Quantitative analysis of metastable wurtzite phase into the self-catalyzed GaP NWs

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Abstract. In this letter, we report the growth of the self-catalyzed GaP nanowires with a high concentration of wurtzite phase by molecular beam epitaxy. Formation of rotational twins and wurtzite polymorph in vertical nanowires was observed by the developed a complex approach based on the transmission electron microscopy and X-ray diffraction method. Microstructural analysis performed by high resolution transmission electron microscopy and micro-Raman spectroscopy gives us insights on the nanowire formation mechanism and vibrational properties of nanowires with mixed crystal phase. We obtained wurtzite polytype segments with thicknesses lying in the range from several tens up to 500 nm. The results of the work open new perspectives for high phase purity phosphide NWs synthesis and its fast investigation with XRD technique using a laboratory X-Ray source.

1. Introduction

Nowadays, there are no reports on the formation of the wurtzite GaP phase in self-catalyzed nanowires (NW) by means of molecular beam epitaxy (MBE), only grown Au-catalyzed WZ GaP NW by CBE or MOVPE methods are reported [1, 2]. Self-catalyzed nanowires presented in this report are free from foreign catalyst impurities acting as deep trapping levels for charge carriers into synthesized NW. Control and analysis of the crystal phase in semiconductor NW are of high importance owing to the high potential of the phase bandgap engineering [3].

The scientific soundness of the presented paper is based on the presentation of both novel material (wurtzite GaP) and original approach for quantitative characterization of this type of nanostructures. Commonly used crystal phase characterization techniques (i.e. transmission electron microscopy (TEM) or X-ray diffraction (XRD)) are lacking both integral and microscopic data. Thus, the TEM studies reveal only microscopic data and do not allow to evaluate lattice parameters with high accuracy. Thus, the use of Rietveld refinement [4, 5] approach to XRD data handling to perform crystal structure
solution, as well as the estimation of volume fraction of the crystalline phases in epitaxial nanoheterostructures are suggested to be inaccurate.

2. GaP nanowires synthesis

GaP NW arrays were synthesized on vicinal silicon (111) substrates with a 4° miscut in $<11\bar{2}>$ direction, using Veeco GEN-III MBE machine equipped with Ga effusion cell and valved phosphorus cracker for P₂ molecular flux ($T_{\text{cracker}} = 900^\circ C$). To establish the influence of the growth temperature on NW crystal structure, three samples were grown at the substrate temperature of 610°C. In this work, a two-stage growth with a change of V/III element fluxes ratio, namely 12 and 18, was presented.

3. Result and discussion

3.1. Raman scattering

Raman microspectroscopy ($\mu$-Raman) technique was used as a complementary approach to spatially distinguished WZ-phase NW segments. Polarization-dependent $\mu$-Raman spectroscopy studies were performed at room temperature (300K) using Horiba LabRAM HR800 single monochromator with 1800 gr/mm grating (Kyoto, Japan) and an optical microscope equipped with a x100 0.9 NA lens for excitation and collection of scattered light in backscattering geometry. Single NWs were “dry-transferred” onto transparent quartz substrate mounted on piezo-based scanning stage of Veeco BioScope Catalyst (USA) atomic force microscope, which allowed spatial mapping of $\mu$-Raman signal. The measurements were carried out with $\lambda = 532$ nm (2.331 eV) frequency-doubled diode-pumped solid-state (DPSS) YAG:Nd (neodymium-doped yttrium aluminium garnet) laser providing the above bandgap excitation of ZB and WZ phases of GaP NWs [1, 2, 6].

The $\mu$-Raman measurements of individual NWs were performed at 300K to investigate the spatial distribution of the NW phase composition. Raman spectra were obtained in $-z(x,x)z$ backscattering configurations, as depicted on the inset of Figure 1, with $x$, $y$, and $z$ axes are aligned along the [111], [112] and [110] GaP ZB phase crystallographic directions. The map of Raman spectra across NW length is presented in Figure 1(a) inset. The sharp increase of optical scattering signal can be observed at NW top and bottom facets, due to the more efficient light scattering and coupling at the NW edges. As can be seen from Figure 1(b) Raman spectra acquired along the NW side facets demonstrate longitudinal optical (LO) mode with low intensity since it is symmetry forbidden. In contrast, Raman spectra obtained at NW top and bottom facets demonstrate bright LO- and surface optical (SO) Raman bands due to selection rules break-down caused by finite size effect [7]. As reported previously, SO mode can be observed in high surface-to-volume ratio nanostructures, this mode is positioned between LO- and TO- modes [1, 8], and can be activated via breakdown of translational symmetry at surfaces under near-resonant laser excitation condition.

It is clearly seen those additional vibrational modes, labelled with blue stars in Figure 1, appear near one of the NW edges, noteworthy LO- and TO- modes are doublet splitted which indicate lower symmetry of the uniaxial WZ crystal structure. In contrast, spectra obtained at the opposite NW edge present only TO-, LO- and SO modes located at 365, 402 and $\sim 395$ cm$^{-1}$, respectively, which is typical for ZB-GaP phase [1, 8]. According to the group theory, the following Raman-active bands for WZ phase III-V semiconductors belonging to P$\acute{e}$6$_3$mc space group can be excited: $A_1$ and $E_1$ modes, where phonons are polarized in $z$ and $xy$ directions respectively, low and high ($E_2^H$) frequency $E_2$ modes [9, 10]. Thus, in a chosen $-z(x,x)z$ backscattering geometry in a Raman spectrum, taken from GaP top facet (see Figure 1(c)), we can identify the following 7 Raman-active modes: namely $E_2^H$ positioned at 357 cm$^{-1}$, $A_1$(TO) - 363 cm$^{-1}$, $E_1$(TO) - 365.5 cm$^{-1}$, $B_1^H$ - 380 cm$^{-1}$, SO - 395 cm$^{-1}$, $A_1$(LO) - 400 and $E_1$(LO) - 402 cm$^{-1}$, as was previously reported by Bruno C. da Silva [6] and Kidong Park [11]. The position of the $E_2^H$ peak of the studied sample is indeed very close to the energy of the TO phonons in GaP at the critical point L on the edge of the Brillouin zone – TO (L) [12, 13]. In addition, the appearance of the Raman-forbidden (“silent”) $B_1^H$ mode can be resolved at NW side facets. It should be noted that $E_2^H$
mode is absent in ZB phase despite the large density of rotational twinning defects, as clearly seen in Figure 1 (b) [14 – 16]. The approximation and visualization of Raman vibrational modes was performed using Lorentz function. Thus, μ-Raman spectroscopy provides clear evidence of the WZ phase in the GaP NW structure.

Figure 1. Profile of the Raman spectra across the NW length of the sample with highest WZ crystal phase content, inset: experiment geometry, b) Raman spectrum obtained from GaP NW middle (ZB phase), and c) Raman spectrum obtained from GaP NW base (WZ phase)

3.2. TEM study
Crystal structure is studied with TEM using JEOL JEM–2100F field emission gun TEM (Tokyo, Japan) operating at 200 kV (with point-to-point resolution of 0.19 nm in TEM mode).

According TEM study (Figure 2(a)) there is the existence of 2 crystal phases – cubic ZB and hexagonal WZ. According to X-ray diffraction reciprocal space mapping analysis, there are the existence of ZB phase twinning and absence of WZ phase twinning (not presented here).

Figure 2. a) HRTEM image of individual studied GaP NW, b) Approximated XRD powder diffraction pattern obtained from disordered GaP NWs into the scotch glue, which was grown at 610˚ C

3.3. XRD study
The study is performed using SuperNova (Rigaku Oxford Diffraction, Japan) diffractometer, radiation generated by IμS microfocus X-ray tube with Cu Kα-radiation (λ = 1.5418 Å, ~8 keV). NW synthesis by the MBE method is always accompanied by the formation of a two-dimensional parasitic island. That
is why, we detached the NW array from the substrate using “scotch-taping” technique for avoiding XRD signal from parasitically grown islands.

As clearly in Figure 2 (b) there are many Bragg reflexes, the highest intensity corresponding to the cubic ZB GaP phase with $P\overline{4}3m$ space group (positions depicted with green sticks) [17] and reflexes with lower intensity can be attributed to WZ phase with P6$_{3}$mc space group (positions depicted with magenta sticks) [18]. Quantitative phase analysis and evaluate the WZ GaP phase lattice parameters ($a = 3.839$ Å, $c = 6.344$ Å), we present a simple express Rietveld refinement method [5]. The WZ phase content in studied sample was 9.7±1.5 percent. The obtained data provide statistics across a large number of disordered NWs in one measurement which makes it more practically useful compared to TEM analysis.

4. Conclusions
We report on the controllable stabilization of the polymorphic wurtzite crystal phase in the MBE grown self-catalyzed GaP NWs and refine the crystal lattice parameters of metastable WZ GaP phase. We observed the appearance of additional Raman bands, which can be attributed to the hexagonal WZ GaP lattice and, thus, we demonstrate features of Raman scattering signal into phase heterostructured individual GaP NW. We employ TEM that enables direct observations of the WZ phase stabilization up to 500 nm long GaP NW segment, that correlated to powder XRD data. The proposed approach can be used for a quantitative evaluation of the mean volume fraction of polytypic phase segments in heterostructured nanowires highly desirable for optimization of growth technologies.

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