Unified mechanism of the surface Fermi level pinning in III-As nanowires

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Received 6 March 2018, revised 9 May 2018
Accepted for publication 14 May 2018
Published 31 May 2018

Abstract
Fermi level pinning at the oxidized (110) surfaces of III-As nanowires (GaAs, InAs, InGaAs, AlGaAs) is studied. Using scanning gradient Kelvin probe microscopy, we show that the Fermi level at oxidized cleavage surfaces of ternary Al_{1-x}Ga_xAs (0 \leq x \leq 0.45) and Ga_{1-x}In_xAs (0 \leq x \leq 1) alloys is pinned at the same position of 4.8 ± 0.1 eV with regard to the vacuum level. The finding implies a unified mechanism of the Fermi level pinning for such surfaces. Further investigation, performed by Raman scattering and photoluminescence spectroscopy, shows that photooxidation of the Al_{1-x}Ga_xAs and Ga_{1-x}In_xAs nanowires leads to the accumulation of an excess of arsenic on their crystal surfaces which is accompanied by a strong decrease of the band-edge photoluminescence intensity. We conclude that the surface excess arsenic in crystalline or amorphous forms is responsible for the Fermi level pinning at oxidized (110) surfaces of III-As nanowires.

Supplementary material for this article is available online

Keywords: nanowires, III-As semiconductors, surface states, oxidized surface, Fermi level pinning, photooxidation, photoluminescence

(Some figures may appear in colour only in the online journal)

1. Introduction

Compound III-As semiconductors (where III atoms are Ga, In, Al) and their ternary alloys, owing to a direct band structure and high carrier mobility, are prospective materials for high electron mobility transistors [1], as well as for a large number of optoelectronic devices [2, 3]. In the last decade, following the general trend to reduce the device sizes down to the nanometer scale, III-As nanowires (NWs) began to be employed for device engineering [4–6]. In addition to the advantageous essential properties of III-As materials, these nanostructures have their own beneficial features which could be used in nano- and optoelectronics. In particular, the III-As NWs can be grown on silicon substrates, which facilitates their compatibility with silicon-based device structures [7, 8]. Also, these NWs possess an increased light absorption and can be employed, therefore, in the fabrication of solar cells with increased efficiency [9]. However, conventional oxidized surfaces of III-As compounds have a high density of surface states that is related, generally, to surface defects [10]. These states are responsible for the surface Fermi level pinning, formation of the near-surface depletion layer, and surface recombination. Owing to the high surface/volume ratio, these surface-induced, negative effects, for III-As NWs are anticipated to be drastically enhanced. For example, the Fermi level mid-gap pinning that occurs in low doped GaAs and AlGaAs NWs can totally switch off the conductivity along the NW, as well as the photoluminescence (PL) [11]. Fixation of the Fermi level in the conduction band known for InAs surfaces
facilitates formation of the ohmic contact in n-type NWs, but gives rise to inversion of the channel conductivity in p-type NWs [12]. It is clear that a comprehensive understanding of the pinning induced phenomena is of fundamental importance and also necessary for the design of device structures based on III-As NWs.

Conventionally, III-As NW surfaces are formed by (110) facets. Surfaces of semiconductor laser mirrors obtained by cleavage have the same orientation. As known, the Fermi level pinning does not occur at clean, cleavage (110) faces of III-As bulk semiconductors, which corresponds to the so-called flat band condition [13]. However, even a submonolayer deposition of O, Ga, In, Au, Al, and other elements leads to fixation of the surface Fermi level at a position that differs from its position in a bulk crystal. The surface pinning positions are usually measured relative to the top of valence band or to the bottom of conduction band. In such coordinates, the pinning positions for (110) surface of III-As semiconductors occur independent of the nature of the adsorbed atoms [14]. As a consequence, the surface states responsible for the pinning are now assigned to intrinsic surface defects. The pinning positions for (110) GaAs are \( \sim 0.75 \) eV and 0.55 eV above the valence band for n-and p-type materials, respectively [15]. For the (110) InAs surface, the Fermi level is fixed at 0.13 eV above the bottom of the conduction band for n-and p-type materials [16]. For Al\(_{1-x}\)Ga\(_x\)As ternary alloys, the Fermi level pinning has been studied much less. For AlGaAs metal-semiconductor interfaces the pinning position conventionally estimated as to be two-thirds of band gap energy according to Mead’s rule [17]. Note that despite the long period of investigations, the nature of the surface states responsible for the Fermi level pinning in III-arsenides is still a controversial issue. It should be noted that the adsorbate—induced surface Fermi level pinning in these materials has been explicitly established only for the (110) surface orientation. For the widely used (001) orientation, the pinning behavior is ambiguous. For example, clean MBE-grown GaAs(001) surface exhibits the near mid-gap Fermi level pinning for all surface reconstructions, while clean InAs(001) surface is found to be unpinned [18].

Here we study the nature of the Fermi level pinning at the oxidized (110) surfaces of the III-As semiconductor NWs. The experimental approach includes the following two stages. Firstly, we determined the pinning positions on the cleavage (110) surfaces of the bulk III-As heterostructures and NWs. Then we investigate a behavior of the PL for III-As NWs under photooxidation. Based on the obtained results, a unified mechanism for the surface Fermi level pinning in the III-As structures and NWs is proposed.

2. Samples and methods

2.1. III-As nanowires

The studied GaAs, Ga\(_{0.66}\)In\(_{0.34}\)As, and Al\(_{1-x}\)Ga\(_x\)As (\( x = 0.2, 0.3, 0.4 \)) NWs were grown on Si substrates by the molecular beam epitaxy (MBE) technique using the vapor–liquid solid growth procedure. In more detail, the samples were grown by MBE using Riber 21 setup equipped with a separate vacuum chamber to deposit gold from an effusion cell heated up to 1150°C. After treatment in HF: H\(_2\)O solution (1:10), the Si(111) substrates were loaded into this vacuum chamber and outgassed at 850°C during 10 min. The subsequent gold deposition was performed at 550°C (with 0.1 nm effective thickness). To improve the droplet size homogeneity, the substrates after were kept at 550°C for 1 min and then cooled down to room temperature. After that, the substrates were transferred to the growth chamber with no vacuum brake. For the NW growth runs, the substrate temperature was set at 580°C for GaAs NWs, 510°C for AlGaAs NWs and 350°C for GaInAs NWs.

The growth rates (AlAs = 0.2 monolayes (ML) s\(^{-1}\), GaAs = 0.8 ML s\(^{-1}\) for Al\(_{0.2}\)Ga\(_{0.8}\)As and GaAs, and InAs = 0.15 ML s\(^{-1}\), GaAs = 0.3 ML s\(^{-1}\)) were calibrated just before the NWs growth on standard GaAs(001) substrates using reflection high energy diffraction (RHEED) oscillation technique. The appearance of pronounced wurtzite-type (WZ) RHEED patterns was documented after \( \sim 20 \) s of the growth for GaInAs NWs, whereas for GaAs and AlGaAs NWs, mixed WZ/ZB patterns kept unchanged until end of the growth. The total growth time for all samples was 20 min. The GaAs NWs were grown without intentional doping, as well as with p\( + \)\((1 \times 10^{18} \) cm\(^{-3}\)) Be doping. GaInAs and AlGaAs NWs were undoped. The lengths of GaAs, Ga\(_{0.66}\)In\(_{0.34}\)As, and Al\(_{0.2}\)Ga\(_{0.8}\)As NWs were in the ranges of 1–2.5 \( \mu \)m, 0.3–1 \( \mu \)m, and 1.5–2 \( \mu \)m, respectively. The diameters were in the range 60–90 nm for GaAs and Al\(_{1-x}\)Ga\(_x\)As NWs, and 30–50 nm for Ga\(_{1-x}\)In\(_x\)As NWs. Scanning electron microscopy images of the NWs are presented in figure S1 in the supplementary material, available online at stacks.iop.org/NANO/29/314003/mmedia.

Composition of a native oxide in the GaAs and Al\(_{1-x}\)Ga\(_x\)As NWs was studied by transmission electron microscopy (TEM) and energy-dispersive x-ray (EDX) analysis. TEM investigations were performed using Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm) equipped with INCA EDX spectrometer Oxford Instruments. The as-grown NWs were transferred to a conventional TEM copper grid with a lacey carbon film by rubbing the latter over the substrate with the NWs.

TEM analysis revealed different sections with zinc blend and wurtzite crystal structures. The Al\(_{1-x}\)Ga\(_x\)As NWs had the core/shell structure Al\(_{0.2}\)Ga\(_{0.8}\)As/Ga\(_{1-x}\)In\(_x\)As [19], in which the first component was the core and the second component was the shell. In figure 1(a) is presented a HAADF-STEM image of Al\(_{1-x}\)Ga\(_x\)As NW exhibiting the core with diameter of 40 nm and an Al-rich shell of 20 nm thickness. The TEM images of the near surface area of naturally oxidized GaAs and Al\(_{1-x}\)Ga\(_x\)As NWs are presented in figures 1(b) and (c), respectively. The oxide shell thickness of the GaAs NW is of 2 nm, while the Al\(_{1-x}\)Ga\(_x\)As NW exhibited a twice thicker native oxide shell with composite structure. We measured EDX spectra in different regions of the oxide shell. Figure 1(d) shows EDX spectra obtained for the outer layer...
(1) and for the inner layer (2) of the oxide for Al\textsubscript{1-x}Ga\textsubscript{x}As NW. For comparison, the EDX spectrum obtained for the Al\textsubscript{1-x}Ga\textsubscript{x}As NW crystal (3) is also presented. As seen, the outer layer of the NW consists mainly of gallium and aluminium oxides, while in the inner layer the arsenic concentration was increased.

2.2. Determination of the pinning positions

Experimentally, the pinning positions were determined by scanning gradient Kelvin probe microscopy (KPM) [20] which allows measuring the energy distance between the surface Fermi level and the vacuum level usually taken as zero. At each scanning point, this technique measures the surface potential $V_s$, which value is given by $V_s = \phi_{\text{tip}} - \phi_s$, where $\phi_{\text{tip}}$ and $\phi_s$ are the work functions of a microscope probe and of a semiconductor surface respectively. The value $\phi_s$ presents the energy difference between the vacuum level and the surface Fermi level. For its accurate determination, before each measurement the work function of the probe was calibrated using freshly cleaved highly oriented pyrolytic graphite (HOPG), whose work function ($\phi_{\text{HOPG}}$) is well defined as 4.48 eV [21]. Then the work function $\phi_s$ can be expressed as $\phi_s = 4.48 + (V_s - V_{\text{HOPG}})/e$, where $V_{\text{HOPG}}$ is the surface potential of the HOPG measured by the same probe as $V_s$, and $e$ is the electronic charge.

For measurements of the $\phi_s$, the NWs were transferred onto the electrically grounded HOPG surface. We studied undoped GaAs, Al\textsubscript{0.3}Ga\textsubscript{0.7}As, Al\textsubscript{0.4}Ga\textsubscript{0.6}As [19] and p\textsuperscript{+} doped GaAs NWs.

For cleavage faces of III-As heterostructures, KPM provides a determination of $\phi_s$ and, hence, of the pinning position for each heterolayer [22]. To verify the validity of such measurements, we obtained the values of $\phi_s$ on the cleavage face (110) of a p–i–n GaAs structure and the laser-diode Al\textsubscript{1-x}Ga\textsubscript{x}As heterostructure. The both structures consisted of relatively thick layers, which allows us to neglect with far field electrostatic effects which could perturb an accuracy of the gradient Kelvin probe measurements. Also, these layers have the well defined doping levels that allows us to study a dependence of the pinning positions on the doping level.

The measurements were performed at room temperature in a low vacuum environment using an NT-MDT Ntegra AURA scanning probe microscope. Conductive NT-MDT W\textsubscript{2}C + AFM probes were used. To eliminate unwanted effect of the cantilever detection laser on the band bending, we used AFM scanning head with infrared (wavelength 1.3 μm) laser. However, the photon energy of the used AFM laser exceeds the band gap of Ga\textsubscript{1-x}In\textsubscript{x},As. That makes impossible a study of the corresponding narrow gap NWs and bulk heterostructures by KPM because of the photoinduced band bending and moving of the Fermi quasi-level by illumination of the AFM detection system.

2.3. Photooxidation study of III-As nanowires

The photooxidation of III-As NWs was studied using a combination of Raman scattering and PL spectroscopy. The former technique was to control chemical composition of the NW surfaces. The experiments were carried out at room temperature (300 K) using Horiba Jobin Yvon T64000 and LabRAM HR spectrometers equipped with a Linkam THMS600 temperature-controlled microscope stage. The measurements were performed with continuous-wave (cw) excitation using the 532 nm laser line of a Nd:YAG laser. We used a Mitutoyo 100× NIR (NA = 0.90) long working-distance objective lens to focus the incident beam into a spot of ~1 μm diameter, which was sufficient to measure the PL signal from a separate NW transferred to a Si/SiO\textsubscript{2} substrate.

The experimental procedure was as follows. First, PL and Raman scattering spectra were measured for the as-received NWs. Then, the NWs were exposed to successive one-minute laser irradiations with a power density of 100, 500, and 2000 kW cm\textsuperscript{-2}. After each laser-light exposure, the Raman scattering and PL spectra were measured at a low pumping density of 10 kW cm\textsuperscript{-2}. 

Figure 1. (a) HAADF-STEM image of the core/shell Al\textsubscript{1-x}Ga\textsubscript{x}As NW. Brighter core indicates increasing of the Ga content. TEM images of the GaAs (b) and the Al\textsubscript{1-x}Ga\textsubscript{x}As (c) NWs obtained near the native oxide shell. (d) EDX spectra measured at the regions 1–3 marked in the figure 1(c).
HOPG substrate. Scale bar is of 100 nm. The vacuum level was taken as zero. From recent studies on n-GaAs [15, 16, 23], we concluded that the minimum of this so-called flat band condition. This was in agreement with the recent studies on n-GaAs NWs [26].

Assuming that the distribution of the surface states density had a ‘U’ shape [27], we concluded that the minimum of this distribution was at a distance of ~4.9 eV from the vacuum level (see figure 3(a)), and the width of the distribution did not exceed 0.25 eV. The density of the surface states on the oxidized surface of III-As semiconductors in the distribution minimum has been reported to exceed 10^{12} cm^{-2} eV^{-1} [28]. Therefore, for low doped p- and n- materials, the Fermi level should be fixed in the vicinity of the distribution minimum. With an increase of the doping level, the surface states at the middle between those found for the p+ layer and the n+ substrate.

To study the Fermi level pinning at the (110) surface of ternary Al_{0.4}Ga_{0.6}As, we used the cleavage face of a laser-diode heterostructure Al_{0.4}Ga_{0.6}As [23]. The heterostructure was grown on n+ (2 × 10^{18} cm^{-3}) GaAs substrate and consisted of the following layers: n+ (5 × 10^{18} cm^{-3})-emitter Al_{0.4}Ga_{0.6}As/p (5 × 10^{16} cm^{-3})-waveguide Al_{0.4}Ga_{0.6}As/p (1 × 10^{17} cm^{-3})-emitter Al_{0.4}Ga_{0.6}As/p, and contact p+ (7 × 10^{18})-GaAs layer. The profile of the surface work function value (−φs) across the heterostructure cleavage face is shown in figure 2(c). Like in figure 2(b), the difference between the pinning positions for p+ and n+ GaAs layers was ~0.2 eV.

As seen from the figure 2(c), the pinning positions for the heavily doped n+ Al_{0.4}Ga_{0.6}As layer and for the heavily doped n+ GaAs substrate were very close. For weakly doped p-Al_{0.4}Ga_{0.6}As layers, the Fermi level was pinned approximately in the middle between the positions for the n+ and p+ layers.

Approximately 20 Al_{0.4}Ga_{0.6}As NWs and 20 heterostructures of GaAs/Al_{0.4}Ga_{0.6}As, in which the Al concentration x varied in the range of 0.1–0.4, were studied. For all x values, the distance between the pinning positions for doped n+ and p+ layers did not exceed 0.25 eV, while for the weakly doped layers and undoped NWs, the pinning positions occurred near the center of this gap. The pinning positions determined with regard to the vacuum level are plotted in figure 3(a). As can be seen, for the (110) surface of Al_{x}Ga_{1−x}As (0 ≤ x ≤ 0.45), the Fermi level was fixed near 4.8 ± 0.1 eV and near 4.9 ± 0.1 eV for the n- and p-type materials, respectively.

To plot the analogous dependence for oxidized surfaces of n-Ga_{x}In_{1−x}As (0 ≤ x ≤ 1), we analyzed the data published in [15, 16, 23]. In figure 3(b), the blue dots mark the known surface pinning positions for n-InAs [16], n-Ga_{0.4}In_{1−x}As [24], and n-GaAs [15]. All these points occurred near the same distance of 4.8 ± 0.1 eV from the vacuum level. A similar result was obtained by Weider who observed that the pinning positions for the components of the Ga_{x}In_{1−x}As MIS structures for all x were also equidistant from the vacuum level [25]. Thus, the obtained results unambiguously demonstrated that at the oxidized (110) surface of III-As compounds, the Fermi levels were fixed at the same energy position calculated from the vacuum level. One can also observe from figure 3(b) that for x ~ 0.2, the positions of the Fermi level coincided with the bottom of the conduction band, which corresponded to the so-called flat band condition.
The oxidized surface can vary from $10^{12}$ up to $10^{13}$ cm$^{-2}$.

The surface states density at the distribution minimum for an

The pinning position. It should also be noted that the value of

minimum, a further increase of the doping level did not shift

As surfaces taken from

levels for n-Ga$_{1-x}$As surfaces taken from [15, 16, 24].

distribution minimum began to be filled and the Fermi level

moved along the distribution curve. As a result, the Fermi level

moved upward or downward in the n- and p-type materials,

respectively.

The higher the doping level, the larger was the shift of

the Fermi level pinning position from the distribution

minimum. However, owing to the sharp increase of the surface

state density at a distance of $\sim 0.1$ eV from the distribution

minimum, a further increase of the doping level did not shift

the pinning position. It should also be noted that the value of

the surface states density at the distribution minimum for an

oxidized surface can vary from $10^{12}$ up to $10^{13}$ cm$^{-2}$ eV$^{-1}$

which can shift the ‘U’ curve in figure 3(a) as a whole to the

lower or higher state density side of the plot.

The presented data unambiguously indicate the existence of a unified mechanism of the Fermi level pinning at oxidized

(110) surfaces of III-As semiconductor structures. Indeed, the positions of the surface Fermi level relative to the vacuum

level occurred to be the same for cleavage faces for all investigated III-As structures and their ternary alloys. We

suppose that excess arsenic atoms emerging at the semi-

conductor surfaces under oxidation are responsible for the Fermi level pinning at the oxidized (110) surfaces of III-

arsenides. To confirm this suggestion, we investigated the effect of the surface As accumulation on the band-edge PL

intensity for III-As NWs in which the pinning-induced effects are strongly enhanced. Additionally, unlike for bulk materials,

chemical and structure changing in the NWs could be easily

studied by transmission electron microscopy. To produce the

controlled accumulation of the surface As at oxide/NW interfaces, we used a photooxidation procedure.

Photooxidation of the NWs was performed via their exposure to focused laser beam at atmospheric ambient. Initially, the NW surfaces were covered by thin layer of the natural oxide. Generation of the electron–hole pairs by the intensive above band gap irradiation promotes further oxidation of the NW material and enhancement of the oxide thickness. Due to partial character of oxidation, the latter process leads to an accumulation of the elemental As at the oxide/NW interface. Using of the focused laser beam makes also possible simultaneous control of the surface As accumulation by Raman scattering technique.

Photooxidation of GaAs and InAs NWs were studied in [28, 29]. A photooxidation-induced decrease of the band gap

PL intensity for GaAs NWs were observed [28]. We have recently shown that the photooxidation leads to the formation of a double layer c-As/GaO$_x$ at the GaAs NW surface and it is the c-As layer that contacts to the crystal lattice of the NW [30].

Figures 4(a) and (b) show the spectra obtained for a GaAs NW. It can be seen that after 500 kW cm$^{-2}$ laser irradiation, the intensity of the initial PL spectrum (black curve in figure 4(a)) decreased by approximately a factor of 10. After the third irradiation (2000 kW cm$^{-2}$), the band-edge PL was hardly detected. In parallel, the intensive laser irradiation resulted in the appearance and growth of the additional lines in the Raman scattering spectra in the spectral region of 200–260 cm$^{-1}$ assigned to TO and LO phonons in amorphous and crystalline arsenic [28] (see figure 4(b)). These results clearly provide evidence that the surface excess arsenic in the crystalline or amorphous forms is the origin of the surface states responsible for surface nonradiative recombination and for the surface Fermi level pinning. These observations agree with the already known results observed on the photooxidation of GaAs NWs [28, 30].

Figures 4(c) and (d) show the optical spectra of the Al$_{0.1}$Ga$_{0.9}$As/Al$_{0.5}$Ga$_{0.5}$As core/shell NW. The initial PL spectrum in figure 4(c) revealed a wide peak at 1.5–1.6 eV which is in consistent with Al-content in the NW core. The width of the peak could be apparently due to optical transitions in WZ and ZB stacks and in the area between them. For exact explanation, more detailed study is needed. The initial Raman scattering spectrum, in addition to the lines of GaAs-like and AlAs-like TO phonons [31], also exhibited the lines corresponding to the phonons in c- and a-arsenic (see figure 4(d)) that is in an agreement with the TEM results shown in figure 1. This arsenic appeared owing to the greater

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**Figure 3.** Band diagrams for III-As ternary alloys, where the red lines indicate the positions of the surface Fermi level pinning. (a) Fermi level positions of Al$_{1-x}$Ga$_x$As heterolayers measured by Kelvin probe microscopy. Blue dots indicate the positions for n-type heterolayers and green squares indicate the positions for p-type. Triangles indicate the positions for NWs (gray for undoped and red for p$^+$ doped NWs). The ‘U’-shaped curve presents a distribution of the surface states density versus the same ordinate axis; (b) Fermi level positions for n-Ga$_{1-x}$In$_x$As surfaces taken from [15, 16, 24].
Presence of the arsenic in the native oxide shell of the AlGaAs NW as well as in the photooxidized GaAs NW shell proofs the validity of the assumption that the structure of natural and photo oxides is the same. Photooxidation simply increases the thickness of the III-element-rich outer oxide layer and As-rich inner oxide layer. TEM images of the GaAs and AlGaAs NWs after photooxidation are presented in figure S2 in the supplementary material.

The PL intensity of AlGaAs NWs significantly exceeded the PL of GaAs NWs, apparently because the NW shell with higher aluminum concentration served as a passivation coating for the NW core. Since the NW shell was not fully oxidized, the oxide did not reach the core/shell interface. After irradiation of the NW by a beam with the power density of 500 kW cm\(^{-2}\), the band-edge PL was not detected, which indicated that the PL intensity decreased by at least 3 orders of magnitude. At the same time, a weak PL appeared near 1.8 eV, which was apparently related to the formation of the GaO\(_x\) layer [30]. The observed elimination of the band-edge PL intensity arose from the entire oxidation of the core/shell interface. In the Raman scattering spectrum, a weak line

Figure 4. Photoluminescence (a), (c), (e) and Raman (b), (d), (f) spectra measured on single NWs before and after intensive laser irradiation. (a), (b) For GaAs NW, (c), (d) for Al\(_{0.1}\)Ga\(_{0.9}\)As core/shell NW, and (e), (f) for Ga\(_{0.7}\)In\(_{0.3}\)As NW. Spectrum measured on Ga\(_{0.66}\)In\(_{0.34}\)As NWs array at 77 K presented in the inset of figure 4(e).
associated with a GaAs-like TO phonon remained. It should be noted that after laser irradiation, the broad arsenic-related spectral pedestal remained.

Owing to a small diameter and low doping level, the Ga$_{0.66}$In$_{0.34}$As NW was completely depleted by charge carriers. Therefore, at the pumping density of 10 kW cm$^{-2}$, the band-edge PL in the NW was not observed (figure 4(c)). The increase of the pump density resulted in a complete oxidation of the PL [33], but in ambient conditions, it also produced a complete oxidation of the NW. The inset in figure 4(e), shows a low temperature (77 K) spectrum obtained for NWs array. Several peaks in this spectrum could be caused by alloy fluctuation in the NWs array and by different optical transitions in WZ/ZB parts of NWs. In the initial Raman spectrum shown in figure 4(f), InAs-like and GaAs-like TO phonons were visible [34]. After laser irradiation with a power density of 100 kW cm$^{-2}$, these lines disappeared and, instead, the lines corresponding to crystalline and amorphous arsenic appeared. The weak PL peak observed in figure 4(e) in the region 1.7–2.2 eV could be explained by the formation of GaO$_x$/Ga$_2$O$_3$ oxides.

4. Discussion

Thus, under photooxidation, the intensity of the band-edge PL in III-As NWs decreased with the simultaneous growth of the arsenic layer just at the crystal NW surface (see figure S2 in the supplementary material). In addition, for all III-As compounds, fixation of the Fermi level at the oxidized (110) surfaces occurred at the same energy interval from the vacuum level. These findings prove that the surface arsenic is responsible for the Fermi level pinning in III-As semiconductors. Indeed, it was shown in [35] that deposition of As on the clean (110) surface led to pinning of the Fermi level. Annealing of the oxidized surface provided a sublimation of As and led to the unpinning of the Fermi level. Unlike the surface As, the Ga-related oxide components of the oxide layers in III-As compounds did not produce the Fermi level pinning. In [36], the Ga$_2$O$_3$ layer was deposited on the GaAs surface and, as a result, the density of mid-gap surface states decreased down to $10^{10}$ cm$^{-2}$ eV$^{-1}$ for the sharp interface between GaAs and Ga$_2$O$_3$.

We now discuss why the surface arsenic created the surface-gap states in III-As. To explain the Fermi level pinning in such compounds, the approaches of the intrinsic defects or of effective work function are conventionally used. In the first approach, initially suggested by Spicer, the electronic states of surface gallium and arsenic vacancies were considered to produce pinning of the surface Fermi level [14]. Later, more detailed calculations indicated that the mid-gap levels could belong to As-antisite defects whose existence at the oxidized GaAs surface was also confirmed experimentally [37]. Very recent studies of the GaAs/oxide interface using density functional theory indicated that the mid-gap Fermi level pinning could be caused by more complicated defect complexes, which included an As vacancy (V$_{As}$) and two As antisites (As$_{Ga}$) [38]. The latter defect also emerged in the form of a V$_{Ga}$–As$_{Ga}$ complex. As a criticism of the native defects approach, a photo-washing experiment is usually cited. In this experiment, the PL intensity of GaAs samples immersed in water was measured [39]. The PL intensity was observed to increase by an order of magnitude after dissolution of surface arsenic. Moreover, a decrease of the surface states density down to $10^{11}$ cm$^{-2}$ eV$^{-1}$ and the unpinning of the surface Fermi level were demonstrated [40]. It is unlikely that an aqueous solution could remove surface native defects. Also, the removal of the surface arsenic layer from GaAs by plasma etching was found to produce a decrease of the surface states density [41].

The effective work function approach, which was presented by Woodal and Freeouf, assumed that surface chemical reactions induced by oxidation or deposition of metals on the III-As surfaces led to the formation of the surface arsenic layer [42]. If the effective work function $\phi_{eff}$ is assigned to this As layer, the level pinning position and Schottky barrier height for the n-type materials can be determined as $\varphi_{bs} = \phi_{eff} - \chi$, where $\chi$ is the electron affinity for the III-As semiconductor. There are not too much data on the work function of arsenic. It is known that $\phi_{eff}$ = 4.66 eV and 5.1 eV for an amorphous [43] and crystalline As layer [44], respectively. The theoretically predicted value of $\phi_{eff}$ has been reported as 4.9 eV [45]. In our case, the pinning positions in figures 3(a) and (b) is in a good agreement with the work function value on the level of 4.8–4.9 eV. However, it is difficult to explain the shift of the Fermi level pinning position by 0.2 eV observed in GaAs when passing from p$^+$ to n$^+$ materials (figure 2(b)) using the effective work function approach.

However, the approach using surface native defects remains as partially applicable. Computations in the framework of numerical models indicated that arsenic defect complexes, such as As–As dimer/DB, are good candidates for amphoteric mid-gap defect levels. Such models also describe the abrupt interfaces of GaAs/Al$_2$O$_3$ quite well [46].

Apparently, the real structure of the natural oxide layer in III-As compounds is quite complex. In particular, surface arsenic can be of a few monolayers of thickness, as has been shown experimentally [30]. To properly explain the Fermi level pinning in III-As compounds and their ternary alloys, the models taking into account surface multi-particle and even cluster arsenic complexes are required.

5. Conclusion

In conclusion, the oxidation or deposition of metal on (110) surfaces of III-As semiconductor NWs provides the formation of surface excess arsenic. The formed arsenic creates surface states which pin the Fermi level at the same distances from the vacuum level of 4.8 ± 0.1 eV and of 4.9 ± 0.1 eV for n-type and p-type materials, respectively. These findings are vitally important for modeling and designing electronic and optoelectronic devices based on III-As NWs. Based on these data, we can predict that the pinning position in ternary GaAs$_x$Sb$_{1-x}$ NWs for (0.01 < x < 0.5) is situated in the
valence band, and explains the formation of an ohmic contact to GaAs$_{0.5}$Sb$_{0.5}$ [47].

Acknowledgments

The reported study was funded by Russian foundation for basic research (RFBR) according to the Research Project 16-32-60147 mol_a_dk. The NW samples were grown under the support of Russian Science Foundation (Project No. 14-12-00393). TEM characterizations were performed using equipment of the Federal Joint Research Center ‘Material science and characterization in advanced technology’ supported by MES RF (id RFMEFI62117X0018). The authors thank S O Slipchenko for providing bulk heterostructures samples.

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