Final report, project ÅForsk 20-108

"Nanowires based on highly mismatched semiconductor alloys for energy-efficient nano-optoelectonics and photonics"
(PI: Prof. I. A. Buyanova)

Summary

Semiconductor nanowires (NWs) made from highly mismatched III-V-V′ alloys represent a promising building block for novel nano-photonic devices with increased device efficiency and low costs. In this project we have characterized and optimized material-related properties of such novel structures, which has led to their reliable and reproducible growth via molecular beam epitaxy (MBE). We have found that clustering of bismuth (Bi) atoms in GaAsBi NWs leads to the spontaneous formation of Bi-rich quantum dots, which could act as single photon emitters, promising for future application of these materials in quantum information technologies. We have also demonstrated that alloying with nitrogen (N) and also lattice engineering represent effective strategies for enhancing and manipulating the second- and third order nonlinear optical responses of subwavelength NWs from Ga(N,Bi)As and GaNP. Moreover, utilizing N-containing alloys in NW heterostructures formed with parental materials, e.g. in GaAsP/GaNAsP core/shell and GaAs/GaNAs/GaAs core/shell/shell NW heterostructures, leads to an efficient energy upconversion in these structures, which could be utilized for harvesting solar energy within a wider spectral range that is not restricted by the bandgap energies of the constituent materials.

1. Purpose and Aims

The aims of this program were:

1) to understand key material-related parameters of novel NWs based on highly mismatched semiconductors (such as dilute nitrides and dilute bismides), and their dependence on structural design;

2) to gain general knowledge on unknown fundamental properties of different crystal polytypes of such NWs, and to exploit band structure engineering for potential applications in optoelectronics and photovoltaics;

3) to single out optimum structural design of prototype NW solar cells for efficient energy harvesting utilizing an intermediate-band approach and of prototype NW LEDs with a high efficiency.

2. Implementation

GaN(P,As) NWs studied in this project were provided by our long-term collaborator Prof. C. W. Tu (Jacobs School of Engineering at UC at San Diego, USA, and EE Department, National Chung Hsing University, Taiwan). Prof. Tu is one of the pioneers in the development of dilute nitrides (including NWs). GaN(Bi)As NWs were grown by Prof. F. Ishikawa (Hokkaido University, Japan) and Prof. P.-P. Chen (Shanghai Institute of Technical Physics, China).

All characterization measurements and modeling of the structures were performed at Linköping University (LiU), Sweden. Structural quality of the NWs was examined by using high resolution X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and cathodoluminescence (CL). Point defects were identified by employing a range of defect-sensitive techniques based on optical and spin resonance spectroscopies including photoluminescence (PL), optically detected magnetic resonance (ODMR) and electron paramagnetic resonance (EPR). Optical techniques, such as continuous wave (cw)- and time-resolved PL and Raman spectroscopies, were also employed to evaluate optical quality and mechanisms of carrier recombination. Second harmonic generation (SHG) and two-photon absorption processes were monitored using optical measurements, which were conducted on both NW arrays and individual NWs with known crystalline structure. All characterization measurements provided feedback to growth, assisting its optimization.

3. Achieved results

3.1. Solving material-related issues

This part of the project was devoted to optimization of the material quality. The performed characterization studies assisted in developing reliable and reproducible MBE growth required for fabrication of desired NW structures. The main obtained results can be briefly summarized as follows:

- We have investigated recombination processes in wurtzite GaAsBi NWs grown by Au-catalyzed MBE. The fabricated NWs formed dense arrays with good structural quality and smooth NW surface, as confirmed from the performed SEM measurements- see Fig.1. By employing the μ-PL and time-resolved PL spectroscopies, we have demonstrated that Bi incorporation causes formation of band-tail states due to alloy disorder. At temperatures below 75 K, this leads to trapping of excitons within band-tail states, which suppresses effects of surface-related non-radiative recombination (SNR) and prolongs exciton lifetime. Furthermore, Bi incorporation in the GaAsBi NW was found to have minor influence on surface states responsible for SNR. Our results, therefore, demonstrated that wurtzite GaAsBi NWs have good structural and optical properties comparable to those of their wurtzite GaAs counterpart, promising for future applications of these novel structures in nano-optoelectonics and nano-photonics.

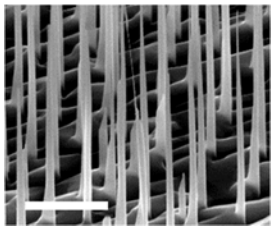

Figure 1. The 30°-tilted view SEM image of typical wurtzite GaAsBi NW array.

- Through detailed cross-sectional high resolution TEM and energy dispersive spectroscopy (EDS) measurements, we have found that Bi favorably segregates within twin planes near the six <112> side corners of the GaAsBi-based NWs, forming the nanodisks – see Figure 2. Their formation is suggested to be strain driven and may also be affected by crystal polarity. The nanodisks induce exciton confinement, giving rise to a series of sharp emission lines with a linewidth below 450 μeV and energies ranging between 1.15 to 1.32 eV. Moreover, the analysis of the variation of the PL linewidth with increasing temperature suggests that accumulation of Bi atoms is facilitated in thinner nanodisks, consistent with the magneto-PL data. Our results, therefore, show that in addition to band structure engineering via bandgap bowing in GaAsBi alloys, the tendency of Bi to segregate within the spatial regions with well-defined crystallographic structure can be used for the fabrication of self-assembled quantum emitters embedded in

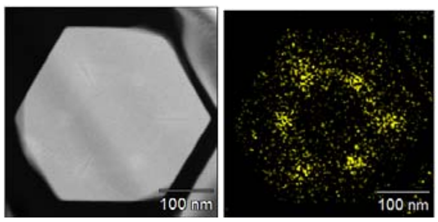

Figure 2. Axial cross-sectional scanning TEM and EDS elemental mapping of Bi in GaAs/GaAsBi/GaAs core/shell/shell NWs.

GaAsBi NWs. This can be promising for future applications of this material system in advanced nanophotonic and quantum information devices.

- By employing PL and ODMR spectroscopies, we have studied defect formation in the MBE-grown Ga(N)AsP NWs. Gallium vacancies were found to be the common grown-in defects in the NWs grown in both vapor-liquid-solid and vapor-solid modes. Based on the similarity of the deduced spin-Hamiltonian parameters with the known parameters of V_{Ga} in bulk GaAs, the defects are concluded to be formed in volume regions of the NW and is favored under As-rich local surroundings. They act as efficient center of non-radiative recombination competing with radiative recombination in the alloys - see Figure 3. Our finding, therefore, calls for future efforts in developing strategies to suppress the defect formation during the growth, crucial for applications of Ga(N)AsP NWs in novel optoelectronic devices.

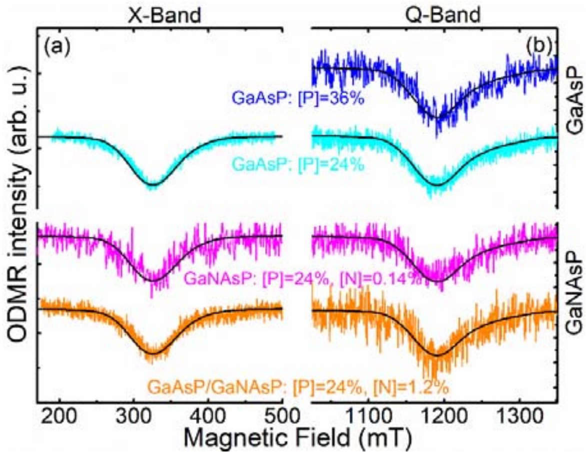

Figure 3: X-band (a) and Q-band (b) ODMR spectra measured under the 532-nm excitation from the uniform $GaAs_{0.64}P_{0.36}$ (the blue curve), $GaAs_{0.76}P_{0.24}$ (the light blue curves), $GaAs_{0.76}P_{0.24}$ with 0.14% N (the pink curves) NWs and GaAsP/GaNAsP core/shell structures with 1.2% N and 24% P (the orange curves). All spectra are normalized to the same maximum intensity. The simulated ODMR spectra using the spin-Hamiltonian parameters of the V_{Ga} surrounded by As atoms are depicted by the solid black curves.

- Post-growth thermal annealing is often involved during device fabrication and can also be used to improve their optical and transport properties. However, effects of such annealing on alloy disorder and strain in core/shell NWs are not fully understood. We have investigated these effects in novel core/shell/shell GaAs/GaNAs/GaAs NWs grown by MBE on (111) Si substrates. By employing polarization-resolved PL measurements, we have shown that annealing (i) improves overall alloy uniformity due to suppressed long-range fluctuations in the N composition; (ii) reduces local strain within N clusters acting as quantum dot emitters; and (iii) leads to partial relaxation of the global strain caused by the lattice mismatch between GaNAs and GaAs. Our results, therefore, underline the applicability of such treatment for improving optical quality of NWs from highly-mismatched alloys. They also call for caution when using ex-situ annealing in strain-engineered NW heterostructures.

- In the quest for further extending the spectral range of light emission from NWs based on highly mismatched alloys, we have grown GaAs/GaNAsBi/GaAs core–multishell nanowires by self-catalyzed MBE on a Si(111) substrate. It was found that the nanowires grown at 350 °C show a regular hexagonal GaNAsBi shell with a width of 20 nm. Based on the cross-sectional STEM-EDS studies, the shell was estimated to contain approximately 1.5% N and 3% Bi, showing a lattice mismatch of less than 0.2%, with the low strain appearing to suppress lattice deformation. Thus, we have obtained room temperature PL at approximately 1300 nm from the GaAs/GaNAsBi/GaAs core–multishell NW ensemble. Our results, therefore, show that co-alloying with Bi and N is promising for future applications of this material system in nanoscale light emitters operating in the near-infrared regime.

3.2. Understanding fundamental electronic properties

In this part of the project, we have analyzed fundamental properties of highly mismatched alloys in the NW architecture aiming to evaluate merits of this material system for solar energy conversion and light emission. The following results were obtained.

- We have successfully fabricated WZ GaAsBi NWs with good optical quality. The electronic band structure of wurtzite GaAsBi NW was revealed by employing spatially resolved optical spectroscopies on individual NWs. The bandgap energy of WZ GaAsBi was found to reduce as compared with parental GaAs. The polarization-resolved micro-PL (μ-PL) and μ-PL excitation spectra indicated that both the A and B valence subbands of the WZ GaAs NW are pushed upwards by anticrossing repulsion following incorporation of Bi atoms, while the symmetry order of the valence band (VB) states is kept unchanged under the current Bi compositions. Surprisingly, the shift is found to be even larger for the C valence subband based on the performed resonant Raman measurement, which is unexpected considering the large energy distance between the C subband and the spin orbit-split Bi level. The extraordinary modifications of the VB states are interpreted by expanding the band anticrossing model and assuming anisotropic hybridization energy in wurtzite GaAsBi NW – see Figure 4. The model also predicts that the ordering of the A and B VB states can be switched in WZ GaAsBi alloys with larger Bi compositions, which could allow control of polarization direction of emitted and absorbed light in thin WZ NWs via alloying. Furthermore, incorporation of Bi into GaAs was found to significantly reduce the temperature sensitivity of bandgap in WZ GaAsBi NW. Our work, therefore, demonstrated that utilizing dilute bismide alloys provides new avenues for bandgap engineering and thus photonic engineering with NWs.

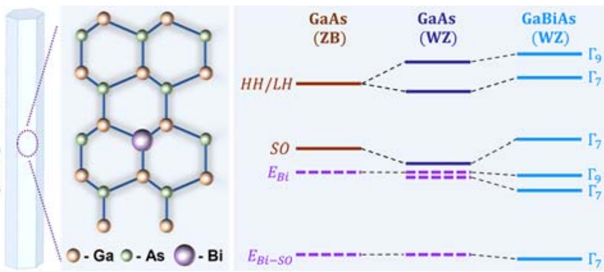

Figure 4. Lattice stucture of WZ GaAsBi NWs together with electronic structure of GaAs and GaAsBi with zinc blende and wurtzite crystalline structure.

- Semiconductor quantum dots (QDs) acting as single-photon-emitters are potential building blocks for various applications in future quantum information technology. For such applications, a thorough understanding and precise control of charge states and capture/recombination dynamics of the QDs are vital. We have studied the dynamics of QDs spontaneously formed in GaNAsP nanowires, belonging to the dilute nitride material system. By using a Random Population Model modified for these highly mismatched materials, we have analyzed the results from photoluminescence and photon correlation experiments and show a general trend of disparity in positive and negative trion populations and also a strong dependence of the capture/recombination dynamics and QD charge states on its surroundings. Specifically, we have shown that the presence of hole-trap defects in the proximity to some QDs facilitates formation of negative trions, which also causes a dramatic reduction of the neutral exciton lifetime. These findings underline the importance of proper understanding of the QD capture and recombination processes and demonstrate the possibility to use highly mismatched materials and defects for charge engineering of QDs.

3.3 Developing optimal designs

This part of the project was devoted to developing optimum structural designs of the NW that provide the maximum efficiency of second harmonic generation SHG and energy upconversion in the NW architecture. Our research efforts have led to the following results.

- We have investigated non-linear optical properties of thin GaAs NWs with zinc blende (ZB) and wurtzite (WZ) crystal structures. The SHG intensity was found to be significantly stronger in WZ NWs as compared with ZB NWs (by about 7 times), reaching the value of $2.5x10^{-5}$ W^{-1} – see Figure 5. This value is among the highest reported in the literature, including complex waveguide and nano-resonator structures, as well as hybrid plasmonic structures. Such enhancement was directly verified by correlative SHG intensity mapping and transmission electron microscopy characterization performed on the same polymorphic NWs. Polarization-resolved measurements showed that the increase of the orthogonal SHG component is chiefly controlled by the surface-induced SHG caused by structural and electric field discontinuity at the NW surface. This component, however, remains weaker than the parallel SHG output by about two orders of magnitude, due to weak out-coupling of the generated light from thin NWs. The dominant parallel SHG component is proven to be enhanced in WZ via electric-field induced SHG, which is activated by the axial built-in electric field related to spontaneous polarization in WZ NWs and can be controlled optically and potentially electrically. This SHG enhancement is found to be robust and does not require high structural quality of the NWs as the presence of structural defects facilitates SHG by enhancing the internal electric field. A more precise control of crystalline structure in MBE-grown NWs could be achievable in future by fine tuning As and Ga fluxes during the growth. Our results, therefore, demonstrate great potential of thin GaAs-based NWs for nonlinear nanophotonics and show that their non-linear properties can be manipulated via lattice engineering.

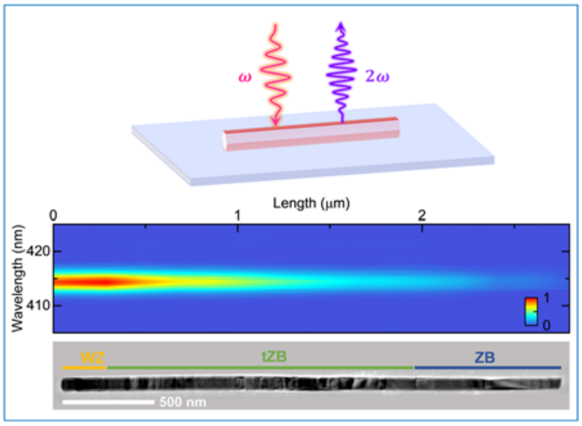

Figure 5. Schematic illustrating second harmonic generation in a lying NW transferred on a Si substrate. SHG intensity distribution along the NW showing that the highest signal originates from the WZ region identified by TEM.

- We have demonstrated an efficient deep subwavelength-scale SHG antenna based on dilute nitride GaNP NWs hybridized with surface plasmons in an Au thin film. The second-order nonlinear susceptibility governing the harmonic efficiency showed a 2-fold increase with 0.45% of N incorporation. The improved nonlinear response is attributed to both valley mixing in conduction band and local crystal symmetry breaking by disordered N cluster states. The presence of rich ZB twin phases in the antennae leads to coherent interference of SHG light between mirrored domains, further tailoring the far-field polarimetric output patterns and providing a new control knob for interfacing with polarization-sensitive nanooptics. The results presented in this work, therefore, manifested dilute nitride-based nanomaterials as a competitive candidate for future chip-integrated optoelectronic technology.

- We have demonstrated a novel type of efficient upconverting semiconductor nanostructures, namely a core/shell NW heterostructure consisting of a nitrogen-free GaAs(P) core and a dilute-nitride GaNAs(P) shell with a smaller bandgap. By monitoring photoluminescence of the NW core with a larger bandgap, we have shown that a dramatic enhancement of the upconversion efficiency, which is about 500-fold in the GaAsP/GaNAsP and 100-fold in the GaAs/GaNAs core/shell NWs, is observed when the excitation photon energy is tuned within the range of band-to-band transitions in the dilute-nitride shell. The revealed upconversion process exhibits a nearly linear dependence on the excitation power and, therefore, can be detected at very low excitation density down to 0.1 W/cm^2. We attribute it to two-step two-photon absorption via the band states of the dilute nitride shell that is promoted in the studied NWs by a favorable band alignment. Based on the performed rate equation analysis supported by the transient photoluminescence, the upconversion efficiency is shown to be strongly dependent on the carrier lifetime in the NW shell, reaching 1.35% in the GaAsP/GaNAsP NW arrays fabricated on a Si substrate under low excitation density. The efficiency can be further enhanced to up to 15% in hybrid NW-on-gold structures, where the electric field distribution is engineered to maximize light absorption within the shell region under upconversion conditions. This is in combination with an overall increase in the emission intensity of these structures caused by a decreased leakage of the laser light outside the NWs. Our findings, therefore, demonstrate the great potential of dilute nitride NWs as energy upconverters in e.g. nano-photonic or next generation photovoltaic applications. They also provide general guidelines for designing efficient nanoscale photon upconverters based on NW heterostructures.

4. Outcome

The obtained results unambiguously show that using highly mismatched alloys in the NW architecture allows efficient tuning of fundamental electronic properties of such materials, attractive for improving performance of novel nano-photonic devices, including nano-LEDs, solar cells and energy converters.

The project results outlined in Sec. 3 were published in the following journal publications:

1) B. Zhang, M. Jansson, Y. Shimizu, W.M. Chen, F. Ishikawa, I. A. Buyanova: Self-assembled nanodisks in coaxial GaAs/GaAsBi/GaAs core-multishell nanowires. Nanoscale 12, 20849 (2020).

2) R. M. Balagula, M. Jansson, M. Yukimune, J. E. Stehr, F. Ishikawa, W.M. Chen, I. A. Buyanova: Effects of thermal annealing on localization and strain in core/multishell GaAs/GaNAs/GaAs nanowires. Sci. Rep. 10, 8620 (2020).

3) M. Jansson, R. La, C. W. Tu, W. M. Chen, I. A. Buyanova: Exciton generation and recombination dynamics of quantum dots embedded in GaNAsP nanowires. Phys.Rev. B 103 , 165425 (2021).

4) B. Zhang, J. E. Stehr, P. P. Chen, X. Wang, F. Ishikawa, W. M. Chen, I. A. Buyanova: Anomalously Strong Second-Harmonic Generation in GaAs Nanowires via Crystal-Structure Engineering. Advanced Functional Materials 31, 2104671 (2021)

5) Z. Luo, C. Ma, Y. Lin, Q. Jiang, B. Liu, X. Yang, X. Yi, J. Qu, X. Zhu, X. Wang, W. M Chen, I. A Buyanova, S. Chen, A. Pan: An Efficient Deep-Subwavelength Second Harmonic Nanoantenna Based on Surface Plasmon-Coupled Dilute Nitride GaNP Nanowires. Nano Letters 21, 3426-3434 (2021)

6) M. Jansson, F. Ishikawa, W. M. Chen, I. A. Buyanova: Designing semiconductor nanowires for efficient photon upconversion via heterostructure engineering. ACS Nano 16, 12666 (2022)

7) K. Nakama, M. Yukimune, N. Kawasaki, A. Higo, S. Hiuta, A. Murayama, M. Jansson, W. M. Chen, A. A. Buyanova and F. Ishikawa: GaAs/GaInNAs Core-Multishell Nanowires with a Triple Quantum-Well Structure Emitting in the Telecommunication Range. Appl. Phys. Lett. 123, 081104 (2023).

8) M. Jansson, V. V. Nosenko, G. Yu. Rudko, F. Ishikawa, W. M. Chen, and I. A. Buyanova: Lattice dynamics and carrier recombination in GaAs/GaAsBi nanowires. Sci. Rep. 13, 12880 (2023)

The obtained results were also presented as **invited talks** at the following international conferences:

- 2020 Int. Conf. Solid State Devices and Materials, Sept 27-29, 2020 (all virtual)
- Compound Semiconductor Week, May 9-13, 2021 (all virtual)
- 244th Meeting of Electrochemical Society, Oct 8-12, 2023, Gothenburg, Sweden