Nitrogen-Polar GaN Nanowires With Coaxial GaInN Quantum Wells

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In this work, position-controlled growth of nitrogen-polar Ga(In)N nanowire heterostructures with aspect ratios up to 20 is presented. By using nanoimprint lithography and dry etching techniques for the mask patterning, nanowires with diameters down to about 300 nm are grown by selective area metal organic vapor phase epitaxy. GaInN quantum wells are realized on the side facets of these structures. Additionally, positioning and alignment of individual wires is demonstrated by application of alternating current dielectrophoresis allowing optical investigations on single wires.

1. Introduction

Besides applications of nanowire heterostructures in general lighting [1] and lasing [2], in particular nanotechnology-based solid-state sensing is expected to become one major focus of research in the next decades [3]. Here, new sensing systems may particularly involve interdisciplinary fields of research beyond classical optoelectronics: e.g. sensors for biomolecules [4], liquids and gases [5–7]. Nanowire heterostructures based on III-nitride ternary alloys are expected to be particularly suitable for optical gas sensing applications due to their large and tunable bandgap [6, 7]. The purely optical sensing principle relies on changes in the photoluminescence signal due to the adsorption of oxidative or reductive gas molecules and atoms on the surface of the nanowires. Models based on near-surface band bending due to the altered Fermi-level pinning as well as induced changes in the non-radiative recombination processes are controversially discussed in literature [7].

Particularly, GaN provides chemical inertness as well as good thermal, chemical and mechanical stability enabling applications in harsh environments, e.g. for combustion monitoring [3, 8, 9]. GaN nanowires have been so far predominantly grown by molecular beam epitaxy (MBE) which also allows integration of AlGaN/GaN nanodiscs [7] while coaxial heterostructures are significantly more difficult to be realized. However, particularly coaxial structures are very promising for sensing applications as quantum wells realized on the side facets of nanowires are expected to benefit from the large surface-to-volume ratio.

Recently, research in the selective area growth of nanowires with Ga- as well as N-polarity by metal organic vapor phase epitaxy (MOVPE) has found increasing interest [1, 10]. Particularly, nanoimprint and holographic lithography have enabled a fast and large area patterning and additionally provide a diameter control of the nanowires [11, 12]. For Ga-polar nanowires usually additional semipolar facets develop during growth at the tips of the wires [1] which seems not to be the case for purely N-polar wires [10]. These additional facets might contribute to the emitted photoluminescence besides the standard m-plane side facets.

In this work, basic studies on the selective area growth of N-polar Ga(In)N nanowires are performed. Characterization of individual wires by micro-photoluminescence spectroscopy, e.g. in different gas ambients, typically requires large distances between the wires or a complete separation of individiual wires due to the limited spatial resolution. Therefore, additionally the application of alternating current (AC) dielectrophoresis as a positioning and alignment method [13] for characterization of individual wires is investigated.

2. Experimental

Position-controlled nitrogen-polar GaN nanowires are realized on structured 2" c-plane sapphire substrates. A 20 nm thick SiO_2 is deposited by plasma enhanced chemical vapor deposition onto the sapphire wafers which serves as a mask material for the selective area growth. Nanoimprint lithography[2] and dry etching is applied in order to create holes with diameters of about 500 nm and 300 nm as well as periods corresponding to 1 µm and 500 nm into the SiO_2 layer, respectively.

Subsequently, in-situ nitridation of the sapphire in ammonia atmosphere at about 1100 °C is performed in order to enforce the N-polar growth by creation of a thin AlN nucleation layer [14]. Nitridation and following selective area epitaxy are carried out in an horizontal flow Aixtron MOVPE reactor using nitrogen and hydrogen as carrier gas, respectively. The development of Ga-polar inversion domains during N-polar GaN growth is a common problem. The polarity of the nanowires is therefore confirmed by wet chemical etching [15] in a hot 5 molar potassium hydroxide solution at 80°C based on the significant difference in etching rates between Ga- and N-polar GaN.

For the positioning of individual nanowires with AC dielectrophoresis a large amount of the wires is separated from the sapphire substrate by scratching them with a TEM-grid and suspending them into isopropanol. Subsequently, the solution is deposited onto a SiO_2 layer on Si with Ti/Au finger structures realized by conventional optical lithography. A voltage of $V = 5\,\mathrm{V}$ with a frequency $f = 10\,\mathrm{kHz}$ is applied at the Ti/Au finger structures in order to position and align the wires at the positions of maximum field strength by AC dielectrophoresis.

3. N-Polar Ga(In)N Nanowires

Generally, vertical growth of GaN nanowires by MOVPE requires very low V/III ratios [1] compared to growth conditions known from planar GaN but also from other three-dimensional structures [16, 17]. However, these growth conditions can be detrimental for selectivity during nucleation. By using a two-step growth mode with a nucleation

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[2] Carried out by the EV Group E. Thallner GmbH

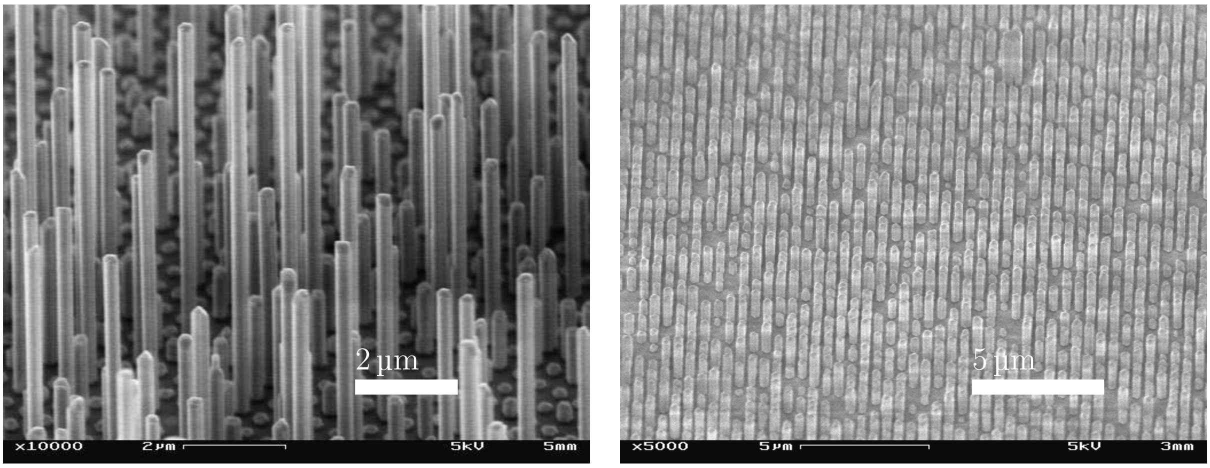

Fig. 1: SEM micrographs of N-polar GaN nanowires selectively grown on a sapphire substrate (left). Improved homogeneity and reduced vertical growth is observed for a reduced silane flow (right).

at high V/III $\approx$ 1000 ratio and reduced temperature in order to fill the mask openings and a subsequent change to lower V/III $\approx$ 60 in order to enhance vertical growth, these two distinct regimes can be combined. Additionally, the introduction of silane has been reported to result in an enhanced vertical growth but may also lead to a passivation during growth [1]. In this work, an additional silane flow is applied in order to enhance the vertical nanowire growth.

A scanning electron micrograph (SEM) of our as-grown nanowires using the two-step growth with silane doping ($n \approx 70\,\mathrm{nmol/min}$) is given in Fig. 1. Nanowires with aspect ratios up to 20 and diameters down to about 300 nm can be realized by using the structured sapphire wafers. In contrast to directly grown nanowires on sapphire, the nanoimprint lithography step enables a much more precise diameter control.

Nucleation conditions have been optimized resulting in an homogeneous filling of all mask openings. However, by changing the growth conditions to enhanced vertical growth homogeneity is reduced which we attribute to a passivation of the nanowires with silicon nitride due to the strong Si-doping. A reduction of the silane flow results in more homogeneous growth and slightly increased lateral growth (Fig. 1, right).

Almost all wires are significantly etched in a hot potassium hydroxide solution which confirmes the predominant N-polarity of the structures. The wires are mainly etched from the top facets, while the $(10\bar{1}0)$ side facets of the rods are surprisingly very stable against the etchant. In areas where growth has stopped after nucleation, the nucleation sites are almost completely removed indicating N-polarity also for the small plateaus.

Coaxial GaInN has been deposited of the side facets of the wires without observing polycrystalline growth on the mask caused by the reduced growth temperatures (Fig. 2). Low temperature integral photoluminescence over a large ensemble of wires shows a dominant contribution of the expected GaInN quantum well luminescence at about 3.15 eV. Spatially and spectrally-resolved investigations on single wires will be presented elsewhere.

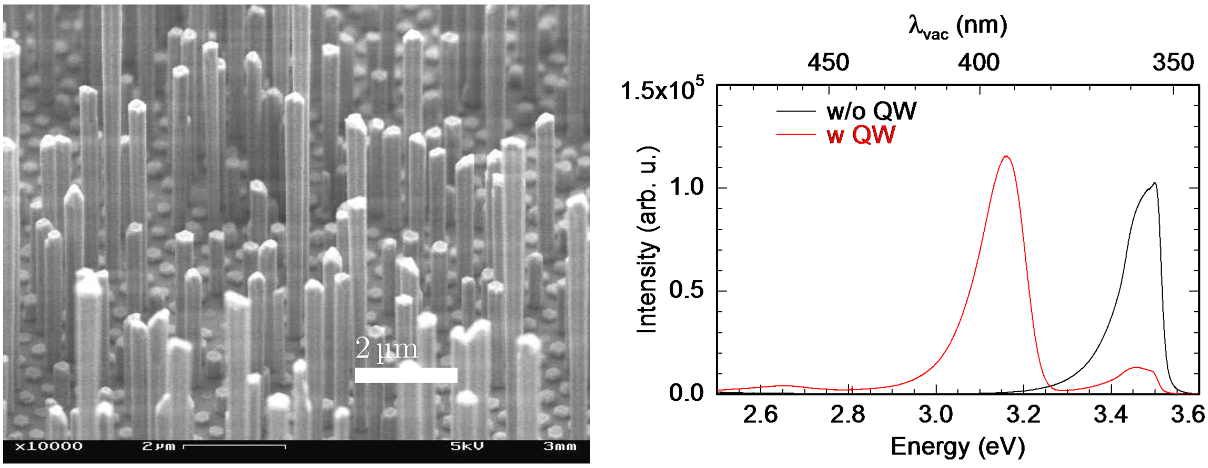

Fig. 2: SEM micrograph of N-polar Ga(In)N nanowires (left) and corresponding integral low temperature ($T \approx 15\,\mathrm{K}$) photoluminescence spectrum of a large amount of wires with and without coaxial GaInN (right).

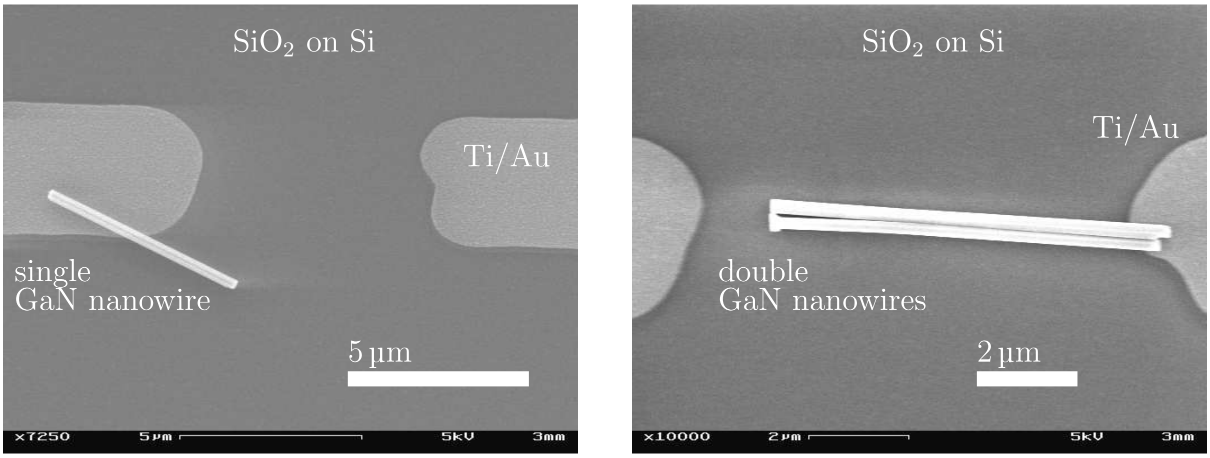

Fig. 3: SEM micrographs of separated GaN nanowires positioned and aligned by AC dielectrophoresis on a SiO$_2$ layer deposited on Si. Trapped but imprecisely aligned nanowire (left) and properly trapped and aligned double wires (right).

4. Dielectrophoresis

Alternating current dielectrophoresis is a common method for positioning and alignment of small particles as well as nanowires based on different material systems [13]. Typical applications mainly include electrical measurements, but the dielectrophoretic positioning can also be used to simplify the locating and separation of single wires on a large area substrate.

By using AC dielectrophoresis, single GaN nanowires and small ensembles of wires can be positioned and subsequently identified by scanning electron microscopy (SEM). While other groups mainly focus on a high yield rate of trapped nanowires for electrical measurements [13], micro-photoluminescence spectroscopy requires a trapping of individual nanowires in order to allow a modal characterization and sensing on a single wire. Therefore, a rather low concentration of nanowires in the suspension and a moderate applied voltage is required. Common difficulties include the unintended trapping of several wires and imprecise alignment (Fig. 3). However, also positioned and aligned double nanowire structures might be interesting for future investigations of the coupling behavior of guided modes between two wires.

5. Summary

In this work, the position-controlled growth of Ga(In)N nanowires with high aspect ratios by MOVPE has been investigated. After separation of the wires from the sapphire substrate, dielectrophoresis allows an positioning and alignment of individual wires. This separation allows an individual characterization, e.g. by micro-photoluminescence, but also investigations on the response of single wires to different gas ambients.

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