MBE growth of GaAs nanowires with modulated crystal structure

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Abstract. In this study, we report on the Au-assisted molecular beam epitaxy of GaAs nanowires using graphene covered SiC substrates. The transmission electron microscopy characterization revealed the quasiperiodic superstructure of the nanowires.

1. Introduction
During recent years, semiconductor nanowires attract great attention due to their original optical and electronic properties. Nanometer size cross-section and high aspect ratio rise to many interesting physical properties which are not seen in bulk materials, such as the possibility to combine lattice-mismatch materials. Indeed, it is not only the possibility to grown the III-V nanowires directly on Si substrates that enables integration of optoelectronic devices with Si-based microelectronics [1], but also to make heterostructures without even the changing material. It is well known that most of III-V materials (with the exception of nitrides III-N) have a zincblende (ZB) crystal structure, whereas nanowires of the same material very often show features of polytypism, i.e. they typically exhibit random intermixing of the ZB and wurtzite (WZ) crystal structures [2]. The existence of uncontrolled intermixing has an impact on the nanowires properties and may pose challenges in future nanoelectronic devices due to electron scattering, low carrier lifetime and carrier mobility [3-5]. In turn, the ability to control the crystal structure during the nanowire growth opens up new opportunities for diverse applications in nanotechnology. For instance, an optical characterization of a crystal-phase quantum dot with demonstration of single photon emissions was reported by Akopian et al. [6]. A periodic structure composed of either single twin planes or alternating WZ/ZB phases showed yield interesting superlattice effects [7-9].

In this letter, we report on the MBE growth of Au-seeded GaAs nanowires with modulated crystal structure on hybrid graphene/SiC substrates.

2. Experiment
The investigations were carried out using 6H-SiC (00001) wafers, having surface covered with several graphene layers. In order to obtain graphene film, we used the method of the thermal decomposition of a SiC surface (detail procedure is described in ref. [10]).

The solid-source Compact 21 TM Riber MBE system equipped with additional high vacuum connected chamber for gold deposition, which also allows to perform the annealing of the samples at the temperatures up to 950°C, was used for the growth experiments. Prior to growth the samples were loaded into additional chamber, where they were degassed at temperature of 500°C. Subsequent gold deposition leading to the formation of Au catalyst particles, was performed. Then the temperature was
decreased, the samples were transferred to the main chamber, which is equipped with standard Ga effusion cell and As cracking cell to provide As dimers. After reaching the growth temperature of 550°C, Ga and As shutters were simultaneously opened. The growth rate was 1 ML/s, the total growth time was equal to 15 minutes. Note, that the growth fluxes are calibrated as 2D equivalent growth rate units, realized by measurements of growth rate oscillations during reflection high energy electron diffraction (RHEED) experiments on GaAs (100) surfaces. Growth was terminated by switching off the Ga supply while maintaining the As supply until the substrate temperature dropped to below 300°C.

The morphology of the nanowires was investigated using Zeiss Supra 25 field-emission scanning electron microscope (SEM).

Structural characterization was performed using Jeol JEM-2100F transmission electron microscope (TEM) operated at 20 kV. Samples for TEM were obtained by depositing nanowires onto carbon film coated Cu grids, by gently rubbing the grid against the sample, in most cases breaking the nanowires off at the base.

3. Results

Typical array of GaAs nanowires formed under condition described above are shown in Figure 1. The result obtained demonstrate freestanding nanowires. Since the diameter of the seed particles can vary greatly in the method used, nanowires have a considerable variation in size. The Au catalyzed GaAs nanowires were found to have a high aspect ratio, with average length of about 4 µm and gradually tapered off cross-section size, which is decreasing from 110 to 10 nm. It is known [11], the carbon layer forming on SiC (0001) presents a highly corrugated surface that leads to a shorter diffusion length of the adatoms and restrains their mobility. This has been shown to lead also to metallic clusters of smaller diameter, and indeed Au catalyst particles with diameter of around 4 nm subsequently were found on the tips of nanowires. Thus, tapered form of nanowires could be related to diffusion limited growth mode [12]. Another salient feature that all nanowires were oriented randomly. Since nanowires typically grow perpendicularly to the substrate normal [13,14], this result suggests that here nanowires nucleate exclusively on the few-layer thick graphene regions created on facets of the SiC substrate [15].

![Figure 1. SEM images of GaAs nanowires: cross sectional view (a), 20 degrees tilted side view (b). Scale bars corresponds to 4 µm.](image)

In order to locally identify the crystal formation, we perform TEM analyses. In Figure 2, we show an example of a structural characterization of GaAs nanowire. As can be seen nanowire has a very special superlattice crystal structure. Periodically appearing WZ segments (bright areas) typically exhibit a constant length of around 10 nm. It has been determined also that this structural variation is diameter-dependent, WZ phase occurring predominantly at smaller diameters, i.e. on the tip of nanowire. As a matter of fact, the numerous WZ/ZB segments stacking are probably a result of the low growth temperature of nanowires [16,17]. The diffraction pattern is a superposition of WZ and ZB diffraction
patterns. Certain ZB diffraction spots appear as doublets/triplets, which corresponds to the rotation twins.

Figure 2. TEM dark-field micrograph image of GaAs nanowire (a), a global diffraction pattern (b).

4. Conclusion
In summary, the GaAs nanowire have been successfully grown directly on graphene. It was found that nanowires have superlattice ZB/WZ crystal structure. Thus, nanowires show indeed great promise for new electronic and optoelectronic devices based on the engineering of crystal phases.

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