Surface state density in wurtzite InP nanowires

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Abstract. The electrical properties of unpassivated wurtzite indium phosphide nanowires were studied by conductive atomic force microscopy. I-V curves of single nanowires with different diameters were obtained. For relatively thin nanowires, surface states caused full depletion of the nanowire volume and low conductivity. With increasing diameter, the conductivity increased significantly due to formation of an undepleted core in the nanowire. A surface state density (~ 6 · 10¹¹ cm⁻² eV⁻¹) was estimated from the radius and doping level of the nanowire. Additionally, experiments were performed to determine whether a piezoelectric current is generated while bending the nanowires. No current was detected.

1. Introduction

Semiconductor A₃B₅ nanowires (NWs) are prospective materials for constructing future nanoelectronic devices. Today the efficiency of solar cells with an active region made of InP nanowires reaches 18% [1]. Wurtzite (WZ) nanowires are of interest for hybrid devices harvesting both solar and mechanical energy due to the strong piezoelectricity of wurtzite [2]. Recently, piezoelectric current generation has been detected in wurtzite GaAs nanowires [3]. The generated current was observed only in passivated nanowires because of a high surface state density ($D_{it}$) in unpassivated nanowires. It is known that a high surface state density in GaAs NWs leads to a reduction in the NW conducting channel due to band bending and depletion [4]. Additionally, surface states lead to increased surface recombination and reduced efficiency of NW solar cells. The surface recombination velocity in InP nanowires is two order lower than in bulk GaAs NWs [5]. Thus, wurtzite InP nanowires are of interest because they combine strongly marked piezoelectricity with pronounced solar efficiency. However, discovering the piezoelectric generation in InP still remains an issue. As nanowires have a high surface-to-volume ratio, its electronic transport is strongly coupled with its surface properties. Surface states are able to trap charge carriers and thereby reduce conductivity. The aim of this research was to determine the density of surface traps in WZ InP nanowires and to detect a generated piezoelectric current.

2. Samples

InP nanowires were grown by molecular beam epitaxy on a highly-doped Si (111) substrate with a gold catalyst. The average NW length was about 5 um and its radius decreased from 100 nm at the base near the substrate to about 10 nm near the top of the NW. Note that the decrease was step-like (see the scanning electron microscopy (SEM) image in figure 1 (a)). An InP underlayer with a thickness of 300 nm was also formed on the surface of the substrate during the growth. Another
sample was grown using graphene on a SiC substrate. InP NWs grown on the graphene were of a typical length of 2 μm and an average diameter of 50 nm without a step-like tapering (figure 1 (b)). Both samples had a pure WZ crystal structure that was proved with transmission electron microscopy (not shown here) [6].

Figure 1. SEM images of investigated InP wurtzite nanowires grown on (a) Si, (b) graphene.

3. Experimental details

The experiment was based on conductive atomic force microscopy (AFM). Measurements were performed on an NTegra AURA microscope (NT-MDT, Russia) with probes covered by a W₂C conductive coating. A conductive AFM probe can be used to bend and deform a single NW and simultaneously measure the electric current flowing through the substrate-NW-probe circuit (see figure 2). Moreover, since the NWs have a step-like shape, it is possible to cut a NW step-by-step (at a step boundary) as shown in figure 2. As a result of this cutting, the probe forms an electrical contact with a 10-nm thick NW, then with a 30-70-nm thick one, and then with a 100-nm thick NW stump near the substrate.

The experimental algorithm of the study was the following: to estimate the level of unintentional doping from the breakdown voltage of the InP underlayer ($N_d$), then to find the diameter ($2r$) where the conductivity significantly increases by measuring $I$-$V$ curves for NWs of different diameters. This increase in conductivity indicates the formation of an undepleted core in a NW. Since the depletion is a known function of the diameter, doping level and surface state density in NWs, it is possible to estimate the $D_{it}$.

Figure 2. Diagram of the experiment. At the first stage, a nanowire was found using the constant height mode and the AFM tip was placed on its top. Next, an $I$-$V$ curve was obtained. After that, several NW bends were made to cut its top. Finally, another $I$-$V$ curve was recorded.
Detection of the piezoelectric current was performed by scanning a NW at a constant height (z), where z is the distance between the probe and the substrate, and is smaller than the NW height. During scanning, the probe bent the NW and a short circuit current was detected. More details of the measuring procedure are presented here [3]. Experiments were performed in dark ambient conditions. About twenty NWs with different diameters were measured.

4. Results and discussion

Figure 3 shows an I-V curve measured on a InP underlayer. The doping level of the InP underlayer can be determined using its relationship with the avalanche breakdown voltage on the I-V curve. The relationship was taken from the Kyuregyan and Yurkov study [7]. The value of the breakdown voltage was 10 V (see figure 3) and the corresponding doping level turned out to be 4·10^{17} cm^{-3}. The NW doping level was considered to be the same.

![Figure 3. I-V curve of the InP underlayer.](image)

Figure 4 shows the series of I-V curves measured on the NWs with diameters ranging from 10 to 100 nm. I-V curves measured for NWs with diameters of 10-70 nm exhibit a very low current (see inset in figure 4), comparable to the sensitivity of our device. Note that the NWs grown on the graphene substrate with a diameter of 50 nm also show a similar low current. Only for a NW with a diameter of 100 nm, the current increases by three order of magnitude. Thus, we can assume that a NW with a 70-nm diameter is fully depleted, while the 100-nm NWs have an undepleted conductive core.

To estimate the surface state density in the studied NWs, we checked for the existence of an undepleted core using the analytical model suggested by Schmidt et al. in [8]. For a nanowire with a radius r, a surface potential \( \psi_0 \), a doping level \( N_D \) and a surface state density \( D_{it} \), the expression for the depleted region \( r_d \) is as follows:

\[
r_d = \sqrt{r^2 - \frac{2r \rho D_{it} \psi_0}{N_D (1 + \frac{r \rho D_{it}}{2e})}}
\]

For the doping level \( N_D = 4\cdot10^{17} \) cm^{-3}, the NW with a diameter of 70 nm is fully depleted when the surface state density is 6·10^{11} cm^{-2}eV^{-1}. On the other hand, a NW with a diameter of 100 nm is fully depleted only with \( D_{it} = 8\cdot10^{11} \) cm^{-2}eV^{-1}. Thus, we can conclude that the surface state density in wurtzite InP nanowires is (6-7)·10^{11} cm^{-2}eV^{-1}. The obtained value is consistent with the value previously measured using the photoluminescence technique (1·10^{12} cm^{-2}eV^{-1}) [9].

![Figure 4. I-V curves measured for InP nanowires of different diameters.](image)
Experiments to detect generation of a piezoelectric current were performed for NWs with diameters in a range of 10-100 nm. Piezoelectric current generation was not detected in non-conducting thin NWs or in undepleted 100-nm-thick NWs. The absence of a generated current may be related to a relatively low doping level and a high surface state density, and will be studied in future.

5. Conclusion
The $I$-$V$ curves of InP nanowires with a wurtzite crystal structure were measured for NWs with diameters ranging from 10 to 100 nm. Measurements were performed by conductive atomic force microscopy. The current in a NW with a diameter of 100 nm is three orders of magnitude higher than the one in a NW with a diameter of 70 nm. This indicates the formation of an undepleted conductive channel in the core of the thicker NW. This difference allows us to estimate the surface state density in naturally oxidized InP NWs as of $(6-7) \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. Experiments designed to detect a generated piezoelectric current during NW bending showed the absence of a generated current.

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