1st International Conference on **C**rystal-**P**hase **S**tructures in **N**anowires

CPSN 1

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Abstracts of the Invited Presentations

(In alphabetic order)

Dingding Ren — NTNU, Norway

Crystal phase engineering in GaAsSb/GaAs nanowires grown by MBE

Due to the catalyst-assisted 1D-growth method, the crystal phase of III-V nanowires can be tuned between zinc blende and wurtzite by controlling the growth conditions. In this presentation, I will present the crystal phase transition mechanism in Au- and Ga-catalyzed GaAsSb/GaAs nanowires grown by molecular beam epitaxy. In addition, the optical properties in heterostructured GaAsSb (zinc blende)/GaAs (wurtzite) nanowires will be discussed including the lasing behavior in a single nanowire with a GaAsSb/GaAs-based superlattice in the active region.

Federico Panciera — C2N, France

Experimental observation of phase selection in self-catalyzed III-V nanowires

In this talk, we present experimental observations of the growth of self-catalyzed GaAs and GaSb nanowires using a modified environmental transmission electron microscope (ETEM) equipped with molecular-beam-epitaxy (MBE) sources. NWs are grown directly inside the microscope and their growth is monitored in situ and in real time with high spatial and temporal resolution. First, we show that by changing the growth conditions and in particular the flux ratio between Ga and As(Sb), we modify the volume of the catalyst droplet and hence the contact angle between the droplet and the crystal. A change in contact angle alters the balance of capillary forces at the triple phase line (TPL) and thus the morphology of the growing interface. We find that the phase change and the modification of the growing front morphology take place simultaneously and at specific contact angles. From this evidence we speculate that the different growing front morphologies offer different nucleation sites that favor the formation of one phase with respect to the other. In the light of these results, we discuss the existing models and we propose a new model to describe the phase selection in III-V nanowires.

Frank Glas — C2N, France

Modelling the growth of wurtzite and zinc-blende GaAs nanowires from liquid droplets with very low As content

Recent in situ TEM experiments have shown that, at least in some conditions, III-V nanowires may grow via strikingly different growth mechanisms depending on their crystal structure. These involve interface truncation and fast step flow for ZB and slow step flow with no truncation for WZ. These two growth modes are likely associated with a very low group V concentration in the catalyst nanodroplet. Based on such *in situ* measurements, we model the kinetics and statistics of growth of the two phases. We perform numerical simulations and analytical calculations, which take into account both the nucleation of each monolayer and its subsequent expansion across the solid-liquid interface.

Gilles Patriarche — C2N, France

Atomic step flow in a limited area: in situ observation of GaAs nanowire growth in a transmission electron microscope

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Molecular beams of Ga and As_4 are implemented in an aberration-corrected transmission electron microscope. GaAs nanowires are grown *in situ* from Au catalyst particles. Real-time observation gives access to their morphological and structural parameters while growing and the formation of atomic planes at the catalyst-nanowire interface can be examined. We use various conditions which can result in solid or liquid catalyst particle. For liquid catalyst, the contact angle of the droplet evolves rapidly with the V/III vapor flux ratio. At contact angles around 120°, the atomic plane stacking switches from hexagonal to cubic, with a transition region of mixed crystal phases. In agreement with recently reported results, but using a different growth technique and higher growth rates, we observe that the formation mechanisms of the two crystal phases differ singularly. Namely, hexagonal monolayers grow by slow and continuous step flow on a flat nanowire top facet (Fig.1)[1]; cubic monolayers appear incrementally and concomitantly with a truncation of the nanowire top facet. By changing the wetting angle of the catalyst, and completely stopping the growth between two different crystal structures, we were able to realize a crystal phase superlattice GaAs heterostructure controlled at the monolayer between the cubic (zinc blende) and the hexagonal (wurtzite) phase structures (Fig.2).

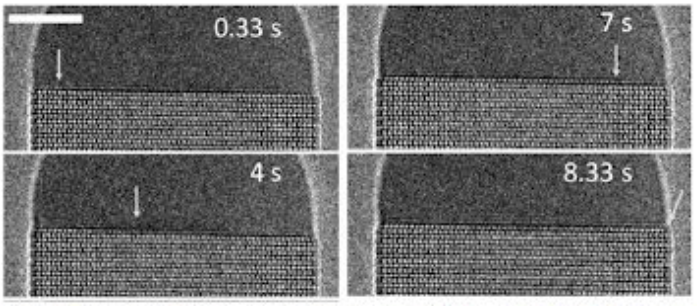

Fig. 1. Flow of a single monolayer step during GaAs nanowire growth in hexagonal (Wurtzite) structure. Scale bar: 5nm.

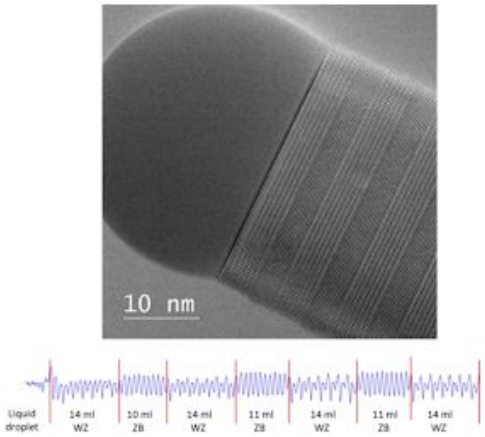

Fig. 2. GaAs crystal-phase heterostructure between the cubic (ZB) and the hexagonal (WZ) structures.

1 Physical Review Letters 121 (2018) 166101

Focus: video – growing a crystal one atomic layer at a time https://physics.aps.org/articles/v11/106

Daniele Barettin — Università Niccolò Cusano, Italy

Modeling of Direct BandGap Wurtzite AlGaAs Nanowires and Quantum Dots

The growth of free standing semiconductor nanowires is one of the most promising solutions for application in nanoelectronics, and nanophotonics, thanks to a better relaxation of the strain field that allows more freedom in combining III–V materials. These wires can include one or several quantum dots. However, GaAa/AlGaAs Nanowires also possess growth mechanisms that might have strong influences on their electronic properties. It is known that the crystal structure of a 1 1 1 nanowire may spontaneously switch during the growth from zinc-blende to wurzite phases. The effect leads to a strong modification of the time-resolved photoluminescence spectra. Similarly, it is expected that optical transitions are sensitive to the crystal phase. We will show how a continuous model for electromechanical fields combined to an 8-band k*p model can both provide excellent parameters for determining the gap of the material in the wurtzite phase, and clearly explain the experimental results obtained for these structures.

George E. Cirlin — Academic University RAS, Russia

Experimental approaches leading to pure phase or unusual phase changes during MBE

In the talk, three different topics will be outlined. First, we discuss how to get pure WZ phase without any structural defects in In-based nanowires via low-temperature Au-mediated growth. Second, we show that if the growth of GaAs and related NWs is started from C-terminated surfaces, regular changes in the crystal phase may appear. Finally, we demonstrate that, under appropriate growth conditions, the nanostructured morphology may change from NWs to nano flowers with cubic insertions at the interface for InGaN system.

Jonas Johansson — NanoLund, Sweden

Zinc blende and wurtzite crystal-phase formation in gold catalyzed InGaAs nanowires

III-V semiconductor nanowires made of materials which have the zinc blende crystal structure in bulk are well known to exhibit either the zinc blende or the wurtzite crystal structure. Understanding and controlling which crystal structure that forms is of highest importance for nanowire applications in a variety of areas. In addition to this, composition control in ternary nanowires is another key technology area for successful nanowire applications. We derive a general model, based on two-component nucleation theory, which we use to explain the so far less understood experimental observations of zinc blende, wurtzite, and mixed crystal structure as a function of growth conditions and composition in gold catalyzed InGaAs nanowires.

Kristian Mølhave — DTU Nanolab, Denmark

Creating silicon nanowire devices in situ TEM

Microchip based heater systems form a unique platform for in situ TEM experiments. We have used Joule heated microfabricated cantilevers for in situ TEM to study the creation of silicon nanowire devices and a range of migration phenomena on the devices. Silicon nanowires were grown by the vapour-liquid-solid (VLS) mechanism, from disiliane catalysed by AuSi eutectic droplets, between adjacent Si cantilever heaters to form freely suspended and electrically contacted bridging nanowire. The chips also allow control of the eutectic droplet shape by electric fields.

Laeticia Vincent — C2N, France

Allotropism in group IV semiconductor nanowires by phase transformation

We report on a stress induced martensitic phase transformation in Ge and Si nanowires attributed to a size effect. The transformation results in quasi-periodic heterostructures constituted of standard cubic-diamond-3C and hexagonal-2H allotropes along the nanowires. This unprecedented nano-structuration may open new properties and functionalities to be explored.

Nanowires are embedded in a Hydrogen silsesquioxane resist-HSQ. The transformation is thermally activated above 400°C and is induced by an external shear-stress produced by the resist matrix surrounding the nanowires. <111>-oriented nanowires with standard diamond structure (3C) undergo plastic deformation under external shear stress leading to a phase transformation toward the 2H diamond-hexagonal (also called lonsdaleite phase). The obtained nanostructures exhibit 2H nano-domains heterogeneously distributed along the nanowire. This polytypism was successfully achieved in Ge and Si nanowires from both bottom-up and top-down fabrication approaches.

First, understanding the origin of this phase formation is critical to evaluate and optimize the possible technological applications. The transformation is dependent upon various key parameters that must be tuned: i) the diameter of the nanowires and the crystallographic direction, ii) the stress that can be viewed as the driving force for the phase transformation, and iii) the temperature at which the transformation occurs. A strain-induced martensitic transformation could account for the transformation in nanowires with a threshold temperature below which the stress induces plastic deformation.

This novel allotropic 3C/2H heterostructure is stable at room temperature and may have very interesting semiconductor and optical properties opening new possibilities of applications of group-IV materials in next-generation devices. Simulations have been performed to give insight into electronic properties and combined DRX, Raman and NIR absorption spectroscopies were carried out to get fundamental physical properties of the 2H phase.

Finally, C-AFM and thermal scanning microscopy measurements are under progress on both 3C and nanostructured 3C/2H Ge NWs to analyze the electronic and thermal conductivities. The main goal is to give an exhaustive insight into the thermoelectric properties of heterostructures 2H/3C in Si and Ge NWs.

Lutz Geelhaar — Paul Drude Institut, Germany

Crystal phase structures in three dimensions and ternary alloys

Along the axis of GaAs nanowires, the crystal structure is prone to exhibit twins, stacking faults and wurtzite/zincblende polytype segments. Due to the differences in band structure between zincblende and wurtzite GaAs, these crystal phase structures can give rise to quantum confinement. The combination of such structures in the axial nanowire direction with compositional heterostructures in the radial direction, e.g. shell quantum wells, results in quantum rings, i.e. structures that are inherently related to the three-dimensional nature of nanowires. Initially, we demonstrated quantum rings in GaAs/(In,Ga)As core-multishell nanowires. Quantum rings are fascinating objects that are interesting for the study of quantum coherence phenomena, but the latter are difficult to observe in ternary alloys. Thus, we turned to the design of quantum rings based on all-binary GaAs/AlAs core-multishell nanowires. In these structures, we measured variations of the exciton energy with magnetic field that evidence the excitonic Aharonov-Bohm effect.

In order to study optical transitions in wurtzite ternary (In,Ga)As quantum wells, we carried out correlated, spatially resolved studies of shell quantum wells around GaAs nanowires exhibiting extended segments of both the wurtzite and zincblende polytype. We find that emission from wurtzite (In,Ga)As is blueshifted by about 70–80 meV. This blueshift results on the one hand from reduced In incorporation and on the other hand from the differences in bandstructure. In particular, the compressive strain of the quantum well has a much stronger impact on the hole ground state in the wurtzite than in the zincblende segment.

Nika Akopian — DTU Fotonik, Denmark

All-optical charging and charge transport in crystal-phase quantum dots

Semiconductor quantum dots are one of the best on-demand sources of single and entangled photons to date, simultaneously merging the highest brightness and indistinguishability of the emitted photons. They are, therefore, among the strongest candidates for practical *single-qubit* quantum photonic devices. However, to exploit the full advantage of quantum physics, *multi-qubit* photonic devices are absolutely necessary.

Here we propose, for the first time, an experimentally feasible *multi-qubit* photonic device, and a method for *individual charging* of multiple quantum dots and *coherent charge transport* between them. We show that charging and charge transport can be implemented in a realistic structure with fidelities greater than 99.9% in a few µs. Our scheme is based on all-optical resonant manipulation of charges in a 1-dimensional array of *crystal-phase quantum dots*. Such structures can be practically realized in view of recent advances in controlling the crystal phases in nanowires during growth.

Peter Krogstrup — Niels Bohr Institute, Denmark

Bi- and tri-crystal epitaxy of hybrid quantum nanowires

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Hybrid nanowire materials with semiconducting, superconducting and magnetic components properties constitute some of the most promising candidates in the search for materials suitable for topological quantum computing [1], [2]. I will present the latest studies of epitaxy of superconductor and ferromagnetic insulator materials on different III-V semiconducting nanowire platforms such as Vapor-Liquid-Solid grown and selective area grown nanowires [3].
I will discuss the growth mechanisms that lead to well defined morphologies and interfaces between crystals with different space groups and fundamentally different electronic properties, and discuss the challenges and material requirements needed for realizing and eventually manipulating topological protected quantum states.

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[2] Krogstrup et al. Nature Mater. 14, 400-406 (2015)
[3] Krizek et al. Phys. Rev. Mat. 2, 093401 (2018)

Riccardo Rurali — ICMAB, Spain

Interface engineering and doping in hexagonal Si nanowires

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Crystal structure and interface engineering are acquiring an increasing importance in nanoscience because of their enormous potential to conceive new properties and functionalities. In the case of nanowires (NWs), the emergence of new stable polytypes of common semiconductors promises to have an important impact in materials design. Driven by this promising evidence, we use first-principles methods based on density functional theory and many-body perturbation theory to investigate the electronic and optical properties of hexagonal–diamond and cubic–diamond Si NWs as well as their homojunctions. We show that hexagonal–diamond NWs are characterized by a more pronounced quantum confinement effect than cubic–diamond NWs. Furthermore, they absorb more light in the visible region with respect to cubic–diamond ones and, for most of the studied diameters, they are direct band gap materials. The study of the homojunctions reveals that the diameter has a crucial effect on the band alignment at the interface. In particular, at small diameters the band-offset is type-I whereas at experimentally relevant sizes the offset turns up to be of type-II. These findings highlight intriguing possibilities to modulate electron and hole separations as well as electronic and optical properties by simply modifying the crystal phase and the size of the junction. Additionally, we present results of an extensive scrutiny of several common dopants revealing similarities, but also unexpected differences with their behavior in cubic and hexagonal Si polytype. We show that an important class of dopants, i.e. acceptors, are much more easily incorporated in hexagonal than in cubic Si, while donors are substantially indifferent to the polytype of the host crystal. This has important consequence in cubic-hexagonal junctions, as different types of dopants will distribute differently across the interface.

Sebastian Lehmann — NanoLund, Sweden

Growth and Characterization of Crystal Phase Engineered III-V (III= Ga, In; V = As, P) nanowires prepared by MOVPE

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Since the first reports continuous efforts have led to precise control of crystal structure formation in III-V nanowires[(1,2)], a deeper understanding of the growth process[(3–6)], and last but not least to numerous studies on the properties of the WZ phase but also combinations of the two crystal phases. These homomaterial heterostructures allow, due to their type-II character of the band alignment between e.g. GaAs Wz and Zb, for the creation of crystal phase quantum dots in related systems[7–9].
Another route to exploit the potential of the high crystal phase control we have achieved for nanowire synthesis is to heteroepitaxially, selectively overgrow the Wz and Zb sections[10,11] and thus allow for an additional degree of freedom for designing heterodevices.
With the increased knowledge of engineering the crystal phase of the nanowires but also designing the 3D architecture of nanowire heterostructures, structurally and compositionally, there is a need for advanced characterization techniques for the structure/composition vs. property relation. Electron channeling contrast imaging (ECCI) in the scanning electron microscope (SEM) is an excellent tool to non-destructively characterize the crystal structure of nanowire devices.

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Vladimir Dubrovskii — ITMO, Russia

Morphologies and related crystal phases of III-V nanowires based on the surface energy analysis

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In this talk, we will discuss some new insights into the crystal phase selection in GaAs and other III-V nanowires grown by the vapor-liquid-solid method with different catalysts. A simple classification of the nanowire morphologies and the related crystal phases (cubic zincblende – ZB or hexagonal wurtzite - WZ) will be presented based entirely on the surface energy analysis. It will be shown that the most important parameter which determines the morphology and crystal phase is the droplet contact angle. At small (< 100o for GaAs nanowires) the tapered nanowire morphology with planar growth interface is preferred, yielding the ZB phase. Intermediate (between 100o and 125o for GaAs nanowires) favor vertical nanowire sidewalls and WZ phase. At larger, the truncated growth interface is preferred, with either vertical (at between 125o and 127o for GaAs nanowires) or inverse tapered (at 127o for GaAs nanowires) sidewalls in the ZB phase. Theoretical considerations will be confirmed by the in situ data obtained in NanoMax transmission electron microscope. Other material systems will also be considered from this viewpoint, explaining, in particular, why GaP nanowires usually form in the ZB phase.