied theoretically and experimentally to show an order of magnitude enhancement in antireflection comparing to the pure Si surface (2.5% vs. 33.8%). In order to determine optimal morphology and doping levels of the structure with maximum possible efficiency we simulated it’s properties using a finite difference method. The carried out simulation showed that a maximum efficiency should be 20%.

1. Introduction

Highly efficient solar cells development and continuous search of new ways for photovoltaic efficiency improvement are topics of great interest for last few decades. Vertically aligned arrays of 1D nanostructures (NWs) due to their unusual properties are potential building blocks for optoelectronic devices, in particular solar cells [1, 2]. Arrays of III-nitride NWs (GaN, AlGaN, InGaN) grown by means of molecular beam epitaxy on crystalline Si substrates are known to possess high crystalline quality and low optical reflectance over the whole visible spectral range. Integrating of A3B5 and Si semiconductor technologies is one of the main priorities in modern photovoltaic researches and A3B5 NWs might be the key to overcome existing difficulties in this field [1].

Schematic image of a tandem solar cell consisting of GaN NWs array on top of emitter of the upper junction is presented on figure 1 a). In the simplest case it may only comprise of GaN NWs grown on Si substrate.

GaN NWs array obtained using AlN mask layer serves as a wide band gap window of the solar cell, has good antireflection properties and provides efficient direct electron transport to contacts (by means of ITO coating for example). It is worth noting that GaN possesses band structure parameters (electron affinity, band gap) good to achieve high quality n-n contact between GaN NW and wide band gap semiconductor used in upper junction of tandem cell.

2. Growth and postprocessing

Prior to the growth process a standard cleaning procedure of a Si substrate has been performed with a final treatment in HF to remove the oxide layer. The substrate was then degased in the growth
chamber at 800 °C (figure 2). After that a thin 4 nm AlN layer was deposited on the substrate and then exposed under N2 flux for 1 minute to form porous material working as a mask for NWs formation.

This thin porous layer works as a wide band gap window to confine charge carriers of both signs photogenerated in Si substrate and also hinders charge transport from Si into unwanted 3D GaN layer (saturated with dislocations) that is grown on top of mask during NWs formation (see figure 1 b). In this technique high crystalline quality GaN NWs providing good carrier transport with high carrier life time grow directly on Si substrate and have no mechanical contact with AlN layer as well as with 3D GaN layer (see inset on figure 1 b).

Array of slightly unintentionally doped n-type GaN NWs on n-type Si substrate was grown using nitrogen plasma-assisted MBE technology with a Ga flux corresponding to the growth rate of 0.3 A/s for GaAs. For nitrogen beam, 2.1 sccm flux was used, with 520 W power providing N-reach growth conditions necessary for the NWs formation. Growth rate of the unwanted 3D GaN layer was two times slower. Typical length of the NWs was measured to be 1 µm, while the 3D layer thickness was...
0.5 μm respectively. Mean NWs diameter was found to be 80 nm, surface density - 10⁹ cm⁻². Elongated geometry of the wires enables us to process a top contact to them isolated with a dielectric from the unwanted GaN layer.

In order to decrease serial resistance of the cell we needed to exclude saturated with dislocation 3D GaN layer from the circuit. To this end we deposited a thin dielectric PMMA resist layer using spinning method on top of GaN layer (figure 2). This PMMA layer was then removed from NWs’ top facets by means of oxygen plasma etching to provide photogenerated carriers transport to the top contact. The top contact was formed with ITO layer covering the entire cell upper surface that was deposited by the magnetron sputtering. A silver net was then made on the ITO surface. Silver paste was also used to derive bottom contact on Si.

3. Experimental results

Band diagram of the solar cell based on n-Si substrate – n-GaN NWs junction is presented on figure 3 a). GaN band gap is 3.2 eV, Si band gap is – 1.1 eV. At the Si-GaN heterojunction an electron transparent tunnel barrier and potential barrier for holes are obtained. Photogenerated in Si electrons travel through NWs to be collected at the face ITO contact. Collection of holes is implemented via back contact with Si.

![Figure 3. a) Band diagram of the n-GaN NWs – n-Si substrate solar cell; b) I(V) characteristic of the n-GaN NWs – n-Si substrate solar cell under AM1.5 illumination.](image)

Experimental current-voltage characteristic of the obtained cell under AM1.5 illumination (1000 W/m²) at a cell temperature of 25 °C is presented on figure 3 b). Open circuit voltage was found to be 0.35 V and corresponds to the potential barrier height for electrons at the Si-GaN heterointerface. Fill factor value was 0.31, which is more likely caused by high value of the ITO face contact serial resistance. Efficiency of the n-n solar cell was measured to be 2.4%. In case of tandem solar cell based on the heterojunction between n-type upper emitter and n-type GaN NWs potential barrier for electrons occurs at the heterointerface which leads to degradation of cell properties. Therefore, an optimization of doping level of both junction materials needs to be performed in order to lower the barrier height.

Dense array of self-assembled NWs having subwavelength diameters is known to have good antireflection properties [3]. Experimental data on antireflection characteristics of GaN NWs grown via molecular beam epitaxy on Si substrate is shown on figure 4. Oscillations of the reflectivity are caused by destructive interference of the incident light in the unwanted 3D GaN layer. Average value of the structure reflectivity was found to be 2.6%.
4. Modelling
In our study we have carried out modeling of a simple solar cell formed by n-type GaN NWs and p-type Si substrate. In such a photovoltaic device photogeneration of electron-hole pairs takes place in volume of Si and separation of the carriers occurs at the heterojunction. Band diagram of the cell is presented on figure 5 a).

In our simulations we have performed independent modeling of semiconductor and antireflection properties of the structure. The main aim of simulations was to obtain optimal NWs morphology, doping levels of both wires and Si substrate to determine maximum theoretical efficiency of the cell.

Antireflection properties modeling has been done via CST Microwave software package. In our simulations we used a geometrical model of hexagonally ordered array of cylindrical NWs on Si substrate (figure 5 b). Experimental data over dependencies of GaN 3D layer thickness on NWs average length and known special features of ITO sputtering on sidewalls of NWs were taken into account in calculations.

Simulations of the antireflection properties included twofold consecutive variation of the NWs surface density, radius and length. The following optimal geometrical parameters were obtained: lateral distance between the wires – 365 nm, radius – 60 nm, length – 1375 nm. Corresponding reflectivity value was 2.5%. For the sake of comparison spectral reflectivity of the pure Si is presented on figure 6 (its mean value equals 33.8%).

![Figure 4](image_url)

**Figure 4.** Antireflection characteristics of GaN NWs grown on Si substrate.

![Figure 5](image_url)

**Figure 5.** a) Band diagram of the p-GaN NWs – n-Si substrate solar cell; b) 3D model of cell.
Figure 6. Modeling results of antireflection characteristics of GaN NWs on Si substrate.

Semiconductor properties of the structure were modeled using Newton method with Fermi statistics. We supposed that NWs have ideal crystal structure with negligible carriers capture at side walls that allowed us to reduce modeling to one dimensional problem. Instead of NWs we introduced GaN layer having thickness equal to an effective minimum distance that carrier needs to overcome between Si substrate and ITO layer (it consists of GaN 3D layer thickness + dielectric thickness, see figure 5 b) multiplied by ratio of substrate surface area to area covered with NWs. In this approximation sum \(h_{\text{bulk GaN}} + h_{\text{PMMA}}\) equals 730 nm and area ratio – 10.2.

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H_{\text{GaN}}^{\text{eff}} = \left(h_{\text{bulk GaN}} + h_{\text{PMMA}}\right) \frac{S_{\text{surf}}}{S_{\text{GaNW}}}
\]

The results of modeling are shown on figure 7. On figure 7 a) you find graphical dependencies of cell efficiencies on substrate doping level at different but fixed levels of wires doping. These curves have strongly marked maxima at substrate acceptors concentration around \(1.3 \times 10^{18} \text{ cm}^{-3}\) and maximum efficiency reaches 20%. Further increase of acceptors concentration leads to fall of both depletion region and mobility of carriers in Si which results in decrement of the cell efficiency.

Figure 7. a) Dependencies of cell efficiencies on substrate doping level at fixed levels of NWs doping; b) dependencies of cell efficiencies on NWs doping level at fixed levels of substrate doping.
On figure 7 b) you find graphical dependencies of cell efficiencies on NWs doping level at different but fixed levels of substrate doping. As can see at donors concentration above $4 \times 10^{18}$ cm$^{-3}$ the curves demonstrate saturation and further increase of wires conductivity doesn’t affect the cell efficiency. Modern MBE technology allows us to reach the obtained doping levels.

5. **Summary**

In this work we study solar cell based on GaN nanowires array grown epitaxially on Si substrate which appears to be the simple case of a tandem cell with an array of GaN nanowires on emitter of the cell’s top junction. Nanowires in this case play a role of a top wide band gap window and provide great antireflection properties.

A simple solar cell consisting of GaN nanowires on top of n-type Si substrate has been obtained using MBE technology. We have shown that the structure has energy conversion efficiency of 2.4% and a high open circuit voltage of 0.35 V which can be explained via low doping level. To increase efficiency of the tandem cell a potential barrier on the boundary between GaN nanowires and top junction emitter should be decreased.

We have also performed properties simulations of the solar cell based on the junction between array of n-type nanowires and p-type Si substrate. It’s been demonstrated theoretically that reflectivity of such a structure is only 2.5% and photovoltaic efficiency can reach 20%.

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