10th International Workshop on Bismuth-Containing Semiconductors

Toulouse, July 21 – 24, 2019

Programme, Abstracts, and General Information
Welcome to LAAS, Toulouse, France, to take part to the 10th International Workshop on Bismuth-Containing Semiconductors.

The International Workshops on Bismuth-Containing Semiconductors have been organized mid-July every year since 2010. This workshop series has been founded by the participants of the Materials World Network “III-V Bismide Materials for IR and Mid IR Semiconductors”, who, for a large part, are still members of the advisory committee.

These workshops focus on the new classes of semiconductors, thermoelectric materials and topological insulators, all containing bismuth, and will treat theory, epitaxial growth, characterization (optical, electrical and structural) of these novel materials, as well as their devices devoted to applications such as low power and energy efficient photonics, electronics, photovoltaics, thermoelectrics, and spintronics. Their goal is to address the issues and boost the development of these emerging compounds taking benefit from the properties of bismuth. These interdisciplinary meetings gather physicists, chemists, materials scientists, and engineers, to address this very active research area, in a condensed three-day workshop.

On behalf of the organizing committee, we would like to thank all the invited speakers and regular participants, who are the core of this 10th workshop, as well as all the institutions and industrial partners who have supported its organization.

We hope that the participants will benefit from this workshop and enjoy the social activities, which we expect to be as exciting and fruitful as the previous editions. We hope that this workshop will contribute to the cohesion of this research community bonded by the goal to advance the fundamental understanding and application perspectives of these emerging alloys.

Chantal Fontaine and Hélène Carrère
Co-chairs
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**Thanks to our sponsors**
Invited speakers

Shane R. Johnson
Center for Photonics Innovation & Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, USA
Molecular beam epitaxy growth of high quality InAsSbBi on GaSb substrates

Joanna Millunchick
University of Michigan, Ann Arbor (USA)
The Atomic-Scale Mechanisms of Mixed Anion Semiconductor Alloy Growth: Self-limited vs. Accumulating Anion Processes

Esperanza Luna
Paul Drude Institute for Solid State Electronics, Berlin, Germany
Transmission Electron Microscopy of (In,Ga)(Sb,Bi) epilayers and quantum wells

Fabio Pezzoli
LNESS and University of Milano-Bicocca, Milan, Italy
Lattice-mismatched heterostructures based on group IV semiconductors as an advanced spin-optronics platform

Stephen Sweeney
University of Surrey, Guildford, United Kingdom
Highly Mismatched and Inhomogeneous Alloys in Photonic Device Applications

Shumin Wang
Chalmers University of Technology, Goteborg, Sweden
Shanghai Institute of Microsystem and Information Technology, Shanghai, China
Progress on Dilute Bismide Near-IR Light Emitting Devices

Joshua Zide
University of Delaware, Newark, USA
Growth of new III-Bi-As materials for new devices
## Workshop Schedule

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Note: Visit of Airbus and of the Aeroscopia Museum on request.
Monday July 22

Session 1. III–Sb–Bi alloys – growth
(Chair: Prof. Shumin Wang)

09:00 – 09:10 Opening

09:10 – 09:50, Invited talk (Mo-1)

Molecular beam epitaxy growth of high quality InAsSbBi on GaSb substrates
Shane R. Johnson, Stephen T. Schaefer, and Rajeev R. Kosireddy
Arizona State University, Tempe (USA)

09:50 – 10:10 (Mo-2)

Molecular-beam epitaxy of Ga(In)SbBi alloys and QWs
Olivier Delorme, L. Cerutti, E. Luna, A. Trampert, E. Tournié, and J.-B. Rodriguez
1IES, Univ. Montpellier (France), 2Paul-Drude-Institut für Festkörperlektronik, Berlin (Germany)

10:10 – 10:30 (Mo-3)

Epitaxial phases of high Bi content GaSbBi alloys
Joonas Hilska, Eero Koivusalo, Janne Puustinen, Soile Suomalainen, and Mircea Guina
ORC, Tampere University (Finland)

10:30 – 11:00 Coffee break

Session 2. III–V–Bi alloys – Surface reconstructions, growth conditions
(Chair: Dr Esperanza Luna)

11:00 – 11:40, Invited talk (Mo-4)

The Atomic-Scale Mechanisms of Mixed Anion Semiconductor Alloy Growth: Self-limited vs. Accumulating Anion Processes
Joanna Millunchick
University of Michigan, Ann Arbor (USA)

11:40 – 12:00 (Mo-5)

Origins of morphology and microstructure of epitaxial GaAsBi
Janne Puustinen, Joonas Hilska, Esperanza Luna, and Mircea Guina
1ORC, Tampere University (Finland), 2Paul-Drude-Institut für Festkörperelektronik, Berlin (Germany)

12:00 – 12:20 (Mo-6)

Impact of growth conditions on Bi incorporation on GaAs grown by Molecular Beam Epitaxy and on the GaAsBi characteristics
Clara Cornille, A. Amoult, Q. Gravelier, and C. Fontaine
1LAAS-CNRS (France), and 2Université Paul Sabatier (France)

12:20 – 13:30 Lunch
Session 3. III–V–Bi alloys – Structural properties, ordering and defects  
(Chair: Prof. Shane Johnson)

13:30 – 14:10, Invited talk (Mo-7)  
Transmission Electron Microscopy of (In,Ga)Sb(Bi) epilayers and quantum wells  
Esperanza Luna¹, O. Delorme², L. Cerutti², E. Tournié², J.-B. Rodriguez² and A. Trampert²  
¹Paul-Drude-Institut für Festkörperelektronik, Berlin (Germany), and ²IES, Univ. Montpellier (France)

14:10 – 14:30 (Mo-8)  
Rutherford backscattering spectrometry investigation of In,Ga, As,Bi, heterostructures  
Matthew K. Sharpe¹, I. P. Marko¹, D. Duffy¹, P. Couture¹, A. Ellis¹, J. England¹, M. Kesaria¹⁺⁻³, V. Fedorov²⁺⁻⁴, E. Clarke², C. H. Tan², T. Hepp³, K. Volz³ and S. J. Sweeney¹  
¹University of Surrey, Guildford (UK), ²University of Sheffield, Sheffield (UK), ³Cardiff University, Cardiff (UK), ⁴Saint Petersburg Academic University (Russia), and ⁵Philipps-Universität Marburg (Germany)

14:30 – 14:50 (Mo-9)  
Surface Diffusion and Disorder in Quaternary (Ga,In)(As,Bi)/InP Heterostructures  
Julian Veletas¹, Thilo Hepp², Kerstin Volz², and Sangam Chatterjee¹  
¹Justus-Liebig-University Giessen (Germany), and ²Philipps-Universität Marburg (Germany)

14:50 – 15:20 Coffee break

15:20 – 15:40 (Mo-10)  
Structural analysis of bismide layers ordering  
S. Stanionytė, V. Pačebutas, M. Skapas, T. Paulauskas, B. Čechavičius, A. Krotkus  
Center for physical sciences and technology, Vilnius (Lithuania)

15:40 – 16:00 (Mo-11)  
Ordering and Droplet-induced Inhomogeneities in GaAsBi Films  
Brandon Carter¹, Veronica Caro¹, Li Yue², and Joanna Millunchick¹  
¹University of Michigan Ann Arbor (USA), and ²Shanghai Institute of Microsystem and Information Technology, Shanghai (China)

16:00 – 16:20 (Mo-12)  
Investigation of Bi quantum dots embedded in GaAsBi matrix by Transmission Electron Microscopy  
M. Skapas, and Renata Butkutė  
Center for physical sciences and technology, Vilnius (Lithuania)

16:20 – 19:00 Poster session and lab visits

20:00 Dinner in the city center
Tuesday July 23

Session 4: III-V-Bi alloys – New III-V-Bi alloys and nanostructures
(Chair: Dr Jean-Baptiste Rodriguez)

09:00 – 09:40, Invited talk (Tu-1)

Growth of new III-Bi-As materials for new devices
Joshua Zide1, Jing Zhang1, Yuejing Wang1, and Greg Haughstad2
1University of Delaware, Newark, (USA), and 2University of Minnesota, Minneapolis, (USA)

09:40 – 10:00 (Tu-2)

Bi localization in GaAs/GaAsBi/GaAs heterostructured nanowires
Teruyoshi Matsuda, Kosuke Yano, Satoshi Shimomura, Fumitaro Ishikawa
Ehime University (Japan)

10:00 – 10:20 (Tu-3)

Compositional profile modelling of bismuth surface segregation in epitaxial III-V-Bi systems
Daniel Fernandez de los Reyes1, S. Flores1, V. Braza1, T. Ben1, N. Ruiz-Marín1, R.D. Richards1, F. Bastiman1, J.P.R. David1 and D. González1
1Universidad de Cádiz (Spain) and 2University of Sheffield (UK)

10:20 – 10:50 Coffee break

Session 5. HMAs and their potential applications
(Chair: Dr Andrea Balocchi)

10:50 – 11:30, Invited talk (Tu-4)

Highly Mismatched and Inhomogeneous Alloys in Photonic Device Applications
Stephen Sweeney
University of Surrey, Guildford (UK)

11:30 – 11:50 (Tu-5)

Impact of band-anticrossing on band-to-band tunneling in highly-mismatched semiconductor alloys
Sarita Das1,2, Christopher A. Broderick1,2, and Eoin P. O’Reilly1,2
1Tyndall National Institute and 2Department of Physics of the University College Cork (Ireland)

11:50 – 12:10 (Tu-6)

Group-IV semiconductor alloys: electronic structure evolution and the indirect- to direct-gap transition
Christopher A. Broderick1,2, Edmond J. O’Halloran1,3, Michael D. Dunne1,2, Amy C. Kirwan1,2, Daniel S. P. Tanner1, Stefan Schulz1, and Eoin P. O’Reilly1,2
1Tyndall National Institute, 2Department of Physics and 3School of Chemistry of the University College Cork, (Ireland)

12:10 – 13:10 Lunch

Session 6. IV and III-V-Bi HMAs: spin and optical properties
(Chair: Prof. Eoin O’Reilly)

13:10 – 13:50, Invited talk (Tu-7)

Lattice-mismatched heterostructures based on group IV semiconductors as an advanced spin-optronics platform
Fabio Pezzoli
LNESS and University of Milano-Bicocca, Milan, Italy
The influence of barrier design on luminescent properties of GaAsBi quantum wells
Simona Pūkienė¹, Mindaugas Karaliūnas¹, Algirdas Jasinskas¹, Evelina Dudutiene¹, Bronislovas Čechavičius¹, Andres Udal², Gintaras Valušis¹ and Renata Butkutė³
¹Center for physical sciences and technology, Vilnius (Lithuania) and ²Tallinn University of Technology, (Estonia)

Growth temperature dependence of GaAsBi tail states probed by sub-band absorption and photoluminescence characteristics
Sho Hasegawa¹ K. Kakuyama, H. Nishinaka² and M. Yoshimoto³
¹Department of Electronics and ²Faculty of Electrical Engineering and Electronics of the Kyoto Institute of Technology (Japan)

Effect of Growth Conditions on the Shape of Bismuth Induced Localized States in GaAsBi
Nicholas J. Bailey¹, T. Wilson⁷, T. B. O. Rockett¹, J. P. R. David¹, R. D. Richards¹
¹University of Sheffield, Sheffield (UK), and ²Imperial College London, London (UK)

15:00-19:00  Airbus visit
20:00  Workshop Banquet

Wednesday July 24

Session 7. III–V–Bi alloys – devices
(Chair : Prof. Masahiro Yoshimoto)

09:00 – 09:40, Invited talk (We-1)
Progress on Dilute Bismide Near-IR Light Emitting Devices
Shumin Wang
Chalmers University, Gothenburg (Sweden) and Shanghai Institute of Microsystem and Information Technology, Shanghai (China)

09:40 – 10:00 (We-2)
Assessing the optical properties of strained and relaxed GaAsBi/GaAs multiple quantum wells
Nada A. Adham¹, Faezah Harun¹, Thomas B. O. Rockett¹, Stephen J. Sweeney⁷, John P. R. David¹, Robert D. Richards¹
¹University of Sheffield (UK), and ²University of Surrey (UK)

10:00 – 10:30  Coffee break

10:30 – 10:50 (We-3)
Temperature and bias dependent photocurrent of GaAsBi/GaAs multiple quantum well devices
Robert D. Richards, M. R. M. Nawawi, F. Harun, and J. P. R. David
University of Sheffield (UK)

10:50 – 11:10 (We-4)
Optical and electrical performance of low temperature MBE-grown InGaAs and InGaAsBi photodetectors
Leh Woon Lim¹, Manoj Kesaria¹, Igor Marko², Pallavi Patil¹, Edmund Clarke¹, Stephen J. Sweeney³, John P. R. David¹, Chee Hing Tan¹
¹University of Sheffield (UK), ²Cardiff University (UK), ³University of Surrey (UK)
Optimization of GaAsBi MQW Growth Parameters for NIR Laser Applications
Algirdas Jasinska, Evelina Dudutiené, Bronislovas Čechavičius, Sandra Stanionytė and Renata Butkutė
Center for physical sciences and technology, Vilnius (Lithuania)

11:30 – 11:50 Closing

11:50 – 13:00 Lunch

Posters

Poster 1
Investigation on the effect of crystal orientation and doping type on the optical properties of bulk GaAsBi thin films
Sultan Alhassan1,2, Saud Alotaibi3, Igor Kazakov3, Helder Vinicius Avanço Galeti4, Yara Galvão Gobato4, Mohamed Henini5
1University of Nottingham, Nottingham (UK), 2Jouf University (Kingdom of Saudi Arabia), 3P.N.Lebedev Russian Academy of Science, Moscow (Russia), and 4 Universidade Federal de São Carlos (Brazil)

Poster 2
The Effect of Bismuth (Bi) as Surfactant on the Optical Properties of InAs/InBiAs Single Quantum Dots Grown on (001) GaAs Substrate
Amra Alhassni1,2, Igor P. Kazakov3, Yara Galvão Gobato4, Helder Vinicius Avanço Galeti4, Mohamed Henini1
1University of Nottingham, Nottingham (UK), 2AL Baha University (BHU), Almakwah, (Saudi Arabia), 3P+N. Lebedev Russian Academy of Science, Moscow (Russia), and 4 Universidade Federal de São Carlos (Brazil)

Poster 3
In situ determination of the growth conditions of GaSbBi alloys
O. Delorme, L. Cerutti, E. Tournié, and J.-B. Rodriguez
IES, Univ. Montpellier (France)

Poster 4
Localization effects and band-gap of GaAsBi/GaAs multi quantum wells
M.S. Nordin, A. Boland-Thoms and A.J. Vickers
University of Essex, Colchester (UK)

Poster 5
Defect-free Bi1-xSbx Nanowires on Si by MBE
Dima Sadek1, Pier-Francesco Fazzini2, Filadelfo Cristiano1, Sébastien Plissard3
1LAAS-CNRS, Université de Toulouse (France), and 2LPCNO-INSA, Université de Toulouse (France)

Poster 6
Novel GaAs1-xBi x based W-Type structures for laser applications
Thilo Hepp, Oliver Maßmeyer, Robin Günkel and Kerstin Volz
Philipps Universität Marburg (Germany)
Molecular beam epitaxy growth of high quality InAsSbBi on GaSb substrates

Shane R. Johnson\textsuperscript{1*}, Stephen T. Schaefer\textsuperscript{1}, Rajeev R. Kosireddy\textsuperscript{2}

\textsuperscript{1}Center for Photonics Innovation & Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, AZ, USA

\textsuperscript{2}Center for Photonics Innovation & Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ, USA

\*shane.johnson@asu.edu

The molecular beam epitaxy growth of the III-V semiconductor alloy InAsSbBi is investigated over a range of growth temperatures and V/In flux ratios. In general, Bi incorporates at growth temperatures around 300 °C, but results in material with limited optical quality. Conversely, higher growth temperatures around 400 °C yield improved optical performance, but with limited Bi incorporation. Both bulk and quantum well structures are grown at temperatures ≥ 400 °C on (100) on-axis and offcut GaSb substrates. The structural, chemical, and optical properties are investigated using Rutherford back scattering, X-ray diffraction, transmission electron microscopy, Nomarski optical microscopy, atomic force microscopy, and photoluminescence spectroscopy. The results indicate that the material is nearly lattice matched, coherently strained, optically active, and contains dilute Bi mole fractions. Large concentrations of Bi-rich surface features are observed on some samples where the incident Bi flux does not fully incorporate or desorb, but instead accumulates on the surface and coalesces into droplet features. Large ~1 μm droplets with densities on the order of \(10^6\) cm\(^{-2}\) are observed when thick InAsSbBi layers are grown with near stoichiometric As flux. Surface droplets are not observed when the As flux is a few percent larger than stoichiometric, indicating that there is an As-Bi interaction that plays a role in the desorption of Bi from the surface. The relationship between the growth conditions and the optical quality, surface morphology, and Bi incorporation is examined.
MO-2

Molecular-beam epitaxy of Ga(In)SbBi alloys and QWs

O. Delorme¹, L. Cerutti¹, E. Luna², A. Trampert², E. Tournié¹, and J.-B. Rodriguez¹*

¹IES, Univ. Montpellier, CNRS, 34000 Montpellier, France.
²Paul-Drude-Institut für Festkörperelektronik, Leibniz-Institut im Forschungsverbund Berlin e.V., Hausvogteiplatz 5-7, D-10117, Berlin, Germany
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Recently, dilute bismuth (Bi) III-V alloys have attracted great attention, particularly due to their properties of band-gap reduction and spin-orbit splitting. Therefore, the incorporation of Bi into antimonide based III-V semiconductor is very attractive for the development of new optoelectronic devices working in the mid-infrared range (2 – 5 μm). However, due to its large size, Bi does not readily incorporate into III-V alloys and the Bi incorporation needs very low growth temperature as compared to the values used for standard antimonide compounds. Moreover, a slight variation of the growth conditions causes the formation of Ga-Bi droplets and a degradation of the crystallographic quality. The epitaxy of III-V dilute bismide alloys is thus very challenging.

We have investigated the molecular beam epitaxy (MBE) of GaSbBi single layers on (001) GaSb substrates. An original method based on RHEED oscillations measurements [1] was used to set the optimum growth conditions (substrate temperature and Sb flux) of GaSbBi. Various sets of samples were grown at different V/III ratios and substrate temperatures to achieve high Bi content GaSb1-xBix (0 < x < 14%) alloys [2] with excellent crystal quality. We also report on the growth of quantum well heterostructures using an active zone composed of GaSbBi/GaSb type-I quantum wells, with different Bi contents and GaSbBi thicknesses. GaSbBi/GaSb QWs demonstrated photoluminescence at RT up to 3.5 μm, but an important degradation of the PL emission was observed as the Bi content becomes higher and the PL wavelength emission longer. To improve the optical performances of the GaSbBi alloys, Indium was added to GaSbBi single layers and QWs. Growth conditions of GaInSbBi alloys were investigated with various In and Bi concentrations. We observed that the addition of In strongly modifies and reduces the Bi incorporation into GaSb. For an In concentration of ~3.7%, we reached a maximum Bi content of 10.5% while the highest Bi concentration falls down to 3% with ~10% of In (Fig. 1). Additionally, droplets appear at lower Bi composition than in GaSbBi alloys. The origin of these features will be discussed. Finally, 15-nm thick GaInSbBi/GaSb QWs with 3.7% In and various Bi contents were grown. These samples exhibit bright PL emission at RT up to 2.6 μm (Fig. 2).

**Fig. 1:** (a) Effect of the addition In on the Bi incorporation in GaInSbBi alloys. (b) PL emission at RT of 15-nm GaInSbBi/GaSb MQW samples with 3.7% In and Bi content between 6 and 10.5%.

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GaSbBi is a relative newcomer in the III-V-Bi family that has experienced rapid development in the past few years, culminating in the first demonstration of a GaSbBi based laser diode [1]. Likewise to other III-V-Bi compounds, while there exists a number of articles on the growth and resulting properties, there is a lack of a comprehensive picture on the intricate details between Bi incorporation, structural properties and epitaxial parameters. This is why we have chosen a systematic methodology [2] based on combinatorial molecular beam epitaxy to investigate a large portion of the growth parameter space in high resolution [3]. Our results reveal three distinct phases in GaSbBi epitaxy, classified by shared properties in terms of Bi incorporation, surface structure and crystallinity. Namely, in phase I we find Ga-Bi compound droplets on the surface, as common in other III-V-Bi compounds, together with decreased crystalline quality and reduced Bi content. In the next phase (phase II), we find optimal structural quality in terms of smooth surfaces with excellent crystallinity and high Bi incorporation. In the last phase (phase III), the Bi incorporation rate is decreased resulting in Bi droplets and, again, poor crystalline quality. In Figure 1, we have mapped these phases as a function of Sb/Ga flux ratio and growth temperature to distinct regimes. In our presentation, we will further show how these phases evolve with increase of the Bi/Ga ratio as well as the growth rate, and discuss these behaviors in the context of different kinetic processes.

Figure 1: A map of the epitaxial phases (shaded regions) as a function of Sb/Ga ratio and growth temperature. The underlying contours correspond to the Bi content, while the scatter points represent x-ray diffraction measurements with good (stars) or bad (circles) crystalline quality.

Alloys of compound semiconductors are necessary to create heterostructures for optoelectronic and electronic devices. Growth of alloys that vary the cation component is fairly straightforward because there are few reactions between the cation species. Growth of mixed anion alloys, such as InAsSb and GaAsBi, are more complex because of the strong tendency for the individual anion species to interact. Both Sb and Bi are known to be surfactants, weakly physisorbing onto the surface and altering the incorporation kinetics of the alloy components. *Ab initio* calculations of the surface reconstructions show that there are strong interactions between the anions. For example, both for Bi- and Sb-containing GaAs, As-terminated surface reconstructions may transform into mixed heterodimer terminated configurations, which cause the roughening by pulling atoms from the terrace. Thus we propose an alternative model for interfacial broadening by intermixing rather than by surface segregation.
Notes
Origins of morphology and microstructure of epitaxial GaAsBi

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In recent years, significant advances have been made concerning the fabrication of III-V-Bi materials, in particular with respect to understanding the incorporation of Bi into different base alloys, and the demonstration of proof-of-concept device functionality. However, challenges in the control and optimization of the material quality still limit the potential of these alloy systems. For example, we recently showed how the Bi incorporation and the structural properties of GaAsBi varied throughout the important stoichiometric flux regime even with minute changes in the As/Ga flux ratio [1], emphasizing the significant challenges in predictable control of the growth process.

The ability to control the growth and the resulting properties requires a fundamental understanding of the specific roles of the Bi surfactant, the low temperature (LT) growth and the flux stoichiometry. To this end, we focus on comparative microscopic analysis of various GaAsBi and LT-GaAs samples throughout the critical near-stoichiometric flux regime, aided by stationary MBE [1]. We investigate the surface morphology and the evolution of bulk microstructure of GaAs(Bi) and the role of growth parameters in this process. As an example, Figs. 1 a) and b) demonstrate the effect of the addition of Bi on the surface, while Fig. 1 c) illustrates various microstructural features in the bulk. The origins of these features are discussed in relation to the extensive works on LT-epitaxy of semiconductors [2] as well as recent reports on III-V-Bi alloys.

Figure 1. a) AFM surface roughness of GaAsBi (150 nm) and LT-GaAs (250 nm) layers grown at 220 °C. b) AFM image from the GaAsBi sample, showing elongated mounds correlated with a variable roughness within the droplet-free As/Ga window. c) TEM image showing lateral composition modulation as well as V-shaped features in a bulk GaAsBi layer.

Notes
Impact of growth conditions on Bi incorporation on GaAs grown by Molecular Beam Epitaxy and on the GaAsBi characteristics

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The applicative interest in extending the operation spectral range of GaAs-based devices further in the near infrared has led to focus research on those III-V alloys, which would meet these requirements. This would allow to use the latter as NIR gain materials in photonic devices/GaAs, or 1.0eV absorbers for multijunction solar cells. In this perspective, the dilute bismides have attracted much attention. Indeed, they provide a large bandgap engineering (88meV/%Bi); moreover adding Bi in GaAs leads to increase the energy between the spin-orbit and valence bands\textsuperscript{1} could also be used to lower the Auger losses in lasers and is of concern for spintronics applications\textsuperscript{2}.

Growth of GaAsBi on GaAs is though challenging, since these alloys are highly mismatched alloys. Therefore, a great attention is still paid to understand the growth mechanisms of these alloys, and to identify those growth conditions, which lead to an efficient incorporation of bismuth while providing good quality materials. Indeed, it was shown in the literature that any small change in growth conditions could lead to low material quality, defects, and/or decrease layer concentration in bismuth.\textsuperscript{3}

The MBE system in LAAS is equipped with real-time measurements of sample incremental stress via curvature monitoring, and RHEED. These are efficient to control the evolution of Bi incorporation and surface reconstruction as the GaAsBi material is growing on GaAs. The information drawn from both techniques has given us insight of the impact of the different growth parameters on the epitaxial growth of GaAsBi/GaAs. We have varied substrate temperature, As/Ga and Bi/Ga atomic ratios and growth rate, while following the evolution of sample curvature and RHEED diffraction patterns. We will discuss the influence of these growth parameters on GaAsBi growth and the set of parameters to be selected in order to grow GaAsBi with controlled Bi content and with proper structural and electronic properties.

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References
Transmission Electron Microscopy of (In,Ga)(Sb,Bi) epilayers and quantum wells

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The recent demonstration of a mid-infrared laser based on Ga(Sb,Bi)/GaSb quantum wells (QWs) [1] has prompted the interest on emerging dilute bismide alloys based on antimonides. Despite the promising perspectives, dilute bismides based on antimonides are far less developed and studied compared to other dilute bismide compounds such as Ga(As,Bi). Fundamental questions such as alloy stability, segregation, or solubility limits are still under investigation, evidencing that material developments are still required for the further use of Ga(Sb,Bi) in practical devices.

As shown here, our recent investigations of the microstructure and chemical homogeneity of Ga(Sb,Bi) epilayers and QWs with Bi contents up to 12% demonstrate its high quality, high stability, and feasibility for use in the active zone of optoelectronic devices. No extended defects, nanoclusters, or composition modulations are detectable in the pseudomorphic layers. There are nevertheless droplets on the surface of Ga(Sb,Bi) epilayers with high Bi content ( > 12%) which lead to surface irregularities and local inhomogeneities.

Ga(Sb,Bi)/GaSb QWs exhibit regular and homogeneous morphologies including smooth and stable interfaces with a chemical width on the same order as in other high-quality III–V heterointerfaces [2] Some QWs are nevertheless affected by (1) lateral thickness fluctuations and slight thickness variations from QW to QW, and (2) a rougher Ga(Sb,Bi)-on-GaSb interface compared to the GaSb-on-Ga(Sb,Bi) one [3]. The morphological smoothing effect at the GaSb-on-Ga(Sb,Bi) interface is attributed to the well-known surfactant behavior of Bi in connection with Bi surface segregation, as evidenced from experimental Bi distribution profiles. The QWs comprising reference laser structures as well as further working laser devices are characterized by narrower and symmetric interfaces with reduced thickness fluctuations.

To date, the maximum Bi incorporated into GaSb is about 14%, which is smaller than the reported maximum 21% Bi incorporation into GaAs [4]. Beyond 12% Bi, the systematic presence of droplets in Ga(Sb,Bi) strongly impacts the optical properties, especially above 3 µm. In this context, the addition of In may enhance Bi solubility into GaSb and allow reaching longer wavelengths. We find that droplet-free (In,Ga)(Sb,Bi) epilayers are of high quality with a microstructure that resembles that of high quality Ga(Sb,Bi). Both In and Bi are simultaneously incorporated in the layer. It seems, however, that In reduces Bi incorporation efficiency into GaSb. In analogy to Ga(Sb,Bi)/GaSb QWs, there is a morphological smoothing at GaSb-on-(In,Ga)(Sb,Bi) interfaces of QW structures, probably due to the surfactant behavior of Bi. Finally, we discuss the challenges in the investigation of the new quaternary (In,Ga)(Sb,Bi) alloy.

Notes
Rutherford backscattering spectrometry investigation of In$_x$Ga$_{1-x}$As$_y$Bi$_{1-y}$ heterostructures

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InGaAsBi alloys offer the potential to enable mid-infrared optoelectronic applications on standard InP substrates [1]. However, the growth of this alloy is complicated and requires significant development to provide both the required Bi composition and high material quality. In this work, we investigate InGaAsBi/InP heterostructures with varying Bi concentrations grown using MBE and MOVPE. For characterisation of the structural and optical properties of the samples, a combination of different techniques were used including Rutherford Backscattering Spectrometry (RBS), high resolution X-Ray Diffraction (XRD) and temperature dependent Photoluminescence (PL). Both PL and conventional XRD are insufficient for compositional analysis since both indium and bismuth atoms increase the lattice constant and decrease the emission peak energy. In contrast, RBS is able to differentiate both the indium and bismuth from the elemental contributions in each layer. This is because the final energy of each primary ion is characteristic of the atomic number of the scattering atom and how deep the atom is located. For these measurements, a helium ion beam energy of 4MeV was found to provide sufficient separation of the In and Bi-related peaks without causing sample damage. Optimisation of RBS channelling measurements was undertaken, enabling a more accurate location of the centre at each channel, as shown by Fig. 1. This is especially useful with regards to the <110> and <111> channels, which are normally challenging to locate accurately. Looking at a range of samples with 2-6% Bi in the InGaAsBi layer, the quality of the crystal is analysed along with presence of defects, for example, bismuth clustering, interstitial defects, etc. The correspondence between the RBS results and the other techniques will be discussed at the workshop.

![Channel Number vs. Ion Yield](image)

Fig. 1 Comparison of the channelling RBS spectra for a InGaAs/InP sample. The aligned direction is for the <100> and the random is for a tilt of 1.5° and -1.5° either side of the same channel along a fixed axis.

Surface Diffusion and Disorder in Quaternary (Ga,In)(As,Bi)/InP Heterostructures

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The incorporation of small amounts of bismuth into III-V semiconductors offers a wide scope for band gap engineering. A band anti-crossing leads to a vast decrease of the band gap energy while introducing more bismuth into the host crystal lattice. This offers the possibility to enhance the performance of future electro optical devices by potentially suppressing non-radiative loss channels. Due to the required growth conditions, the incorporation of bismuth into the host crystal lattice is challenging for both growth techniques, MBE and MOVPE as well. Since bi-atoms segregate towards the surface and, thus, will not incorporate into the crystal lattice, the incorporation of bismuth requires low growth temperatures.

Our work addresses the influence of varied growth parameters on the surface segregation process of bismuth atoms during growth and the associated surfactant effect. We use temperature dependent photoluminescence spectroscopy to analyze disorder effects on a systematic sample series of (Ga,In)(As,Bi)/InP heterostructures where the different partial pressures of the precursors are varied. Additionally, we use X-ray photoelectron spectroscopy as a surface sensitive method to research the surface diffusion process of the bismuth atoms. A comparison to both, high temperature and low temperature grown (Ga,In)As/InP heterostructures reveals the qualitative influence of the surfactant effect. Secondly, we observe a clear trend for the bismuth segregation as a function of the varied partial pressures of the precursors.
Notes
Structural analysis of bismide layers ordering

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A\textsubscript{III}B\textsubscript{V} group bismide layers are significantly attractive due to their exclusive properties, such as large bandgap reduction, strong enhancement of spin-orbit splitting and temperature insensitive bandgap. These properties allow using bismides for applications in long wavelength optoelectronic devices, lasers, photodetectors, terahertz optoelectronic and spintronic devices. However, formation of A\textsubscript{III}B\textsubscript{V} group bismide layers is complicated due to differences in atomic sizes of As and Bi atoms. An atomic size mismatch can result in a specific atomic ordering during growth and was examined in this work for layers grown on different substrates by MBE.

Ordered A\textsubscript{III}B\textsubscript{V} group layers can have different properties along different crystal axes, such as polarized photoluminescence in perpendicular crystal directions, so the growth of ordered materials could be prospective for lasers with well polarized output. Ternary A\textsubscript{IIIBV} group layers tend to order spontaneously and usually along <111> cubic lattice diagonals which is called CuPt ordering [1, 2]. In figure 1 CuPt\textsubscript{8} ordering in GaAsBi alloy with Bi atoms occupying As planes is shown. This ordering can be described as \{½ ½ ½\} planes because their interplanar distance is twice longer than \{111\}.

![Figure 1: CuPt\textsubscript{8} ordering in GaAsBi layer [3].](image)

In this work atomic ordering in GaAs\textsubscript{1-x}Bi\textsubscript{x} layers grown by MBE at low temperature on different substrates was revealed by transmission electron microscopy and high resolution X-Ray diffraction. For layers grown on GaAs substrates CuPt\textsubscript{8} ordering was observed in two perpendicular directions, while on Ge layers with 6° offcut – only in one direction. It was also shown that ordering has significant effect on optical properties of the bismide layer. However, further investigation is needed to determine the importance of ordering effects for possible applications.

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Notes
Bismuth containing semiconductor alloys have recently enjoyed growing interest due to their unique properties. For example, III-V compounds with Bi exhibit large spin orbit interactions, making them exciting candidate for topological insulators. However, high Bi concentrations alloys are particularly difficult to grow with good quality. Bi has a low solubility in III-V compounds such as GaAs and GaSb, leading to Bi droplet formation on the growth surface with increasing Bi flux. The incorporation rate can be increased by lowering the group V flux such that the growth front is group III terminated. However, growth of GaAsBi films in the presence of Ga-droplets can lead to nonuniform incorporation of Bi parallel to the growth surface. This compositional inhomogeneity is primarily kinetic in nature, as it results from a droplet-induced variation in Ga concentration along the surface. Figure 1a shows a High Angle Annular Dark Field (HAADF) Transmission Electron Micrograph of a GaAsBi film grown under conditions that results in both Ga and Bi droplets showing these nonuniformities. High resolution images (Fig. 1b) in the vicinity of the Bi-rich exhibit Cu-Pt ordering. Fast Fourier Transforms (FFT) from the Bi-rich region (Fig. 1c) exhibit additional spots compared to the Bi-deficient regions (Fig. 1d). Restricting growth to the regime where droplets do not form (at low Bi flux and high Group V flux), however, is not enough to do away with inhomogeneities, as lateral composition modulation and Bi-rich nanostructures can be present. These inhomogeneities are likely the result of phase separation.

Figure 1: HAADF TEM images of a GaAsBi films with Ga-Bi droplets grown at 315C and As:Ga Beam Equivalent Pressure ratio of 3.5 (a) showing non-uniform Bi incorporation; (b) high resolution image showing that the Bi-rich regions exhibit ordering; (c) FFT from the Bi-rich region in (b) showing extra spots (arrowed) indicating ordering; (d) FFT from the Bi-deficient region in (b) without extra spots.
Investigation of Bi quantum dots embedded in GaAsBi matrix by Transmission Electron Microscopy

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Devices based on A\textsuperscript{III}B\textsuperscript{V} group semiconductors have been used for a long time, but bismide compounds were only scarcely investigated. Growth and characterization of diluted bismide layers and structures are carried on only a few scientific groups in the world, and only part of them investigates the internal structure (especially of Bi Quantum dots) by transmission electron microscopy, so there are a few papers on detailed structure of these layers, so this work was mainly attributed to investigate the internal structure of Bi quantum dots, formed in GaAsBi or GaAsBi/AlAs matrix.

In this work, MBE and MEE grown GaAsBi/AlAs MQW structures were investigated by Transmission Electron Microscopy. Both HRTEM and HAADF STEM modes were used, together with EDS spectrometer, thus providing accurate identification of Quantum dots. Geometric Phase Analysis (GPA) technique was applied for GaAsBi and individual Bi QD strains measurement. Figure 1 shows HRTEM micrograph of individual Bi QD embedded in GaAsBi/AlAs layers (a) and the corresponding $d_{002}$ (b) and $d_{220}$ (c) interplanar spacing maps. GaAsBi layers are fully strained in respect to AlAs and GaAs, while Bi quantum dot is fully relaxed.

Figure 1: HRTEM micrograph of individual Bi QD (a) and corresponding $d_{002}$ (b) and $d_{220}$ interplanar spacing maps. Arrows indicates interplanar spacings of unstrained rh-Bi and GaAs
We present our latest results on the growth of (In/Ga/Al)BiAs materials and heterostructures by molecular beam epitaxy. InGaBiAs-based materials hold promise for infrared devices on InP platforms, while InAlBiAs-based materials are useful for the upconversion of photons. InGaAlBiAs is useful for photoconductive switches and other terahertz devices. GaBiAs can also be used to tailor hole wavefunction coupling in quantum dot molecules. Finally, some of these materials hold promise for thermoelectrics based on control over band alignments and phonon scattering.

We discuss our experiences with the growth of these materials and their device implications. We will also briefly discuss the newly opened Materials Growth Facility at the University of Delaware, which is being operated as a (staff-assisted) user facility for MBE growth, including of bismuth-containing semiconductors.
Semiconductor nanowires (NWs) are of materials of interest for these decades because of their potential application in nanoscale electronic and optoelectronic devices, and we have studied the growth and characteristics of Bi containing semiconductor nanowires.[1] We report the structural characteristics of GaAs/GaAsBi/GaAs core-multi shell nanowires having Bi concentration of 2% at the GaAsBi shell. We observed clear formation of three-multi-layered core-shell structure from the cross-sectional scanning transmission microscopy (STEM). Even though the wire surface showed very rough surface from the SEM observation, the cross section showed hexagonal structure. That suggests the sample have faceted structure showing a certain crystal orientation. The longitudinal and lateral cross section showed characteristic intensity modulation of the Bi element at the energy dispersive x-ray spectrometry (EDX). Figure 1 shows the results of laterally cross sectional STEM/EDX results for a nanowire investigated. As seen in the figure, the Bi showed accumulation at the localized area, forming clustered like localization. The Bi rich area probably have smaller band gap, larger lattice constant, and three dimensionally specific strain status. These Bi accumulation may be applicable to quantum confined nanoscale structure and light sources.

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Figure 1: Observed Bi accumulation in cross sectional STEM/EDX observation of GaAs/GaAsBi/GaAs core-multishell nanowires.

Notes
Compositional profile modelling of bismuth surface segregation in epitaxial III-V-Bi systems

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In recent years, diluted III-V-Bi alloys have attracted the attention of researchers for their potential to optimize optoelectronic, thermoelectric and electronic devices. However, these III-V-Bi alloys so far have inherent problems during their epitaxial growth, which could result in a high tendency to segregation, alloy clustering and/or atomic ordering. The present work analyzes the surface segregation of Bi in two different III-V-Bi (1–3% of Bi) alloys grown by molecular beam epitaxy by means of High Angle Annular Dark Field and Energy Dispersion X-Ray (EDX) analysis in an FEI Titan Cubed Themis transmission electron microscope, and completed with X-Ray Diffraction and Photoluminescence measurements.

First, a set of four InAsBi/InAs superlattice samples was used to model the Bi segregation profiles (Fig. 1a) using a three-layer fluid exchange mechanism, extracting the values of the As/Bi exchange energies in the InAs matrix (E1, 1.26±0.01 eV and E2, 1.36±0.02 eV). A relationship is proposed to calculate the activation energies for the exchange in III-V alloys from the bonding energies (Fig. 1b), which would allow predicting them for other previously unknown compounds. Finally, the estimated As/Bi exchange energies for the GaAsBi/GaAs alloys (E1, 1.24±0.01 eV and E2, 1.31±0.02 eV) have been successfully used to describe the Bi profile in different GaAsBi alloys corroborating the effectiveness of our adjustment.

Figure 1: a) EDX map (top) and the experimental and calculated profiles (bottom) for an InAsBi/InAs superlattice sample. b) Plot of the fitted E1 and E2 energies versus the experimental ones for different III-V systems (from us and other authors). The solid line represents equality between the calculated and measured energies.
Notes
Over a number of years there has been considerable effort devoted to developing new semiconductor systems and approaches to overcome the fundamental limitations of well-established materials for use in photonic devices [1,2]. Of these, the dilute bismide and dilute nitride systems have been of particular interest owing to the degree to which Bi or N atoms perturb the band structure, promising lasers with reduced losses, facilitating access to new wavelength ranges on conventional substrates, or as new approaches to spin-based devices. Other materials, such as GeSn or InAs quantum dots have separately been explored for their potential as laser active regions that may be directly integrated on silicon for photonic integrated circuit applications [3,4].

In all of these materials, a common theme is the challenge in achieving the optimum growth conditions required to produce high quality and uniform material that is suitable for the production of reliable devices. In this paper we explore the development of these systems and consider their common properties in terms of device applications. In particular, we show how the effects of inhomogeneity lead to carrier localization and unusual temperature-dependent behaviour which can be exploited to give rise to temperature stability [1]. We will also discuss the influence of defect-related recombination in a variety of materials systems and the extent to which this limits (or not) device performance [1]. The paper will conclude with a prognosis for the future development and exploitation of devices based upon these material systems.

Notes
Impact of band-anticrossing on band-to-band tunneling in highly-mismatched semiconductor alloys

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There has been growing interest in the use of dilute bismides and related highly-mismatched alloys (HMAs) to develop light-emitting devices for the application-rich 3-5 µm spectral range [1]. However, there also exists broad scope for the development of mid-infrared sensing technologies. It has been proposed to exploit the strong reduction in hole mobility associated with Bi incorporation to develop low-noise mid-infrared avalanche photodiodes (APDs). In mid-infrared APDs, leakage currents associated with band-to-band tunneling (BTBT) contribute significantly to the dark current, limiting the signal-to-noise ratio. It is therefore of interest to quantify the extent to which the unusual band structure of narrow-gap HMAs can be exploited to mitigate such losses. We present a theoretical analysis of the impact of band-anticrossing (BAC) on BTBT in narrow-gap HMAs, and characterise associated general trends via comparison of results for HMAs and conventional III–V semiconductor alloys [2].

Incorporation of N or Sb in InAs causes a rapid reduction of the band gap, providing access to mid-infrared wavelengths up to ≈ 5 µm in structures compatible with epitaxial growth. While InAs1−ySby is a conventional semiconductor alloy, dilute nitride InN xAs1-x is highly-mismatched: N incorporation introduces impurity states lying energetically within the InAs conduction band (CB), which interact with the CB states of InAs via a BAC interaction [3]. This BAC interaction leads to the unusual combination of decreasing band gap and increasing CB edge effective mass with increasing N composition x. This behaviour is qualitatively similar to that in dilute bismide In(Ga)As1−xBix, where Bi-related impurity states and BAC impact the valence band (VB) structure [1].

We establish theoretical calculations of the BTBT current in HMAs, and analyse the impact of BAC on the BTBT current as a function of applied electric field [2]. At fixed band gap, we find that the BAC in InN xAs1-x leads to decreased (increased) BTBT current at low (high) applied fields compared to that in InAs1−ySby. Analysis of the BTBT transmission coefficient demonstrates the presence of a field-dependent competition between the BAC-induced modifications to the CB edge density of states and to the dispersion of the complex band linking the VB and CB: the former and latter respectively act to increase and decrease the BTBT current. Given the strong qualitative similarity between the band structure of InN xAs1-x and In(Ga)As1−xBix, our results provide general guidelines regarding BTBT in HMAs. The implications of our results for device applications are discussed.

Figure 1: (a) Complex band structure of InN0.083As0.917 (solid lines) and InA0.882Sb0.118 (dashed lines) alloys having band gap Eg = 0.257 eV at k┴ = 0. In both cases the zero of energy is taken at the valence edge. (b) BTBT transmission coefficient T as a function of in-plane wave vector k┴ for InN0.083As0.917 (solid lines) and InA0.882Sb0.118 (dashed lines) alloys, for applied electric fields F = 50 kV cm−1 (upper panel) and 1 MV cm−1 (lower panel). (c) BTBT current density J as a function of the k┴ = 0 band gap Eg for InN xAs1-x (solid lines) and InA1−ySby (dashed lines), for applied electric fields F = 50 kV cm−1 (upper panel) and 1 MV cm−1 (lower panel). The inset in each panel shows the ratio of the InN xAs1-x current density to that of InA1−ySby.

Notes
The elemental group-IV semiconductors silicon (Si) and germanium (Ge) are ubiquitous in conventional micro-electronics, and have been used to develop a wide range of passive photonic components. However, their indirect fundamental band gaps severely limit their application in the development of active photonic components, such as light emitting diodes or lasers, fundamentally limiting the development of Si photonics. Due to the fact that the fundamental indirect band gap of Ge is only ≈ 145 meV lower than its direct gap, there has recently been a surge of interest in engineering a direct band gap from Ge. In particular, alloying Ge with other group-IV elements - carbon (C), tin (Sn) and lead (Pb) - is attracting increasing attention.

Initial theoretical analysis of dilute Ge$_{1-x}$C$_x$ alloys suggested the emergence of a direct band gap via a band anti-crossing interaction similar to that in dilute nitride alloys. For Ge$_{1-x}$Sn$_x$, theoretical and experimental analysis suggests that incorporation of ≈ 9% Sn is sufficient to bring about a direct band gap. For Ge$_{1-x}$Pb$_x$, initial theoretical analysis has suggested the presence of an indirect- to direct-gap transition for Pb compositions as low as 1%. Optically and electrically pumped lasing has recently been demonstrated in Ge$_{1-x}$Sn$_x$-based structures, confirming the promise of group-IV alloys. To develop devices based on group-IV alloys a detailed understanding of the electronic structure evolution is required, including identification and quantification of the mechanism(s) driving the indirect- to direct-gap transition, and consequences for technologically-relevant material properties.

In this talk we firstly describe ab initio calculations of the electronic structure evolution in Ge$_{1-x}$(C,Sn,Pb)$_x$ alloys based on density functional theory (DFT). For dilute carbide Ge$_{1-x}$C$_x$ alloys we demonstrate, contrary to the existing literature, that C incorporation does not lead to the emergence of a direct band gap. For Ge$_{1-x}$Sn$_x$ and Ge$_{1-x}$Pb$_x$ alloys we verify the presence of the indirect- to direct-gap transition, and in each case we additionally identify and quantify the mechanism driving this transition. For Ge$_{1-x}$Sn$_x$ alloys we demonstrate the presence of strong alloy band mixing effects close in energy to the conduction band edge, which will have significant implications for optical and transport properties. We then secondly describe the establishment of a semi-empirical framework - based on valence force field (VFF) structural relaxation and tight-binding (TB) electronic structure calculations - to calculate the properties of (Si,Ge)$_{1-x}$(C,Sn,Pb)$_x$ alloys. The VFF and TB models are parametrised directly from DFT calculations, provide excellent quantitative agreement with full DFT calculations for small alloy supercells, and provide the capability to scale efficiently to systems containing ≈ 10$^5$ atoms, allowing for direct atomistic calculations of the properties of realistic (disordered) group-IV alloys and their heterostructures. Our results provide fundamental insight into the properties of emerging Ge$_{1-x}$(C,Sn,Pb)$_x$ group-IV alloys, and provide information relevant to inform the use of these alloys in proposed device applications.

Figure 1: (a) DFT-calculated conduction band structure for a 64-atom Ge$_{64}$ supercell, and ordered Ge$_{64}$(C,Sn,Pb)$_1$ ($x = 1.56\%$) alloy supercells containing a substitutional C, Sn or Pb atom. The zero of energy in each case has been chosen to lie at the valence band edge. (b) DFT-calculated evolution with $x$ of the pressure coefficient associated with the CB edge state in Ge$_{256}$C$_1$ ($x = 0.78\%$). (c) DFT-calculated evolution with $x$ of the fundamental band gap and its pressure coefficient in 128-atom Ge$_{1-x}$(Sn,Pb)$_x$ special quasi-random structures.
Group IV semiconductors are emerging as solid-state hosts of spin-based information. Besides being low-cost and readily-available substances, they possess highly desired features, such as long spin lifetimes and diffusion lengths [1]. Group IV semiconductors can additionally leverage wafer-scale epitaxy, which introduces confinement, alloying and strain as effective degrees of freedom for the simultaneous manipulation of electronic, photonic and spin-dependent properties [2].

Here we will discuss how band-structure engineering of the hetero-interface between Ge and Si offers the exciting possibility of studying the impact of spin-orbit coupling on conduction band electrons. We experimentally demonstrate the manipulation of the Landé g-tensor over a record-high tuning range for group IV materials [3]. Finally, by combining time- and polarization-resolved photoluminescence with electron spin resonance we unveil spin relaxation times approaching few $\mu$s in Ge and rivaling with the one of the lighter Si counterpart.

These findings are contributing to stimulate the emergence of new research frontiers at the intersection between magnetism, electronics and optics. Finally, we will discuss prospects for heteroepitaxial architectures based on novel SiGeSn alloys and how they can possibly enrich conventional devices with photonic and spintronic benefits in terms of energy efficiency and information processing speed [4,5].

Notes
The influence of barrier design on luminescent properties of GaAsBi quantum wells

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The bandgap engineering with bismuth opens the possibility to achieve longer wavelength emission on a GaAs platform. It is already illustrated with examples of successful operation of electrically injected GaAsBi quantum well (QW) laser diodes (LD) starting from 2013 [1, 2]. Despite the achievements, the progress in LDs operating at longer wavelengths is held back by the technology of bismides, and today the efficient photoluminescence (PL) is still a big challenge.

In present work, the influence of barrier material and structure on implementation of the quantum confinement in GaAsBi QWs was studied by changing the composition and design of barriers from conventional rectangular to step-like barrier. The samples were grown using solid-state MBE.

The optical investigations discovered that room temperature photoluminescence is increased by more than 50 times in the GaAsBi QWs with step-like barriers in comparison to standard rectangular QW structures (see Fig. 1). It was suggested, that carrier localization and increase of trapping efficiency in GaAsBi QWs is responsible for observed enhancement of radiative properties. These findings open the window for fabrication of NIR lasers based on GaAsBi QWs surrounded by step-like (Al,Ga)As barriers.

Fig. 1 Room temperature PL spectra of rectangular (a) GaAsBi MQW and GaAsBi SQW structures with step-like (Al,Ga)As barriers (b).

Growth temperature dependence of GaAsBi tail states probed by sub-band absorption and photoluminescence characteristics

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Crystal growth of GaAsBi alloys requires non-equilibrium state such as low temperature growth (< 400°C), because of the low solubility of Bi to GaAs. At low temperature growth, compositional fluctuations and atomic clustering can be caused by lacking of atom migrations. This can lead to introduce the potential fluctuations in the alloys, and adversely affect the device performance, which is non-negligible problem. For instance, the threshold current of GaAsBi laser diode is limited by non-radiative defect-related recombination and an inhomogeneous carrier distribution [1]. Under these circumstances, investigations of the potential fluctuations and the non-homogeneous Bi distribution have attracted the interest of many groups, and many studies have been reported by analysis of photoluminescence characteristics, TEM observation, etc. [2, 3]. In addition to these quantitative evaluations, it is considered that the search for growth conditions that suppress the generation of GaAsBi tail states is indispensable for obtaining GaAsBi thin films of device quality.

In this study, GaAsBi tail states were systematically investigated from sub-band absorption and photoluminescence characteristics. GaAs\textsubscript{1-x}Bi\textsubscript{x} thin films (0 ≤ x ≤ 0.05) were grown by solid source MBE at substrate temperatures of 360 °C and 380 °C. The Bi composition was adjusted by varying Bi flux. GaAs\textsubscript{1-x}Bi\textsubscript{x} photodiodes were fabricated to evaluate sub-band absorption characteristics. Figure 1 shows EQE obtained from the fabricated photodiodes with the almost same Bi composition (~5%). The slope below the absorption edges (Urbach tail) was more gradual for the sample with lower growth temperature. The photoluminescence from GaAs\textsubscript{1-x}Bi\textsubscript{x} thin films at 20 K are shown in Figure 2. The sample grown at 380 °C has stronger luminescence and narrower peak width than the sample grown at 360 °C. In this presentation, we will discuss the quantification of tail states focusing on the Urbach tail and the temperature dependence of the PL peak energy.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{EQE obtained from the GaAs\textsubscript{1-x}Bi\textsubscript{x} photodiodes grown at 360°C and 380°C.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Photoluminescence at 20K from the GaAs\textsubscript{1-x}Bi\textsubscript{x} thin films grown at 360°C and 380°C.}
\end{figure}

Effect of Growth Conditions on the Shape of Bismuth Induced Localized States in GaAsBi

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Recent work has investigated the effect of growth conditions on the optical quality of GaAsBi [1-2]. As yet, however, literature has not covered how changing the growth conditions affects the widely reported formation of Bi-induced localized states within the bandgap. In this work, temperature and power dependent photoluminescence measurements on a series of samples previously reported in [1] have been fitted using the model developed in [3]. In [3] T. Wilson demonstrated that a Gaussian profile best represented the distribution of localized states in the sample that was analyzed. Here, we show that some samples display a better fit using an exponential distribution of states. This suggests the growth conditions affect the shape of the distribution of localized states as well as its density, which may reconcile conflicting reports in literature which present evidence for Gaussian and exponential shaped distributions. Potentially, analysis of the photoluminescence line shape may be used to determine whether a sample was grown under Bi flux, or temperature, limited conditions.

![Figure 1: Localized model fit to photoluminescence of a sample using (a) an exponential profile and (b) a Gaussian profile. Note in [3] it was found that a Gaussian profile produced a better fit.](image)

Progress on Dilute Bismide Near-IR Light Emitting Devices

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Dilute bismide exhibits a variety of interesting physical properties such as large bandgap bowing effect, large spin-orbit splitting energy, temperature insensitive bandgap, strong and broad photoluminescence (PL) etc. By optimizing growth parameters and heterostructures, we demonstrate very broad near IR PL at room temperature with a line-width of 700 nm from InPBi and 1000 nm from GaAsBi. Electrically pumper GaAsBi quantum well lasers reveal lasing wavelength up to 1.142 μm at room temperature, while the longest wavelength from a GaAsBi light emitting diode reaches 1.25 μm. For optically pumped disk lasers, we demonstrate tunable lasing wavelength from 1.27 to 1.41 μm by varying the disk diameter.
Assessing the optical properties of strained and relaxed GaAsBi/GaAs multiple quantum wells

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GaAsBi has been recently recognized for its potential application as a multijunction photovoltaic 1 eV subcell, due to the large reduction of the band gap caused by the interaction of Bi induced localised states with the host valence band edge. Quantum wells (QWs) based upon GaAsBi offer a route towards the development of solar cells with band gaps around the important 1 eV range. For multijunction photovoltaics, strong absorption and current matching are essential which requires the incorporation of a large number of QWs.

In this work, the optical properties of multiple quantum well (MQW) samples, shown in Fig. 1 left, are investigated using room temperature and low temperature (18 K) power dependent photoluminescence (PL), focusing on the effects of strain and relaxation. The layers relax for high quantities of QWs. It was found that the relaxed samples with 54 and 63 QWs show a smaller overall integrated PL compared to the strained samples. However, strain relaxation appears to have negligible effect on the slope of the log integrated PL vs. log excitation power. Fig. 1 right shows the power dependent PL spectra at 18 K for a 3 period MQW GaAsBi/GaAs sample. The interpretation of this behaviour in terms of structure design and optimization will be discussed at the workshop.

Figure 1: The left is the structure of the GaAsBi/GaAs MQW samples [1]. The right is the power dependent PL spectra for a 3 QW sample at 18 K.

Notes
Temperature and bias dependent photocurrent of GaAsBi/GaAs multiple quantum well devices

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Recent work has indicated the potential of GaAsBi for multi-junction photovoltaics [1]. It also highlighted the areas in which progress remains to be made. More recently, the low temperature illuminated IV of a GaAsBi/GaAs multiple quantum well device was measured to investigate the effect of the large valence band offset on the quantum efficiency of the same devices [2].

In this work, the quantum efficiencies of a series of GaAsBi/GaAs multiple quantum well diodes are measured at high temperature. The results show a redshift of the photocurrent with increasing temperature, and a reduction in the magnitudes of the spectra. A reduction in the magnitudes of the spectra is also observed with increasing forward bias, indicating that incomplete carrier extraction is still a potential issue at high temperature.

Figure 1: Photocurrent of a 40 quantum well GaAsBi/GaAs multiple quantum well pin diode at a bias of + 0.4 V. The arrows indicate increasing temperature from room temperature to 120 °C.


Notes
Optical and electrical performance of low temperature MBE-grown InGaAs and InGaAsBi photodetectors

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Conventional short-wave infrared sensors use In₀.₅₃Ga₀.₄₇As and extended wavelength InGaAs (with increased indium content) as the detector material. However, the former, while offering good optoelectronic properties, is limited to a cutoff wavelength of 1.7 μm and the latter is grown lattice mismatched on InP substrates. It has been demonstrated that the incorporation of Bi in InGaAs can increase the cutoff wavelength up to 2.1 μm [1] while maintaining lattice match capability to InP by adjusting the In and Ga composition. However, the inclusion of Bi in III-V materials requires reduced growth temperature which leads to increased defect density.

Dark current and responsivity characteristics in InGaAsBi p-i-n diodes have been found to be relatively poor. To investigate whether the poor performance is due to growth at low temperatures, the effects of growth temperature on the optoelectronic properties of bismuth-free In₀.₅₃Ga₀.₄₇As photodiodes are investigated. InGaAs p-i-n wafers have been grown under two different sets of temperature conditions. In the first set, set A, the epilayers were grown at a uniform temperature ranging from 350°C to 595°C. And in the second set, set B, the growth temperature of the p- and n- layers were kept at 595°C while the i-layer growth temperature was varied from 350°C to 595°C. For each set, p-i-n diodes were processed and the current-voltage and light-current characteristics were compared to determine the influence of low temperature growth on device properties, as will be discussed at the workshop.

Optimization of GaAsBi MQW Growth Parameters for NIR Laser Applications

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The increasing need for efficient light sources emitting at different wavelengths forces engineering of novel compounds and progress in material science. One of the main problems of modern semiconductor lasers – bandgap sensitivity to the temperature deviations, makes such laser systems require additional cooling, reducing their efficiency, compactness and affordability. It was shown previously, that incorporation of 1% of Bi to the GaAs lattice reduces bandgap by up to 88 meV [1]. Moreover, spin-orbit splitting increases at higher Bi fractions, which opens up a possibility to suppress Auger and other non radiative losses [2]. Finally, dilute bismide alloys were shown to have unusually low bandgap temperature dependence compared to widely used III-V compounds [3]. These three properties make GaAsBi and other bismides attractive for various optoelectronics device applications, including lasers [4].

This study focuses on research of GaAsBi alloy as an active region of NIR lasers, emitting at around (1-1.3) μm. The aim of this work is to optimize technological growth conditions of GaAsBi Multiple Quantum Well (MQW) structures in order to achieve high intensity Photoluminescence (PL) signal. The influence of different element ratios, growth rate and temperature, QW and barrier layer thickness and composition to the optical and structural properties was investigated.

GaAsBi MQW structures were grown by molecular beam epitaxy (MBE) on semi-insulating GaAs (100) substrates. High resolution X-Ray Diffraction (HR-XRD) and Transmission Electron Microscopy (TEM) were employed to evaluate crystalline structure and content of bismuth (Fig 1). Atomic Force Microscopy (AFM) was used to determine surface quality, while PL measurements were performed to investigate optical properties. After the optimization of growth conditions, enhancement of RT PL intensity by more than three orders of magnitude was observed (Fig. 2).

Fig. 1. HR-XRD measurement of a sample with 7 GaAsBi QWs indicating excellent crystalline quality.

Fig. 2. Room temperature PL intensity map of all the samples, grown under different technological conditions.

posters
Investigation on the effect of crystal orientation and doping type on the optical properties of bulk GaAsBi thin films.

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Semiconductors containing bismuth (Bi) have draw attention of several researchers in recent years, particularly for near to mid-infrared optoelectronic applications. This is mainly due to the large band gap reduction of GaAs (~88meV for each percent of bismuth) by incorporating small amounts of dilute Bi [1]. The growth of GaAsBi is more complex than the growth of other conventional III–V alloys, due to high tendency that Bi caused to surface segregate during growth. To avoid Bi segregation during growth, low growth temperature, usually between 270 °C and 400 °C, is necessary [2, 3]. Doping can generates defects in the crystalline lattice during growth, lead to reduce the photoluminescence (PL) intensity significantly. In this work, we have studied the optical properties of bulk doped (n and p type) GaAsBi thin films grown on different high index planes (100) and (311)B GaAs substrates. Furthermore, the effect of doping type on (100) and (311)B oriented substrates on the optical properties of GaAsBi is investigated by using Photoluminescence measurements. The nominal Bi concentration incorporated into GaAs in all samples is 0.5 %. In order to understand the effect and role of doping, the results of doped samples were compared with samples have same structure without intentional doping. Further, the temperature dependence of the PL peak energy over temperature range 10K – 100K revealed an energy decrease, and no s-shaped profile observed in all samples. N and p-types samples grown on (311)B GaAs substrates, have small intensity than samples grown on (100). PL peaks energy showed a strong red shift (to low energy) for all samples, and it displayed a higher shift on samples grown on (311)B than for samples grown on (100), which may signify a higher Bi incorporated to (311)B than (100) GaAs substrates. In addition, it was found that the effect of doping type on samples grown on (100) resulted in a substantial shift of the PL peaks to low energy compared to samples without doping by energy (~ 60meV).

The Effect of Bismuth (Bi) as Surfactant on the Optical Properties of InAs/ InBiAs Single Quantum Dots Grown on (001) GaAs Substrate

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Heterostructures with self-assembled InAs quantum dots (QDs) grown on GaAs substrates have drawn intensive interest due to their potential for basic physics studies and optoelectronic device applications. These require InAs QDs with good optical properties and the ability to control their density. Typically, InAs QD density is controlled by tuning the growth temperature, growth rate and InAs thickness [1]. For example, using a higher growth temperature or a lower growth rate will result in longer diffusion lengths of In adatoms and thus a lower density of InAs QDs [1, 2]. However, the tunability of the density of InAs QDs using growth temperature and growth rate is usually limited [1]. In order to further improve the controllability of InAs QD growth, surfactants are used as a powerful tool to control the growth process. Bismuth (Bi) has been used as surfactant to promote layer-by-layer growth and improve photoluminescence (PL) efficiency of GaAs, either using molecular beam epitaxy (MBE) or metal organic chemical vapour deposition (MOCVD). In addition, Bi seems to be the most suitable entrant for the role of surfactant for the InAs/GaAs system. Due to a rather large covalent radius compared to that of As, Bi is not expected to be incorporated into the QD material but to segregate on the growth surface. Also, since Bi is a V group element, it was expected not to change the material properties significantly even if incorporated in large amounts [2, 3].

In this work, we investigated the use of Bi as surfactant, which provides an effective method to reduce the density and improve the optical quality of InAs QDs. For this purpose, two types of InAs QDs samples were grown at similar conditions at low temperature (3500C) on (001) GaAs substrate by using solid source MBE with and without the presence of Bi-contained layer. The PL emission was studied as a function of laser power at 10K. Two sets of InAs QDs were observed in the Bi-free and Bi-mediated grown samples with energies of 1.32eV and 1.35eV, and 1.26eV and 1.36eV, respectively. In addition, PL peaks were detected in both samples at 1.49eV and 1.4eV, which were assigned to GaAs and InAs wetting layer, respectively. It was found that the use of Bi as surfactant resulted in a substantial improvement of the PL intensity, e.g. the peaks due to large and small QDs at 1.26 eV and 1.36 eV improved by a factor of 5 and 1.5, respectively, under a laser excitation intensity of 7mw at 10K. The presence of Bi caused a large red shift of the PL energy of the large QDs (from 1.32eV to 1.26 eV) and no appreciable shift was observed of the smaller QDs (from 1.35eV to 1.36 eV). The integrated PL intensity of the QDs as function of laser excitation power (0.5 mW-25 mW) was found to be linear indicating that the samples have low defects and dislocation densities [1]. Furthermore, the temperature dependence of the peaks energy over the temperature range 10K-80K showed an energy decrease. The large enhancement of the PL intensity of InAs QDs grown by MBE using Bi as surfactant can be explained by the improvement of the diffusion of In adatoms during the growth of the dots and possibly by a decrease of the incorporation of background impurities [1].

Notes
In situ determination of the growth conditions of GaSbBi alloys

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Recently, dilute bismuth (Bi) III-V alloys have attracted great attention, particularly due to their properties of band-gap reduction and spin-orbit splitting. Therefore, the incorporation of Bi into antimonide based III-V semiconductor is very attractive for the development of new optoelectronic devices working in the mid-infrared range (2 – 5 μm). However, due to its large size, Bi does not readily incorporate into III-V alloys and has indeed a strong tendency to surface segregate and form droplets. Nonetheless, the growth of GaSbBi alloys can be achieved using unusually low growth temperatures and V/III flux ratio close to unity [1]. But overall, the conditions (temperature and flux ratio) allowing the growth of high quality GaSbBi are extremely challenging to set since any slight deviation easily leads to the formation of droplets or to a low incorporation of Bi into the GaSb matrix. A large number of calibration samples is thus generally required to correctly set these parameters by a trial-and-error approach, which is both time- and money-consuming.

In this work, we present an original in-situ method to determine the optimal growth conditions (flux ratio and substrate temperature) of GaSbBi alloys based on RHEED oscillations measurements [2]. Strong RHEED intensity oscillations were measured for both GaSbBi and GaSb for different Bi fluxes at very low temperature, even during group-V induced growth. To set the critical V/III flux ratio and the growth temperature, the influence of the Sb flux and the temperature on the growth rate of GaSbBi and GaSb was studied. The variation of the Bi incorporation rate was clearly observed. Finally, several GaSbBi layers with Bi content between 2 and 13% were grown under different temperatures and fluxes using the indications given by the RHEED measurements. This new technique could also be useful for other III-V-Bi alloys and help overcome the growth difficulties caused by the challenging Bi incorporation.

Fig. 1: (a) RHEED oscillations from GaSbBi grown at different temperatures using fixed fluxes (Sb BEP: 2.00 x 10⁻⁷ Torr, Bi BEP: 3.7 x 10⁻⁸ Torr). The calculated growth rates are indicated for each curve. The curves have been vertically shifted for clarity. (b) GaSbBi growth rate calculated from the RHEED oscillations as a function of the growth temperature. The dashed line was calculated using a kinetic model.

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Notes
Novel GaAs$_{1-x}$Bi$_x$ based W-Type structures for laser applications

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In this work we will present different GaN$_y$As$_{1-y}$/GaAs$_{1-x}$Bi$_x$/GaN$_y$As$_{1-y}$ W-type structures grown on GaAs in terms of their photoluminescence (PL) and growth properties. These structures can be grown strain balanced on GaAs, since GaAs$_{1-x}$Bi$_x$ is compressively strained while GaN$_y$As$_{1-y}$ is tensile strained. Due to the strong reduction of the band gap by incorporation of nitrogen (N) and bismuth (Bi) respectively, it is possible to shift the emission wavelength of such structures into the mid infrared region [1].

The samples were grown in an Aixtron AIX 200 horizontal reactor system. Since deposition of GaAs$_{1-x}$Bi$_x$ requires low growth temperatures around 400 °C, triethylgallium, tertiarybutylarsine and trimethylbismuth were chosen as precursors. For incorporation of N into GaAs 1,1-dimethylhydrazine was used. The layer thicknesses and compositions were determined using high resolution X-Ray diffraction (HR-XRD). The PL signal was recorded using a wavelength of 532 nm for excitation.

Fig. 1 (a) shows a HR-XRD diffractogram of a GaN$_y$As$_{1-y}$/GaAs$_{1-x}$Bi$_x$/GaN$_y$As$_{1-y}$ W-type 3x QW structure. The satellite peaks corresponding to the W-type structure are clearly visible. Furthermore, the good agreement between dynamic modelling and experimental data suggests good crystalline quality.

The corresponding PL measurement of this sample is shown in Fig. 1 (b). The peak arising at 1.06 eV is in good agreement to the theoretical calculation of a type-II transition between GaN$_{0.0085}$As$_{0.9915}$ and Ga$_{0.942}$Bi$_{0.058}$ QWs, which will further be discussed in the presentation.

Figure. 1: (a) Shows a HR-XRD of the GaN$_y$As$_{1-y}$/GaAs$_{1-x}$Bi$_x$/GaN$_y$As$_{1-y}$ W-type 3x QW structure. In (b) the corresponding PL spectrum is shown.

Localization effects and band-gap of GaAsBi/GaAs multi quantum wells

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The band-gap of GaAs$_{1-x}$Bi$_x$ suitable for use in tandem solar cells is determined using the Valence Band Anti Crossing (VBAC) model. Unlike the incorporation of Nitrogen (N) into GaAs, which perturbs the conduction band, Bismuth (Bi) interacts more with the valence band of GaAs than its conduction band. Incorporation of Bi into GaAs lattice forms a Bi resonant level closer to the valence band maximum (VBM). Two structures are considered, both consists of ten 10-nm quantum wells grown by using Molecular Beam Epitaxy on a highly doped GaAs substrate with different intrinsic Bi concentration of 1% and 2%. All the Bi containing layers are grown at relatively lower temperature of 360°C to ensure Bismuth is incorporated [1, 2]. Photoluminescence (PL) measurements are performed to investigate the power response and temperature dependence of the structures. The PL peak emission energy becomes independent of the excitation power. The results indicate the presence of localized energy states which trap carriers at low temperatures and that the majority of the carriers become delocalized at higher temperature. Furthermore, the temperature dependent PL also shows an S-shape behavior, which is a signature of localization effects.

Notes
Defect-free Bi$_{1-x}$Sb$_x$ Nanowires on Si by MBE

Dima Sadek$^{1,*}$, Pier-Francesco Fazzini$^2$, Filadelfo Cristiano$^1$, Sébastien Plissard$^1$

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1D nano structures of Bismuth Antimonide (Bi$_{1-x}$Sb$_x$) alloys, especially nanowires, are promising for quantum computing, nanoelectronics, thermoelectrics and spintronics.\(^1\) Varying Sb composition (x), Bi$_{1-x}$Sb$_x$ should behaves as: semi-metal (x<0.07), indirect bandgap semiconductor (0.07<x<0.09), direct bandgap semiconductor (0.09<x<0.15), indirect bandgap semiconductor (0.15<x<0.23) and again semimetal (x>0.23).\(^1,2\) Thus, a precise control of this parameter holds promises for future quantum devices. For instance, if x=0.03, 3D dirac cones should be observed in the structure and could be used to host Majorana zero mode when coupled with superconducting contact. If 0.08<x<0.24 the material should behave as a 3D-topological insulator, and for x>0.23, the high electron mobility and strong spin-orbit interactions make it an interesting candidate for spintronics.\(^3\)

Hence excellent quality of 1D nanostructure, with control over Sb content, is necessary in order to understand and engineer the material. This study is the initial step on addressing these existing hurdles and explore opportunities. Epitaxial Bi$_{1-x}$Sb$_x$ nanowires with controlled Sb concentrations are integrated on Si(001) and Si(111) substrates for the first time.

The process starts with the removal of native oxide from unpatterned Si(001) wafers with the help of hydrofluoric acid (HF 5%). The degassing of substrates at 200 °C follows next. Then self-catalyzed growth of Bi$_{1-x}$Sb$_x$ nanowires (varying x) occurs on these substrates in a solid source molecular beam epitaxy (MBE) system. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) characterizations are carried out for morphology, composition and crystallographic studies. Electrical characterizations will be performed to extract intrinsic properties (electron mobilities, resistivity, etc).

SEM characterizations confirm high density of BiSb nanowires with diameters around 25 nm and lengths up to 15 µm. As expected, the composition has a significant impact on these nanostructures including density, morphology, and crystallography. Finally, the electrical characterizations will be presented.

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✓ How to come to LAAS-CNRS
✓ How to go to the restaurant « caves de la Maréchale »
✓ How to go the restaurant “le Moaï”
Subway lines in Toulouse

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les caves de la Maréchale
Esquirol Station (A)

Mercure Compans
Compans Cafarelli station (B)

to LAAS
Faculté de Pharmacie station (B)

Restaurant
Le Moaï
Palais de justice Station (B)

Jean Jaurès Station (A&B)
How to come to LAAS

Subway - line B Borderouge (north) to Ramonville (south), every 3min.
It takes 15mn from the Compans-Cafarelli station to the Faculté de Pharmacie station

Buses
you can download the iphone application "TISSEO". It is very convenient and provides direct information on next bus arrivals.
In summer, the service frequency is reduced.

line 78 (Buses run every 20min)
From Faculté de Pharmacie stop to LAAS stop: 08:10  08:30  08:50  etc.
From LAAS stop to Faculté de Pharmacie stop: 08:00  08:20  08:40  etc.

line 27 Giordiano Bruno stop - LAAS stop: every 25 min.
line 37 Giordiano Bruno stop - LAAS stop: every 25 min.
On Monday July 22, dinner at the restaurant:

Caves de la maréchale, 3 rue Jules Chalande
phone: +33/0.561.23.89.88

Restaurant les Caves de la Maréchale
On Tuesday July 23 (20:00): Workshop banquet at the restaurant

Le Moaï, 35 Allée Jules Guesde
phone: +33/0.5. 34.31.67.85
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