Probing electric properties of GaP nanowires with Kelvin probe force microscopy

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Abstract. Surface electronic properties of GaP nanowires were investigated using scanning probe force microscopy. I-V curves of individual free-standing NWs with different doping types were obtained. Surface Fermi level positions in the nanowires of different crystal phases and doping types were extracted using phase-modulated Kelvin probe force microscopy. The results indicate on weak Fermi level pinning in GaP nanowires. The difference between wurtzite and zinc blende GaP work function is observed.

1. Introduction
Semiconductor nanowires (NWs) stay in focus of attention. NW Mechanical strength and the ability to be grown on highly mismatched substrates as well as significant progress in growth and characterization techniques opened paths to fabrication of a wide range semiconductor NW-based devices in nanoelectronics, photovoltaics, sensing and energy harvesting. In this case, comprehensive understanding of NW electronic transport is of interest. Surface phenomena play critical role in the transport properties of low-dimensional semiconductor structures. In the case of nanowires, the surface effects are especially critical due to the high surface to volume ratio. Termination of the lattice periodicity leads to the formation of dangling bonds on the surface. These bonds, coupled with surface defects and native oxide states, accounts for surface electronic states inside energy gap. At a high density of surface states, their influence on the surface conductivity becomes dominant. In particular, presence of surface states leads to Fermi level pinning. In this case, the conductivity of the III-V NWs with oxidized surface is governed mainly by surface states. Conventionally, III-V NW surface is terminated by (110) facets. Surface electronic properties of III-As semiconductors are widely investigated via Kelvin probe force microscopy (KPFM), scanning tunneling spectroscopy (STS) and other characterization techniques. Fermi level in GaAs and in InAs (110) surface with native oxide layer is pinned in the midgap and near the conduction band respectively, resulting in different transport properties. The surface Fermi level does not coincide with the bulk level, which leads to the transfer of carriers and energy band bending. Midgap-pinned Fermi level leads to the formation of near-surface depleted area whose width is governed by doping level ND, NW diameter a, surface state density, and work function. The difference between $E_F$ in n + and p + (110) GaAs doesn’t exceed 200 meV [1] due to strong pinning effect so the conductivity of thin NWs is terminated.
Early studies of electronic surface states on UHV cleaved GaP (110) revealed Fermi level pinning 1.5-2.1 eV above the valence band depending on cleavage-induced surface states. Unlike other III-Vs, the tail of intrinsic surface band lies in the band gap in case of GaP [2]. To quantitatively analyze transport properties of GaP NW, one should know a position of the surface Fermi level pinning (work function) as it is necessary for calculating the Schottky barrier height and optimizing ohmic contacts. A strong Fermi level pinning effect induces high contact resistance and obstructs realization of ohmic contact. However, surface Fermi level position in III-P NWs with native oxide layer is still poorly studied. Gallium phosphide (GaP) NWs are prospective for betavoltaic devices and photodetectors, while wurtzite GaP is promising for green-range optoelectronics due to direct band gap. GaP window is often used as a window layer in AlInGaP LEDs [3]. For designing GaP NW-based devices with controllable electronic parameters, the rate of pinning effect and the work function value have to be obtained. GaP NWs are still poorly studied from this point of view.

2. Results and discussion

In phosphides and arsenides, it has been shown that the appearance of the wurtzite phase is restricted to the nanowire form and is never observed in the bulk. Wurtzite III-V NWs are attracting a great interest in opto- and nanoelectronics. The influence of the crystal phase on transport properties is questionable.

It was shown, that the work function of (110) ZB and (1010) WZ InAs NWs differs at least by 50 meV [4]. In this work, we discuss the effect of the crystalline phase on the work function of GaP NWs. We obtain WF values of ZB and WZ i-GaP as well as n- and p-GaP. Fermi level pinning is studied with respect to NW diameter. GaP nanowires were synthesised in self-catalysed mode on Veeco Gen-III MBE setup on (111) Si substrates. Gallium drops were used as catalytic caps instead of Au in order to improve crystal quality. Three samples with different doping type and crystal structure were studied. Sample 1 is 5 μm long i-GaP (see figure 1, a). Sample 2 is silicon-doped (see figure 1, b). Silicon is known to be n-dopant in gap. Sample 3 is p-GaP doped with Be. NW crystal structure of sample 1 was studied with transmission electron microscopy (TEM) and turned out to be polytypic with mainly twinned zinc blende crystal structure and wurtzite base and top (see inset in figure 1, a). Self-catalysed VLS mode, which has been realized mainly in molecular beam epitaxy (MBE), allows one to modify the droplet volume during growth by changing the ratio of the fluxes of group III and group V species. During the end of growth process Ga droplet was expended resulting in the formation of 500 nm long wurtzite (WZ). WZ phase in III-V nanowires is being formed in case of triple line nucleation – at specific volume and contact angle of Ga droplet [5]. Thus, WZ segments in NW bases may be formed due to droplet formation while that in tops emerged due to it consumption. Sample 2 and 3 possess zinc blende crystal structure.

Figure 1. (a) SEM image of sample 1 (polytypic WZ/ZB i-GaP NWs), TEM image of the NW top is shown in the inset; (b) and (c) SEM images of sample 2 (n-GaP ZB NWs) and sample 3 (p-GaP ZB NWs).
WZ inset on a big number of NWs on sample 1 was confirmed by micro-Raman mapping. For mapping we used Horiba Lab RAM setup with 532 nm excitation laser and x100 lens. 1D Raman scan along a NW is shown in figure 2. The 1D profiling revealed strong signal from base and top of NW caused by waveguiding effect. Black and red curves represent Raman spectra from base and top respectively. Left shoulder on transverse optical mode at 357 cm\(^{-1}\) corresponds at the presence of WZ phase and is observed only near the NW top. WZ phase is absent relating to samples 2 and 3 because the droplet wasn’t consumed because of rapid temperature decreasing in the end of the growth.

![Figure 2](image-url)

**Figure 2.** Micro-Raman mapping of ZB i-GaP nanowire with WZ inset. Left: 1D micro-Raman profile along a NW. Right: Raman spectra from bottom (black) and top (red) NW ends.

We check individual NW conductivity with conductive atomic force microscopy (c-AFM) study by obtaining its I-V curve. The first conductive electrode was created using conductive AFM probe being accurately positioned on the NW top. The second one was formed between the highly doped Si growth substrate and an AFM sample holder. scheme of this experiment and the results for sample 2 are shown in figure 3, a. The curve slope as well as knee and breakdown voltage values correspond at n-type doping. The I-V curve from individual NW from sample 3 is shown in figure 3, b.

![Figure 3](image-url)

**Figure 3.** I-V curves from individual n- (a) and p- (b) doped GaP nanowires

Kelvin probe force microscopy (KPFM) is specializing in structural and electronic surface characterization of semiconductors. KPFM allows mapping contact potential difference (CPD) between a sample and a metallic probe. Knowing the probe work function, one can calculate the sample work function from CPD. KPFM is typically utilized for investigating planar structures such as p-n junctions and segnetoelectrics. Recently, a publication activity over nanowire-related KPFM studies increased. GaN and InP NWs with axial p-n junction were investigated [6-8]. It was shown
that the Fermi level at oxidized cleavage surfaces of AlGaAs and GaInAs is pinned at the same position, which is attributed to excess surface arsenic [9] CPD value and band bending of individual GaN and Si nanowires were studied with respect to diameter [10]. These studies prove that KPFM spatial resolution allows distinguishing and qualitative analysis of work function of n- and p- regions in a single nanowire. However, the effect of crystal phase on work function is more delicate, and convenient amplitude-modulated (AM) KPFM that was used in these works seems to lack spatial sensitivity for its registration.

KPFM measurements were performed on NT-MDT NTegra Aura setup under low-vacuum (5×10⁻⁵ Bar) conditions. The NW arrays were transferred from the growth substrates on the surface of freshly cleaved highly oriented pyrolytic graphite (HOPG). HOPG work function (4.48 eV) was well defined [11] which is helpful for quantitative data analysis. The main idea of KPFM may be summarized to utilizing relations between electrodynamic force between probe and sample and the probe amplitude and phase. We utilize double-pass phase-modulated (PM) KPFM, which is described in detail in [12]. Firstly, the morphology was acquired using the semi contact mode. Secondly, based on the morphology profile obtained, the tip was retracted from the surface and vibrated at a low amplitude. Then, the dc tip to sample polarization was applied only during the second pass and frequency or phase shifts were detected. Thus, constant distance explorations of long-range force gradients can be achieved and linear conditions can reasonably be obtained. Gradient KPFM techniques have much higher spatial resolution which is crucial for nanostructures analysis. We used rigid TipsNano HA NC/W2C probes (force constant k=12 N/m, resonant frequency f=235 kHz). After sampling several probes, we have found that rigid ones have better spatial resolution and signal-to-noise ratio in KPFM due to higher quality factor.

AFM topography and CPD scan of sample 1 are shown in figure 4. CPD value on HOPG is stabilized at -0.05 V so one can estimate the probe work function as \( \phi_{probe} = 4.48 - 0.05 = 4.43 \) eV. The CPD value significantly varies along the NW. Thus, in the bottom side of NW (top side of scan) it amounts to -0.1 V, against 0 V and 0.15 V at the middle and at the very end of NW. We associate the increased value of CPD at the NW top with WZ crystal structure. In this case, KPFM measurements are in agreement with TEM, CL and micro-Raman mapping. Surface potential gradient along the NW may be connected with gradient of flat defects density arising from changed growth conditions. Thus, work function of ZB and WZ GaP are 4.43 and 4.28 eV respectively. The electron affinity in GaP is 3.8 eV, so for both cases surface Fermi level is pinned near the middle of band gap.

![Figure 4. AFM topography and CPD scans of ZB i-GaP nanowire with WZ inset.](image-url)
KPFM results for sample 2 are shown in figure 5. CPD value on n-GaP is 0.6 V and doesn’t significantly change along the NW. Thus, we estimate n-GaP work function as 5.0 eV. The significant difference between i- and n- GaP WF indicates on weak Fermi level pinning in GaP in comparison with GaAs.

![AFM topography and CPD scans of n-GaP nanowire](image)

**Figure 5.** AFM topography and CPD scans of n-GaP nanowire

KPFM results for sample 3 are shown in figure 6. CPD value on p-GaP is 0.05 V and doesn’t significantly change along the NW. The increased value of CPD near the NW base in the bottom of the scan may be attributed to growth instability. Thus, we estimate p-GaP work function as 4.33 eV that is close to the data obtained on i-GaP indicating on low Be-doping level.

![AFM topography and CPD scans of p-GaP nanowire](image)

**Figure 6.** AFM topography and CPD scans of p-GaP nanowire

3. Conclusion
In this work we present a study of surface potential of GaP nanowires with different crystal structure and doping type. We observe different work function between wurtzite and zinc blende GaP (4.43 and 4.28 eV respectively). The response from nanoscale regions possessing different crystal phases within the same nanowire was quantified due to high spatial resolution of force gradient Kelvin probe force.
microscopy. Work function values for n- and p- doped ZB GaP were 5.0 eV and 4.33 eV respectively. Significant difference between the work function with respect to doping type indicates on relatively weak pinning in gallium phosphide.

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References
[1] Alekseev P, Dunaevskiy M, Cirlin G, Reznik R, Smirnov A., Kirilenko D, Davydov V and Berkovits V 2018 Nanotechnology 29 314003
[2] Guichar G, Sebenne C and Thuault C 1979 Journal of Vacuum Science and Technology 16 1212-15
[3] Tseng M, Chen C, Lai N, Chen S, Hsu T, Peng Y and Horng R 2014 Optics express 22 A1862-67.
[4] Hjort M, Lehmann S, Knutsson J, Zakharov A, Du Y, Sakong S, Rainet T, Nylund G, Lundgren E, Kratzer P, Dick K and Mikkelsen A 2014 ACS nano 8 12346-55
[5] Dubrovskii V 2015 The Journal of chemical physics 142 204702.
[6] Minj A, Cros A, Auzelle T, Pernot J and Daudin B 2016 Nanotechnology 27 385202
[7] Sun X, Wang X, Wang P, Sheng B, Li M, Su J, Zhang J, Liu F, Rong X, Xu F, Yang X, Qin Z, Ge W and Shen B 2017 Optical Materials Express 7 904-12
[8] McKibbin S, Colvin J, Troian A, Knutsson J, Webb J, Otnes G, Dirscherl K, Sezen H, Amati M, Gregoratti L, Borgstrom M, Mikkelsen A and Timm R 2019 Nano letters 20 887-95
[9] Parida S, Sahoo A, Madapu K, Jaya S and Dhara S 2020 Applied Surface Science 510 145502
[10] Koren E, Hyun J, Givan U, Hemesath E, Lauhon L and Rosenwaks Y 2011 Nano letters 11 183-7
[11] Hansen W and Hansen G 2001 Surface science 481 172-84
[12] Portes L, Girard P, Arinero R and Ramonda M 2006 Review of Scientific Instruments 77 096101