µLaue diffraction and excited luminescence in nitrides optoelectronics: physics, operando, serial crystallography

Keywords: X-ray synchrotron, µLaue, XEOL, Data analysis, opto-electronics
Location: The PhD candidate will be located at CEA Grenoble (IRIG/MEM/NRX) and ESRF, France and affiliated with University of Grenoble Alpes (UGA) in the Physics doctoral school.
Time: PhD expected starting date: fall 2023 (3 years contact). Funded by CEA grant.

Summary

The Laue microdiffraction instrument (µLaue), installed at the European Synchrotron (ESRF) in Grenoble (BM32 beamline), is unique in Europe and probes the matter by diffracting a polychromatic beam of a few hundred nanometers. The acquisition of the Laue diffraction diagram is very fast and allows the scanning of the samples with high precision to get the structural parameters of mono or polycrystalline materials in terms of orientation, crystallographic lattice parameters, and lattice strains. The possibility to measure the emitted visible and near IR light excited from X-ray (called XEOL for X-ray Excited Optical Luminescence) has been recently added to this instrument. The acquisition of XEOL spectrum is synchronized to the diffraction pattern collection to measure the same sample's location. The Ph.D. subject consists in participating in the development of new ESRF experiments with our team (improvement of light collection and setup), performing materials science physics and optimizing data processing using image analysis algorithms, intelligent Laue diagram recognition and artificial intelligence. A specific focus will be laid on the determination of strain fields/rotations, and on the nature of defects in epitaxial nitride materials (In, Al, Ga-N), and their correlation with the emission properties. This new analysis method will allow the systematic treatment of a large amount of data by "serial crystallography" (a term used in biology). We will study nitride materials that are of paramount industrial importance in optoelectronic and high-power devices. This work will benefit from the Extremely Brilliant Source (EBS) upgrade of the ESRF, recent fast pixel detector, and continuous development of the LaueTools program for diffraction pattern analysis. It will participate in two French ANR initiatives: MAGNIFIX (upgrade of the 5 French-CRG beamlines: optics and new setups) and DIADEME (French research priority program: automation, artificial intelligence). The student will belong to the CEA synchrotron X-ray team and will benefit from the French-CRG infrastructure. He will be registered at Univ. Grenoble Alpes (UGA) and have a CEA grant.

Full description of the subject

Context and in-house development: Nitride heterostructures recently demonstrated novel optical, transport and electronic properties making use of quantum confinement effects and strain engineering. The emergence of disruptive functionalities is strongly related to their growth and technology controls, but also to the development of advanced characterization techniques having high spatial and spectral resolution, as such as focused X-ray beams that provide innovative solutions to analyse quantitatively the morphology, defects, strain, and composition of these materials.

This Master/PhD project proposes to correlate the crystalline state properties and visible emission efficiency in nanoscale nitride heterostructures used in lighting emitters and µdisplays by mapping *at the same time* µLaue and XEOL. This brand-new (in the world) experimental development performed on the BM32@ESRF beamline **[0]** combines the advantages of adapted beam size to get full and fast information on *single objects/areas*, but also on *assemblies* with significant statistical information. It will provide unique information on growth, relationships between emitting performance and structure, and integration of these heterostructures in every day's life devices.

X-ray excited optical luminescence (*XEOL*) is an efficient technique to measure the optical properties of materials. As an example, some original studies have been performed by our team at the ID22 and ID16B@ESRF beamlines with focused hard X-ray beam (size around 63x63 nm^2, pink beam @ 29.6 keV & 17.5 keV) to study the exciton confinement and radiative time decays for blue light emission in InGaN/GaN multiple quantum core-shell wells (MQW) deposited around GaN wires **[1]**, as well as the effect of crystalline polarity on Si-dopant incorporation and wire emission **[2]**. These very small beams providing a high spatial resolution are well suited to study nanostructures, but mappings are quite long and only small area can be recorded (*e.g.,* several hours of measurements per single dispersed wires on ID16). For these experiments, XEOL measurements have been combined advantageously with X-

ray fluorescence (XRF) to correlate optical properties and indium composition inside multiple quantum wells (one of the most important parameters driving the emission color). It has been demonstrated that these wires have a very bright blue light emission and can be electrically excited. RGB color mixing is still not completely mastered and basic researches are still needed to understand device properties. Importantly, the measurements of *strain and emission* fluctuations *inside* and *in-between* devices are required. As an example, Ref. [3] shows our realization of flexible white LED based on nitride wires and phosphors. These scientific questions in terms of *structural (strain) and optical fluctuations at the pitch scale and on the assemblies* also apply in nitrides µ-Displays developed at CEA, for display applications. One challenge is to quantify the emission losses at the edges of the small patterns and to understand the impact of structural defects. These structures can be based on c-planes planar InGaN MQWs and are electrically contacted to emit very bright light [4] with a main emission wavelength in the 400-450 nm range.
The µLaue/XEOL setup has been significantly improved during the last years (new detector & higher stability of the beam) and is still underway with a new instrument in preparation with the beamline upgrade (French ANR PIA3 Magnifix and PEPR DIADEME). In the older setup, the XEOL is collected by an off-axis parabolic Al-mirror (X-rays are going through the mirror), which is re-focused by means of a second parabolic mirror to the entrance of an optic fiber going to a spectrometer. The light is dispersed by a diffraction grating on a back-illuminated pixels CCD camera cooled by Peltier effect (see Fig. 1).

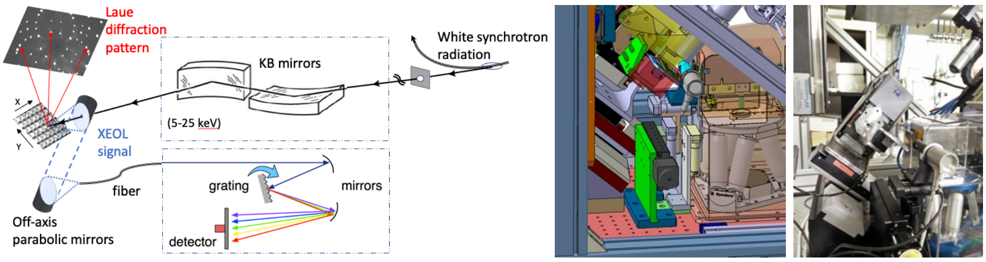

Fig. 1: Left: *Schematics of the experimental setup.* ***Right:*** *drawings and picture of the µLaue setup (2022 config., before upgrade) of the BM32 beamline at ESRF.*

Note that by using polychromatic wavelength, the sample (see Fig. 2) does not need to be aligned to record the Laue diffraction pattern and it needs only to be scanned. At each position, we can measure the Laue diffraction, the XEOL signal and supplementary signals: fluorescence, photon beam induced current, as well as control signal: temperature, injected current in devices… (multivariate analysis).

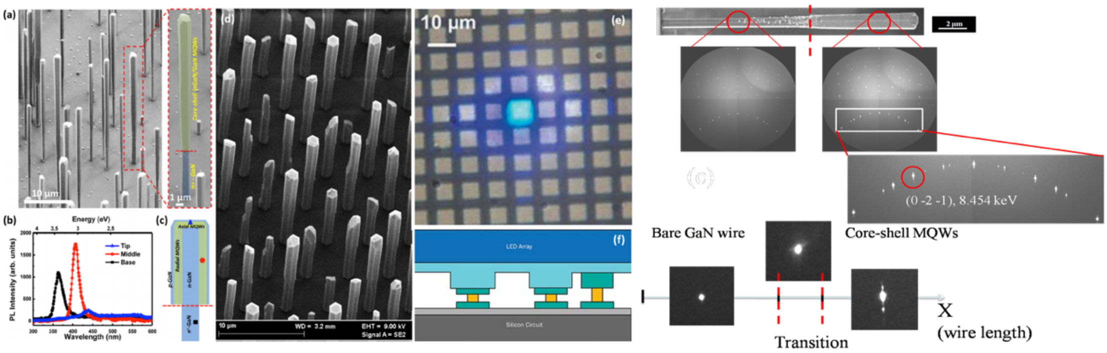

Fig. 2: Left: *Samples to be studied: (a) self-organized wires that will be dispersed on glass, (d) standing wires grown on sapphire. (c) shows the MQW heterostructures and (d) example of photoluminescence spectra. (e) µDisplay structure with its technological integration shown in (f).* ***Right:*** *Evolution of the scattering patterns collected by Laue Microdiffraction as a function of beam location along the nanowire. At the wire tip (right hand side) the multiple components shape of Laue peaks correspond to the periodic structure of the MQWs.*

The major upgrade of the ESRF synchrotron has increased the brilliance and decreased the beam size, urging the necessity to speed-up the acquisition and analysis treatment to increase the throughput of the scientific & technological impact of this instrument. A recent 4096x4096 pixels X-ray SCMOS seamless camera array with 0.072 s readout time (Photonic Science) will be used. A small map of 200x200 positions (for example with a probe size of 0.5 µm and a counting time of 01. s/point) generates ≈320 Go of data (40000 images of diffraction pattern of about 8 Mo). In the next years, a completely new energy-dispersive pnCCD technology where each pixel is encoded in X-ray energy will expand again the quantity of data. Presently, the µLaue analysis is performed by the LaueTools program (with artificial intelligence options) developed by J.S. Micha at the beamline [5]. For the XEOL signal that is less heavy (1024 wavelength channels), we are developing a specific python library to analyze hyperspectral data.
The candidate will be trained to complementary techniques (e.g., SEM, cathodo-luminescence, photoluminescence, SIMS) present at IRIG and PFNC (the characterization platform of the CEA Grenoble).

Objectives: To tackle the physical opto-electronics questions and estimate their fluctuations related to growth and technology defects, we need a statistical information on a large number of emitters/zones. A new analysis method has to be implemented that must combine high-level experiments and data analysis. The Master work will be performed at BM32 on (i) dispersed rods/wires and standing wires on sapphire with core-shell InGaN MQWs (diameter ~1.5 µm, length of the MQW ~10 µm) and (ii) µDisplays grids. The samples will be selected from MOVPE growths (laboratory in-house research and collaborations) having good photo- and electro-luminescence properties. Already acquired datasets are also available to check the analysis procedures before experimental beamtime.

The PhD candidate (3 years) will strongly interact with experimentalists and scientists to:

- **perform mapping experiments** related to nitride opto-electronics materials,
- **design better experiments**: participation in the installation/test of the new Laue instrument and in the implementation of a new pnCCD detectors
- **analyse the heterostructures** in terms of strains, orientation and emission mappings [6]. A specific task will be the representation of disorientation and strain elasticity tensors to identify the nature of the defects that have different impacts of *hkl* diffraction peak shapes, shifts and broadenings. It will allows proposing some physical models of the defects (dislocations, epitaxial defects) and their distributions. New interesting questions are also related to experimental energy-resolved measurements that will provide the missing parameter for a complete knowledge of crystallographic parameters.
- **operando measurements** LED structures under electric excitation. Strain induced by current, defect development. Analyses of intensity distribution in planar InGaN/GaN LEDs when excitation is increased.
- **develop the data analysis workflow** by improving the methods: e.g., automation scripts, data reduction, combination of machine learning and physical modelling, hyperspectral treatment of XEOL data with Principal Component Analysis (PCA and NMF variants), integration of the work in an HyperSpy extension. For this aspect, the candidate will benefit from the interactions with data analysis specialists at CEA & ESRF (see PaNdata ESRF contributions) and from the general efforts of the French-CRG beamlines in the big data challenge. A 2 years post-doc is planned on these topics with a strong numerical background.

Expected impact and perspectives: Large-scale facilities are facing recently the "data deluge" due to the continuous development of new techniques with powerful excitation sources, improved sample and sensor positioning, faster detectors with a strong increase in size and number of pixels. The digitization of these tools has also been a revolution that is still ongoing. It will contribute actively to the materials characterization at the nanoscale, often mandatory for many process and device developments. This PhD will provide the missing element to reduce considerably the operation time of the µLaue/XEOL nano-characterisation which has the capability to improve the physical understanding of the growth and to control the quality of complex nanomaterials and opto-electronic devices. A new methodology, which will combine different analysis techniques of nano-characterisation and new computational tools is proposed. It corresponds to a new and necessary improvement of the nanomaterial's characterization chain.

In addition to addressing important materials for applications: in Europe the Aledia and Plessey companies are developing actively nitrides µLEDs (as well as many companies in Asia), the data analysis developed for these techniques will benefit to academic studies and to the synchrotron community (the French Collaborative Research Group, the ESRF and more generally Large-Scale infrastructures). Several other families of materials (focusing on green and red emission) will directly benefit from this serial-crystallography approach such as the MQW nitride growth on patterned non-polar and semi-polar surfaces (e.g., CNRS/CHREA), on porous GaN (e.g., CEA/Leti) to benefit from strain relaxation, on Sapphire Nanomembranes (e.g., KENTECH, Korea) … We believe that this technique will be also interesting to analyse bulk GaN crystal, but also crystals for non-linear optics. Extension to other materials is quite straightforward and we have already tested phosphor crystals for white LED emission & perovskites.

This project will foster collaborations between experimenters developing advanced characterization techniques, growers and technologists and computer scientists, bringing their necessary skills in data analysis.

This PhD work will motivate beamtime proposals on the ESRF ID16 beamline to benefit from fluorescence mapping and high resolution (correlation composition/light), as well as time-resolved analysis (to get efficiency mapping by measuring the emission time-decay). Furthermore, the first experiments involving monochromatic diffraction have been performed on BM32 to study the X-ray / matter interaction and light extraction with nitrides MQWs. Extensions to absorption measurements could be straightforward with transparent membranes. The student will be also associated to this innovative research.

Candidate profile: Requested skills: A master of science (physics or nanoscience disciplines) with strong motivations in semiconductor physics and data analysis. Skills in machine learning, image analysis, and Python/Notebooks (programming language at ESRF) would be an asset.
You should be motivated by experimental work. In addition, you should have:

- Ability to get to the heart of the problem and take it effectively through to completion;
- Good organizational and planning skills;
- Self-motivation and initiative attitude;
- Good interpersonal, communication, and presentational skills;
- Will to work as part of a multi-disciplinary team.

He/She should demonstrate excellent oral and written communication skills in English.

Benefits:

• Legal work time, paid holidays and 10 days of public holidays.

• Maternity, sick and accident leave. Same social advantages as CEA employees in terms of contribution to parental leave, health and accident insurance.

• Retirement. Like permanent researchers, this grant fellows benefit from a pension fund and contribute to a retirement pension scheme.

• PhD fellows are considered permanent staff regarding social benefits such as access to catering and company transportations. Lunches onsite are partially supported by CEA. CEA's contribution depends on personal income. Participation in public transportation (85%).

• PhD fellows have access to the library and social activities such as musical, cultural and sport activities. Benefit from discount holiday travel and theatre, opera and movie tickets.

• In most cases, and like all international scientists routinely welcomed by CEA, PhD fellows will be helped by associations co-funded by CEA to find housing and school for children, fulfill administrative forms, and open a bank account.

• Like all CEA employees, PhD fellows are required to complete a Security Background Investigation. In total respect to the national law, CEA conducts a medical examination and a background investigation before any employment. Fellows are required to answer personal questions about themselves and their families such as place and date of birth, employment, and address. This information is necessary for CEA to allow access and work in CEA premises and facilities.

Location: The PhD candidate will join the Nanostructures X-ray Radiation Laboratory of the CEA including research scientists in physics and instrumentation. NRS contributes to the scientific and technological objectives defined by CEA and by the French community within the framework of the French X-ray synchrotron large-scale facilities. These tasks require very specific synchrotron equipment and scientific skills to carry out high-level experiments on a broad range of subjects supporting both academic research and societally relevant applications.

Application: Please submit electronically (in PDF format) a detailed resume and a motivation letter. Applications must be sent to Dr. Joël Eymery (joel.eymery@cea.fr) and Dr Jean-Sébastien Micha (micha@esrf.fr). In the object of your application email, please include the reference "[PhDThesis-Application]" followed by your Name and Surname.

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