Work function of polytypic gallium phosphide nanowires

V A Sharov$^{1,2}$, P A Alekseev$^2$, V V Fedorov$^1$, A V Ankudinov$^2$ and I S Mukhin$^{1,3}$

$^1$ Alferov University, Saint-Petersburg 194021, Russia  
$^2$ Ioffe Institute, Saint-Petersburg 194021, Russia  
$^3$ ITMO University, Saint-Petersburg 197101, Russia

E-mail: vl_sharov@mail.ru

Abstract. In this work we investigate the work function of gallium phosphide nanowires by the means of frequency-modulated Kelvin probe force microscopy. Polytypic wurtzite/zinc blende nanowires were synthesized via self-catalytic molecular beam epitaxy. Mixed crystal phase was achieved by controlling the catalytic droplet contact angle and confirmed via transmission electron microscopy and Raman spectroscopy. Kelvin probe study showed a contrast between the work function of (110) zinc blende and (11\bar{2}0) wurtzite gallium phosphide: $\phi_{\text{ZB}} = 4.28$ eV and $\phi_{\text{WZ}} = 4.2$ eV. Also, it was shown that sub-monolayer arsenic shell increases the work function up to 4.75 eV. Thus, two mechanisms for work function adjustment in the range 4.2-4.75 eV are shown. The results are important for optimization of Schottky barriers in nanowire-based devices.

1. Introduction

Semiconductor nanowires (NWs) provide new design strategies for nano-electronic and photonic devices [1]. Crystal phase engineering is one of the key advantages of non-nitride III-V NWs. Depending on the growth conditions, they can be synthesized in cubic (zinc blende, ZB), hexagonal (wurtzite, WZ) or mixed crystal phase [2]. This provides an additional degree of freedom for optical and transport properties adjustment [3].

Gallium phosphide (GaP) is a perspective material for nanophotonics as it exhibits broad transparency range, high values of nonlinear refractive index and good thermal conductivity. WZ GaP NWs attract interest due to pseudo-direct band structure and good photocatalytic properties [4,5]. For the further progress in the functional applications of GaP NWs, a study of their surface electronic properties, governed by a work function ($\phi$) value, is demanded. Work function tailoring allows increasing the efficiency of photocatalysis as well as reducing the Schottky barrier height between semiconductor nanostructure and metal contact providing better electric properties. There are recent theoretical papers on the work function tuning in GaAs NWs [6]. However, there is no such studies for GaP NWs as the interest in their investigation appeared relatively recently.

Work function corresponds to a gap between surface Fermi level ($E_{\text{FS}}$) and the vacuum level ($E_{\text{VAC}}$), $\phi = E_{\text{VAC}} - E_{\text{FS}}$ or $\phi = \chi + (E_C - E_{\text{FS}})$, where $\chi$ - electron affinity, $E_C$ - conduction band minimum. The work function of semiconductor nanostructures is sensitive to the microscopic structure of the surface. The surface Fermi level $E_{\text{FS}}$ does not coincide with the bulk Fermi level due to its pinning caused by surface states of various nature (dangling bonds, surface defects, native oxide formation). Since NWs have high surface to volume ratio, their electronic properties are controlled by the $E_{\text{FS}}$ and by the surface state density. Besides variation of the $E_{\text{FS}}$, the work function can be controlled by changing the electron affinity.
Despite the well known effects of the phase polytypism in III-V NWs, the influence of the crystal phase on its electronic properties remains ambiguous. Among the latest results, it is demonstrated, that the value of $\phi$ in case of ZB (110) and WZ (10\overline{2}0) surfaces of InAs NWs differs by at least 50 meV [7]. Work function of both ZB and WZ GaP NWs is rather poorly studied.

The present study presents experimental data on work function distribution over polytypic ZB/WZ GaP NW and showing the difference between different crystal phases. We also show the ability to control electron affinity by covering the NW with arsenic shell.

2. Materials and methods

The NW growth was carried out in self-catalytic mode using Veeco Gen-III molecular beam epitaxy setup. NW crystal structure was investigated via transmission electron microscope (TEM) and Raman micro-spectroscopy (Horiba LabRam HR-800 with 532 nm excitation laser and \times 100 lens with 0.9 numerical aperture), NW geometry was studied via scanning electron microscopy (SEM) and atomic force microscopy (AFM). Surface electronic properties were investigated via frequency-modulated Kelvin probe force microscopy (FM-KPFM) under low-vacuum ($5 \times 10^{-5}$ Bar) using NT-MDT NTegra Aura setup. FM-KPFM mapping provides information about contact potential difference (CPD) between a sample and a conductive probe. CPD corresponds to work function difference between the probe and the sample: $CPD = \phi_{\text{probe}} - \phi_{\text{sample}}$. For quantitative data analysis, before FM-KPFM measurements the sample was transferred onto auxiliary substrate made of freshly-cleaved highly oriented pyrolytic graphite (HOPG) which work function (4.48 eV) is well defined. Rigid TipsNano HA_NC/W\textsubscript{2}C probes were used (force constant $k=12$ N/m, resonant frequency $f=235$ kHz, curvature radius less than 35 nm). Estimated FM-KPFM Spatial resolution is less than 60 nm [8] which enables distinguishing of the work function fluctuations along a NW.

3. Results and discussion

SEM image of the grown array is shown in Figure 1. On average, the NWs possess 5 $\mu$m length and pronounced thickness change along the growth direction: from 270 nm near base to 200 nm near top. The inset in Figure 1 shows TEM image of a NW top region.

Figure 1. SEM image of the NW array on the growth substrate. The inset shows TEM image of the top region of a single NW confirming the presence of wurtzite phase.

TEM study confirms mixed crystal phase. For the most part, the crystal structure is zinc blende with multiple twinning while the top region is pure wurtzite. The formation of WZ phase in III-V nanowires is associated with the triple line nucleation occurring at specific volume and contact angle of Ga droplet [9]. Phosphorus flux during the upper NW segment growth was increased to promote consumption of the droplet and, consequently, the formation of WZ crystal phase resulting in 500 nm WZ region near NW top. Remarkably, stabilization of the WZ GaP phase has only been previously demonstrated in gold- and silver- catalyzed NWs grown by metal organic chemical vapor deposition or chemical beam epitaxy [10]. Unintentional doping induced by foreign catalyst or organic precursors can significantly...
alter electronic structure of GaP [4]. Thus, WZ self-catalyzed NWs, which are free from this problem, are of great interest.

Also, 30 nm thick WZ GaPAs nanodisks were grown in the middle of the NWs. Due to inevitable radial NW growth, shell formation occurs. Thus, NWs bottom segments can be covered with As-containing GaPAs shell which thickness should be in the range of 1.5-2 Å based on the estimated radial growth rate value of 3-4 Å/min.

For subsequent measurements, NWs were transferred on HOPG substrate. In order to additionally prove the polytypic structure of the NW of interest, Raman study was conducted. Figure 2 shows Raman spectra near transverse optical (TO) mode in the NW middle region (black curve) and top region (red curve).

![Figure 2](image.png)

Figure 2. Raman study of individual polytypic GaP NW. The inset shows optical image with marked positions of the pumping spot.

The red curve has, in addition to TO mode at 367 cm\(^{-1}\), a pronounced peak at 357 cm\(^{-1}\). This peak is attributed to \(E_2^H\) mode, which is a common marker for the presence of WZ phase [11] as other WZ modes merge with ZB spectrum.

The same NW was investigated by the means of FM-KPFM. The results are shown in Figure 3. Figure 3a and b show topography and CPD scans over three NWs. Figure 3c shows 1D profiles along the left NW. It can be seen that the NW length is 4.5 µm while its thickness is 250-300 nm in the bottom part and decreases to 200 nm near he top. In the CPD profile, zero value corresponds to the surface potential of HOPG. Thus, The CPD was recalculated into the work function \(\phi\) by subtracting it from the value of 4.48 eV corresponding to \(\phi_{\text{HOPG}}\). The CPD value changes along the NW, the profile contains two main features. First, drastic increase appears in the NW middle: CPD is -0.15±0.1 V in the left part against 0.15±0.05 V in the right part. We associate this 0.3 V increase with the presence of As-containing shell in the left part affecting the electron affinity. The value of \(\phi\) in the bottom GaPAs-covered NW part lies in the range of 4.6-4.75 eV, which is consistent with the recently observed value in GaP NWs with thicker GaPAs shell (4.75 eV) [12]. Thus, even sub-monolayer GaPAs shell drastically affects the work function of GaP NW.

Second, an increase of CPD value by 80 mV is observed near the NW top end, in the area which is expected to have wurtzite crystal structure, according to TEM and Raman study. We attribute this change to crystal phase switching. The corresponding work function values for ZB and WZ parts are following: \(\phi_{\text{ZB}} = 4.28\) and \(\phi_{\text{WZ}} = 4.2\) eV. The difference between \(\phi_{\text{ZB}}\) and \(\phi_{\text{WZ}}\) can be explained with discontinuity of energy bands at the interface between the crystal phases. Recently, band offsets \(\Delta E_C = -20\) meV and \(\Delta E_V = 136\) meV were reported [13]. In case of p-GaP, the valence band behaviour is dominant. It must be stressed, that the ZB region of studied NWs possesses high twinning density. Twin defects may affect the work function, and taking them into account is a subject for future research.
Figure 3. KPFM study of polytypic GaP NW. (a) AFM topography of three NWs, (b) CPD map of three NWs, (c) 1D profiles of topography and CPD along the left NW.

4. Conclusion

The work function of polytypic p-type gallium phosphide nanowires is directly investigated via frequency-modulated Kelvin probe force microscopy. The distinction between the work function of (110) zinc blende ($\varphi_{ZB} = 4.28$ eV) and (1020) wurtzite ($\varphi_{WZ} = 4.2$ eV) GaP is shown experimentally and discussed within the energy structure model. The impact of sub-monolayer arsenic-containing shell on the work function is shown. Thus, the ability for GaP work function tailoring in the range 4.2–4.7 eV is shown. This result is important for optimization of Schottky barriers in nanowire-based devices as well as for photoelectrochemical water splitting.

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