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BOOK OF ABSTRACTS

Germanium Nanowire Growth in Scanning Electron Microscope

 $\frac{\text{Miroslav Kolíbal}^{1,2}, \text{Tomáš Vystavěl}^3, \text{Libor Novák}^3, \text{Tomáš Pejchal}^1, \text{Peter Varga}^1 \text{ and Tomáš Šikola}^{1,2}$

¹ Central European Institute of Technology – CEITEC, Technická 2, 61669 Brno, Czech Republic

The nanowire shape (cross-section, sidewalls' orientation etc.) and orientation plays a major role in determining electrical transport or sensing properties of nanowire-based devices. The ability to fully control the nanowire morphology is, of course, based on our understanding of the growth process. In this respect, in-situ Transmission Electron Microscopy (TEM) studies have provided vital information on this issue [1].

In this contribution, we will present our results on the vapor-liquid-solid (VLS) germanium nanowire growth by evaporation from a solid Ge source inside a scanning electron microscope (SEM) vacuum chamber. As the group IV nanowires grown by evaporation are highly faceted, we will focus on the effects where SEM can give substantial information. In particular, the initial formation of the growth interface between the gold droplet and the substrate (Fig. 1) will be discussed in detail [2,3] with respect to the formation of new facets [4]. In another example, we will demonstrate that the droplet on top of a nanowire is not necessarily pinned to the growth interface. Instead, under certain growth conditions it slides down the sidewalls and then climbs up again to the top [5]. We will also present our latest results showing in-situ growth under the presence of hydrogen, which drastically affects the growth morphology.

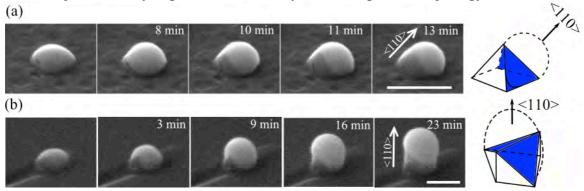


Figure 1: The formation of a V-shaped growth interface, which is an intrinsic feature of nanowires growing in <110> direction. a) An image sequence captured using a scanning electron microscope at elevated temperature (400 °C) during Ge evaporation onto Ge(100) substrate covered with Au nanoparticles (bright droplet in the middle of the image). Initially, a germanium island having a pyramidal shape with four {111}-oriented sidewalls is formed. However, the droplet dewets two of these facets and finally pins to the edges of the remaining two, thus forming the V-shaped interface made of two inclined {111} planes (marked blue in the schematic to the right). b) Similar experiment performed on Ge(110) substrate. Scale bars, 200 nm. The images are tilted by 52° to the surface normal.

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- [2] Kolíbal M., Vystavěl T., Novák L. et al., Applies Physics Letters 99 (2011) 143113.
- [3] Kolíbal M., Kalousek R., Vystavěl T. et. al., Applied Physics Letters 100 (2012) 203102.
- [4] Schwarz, K. W., Tersoff, J., Nanoletters 11 (2011) 316.
- [5] Kolibal M., Vystavěl T., Varga P., Šikola T., Nano Letters 14 (2014) 1756.

² Institute of Physical Engineering, Brno University of Technology, Technická 2, 61669 Brno, Czech Republic

³ FEI Czech Republic, Vlastimila Pecha 111982/12, 61669 Brno, Czech Republic

Sub-Eutectic Vapour-Liquid-Solid Growth of Ge Nanowires Enabled by Sidewall Hydrogen

Saujan V. Sivaram¹, Ho Yee Hui¹, Jane Y. Howe², and Michael A. Filler¹

¹ School of Chemical & Biomolecular Engineering, Georgia Institute of Technology ² Hitachi High Technologies America, Inc.

Vapour-liquid-solid growth of semiconductor nanowires below the catalyst eutectic temperature occurs in a handful of systems, yet it remains unclear what factors enable this undercooled state. Our previous work revealed that sidewall hydrogen atoms, reactive intermediates in the heterogeneous decomposition of the precursor Ge₂H₆, suppress the taper of Ge nanowires and must be present above a critical coverage to sustain stable growth¹. Here, we couple in situ infrared spectroscopy and electron microscopy to show that these species are, in fact, responsible for maintaining the catalyst as a liquid below the eutectic temperature. We quantitatively determine this connection by measuring both hydrogen atom coverage and catalyst phase as a function of time. The ability of atomic hydrogen, which we deliver to the nanowire sidewall in the absence of Ge₂H₆, to maintain the catalyst as a liquid unambiguously confirms the role of surface chemistry. Our data indicate a mechanism whereby catalyst atoms begin to sample the nanowire sidewall as hydrogen coverage decreases, eventually finding a location favourable for Au nucleation. We also find that desorption of H₂ from the sidewall is fastest near the catalyst, presumably due to the presence of Au. This observation indicates that sidewall-adsorbed hydrogen atoms must result from the decomposition of Ge₂H₆ on the sidewall itself, rather than in/on the catalyst. Our findings demonstrate that changes to sidewall chemical bonding are critical to understand semiconductor nanowire growth and provide new guidelines for tuning catalyst phase and composition.

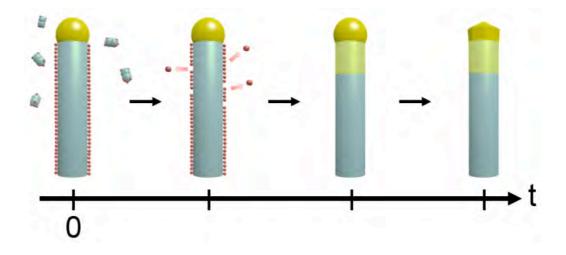


Figure 1: Schematic illustration of H₂ desorption from a Ge nanowire, which leads to AuGe catalyst solidification below the eutectic temperature.

¹ S. Sivaram, et al., J. Am. Chem. Soc. under revision (2015).

Coalescence of spontaneously formed GaN nanowires in plasma-assisted molecular beam epitaxy

<u>Vladimir Kaganer</u>¹, Sergio Fernández-Garrido¹, Pinar Dogan^{1,2}, Karl Sabelfeld³, Oliver Brandt¹

¹ Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany

Spontaneously formed GaN nanowires may inadvertently undergo coalescence resulting in irregularly shaped nanowire aggregates which are easily perceived in top-view scanning electron micrographs [see, e. g., the inset in Fig. 1(a)]. This unintentional coalescence of spontaneously formed nanowires has a detrimental impact on their optoelectronic properties, and it is thus highly desirable to understand the mechanisms governing the coalescence process.

In the present work, we study the temporal evolution of coalescence during the spontaneous formation of GaN nanowires in plasma-assisted molecular beam epitaxy. For this purpose, we prepare series of GaN nanowire ensembles on Si(111) under identical growth conditions, differing only in growth time. By analyzing top-view scanning electron micrographs of these ensembles, we quantify their properties such as coverage, coalescence degree, density and the average diameter of the nanowires/aggregates. Side-view micrographs give access to the nanowire length. The experimental data directly show that coalescence already takes place during the nucleation stage. When the nanowires grow in length, a second mechanism is found to set in which induces further coalescence, namely, nanowire bundling facilitated by their bending.

For a quantitative understanding, we perform Monte Carlo simulations of nanowire growth and coalescence. The model incorporates spatially random nucleation of nanowires with a certain out-of-plane misorientation as observed experimentally, radial growth, and nanowire bundling. For a nanowire length less than 200 nm and a coverage below 0.15, continuous nucleation results in a sharp increase of nanowire density [see Figs. 1(a) and 1(b)] which is slowed down by radial-growth induced coalescence. Radial growth ceases after an equilibrium nanowire diameter is reached,³ and nucleation stops when the substrate is shadowed from the impinging fluxes by nanowires of sufficient length. At this stage, however, nanowire bundling is energetically favourable, since the energy of the free side facets is reduced at the cost of the elastic energy of bending. This process is fully taken into account in our model and results in the decrease of nanowire density seen in Figs. 1(a) and 1(b). For fully developed ensembles, it eventually results in a coalescence degree near unity.

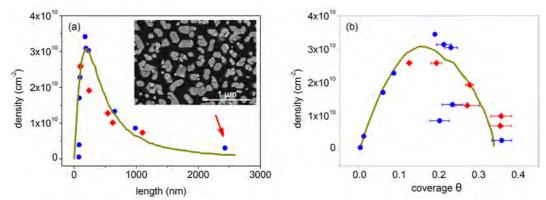


Figure 1: Evolution of the density of spontaneously formed GaN nanowires with (a) height and (b) coverage. Symbols represent two sets of samples, solid lines the results of a Monte Carlo calculation.

- ¹ O. Brandt et al., Crystal Growth & Design 14, 2246 (2014).
- ² S. Fernández-Garrido et al., Nanotechnology 25, 455702 (2014).
- ³ S. Fernández-Garrido et al., Nano Letters 13, 3274 (2013).

² Department of Electrical and Electronics Engineering, Mugla Sitki Kocman University, Mugla, Turkey ³ Institute of Computational Mathematics and Mathematical Geophysics, Russian Academy of Sciences, Novosibirsk, Russia

Polytypism in growing self-catalyzed GaAs nanowires probed by timeresolved in-situ high-resolution X-ray diffraction

Philipp Schroth^{1,2}, Seyed Mohammad Mostafavi Kashani¹, Julian Jakob³, Martin Köhl³, Jonas Vogel¹, Arman Davtyan², Jörg Strempfer⁴, Tilo Baumbach^{2,3} and Ullrich Pietsch¹

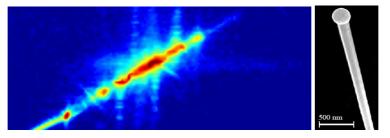
- 1) Universität Siegen, Siegen, Germany
- 2) Laboratory for Application of Synchrotron Radiation, Karlsruhe Institute of Technology
- 3) Institute for Photon Science and Synchrotron Radiation (IPS) / ANKA, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
 - 4) Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany

Time-resolved X-ray measurements can provide valuable insight in the dynamics of the growth of GaAs nanowires, in particular in the evolution of their crystallographic properties¹. Here, we report on the growth of self-catalysed GaAs nanowires onto Silicon (111) substrates using the portable molecular beam epitaxy setup of ANKA². We probe the crystallographic properties of the growing nanowires by means of time resolved high-resolution X-ray diffraction.

The X-ray experiment has been performed at the P09 beamline of PETRA III with a beam spot size of approx. $\sim 70 \times 50 \mu m$. Using a photon energy of 15keV, the symmetric (111) and the asymmetric (311) and (220) zinc-blende and (10.3) wurtzite Bragg reflections have been monitored during growth: after a substrate annealing step, liquid Gallium droplets were seeded before the axial nanowire growth was initiated by supplying both Gallium and Arsenic at 600°C substrate temperature. After the growth, the temperature was reduced to room temperature by a constant cooling rate of 20°C per minute.

We observe that twinned GaAs zinc-blende and wurtzite form first. The X-ray signal of the twinned zinc-blende evolves facet-streaks common for vertical NWs, whereas the facet-signal is missing for the substrate-oriented zinc-blende GaAs even at the end of growth. During the cooldown, the signal of wurtzite becomes more pronounced. Compared to growth temperature, the coherent intensity of the monitored Bragg reflections was increased after cooldown, but at the same time the intensity of diffuse scattering was significantly reduced - beyond expectations from considering the effect of the Debye-Waller factor alone.

Since some of the grown NWs are not strictly parallel to the (111) direction but exhibit a slight tilt, the X-rays scattered at these NWs appear at well separated positions at the detector. The small beam size in combination with the high photon flux at P09 allowed the time-resolved monitoring of these individual NWs. Therefore, we obtained insight in the evolution of the crystalline properties during growth, for a large ensemble of wires, as well as for a small number of individual wires.



 $Fig. 1-Left: Ga As\ 220\ Reflection\ with\ multiple\ signals\ originating\ from\ single\ objects.\ Right:\ Grown\ Ga As\ Nanowire$

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¹ P. Schroth, et al., Phys. Rev. Lett. 114, 055504 (2015).

² T. Slobodskyy, et al., Rev. Sci. Instrum. 83, 105112 (2012).

Real time imaging of growing GaAs nanowires under transient growth conditions

<u>Daniel Jacobsson</u>^{1,*}, Federico Panciera², Sebastian Lehmann¹, Mark C. Reuter³, Jerry Tersoff³, Frances M. Ross³, and Kimberly A. Dick^{1,4}

To grow Au-seeded GaAs nanowires, the Au seed particle alloys with Ga. For growth temperatures above ~500°C, no thermodynamic upper limit on the Ga fraction in a liquid Au-Ga alloy droplet exists at typical growth conditions. Hence, the droplet can easily increase or decrease in size depending on the Ga kinetics, in other words the difference between Ga arrival rate into the droplet and incorporation into the nanowire. In an As-limited growth regime, the Ga incorporation rate will be directly dependent on the As arrival rate, and directly shown by the nanowire growth rate. As Ga has a relatively long migration length, the arrival rate of Ga to the seed droplet is dependent on the nanowire geometry, growth conditions, and the surroundings. Ga adatoms may potentially be collected from a large area. However, for the more volatile As, the migration length is negligible, and the collection area is much smaller compared to Ga. To contribute to growth of the nanowire, the As adatoms are required to reach the nanowire growth front at the interface between the droplet and the solid nanowire. However, it remains unclear where the As is actually collected before getting to the growth front.

We have therefore used *in situ* transmission electron microscopy to examine the details of GaAs growth, in particular measuring kinetics and structure under transient growth conditions. By monitoring the nanowire growth rate with an accuracy of single bilayers, we can compare droplet area and local growth rate. The data suggests that As is collected on the surface area of the droplet. Within a certain range of V/III ratio, we find that the droplet size at steady state depends on both the group V and the group III flows, with a lower V/III ratio resulting in larger seed droplet size. The larger As collection area for lower V/III ratio gives a sub-linear growth rate dependency on As flow, as well as a Ga-dependent growth rate, even in an otherwise As limited growth regime. Furthermore, we observe a temporal delay between variations in the precursor flow and changes in the droplet volume, leading to transient regions where the local growth rate can be either higher or lower than the steady-state growth rate at a given precursor flow. We believe our findings should be applicable to self-seeded growth, as well as other III-V systems, and are crucial for precise control of axial nanowire heterostructures.

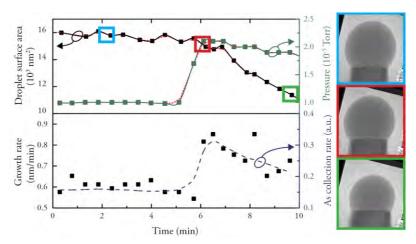


Figure 1. Local growth rate dependence on AsH₃ pressure and droplet surface area. Single images are extracted from the video at the times indicated by colored boxes in the plot, illustrating the droplet volume changes.

Solid State Physics/The Nanometer Structure Consortium, Lund University, Box 118, 221 00 Lund, Sweden
 Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom

³ IBM T. J. Watson Research Center, 1101 Kitchawan Road, Yorktown Heights, New York 10598, USA ⁴ nCHREM / Centre for Analysis and Synthesis, Lund University, Box 124, 221 00 Lund, Sweden

^{*} corresponding author: Daniel.Jacobsson@ftf.lth.se

Hybrid Si/III-V nanowire heterostructures

Moïra Hocevar

Institut Néel CNRS/UJF UPR2940, 25 rue des Martyrs, 38042 Grenoble, France

Fabricating heterostructure nanowires based on group IV and III-V materials will potentially bring new functionalities to semiconductor based nanodevices.

Here I present Si/III-V nanowire heterostructures fabricated in the vapor liquid solid growth mode from gold catalysts in a MOCVD reactor. We combined GaP and Si in a unique nanowire in order to study the growth mechanisms of Si/III-V heterostructures, as these two materials have a small lattice mismatch of 0.3%. We developed a method to control the growth of straight Si sections on GaP nanowires and vice versa, as well as Si shells around GaP core nanowires.

Axial heterostructures were grown by switching between source gases at a constant growth temperature. In opposition, core-shell nanowires, whose composition changes in the radial direction, were fabricated by first growing the core nanowire and then by raising the temperature, in such a way non-catalyzed Si shell growth occurs on the surface of the GaP core. Our results show defect free epitaxial Si/GaP heterostructures in both radial and axial geometries (see Fig. 1). They demonstrate that the nanowire geometry is a major platform to reach high crystalline quality at Si/III-V interfaces. Finally these results pave the way to more challenging Si/III-V combinations and to the development of novel opto-electronic nanodevices such as single photon detectors or electron spin memories.

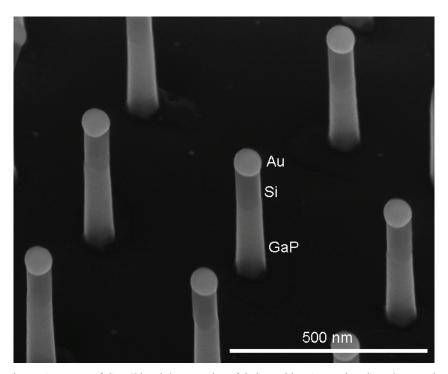


Figure 1: array of GaP/Si axial nanowires fabricated by Au-assisted VLS growth.

GaP/GaAs AXIAL HETEROSTRUCTURES IN SELF-CATALYZED NANOWIRES

<u>Giacomo Priante</u>, Gilles Patriarche, Fabrice Oehler, Frank Glas and Jean-Christophe Harmand CNRS-Laboratoire de Photonique et de Nanostructures, Route de Nozay, 91460 Marcoussis, France

giacomo.priante@lpn.cnrs.fr

GaAs_{1-x}P_x nanowires (NWs) have potential applications in photovoltaics and photonics, thanks to the possibility to adjust their group V composition and thus the band gap, over a wide range. Self-catalyzed NWs are grown using a droplet made of the group III element. This avoids contamination from foreign materials and opens new possibilities such as diameter tailoring. While the self-catalytic method of growing GaAs NWs has attracted much attention in the recent years, its extension to other Ga-V semiconductors has rarely been investigated, especially concerning the fabrication of axial heterostructures^{1,2}. Here, we present the self-catalyzed growth of pure GaP NWs by molecular beam epitaxy, using growth conditions compatible with those used for GaAs NWs. By commuting the group V fluxes, we fabricate purely axial GaP/GaAs heterostructures, composed of multiple and reproducible segments of binary and ternary compounds. We test different flux switching schemes and measure the corresponding interfacial composition profiles with atomic resolution, using high-angle annular dark field (HAADF) scanning transmission electron microscopy. We show that the interface abruptness is drastically improved by switching off all the molecular fluxes for a short time at the group V commutation. Finally, we demonstrate that the morphology of the growth front can be either flat or truncated, depending on the growth conditions.

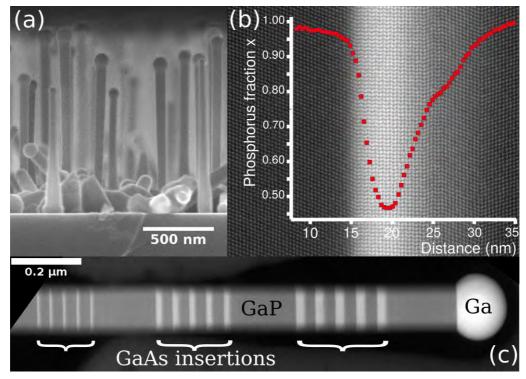


Figure 1: a) Pure self-catalyzed GaP NWs grown on Si(111); b) Example of compositional profile extracted from a high-resolution HAADF TEM image; c) Medium-resolution HAADF TEM image showing GaAs insertions in a GaP NW.

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² Y. Zhang, et al., Nano Lett. **13**, 3897 (2013).

³ G. Priante, et al., submitted

Growth of GaAs/InAs and InAs/GaAs axial heterostructured nanowires by Chemical Beam Epitaxy

<u>V Zannier</u>¹, D. Ercolani¹, U. Prasad Gomes¹ M. Gemmi², J.David² and L. Sorba¹

¹NEST, Istituto Nanoscienze -CNR and Scuola Normale Superiore, P.zza S. Silvestro 12, 56127 Pisa, Italy ² Istituto Italiano di Tecnologia IIT, P.zza S. Silvestro 12, 56127 Pisa, Italy

Semiconductor nanowires (NWs) are widely considered one of the most promising technologies for future device applications. One of the greatest advantages of these structures is the ability to form axial heterostructures using lattice-mismatched materials. The epitaxial growth of axial nanowire heterostructures has been reported since 1996, however the growth is not straightforward and far from fully understood. The two main issues when growing axial heterostructures are to have straight nanowires and sharp interfaces between the two materials. Concerning Au-assisted III-V semiconductor NWs, straight wires with atomically sharp heterointerfaces are easier to obtain when group V interchange occurs, due to the lower solubility of the group V species than that of the group III ones into the Au seed nanoparticles.^{2,3} In the specific case of InAs/GaAs heterostructured nanowires, straight nanowire growth has been reported for the growth of GaAs on top of InAs, whereas in the other direction kinked nanowires are generally obtained.^{2,4} Moreover, it is observed that the Ga-to-In switch is much sharper than the In-to-Ga one. These results have been explained taking into account the crystal structure of the two materials and the different affinity of the Au catalyst for In and Ga.⁴ In this contribution we report on the growth of both InAs/GaAs and GaAs/InAs heterostructured NWs, as well as the growth of double heterostructured NWs (InAs/GaAs/InAs and GaAs/InAs/GaAs) by means of Chemical Beam Epitaxy. A careful investigation of the NWs morphology as a function of growth parameters like growth temperature, III/V flux ratio and chemical composition of the catalyst nanoparticle has been performed by means of SEM, TEM and EDX. The results suggest that the thermal history and the chemical composition of the nanoparticle strongly affect the growth. We found that, while GaAs on InAs easily grows straight, InAs on GaAs grows straight only if the chemical composition of the nanoparticle is properly tuned. Straight heterostructured NWs in both sequences can therefore be obtained by carefully controlling the alloy nanoparticles.

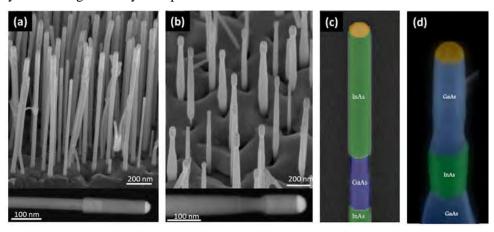


Figure 1: (a, b) 45°-tilted SEM images of InAs/GaAs (a) and GaAs/InAs (b) heterostructured NWs grown on InAs(111)B and GaAs(111)B substrates respectively. The insets at the bottom are STEM images of representative NWs reported in each panel. (c, d) False-colour SEM images of the double heterostructured NWs: InAs/GaAs/InAs (c) and GaAs/InAs/GaAs (d). The colours highlight the various segments: InAs (green), GaAs (blue) and catalyst nanoparticle (yellow).

- ¹ K. Hiruma et al., Journal of Crystal Growth, **163**, 226-231 (1996)
- ² K. Dick *et al.*, *Nano Letters*, **7**, 1817-1822 (2007)
- ³ K. Dick et al., Nano Letters, **12**, 3200-3206 (2012)
- ⁴ M. Paladugu *et al.*, *Small*, **3**, 1873-1877 (2007)

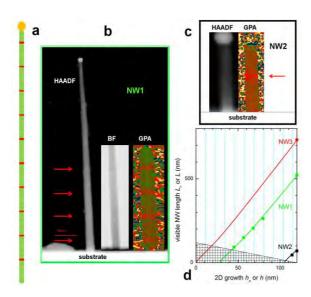
Single-temperature growth of II-VI dots in core-shell nanowires

P. Rueda-Fonseca, ^{1,2,3} M. Orrù, ^{1,2,3} A. Artioli, ^{1,2} M. Jeannin, ^{1,2} M. Den Hertog, ^{1,2} M. Lopez-Haro, ^{1,3} G. Nogues, ^{1,2} D. Ferrand, ^{1,2} Y. Genuist, ^{1,2} R. André, ^{1,2} E. Robin, ^{1,3} S. Tatarenko, ^{1,2} J. Cibert, ^{1,2} and <u>E. Bellet-Amalric</u> ^{1,3}

Univ. Grenoble Alpes, Grenoble, France,
 CNRS, Institut NEEL, Grenoble, France,
 CEA, INAC-SP2M, Grenoble, France.

The dot-in-a-nanowire configuration is extremely flexible and virtually any material combination, any dot shape and any built-in strain can be realized. It allows one to engineer the hole states in semiconductor dots, and tailor their orbital and spin states. This opens the opportunity to fully design the photonic properties of the nanostructure, and its magnetic properties if magnetic impurities are added.

We used gold-catalysed molecular beam epitaxy to grow Cd(Mn)Te quantum dots in ZnTe-Zn(Mg)Te core-shell NWs at low temperature (350°C). The whole structure can be grown at the same temperature, which ensures a good balance between axial growth and radial growth, a good morphology of the interfaces and surfaces, and a good insertion of the magnetic impurities. The overall structure was characterized by transmission electron microscopy, including high angle annular dark field (HAADF), geometric phase analysis (GPA), and energy dispersive x-ray spectroscopy (EDS), cathodoluminescence and (magneto-optical) photoluminescence. We here focus on the NWs with the zinc-blende structure, which exhibit a cone shape 1 and good luminescence properties. 2



These NWs exhibit a broad distribution of their length, with one order of magnitude between the longest and the shortest NWs. In order to model the growth we inserted 10 thin CdTe markers along ZnTe NWs (fig. a). The analysis by TEM on the cleaved sample of several nanowires reveals:

- i) a large dispersion in the number of insertions 8 for NW1 (fig b) and 1 for NW2 (fig c and
- ii) a cone shape which is due to the combination of a small contact area of the gold catalyst (6 to 8 nm in diameter) and significant lateral growth (base diameter up to 200 nm for several microns long NWs).

The inclusion of several CdTe dots reveals therefore that the nucleation of the NW occurs randomly and involves a long delay for the shortest NWs (fig d). A diffusion-limited model taking into account the incidence angle of the molecular beams describes well the growth characteristics (axial and radial growth, composition) and the effect of temperature and deviation from a stoichiometric molecular beam.

¹ P. Rueda-Fonseca, E. Bellet-Amalric, R. Vigliaturo, M. Den Hertog, Y. Genuist, R. André, E. Robin, A. Artioli, P. Stepanov, D. Ferrand, K. Kheng, S. Tatarenko, and J. Cibert, Nano Lett. **14**, 1877 (2014).

² A. Artioli, P. Rueda-Fonseca, P. Stepanov, E. Bellet-Amalric, M. Den Hertog, C. Bougerol, Y. Genuist, I. F. Donatini, R. André, G. Nogues, K. Kheng, S. Tatarenko, D. Ferrand, and J. Cibert, Appl. Phys. Lett. **103**, 222106 (2013).

Adding functionality: InSb nanowires with built-in tunnel barriers

<u>Diana Car</u>¹, Sonia Conesa-Boj², Saša Gazibegović², Roy op het Veld¹, Michiel de Moor², Marcel A. Verheijen^{1,3}, Sebastien Plissard^{4,5}, Leo P. Kouwenhoven², Erik P. A. M. Bakkers^{1,2}

In the world of III-V semiconductors, InSb is a material of extremes: it has the narrowest bandgap, the lowest electron effective mass (the largest electron mobility) and a giant Lande g factor of ~50.^{1,2} These superior characteristics make it interesting for a variety of applications: from infrared optoelectronics and thermoelectrics to high-speed, low-power electronics and quantum computing.^{3–8} Currently, we use tunnelling spectroscopy to study Majorana zero bias peaks in InSb wires. We want to investigate whether a heterostructure tunnel barrier can outperform an electrostatically-induced barrier. As InSb has the largest lattice parameter of all the III-V's it is highly lattice-mismatched even to its nearest neighbour GaSb: the lattice mismatch between InSb and GaSb is ~6.3%. This is a serious drawback in planar geometries where stacking of lattice mismatched materials is impossible to realize.

Here, we investigate the growth and electrical properties of InSb nanowires with built-in Ga_xIn_1 - $_xSb$ barriers. By controlling the precursor molar fraction and the growth time, we can tune the composition and the length of the barriers. Structural and chemical characteristics of the nanowires have been assessed by means of high-resolution transmission electron microscopy and x-ray energy dispersive spectroscopy. Strain in the structures has been calculated via Geometrical Phase Analysis. Finally, the temperature-dependent transport measurements have been performed to determine the height of the barriers.

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¹ Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands

 ² Kavli Institute of Nanoscience, Delft University of Technology, 2628CJ Delft, the Netherlands
 ³ Philips Innovation Services Eindhoven, High Tech Campus 11, 5656AE Eindhoven, the Netherlands
 ⁴ CNRS-LAAS, 7 avenue du Colonel Roche, F-31400 Toulouse, France
 ⁵ Univ. Toulouse, LAAS, F-31400 Toulouse, France

Elastic and plastic strain relaxation in GaAs/(In,Ga)As core-shell nanowire heterostructures

Ryan B. Lewis, Oliver Marquardt, Pierre Corfdir, Hanno Küpers, Manfred Ramsteiner, Uwe Jahn, Oliver Brandt and Lutz Geelhaar

Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

III-V core-shell nanowire (NW) heterostructures are promising for future optoelectronic devices due to their large active area for small planar footprint and their ability to integrate on foreign substrates such as the Si platform. In these structures, misfit strain can relax elastically in both lateral and axial directions, and the strain is shared between the core and the shell. This efficient elastic strain relaxation allows core-shell NWs to be grown free of strain-relieving dislocations to larger lattice mismatches and thicknesses than those possible for planar films, extending the operating wavelength range for perspective optoelectronic devices for a given material system. However, the strain state of these heterostructures depends nontrivially on both the core and the shell dimensions and compositions, and will impact the bandstructure and ultimately device operating wavelengths and performance. Therefore, strain in core-shell heterostructures must be understood and incorporated into device designs. In this work, GaAs/(In,Ga)As-based core-shell NW heterostructures, where the lattice mismatch is systematically varied by varying the shell In content, are grown for a range of core and shell dimensions. The elastic and plastic strain relaxation in the NWs and its effect on optoelectronic properties are investigated. This work opens the door to GaAs/(In,Ga)As core-shell NW devices operating in the technologically

important 1.3 µm wavelength range.

 $GaAs/In_xGa_{1-x}As/GaAs$ core-shell heterostructures with core diameters of 40 and 140 nm, 0<x<1 and predominantly zincblende crystal structure were grown on Si (111) substrates by molecular beam epitaxy. X-ray diffraction (XRD) reciprocal space maps, recorded around the axial (111) reflection of NW ensembles for varying In contents, show that for x < 0.4-0.5 the heterostructures are pseudomorphic, sharing a single lattice constant in the axial direction which increases with increasing In content. However, above a critical In content (which depends dimensions), further increasing the In content decreases the (111) NW lattice spacing, indicating a decrease in the strain of the GaAs core (see Fig. 1). At the same time, an increasing presence of fully

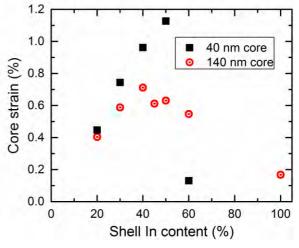


Figure 1: Core axial strain as measured by XRD as a function of the In content in GaAs/(In,Ga)As/GaAs core-shell-shell NW ensembles. Shell thicknesses are 20 nm and 35 nm for the series' with 40 nm and 140 nm cores, respectively.

relaxed (In,Ga)As is observed. These observations are interpreted as the onset of plastic relaxation in the heterostructure, which occurs much beyond the planar limits for pseudomorphic growth. Complementary measurements with Raman spectroscopy corroborate the evolution of the strain in the GaAs NW heterostructures.

Photo- and cathodo-luminescence measurements were carried out on NWs with $x \leq 0.5$ at 10 K and reveal emission wavelengths lying between those for corresponding fully strained and fully relaxed planar films. The measurements agree well with three-dimensional $\mathbf{k} \cdot \mathbf{p}$ simulations where the strain distribution was adjusted to minimize the elastic energy. The simulations show that the emission wavelengths of core-shell NWs depend strongly on core and shell dimensions, as they determine the strain state of the (In,Ga)As shell. This work underscores the crucial importance of strain consideration when designing core-shell NW devices.

Molecular-beam epitaxy of high-quality InAs/InSb heterostructure nanowires on Si(111)

Jianhua Zhao

State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, China

The uniquely intrinsic properties, like narrow bandgap, extremely high electron mobility, strong spin-orbit interaction and giant g factor, make III-V compound semiconductor InSb nanowires (NWs) attractive for both high-frequency and low-power functional devices as well as fundamental studies. In recent years, heterostructure NWs containing a high quality InSb segment have been realized by some means, such as metal organic vapor phase epitaxy, chemical beam epitaxy and molecular-beam epitaxy (MBE) on III-V substrates, but none on Si substrates. In this talk, after a brief introduction of our recent work related with high-quality GaAs and InAs nanowires grown on Si substrates¹⁻³, I will focus on the growth of high-quality InAs/InSb heterostructure NWs on Si (111) substrates by MBE employing Ag catalysts. It is found that the Sb/In flux ratio can be varied to effectively control the morphology and the size of the InSb NWs. High-resolution transmission electron microscope (TEM) images confirm that the InSb NW is fully single-crystalline and has a sharp interface with the InAs stem, as shown in Fig. 1. I also provide their electrical properties, for example, the temperature dependence of the field effect mobility, measured from the globe top-gate NW field-effect transistors based on InSb NW segments⁴.

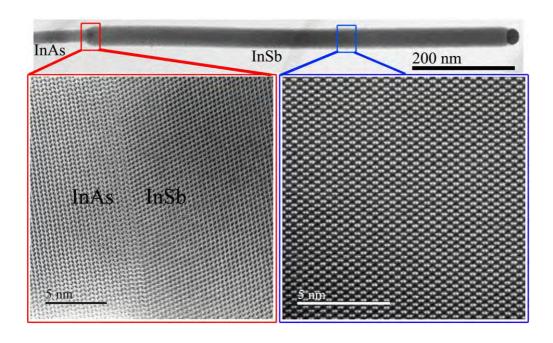


Figure 1: High-resolution TEM images of an InAs/InSb heterostructure nanowire

This work has been carried out in collaboration with Dr. Dong Pan and Prof. Hongqi Xu et al.

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⁴D. Pan et al., to be submitted

Direct Nucleation, Morphology and Compositional Tuning of InAs₁. _xSb_x Nanowires on InAs (111) B Substrates

Luna Namazi¹, Sepideh Gorji Ghalamestani¹, Kimberly A. Dick ^{1, 2}

¹ Solid State Physics, Lund University, Box 118, SE-22100 Lund, Sweden ² Centre for Analysis and Synthesis, Lund University, Box 124, 221 00, Lund, Sweden

InAs_{1-x}Sb_x nanowires have high potential for future optical applications such as Infrared photodetectors ¹ and electronics such as quantum computing, due to their tunable material composition. Further, their compositional tunability offers the narrowest band gap at room temperature among all the III-V semiconductor materials.

Gowing Sb-based nanowires from Au seed particles on III-V substrates mainly requires using a stem of the same material as the substrate due to nucleation difficulties caused by the surfactant properties of Sb 2 . Although growing InAs_{1-x}Sb_x nanowires on an InAs stem eliminates nucleation failures, the stem can result in other complications such as stem decomposition when turning the AsH₃ flow off for As-free material synthesis, hence nanowire breakage during growth. Noting that, due to the low contact angle of the Au particle when growing InSb, direct nucleation of this material on InAs substrates is complicated, meaning that the Sb content in the ternary InAs_{1-x}Sb_x material system plays a key role in achieving direct vertical growth of these nanowires. Therefore, studying the direct growth from substrate of this ternary system where, the Sb content can be tuned up to a point where growth fails, can offer further understanding of nucleation, and in which way Sb affects it. Moreover, although there have been reports on Au-seeded growth of InAs_{1-x}Sb_x nanowires on InAs (111) B substrates 3,4 , a full attempt to understand and control the radial and axial growth rates, and the morphology of these nanowires at different compositions has not yet been carried out 5 .

We demonstrate direct nucleation and growth of $InAs_{1-x}Sb_x$ nanowires over a range of compositions for different Au particle diameters and surface densities by means of metalorganic vapor phase epitaxy (MOVPE). TMIn is used as the group III precursor, while AsH_3 , and TMSb are used as the group V precursors. We investigate how the nucleation, morphology, axial and radial growth rate of these nanowires depend on the particle diameter, density, and growth conditions such as Sb content, temperature, total precursor flows, nominal V/III ratio, and growth time. Independent of the growth conditions, The nanowires show a tapered morphology, where the Sb content changes over the length of the nanowires, usually from a higher Sb content at the base, decreasing to lower amounts towards the tip.

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Regimes of self-catalysed nanowires growth

Y. Berdnikov¹, N.V. Sibirev^{1,2}, V.G. Dubrovskii^{1,2}

¹ St. Petersburg Academic University, Khlopina 8/3, 194021 St. Petersburg, Russia ² ITMO University, Kronverkskiy pr. 49, 197101 St. Petersburg, Russia

Self-catalysed growth recently became a very popular approach to synthesis of Au-free nanowires compatible with Si technology. In implementation of this mechanism, initially formed Ga droplets induce the epitaxial growth of the NWs in case of appropriate choice of growth parameters. In contrast with Au-assisted process - when metal droplet does not change appreciably during the growth under the optimized conditions - in Ga-catalyzed mechanism size of the droplet is not necessarily constant and is highly sensitive to the V/III flux ratio and Ga desorption which depends on growth temperature. In this contribution we present the model for quantitative prediction for dynamic behaviour of Ga droplet size and thus NW radius. The results are presented as a parameter map where different regions correspond to different regimes of growth.

In a modelling case a nanowire starts the growth with a droplet of diameter R_0 . Its further formation is described by following equations for scaled NW length (I) and radius (r):

$$c\frac{dL}{d\tau} = \frac{A(r)}{1 + A(r)} \tag{1}$$

$$c\frac{dL}{d\tau} = \frac{A(r)}{1 + A(r)}$$

$$\frac{dr}{d\tau} = \frac{1}{F_{53}} - \frac{A(r)}{1 + A(r)} + \frac{\alpha}{r^p}$$

$$\tag{2}$$

Here $A(r) = \frac{v}{i_c} W[r^2]$ with W[x] – Labert W-function and $R_* = \left(\frac{v \chi v_5}{i_c \pi h J(\Delta \mu)}\right)^{1/2}$ scales length $l = L/R_*$ and radius of nanowire $r = R/R_*$. Right-hand side of eq. (1) and the second term in eq. (2) correspond to group V adsorption which in case of Ga-rich self-catalysed mechanism moderates the growth process. Diffusion of Ga adatoms contributes to the third term in eq. (2) where α is defined as $\alpha = \left(\frac{\Lambda}{R_*}\right)^p \left(\frac{1}{F_{53}} - \frac{1}{F_d}\right)$ and could be either positive or negative depending on parameter F_d ($\sim \tau$ – adatom lifetime defined by temperature) and F_{53} - V/III flux ratio.

The solution of eq. (2) predicts different character of changes of Ga droplet size depending on two growth parameters F_{53} and F_d . The map of growth regimes is shown on Fig. 1(a). At high F_d and thus low adatoms desorption rate droplet radius either grows unlimitedly (azure region) or saturates at some limit value (purple region) depending on fluxes ratio F_{53} .

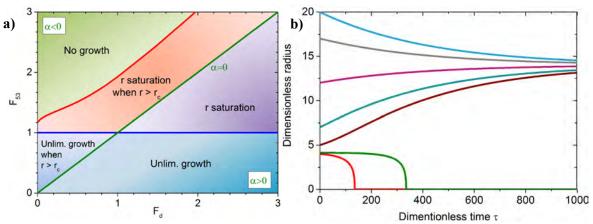


Figure 1: a) Parameter map of NWs growth regimes. b) Typical $r(\tau)$ dependences for red region of (a)

Small values of F_d correspond to intensive desorption which results in droplet decomposition below some critical radius r_c . Red and green curves on Fig. 1(b) illustrate this case while other curves show saturation of droplet size when initial value is above r_c (red region). Finally, in green region, which corresponds to high V/III flux ratio, droplet decomposes fast and selfcatalysed mechanism of growth is no more applicable.

New possibilities in the self-catalyzed growth of GaAs nanowires using a modification of migration-enhanced epitaxy

L. Balaghi, L. Bischoff, R. Hübner, H. Schneider, M. Helm, <u>E. Dimakis</u>

Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, 01328 Dresden, Germany

The self-catalyzed (or Ga-induced) growth of vertical GaAs nanowires on Si(111) by molecular beam epitaxy has offered the possibility to obtain nanowires with fairly good control of the structural polytypism (especially in favor of the zinc-blende phase), without the risk of contamination by foreign elements like Au. The growth is typically performed close to the congruent temperature of GaAs (580-630 °C) in combination with relatively high V/III ratios. Those conditions ensure the efficient surface diffusion of Ga adatoms from the substrate and the nanowire side-walls to the apex of the nanowires, and suppress the thermal decomposition of the $\{1\overline{1}0\}$ side-walls. Nevertheless, the specific growth conditions impose several limitations: 1) the growth temperature exceeds largely the thermal budget limit of the Si-CMOS technology, rendering the future integration of the two material technologies impossible; 2) the interruption of the axial growth cannot be abrupt because of the long shut-off transient of the As-flux, which is typically accompanied by the formation of a segment that is rich in stacking faults below the Ga droplet; 3) significant inter-diffusion at high temperatures will deteriorate the compositional/doping profile of axial heterostructures; 4) it is difficult to avoid the unintentional radial (shell) growth, which is undesirable in axial heterostructures.

Aiming to surmount the inherent limitations of the conventional self-catalyzed growth mode, we developed a new growth scheme that expanded successfully the growth window to temperatures as low as 450 °C, minimized the radial growth, and allowed for accurate and defect-free interruptions of the axial growth. Our scheme is inspired by the migration-enhanced epitaxy of GaAs thin films, where the Ga and As fluxes are supplied alternately and in doses comparable to the atom sheet-density of the growth interface. In the case of nanowires, though, we adapted the alternate supply of Ga and As to achieve targeted delivery of the Ga atoms to the apex of the nanowires, minimizing in that way the radial growth. This work did not concern the nucleation stage, thus nanowires grown in a conventional way were used as templates for all experiments.

The results of our study include quantitative descriptions of the Ga adatom migration kinetics, the incorporation efficiency of As through the Ga droplet, and the dependence of both on the growth temperature. Having constructed a complete picture of the growth kinetics, we were able to identify the optimal growth conditions and beam-shutter sequence for different growth temperatures, covering the range from 550 to 450 $^{\circ}$ C. The structural analysis of our nanowires by transmission electron microscopy showed a zinc-blende structure with a small number of twin defects (Fig. 1). However, the spacing between the twins is irregular and does not correlate with the periodic beam-shutter sequence. The success of our growth scheme is interpreted on the basis of the atomic arrangement of the non-reconstructed $\{110\}$ side-facets.

Ongoing work concerns the nucleation stage at 450 °C, as well as the fine tuning of the growth scheme parameters in order to eliminate the formation of twin defects.

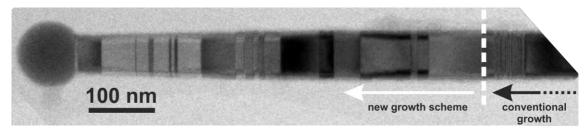


Figure 1: Transmission electron microscopy image of a GaAs nanowire grown at 450 °C using the proposed growth scheme. The bottom part of the nanowire (partly shown on the right side of the dashed line) was grown in a conventional way at 600 °C. A segment with a high density of stacking faults was formed only at the end of the conventional growth.

Critical examination of the mononucleation hypothesis and joint modelling of the kinetics and statistics of self-catalyzed NW growth

Frank Glas¹, Jean-Christophe Harmand¹ and Vladimir Dubrovskii^{2,3,4}

¹CNRS - Laboratoire de Photonique et de Nanostructures, 91460 Marcoussis, France ²Saint Petersburg Academic University, Saint Petersburg, Russia ³Ioffe Physical Technical Institute RAS, Saint Petersburg, Russia ⁴ITMO University, Saint Petersburg, Russia

In the recent years, self-catalyzed growth has emerged as a powerful technique for growing nanowires (NWs) of certain III-V semiconductors. In this variant of vapor-liquid-solid (VLS) growth, which has been mainly applied to Ga-based materials elaborated by molecular beam epitaxy (MBE), the foreign metal that forms the basis of the catalyst droplet is replaced by the group-III constituent(s) of the NW. At variance with standard MBE of planar III-V structures, the steady state growth velocity is then determined by the group-V flux 1,3 and, ultimately, by the concentration of group-V element in the droplet, which is only of the order of 1%.4

Our current understanding of VLS growth in general is largely based on the nucleation of 2D monolayers (MLs) at the solid-liquid interface. We first recall briefly how the self-catalyzed growth of GaAs NWs can be modelled quantitatively⁴ assuming 2D mononucleation (a single nucleation event for each ML), on the basis of a comparison with quantitative data about the growth kinetics under various conditions.³ However satisfactory these fits are, they raise several questions, in particular with respect to the size of the critical nuclei that they yield. Moreover, the single nucleation scheme is not the only one conceivable. To clarify these questions, we will thus compare critically and quantitatively this scheme to polynucleation^{5,6} (possibility of several nucleation events for a single ML) and to other scenarios that do not even involve nucleation.

The critical examination of the validity of the mononucleation hypothesis can be carried out a step further by analysing the statistics of formation of successive NW MLs. Recall that VLS growth exhibits an effect that we termed 'nucleation antibunching' and which consists in a temporal anti-correlation of the formation of successive MLs. The ensuing sub-Poissonian statistics can be modelled quantitatively and analytically assuming 2D nucleation and allowing for the depletion of the catalyst droplet in the dilute group-V element, following the formation of each ML. Physical parameters that determine the magnitude of this effect, be they system-dependent or specific to a single NW in certain growth conditions, are the same that those which govern growth kinetics. We will thus be able to show how, in the framework of mononucleation, a single set of model parameters allows one to model jointly and to reproduce quantitatively the experimental results about kinetics and statistics. In particular, this allows one to set narrow bounds on the key system parameter of both models, namely the energy of the edge of the 2D nuclei that form at the liquid-solid interface.

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Plateau-Rayleigh Crystal Growth of Periodic Shells on Synthesized and Fabricated 1D Substrates

Robert W. Day¹, Max N. Mankin¹, Shota Kita², Marko Loncar² and Charles M. Lieber^{1,2}

Nanoscience offers the promise of driving revolutionary advances in many areas of science and technology, yet the realization of this promise depends critically on the rational development of nanoscale structures whose properties and/or function are controlled during materials synthesis. Recently, we reported a growth phenomenon specific to one-dimensional (1D) materials, termed Plateau-Rayleigh crystal growth (PRCG)¹. For well-defined conditions, the chemical vapor deposition of Si onto uniform-diameter Si cores, Ge onto Ge cores, and Ge onto Si cores can generate periodic shell nanowires with tunable diameter-modulation periodicities and amplitudes. Here, we first review key details of PRCG and discuss our underlying physical model¹. Then, we will focus on some unique predictions/opportunities that have not been realized previously with PRCG. First, we demonstrate that Si periodic shells can be grown successfully onto Ge cores. Second, by modulating the time and pressure during growth of core/shell heterostructure nanowires, coiled, or spring-like structures can develop where shells form predominantly on one side of the core in contrast to the radially conformal, periodic shells reported previously. Transmission (TEM) and scanning electron microscope (SEM) images of these structures indicate that one-sided Ge shells induce bending of the Si core away from the shell, whereas one-sided Si shells deform the Ge core toward the shell, consistent with stress from lattice mismatch. Last, we will show that our PRCG concept can be applied to growth of periodic shells on top-down fabricated 1D substrates (Fig. 1) in addition to bottomup, VLS-grown nanowire cores. The potential benefits of combining top-down methodology with bottom-up growth for expanding synthetic capabilities as well as for enabling unique applications will be discussed.



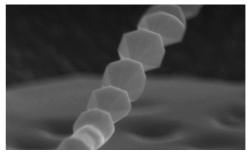


Figure 1: Plan-view (left) and angled (right) perspective SEM images of bottom-up grown Si periodic shells on top-down fabricated Si substrates. Suspended, one-dimensional Si substrates were fabricated using electron beam lithography and reactive ion etching. Si periodic shells were deposited from SiH_4 in a chemical vapour deposition chamber.

¹ Department of Chemistry and Chemical Biology, Harvard University. ² School of Engineering and Applied Sciences, Harvard University.

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Synthesis of Au- or In-seeded Si NWs on flexible or ganic substrates

<u>Lin Tian</u>, Lorenzo Di Mario, Antonio Minotti and Faustino Martelli IMM-CNR, via del fosso del cavaliere 100, 00133 Rome, Italy

Semiconductor NWs can be grown on any substrate that stands up the growth condition, as a result of lacking of lattice mismatch constrains. Such merit allows integration of NWs with low-cost, flexible substrates, without the need of complex procedures to transfer NWs grown on rigid substrates onto any arbitrary substrate. The direct growth simplifies the process, is more cost-effective, and avoids damages of NWs caused by the transferring. To date, Si NWs have been grown on metallic foils¹⁻³ and C-fibers⁴, but not on plastics, yet, despite its low-cost, scalability and easily manufacturing. Those works use growth temperatures larger than 450°C, values incompatible with organic substrates.

Most growths of Si NWs use Au as seed. However, Au forms deep carrier traps in Si and should be avoided in any Si-based technology. Indium, a shallow acceptor in Si, has aroused attention as alternative seed⁵. Featuring a low-melting temperature (157°C), In also endows polymer-compatible deposition environment. Nevertheless, the high Au efficiency as NW seed can be exploited to set the growth conditions to be then used with alternative seeds. Using both Au- and In- seeds, we have grown dense Si NWs arrays on polymer substrates by plasma enhanced chemical vapor deposition (PECVD).

The growth of Si NWs was carried out at 350°C in PECVD with a gas mixture of SiH₄/H₂ on a stack of oxidized Si/polyimide/a-Si/In (or Au) substrate. A 4-8µm thick polyimide layer was spin-coated on oxidized Si substrates, followed by a thin a-Si (50-100nm) layer deposited by PECVD and subsequently by Au (2nm) or In (4-10nm) film via e-beam evaporation. The employment of a-Si thin layer between polyimide and seed layer has great importance to accelerate the supersaturation of the seed NPs formed by dewetting, and promote a quick nucleation. Otherwise, the seed NPs will be buried under the parasitic deposition of a-Si and as a result little NWs will sprout out. It should be pointed out that In gets oxidized very fast and a reductive treatment has been necessary. Therefore, a H₂ plasma was applied prior to grow the Si NWs to restore In and prompt NWs growth. Figure 1 presents an In-seeded Si NWs sample on polyimide substrate. The circular In-patterned regions host a high density of Si NWs and appear brownish due to largely diffused light by Si NWs. The inset shows the easy peeling-off process of that sample.

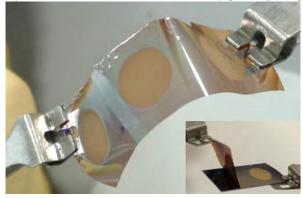


Figure 1.In-catalyzed SiNWs on polyimide substrate

This work has received funding from the EU's 7th Framework Programme [agreement no. 316751 (NanoEmbrace)]

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Growth of InP nanoflags and planar nanowires by *in situ* catalyst manipulation.

A. Kelrich, Y Calahorra, S. Cohen and D. Ritter Department of Electrical engineering, Technion, Haifa 32000, Israel

E-mail: skelrich@tx.technion.ac.il

Au-assisted growth is a common method for bottom up III-V semiconductor nanowire (NW) synthesis owing to the high degree of control over NW aspect ratio, crystal phase purity and heterostructure interface sharpness, contributing to demonstrated applications such as single electron transistors, lasers and nanomechanical devices. In the following we extend the concept of catalyst assisted growth of nanowires to span an additional growth dimension to form bi-axial nanomaterials. Despite crystal structure flexibility achieved in NWs, materials in the form of single-crystal thin film are still desirable in many applications due to their unique physical, and chemical properties as well as possible device integration¹.

We report here on the synthesis of novel, free standing, quasi two-dimensional (2D) nanostructures and planar NWs, in a process of comparable complexity to standard NW growth – only by changing basic growth parameters. We'll describe the growth-modes for the creation of nanoflag type structures, starting from selective area catalyzed NW growth², going through *in-situ* controlled displacement of the catalyst, and concluding with catalyst guided radial growth.

At the heart of proposed technique lays the ability to shift the catalyst from the top of the NW and induce its migration downwards along a single NW sidewall. We'll discuss the mechanism behind this phenomenon, as well as the criteria for the migration stop with particular consideration of catalyst-NW interaction and structural defect density control along the NW³. The last aspect is especially important as the "pole" crystal structure is epitaxially transferred to the nanoflag, resulting in some cases in nearly pure thin films of wurtzite (WZ) InP. Optimizing the process with additional flux related steps, enabled us to achieve more than 90% yield of such 2D WZ nanostructures.

In addition, guiding the catalyst to the NW base, followed by axial NW growth conditions, we achieved planar NWs on amorphous SiN_x layer, resulting in an "easy to handle" epitaxial NW configuration with a potential for implementation in future nano-devices.

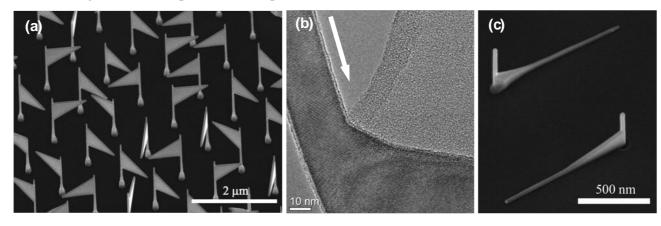


Figure 1: (a) 30° tilted view SEM image of InP nanoflag array. The flag directions follow arbitrary the six $\{1\text{-}100\}$ facets of the NW (b) HRTEM image of the nanoflag, emphasizing pure WZ phase of the entire structure and epitaxial transition from the nanowire to the flag. The arrow indicates the NW growth direction. (c) 30° tilted view SEM image of planar InP nanowires grown on top of SiN_x mask.

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Tunable quantum confinement in ultrathin GaAs based nanowires via reverse reaction growth

<u>Bernhard Loitsch</u>¹, Daniel Rudolph¹, Stefanie Mörkotter¹, Julia Winnerl¹, Gianluca Grimaldi¹, Jakob Wierzbowski¹, Sonja Matich, Markus Döblinger², Gerhard Abstreiter^{1,3}, Jonathan Finley¹, and Gregor Koblmüller¹

Most properties of GaAs Nanowires (NWs) and their devices are, despite their manifestly 1D (high aspect ratio) geometry, still described by 3D bulk-like properties. A truly 1D NW platform, with NW diameters below the exciton Bohr radius would enable new opportunities in mesoscopic devices for advanced quantum photonics, quantum transport and nanoelectronics. In this contribution we present a novel "reverse-reaction-growth" scheme to controllably tune the diameter of GaAs NWs, grown by self catalyzed droplet epitaxy on silicon substrate, down to 7 nm in diameter via in-situ thermal evaporation in a molecular beam epitaxy (MBE) chamber. After surface passivation by an AlGaAs shell the ultrathin GaAs NWs exhibit a very high luminescence efficiency. The photoluminescence (PL) energy systematically increases with decreasing NW diameter, in good agreement with the calculated transition energy of an exciton confined in a hexagonal GaAs NW core. By direct correlation of PL and transmission electron microscopy (TEM) we observe a transition from 1D quantum confinement in phase pure zincblende (ZB) NWs towards 0D quantum dot like (QD) emitters in NWs with wurtzite (WZ) segments embedded along the NW axis. PL-excitation measurements further confirm the presence of strong quantum confinement effects in ultrathin GaAs NWs.

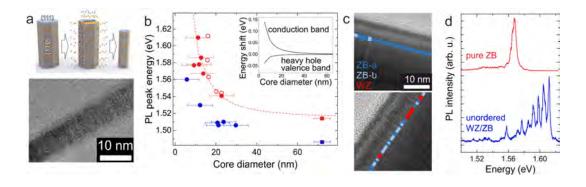


Figure 1: (a) Schematic of reverse reaction growth and TEM image of resulting ultrathin GaAs NW. (b) Transition energy of excitons confined in ultrathin 1D GaAs NW cores. (c) and (d) TEM image and corresponding PL spectrum of GaAs-AlGaAs core-shell NWs with ultrathin GaAs core and different crystal structure.

Walter Schottky Institut and Physik Department, Technische Universität München, Garching, Germany
 Department of Chemistry, Ludwig-Maximilians-Universität Munich, Munich, Germany
 Institute of Advanced Study, Technische Universität München, Garching, Germany

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Self-assembled InAs nanowire junctions on Si substrates

<u>Torsten Rieger</u>¹, Daniil Vakulov¹, Daniel Rosenbach¹, Sebastian Heedt¹, Detlev Grützmacher¹, Thomas Schäpers¹, Mihail Ion Lepsa¹

¹ Peter Grünberg Institute 9 and JARA-FIT, Forschungszentrum Jülich GmbH, Germany

Nanowire junctions combining individual nanowires present a particular interest for the search and investigation of Majorana fermions^{1,2} in semiconductors. So far, these junctions have been obtained with Au-assisted grown nanowires. However, the Au seed particles can have a strong impact on the crystalline quality of the junction, partially etching into the existing nanowires². Nanowire junctions obtained without the use of any seed particle represent therefore an attractive alternative.

We present the growth, structural characteristics and electronic transport properties of self-assembled InAs nanowire junctions. To obtain these junctions, Si (100) substrates with patterned V-grooves having (111) facets have been used. The InAs nanowires were grown by molecular beam epitaxy in a self-assisted manner without the use of any seed particle. Due to relative orientation of the V-groove facets, the nanowires merge into junctions of different geometries. Figure 1a shows a representative sample, evidencing nanowire growth only on the facets of the V-grooves. In Fig. 1b, nanowire junctions having a "T" shape are illustrated. Apart from this junction geometry, also L- and X-shaped junctions are obtained. The self-assisted grown InAs nanowires have a high density of stacking faults. Surprisingly, the crystal structure of the junctions turns into a pure zinc blende one (see Fig. 1c). Shockley partial dislocations were identified to be the driving force for this transformation.

Electrical measurements performed on the different junctions do not show any impact of the junction. Exemplarily, this is presented in Fig. 1d showing a contacted T-shaped InAs nanowire junction and the I-V and transfer characteristics for all the combinations of the contacts.

The results demonstrate the excellent suitability Au-free InAs nanowire junctions for future electronic devices.

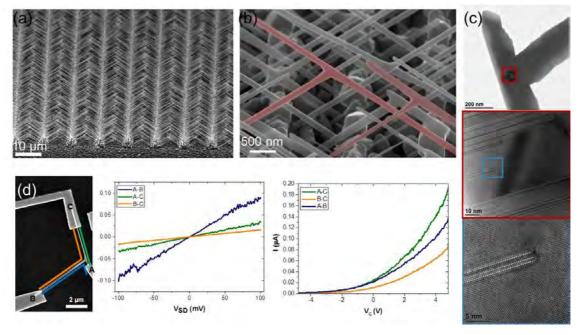


Figure 1: (a) SEM image of InAs nanowires grown on Si (100) substrates with V-grooves having (111) facets. (b) SEM image of T-shaped junctions. (c) (HR)TEM images of a T-shaped junction. (d) SEM image and RT electrical characteristics of a contacted T-shaped junction.

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Template-Assisted Selective Epitaxy: Highly controlled III-V nanowire integration on Si

Mattias Borg¹, Heinz Schmid, Kirsten E. Moselund, Davide Cutaia, Heike Riel

¹ IBM Research – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland

III-V semiconductor nanowires have emerged as promising materials for applications in highspeed electronics, optoelectronics, solar energy harvesting, thermo-electrics and sensing. The most successful nanowire synthesis methods are vapour-liquid-solid growth and selective area epitaxy, and by now the understanding of the nanowire growth process by these methods is extensive. However, to bring nanowires into high-volume production of electronic and optoelectronic components, it is required to integrate III-V nanowires with Si technology and to achieve a level of control and low variability that is very challenging to achieve by mere epitaxial growth control. Here we describe a novel method called Template-Assisted Selective Epitaxy (TASE) that combines top-down fabrication with bottom-up epitaxy to realize highly controlled synthesis of III-V nanowires and nanostructure devices on Si substrates of any orientation.¹⁻⁴ TASE utilizes optimized CMOS-compatible processes to fabricate silicon oxide nanotube templates for subsequent epitaxial growth. The orientation of these templates can be either vertical (Fig. 1a) or horizontal (Fig. 1b) and may have varied diameter if desired (Fig. 1c-d). The nanotube templates guide the growth of the III-V crystals such that they take on the same shape as the templates, thus transferring the highly controlled morphology of the template into III-V nanowires. A key feature of the TASE method is to limit the extent of the Si/III-V junction to confine detrimental strain-induced defects at the heterojunction, resulting in a high-quality crystal in the bulk of the III-V nanostructure. We furthermore demonstrate that the crystal quality of the TASE-grown nanowires match that of other selective-area grown nanowires, and may be further improved by tuning the growth parameters. Using grown cross-bar nanostructures (Fig. 1e-f) we also evaluate the Hall electron mobility of InAs nanostructures to be higher than 5000 cm²/Vs. Finally, we present nanowire MOSFETs with excellent performance metrics.

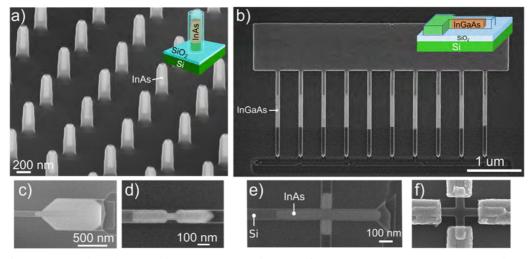


Figure 1: Scanning electron microscopy (SEM) images of TASE-grown III-V nanostructures in (a) vertical and (b) horizontal nanotube templates. The insets schematically visualize the structures. SEM image of horizontal InAs nanostructure with (c) expanded and (d) constricted in-plane width. SEM image showing a horizontal InAs cross structure (e) as-grown and (f) as a finished Hall device.

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In As Growth in Si/SiO2 Nanotubes by Molecular Beam Epitaxy

<u>Jelena Vukajlovic Plestina</u>¹, Gözde Tütüncüoglu¹, Heidi Potts¹, Federico Matteini¹, Esther Alarcon Llado¹ and Anna Fontcuberta i Morral¹

¹LMSC, Ecole Polytechnique Federale de Lausanne, Switzerland

Position controlled and self-assisted growth of nanowires (NW) on silicon (Si) substrates is needed to obtain functional, high performances devices. Control over the position can be done by different methods of patterning by defining arrays of holes on the dielectric mask. E-beam lithography (EBL) is the most frequently used patterning method in the literature [1, 2]. Even though it offers impressive precision, an alternative technique should be explored to enable large scale implementation of NWs. One possible alternative is phase shift photolithography (PSL), which was used in this work to define arrays of silicon oxide nanotubes. As Borg et al. reported, tube template should allow growth of the vertical NWs on any kind of the substrate crystalline orientation [3]. Beside this more practical point of view, oxide nanotubes based substrates are interesting platforms for more fundamental investigations of different phenomena that are present during MBE NW growth, such as surface diffusion, adsorption-desorption mechanisms and capillarity effects in VLS growth.

Here we present the growth results for InAs NWs grown on the silicon oxide tubes based substrate. We have successfully grown high yield nanowire arrays as presented in Fig. 1.a) and more detailed SEMs in Fig 1.b) and c). As most interesting result we present In droplets that we were able to capture during In deposition experiment. Fig 1.d) and e) show the In droplets captured within the tubes while Fig 1.f) presents In droplet on top of the Si pillars coated with silicon oxide. This shows that within the tube InAs NWs grow through VLS mechanism what can provide a novel approach for controlling the crystalline structure as reported in [4].

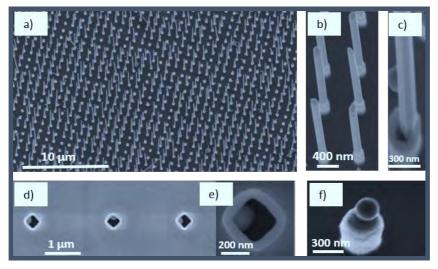


Figure 1: a) SEM image of the small part of the high yield of InAs NWs grown in on the tube substrate, b) and c) more detailed SEM of InAs NWs in the silicon oxide tubes, d) and e) In droplets captured inside the tubes in the In deposition experiment, f) In droplet on top of the silicon pillar wrapped with silicon oxide.

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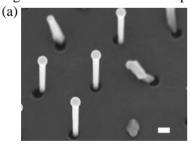
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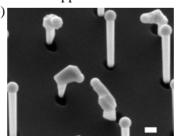
High-yield Self-catalyzed GaAsSb/GaAs Heterostructured Nanowire Array on Si(111) by Molecular Beam Epitaxy

<u>Dingding Ren</u>¹, Dasa L. Dheeraj², Junghwan Huh¹, Johannes F. Reinertsen¹, A. Munshi Mazid², Dong-Chul Kim^{1,2}, Antonius T. J. van Helvoort³, Helge Weman^{1,2}, and Bjørn-Ove Fimland^{1,2}

One-dimensional nanowire (NW) arrays are promising structures for nanoscale electronic and optoelectronic devices, for example solar cells¹. GaAs NW array grown on Si is one of the solutions for low-cost high-performance device architecture.² However, the low yield of vertical GaAs NWs in the NW array on Si(111) is still a limiting factor for wafer-scale application. One of the major reasons for the low yield is that the NW growth is sensitive to the pre-growth pattern fabrication; another reason is due to a high density of twins close to the nucleation interface.^{3,4} It has been reported that GaAsSb NWs adapt twin-free stable zinc blende structure down to first bi-layer that leads to high yield for positioned growth,^{5,6} which could be used as a bottom stem for high yield GaAs NW arrays.

In this work, we have successfully demonstrated the growth of GaAsSb/GaAs heterostructured NW arrays on Si(111) substrates. Nanohole patterns are defined in a SiO₂ mask using either nanoimprint lithography (NIL) or electron beam lithography for the growth of the NWs. Figure 1(a) shows a SEM image of low yield GaAs NW arrays grown on a NIL patterned substrate with a hole diameter around 220 nm. By growing a GaAsSb stem before the growth of the GaAs NWs, the NW yield is greatly improved, although quite a few kinked NWs can be observed in figure 1(b). We have adapted the growth of a graded transition region (GTR) to prevent the change in the growth direction and morphology at the GaAsSb/GaAs interface in the NWs. This is found to be a crucial step to maintain the growth of NWs in (111)B direction, and minimize the formation of kinked NWs. The yield of GaAsSb/GaAs heterostructured NW arrays with GTR is found to be around 90%, as shown in figure 1(c). This routine has a higher tolerance with the pre-growth patterning process, delivering a similar yield between 90 and 230 nmdiameter opening sizes. In addition, the GaAsSb stem has a higher radial growth rate compared to bare GaAs NWs, which can fill up the SiO₂ openings during axial growth. We believe that the GaAsSb/GaAs heterostructured NW arrays could be an effective high-yield platform for high-efficient low-cost nano-optoelectronic applications.





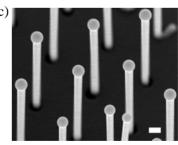


Figure 1: SEM images of NW array grown on NIL patterned Si(111). (a) GaAs NWs (b) GaAsSb/GaAs NWs without GRT (c) GaAsSb/GaAs NWs with GRT. The scale bars are 200 nm.

¹ Department of Electronics and Telecommunications, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway

² CrayoNano AS, Otto Nielsens vei 12, NO-7052, Trondheim, Norway

³ Department of Physics, Norwegian University of Science and Technology (NTNU), NO-7491,

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Narrowing the radius distribution of Ga-catalyzed GaAs nanowires

<u>V.G. Dubrovskii</u>^{1,2}, T. Xu³, A. Díaz Álvarez^{3,4}, S. Plissard⁵, P. Caroff⁶, F. Glas⁷, B. Grandidier³

¹Ioffe Physical technical Institute RAS, Politekhnicheskaya 26, 194021, St. Petersburg, Russia ²ITMO University, Kronverkskiy pr. 49, 197101 St. Petersburg, Russia

³IEMN, CNRS, UMR 8520, Département ISEN, 41 bd Vauban, 59046 Lille Cedex, France, ⁴Key Laboratory of Advanced Display and System Application, Shanghai University, 149 Yanchang Road, Shanghai 200072, People's Republic of China

⁵CNRS-Laboratoire d'Analyse et d'Architecture des Systèmes (LAAS), Univ. de Toulouse, 7 avenue du colonel Roche, F-31400 Toulouse, France

⁶Department of Electronic Materials Engineering, Research School of Physics and Engineering, The Australian National University, Canberra, ACT 0200, Australia

⁷CNRS-LPN, Route de Nozay, 91460 Marcoussis, France

Designing strategies to reach radius-uniformity in fabrication of semiconductor nanowire ensembles is essential for numerous applications. When Ga-catalyzed GaAs nanowires are grown by droplet-engineered molecular beam epitaxy on Si substrates, we observe a significant narrowing of the radius distribution of the final nanowire array with respect to the size distribution of the initial Ga droplets¹ [Fig. 1 (a)]. Considering that the droplet serves as a non-equilibrium reservoir of a group III metal, we develop a model that demonstrates a self-equilibration effect on the droplet size in self-catalyzed III-V nanowires. In particular, we find the following equation for the nanowire radius

$$dR/dt = -A + B/R$$
,

where B is a positive diffusion-induced term and $A \propto dL/dt - \chi_3 v_3$. Thus, in situ self-equilibration of the nanowire radius is observed in As-rich conditions where the arsenic-limited elongation rate dL/dt is larger than the effective Ga deposition rate $\chi_3 v_3$. Figure 1 (b) shows the time evolution of the nanowire diameters 2R starting from differently sized droplets and demonstrates that the diameter distribution acquires a delta-like shape after 300 s of growth, with a stationary diameter of ~ 50 nm for a 250 nm array pitch.

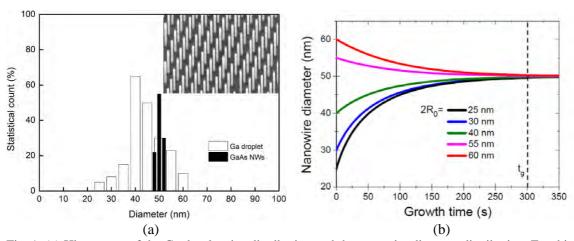


Fig. 1. (a) Histograms of the Ga droplet size distribution and the nanowire diameter distribution. For this array, the hole size and pitch are 60 nm and 250 nm, respectively. (b) Theoretical time-dependent variations of the nanowire diameters for different R_0 . The vertical dash segment indicates the growth time t_q of 300 s.

This effect leads to arrays of nanowires with a high degree of uniformity, while the stationary radius can be further finely tuned by varying the spacing of the array pitch on patterned Si substrates.

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VLS growth from chloride gaseous precursors: fast atomistic growth process for polytypism-free III-V NWs with record aspect ratio

E. Gil 1,2

Hydride vapor phase epitaxy (HVPE) involves high mass inputs of chloride III-Cl and hydride V-H₃ gaseous growth precursors, providing the largest range of growth rates (1 to 300 µm/h) for the planar growth of III-V semiconductors. When it comes to metal catalyst-assisted vapor-liquid-solid (VLS) growth of nanowires (NWs), the high mass input of precursors assisted by high dechlorination frequency yields high axial growth rate of NWs (> 150 µm/h)^{(a)(b)}. Remarkable polytypism-free NWs showing constant diameter over length of several tens of microns are then grown in a few minutes. As a result, record pure zincblende phase in GaAs NWs was shown with a radius as small as 5 nm^(c). A first interpretation of growth involves high Ga concentration in the liquid catalyst droplet, which decreases the droplet surface energy, disabling nucleation at the triple phase line thus preventing the formation of wurtzite stacking sequences. This holds for any nanowire radius^(c). Recent HVPE growth of (In,Ga)N NWs showing a wide range of In composition may call for another understanding: catalyst-assisted HVPE growth could be purely atomistic, so that any nucleation step would no longer take place. Both the polytypism-free crystal structure and the possibility to process a wide range of alloy compositions could be explained by simple atomistic growth. Such atomistic growth is expected to minimize reservoir effects, which is of benefit to the growth of NW heterostructures with controlled variations of composition. In this talk, we will address the properties of NWs grown by HVPE and discuss the physics of growth associated with chloride gaseous precursors.

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¹ Université Clermont Auvergne, Université Blaise Pascal, Institut Pascal, BP 10448, F-63000 Clermont-Ferrand, France

² CNRS, UMR 6602, IP, F-63178 Aubière, France

Decoding crystal phase switching in nanowires

S. Assali¹, L. Gagliano¹, D. S. Oliveira², M. A. Verheijen^{1,3},

L.-F. Feiner¹, S. R. Plissard⁴, and E. P. A. M. Bakkers^{1,5}

The development of nanowire homostructures formed by the combination of the zinc blende (ZB) and wurtzite (WZ) crystal phases has drawn a lot of attention in the last few years^{1,2}. Gallium Phosphide (GaP) in the normal cubic phase has an indirect band gap, but the predicted direct band gap in the WZ crystal structure has been recently shown in WZ GaP wires by photoluminescence measurements³ and photoelectrochemical hydrogen production⁴. Large spontaneous polarization fields are predicted for WZ GaP⁵, which can induce surface charges across a thin ZB GaP nanowires segment⁶. This would allow the growth of crystal phase quantum well (CPQW) and quantum dot (CPQD) structures in this material system⁷.

Here, we study the growth kinetics of pure and thus defect-free WZ/ZB homostructures in GaP nanowires with the aim to obtain monolayer control of the ZB and WZ segment lengths. We find that the Ga concentration and the supersaturation in the catalyst particle are the key parameters determining the growth kinetics. These parameters can be controlled by the gallium partial pressure and the temperature. The formation of WZ and ZB can be understood with a model based on nucleation either at the triple phase line (TPL) for the WZ phase and in the center (C) of the solid-liquid interface for the ZB phase. With this knowledge, a WZ/ZB superlattice with multiple WZ and ZB segments with constant length has been fabricated.

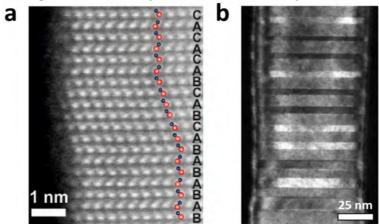


Figure 1: (a) HRSTEM image of a WZ/ZB/WZ junction showing atomically sharp interfaces. By choosing a growth time of 4.2 s the growth of 7 ZB MLs is observed. The red and blue dots indicate the Ga and P atoms, respectively. (b) Dark-field TEM image of a WZ/ZB superlattice. No stacking faults are observed in both crystal phases.

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¹ Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

² Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, UNICAMP, 13083-859, Campinas, SP, Brazil

³ Philips Innovation Services Eindhoven, High Tech Campus 11, 5656AE Eindhoven, The Netherlands ⁴ CNRS-Laboratoire d'Analyse et d'Architecture des Systèmes (LAAS), Univ. de Toulouse, 7 avenue du colonel Roche, F-31400 Toulouse, France

⁵ Kavli Institute of Nanoscience, Delft University of Technology, 2600 GA Delft, The Netherlands

Group V-flow induced zinc blende – wurtzite – zinc blende transition in Au-seeded GaAs nanowires grown by MOVPE

Sebastian Lehmann¹, Daniel Jacobsson¹, and Kimberly A. Dick^{1,2}

¹ Lund University, Solid State Physics, Box 118, 22100, Lund, Sweden, ² Centre for Analysis and Synthesis, Lund University, Box 124, 22100, Lund, Sweden

corresponding author - Sebastian Lehmann: Sebastian.Lehmann@ftf.lth.se

Keywords: GaAs, nanowire, wurtzite, zinc blende, MOVPE

Wurtzite (WZ) to zinc blende (ZB) transitions have been observed in Au-seeded GaAs nanowire growth by metal organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE), respectively. A major parameter which was effectively used to control this structural transition has been the nominal [V/III]-ratio – or more precisely the group V flow. However, it is of special interest that the structural transitions observed in MOVPE and MBE are of opposite sign. Namely, for nominally increasing the [V/III]-ratio a WZ to ZB transition has been reported for MOVPE¹ but a ZB to WZ transition has been observed for MBE².

In this contribution we show that the structural transitions observed in Au-seeded GaAs nanowire growth in MOVPE and MBE, respectively, are not necessarily contradictory. We found that MOVPE-grown GaAs nanowires show a ZB – WZ – ZB transition for increasing nominal [V/III]-ratios but extending the range to very low nominal [V/III]-ratios of 0.6 compared to previous work¹. These results hold the potential of explaining the opposite structural preferences in Au-seeded GaAs nanowires previously reported for MOVPE and MBE growth which might be of fundamental interest for nanowire growth modelling.

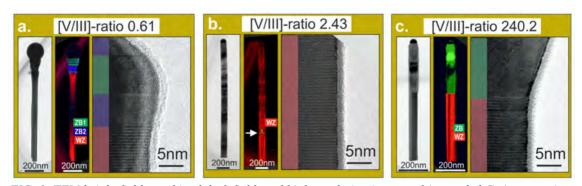


FIG. 1: TEM bright field, combined dark field, and high resolution images of Au-seeded GaAs nanowires with a WZ stem grown at a nominal [V/III]-ratio of 2.43. The ZB top segment was grown at a nominal [V/III]-ratio of 0.61 for (a.) and 240.2 for (c.), respectively, with the wurtzite reference grown at 2.43 (b.).

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Nitride nanowire light emitting diodes: from single wire properties to flexible light emitters

M. Tchernycheva¹, X. Dai¹, H. Zhang¹, A. Messanvi^{1,2}, V. Neplokh¹, P. Lavenus¹, N. Guan¹, F. H. Julien¹, L. Rigutti³, A. Babichev⁴, G. Jacopin,⁵ L. Largeau,⁶ R. Ciechonski,⁷ G. Vescovi,⁷ O. Kryliouk⁸, M. Foldyna⁹, J. Eymery², and C. Durand²

Ioffe Institute, Polytechnicheskaya 26, 194021 St. Petersburg, Russia
 ICMP LOEQ Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
 LPN-CNRS, Route de Nozay, 91460 Marcoussis, France
 GLO AB, Ideon Science Park, Scheelevägen 17, S-223 70 Lund, Sweden
 GLO-USA, 1225 Bordeaux Dr, Sunnyvale, CA, 94086, USA

⁹ CNRS, Laboratoire de Physique des Interfaces et Couches Minces (LPICM), Ecole polytechnique, 91128 Palaiseau, France

We will present our recent work on nitride nanowire based light emitters. These nanomaterials have the potential to boost the device performance, to improve the energy efficiency, to reduce the cost and to bring new functionalities. In particular, we will discuss our recent progress towards flexible nitride nanowire devices. We propose a method to combine high flexibility of polymer films with high quantum efficiency provided by nitride nanowires to achieve flexible inorganic light emitting diodes and light sensors [1]. We will also discuss the fabrication and characterization of single nanowire light emitting diodes with graphene transparent contacts [2], the structural characterization of these nanowires using charge collection microscopy [3], the possibility to control the LED color by a post-growth treatment [4] as well as the coupling of single nanowire emitters with waveguides in order to form a functional photonic platform [5].



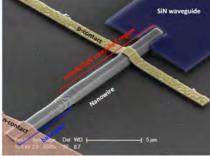


Figure: Left – flexible nanowire-based blue LED; Right – nanowire LED integration with an SiN waveguide

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 ¹ Institut d'Electronique Fondamentale, UMR 8622 CNRS, Université Paris Sud XI, 91405 Orsay, France
 ² Equipe mixte "Nanophysique et semiconducteurs," CEA/CNRS/Université Joseph Fourier, CEA, INAC, SP2M, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

³ Groupe de Physique des Matériaux, UMR CNRS 6634, Normandie University, University of Rouen and INSA Rouen, 76801 St. Etienne du Rouvray, France

Molecular beam epitaxy growth of InGaN/GaN nanowire heterostructures

Xin Zhang^{1, 2, 3}, Hugo Lourenço-Martins⁴, Sophie Meuret⁴, Luiz Tizei⁴, Mathieu Kociak⁴, Pierre-Henri Jouneau⁵, Catherine Bougerol^{1,6}, and Bruno Daudin^{1,2}

Corresponding author: bruno.daudin@cea.fr

¹Univ. Grenoble Alpes, F-38000 Grenoble, France

²CEA, INAC-SP2M, "Nanophysique et semiconducteurs" group, F-38000 Grenoble, France

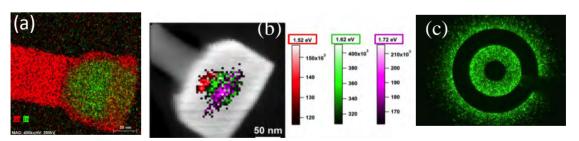
³ALEDIA, 17 rue des martyrs, Bât. M23, 38054 Grenoble CEDEX 9, France

⁴Lab. de Physique des Solides, UMR 8502 Université Paris Sud bât 510, 91405 Orsay Cedex, France

⁵CEA, INAC, MINATEC Campus, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France

⁶CNRS, Institut Néel, "Nanophysique et semiconducteurs" group, F-38000 Grenoble, France

We report on the growth, structural and optical characterization of InGaN nanowire (NW) heterostructures grown by molecular beam epitaxy, in view of realizing green and red light emitting diodes (LEDs). The InGaN NWs have been grown by molecular beam epitaxy (MBE) on a GaN base. The slight excess of metal during growth led to an enlargement of the InGaN section, with formation of characteristic pinhead structures nucleated in the center of the GaN base [1]. As evidenced in figure (a) by Energy Dispersive X-rays Spectroscopy (EDS) the InGaN section is surrounded by a Ga-rich shell, consistent with previous results [2,3,4], Indium content could be as large as 60%. NWs exhibited intense photoluminescence (PL) signal in a 1.7-3.0 eV range depending on In content, due to the absence of extended defects in the InGaN section, a feature directly linked to the specific elastic strain relaxation mechanism in NWs [5]. In composition inhomogeneities were observed by EDS and resulted in emission wavelength scattering put in evidence by mapping of cathodoluminescence at the nm scale as shown in figure (b). Interestingly, as a consequence of N-polarity of InGaN NWs, the temperature stability of N-polar InGaN as a function of In content (0-60% range) was experimentally established and found significantly higher than for 2D metal-polar alloys, a key advantage for practical realization of long wavelength LEDs. Finally, green and red electroluminescence of processed LEDs consisting of n-GaN/InGaN/p-GaN NW heterostructures was observed, as an experimental evidence that the NW route may contribute to close the green gap and open a path towards full color emitting devices.



(a) Energy dispersive Xrays spectroscopy mapping of an InGaN NW section on top of a GaN NW. Red: Gallium; green: Indium (b) Nano-CL map of an InGaN section similar to the one in (a). The intensity scale has been chosen to make clear the spatial origin of three different emission lines at 1.52, 1.62 and 1.72 eV (c) electroemission of a NW-based LED

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Characterization of III-V nanowires towards the realisation of intermediate band solar cells

<u>Vilgailė Dagytė</u>¹, Magnus Heurlin¹, Gaute Otnes¹, Mats-Erik Pistol¹, Lars Samuelson¹, and Magnus T. Borgström¹

¹ Solid State Physics, Lund University, Box 118, S-221 00 Lund, Sweden

With the single p-n junction solar cell approach, photovoltaic energy conversion efficiencies up to 33% can be reached under 1-sun illumination and 41% under concentrated light. A common approach to reach higher efficiencies is to stack multiple materials with different bandgaps in a multi-junction solar cell. However, such an approach is quite complex and expensive to realize. One of the emerging alternatives is a multiband solar cell, for example, an intermediate band solar cell (IBSC), which contains an additional band between the conduction and valence bands. In addition to single-photon absorption through transitions from the valence band to the conduction band, an IBSC can use the intermediate band to absorb two lower energy photons to produce an electron-hole pair. IBSC has been predicted to have the potential to be more efficient (47% under 1-sun illumination and 63% under concentrated sun light) than a single junction solar cell or even a 2-junction solar cell by covering a larger part of the solar spectrum or reducing thermalisation losses, without decreasing the $V_{\rm oc}$. $V_{\rm oc}$.

Semiconductor nanowires are, among other applications, being intensively researched for single junction and tandem solar cells.⁵ Semiconductor nanowires show promise for reduced material consumption with bulk like photocurrent generation, more efficient carrier collection, and single junction efficiency limit slightly exceeding that of a bulk cell, as well as the flexibility in the choice of lattice-mismatched materials.^{5,6,7} However, the concept of multiband nanowire solar cells has not been investigated. The use of nanowires could reduce the fabrication cost as well as open up for optimized, but lattice-mismatched, material combinations for the IBSC.

Here we present transmission electron microscope and optical characterisation of GaInP nanowires with an InP quantum well (the structure shown in Figure 1), grown by MOVPE from a hexagonal pattern of Au catalysts with a pitch of 500 nm, defined on InP wafer by nano-imprint lithography, metal evaporation and lift off. The material choice is GaInP since its room temperature bandgap can be tuned from 1.34 to 2.26 eV, which offers materials combinations close to the predicted optimum for IBSC.³ As a first step we performed temperature and power dependent photoluminescence spectroscopy. These studies reveal interesting carrier distribution and thermalisation effects in a p-i-n nanowire structure with an axial quantum-well segment with respect to its undoped counterpart.

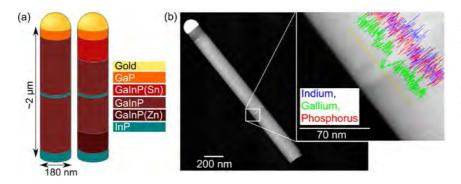


Figure 1: (a) Schematics of the studied intrinsic (left) and p-i-n (right) nanowires with InP quantum well; (b) TEM of an intrinsic wire with the InP segment.

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Bottom-up grown direct bandgap $Ge_{1-x}Sn_x$ (x> 0.09) nanowires

Subhajit Biswas¹, Jessica Doherty¹ and Justin D. Holmes^{1,2}

¹Materials Chemistry & Analysis Group, Department of Chemistry and the Tyndall National Institute, University College Cork, Cork, Ireland. ²AMBER@CRANN, Trinity College Dublin, Dublin 2, Ireland.

The development of direct bandgap, group IV one-dimensional nanoscale systems is critical for the advancement of silicon compatible device modules. In particular, direct bandgap semiconductor materials are needed for new device architectures such as "band-to-band tunnelling (BTBT)" tunnel FETs (TFET), optical interconnects and for the development of group IV photonics because these technological modules are based on the direct transition of carriers between energy bands. Here, we describe for the first time the fabrication of uniform diameter, direct bandgap $Ge_{1-x}Sn_x$ alloy nanowires, with a Sn incorporation up to 9.2 at.%, through a conventional catalytic bottom-up growth paradigm employing innovative catalysts and precursors. Sn inclusion in the Ge nanowires far exceeded the equilibrium solubility (~ 1 at.%) of Sn in bulk Ge. The addition of an annealing step close to the Ge-Sn eutectic temperature (230 °C) during cool-down, facilitated the excessive dissolution of Sn in the nanowires. Sn was uniformly distributed throughout the Ge nanowire lattice, as determined by atomic resolution energy electron loss spectroscopy, with no metallic Sn segregation or precipitation at the surface or within the bulk of the nanowires. A direct bandgap has been identified for $Ge_{1-x}Sn_x$ nanowires with 9.2 at.% Sn through low temperature photoluminescence. The non-equilibrium incorporation of Sn into the Ge nanowires can be understood in terms of a kinetic trapping model for impurity incorporation at the triple-phase boundary during growth.

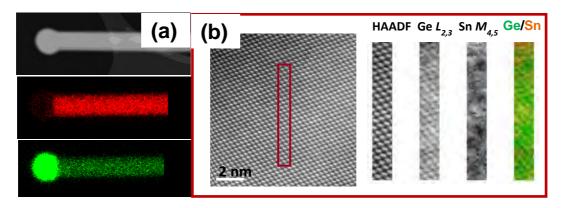


Figure 1: (a) EDX mapping in HAADF mode of $Ge_{1-x}Sn_x$ nanowire with greater than 9 atomic% Sn incorporation. (b) High resolution EELS mapping from nanowire core shows sparse distribution of Sn in Ge lattice.

Band gap blueshift induced by Wurtzite crystal phase in InAsSb nanowires grown by selective-area MOCVD

<u>Diana L. Huffaker^{1,2}</u>, Alan C. Farrell¹, Wook-Jae Lee¹, Pradeep Senanayake¹

¹ Electrical Engineering,, University of California at Los Angeles, Los Angeles, CA 90095, USA ² California NanoSystems Institute, University of California at Los Angeles, Los Angeles, CA 90095, USA

We report on the growth and characterization of InAs_{1-x}Sb_x nanowires grown by selective-area metal-organic chemical vapor deposition (SA-MOCVD). Uniform arrays of high aspect-ratio hexagonal nanowires (Fig. 1a) are achieved only with very slow vertical growth rates (< 30 nm/min) and V/III ≥ 2 . Antimony composition—determined with energy dispersive x-ray spectroscopy (EDX)—increases with a decrease in growth temperature and the (77 K) photoluminescence peak shifts to lower energy (Fig. 2b). The intensity of the nanowire PL is comparable to the substrate (at 395 meV), despite a fill factor of less than 10%. The peak energy E_p as a function of temperature is used to determine the appropriate correction to calculate the bandgap. The bandgap is estimated by subtracting k_BT/2 (typical for binaries) and 2k_BT (typical for ternaries) and comparing the data to the prediction of the Varshni equation. The best fit to the data is the correction by k_BT/2, and the bandgap vs. composition is plotted in Fig. 1c. We find that for low antimony composition, the bandgap is larger than expected by as much as 60 meV (Fig. 1c inset). There exists both theoretical and experimental evidence² that the bandgap of wurtzite (WZ) InAs is blueshifted with respect to zinc-blende (ZB) InAs. In addition, it has been shown that there is significant structural evolution of InAsSb nanowires with increase of Sb incorporation, from mostly WZ at low antimony composition to entirely ZB at higher antimony composition3. These two facts suggest that we should expect to see this structural evolution mirrored by a similar evolution of the bandgap of InAsSb nanowires for increasing antimony composition. This is indeed what is observed up to x = 0.07 when the bandgap blueshift vanishes, suggesting the transition to the ZB crystal phase is complete. High-resolution transmission electron microscopy analysis on an InAsSb nanowire with x = 0.07 confirms that the crystal phase is predominantly zinc-blende (Fig. 1d). Based on these results, we conclude that the blueshift at low antimony composition is caused by the difference in band gap energy between WZ and ZB and decreases until vanishing for $x \ge 0.07$, mirroring the evolution of the crystal phase.

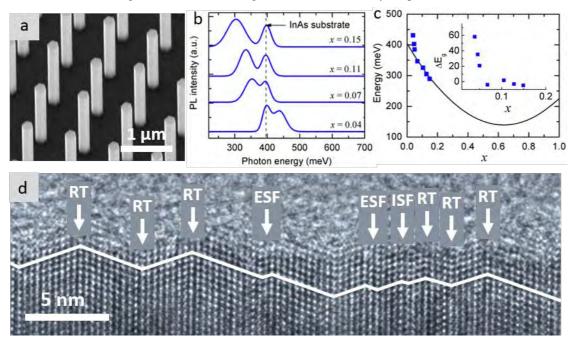


Figure 1: a) Tilted SEM of InAsSb nanowire array. b) 77 K photoluminescence of InAsSb nanowires with increasing antimony composition. The peak at 395 meV is due to the InAs substrate. c) Estimated bandgap calculated with $k_BT/2$ correction. The solid line is calculated with a bowing parameter of 662 meV. Inset: Blushift of bandgap as function of composition d) HR-TEM image showing zinc-blende structure, rotational twins (RT), intrinsic (ISF) and extrinsic (ESF) stacking faults with no polytypism.

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Controlled growth and enhanced thermoelectric properties of topological crystalline insulator nanowires

Shixiong Zhang

Department of Physics, Indiana University, Bloomington, IN, USA

Topological crystalline insulators (TCIs) are a class of quantum materials that host topological surface states protected by crystalline mirror symmetry. Immediately after theoretical predictions, tin telluride (SnTe) and its alloy compounds were experimentally demonstrated to be TCIs. The SnTe-based TCIs have intriguing surface properties, including a Van-Hove singularity in the density of states, which could be useful for enhancing thermoelectric properties. One dimensional nanowires have large surface-area-to-volume ratio and hence increased contributions from surface states. Here I will discuss the controlled synthesis and thermoelectric studies of nanowires of SnTe and its alloy compounds. The nanowires were grown using a vapor transport approach and are single crystalline with a broad diameter distribution. Correlated measurements of electrical conductivity, thermopower and thermal conductivity were performed on the same, individual nanowires to accurately determine their thermoelectric figure of merit ZTs. While their electrical conductivity is comparable with that of bulk samples, the thermopower of nanowires is higher than the bulk values and it shows a strong diameter dependence. The thermal conductivity of nanowires is lower than bulk values, which may arise from the enhanced phonon-surface scattering. The simultaneous improvement of thermopower and suppression of thermal conductivity give rise to a significantly enhanced figure of merit ZT in TCI nanowires.

CHARACTERIZATION OF Mg DOPING IN GaN NANOWIRES WITH RAMAN SPECTROSCOPY

Kris A. Bertness, Lawrence Robins, Shannon Duff, Matt Brubaker, and Norman Sanford

NIST, 325 Broadway, Boulder, CO 80305 Corresponding author: kris.bertness@nist.gov

We apply Raman spectroscopy to characterize Mg dopants in GaN nanowires and films grown by molecular beam epitaxy. Although Mg is the only impurity known to generate *p*-type conduction in GaN, the dopant atom states are far from the valence band and therefore Mg atoms are only partially ionized at room temperature. Activation of Mg as a dopant can also be blocked if hydrogen bonds to the dopant atoms or if the Mg incorporates as an interstitial instead of substitutionally on the Ga site. In order to distinguish active Mg from inactive Mg, we measure the peak intensity of a Raman peak with a wavenumber shift of around 655 cm⁻¹. This peak has been shown to be related to a N-Mg bond in the correct lattice position for doping and in the absence of hydrogen passivation. To compensate for variations in specimen volume, the Mg peak intensity is normalized by the total signal measured for the strong TO phonon and E₂ peaks of GaN in the range of 520 to 580 cm⁻¹.

As shown in Fig. 1, we find that nanowire growth temperatures are in general too hot for effective Mg incorporation. The active Mg peak is not present in samples grown at 790 °C and above (black shells in Fig. 1), and nanowire growth morphology is poor at and below this temperature. Unlike films, however, nanowires can be grown with a very high V:III ratio, and thus the Mg activation and incorporation can be increased with high N flux. Nanowires are thus most effectively doped with Mg in two-stage growth (green shells) in which nanowires are nucleated at high temperature and under high N flux and then extended or overcoated with a second step at lower temperature. These trends are also evident in GaN films (red spheres) grown at conditions approaching those of nanowire growth. Comparisons with Mg atomic density as measured by SIMS and atom probe tomography will also be presented.

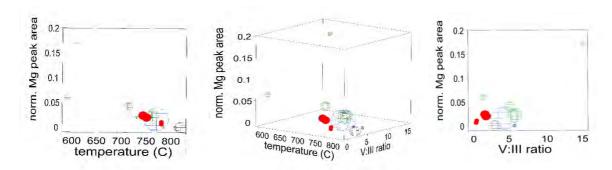


Figure 1: Dependence of active Mg Raman signal on growth parameters. Solid red spheres are planar film samples. Green sphere shells represent two-stage growth runs (see text), plotted against the lowest growth temperature from the run. Blue and black shells are single-stage nanowire growths, most of which had little or no active Mg peak. The size of the sphere roughly represents the ratio of Mg flux to Ga flux, and the symbols corresponding to this films have been increased in size relative to the nanowire symbols in order to be clearly visible.

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Te doping for high electron densities in self-assisted GaAs nanowires

Marta Orrù¹, Eva Repiso^{1,2}, Stefania Carapezzi³, Alex Henning ⁴, Faustino Martelli⁵, Stefano Roddaro^{1,6}, Alfonso Franciosi^{1,2}, Yossi Rosenwaks⁴, Anna Cavallini³, and Silvia Rubini¹

It is well assessed that Si, the typical donor in III-As compounds grown by molecular beam epitaxy (MBE) is not efficient as donor in GaAs NWs[1]. Due to different growth mechanisms and conditions between epitaxial layers and NWs, the Si amphoteric character reveals itself through the preferred incorporation at the As instead of the Ga sites in NWs, giving them a p- or compensated character [1,2]. Tellurium is a possible alternative, as demonstrated in p/n GaAs core/shell NWs obtained by Au-assisted gas source-MBE using Te as donor [3].

We demonstrate here that n-type GaAs NWs with electron concentration as high as 10^{20} cm⁻³ can be efficiently grown by Ga-assisted MBE. Moreover we give a comprehensive study of the electrical and optical properties of the Te-doped GaAs NWs, by availing of several electrical measurements [I-V and transconductance in field-effect transistor (FET) geometry], Kelvin-probe force microscopy (KPFM) and photoluminescence (PL).

NWs were grown by solid source MBE, co-evaporating GaTe from a standard Knudsen cell. The presence of Te flux during the growth revealed itself already in the NW morphology by the progressive reduction of the NW diameter and appearance of parasitic lateral branches as Te flux increases. Te incorporation was studied exploring a wide range of growth (T_g) and GaTe source temperatures.

Transport measurements (Fig. 1) allowed estimating the carrier density and the mobility for the NWs grown with the highest Te fluxes. Highly efficient doping was observed in NWs grown up to 640°C, i.e. at temperatures well above those used to dope epitaxial layers.

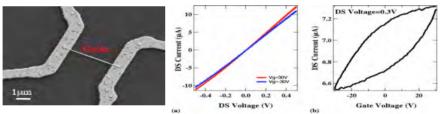


Fig. 1. (left) SEM image of a typical NW-FET. (right) Curves of a NW-FET device based on a single Te-doped GaAs NW from a sample grown at 580°C. (a) I-V curves as a function of back-gate bias indicates *n*-type doping. (b) the transconductance.

Additionally, KPFM was used to measure the surface potential of NW-based FETs under bias, by nullifying the work function difference between sample surface (NW) and the tip of the atomic force microscope [4]. The NW mobility was extracted by combining KPFM and I-V measurements.

A systematic analysis of the low-temperature PL provided a semi-quantitative, independent control of the doping level estimates, and allowed the detection of Te incorporation also at very low levels. PL spectra indicate that at low Te fluxes, the increase of $T_{\rm g}$ hinders Te incorporation into the nanowires. Transport as well as PL data point to a more efficient Te incorporation in NWs than in bulk. Our investigation shows that the best compromise between a good NW morphology, a low incorporation of unwanted impurities and a high electron density is obtained for $T_{\rm g}$ =610 °C.

¹IOM-CNR Laboratorio TASC- Trieste Italy; ²Università di Trieste, Italy; ³Università di Bologna, Italy; ⁴Tel Aviv University, Ramat Aviv, Israel; ⁵IMM- CNR, Roma, Italy; ⁶Nano-CNR, Pisa, Italy

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Terahertz Spectroscopy of Modulation Doped GaAs/AlGaAs Core-Shell Nanowires.

<u>Jessica L. Boland¹</u>, S. Conesa-Boj², G. Tütüncouglu², F.Matteini², D. Rüffer², A.Casadei², F.Gaveen², F. Amaduzzi², P. Parkinson¹, C. Davies¹, H.J.Joyce³ L.M.Herz¹, A.Fontcuberta i Morral² and Michael B. Johnston¹

 Department of Physics, University of Oxford, Oxford, OX1 3PU, United Kingdom
 École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
 University of Cambridge, Centre for Advanced Photonics and Electronics, 9 JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom

III-V semiconductor nanowires have already shown great potential as building blocks for many optoelectronic devices, from solar cells¹ to light-emitting diodes², with some prototype nanowire-based devices having already been developed³. For such devices, controllable and effective doping of nanowires is a key requirement for controlling the nanowire conductivity. However, achieving reliable doping of III-V nanowires without loss of other electrical properties, such as mobility, has proven difficult.

Here, we examine MBE-grown GaAs/AlGaAs core-shell nanowires with modulation n-type silicon doping within the shell, situated at a distance of 12nm from the GaAs/AlGaAs interface. We use a non-contact optical pump-probe terahertz spectroscopic technique⁴ to extract a doping density, carrier lifetime and electron mobility. Figure 1a plots the photoconductivity decay at different fluences for these modulation-doped nanowires, showing extremely long lifetimes of over 3.92ns. The photoconductivity spectra (Figure 1b) exhibit a Lorentzian response, showing localised surface plasmon modes in the terahertz range. By fitting a Lorentzian function to these spectra, an electron mobility of $2200 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ was extracted and the doping density measured to be $1.1 \times 10^{16} \text{ cm}^{-3}$. Remarkably, the doping did not affect the high mobility seen for undoped core-shell GaAs/AlGaAs nanowires. The long lifetime and maintained high electron mobility exhibited by these nanowires indicate their suitability for use in optoelectronic devices⁵.

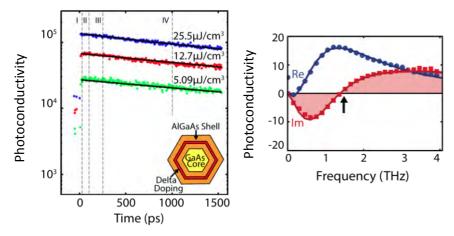


Figure 1: Pump-induced change of free carrier concentration against pump-probe delay at different photoexcitation fluences (left) and time-resolved photoconductivity at 25ps after photoexcitation (right) for modulation n-type doped GaAs nanowires.

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Photon Upconversion and Charge Carrier Dynamics in Highly Doped InP Nanowires

<u>Kilian Mergenthaler</u>¹, Sebastian Lehmann¹, Wei Zhang², Neimantas Vainorius¹, Jesper Wallentin³, Magnus T. Borgström¹, Arkady Yartsev², Mats-Erik Pistol¹

¹ Solid State Physics, Lund University, Box 118, S-221 00, Lund, Sweden ² Division of Chemical Physics, Lund University, Box 124, 221 00 Lund, Sweden ³ Institute for X-ray Physics, University of Göttingen, Friedrich-Hund-Platz 1, 37077, Göttingen, Germany

We investigated highly sulfur doped InP nanowires with scanning electron microscopy, transmission electron microscopy including energy dispersive x-ray spectroscopy, microphotoluminescence, time-resolved photoluminescence spectroscopy (PL) and photoluminescence excitation spectroscopy (PLE).

The high doping concentration causes a strong blue-shift of Fermi edge emission and absorption, well into the visible range, as the carriers fill the conduction band [1]. For exciting laser energies above the band gap, but below the Fermi energy a photon upconversion process was discovered [2], which enables observations of charge carrier dynamics not only through time resolved luminescence measurements, but also in PL with continuous wave excitation.

The observed photon upconversion is based on the absorption of photons with energies above the band gap but below the Fermi energy, which is possible due to an elevated electron gas temperature induced by laser heating. Figure 1 (a) shows that for exciting laser energies above the band gap and below the Fermi energy luminescence is observed energetically on both sides of the laser.

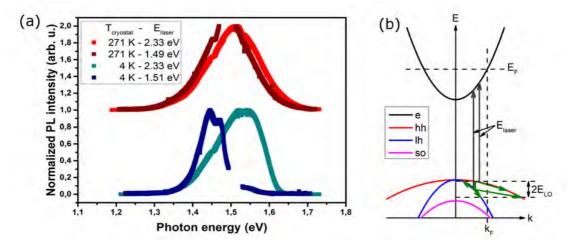


Figure 1: (a) PL at 271 K (red) and at 4K (blue) with excitation far above the Fermi energy (light colors) and excitation below the Fermi energy (dark colors). (b) Schematic image of absorption of 1.52 eV photons in InP and the relaxation of the photo-excited holes via LO phonon scattering. The phonon assisted transitions are indicated by green arrows. InP ZB masses were used for the bands. Band gap is not in scale.

We propose that the upconversion in highly doped nanowires is dominantly caused by phonon assisted hole scattering to higher k-values followed by k-conserving recombination with conduction band electrons. The main hole-LO phonon scattering processes are depicted in Figure 1 (b). We support our hypothesis by temperature dependent PL, selectively excited PL and simulations.

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Carrier Dynamics in Ge and Ge-Core/Si(Ge)-Shell Nanowires: Effects of Diameter, Growth and Surface Conditions

Paul C. McIntyre¹

¹ Department of Materials Science & Engineering, Stanford University, Stanford, CA, U.S.A.

Germanium and germanium-silicon core-shell nanowires (NWs) are promising building blocks to enable improved performance of nanophotonic and nanoelectronic devices. However, surface defect passivation is an important requirement for such devices: Small diameter wires have a very large surface area-to-volume ratio, and surface defects can cause carrier scattering and recombination in NWs. Summarizing recent photoluminescence and ultra-fast pump probe absorption data obtained from epitaxial Ge NW assemblies, this presentation will begin by examining the influence of nanowire diameter and surface condition on carrier recombination dynamics. The germanium-to-oxygen stoichiometry of a surface oxide, either a native oxide or one intentionally grown, on the NW sidewalls is found to have a strong effect on nonradiative recombination of photoexcited carriers in the wires. Transient absorption results are consistent with the presence of negative charges in the defective surface oxide layer that promote relatively long-lived non-equilibrium electron populations. Interestingly, this effect is enhanced with decreasing wire diameter.

Growth of an epitaxial silicon or SiGe shell around a germanium NW core can achieve both displacement of surface defects from the core and carrier confinement, but these structures must remain stable with respect to relaxation of misfit strains. The effects of nanowire surface conditions, both during growth and subsequent annealing, and how they control the key strain relaxation mechanisms - misfit stress-driven roughening, dislocation climb, dislocation glide, and Ge-Si interdiffusion – will be summarized. Coating 40 nm diameter Ge NWs with thin and coherently strained SiGe shells produces strong radiative recombination consistent with the indirect gap transition of bulk-like Ge, and suppresses the influence of surface states.

PROBING STRUCTURAL DEFECTS AND CHEMICAL HETEROGENEITIES IN NANOWIRES WITH A MULTIMODAL HARD X-RAY NANOPROBE

<u>Damien Salomon</u>^{1,*}, Julie Villanova¹, Rémi Tucoulou¹, A. Messanvi^{2,3}, Christophe Durand², Joel Eymery², Gema Martinez-Criado¹

¹ European Synchrotron Radiation Facility, Experiment Division, 38000 Grenoble, France
² University Grenoble Alpes, CEA, INAC-SP2M, F-38000 Grenoble, France
³Institut d'Electronique Fondamentale, UMR 8622 CNRS, Université Paris Sud, Orsay, France

Semiconductor nanowire heterostructures offer new opportunities for the development of optoelectronic and photonic devices. To tune their electronic and optical properties, a high control of their shape, composition and defects is needed, and tools with high spatial and chemical resolution are therefore crucial to characterize them. Here we will illustrate how structural defects and chemical heterogeneities impact the optical and electronic properties of nanowires heterostructures by using a multimodal hard X-ray nanoprobe.¹

In particular, we have studied nitride core/shell wires heterostructures grown by metal organic vapour phase epitaxy^{2, 3} by combining X-ray fluorescence (XRF) and X-ray excited optical luminescence (XEOL) at the nanoscale. XEOL results reveal two main contributions: the InAlN/GaN multi quantum wells (MQWs) and the yellow band. The 2D distributions exhibit the presence of different and well defined regions on the top facet of the wire (Figure 1). The XRF maps show a strong correlation between these regions and the indium signal. These findings could be caused by the presence of inversion domain boundaries.⁴ This is the first time that the spatial relationship between the inversion domain boundaries and the indium composition is shown at the nanometer level.

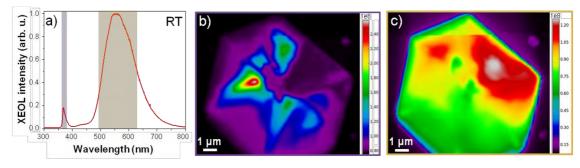


Figure 1: a) XEOL spectrum acquired from the top of GaN wire covered with 10xInAlN/GaN QWs, b-c) XEOL intensity map at the emission wavelength of the MQWs (370 nm) and the yellow band respectively.

In addition, the analysis of the electrical properties of a connected nanowire heterostructure via X-ray beam induced current (XBIC) measurements has been probed at the nanometer scale, giving access to complementary information such as non-radiative recombination centers and the electrical homogeneity inside the wires.

Finally, further insights into the nanowires properties will be provided by low temperature measurements (10 K), using a He cryostat currently under commissioning.

^{*} Corresponding author: damien.salomon@esrf.fr

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InAsSb nanowires grown by molecular beam epitaxy for long wavelength infrared optoelectronics

Q. D. Zhuang¹, H. Alradhi¹, Zh. M. Jin¹, Ezekiel A Anyebe¹, X. R. Chen², J. Shao², Ana M Sanchez³, A. A. Zhukov⁴, S. H. Shu², N. Dai²

1 Physics Department, Lancaster University, Lancaster LA1 4YB, UK 2 National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, 200083 Shanghai, People's Republic of China.

3 Department of Physics, University of Warwick, Coventry CV4 7AL, UK 4 Department t of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK.

Semiconducting nanowires (NWs) material has shown promise for novel high-performance photonic and nanoelectronic devices including light emitting diodes, detectors, solar cells, lasers and high-speed transistors etc. a variety of semiconductor NWs have been demonstrated, of particular interest is InAsSb NWs which possess direct bandgap, high electron mobility, light effective mass and lowest bandgap energy in III-V compounds. These features enable InAsSb NWs be promising candidate leading optoelectronics operating at long wavelength range and compatible with Si technology. However, the synthesis of Sb-rich InAsSb NWs remains challenging due to the strong surfactant effect of Sb during epitaxy [1]. Here we report the realization of InAsSb NWs grown by molecular beam epitaxy with Sb composition up to 20%. The effect of Sb incorporation to the geometry of the resulting NWs, Sb distribution, and the phase mixture were investigated by scanning electron microscopy and transmission electron microscopy. We observed that the incorporation of Sb into InAs NWs significantly modifies the NWs geometry, suppresses crystalline defects, reduces phase mixture and increases Sb nonuniformity [2]. In addition, we performed photoluminescence measurements on these nanowires to investigate their optical properties. PL emission at long wavelength of 5.5 µm was obtained. This study provides new insights on exploiting InAsSb NWs for long wavelength infrared optoelectronics.

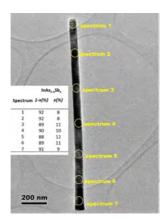


Fig.1 EDX measurement shows the Sb composition in a single nanowire at different positions

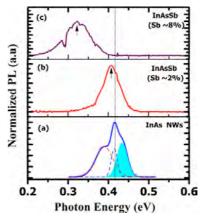


Fig.2 10 K photoluminescence of InAsSb nanowires with different Sb compositions

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Structure Study of III-V heterostructured Nanowires: Polarity and Interfaces

Reza R. Zamani¹, Sebastian Lehmann¹, Ruth L. Chantry², Fredrik S. Hage², Quentin M. Ramasse², Kimberly A. Dick^{1,3}

Solid State Physics, Lund University, Box 118, Lund, Sweden
 SuperSTEM Laboratory, STFC Daresbury Campus, Daresbury, United Kingdom
 Centre for Analysis and Synthesis, Lund University, Box 124, Lund, Sweden

Nanoscale heterostructures are promising candidates with potential in several applications such as optoelectronics and electronics. III-V nanowires, in this context, are excellent examples as they offer an ample range of possibilities for modulating the properties. On the other hand, their morphology allows accommodation of different compounds with larger lattice mismatch compared to bulk.

Nanowires are grown by metal organic vapor phase epitaxy (MOVPE) using size-selected Au aerosol particles,³ as catalysts, which were deposited onto <111>B-oriented GaAs wafers. The nanowire growth was carried out in an AIXTRON 3x2" close coupled showerhead MOVPE growth reactor at set temperatures of 510°C for GaAs and GaSb and 460°C for InAs, respectively.

The nanowires are characterized by means of aberration-corrected scanning electron microscopy (STEM). The polarity of the nanowires is determined by means of HAADF-STEM imaging. It is shown that each accommodating material inherits the polarity from its base. An As-polar GaAs segment grows on the GaAs (111)B substrate. Then GaSb accommodates with Sb polarity, the heavier element is on top in the dumbbell units; and the InAs shell grows with As polarity (lighter element on top). Therefore, a switch in the dumbbell units is observed along the diameter of the nanowires caused by the change in the chemical composition (from GaSb core to InAs shell). EELS compositional maps confirm this change. See Figure 1.

In addition, the heterointerfaces are studied. In the MAADF-STEM micrograph (Figure 1(i)) one can see that at the interfaces the intensity increases which is related to strain due to the difference between the lattices of the dissimilar compounds. It is also observed that where a crystal structure defect occurs at the heterointerface, the group III element from the shell diffuses in. HAADF-STEM and EELS compositional maps prove this.

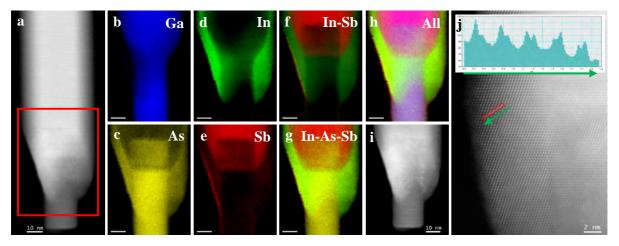


Figure 1: (a) HAADF-STEM image of the heterostructured GaAs-GaSb-InAs nanowire, (b-h) EELS maps, (i) MAADF-STEM image showing the strain in the interface, and (j) atomic resolution HAADF-STEM image showing the polarity (the inset is the intensity profile along the green arrow).

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III-V Nanowires: an Atomic Resolution Approach

María de la Mata^{1,2}, Martin Eickhoff³, Philippe Caroff⁴, Jordi Arbiol^{2,5}

¹ Instituto de Ciencia de Materiales de Barcelona, ICMAB-CSIC, Bellaterra (Spain) ² Institut Català de Nanociència i Nanotecnologia, ICN2, Bellaterra (Spain)

³ I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Gießen (Germany)

⁴Department of Electronic Materials Engineering, Research School of Physics and Engineering, The Australian National University,

Canberra, (Australia)
⁵ Institució Catalana de Recerca i Estudis Avançats, ICREA, Barcelona (Spain)

(Nanowire Growth Workshop preferred)

One of the main challenges for growing high quality nanostructures is the understanding of the underlying growth mechanism. In order to achieve the desirable knowledge about their development and behaviour, we analyse the materials at the atomic scale by means of aberration-corrected scanning transmission electron microscopy (STEM). In the case of binary semiconductor materials, several issues, as their crystalline phase; namely, wurtzite or zincblende (or intermediate polytypes), their polarity [1] and its preservation or inversion, the presence of strain and induced lattice deformations [2], etc., influence the growth and finally modify the optoelectronic response. Therefore, an atomic view of these nanostructures allows us relating the observed morphology (shape, size and orientation) and the measured opto-electronic response with the actual atomic arrangements. In the present work, we perform careful atomic resolution analyses concerning the unidirectional polar growth at the nanoscale and the creation of heterostructures under the nanowire morphology, to better understand how the growth proceeds and correlate the final structure and 3D morphology with the optical and electronic properties of the complex NW heterostructures, including embedded quantum structures.

- [1] M. de la Mata, C. Magen, J. Gazquez, M.I.B. Utama, M. Heiss, S. Lopatin, F. Furtmayr, C.J. Fernandez-Rojas, B. Peng, J.R. Morante, R. Rurali, M. Eickhoff, A. Fontcuberta i Morral, Q. Xiong, J. Arbiol, *Nano Letters*, **12**, 2579 (2012)
- [2] M. de la Mata, C. Magen, P. Caroff, J. Arbiol, *Nano Letters*, **14**, 6614 (2014)
- [3] M. de la Mata, X. Zhou, F. Furtmayr, J. Teubert, S. Gradecak, M. Eickhoff, A. Fontcuberta i Morral, J. Arbiol, *Journal of Materials Chemistry C*, **1**, 4300 (2013)

Group III-nitride nanowire hetero- and quantum structures

Martin Eickhoff

I. Physikalisches Institut, Justus-Liebig-Universitaet Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

Group III-nitride (III-N) nanowires (NWs) and nanowire heterostructures (NWHs) are a topic of intense current research. Part of these activities is motivated by the possibility of realizing novel, nanoscaled optoelectronic devices with improved stability and efficiency or the perspective of improving electronic devices due to the low density of structural defects. In addition, nanowire heterostructures can also serve as ideal model system for the analysis of carrier confinement, carrier dynamics and internal electric fields, as the influence of structural defects on the optical properties is significantly reduced.

In this line we will report on the growth of AlGaN/GaN NWHs and the relation between structural and optical properties with a focus on internal electric fields in GaN nanodiscs (NDs) axially embedded in NWHs. We show that electric fields in III-N NWHs can be probed by studying the effect of superimposed external electric fields on the photoluminescence properties of single NWHs. Efficient n-type doping of GaN NWs can be achieved with Germanium as a donor. Temperature-dependent analysis of the Seebeck coefficient for single NWs yields a free carrier density of up to $4x10^{19}$ cm⁻³ and Ge-doping of optically active GaN NDs in AlN/GaN NWHs facilitates electrostatic screening of polarization-induced internal electric fields.

We will further demonstrate that control of the growth conditions allows the realization of selforganized GaN quantum wires with diameters below 5 nm on AlN/GaN NW templates and report on their structural and optical properties.

With regard to novel applications we show that the photoluminescence properties of GaN- and InGaN-NWs in electrolyte solutions sensitively depend on the applied bias and the pH-value. We discuss this behavior in terms of photoactivated hole-transfer to RedOx-levels in the electrolyte, facilitating the application as electrochemical sensors with spatial-resolved optical readout.

Optical anisotropy in single InAs/InP quantum dot and quantum rod nanowires

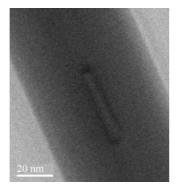
R. Anufriev^{1a}, J.B. Barakat^{1b}, G. Patriarche², X. Letartre^{1b}, P. Regreny^{1b}, C. Bru-Chevallier^{1a}, J.-C. Harmand², M. Gendry^{1b}, and <u>N. Chauvin</u>^{1a,*}

*nicolas.chauvin@insa-lyon.fr

The growth of nanowires (NWs) using Vapor-Liquid-Solid (VLS) method is well adapted to integrate III-V semiconductors on silicon (Si) which gives to NWs a great potential in nanoelectronics and optoelectronics. The integration of NW heterostructures in more complex photonic structures requires to understand and to control the orientation of the dipole in the quantum emitter. The dipole orientation can be accessed through polarization-resolved micro-photoluminescence (PL) measurements on single NWs

In the present work, the degree of linear polarization (DLP) is investigated for InAs quantum dots (QDs) and quantum rods (QRs) embedded in wurzite InP NWs. All these measurements are performed at telecom wavelengths. It is known that in unstrained InP and InAs wurtzite materials, the dipole polarization is expected to be perpendicular to the [0001] direction which is usually the NW axis. This is a direct consequence of the heavy hole-light hole splitting induced by the spin orbit coupling and crystal field splitting. Measurements performed on the InAs/InP NWs revealed that the emission polarization is mainly perpendicular to the [0001] NW axis for the QD-NWs but strongly parallel in the case of the QR-NWs (Fig. 1). To understand these results, we must take into account that the measured DLP is not only due to the intrinsic DLP of the emitter but also to its environment. For instance, a NW of high-refractive material can screen the electric field perpendicular to the NW axis when the NW diameter becomes much smaller than the emission wavelength. Moreover, the investigated NWs are lying on a substrate which can also alter the measured DLP. Consequently, finite difference in time domain (FDTD) calculations were performed to take into account the impact of the environment on the emitter and then to extract its intrinsic polarization.

From this experimental and theoretical study, we have shown that the intrinsic QD-NW emission polarization is nearly 100% perpendicular to the NW axis as expected for bulk wurtzite material. As far as the QR-NWs are concerned, the intrinsic polarization contains a component parallel to the NW axis. This means that, despite the heavy hole-light hole splitting in wurtzite InAs, a mixing occurs between these two bands for emitters presenting a high height to diameter ratio.



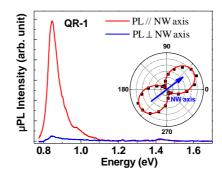


Figure 1: TEM picture of a QR-NW and polarization resolved micro-PL spectrum of a single QR-NW at room temperature.

¹ Université de Lyon, Institut des Nanotechnologies de Lyon (INL)-UMR5270-CNRS, ^aINSA-Lyon, 7 avenue Jean Capelle, 69621 Villeurbanne, France.

^bEcole Centrale de Lyon, 36 avenue Guy de Collongue, 69134 Ecully, France.

² Laboratoire de Photonique et de Nanostructures (LPN), UPR20-CNRS, route de Nozay, 91460 Marcoussis, France.

A QUANTUM FIBER-PIGTAIL

<u>Davide Cadeddu</u>¹, Jean Teissier¹, Floris Braakman¹, Niels Gregersen², Petr Stepanov^{3,4}, Jean-Michel Gerard^{3,4}, Julien Claudon^{3,4}, Richard J. Warburton¹, Martino Poggio¹, and Mathieu Munsch¹

¹ Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland ² DTU Fotonik, Department of Photonics Engineering, Technical University of Denmark, Building 343, DK-2800 Kongens Lyngby, Denmark ³ Université Grenoble Alpes, F-38100 Grenoble, France ⁴ CEA, INAC-SP2M, 17 rue des Martyrs, F-38054 Grenoble, France

We report the direct coupling of QD single photons to an optical fiber with a new approach¹. Our device, the quantum fiber-pigtail, consists of a QD embedded in a tapered photonic wire (PW), a photonic "trumpet", that is directly attached to the cleaved end of a single mode fiber. Our quantum emitter consists of a self-assembled InAs quantum dot grown by Molecular Beam Epitaxy embedded 110nm away from the sharp end of a 12µm long conical PW². These conical wires are obtained through a top-down approach. We demonstrate a photon collection efficiency at the output of the fiber of 5.8% and suggest realistic improvements for the implementation of a useful device in the context of quantum information. Due to its attractive features, we think that our device could also find potential applications in scanning probe microscopy such as quantum plasmonics³ and local electric field sensing⁴.

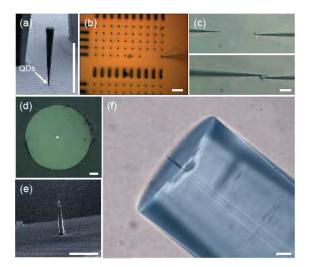


Figure 1: Fabrication procedure. a) SEM picture of the photonic trumpet. b) Removing a single PW from its original substrate with glass micromanipulator (right side). c) Orientation of the PW for subsequent gluing onto the fiber. d) Top view of the bare fiber with a drop of UV glue (bright spot) deposited at its center. e) SEM picture of the fiber-wire connection. f) Side view of the final device (optical microscope image). The white scale bars represent 10 µm.

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Interband and intersubband transitions in GaN/AlN nanowire heterostructures

E. Monroy¹, M. Beeler¹, J. Lahnemann¹, C. B. Lim¹, J. Bleuse¹, P. Hille², J. Schörmann², M. de la Mata³, J. Arbiol^{3,4}, and M. Eickhoff²

¹ CEA-Grenoble, INAC-SP2M, 17 av. des Martyrs, 38054 Grenoble, France
² I. Physikalisches Institut, JustusLiebigUniversität Gieβen, 35392 Gieβen, Germany
³ Institut de Ciencia de Materials de Barcelona, ICMABCSIC, 08193 Barcelona, Catalonia, Spain
⁴ ICREA and Institut Català de Nanociència i Nanotecnologia (ICN2), 08193 Barcelona, Catalonia, Spain

Nanowires (NWs) are seated to improve the performance of intersubband (ISB) devices, by increasing the escape probability of photoexcited carriers, reducing thermal scattering, and reducing the electrical capacitance without degradation of the light absorption. Furthermore, their large surface-to-volume ratio allows misfit strain to be elastically released, extending the viable active region size and composition beyond the limits of planar systems. GaN is a model material for the study of ISB transitions in NWs, since the presence of stacking faults or extended defects can be limited to the first hundred nanometers close to the substrate. III-nitrides have recently emerged as promising materials for ISB technologies in a large spectral region, from $1.3~\mu m$ reaching into the far infrared.

In this work, we present a study of the electronic properties of (000-1)-oriented Ge-doped GaN/AlN NW heterostructures grown by plasma-assisted molecular-beam epitaxy on Si(111), correlating structural and optical (interband and intersubband) measurements, and theoretical calculations. The photoluminescence (PL) emission from these heterostructures blueshifts with increasing doping levels, pointing to a significant screening of the polarization-induced internal electric field. Measurements in the time-resolved regime show that increasing the Ge dopant level, the PL relaxation times drop exponentially. The blueshift and decrease in carrier lifetime are larger than expected from the screening of the electric field along the growth axis in quantum well structures. Furthermore, relaxation times of undoped NWs are one order of magnitude longer than those of quantum wells emitting at the same wavelength. These results are understood by comparison with three-dimensional (3D) calculations of the electronic structure. At low dopant levels, the electron is confined towards the vertical bottom and radial center of the GaN disk, whereas the hole is vertically at the top of the disk and radially at the edge, due to the piezoelectric field induced by the shear component of the strain in the disk. With increasing Ge concentration, this radial electric field is screened and the hole centralizes under the electron.

On the other hand, we demonstrate room-temperature TM-polarized infrared absorption assigned to the s- p_z intraband transition in the GaN disks. The absorption line blueshifts with increasing Ge concentration and redshifts with increasing disk thickness. Experimental results are compared to theoretical calculations that take into consideration the 3D strain distribution and the presence of surface states. From the theoretical analysis we conclude that the formation an AlN shell, which is known to blue shift the PL emission, has little influence on the intraband transitions. Upon the inclusion of many body effects; namely the carrier screening of the internal electric field, exchange interaction and the depolarization shift, the ISB transitional wavelength can be simulated with reasonable accuracy.

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Ritesh Agarwal

Department of Materials Science and Engineering, University of Pennsylvania

riteshag@seas.upenn.edu

3231 Walnut St., Philadelphia, PA 19104 USA

Title: Novel classical and quantum photonic devices by manipulating light-matter interactions in low-dimensional systems

Abstract: Strongly confined electrical, optical and thermal excitations drastically modify material's properties and break local symmetries that can enable precisely tunable novel responses and new functionalities. With an emphasis on low-dimensional materials such as nanowires and monolayer MoS₂, we will discuss how extreme confinement of fields interacting with materials produces new and unexpected materials response. For example, we will discuss how the strong plasmonic fields can lead to a new paradigm of nanoscale Si-based photonics such as optical emission in the visible region and nonlinear optical devices. Furthermore, by utilizing the fundamental symmetry breaking properties of fields, new quantum phenomena such as chirality-dependent optical and electronic properties will be discussed in non-chiral materials and utilized to enable new functionalities that are only possible in strong spin-orbit coupled materials. The role of geometry such as in nanowires to produce new properties in the presence of symmetry breaking fields will be discussed. Finally, effect of plasmons on light matter interactions in 2D excitonic crystals will be discussed, which can be engineered to produce novel responses such as enhanced emission and Fano resonances.

Directional and polarized nanowire emission governed by waveguide modes

<u>Dick van Dam</u>¹, Diego R. Abujetas², Meng Liu¹, Jose A. Sanchez-Gil², Erik P.A.M. Bakkers^{1,3}, Jos E.M. Haverkort¹, Jaime Gomez Rivas^{1,4}

¹ Applied Physics, Eindhoven University of Technology, The Netherlands
² Insituto Estructura de la Materia, CSIC, Madrid, Spain
³ Kavli Institute of Nanoscience, Delft University of Technology, The Netherlands
⁴ Surface Photonics, FOM-institute AMOLF c/o Philips Research, Eindhoven, The Netherlands

E-mail: a.d.v.dam@tue.nl

Full control over directionality and polarization of nanowire emission is required for applications in LEDs, solar cells and single-photon devices. The emission of nanowires has been associated with coupling to waveguide modes that are supported by the nanowire geometry, and affect both emission properties.

Here, we present measurements of the directional and polarized emission of vertically and horizontally oriented InP nanowires obtained with a Fourier microscope. We demonstrate that we can completely change the directionality of the emission from individual vertical nanowires by coupling the emission to different waveguide modes¹. Simultaneously, the polarization of the emission is modified according to the polarization of the relevant waveguide mode. In such way, the emission cone can be designed to be either broad or narrow, and either p-, s- or unpolarized. We have also investigated the directional emission from horizontal nanowires and demonstrated tuning of the emission direction.

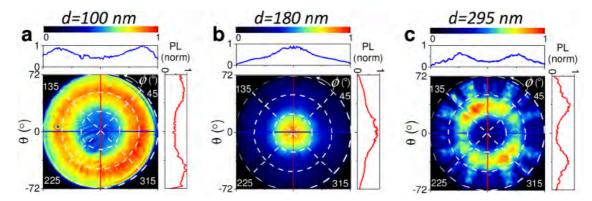


Figure 1: Fourier photoluminescence (PL) emission patterns from vertical nanowires with diameters d equal to a) 100 nm, b) 180 nm, and c) 295 nm. At each top and right side of the color plot the cuts through the center of the image are displayed.

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Single-electron tunnelling in InAs nanowire quantum dots formed by crystal phase engineering

<u>Malin Nilsson</u>¹, Luna Namazi¹, Sebastian Lehmann¹, Martin Leijnse¹, Kimberly A. Dick^{1,2} and Claes Thelander¹

¹ Solid State Physics, Lund University, Box 118, S-221 00 Lund, Sweden ² nCHREM / Centre for Analysis and Synthesis, Lund University, Box 124, 221 00 Lund, Sweden

In contrast to conventional layer-growth, where most of the III-V semiconductors form in the zinc blende (ZB) crystal phase, studies have shown that it is possible to tune the crystal phase between ZB and wurtzite (WZ) with high precision in nanowire growth. In the case of InAs, a material with strong relevance for future low-power electronics, it has been theoretically predicted that WZ has a larger bandgap than ZB, with a positive conduction band off-set of approximately 30 - 90 meV at the crystal phase interface. Efforts have been made to study the band alignment at the interface between ZB and WZ in InAs nanowires, yet few experimental results have been reported to support the theoretical predictions, partly explained by the difficulties involved in optical studies due to the narrow band gap. However, it has been demonstrated that thin WZ segments, in an otherwise ZB InAs nanowire, act as tunnel barriers for electrons, and two closely spaced WZ segments form a quantum dot (QD).¹

In this work, QDs defined by crystal-phase engineering in InAs nanowires are studied. We employ a novel nanowire growth method, using higher temperatures and a new procedure to induce structural changes, leading to improved nanowire quality and crystal phase control. By means of electrical characterization at 4.2 K, the functionality of the WZ segments as tunnel barriers over a large range of gate voltages is demonstrated. A typical device with a ZB QD length of ~ 50 nm (WZ barrier ~ 20 nm) show periodical Coulomb oscillations over ~ 7 V and a gate capacitance of ~ 3.8 aF (Figure 1). From high resolution SEM images, dimensions of the measured QDs can be extracted (insets in Figure 1). By tuning the spacing between the WZ segments, electrical properties of the QD can be controlled. When the QD length is reduced to ~ 30 nm, we see the effect of single particle energy levels in the conductance. In charge stability diagrams, conductance via excited states is clearly visible. Finally, a lower limit for the tunnel barrier height of ~ 120 meV is estimated.

A major motivation for studying crystal-phase defined QDs is the possibility to use these as building blocks in more complex core-shell QDs. Recently, selective radial heterostructure growth of GaSb on crystal-phase engineered InAs nanowires was reported.² Such core-shell QDs are of considerable interest for studies of electron-hole interactions,³ which is an ongoing project.

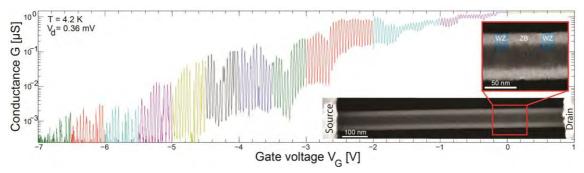


Figure 1: Conductance as a function of gate voltage for a crystal phase defined QD, multiple separate recordings have been merged, indicated by different colors. Inset: SEM top view image of the measured QD device and a close up of the QD structure (WZ barriers visible by crystal-phase related contrast differences are partly colored blue to guide the eye).

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³ B. Ganjipour, et al., *Phys. Rev. B.* **91**, 3494–3499 (2010)

High-aspect ratio core-shell InGaN/GaN microrods for future high-efficiency lighting

Adrian Avramescu¹, Tilman Schimpke^{1,2}, Martin Mandl^{1,2}, Xue Wang^{1,2}, Ion Stoll¹, Tansen Varghese¹, Hans-Jürgen Lugauer¹, Matthias Sabathil¹, Johannes Ledig^{2,3}, Jana Hartmann², Andreas Waag^{2,3}, and Martin Strassburg^{1,*}

¹ OSRAM Opto Semiconductors GmbH, Leibnizstr. 4, Regensburg, Germany ² Institute of Semiconductor Technology, Braunschweig University of Technology, Germany ³ Epitaxy Competence Center, Hans-Sommer-Strasse 66, 38106 Braunschweig, Germany *Email: Martin.Strassburg@osram-os.com

Core-Shell micro- and nanorods (NAMs) have attracted attention in the past due to the promise of increasing the internal quantum efficiency with their increased effective area of the quantum wells on the side walls and the growth of nonpolar quantum wells on these which reduces the quantum confined stark effect and thereby the droop phenomenon. By using the third dimension, NAMs achieve lower current densities by increasing the total pn junction area for a given chip footprint area. Therefore, core-shell NAM LEDs are considered as a very promising candidate for future generations of highly efficient, LEDs for e.g. for display and for solid-state lighting applications.

However for operation at reduced current densities other loss mechanisms such as Shockley-Reed-Hall (SRH) recombination become more important. SRH contributions strongly affect the performance and the carrier lifetime and therefore particular attention needs to be given to the crystalline quality. Detailed insight into MOVPE growth mechanisms has been gained for both, core and shell structures. Such core-shell structures can reproducibly be fabricated with high aspect ratios and excellent homogeneity across 4 inch wafer and in series of MOVPE runs. For example, a homogeneous array of NAMs with a $\sim 1 \mu m$ -diameter and a $40 \mu m$ -height has been grown. Such high aspect ratio is expected to give a significant efficiency increase [2] providing a 10-fold surface area increase (Fig. 1). Further processing into blue LEDs as well as performing analysis of these NAM structures is a challenge and calls for novel approaches.

In combination with micro-grain phosphor particles white LEDs are achieved. In this way, internal efficiency gains are enabled taking full advantage of highest conversions efficiency via closely coupled phosphor particles densely packed between the NAMs (Fig. 2). Such an approach offers also advantages regarding conversion efficiency, enhanced light extraction and better heat extraction from the conversion material [3]. Leaving the standard path of planar devices opens up a new world of opportunities in the realm of 3D nanostructures.

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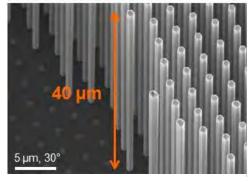


Fig.1 GaN rods with an aspect ratio of ~40 and an effective area increase of ~10.

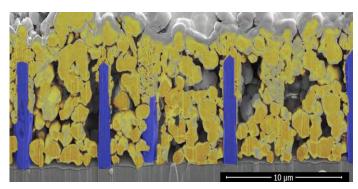


Fig.2 Phosphor grains are closely packed in the space between the GaN rods.

Dielectric confinement of excitons in ultrathin GaN nanowires

P. Corfdir, J. K. Zettler, C. Hauswald, S. Fernández-Garrido, E. Luna, A. Trampert, U. Jahn, T. Flissikowski, H. T. Grahn, L. Geelhaar, and O. Brandt

Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

In 1979, Keldysh demonstrated that the excitonic properties of a semiconductor nanostructure are not only affected by quantum confinement, but also by the mismatch in dielectric constants between the semiconductor and its immediate environment. This so-called dielectric confinement of the exciton is particularly strong when the surrounding material is air or vacuum. It gives rise to an important increase in exciton binding energy and oscillator strength, which is interesting for room temperature applications involving excitons. Unfortunately, the unpassivated surfaces of III-V semiconductor nanostructures usually induce efficient surface recombination, making these structures and thus exciton dielectric confinement incompatible with optoelectronic applications.

In this context, the low surface recombination of 210 cm/s reported recently for GaN nanowires makes this system promising for studying the impact of the dielectric confinement on the radiative properties of GaN nanowires. Independent of the substrate, GaN nanowires are also free of threading dislocations, making them a promising candidate for the realization of optoelectronics devices with high internal quantum efficiency. However, the diameter of GaN nanowires is typically between 50 and 100 nm, a value smaller than the emission wavelength (360 nm), but much larger than the Bohr radius of free excitons in the bulk (3 nm). Therefore, whereas the nanowire geometry alters significantly the coupling with light, the impact of dielectric confinement is negligible, and the excitonic properties of spontaneously formed GaN nanowires closely resemble those of freestanding GaN layers.³

In this work, we study the photoluminescence properties of ultrathin GaN nanowires with a diameter down to 5 nm (Fig. 1). The emission energy of nanowires at 300 K increases with decreasing diameter, as a result of the dielectric confinement of the exciton in these nanostructures. Despite the fact that their sidewalls surfaces are unpassivated, these ultrathin

exhibit intense nanowires excitonic recombination at room temperature. The thinner the nanowire, the weaker the photoluminescence quenching of the intensity with increasing temperature (Fig. 1). We demonstrate that the dielectric confinement in ultrathin nanowires leads to a reduction in the dimensionality of the exciton's density of states and to a decrease in the radiative lifetime of the exciton. As a result, ultrathin GaN nanowires exhibit an improved radiative efficiency at 300 K.

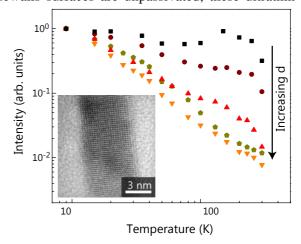


Figure 1: Temperature dependence of the photoluminescence intensity of ultrathin nanowire ensembles of various diameters d. The intensities at 9 K have been normalized to one. Inset: High-resolution transmission electron micrograph of a segment of an ultrathin GaN nanowire with d \approx 6 nm.

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Nanophotonics in III-V nanowire arrays

Nicklas Anttu

Division of Solid State Physics and the Nanometer Structure Consortium (nmC@LU), Lund University,

22100 Lund, Sweden

We have studied how light interacts with arrays of vertical nanowires made of the optoelectronically important III-V materials. Our combined theoretical and experimental investigations [1-8] have yielded guidelines for efficient light-management in these arrays. With proper tuning of the nanowire geometry, the absorption per volume semiconductor material can be 20 times higher than in a planar geometry [1]. At the same time, the arrays show low reflection losses, thus combining anti-reflection properties with light-trapping to enhance the absorption. Based on these guidelines, we have fabricated solar cells of InP nanowires [2]. These arrays show an efficiency of 13.8 % under the AM1.5 solar spectrum illumination and convert more than 70 % of above-bandgap photons into electric current, despite covering only 12 % of the surface.

Furthermore, we have shown through electromagnetic modelling that the Shockley-Queisser efficiency limit for an optimized nanowire array solar cell is higher than for a conventional, planar solar cell [9]. This fundamental limit is calculated by considering how many photons the cell absorbs, how many photons the cell emits at a given voltage, and how much current remains for extraction. In this way, the current-voltage curve of the solar cell can be constructed, from which the efficiency is obtained. First, for a nanowire diameter of 180 nm, nanophotonic resonances in the nanowires enhance the absorption [1,2,6,8]. The nanowires produce a short-circuit current of 95 % of that obtainable in a perfectly absorbing InP bulk cell, even though the nanowires cover only 10 % of the substrate surface. Second, the nanowire cell emits less photons than the bulk cell. This weaker emission allows for a 10 % higher opencircuit voltage than in the bulk cell. In this way, the nanowire array solar cell shows a higher Shockley-Queisser efficiency limit than a bulk cell. Thus, nanowire arrays show indeed great promise for photovoltaics with the prospect of reaching efficiencies beyond that obtainable in conventional bulk cells.

Finally, we have found how the geometry of nanowire arrays can be tuned to enhance both the out-coupling and the emission rate of photons. This emission enhancement is reciprocal to the more well-studied absorption enhancement [1-8] where optical resonances in the nanowires are employed. With these guidelines, the design and performance of nanowire array based light emitting diodes can be optimized in a systematic manner.

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Ramsey fringes and ultrafast coherent pulse emission from GaAs-AlGaAs nanowire lasers

Sabrina Sterzl¹, B. Mayer¹, T. Stettner¹, B. Loitsch¹, G. Abstreiter², G. Koblmüller¹ and J. J. Finley¹

¹Walter Schottky Institut and Physik Department, TU-München, Am Coulombwall 4, Garching 85748, Germany

²Institute of Advanced Study, TU-München, Lichtenbergstr. 2a, 85748 Garching, Germany

Email: sabrina.sterzl@wsi.tum.de

The drive towards enhanced data processing speeds whilst minimizing the energy cost per bit requires ultra-compact all-optical interconnects on silicon. Semiconductor III-V nanowires (NWs) provide very strong potential for new generations of nanoscale photonic devices since their small footprint facilitates direct monolithic growth of III-V materials on silicon. Very recently, lasing up to room temperature from individual GaAs-AlGaAs core-shell NWs has been demonstrated substantiating their applicability in practical photonic devices [1,2].

In this work, we investigate the gain dynamics of GaAs-AlGaAs core-shell nanowire lasers using ultrafast pump-probe spectroscopy where we excite the NWs optically with two subsequent ~200fs excitation pulses with variable time delay. Remarkably, the NW lasers exhibit sharp fringes within their lasing peaks when subject to excitation pulse sequences in the range of a few picoseconds. We attribute this observation to Ramsey fringes that constitute a basic type of frequency combs that are a direct result of the coherent nature of subsequent NW laser pulses and their temporal interference [3]. Fig. 1a) shows the NW laser spectra as a function of time delay between the pump $(P/P_{th}=4)$ and the probe $(P/P_{th}=2)$ pulse whereas Fig.1b) depicts selected spectra. The frequency spacing between two adjacent fringes corresponds to the inverse of the NW pulse separation in the time domain and can be used as a direct measure of the repetition rate of the NW laser as shown in figure 1c). The blue data points are depicted from the spacing of the Ramsey fringes and

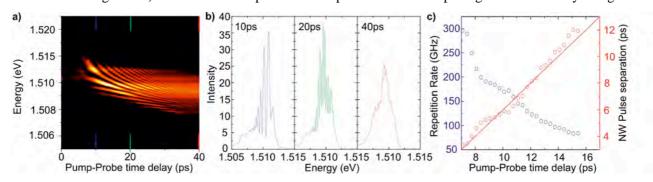


Figure 1: a) NW Laser spectra as a function of time delay between the pump and the probe pulse. b) Selected spectra of the NW laser for pulse separations between pump and probe pulse of 10ps (blue curve), 20ps (green curve) and 40ps (red curve). c) NW laser repetition rate (blue data points) and pulse separation (red data points) as a function of time delay between the pump and the probe pulse.

represent the repetition rate of the NW laser. The NW laser pulse separation in the time domain consequently increases linearly with the time delay between the two excitation pulses as shown by the red data points in Fig. 1c). Remarkably, the NW laser reaches extraordinary high repetition rates of ~300 GHz corresponding to a pulse separation of only 3.3 ps.

In summary, the results give an insight into the fundamental gain dynamics of GaAs-AlGaAs NW lasers and reveal ultrafast pulse emission with repetition rates up to 300GHz. Furthermore, we demonstrate the potential of GaAs-AlGaAs NW lasers as coherent frequency comb sources at the nano scale.

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Sensing with Nanowires

Martino Poggio¹

¹ University of Basel, Department of Physics, 4056 Basel, Switzerland

Researchers can now produce nanometer-scale nanowire (NW) structures from the bottom-up with unprecedented mechanical properties. Due to their favorable geometry and potentially defect-free growth, NW cantilevers are promising as ultrasensitive force transducers for scanning probe microscopy. Their high mechanical resonance frequencies decouple their motion from external noise sources and permit exquisite sensitivity in mass-sensing and scanning probe applications.

Meanwhile, heterostructure engineering has developed such that devices including field effect transistors, single photon sources, and quantum dots (QDs) can be produced within a NW. NWs have also become attractive hosts for optical emitters as their geometry favors the efficient extraction of photons. All of these properties, combined with the fact that NWs are ideal scanning probe tips, may lead to new measurement modalities, such as sensing of local electric or magnetic fields. At the same time, this multi-functionality makes NWs ideal hybrid systems, since they are both good candidates to exhibit quantum states of motion and – with embedded QDs – they can be integrated with electronic spins or quantized charge degrees of freedom. Hybrid systems, in which a mechanical oscillator is coupled to another microscopic quantum system, may provide new approaches to the quantum control of mechanical objects, to precision sensing, and to quantum information processing.

I will discuss our experiments on NWs as mechanical resonators, hybrid systems, and scanning sensors. I will focus first on the mechanical properties of as-grown GaAs NWs in both the linear and non-linear regime¹. I will then demonstrate a scanning vectorial force sensor implemented using two orthogonal NW modes. Furthermore, I will show how the strong coupling of these modes allows for the coherent control of this classical two-level system². I will then discuss a QD-in-NW hybrid system, in which QD states are coupled to NW mechanical motion³. Finally, I will present our recent work realizing a quantum fiber-pigtail, i.e. a semiconductor quantum-dot embedded into a conical photonic nanowire that is directly connected to the core of a fiber-pigtail⁴.



Figure 1: Optical micrograph of a quantum fiber-pigtail⁴.

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Digital emission tuning in GaP crystal phase quantum wells

<u>Jos E.M. Haverkort¹</u>, Simone Assali¹, <u>Thuy T.T. Vu</u>¹, Nika Akopian^{1,2}, Maaike Bouwes Bavinck², Klaus D. Jöns², Marcel A. Verheijen^{1,3}, Erik P.A.M. Bakkers^{1,2}

¹ Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands ² Kavli Institute of Nanoscience, Delft University of Technology, 2600 GA Delft, The Netherlands ³ Philips Innovation Services, High Tech Campus 11, 5656AE Eindhoven, The Netherlands

GaP nanowires enable the growth of both pure zincblende (ZB) and pure wurtzite (WZ) nanowire sections. Due to the band gap difference, a WZ/ZB/WZ homojunction provides a crystal phase quantum well (CPQW) [1] in a WZ GaP nanowire [2]. The atomically flat interfaces result in extremely high quality quantum wells, with controlled length of the ZB segments [3]. This structure can be exploited as building blocks for solid state quantum systems.

Wurtzite GaP shows a large spontaneous polarization [4], which creates a large surface charge across a thin ZB GaP nanowires section [5]. The resulting band-bending forms a type II quantum well as shown in Fig. 1a. The nanowire CPQWs show narrow emissions with a FWHM of 100-400 μ eV at visible wavelengths, in between the bandgaps of WZ and ZB GaP. Moreover, by adding a single monolayer of ZB GaP, the emission wavelength of the CPQW is shifted by a fixed amount. We demonstrate digital emission tuning in a single nanowire in Fig. 1b. We will present a histogram of all photoluminescence emission peaks observed for different thickness CPQWs, clearly showing a regular spacing between the emission peaks.

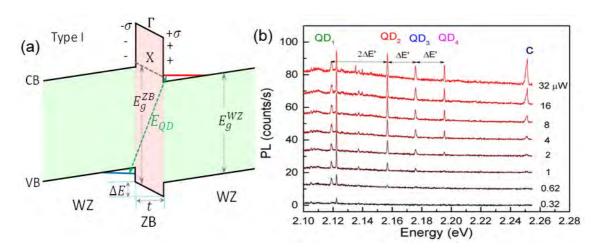


Figure 1. (a) Schematic picture of a crystal phase quantum well in GaP. (b) Digital tuning of the emission wavelength in GaP CPQWs.

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Nanowire-based Tandem Solar Cells

Magnus T Borgström¹, Frank Dimroth², Mikael T Björk³, Maria Tchernycheva⁴, Willie J G M Peijnenburg⁵, Heike Riel⁶, Lars Samuelson¹,

Lund University, Solid State Physics/NanoLund, Box 118, SE-221 00 Lund, Sweden
 Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany
 Sol Voltaics AB, Scheelevägen 22, SE-223 63 Lund, Sweden
 Institut d'Electronique Fondamentale, UMR 8622 CNRS, Universite Paris-Sud XI, 91405 Orsay, France
 Institute of Environmental Sciences (CML), Leiden University, Leiden, The Netherlands
 IBM Research-Zurich, Säumerstrasse 4, 8803, Rüschlikon, Switzerland

This will be a first presentation of a just started Horizon2020-project, NANO-TANDEM, which engages researchers from six partner laboratories: Lund University (Coordinator), Fraunhofer Institute for Solar Energy Systems (ISE) in Freiburg, Sol Voltaics AB in Lund, University of Paris Sud, University of Leiden, and IBM Research in Rüschlikon. Although we have barely started the research, we are very excited about what we believe we will achieve.

Silicon-based photovoltaic cells are the dominant technology for terrestrial solar energy conversion. After many decades of research and development, efficiencies have essentially saturated with the best devices measuring 25.6 % in the laboratory [1]. Significantly higher conversion efficiencies up to 37.8 % can be reached with multi-junction cells based on III–V semiconductors in flat plate configuration [2]. However, these materials are too expensive for use in flat-plate modules.

Nanowires allow a significant reduction in material needs without compromising absorption or performance. Members of the consortium have already demonstrated single-junction nanowire (NW) solar cells, reaching efficiencies of 13.8 %, and GaAs NW solar cells, with efficiencies of 15.3 %, with the active material occupying only about 12 % of the volume of a conventional bulk solar cell [3, 4, 5]. III–V nanowires in combination with today's silicon photovoltaic (PV) technology have the potential of simultaneously reaching very high performance devices, efficient use of materials, and low cost. In this project we aim to demonstrate for the first time an experimental proof of a tandem flat-plate solar cell composed of a top *pn*-junction formed in III–V nanowires, connected in series with a bottom *pn*-junction formed in silicon.

Today's state-of-the-art high-efficiency Si solar cells will be combined with an additional *pn*-junction formed in an array of nanowires. Such solar cell devices will be fabricated either by direct growth of the nanowires on Si or by transferring a film of nanowires embedded in a polymer [6] onto a Si bottom cell. Besides developing the best process to demonstrate such tandem solar cells with > 25 % efficiency, we are also addressing the important aspect of scaling up the technology to large areas. To reach this objective, we are developing technologies for large area III–V nanowire arrays (10 x 10 cm2) based on nano-imprint technology and epitaxial growth or on a new vapour phase nanowire growth method called Aerotaxy [7]. The anticipated large-scale application of nano-materials and III–V compounds in photovoltaics further requires an in-depth analysis of ecological and health related risks. In this project we are addressing this important issue already at an early stage of the development.

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Heat Transport in Nanowires Supporting the Propagation of Polaritons and Phonons

Jose Ordonez-Miranda*, Shiyun Xiong, and Sebastian Volz

Laboratoire EM2C, CNRS, CentraleSupélec, Université Paris-Saclay, Grande Voie des Vignes, 92295 Chatenay-Malabry cedex, France.

The blossoming of nanotechnology involving the miniaturization of devices with enhanced rates of operation requires a profound understanding and optimization of their thermal performance. This is particularly critical in nanowires, due to the significant reduction of their thermal conductivity/conductance as their size is scaled down. Surface phonon-polaritons (SPhPs) have shown wide potential to enhance the energy transport through these nanomaterials [1,2]. The mean free path of these energy carriers can be much longer than that of phonons, however their contribution to the heat transport is not well understood to date.

In this work, the SPhP thermal conductance of polar nanowires and the phonon thermal conductivity of Si nanowires with a twining superlattice structure are investigated in detail. Based on the Maxwell equations and the Landauer formalism, it is shown that the SPhP thermal conductance is independent of the material characteristics and is given by $\pi^2 k_B^2 T/3h$, where k_B and h are the Boltzmann's and Planck's constants, respectively and T is the nanowire temperature. This universal quantization holds not only for temperatures much smaller than 1 K, as is the case of electrons and phonons, but also for temperatures comparable to room temperature [3]. Furthermore, by means of nonequilibrium molecular dynamic simulations, we show that the twining modulation of a Si nanowire at room temperature can reduce its thermal conductivity by 65% compared to that of a straight one [4]. This thermal conductivity increases with the nanowire diameter and exhibits a minimum at a given lattice period, as a result of the zigzag phonon propagation. The obtained results could have promising applications to enhance the thermal and thermoelectric performances of nanowires through polaritons and phonons, respectively.

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^{*}Corresponding author's email: jose.ordonez@centralesupelec.fr

Nonlinear thermoelectric response due to energy-dependent transport properties of a quantum dot

Adam M. Burke¹, Artis Svilans¹, Sofia Fahlvik Svensson¹, Martin Leijnse¹ and Heiner Linke¹

¹NanoLund and Solid State Physics, Lund University, Box 118, 221 00 Lund, Sweden

Quantum dots' electrostatically tuneable, energy-dependent transport properties make them useful model systems for studying quantum thermoelectric behavior. Due to their strong energy dependence, the thermoelectric response of quantum dots is expected to have a nonlinear relationship to an applied thermal bias. However, this effect has been challenging to observe experimentally since sufficiently large thermal bias is difficult to apply at the nano-scale without overall heating in the device. We take advantage of the novel top-heating architecture to demonstrate a nonlinear thermoelectric response in a quantum dot, which is defined in an InAs/InP heterostructured nanowire. We further show that the observed nonlinear thermoelectric response can be fully explained in a theoretical model based on the Master equations; given the energy-dependent transport properties of the quantum dot.

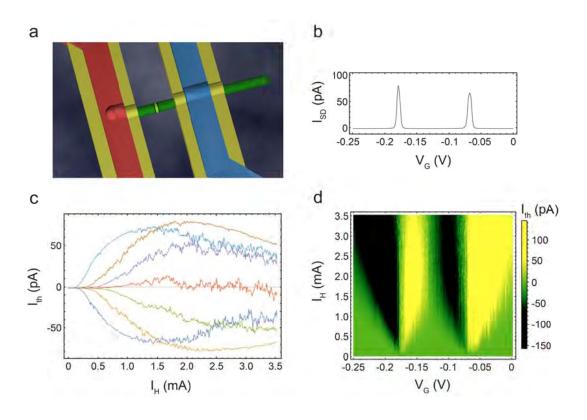


Figure 1: a) Device schematic with source/drain contacts in yellow, heaters in red and blue, the nanowire in dark green and the quantum dot in light green. Driving a current through the red heater creates a temperature bias across the device. b) Source-drain current through the device with respect to backgate bias at +100 μ V V_{SD} in the absence of heating. c) Nonlinear thermocurrent as a function of heating current at V_{SD} = 0. The different traces represent backgate biases of: -165, -154, -141, -131, -115, -101 and -85 mV. d) Thermocurrent (color) as a function of backgate bias and heating current.

Thermal rectification by design in telescopic Si nanowires

Xavier Cartoixà¹, Luciano Colombo², Riccardo Rurali³

Thermal diodes are systems whose thermal resistance depends on the sign of the applied thermal gradient and where, accordingly, heat current preferentially flows in one direction¹. These devices are one of the key building blocks of phononics, the discipline that investigates the manipulation of heat with the goal to engineer devices with the same functionalities as electrical diodes and transistors².

In bulk semiconductors thermal rectification can be achieved in heterostructures made of materials whose thermal conductivity κ has a sufficiently different dependence on the temperature to produce a sizeable rectification³. However, a general heterojunction will present a large lattice mismatch and a disordered interface, which would cause a large interface thermal resistance (ITR) masking the effect of the bulk materials.

Nanowires (NWs), with their ability to release strain laterally and their strong dependence of physical properties on NW diameter and other aspects, κ not being an exception⁴, are a perfect candidate to tailor thermal transport properties and achieve a large amount of thermal rectification.

We will present molecular dynamics simulations on thermal transport and thermal rectification in *telescopic* nanowires, i.e. NWs with an abrupt variation of diameter⁵; we also provide evidence that we can predict the thermal rectification by means of an atomically-informed continuum model that allows avoiding time-consuming non-equilibrium simulations, and which can also be applied to available experimental data. Based on this model, we predict thermal rectification values of ~15% for junctions of experimentally produced NWs⁴, reaching 50% when one of the edges is at cryogenic temperatures.

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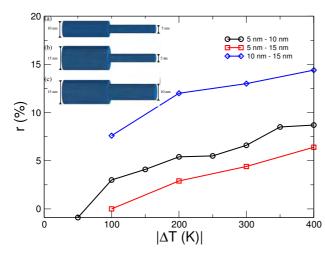


Figure 1: Thermal rectification obtained from NEMD calculations of three different telescopic Si NWs. Phonons are found to preferentially flow from the thick to the narrow

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¹ Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

² Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (Ca), Italy ³ Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de Bellterra, 08193 Bellaterra, Barcelona, Spain

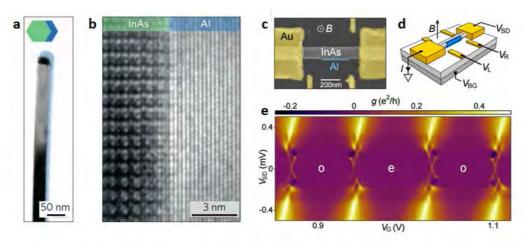
Transport in Epitaxial Semiconductor/superconductor nanowire hybrid quantum dots.

A. P. Higginbotham^{1,2}, S. M. Albrecht¹, P. Krogstrup¹, W. Chang^{1,2}, N. L. B. Ziino¹, M. H. Madsen¹, E. Johnson³, G. Kirsanskas¹, F. Kuemmeth¹, J. Nygård¹, K. Flensberg¹, C. M. Marcus¹, T. S. Jespersen¹

We present molecular beam epitaxy grown InAs semiconductor nanowires capped with a shell of aluminum (superconductor). The hybrid wires are grown without breaking vacuum, resulting in an epitaxial interface between the two materials as demonstrated by detailed transmission electron microscopy and simulations¹.

Incorporating the epitaxial nanowire hybrids in electrical devices we performed detailed tunneling spectroscopy of the proximity induced superconducting gap in the InAs core at 20 mK. The epitaxial hybrids seem to solve the soft gap problem associated with the use of nanowire hybrids for future applications in topological quantum information based on Majorana zero modes².

By selectively etching the Al shell except at a short ~300-1500nm section, hybrid semiconductor/ superconductor quantum dot devices were fabricated (see figure)³. We identify Andreev-like bound states in the semiconductor via bias spectroscopy, determine the characteristic temperatures and magnetic fields for quasiparticle excitations, and extract a parity lifetime (poisoning time) of the bound state in the semiconductor exceeding 10 ms. In the topological regime the hybrid quantum dots may host Majorana bound states, and a potential implementation for testing Majorna fusion rules is discussed.



a) TEM micrograph of an epitaxial InaAs/Al hybrid nanowire. b) Hi resolution TEM of the epitaxial interface. c,d) False color SEM and schematic illustration of hybrid semiconductor/superconductor quantum dot device. e) Bias spectroscopy of the device at 20mK.

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¹ Center for Quantum Devices, Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

² Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA ffiliation (Times New Roman 10 italic)

³ Department of Wind Energy, Technical University of Denmark, Risø Campus, Roskilde, Denmark

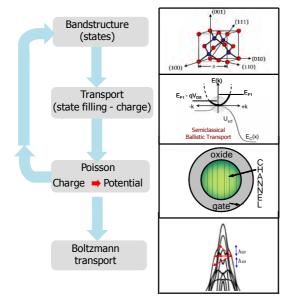
Thermoelectric properties of gated Si nanowires

Submission for Nanowires Workshop (NW)

Neophytos Neophytou

School of Engineering, University of Warwick, Coventry, CV4 7AL, UK

This work introduces a self-consistent atomistic sp³d⁵s* tight-binding bandstrusture simulator that computes the electronic structure of ultra-narrow semiconductor nanowires in the presence of a gating electrostatic potential. The sp³d⁵s* tight-binding model is coupled iteratively to the 2D Poisson equation, as shown in Fig. 1 [1]. Upon convergence, the mobility is extracted using the full band information and linearized Boltzmann transport theory, considering all relevant scattering mechanisms, i.e. acoustic phonons, optical phonons, surface roughness scattering, and ionized impurity scattering [2]. The model is computationally robust to allow atomistic description of the electronic properties for NWs with diameters even up to 25nm, consisting of several thousands of atoms in the computational domain. Using the simulator we compute the electronic and thermoelectric properties of p-type NWs of D=12nm in the [110] transport orientation. Figure 1b shows the carrier mobility versus density for two different device cases: i) the gated channel, considering phonon (red-solid-dot line) and surface roughness (red-dashed-dot line) scattering, and ii) the doped channel, considering phonons, surface roughness, and ionized impurity scattering (black-solid line). It can be observed that the mobility of the gated channel is largely increased compared to the mobility of the doped channel because of the absence of ionized impurity scattering, but also because electrostatic confinement (at concentrations p~10¹⁹/cm³) causes a severe valence bandstructure modification, increasing the band curvature, increasing carrier velocities, and thus mobility, even in the presence of surface roughness scattering. Figure 1c shows the thermoelectric power factor of the NW under direct doping and under gating. A large improvement in the power factor is observed as a result of the improved conductivity of the NW upon absence of ionized impurity scattering and bandstructure modifications under electrostatic confinement [3].



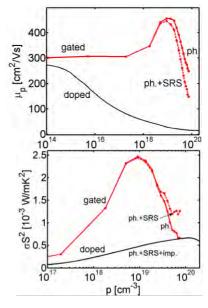


Figure 1: (a) The self-consistent atomistic bandstructure model for examining the transport properties of NWs. (b) The [110] D=12nm Si NW mobility under doped and gated conditions. (c) The thermoelectric power factor for the same NW and conditions.

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Hybrid nanophotonics systems based on sub-wavelength nanowires

 $\underline{\text{M. Notomi}}^{1,2}$, A. Yokoo^{1,2}, M. D. Birowosuto^{1,2}, M. Takiguchi^{1,2}, M. Ono^{1,2}, K. Tateno^{1,2}, G. Zhang^{1,2}, and E. Kuramochi^{1,2}

¹ Nanophotonic Center, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi, Japan ² NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi, Japan

Photonic integration differs fundamentally from electronic integration, especially because the former needs a variety of functional materials in order to realize sophisticated integrated circuits, though the latter can work mostly with Si. In order to realize low-power dense integrated circuits, it is very important to employ functional materials with a substantially small volume because the size of the functional volume mainly determines the power consumption of photonic devices [1]. However, such heterogeneous integration is a difficult task. One possible way to overcome this issue is employing ultrasmall materials (such as semiconductor nanowires) for a building block for photonic integration. Although various nanomaterials have been investigated for photonics application, the light-matter interaction is reduced because their size is much smaller than the wavelength of light. In this talk, we describe our effort in constructing novel hybrid nanophotonics platforms with sub-wavelength nanowires.

First example is a combination of photonic crystals and nanowires. Recently, we have demonstrated that a high-Q nanocavity can be created if a semiconductor nanowire is placed within a line defect of a photonic crystal. This is achieved by the "modulated mode-gap cavity" formation mechanism, by which a number of high-Q nanocavities have been demonstrated [2]. Although the modulation is normally induced by distorting the photonic crystal lattice itself, here we do this by placing a nanowire on the photonic crystal. In experiment, we placed an InAsP nanowire (90 nm in diameter, grown with VLS method) by employing a nano-probe manipulation technique on Si photonic crystal line defect, and observed unprecedented strong light confinement in a sub-wavelength nanowire [3]. An important feature of this method is that we can give various optically-active functionalities on Si photonic platforms, by just placing functional nanowires on them. In addition, this method enables us to realize movable high-Q nanocavities on photonic circuits, which is also nontrivial task in general.

Second example is a combination plasmonic nanoantenna and sub-wavelength nanowires. After fabricating gold bowtie antennae by electron beam lithography, we employed the "nanofactory" setup which consists of a focused ion beam equipped with in-situ nanomanipulators and an electron microscope. This "nanofactory" enables us to pick up a single nanowire and place it at desired place, and finally glue it. By using it, we successfully place a InP nanowire with a diameter of 50 nm within a gap of the bowtie antenna [4]. As a result of the spatially-resolved photoluminescence study, confirmed that light emission from the nanowire in the gap was resonantly enhanced. We estimated that total intrinsic enhancement of light emission is as large as over 100, which corresponds to double

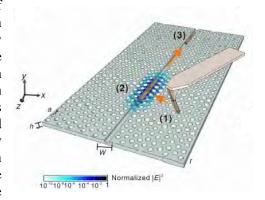


Fig. 1. Nanowire-induced nanocavity in a photonic crystals fabricated by AFM manipulation method.

enhancement due to the fact that the excitation and emission wavelengths are both within the region of plasmonic enhancement of the bowtie antenna.

We will show some examples in which we employ functional nanowires to achieve device operation, and also discuss related technologies for other combinations of nanomaterials with nanophotonics and possible impacts for future photonic integrations.

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Hot electroluminescence in Si nanowires

Alois Lugstein, Sebastian Glassner, Sebastian Kral, Emmerich Bertagnolli

Institue for Solid State Electronics, Technical University of Vienna

Monolithically integrated, active photonic devices on Si are key components in Si-based large-scale electronic-photonic integration for future generations of high-performance communication systems. Although a number of photonic components can be manufactured in mature Si technology, the realization of a Si-based light source in this platform technology is still in the focus of research. The manipulation of the Si band structure by exploiting quantum confinement, has been one approach to generate light. Another promising strategy is to increase transition possibilities within the band structure by generating hot-carriers. Thus a plausible yet less explored route for light emission is hot-carrier recombination, where the advantage of nanowires is the mitigation of phonon scattering under quantum confinement conditions.

In this work, we address the electrical and optical properties of hot-carrier electroluminescent devices (HELDs). Their ability to emit light is a direct response to high electric fields of up to 300 kV/cm that initiate stable impact ionization in nanowire heterostructures. In an effort to reduce the operating voltage, and at the same time increase the average electron energy, short semiconductor segments monolithically integrated in metallic nanowires are realized.

The HELDs consist of an intrinsic Si nanowire segment, enclosed by two self-aligned and atomically sharp, quasi-metallic nickel-silicide contacts (Figure 1a). The segment length ($L_{\rm S}$) can be controlled by adapting the silicidation process. The nanowires used for the device implementation were grown via a gold catalyst assisted vapour-liquid-solid method and are typically 10 μ m long with diameters ranging from 58 to 125 nm. Figure 1b shows a scanning electron micrograph (SEM) of a fully featured HELD.

The HELDs demonstrate efficient, power-dependent, super-bandgap emission of visible light that is mainly linearly polarized parallel along the nanowire axis covering a spectral range of 400 to 950 nm. Optical images of the device switched either off (Figure 1c) or on (Figure 1d) demonstrate the emission of white light.

We assign phonon-assisted inter- and intraband transitions of both electrons and holes to be the dominating light generating mechanism. The reduced phonon scattering slows down hot-carrier cooling, thereby enabling light emission by the phononless recombination of hot-carriers, whose quantum yield increases by up to three orders of magnitude when compared with bulk Si (from 10^{-7} to 10^{-4}).

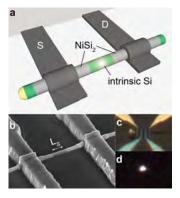


Figure 1: Hot-carrier electroluminescent device illustration. a) schematic and b) tilted SEM image of the device: Two atomically sharp and thermally intruded $NiSi_2$ segments contact the intrinsic Si segment. The segment length L_s of this particular device is 255 nm. c) Image of a non-avalanching impact device recorded with an optical microscope. The central, current carrying electrodes are highlighted and overlaid with the corresponding SEM. d) Visible light spot after long-term exposure of the identical but avalanching device with microscope illumination turned off.

Nanowires Are Not So Cool

M. De Luca^{1,2}, D. Tedeschi¹, H. A. Fonseka³, Q. Gao³, F. Mura¹, H. H. Tan³, C. Jagadish³, M. Capizzi¹, and A. Polimeni¹

¹ Dipartimento di Fisica, Sapienza Università di Roma, Roma, Italy ² Department of Physics, University of Basel, Basel, Switzerland

martadeluca.roma1@gmail.com

In optoelectronic and thermoelectric devices based on semiconductor nanowires (NWs), a pivotal role is played by the carrier cooling and heat management mechanisms. For instance, the reduced thermal conductivity of NWs with respect to their bulk counterparts has enabled an increase in the figure of merit of thermoelectric devices. Also, the rate at which charge carriers cool down after an optical or electrical excitation is crucial in relation to the efficiency of solar cells and high-speed devices. So far, surface roughness¹ and polytypism,² as well as several point defects, have been invoked as possible mechanisms able to hamper carrier-phonon interaction usually driving carrier thermalization.

We investigate here the thermalization properties of charge carriers in InP NWs.³ Photoluminescence (PL) measurements on single NWs and NW ensembles unveils the existence of a difference (ΔT) between the temperature of photo-generated carriers ($T_{\rm C}$) and that of the lattice ($T_{\rm L}$). Figure 1 (a) and (b) show PL spectra (thick lines) recorded at room temperature on WZ and ZB NWs with different diameters d, respectively. $T_{\rm C}$ is determined by fitting the PL spectra by a model (dashed lines) including both excitonic and continuum states. Clearly, $T_{\rm C}$ increases with decreasing d, as also summarized in (c). $T_{\rm C}$ as high as 500 K is reached at $T_{\rm L}$ =310 K in NWs with the smallest d. This hot carrier phenomenon is found to be a general feature of NWs regardless of NW growth technique (vapour-liquid-solid vs catalyst-free selective area epitaxy), crystal structure (WZ vs ZB), and shape. Thus, charge carriers in NWs can harvest a thermal budget up to the long times probed by steady-state PL that is of relevance for photovoltaic and thermoelectric applications.

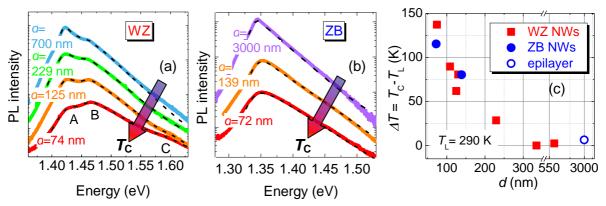


Figure 1 (a), (b) PL spectra (thick lines) recorded at lattice temperature T_L =290 K on some representative WZ (a) and ZB (b) InP samples with the indicated diameter d. Notice the semilog scale, allowing to qualitatively estimate carrier temperature T_C from the slope of high-energy tails. T_C was quantitatively determined by the fits of PL spectra (dashed lines). In WZ samples, high-energy transitions (labelled B and C) get more populated as T_C increases. (c) $\Delta T = T_C - T_L vs d$ estimated at T_L =290 K for all WZ (squares) and ZB (circles) samples.

³ Department of Electronic Materials Engineering, Research School of Physics and Engineering, The Australian National University, Canberra, Australia

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Nanowire Antenna Absorption Probed with Time-Reversed Fourier Microscopy

J. Gómez Rivas^{1,2,*}, R. Paniagua-Domínguez³, D.A. van Dam², and J.A. Sánchez-Gil³

FOM Institute AMOLF, Amsterdam, The Netherlands
 COBRA Research Institute, Eindhoven University of Technology, The Netherlands
 Instituto de Estructura de la Materia (IEM-CSIC), CSIC, Madrid, Spain
 rivas@amolf.nl

Semiconductor nanowires have attracted broad interest as building blocks for novel photodetectors and photovoltaic devices. Similarly to other resonant nanostructures, nanowires support optical modes to which the incident light can resonantly couple due to their small dimensions comparable to optical wavelengths. In this way, nanowires have proven to efficiently concentrate light and enhance absorption. Despite extensive theoretical and experimental investigations on light absorption in nanowire arrays and in solar cells, the angle-dependent light absorption in individual nanowires remains largely unexplored. Typically, only the two limiting cases for the illumination are reported in the literature: (i) nanowires lying on the substrate illuminated perpendicular to their axis that are described as Mie scatterers, and (ii) vertical nanowires illuminated parallel to their axis that support guided modes to which the incident light can couple and be absorbed.

In this contribution, we demonstrate the angle-dependent light absorption in a dilute array of optically uncoupled nanowires that behave as individual nanowires, ¹ following a purely optical approach without using any electrical contacts to the wires. Such measurements rely on analyzing the light emission from nanowires and constitute an experimental challenge due to the very low intensity emitted to the far field by dilute nanowire arrays. We address this challenge by introducing a novel technique that we call time-reversed Fourier microscopy. With this technique, we are able to illuminate nanostructures under a microscope objective with a controlled and variable polarization and angle of incidence and efficiently collect their emission with the same objective. In this way, we can map the directional absorption of nanowires for the angles within the numerical aperture of the objective. We find that at small angles of incidence, measured from the nanowire axis, light predominantly couples to the HE₁₁ guided mode, which is absorbed as it propagates through the wire. At large angles, however, the coupling to the guided mode weakens and the incident light excites Mie resonances that become the major absorption mechanism.

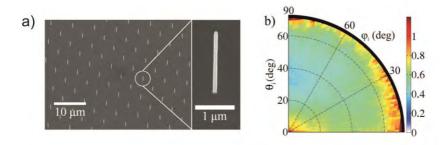


Figure 1: (a) SEM image of a diluted arrays of InP nanowires. (b) Polar plot of the normalized directional absorption of the individual nanowires in the array.

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Quantum transport in core-shell nanowires

Jan G. Gluschke^{1,2}, Bahram Ganjipour¹, Martin Leijnse¹, Lars Samuelson¹, Hongqi Xu^{1,3}, Kimberly A. Dick^{1,4}, Heiner Linke¹, and Claes Thelander¹

¹Solid State Physics and Nanometer Structure Consortium (nmC@LU), Lund University, Lund, Sweden ²School of Physics, The University of New South Wales, Sydney, Australia

Heterostructures of GaSb and InAs show an uncommon type II-broken gap band alignment which is tunable by confinement, making them interesting for a range of applications such as tunneling based devices and far-infrared detectors, as well as for fundamental physics studies of electron-hole hybridization and topological states of matter. Recently, this heterostructure has been realized in a nanowire core-shell geometry (for example a GaSb core covered with a thin InAs shell). Here we present two studies aimed at uncovering the fundamental physics of these novel nanowires through different quantum transport measurements combined with theoretical modeling.

First, we present measurements of the thermovoltage¹, i.e., the open circuit voltage resulting from an applied temperature gradient, of GaSb-InAs core-shell nanowires. We show that such thermovoltage measurements can be used to reliably identify the dominant carrier type, which can be changed between electrons and holes with a global back gate. This works all the way from 4.2 K up to room temperature, even in regimes where a conductance measurement does not allow for such a distinction. In addition, we show that theoretical modeling using the measured conductance as input can reproduce the measured thermovoltage under the assumption that electron and hole states shift differently in energy with the applied gate voltage. The thermovoltage also reveals evidence of 0D-like states for gate voltages where the nanowire is almost depleted of both electrons and holes.

Second, we present a detailed investigation of the regime where a GaSb-InAs core-shell nanowire is populated with both electrons and holes². Here, we investigate devices based on short nanowire segments hosting core-shell nanowire quantum dots and perform measurements at temperatures down to 50 mK. The conductance measured as a function of gate and bias voltages shows peculiar Coulomb blockade features, which model calculations show are consistent with simultaneous transport of electrons through a quantum dot formed in the InAs shell and of holes through a quantum dot formed in the GaSb core. Adjusting the gate voltage allows us to controllably add single charge carriers, and we can extract the energy scale associated with the attractive interactions between the spatially separated electrons and holes.

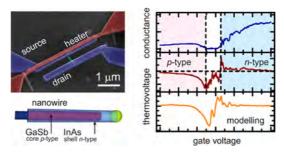


Figure 1: Core-shell nanowire and SEM image of a typical device used for thermoelectric measurements (left), together with the measured conductance and thermovoltage, and the simulated thermovoltage. The figure is taken from Reference 1.

³Department of Electronics and Key Laboratory for the Physics and Chemistry of Nanodevices, Peking University, Beijing, China

⁴Center for Analysis and Synthesis, Lund University, Lund, Sweden

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Controlled growth and enhanced thermoelectric properties of topological crystalline insulator nanowires

Shixiong Zhang

Department of Physics, Indiana University, Bloomington, IN, USA

Topological crystalline insulators (TCIs) are a class of quantum materials that host topological surface states protected by crystalline mirror symmetry. Immediately after theoretical predictions, tin telluride (SnTe) and its alloy compounds were experimentally demonstrated to be TCIs. The SnTe-based TCIs have intriguing surface properties, including a Van-Hove singularity in the density of states, which could be useful for enhancing thermoelectric properties. One dimensional nanowires have large surface-area-to-volume ratio and hence increased contributions from surface states. Here I will discuss the controlled synthesis and thermoelectric studies of nanowires of SnTe and its alloy compounds. The nanowires were grown using a vapor transport approach and are single crystalline with a broad diameter distribution. Correlated measurements of electrical conductivity, thermopower and thermal conductivity were performed on the same, individual nanowires to accurately determine their thermoelectric figure of merit ZTs. While their electrical conductivity is comparable with that of bulk samples, the thermopower of nanowires is higher than the bulk values and it shows a strong diameter dependence. The thermal conductivity of nanowires is lower than bulk values, which may arise from the enhanced phonon-surface scattering. The simultaneous improvement of thermopower and suppression of thermal conductivity give rise to a significantly enhanced figure of merit ZT in TCI nanowires.