

Photovoltaic Properties of p-Doped GaAs Nanowire Arrays Grown on n-Type GaAs(111)B Substrate

G. E. Cirlin · A. D. Bouravleuv · I. P. Soshnikov ·
Yu. B. Samsonenko · V. G. Dubrovskii · E. M. Arakcheeva ·
E. M. Tanklevskaya · P. Werner

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Abstract We report on the molecular beam epitaxy growth of Au-assisted GaAs p-type-doped NW arrays on the n-type GaAs(111)B substrate and their photovoltaic properties. The samples are grown at different substrate temperature within the range from 520 to 580 °C. It is shown that the dependence of conversion efficiency on the substrate temperature has a maximum at the substrate temperature of 550 °C. For the best sample, the conversion efficiency of 1.65% and the fill factor of 25% are obtained.

Keywords Molecular beam epitaxy · Nanowires · GaAs · Solar cells · Photovoltaic properties

Introduction

Aligned NW arrays are very promising building blocks for various nanoelectronic devices, such as nanolasers [1, 2],

field-effect transistors [3], light-emitting diodes [4, 5] and field emitters [6, 7]. Compared to polycrystalline films, vertically oriented NW arrays are particularly advantageous for photovoltaic (PV) application, because the oriented geometry provides direct conduction paths for photo-generated carriers to transport from the junction to the external electrode, thereby resulting in a high carrier collection efficiency [8, 9]. Moreover, NW arrays have significantly smaller optical reflectance and enhanced light absorption in comparison to thin films [10, 11]. Due to the strain accommodation at the nanowire sidewalls, NWs are less restricted by lattice mismatch, which provides greater freedom in the bandgap engineering and the substrate selection [12]. In most cases, NWs arrays can be formed via the vapor–liquid–solid growth mechanism [13] using different epitaxial techniques, such as metal organic chemical vapor deposition or molecular beam epitaxy (MBE). One of the most important features of MBE growth is the ability to precisely control the shape, the height, the diameter and the surface density by an appropriate choice of technological parameters by exploring the diffusion-induced growth mode [14, 15], as well as to monitor the formation and time evolution of NWs in situ by the reflection high-energy electron diffraction (RHEED) technique [16]. PV properties of NWs have been investigated for different semiconductor combinations, like Si axial and core–shell single NWs [17], GaAs core–shell single NW and NW arrays [18, 19], and InAs/Si(111) NW arrays [20]. For the GaAs-based NW arrays, the best conversion efficiency has been demonstrated at the level of 1% at room temperature [18]. In this note, we report on the growth of Au-assisted GaAs p-type-doped NW arrays on the n-type GaAs(111)B substrate and their photovoltaic properties at different substrate temperatures. In our case, the highest efficiency of 1.65% is obtained, which is, to the best of our

G. E. Cirlin (✉) · Yu. B. Samsonenko
Institute for Analytical Instrumentation RAS, Rizhsky 26,
190103 St.-Petersburg, Russia
e-mail: cirlin@beam.ioffe.ru

G. E. Cirlin · A. D. Bouravleuv · I. P. Soshnikov ·
Yu. B. Samsonenko · V. G. Dubrovskii
St.-Petersburg Physics and Technology Centre for Research and
Education RAS, Khlopina 8/3, 194021 St.-Petersburg, Russia

G. E. Cirlin · A. D. Bouravleuv · I. P. Soshnikov ·
Yu. B. Samsonenko · V. G. Dubrovskii ·
E. M. Arakcheeva · E. M. Tanklevskaya
Ioffe Physical Technical Institute RAS, Politekhnikeskaya 26,
194021 St.-Petersburg, Russia

P. Werner
Max Planck Institute for Microstructure Physics, Weinberg 2,
06120 Halle/Saale, Germany

knowledge, higher than the values reported in the literature for the GaAs NW arrays.

Experimental Details

Growth experiments are carried out in EP1203 MBE reactor equipped with the effusion Au cell, on GaAs(111)B n-type ($n = 2 \times 10^{18} \text{ cm}^{-3}$) substrates. After the desorption of an oxide layer in the MBE growth chamber, ~ 100 -nm thick GaAs Si-doped ($n = 2 \times 10^{18} \text{ cm}^{-3}$) buffer layer is grown on the GaAs(111)B substrate. To ensure n-type doping of the buffer layer, a separate sample has been grown on the GaAs(111)B semi-insulating substrate at the same growth conditions as used for the NWs samples. Electrical measurements (van der Pauw method) confirm n-type doping of the layer with the carrier concentration $n = 2 \times 10^{18} \text{ cm}^{-3}$ at the Si cell temperature of 1100 °C. To promote the NW formation by the growth catalyst, the deposition of 0.3-nm thick Au layer is performed at 550 °C. The samples are then kept for 1 min at the same temperature in order to form liquid drops of alloy of Au with the semiconductor material of the substrate. The MBE growth of GaAs Be-doped ($P = 1 \times 10^{18} \text{ cm}^{-3}$, as measured from a planar layer) NWs is carried out by the conventional MBE at desired substrate temperature (520–580 °C) with a GaAs growth rate 1 monolayer (ML)/s. The process of NW formation is monitored in situ by RHEED technique. The nucleation of NWs is normally detected after 15 s. The transition to the wurtzite phase is typically observed after the deposition of ~ 30 ML of GaAs, which

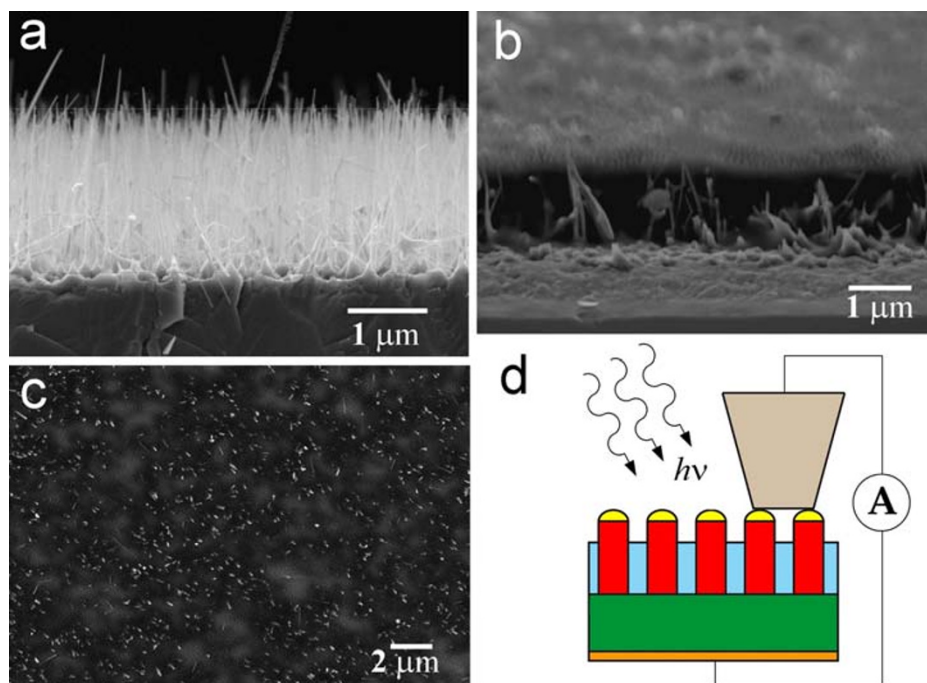
is consistent with earlier results for pure GaAs NWs [21]. Total NW growth time is set at 12 min. Four samples are grown at different substrate temperatures, resulting in different morphological properties. The final NW height varies from 1.7 to 2.2 μm , the NWs surface density amounts to 5×10^8 – $1 \times 10^9 \text{ cm}^{-2}$, and the average diameter is typically 50 nm.

To demonstrate the viability of our GaAs NW arrays for the use in PV application, several prototypes of solar cell devices are fabricated. To prepare the p–n junction, the spaces between the NWs are filled with the insulating photoresist (PMMA) via spin coating. After photoresist deposition, the sample surface is treated in oxygen plasma until the tips of GaAs NWs are exposed. Conventional Ohmic contacts for the backside of n-type substrate are fabricated by electron-beam evaporating of AuGe (30 nm) and Ni/Au (10/150 nm) combination having resulting contact resistance $\sim 1 \times 10^{-6} \text{ Ohm/cm}^2$. After each stage, the samples are studied by scanning electron microscopy (SEM) technique. SEM images are shown in Fig. 1a–c, where we also present the schematics of device structure (Fig. 1d).

Results and Discussion

I–V characteristics are measured using a Keithley 238 source meter. The samples are placed on a copper base from backside; a metallic sharp tip ($D = 0.5 \text{ mm}$) is used as top contact to the NWs/PMMA array. The energy conversion efficiency is determined by illuminating the

Fig. 1 SEM images taken at different stages of device structure preparation. **a** As grown GaAs NWs array, **b** after PMMA deposition, **c** top view of the resulting structure (after oxygen plasma treatment), **d** schematic view of the device structure testing



structures using a halogen arc-lamp with the calibrated power density of $P = 100 \text{ mW/cm}^2$.

Figure 2a shows typical current density–voltage (J – V) characteristic of the device structure measured in dark. The fabricated cells exhibit a clear diode behavior. Under the forward bias, a turn on of the device is observed at 0.7 V. At +0.5 V bias, the forward current density is varied within the range of 1.2 – 5.5 mA/cm^2 , while the reverse leakage current density is typically about 0.01 mA/cm^2 at -0.5 V . The rectification ratio is therefore greater than 10^2 at $\pm 0.5 \text{ V}$, which demonstrates a reasonable p–n junction between the p-type GaAs NWs and n-type GaAs(111)B substrate.

The fill factor (FF) and the power conversion efficiency (η) are calculated according to the following equations:

$$\text{FF} = (V_M J_M) / (V_{\text{OC}} J_{\text{SC}}); \quad (1)$$

$$\eta = V_M J_M / P, \quad (2)$$

where V_{OC} and J_{SC} are the open-circuit voltage and the short-circuit current; V_M and J_M are the voltage and the current density at the maximum power output, respectively, and P is the incident optical power density from the lamp.

In Fig. 2b, we present the J – V characteristics of the best sample (with the highest NWs) in dark and under illumination. Upon illumination of the front surface with the light, the structure yields an obvious photocurrent. The short-circuit current density J_{SC} equals 27.4 mA/cm^2 , and the open-circuit voltage V_{OC} amounts to 0.245 V . This corresponds to the conversion efficiency of 1.65% and the fill factor of 25% .

In Table 1, we summarize the conversion efficiency for different NW morphology. It is seen that the substrate temperature variation even within the range of 60° leads to significant (up to 20 times) change in the conversion efficiency. The morphology of NW arrays therefore strongly influences the device properties. This should be due to geometrical factors as well as different Be

incorporation processes at different temperatures (resulting in variable doping concentration profiles). Previously, it has been shown that the substrate temperature $\sim 550^\circ \text{C}$ is optimal for MBE growth of GaAs NWs at the GaAs growth rate of 1 ML/s [21, 22]. At this temperature, GaAs NWs exhibit better homogeneity as well as the highest NW/2D growth rate ratio. When the temperature is above or below this optimal value, a rapid decrease in the NW height is observed, which is consistent with the results of previous studies [21, 22]. We also observe the decrease in surface density as the temperature is increased to 580°C , which can also affect the conversion efficiency. The lowest efficiency corresponds to the sample grown at lowest temperature of 520°C , although its morphological characteristics are similar to other samples. Most probably, at this temperature, Be atoms incorporate in different sub-lattice site leading to a higher compensation level. All above mentioned factors could influence significantly the quality of device structures. For example, the results of Ref. [18] show that the substrate temperature variation of 20° (due to the inhomogeneity of the substrate heater) could change the conversion efficiency by the factor of 5.5, which is also in agreement with our study. Additionally, electrical properties of the device structures (V_{OC} and J_{SC}) still have to be optimized. In particular, for GaAs material we could expect higher open-circuit voltage. Two possible reasons may influence on relatively low V_{OC} . First, the

Table 1 Morphological characteristics and conversion efficiencies of different samples

T_s ($^\circ \text{C}$)	NWs surface density (cm^{-2})	NWs height (μm)	Conversion efficiency (%)
520	1×10^9	1.7	0.08
535	1×10^9	1.9	0.27
550	1×10^9	2.2	1.65
580	5×10^8	1.7	0.29

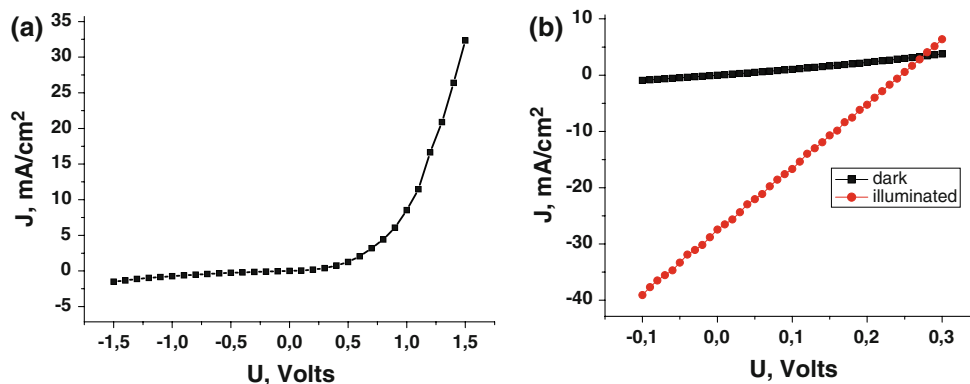


Fig. 2 **a** J – V characteristic of the device structure measured in dark, **b** J – V characteristics in dark and under illumination with an intensity of 100 mW/cm^2

parasitic two-dimensional layer is formed between the NWs and an additional p–n junction is created. Second, Be adatoms may segregate on the NW sidewalls forming depletion regions inside the NWs. Moreover, the fill factor FF ($\sim 25\%$) is also rather low. Further optimization may include the study of Be doping level influence on V_{OC} and J_{SC} . A heterostructured scheme may be considered in order to increase V_{OC} (e.g., GaAs/AlGaAs core–shell structures).

To conclude, we have investigated the PV properties of p-doped GaAs NWs array grown on the n-GaAs(111)B substrate at different substrate temperatures. The highest conversion efficiency 1.65% is achieved at 550 °C. To the best of our knowledge, this is the highest value obtained for the GaAs-based NW arrays.

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