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Observation of linear I-V curves on vertical GaAs nanowires with atomic force microscope

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Abstract. In this work we demonstrate the possibility of studying the current-voltage characteristics for single vertically standing semiconductor nanowires on standard AFM equipped by current measuring module in PeakForce Tapping mode. On the basis of research of eight different samples of p-doped GaAs nanowires grown on different GaAs substrates, peculiar electrical effects were revealed. It was found how covering of substrate surface by SiO₂ layer increases the current, as well as phosphorous passivation of the grown nanowires. Elimination of the Schottky barrier between golden cap and the top parts of nanowires was observed. It was additionally studied that charge accumulation on the shell of single nanowires affects its resistivity and causes the hysteresis loops on I-V curves.

1. Introduction

Semiconductor nanowires (NWs) attract significant attention as structural elements of electronic and optoelectronic devices [1]. Remarkable progress was achieved in application of NWs for solar cells, e.g. efficiency of such structures has grown already on one order during the last decade [2]. Typical solar cell based on NWs is a regular array of vertically oriented NWs grown on a semiconductor wafer. After the growth the array is covered by a transparent dielectric matrix, which is then covered with a transparent electrode. Despite the achieved progress, efficiency of NW-based solar cells is relatively low. Exist several factors limiting the efficiency of solar cells, e.g. high surface recombination velocity [3], difficulty of creating the ohmic contact with nanowires etc. Thus, study of the influence of surface modifying on electrical and photoelectrical properties of nanowires and electrical contacts to them is still topical.

Electrical contacts are required to study photoelectrical and electrical properties of NWs. Two most developed paths for creating such contacts are: contacting the horizontally lying nanowire with electron beam lithography (EBL) [4] and using a nanoprobe to form the contact with a vertically standing NW [5]. Creating contacts with EBL has few drawbacks, connected with laboriousness of this procedure. Besides that, substrate and resistance of the barriers, which appears between the contact and NW, are affecting the electrical properties of the NW [6]. Application of nanopores seems to be the most preferable method to investigate characteristics of individual nanowires. Geometry of such experiment
corresponds well with working conditions of solar cells [7]. Moreover, using such method doesn't require laborious processing and allows measuring large quantities of NWs.

Precise positioning of the nanoprobe is required for measuring the current-voltage characteristics (I-V curves). This is usually achieved by using a system, where the nanoprobe is accurately positioned on top of a NW in a scanning electron microscope (SEM) chamber. I-V curves of Ge [8], InAs [9], GaAs [10] etc. were measured with such method. Newly appeared results of measurements of I-V curves by scanning probe microscopy: scanning tunneling microscopy (STM) [11], conductive atomic force microscopy (C-AFM) [12] and photocurrent (PC)-AFM [7] demonstrate possibility to obtain conductivity and photoconductivity maps of NW arrays. Worthily note that obtaining the conductivity maps has been carried only for covered arrays, because uncoated NWs are flexible and become bended during scanning.

Recently, I-V curves were measured with nanometer scale lateral resolution on free standing NWs without SEM controlling procedure by the STM technique [11]. Despite the advantages of this method such as high lateral resolution and low resistance of probe-NW contact, construction of the microscope impedes the additional illumination and requires vacuum conditions. Instead of STM, the AFM provides wider opportunities for studying the photoelectrical properties of NWs. However, it is rather difficult to control the force of probe-NW interaction. In standard contact and semicontact AFM modes it is not possible to obtain stable electrical contact as NW can bend and break during scanning. In 2009 a technique called PeakForce Tapping® was introduced, which allows to control the maximum force, i.e. "peak force" of probe-surface interaction. This method was extensively used for nondestructive scanning of conductive arrays of carbon nanotubes in polymer matrix [13].

Present study is concerned with modification of surface and its influence on electrical and photoelectrical properties of GaAs NWs, including NWs with p-n junction. Two types of modification were examined: 1. passivation of the structure's surface by epitaxial GaP layer; 2. covering with SiOx, spin-on-glass (SOG) layer. Measurements were carried by C-AFM method in PeakForce mode. It is worth noting that individual current-voltage characteristics were obtained for single nanowires.

2. Materials and Methods

NWs were grown by VLS technique with Au-catalyst in MOVPE chamber. Eight different samples were investigated in this work and they were varied by three parameters: (1) two types of substrates with p- and n-type doping, with carrier concentration 1.3-1.6·10¹⁹ cm⁻³ and 1.6-3.9·10¹⁸ cm⁻³, respectively; (2) two alternatives of GaP-passivation [14], phosphorous passivation parameters are indicated in Table 1; (3) two variants of coating, i.e. with SOG and without SOG layer of thickness ~1 um (See Fig. 1 (b), (d)).

<table>
<thead>
<tr>
<th>Passivation</th>
<th>GaP-passivated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth time</td>
<td>120 sec</td>
</tr>
<tr>
<td></td>
<td>45 sec</td>
</tr>
<tr>
<td>Height</td>
<td>2.3 μm</td>
</tr>
<tr>
<td></td>
<td>1.1 μm</td>
</tr>
<tr>
<td>Diameter</td>
<td>~100 - 200 nm</td>
</tr>
<tr>
<td>DEZn flow</td>
<td>1 sccm</td>
</tr>
<tr>
<td></td>
<td>5 sccm</td>
</tr>
</tbody>
</table>

With such combination of samples it was expected to distinguish the influence of pn-junction, GaP-passivation and SOG coating separately on the IV-curves of individual nanowires. Additionally, it was expected to study the carrier excitement due to light illumination and localized NW surface charges.
Figure 1. SEM (a), (b) and AFM 3D (c), (d) images of GaAs NWs array. a), c) uncoated; b), d) coated by 1 μm SiO$_X$ layer. The conductivity skin (black conductive spots) is imposed on AFM topography image. The conductivity was measured with -2V applied to the substrate.

AFM studies were performed using the PeakForce Tapping® technique, based on the measurement of force-distance curves at each point of the scan, with periodic modulation of the tip-surface distance. During the topography imaging, it is also possible to measure the I-V curves of each point at the contact between the probe and surface. Studies were performed on Bruker Multimode 8 AFM under ambient conditions. The conductive PFTuna probes (Bruker) with Pt/Ir coating were used. In this device, the cantilever deflection is controlled by using an optical system consisting of a red laser and a 4-quadrant photodiode. Since the diameter of the laser beam exceeds the width of the cantilever, a portion of the radiation reaches the scanned sample, so all measurements were performed in the overilluminated conditions.

SiO$_X$ deposition does not lead to breaking of NWs away from the substrate and all NWs remain conducting, which is seen on Figure 1 (c), (d) as colored conductivity spots near top parts of NWs. Due to the convolution of the pyramidal shape of the AFM probe and the actual cylindrical shape of NWs, uncoated NWs have the pyramidal shape in the 3D image. Topography image of NWs have almost no noise, moreover changing of scanning direction did not alter the image which indicates absence of NWs bending during the scanning procedure. Interestingly, the areas of the highest conductivity, are located not in the top of the pyramid, but on their side faces. This effect is caused by practical observation of fact that conductive coating thickness at the end of the probe’s tip is small. Moreover, contact area of the tip and the NW Au cap is smaller than the contact area of pyramid faces of the probe and the Au cap, therefore face of the pyramid provides better conductivity. Furthermore, conductive coating can be ripped off the probe’s tip because of the scanning effort, which is a feature of the probes with Pt/Ir coating. Wear-resistant probes with conductive diamond-like coating could be used, but their resistance is in the scale of tens of MΩ, which drastically limits their applicability in NW I-V measurements.
Measurement of the I-V curves was performed as following: firstly, the conductivity map of NWs array was taken, and then the I-V curves were measured in the points with the highest conductivity. The experimental scheme is shown in Figure 2. Worth noting that in this configuration, the probe was grounded and voltage was applied to the substrate. The bottom contact was created by bonding of substrate to a metal wafer using special conductive silver paste. Since the area of such Ag contact and its conductivity are high, then such contact may be considered as ohmic. Moreover, substrates were highly doped and their resistance were only several Ohms.

3. Experimental results

3.1. p-NWs on p-substrate

Figure 3 shows the current-voltage characteristics for uncoated and coated by SiO$_x$ layer NWs of unpassivated (a) and GaP-passivated (b) samples, respectively, grown on the p-substrate. I-V curves for the passivated NWs are almost linear (coated) and linear ohmic (uncoated), while for the unpassivated NWs they are non-linear.

The linear shape of the I-V curves for uncoated passivated NWs indicate the absence of barriers between NW and substrate, as well as between Au cap and NW (Fig. 3 (c)). Thus, in the case of passivated samples Au cap has formed ohmic contact with NW that is not consistent with the previously
known data where Schottky barrier between Au cap and GaAs NWs was observed [15]. A possible explanation of this discrepancy, is the high doping level of studied NWs, which can lead to the formation of an ohmic contact [16], that is confirmed by the fact that in unpassivated NWs, which were less doped, the rectifying contact was formed. In addition, possible that GaP-passivation also contributed to the creation of an ohmic contact.

It is needed to be emphasized that for uncoated passivated NWs, the slope of I-V curve corresponds to resistance of 7 kΩ, which corresponds to the resistance of heavily doped GaAs NWs. Further, it seems possible to estimate the range of resistance $R$ of p-NW assuming that level of doping was $N_A = 10^{18}$, $10^{19}$ cm$^{-3}$, mobility $\mu = 400$ cm$^2$/V·s, length $l = 1$ µm and radius $r = 80$ nm. Geometrical dimensions were taken from the AFM topography data. Then, assuming that for highly doped and passivated NWs depletion near surface region is negligible, and according to the equation $R = l/en\mu\pi r^2$, where e-electron charge, we find that $R = 0.7 - 7$ kΩ. When calculating, we took the value of mobility corresponding to bulk GaAs. However, due to scattering by surface defects, as well as on the bulk structural defects, the charge carrier mobility in NWs is typically several orders of magnitude smaller [17]. In this case, assuming that the doping level is $10^{19}$ cm$^{-3}$, the mobility will be only one order of magnitude less than in bulk GaAs. Such high values of mobility are likely caused by the reduction of the surface influence due to the GaP-passivation.

The abovementioned arguments do not take into account the influence of the contact resistance between probe and NW, which can be higher than nanowire self-resistance and be responsible for the slope of I-V curves. However, taking into account the contact resistance will not lead to a change in the order of the estimated values. Additionally, it can be concluded that contact resistance between probe and uncoated NW is even less than 7 kΩ. Increased resistance of coated passivated NWs we associate with a significant increase in contact resistance, because after applying SiO$_X$ coating the height of the NWs is decreased up to 100 – 200 nm and in this case only the probe’s tip with relatively high resistance is contacting the NW. For higher NWs (unpassivated) such problem was not observed. Besides that, SiO$_X$ coating led to increase in the current through the NW, which can be explained by the passivation effect of SiO$_X$ coating.

### 3.2. p-NWs on n-substrate

Figure 4 shows the I-V curves for unpassivated (a) and GaP-passivated (b) NWs on n-substrate. Presence of p-n junction between the NW and the substrate affects the shape of I-V curve from linear to the diode shape. Fig. 4 also demonstrates that SiO$_X$ coating does not noticeably change the I-V curves of passivated sample, while it significantly changes its character for the unpassivated sample.

![Figure 4. I-V curves of the GaAs NWs grown on n-substrate: uncoated (black/blue) and coated (red) by SiO$_X$ layer for (a) unpassivated and (b) passivated samples. Black/blue curves indicate current during increasing/decreasing of the input voltage for uncoated NWs.](image-url)
I-V curves of unpassivated NWs have a pronounced hysteresis. Moreover, these I-V curves have saturation in the -2 – -3V range, whose presence can be explained by influence of the Schottky barrier between NW and Au cap. Indeed, in this case the current is determined by serial resistance of two diodes connected towards each other, i.e. p-n junction and Schottky barrier. Saturation in -2 – -3V range corresponds to the case with open Schottky barrier, and still closed p-n junction. Sufficiently high reverse current in this range is caused by effects of illumination and photoconductivity.

It is worth noting that such shape of I-V curves occurs in approximately 80% of uncoated unpassivated NWs. In rest 20% cases, the I-V curves had shape similar to the passivated samples. Differences in the shape of the I-V curves can be explained by various height of the Schottky barrier in the structure of unpassivated NWs. Schottky barrier height can be changed under the influence of charge accumulated by the NW surface states [18]. It was previously shown that this charge accumulation on the surface is possible for p- GaAs NWs near the Schottky barriers with applying an external electric field [19]. Hysteresis of I-V curves confirms charging and discharging of the NW surface near the barriers area.

Coating of NWs by SiO$_X$ layer leads to elimination of the hysteresis. Thus, SiO$_X$ passivates surface and blocks the capturing of charges on the NWs shell. It is known that presence of the pn-junction between NW and substrate can cause the photo voltage [20]. Since in our case I-V curves were measured under illumination, they were expected to be shifted along the axes. However, this effect was not observed even for passivated samples. This can be explained by the small pn-junction area, and by high doping level, which significantly reduces the lifetime of non-equilibrium charge carriers.

4. Conclusion
The effect of surface modification on the electrical and photoelectric properties of GaAs nanowires was investigated with AFM in PeakForce Tapping® mode. This method was successfully applied for measuring I-V curves of single freestanding vertical NWs. Contact resistance between the probe and NW was found to be less than 7 kΩ that allows investigating heavily doped GaAs NWs. The absence of Schottky barrier between Au catalyst cap and heavily doped NW with a GaP passivation layer was found. Charge accumulation on the surface of unpassivated GaAs NWs is found to change the height of the Schottky barrier between the cap and NW and produce hysteresis observed on I-V curves. The SiO$_X$ coating leads to surface passivation and suppresses the process of charge trapping on the surface.

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