Studying surface Fermi level pinning in GaP nanowires with gradient Kelvin probe microscopy

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Abstract. In this work, we use scanning Kelvin probe force microscopy to study surface Fermi level pinning in horizontal undoped nanowires with axial GaP/GaPAs heterojunction. The nanowires were separated from the growth substrate and dispersed on smooth surface of Ni/Si substrate. Then longitudinal and transverse surface potential profiles of several nanowires were captured. The study revealed a distinction between the work function of GaP and GaPAs regions. It was shown that the Fermi level in undoped GaP nanowires was pinned in the middle of the energy gap.

1. Introduction
Semiconductor nanowires (NWs) remain prospective building blocks for the next generation of nanoscale electronic devices. Mechanical strength and the ability to be grown on highly mismatched substrates have led to the development of NW-based optoelectronics [1] and photovoltaics [2,3]. In this case, understanding NWs transport properties is of interest. It is well known that surface effects in one-dimensional nanostructures are strong due to high surface to volume ratio. In particular, surface Fermi level pinning leads to a surface band bending and to a formation of the near surface depleted area. In this case, the conductivity of the III–V NWs with an oxidized surface is governed mainly by surface states. The depletion area width is governed by doping level, NW diameter, surface state density, and position of the Fermi level pinning [4]. To quantitatively analyse transport properties of NW, one should know a position of the surface Fermi level pinning (work function). Conventionally, NW surface is terminated by [110] facets. Fermi level in GaAs and in InAs [110] surface with native oxide layer is pinned in the midgap and near the conduction band, respectively [5,6], resulting in different transport properties [7]. Scanning Kelvin probe force gradient microscopy (KPFGM) proved to be an effective tool to directly investigate NW work function. Recently, in has been shown that excess arsenic is responsible for the Fermi level pinning in III-As NWs with native oxide [8]. However, surface Fermi level position in III-P NWs with native oxide layer is still poorly studied. GaP NWs are prospective for betavoltaic devices [9] and photodetectors [10], while wurtzite GaP is promising for green-range optoelectronics due to direct band gap [11]. For designing GaP NWs based devices with controllable electronic parameters, the position of the Fermi level pinning has to be obtained. In this work, we measure the work function on the [110] crystal plane of NWs with GaP/GaPAs axial heterojunction.

2. Experimental
Undoped Gallium phosphide NW arrays were synthesized by solid source molecular beam epitaxy using Veeco GEN-III machine on (111) silicon substrate (Fig. 1a). Self-catalytic vapour-liquid-solid
mechanism with the use of gallium droplet acting as a catalyst was used. The average NWs length was approximately 5 μm. Arsenic source was turned on after 2 μm growth. The bottom part of NWs is 130 nm thick GaP with arsenic shell, while the top part is 150 nm thick GaPAs. NW crystal structure was studied with transmission electron microscopy (TEM) (Fig. 1b) and turned out to be cubic with a lot of stacking faults with 200 nm wurtzite insertion near GaP/GaPAs interface. The top 250 nm GaP region has a zincblende structure with small number of twin-defects. Phase features in the top of III-V NWs may be due to the contact angle behaviour during the catalytic drop disappearance in the end of the growth process [12]. Energy-dispersive X-ray spectroscopy (EDS) confirmed that NW array was separated from the growth substrate and dispersed on a Si/Ni substrate for subsequent atomic force microscopy (AFM) measurements. AFM topography of individual horizontal NW is shown in Figure 1f. AFM measurements were carried out using Ntegra Aura setup (NT-MDT, Russia). We used silicon probes with W2C conductive coating, 3.5 N/m average force constant, and 30 nm tip curvature radius. Fermi level pinning position was determined by phase-modulated Kelvin probe force gradient microscopy (KPFGM) [13]. At each scanning point, this technique measures the surface potential, which is the difference between the work functions of a microscope probe and of a semiconductor surface. The latter value presents the energy gap between the vacuum level and the surface Fermi level pinning position. The scanning process is one-passed and includes two steps in each scanning point. First, the topography is measured in semi-contact regime. Second, the probe magnitude is being reduced by one order, the tip-sample distance is 20 nm, constant voltage $U_{\text{sample}}$ is applied on the sample, and the cantilever phase $\phi$ is measured with respect to the $U_{\text{sample}}$. The phase is proportional to squared contact potential difference $U_{\text{CPD}} = U_{\text{tip}} - U_{\text{NW}}$. In each scanning point the parabolic fit $\phi(U)$ is obtained. The voltage of the parabola apex is $U_{\text{CPD}}$. Inherently, KPFGM technique is very similar to electrostatic force microscopy (EFM), but output signals are different as EFM shows only phase of cantilever oscillations and does not show surface potential. More detailed KPFGM description can be found elsewhere [14]. The force gradient technique is much more sensitive than a regular KPFM [15] and allows studying low-dimensional nanostructures such as NWs. Before each measurement, the work function of the probe was calibrated using freshly cleaved highly oriented pyrolytic graphite (HOPG) with well-known work function ($\Phi_{\text{HOPG}}$) of 4.48 eV [16]. Then the NW work function $\Phi_{\text{NW}}$ can be expressed as $\Phi_{\text{NW}} = 4.48 + (U_{\text{HOPG}} - U_{\text{NW}})/e$, where $U_{\text{HOPG}}$ is the surface potential of the HOPG measured by the same probe as $U_{\text{NW}}$ and $e$ is the electronic charge. The measurements were carried out in medium vacuum (around 1 Torr) in order to increase cantilever Q-factor up to ~2500 and decrease the role of potential shielding by the surface water layer.

**Figure 1.** (a) Scanning electron microscopy image of GaP/GaPAs NWs array, (b)-(e) TEM and EDS study of individual NW, (f) AFM scan of individual NW.
Figure 2. KPGFM scans of individual NW containing topography and surface potential: (a) longitudinal scan containing GaP/GaPAs interface; (b) transverse scan of GaP part; (c) transverse scan of GaPAs part.

3. Results and discussion
Figure 2 shows the main AFM results. The KPGFM profile along the NW is shown in Figure 3a. The GaP/GaPAs interface is in the middle of the profile, at 1000 nm. The right part is thicker; therefore, this NW region corresponds to GaPAs. Figure 2b, c shows KPGFM profiles across GaP and GaPAs regions, correspondingly. All profiles indicate that the surface potential is about 70 mV higher in GaP part. It means that GaPAs work function is 70-100 meV lower than that of GaP. This is confirmed by multiple measurements on several NWs. The transverse profiles overestimate the potential signal on NW sides, so only the signal from the central [110] facet (-50 mV on GaP and -120 mV on GaPAs) should be taken into account. The probe work function was checked out on freshly cleaved HOPG and turned out to be 4.9 eV. KPGFM lateral resolution is less than 50 nm for 30 nm probe radius and 20 nm tip-sample distance during the phase measurement [15]. Taking into account that the width of top [110] facet is 2-3 times larger, we assume that the measurement error is mainly due to the KPGFM noise that does not exceed 20 mV. Thus, GaP and GaPAs work functions are 4.95±0.01 and 5.02±0.01 eV. Taking into account that GaP electron affinity is 3.8 eV, one can conclude that the Fermi level of undoped NWs is pinned in the midgap. The obtained work function value is in a good agreement with Ref. [17]. The surface states responsible for the pinning have energy around 1.2 eV below the conductive band minimum. It is shown in Ref. [18] that such pinning position can be attributed to P-derived dangling bond states.

4. Conclusion
Surface electronic properties of undoped GaP/GaPAs nanowires were studied with Kelvin probe force gradient microscopy. The values of surface Fermi level pinning position at [110] facet turned out to be 4.95±0.01 and 5.02±0.01 eV in GaP and GaPAs, respectively. Fermi level of undoped GaP NWs was
pinned in the midgap. The obtained data are important for calculation of the surface depletion layer thickness that is crucial for understanding the transport properties of nanowires.

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