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RPPR Final Report
as of 05-Apr-2019

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STEM Degrees: 0 **STEM Participants:** 5

Major Goals: The major goal of this project was for the Center for High Technology Materials (CHTM) at the University of New Mexico (UNM) to specify, order, acquire, install, and qualify a new state-of-the-art high-resolution X-ray diffractometer to support Department of Defense (DoD) research related to advanced epitaxial thin-film and nanoscale materials growth and characterization.

More details are given in the attached pdf report.

RPPR Final Report
as of 05-Apr-2019

Accomplishments: The goal of this project was completed. A PANalytical Empyrean X-ray diffractometer was purchased, installed at CHTM, and qualified. The tool is being used to support epitaxial growth of compound semiconductors, including novel nanoscale materials, short-period superlattices, and conventional electronic and optoelectronic devices. The new system provides a wealth of conventional structural information related to the strain state, alloy composition, layer thickness, density, layer tilt and distortion, interfacial roughness, and defect density/distribution of materials. In addition, the new system provides novel capabilities that are specifically targeted to advanced epitaxial thin-film and nanoscale materials characterization, including high-resolution triple-axis scanning, ultra-fast (sub-minute) reciprocal space mapping (RSM), high-temperature X-ray measurements, grazing incidence small-angle X-ray scattering (GISAXS), topography analysis using diffraction contrast imaging, and analysis of non-basal-plane wurtzite materials. The system is being used to support research in the areas of III-nitride high-speed light-emitting diodes (LEDs), near-UV vertical-cavity surface-emitting lasers (VCSELs), high power vertical external-cavity surface-emitting lasers (VECSELs), multi-junction solar cells, strained nanowire transistors, semiconductor nanomembranes, and carbon nanotube fiber-reinforced polymers.

More details are given in the attached pdf report.

Training Opportunities: Two training sessions on the tool were provided by the manufacturer (PANalytical). The training sessions were composed of classroom instruction and hands-on operation of the X-ray diffractometer. Four postdoctoral researchers and several students attended the training sessions. In addition, the training sessions were also attended by Dr. Tito Busani (CHTM Nanofabrication Facility manager) and by Mr. Douglas Wozniak (Nanofabrication Facility staff). Future training to other researchers, students, staff, and external users will be provided by Dr. Busani and Mr. Wozniak.

More information is given in the attached pdf report.

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Daniel Feezell
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI
Participant: Tito Busani
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 05-Apr-2019

High-Resolution X-Ray Diffractometer for Advanced Epitaxial Thin-Film and Nanoscale Materials Characterization

Final Report

Contract Number: W911NF-17-1-0476

Reporting Period: 9/5/17 – 1/4/19

PI: Daniel Feezell

Other Key Personnel: Ganesh Balakrishnan, Sang. M. Han, Tito Busani, Francesca Cavallo, Mahmoud Taha

Center for High Technology Materials (CHTM), The University of New Mexico, Albuquerque, NM 87106, USA

1. Introduction

The Center for High Technology Materials (CHTM) at the University of New Mexico (UNM) has specified, ordered, acquired, installed, and qualified a new state-of-the-art high-resolution X-ray diffractometer to support Department of Defense (DoD) research related to advanced epitaxial thin-film and nanoscale materials growth and characterization. The acquired tool, which will be described below, is the PANalytical Empyrean X-ray diffractometer. The tool is being used to support epitaxial growth of compound semiconductors, including novel nanoscale materials, short-period superlattices, and conventional electronic and optoelectronic devices. The new system provides a wealth of conventional structural information related to the strain state, alloy composition, layer thickness, density, layer tilt and distortion, interfacial roughness, and defect density/distribution of materials. In addition, the new system provides novel capabilities that are specifically targeted to advanced epitaxial thin-film and nanoscale materials characterization, including high-resolution triple-axis scanning, ultra-fast (sub-minute) reciprocal space mapping (RSM), high-temperature X-ray measurements, grazing incidence small-angle X-ray scattering (GISAXS), topography analysis using diffraction contrast imaging, and analysis of non-basal-plane wurtzite materials. The system is being used to support research in the areas of III-nitride high-speed light-emitting diodes (LEDs), near-UV vertical-cavity surface-emitting lasers (VCSELs), high power vertical external-cavity surface-emitting lasers (VECSELs), multi-junction solar cells, strained nanowire transistors, semiconductor nanomembranes, and carbon nanotube fiber-reinforced polymers.

2. System Specifications and Bidding Process

The system specifications were initially developed to fit the research needs at CHTM. In addition to conventional XRD features, the following capabilities were targeted:

- high-resolution triple-axis scanning
- ultra-fast reciprocal space mapping (RSM)
- high-temperature x-ray measurements
- grazing incidence small-angle x-ray scattering (GISAXS)
- topography analysis using diffraction contrast imaging
- analysis of non-basal-plane wurtzite materials

To identify the best value for the research needs and to optimize the awarded money from the grant, a bidding process was opened through the purchasing department at UNM. The winner of the bidding process was PANalytical, due to their ability to meet all of the needed capabilities within the constraints of the grant funding.

The tool identified to meet the research need was the PANalytical Empyrean X-Ray Diffractometer. This is a multi-purpose tool capable of measuring thin-films, nanoscale materials, powders, and solid objects. The tool contains a high-resolution goniometer (step size 0.0001^{o}), universal PreFIX optics and stages with a 3-axis cradle, a copper-anode long fine focus X-ray tube, hybrid 2 bounce Ge(220) monochrometer, Bartels 4 bounce monochrometer for improved resolution, PIXcel^{3D} detector, GISAXS upgrade, DHS 1100 domed hot stage, and a comprehensive software suite for data collection and analysis. Several of the optics available on the PANalytical Empyrean diffractometer offer measurement resolutions that are higher and cover a broader range than are currently available at UNM. In addition, the instrument is equipped with the Bragg Brentano HD optic that is unique to PANalytical and offers significantly improved diffraction performance. The included PIXcel^{3D} detector also offers higher spatial resolution (55 µm), a high dynamic range (>10^{10}), and point spread function equal to 1 pixel. The PIXcel^{3D} detector technology enables additional new capabilities that are not available on the other UNM diffractometers, including GISAXS, which supports research of nanostructured surfaces and interfaces, and unique ultrafast (sub-minute) reciprocal space mapping.

A quotation was provided by PANalytical for an Empyrean X-ray diffractometer with the following summary of capabilities:

1) X-Ray powder diffraction (XRPD) using Bragg-Brentano parafocusing geometry and a linear (1D) position sensitive detector (or area detector operating in 1D mode) for fast measurements

2) Grazing incidence X-ray diffraction (GIXRD) with parallel beam optics using asymmetric Bragg diffraction measurements for thin film and surface analysis

3) High-resolution X-ray diffraction (HRXRD) of epitaxial thin films, including rocking curve (RC) and triple-axis scanning (TA) measurements

4) Reciprocal space mapping (RSM) using conventional triple-axis measurements and using faster single-pass mapping with an area detector

5) In-plane X-ray diffraction (IP-XRD) using both parallel beam and high resolution optics for in-plane analysis of nanostructured materials and epitaxial thin films

6) X-ray reflectometry (XRR) of films ranging in thicknesses from 2 nm to 200 nm multilayers

7) Topography analysis using diffraction contrast imaging

8) Grazing incident small angle x-ray scattering (GISAXS) with 2D imaging

9) Diffuse scatter analysis of off-specular reflection (resonant diffuse scattering) and diffuse intensity distribution in reciprocal space around a Bragg reflection

10) Wafer mapping with xy translation using XRR, RC, and RSM

11) High-temperature x-ray measurements with the ability to perform XRPD, RC, TA, RSM, and XRR measurements at elevated temperatures up to 1100 ^{o}C

Software Packages	**Functionality**
XRD 2D scan	1D and 2D micro-diffraction
Highscore	Material Phase analysis and its identification including HKL identification and reciprocal space mapping
Epitaxy	Composition, thickness, strain and

	orientation, lateral coherence and twist of epitaxial and heteroepitaxial structures, rocking curves, and wafer mapping
Reflectivity	X-ray reflectivity: single and multi-film thickness, roughness and density

Before final acceptance of the PANalytical system quotation, UNM requested PANalytical to demonstrate the tool's capabilities for our research needs. To this end, seven epitaxial samples were sent to PANalytical for various measurements. The samples included an InGaN/GaN superlattice, a GaAs substrate with GaSb grown on top, an InP substrate with InGaAs on top, planar GaN on silicon, GaN nanowires on sapphire, *m*-plane AlGaN/GaN superlattice, and a semipolar InGaN/GaN superlattice. PANalytical performed a variety of measurements on these samples. The results from a selection of the measurements are shown in the figures below.

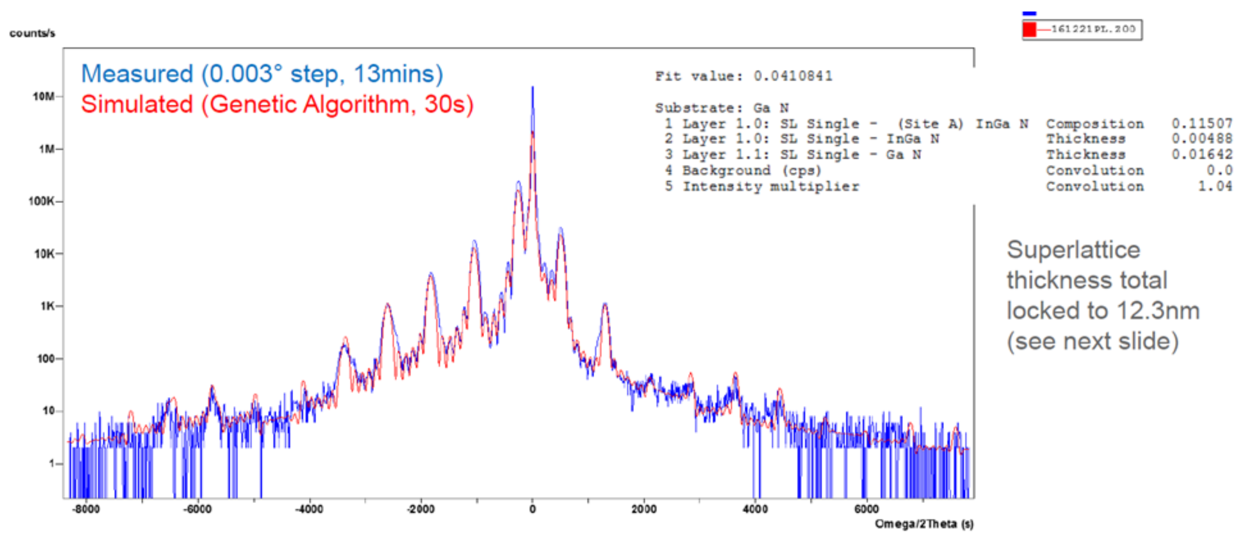


Figure 1. X-ray rocking curve of an InGaN/GaN superlattice sample and the associated curve fit, indicating a superlattice thickness of 12.3 nm.

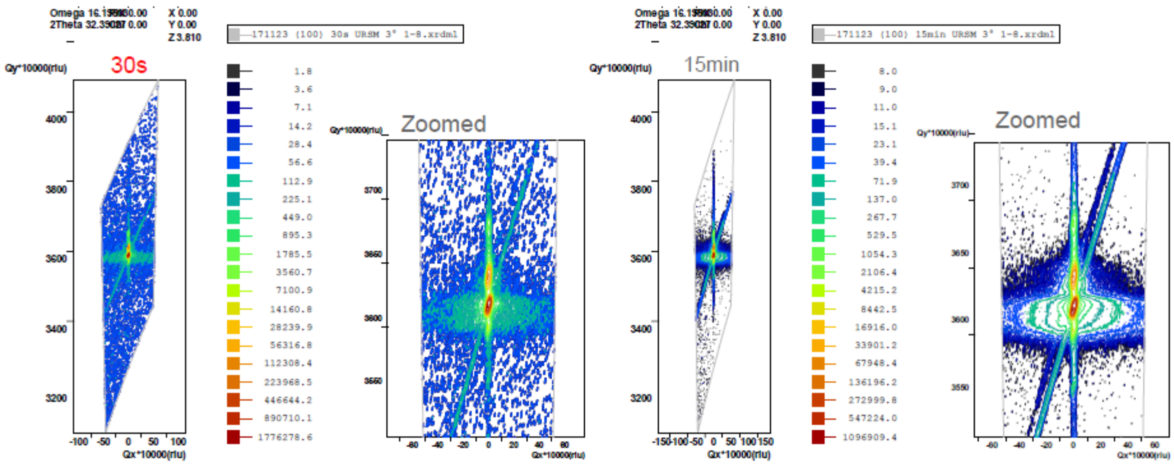


Figure 2. Reciprocal space maps of an AlGaN/GaN superlattice using short (30 seconds) and long (15 minutes)scanning times. Despite the short scanning time, the main peak features are resolvable in the 30 second RSM. The 15 minute scan resolves superlattice features.

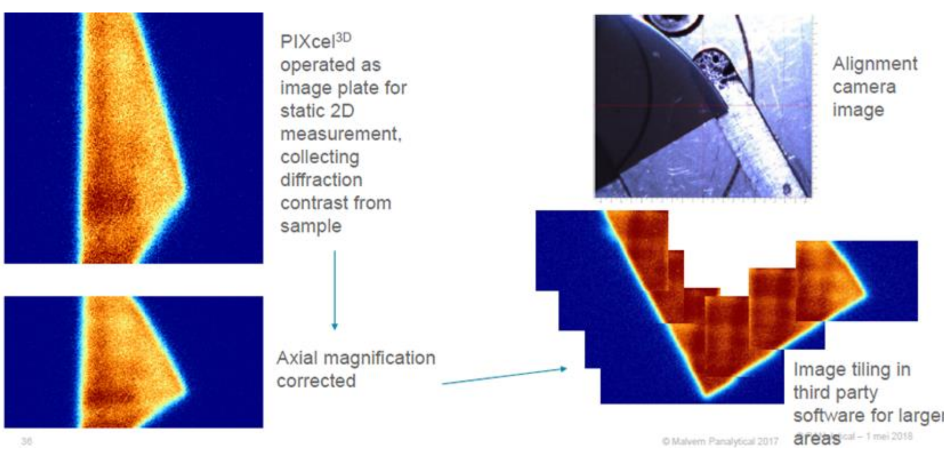


Figure 3. Topography measurement of an m-plane GaN sample using the Berg-Barrett method and the PIXcel^{3D} detector. Images can be stitched together to show the entire wafer.

PANalytical provided UNM with a full report on the measurements of our samples. Based on this report, we concluded that the tool's measurement capabilities were more than suitable for our research needs. Finally, before finalizing the order, a webinar software demonstration was also provided by the PANalytical engineers to demonstrate the analysis capabilities of the tool.

The order for the PANalytical Empyrean X-ray diffractometer was placed on June 13, 2018.

3. Installation, Training, User Facility

The PANalytical Empyrean X-ray diffractometer was delivered in December 2018. Installation of the tool by PANalytical technicians was performed in an available laboratory space at CHTM. Two days of basic training by PANalytical engineers was completed by January 4, 2019 (see

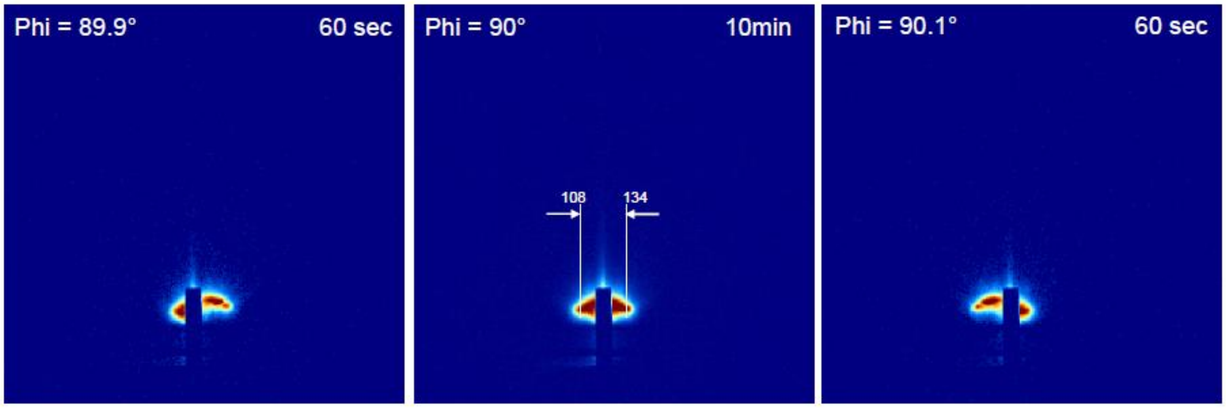


Figure 4. GISAXS measurement of GaN nanowires on sapphire. A simple Bragg spacing interpretation of lobe spacing corresponds to a feature size of 25.8 nm.

Figures 5(a) and 5(b)). Four people were trained during the initial training session: three postdoctoral researchers that are supervised by Dr. Feezell (PI), Dr. Balakrishnan (Other Key Personnel), and Dr. Busani (Other Key Personnel), and a staff member of the CHTM Nanofabrication Facility, Mr. Douglas Wozniak. The training sessions consisted of classroom presentations and hands-on operation of the tool. Beyond this initial training, we received an additional three-day training session with another PANalytical application engineer, for a total of five days of training.

After January 4, 2019, the XRD was made available to general internal users (students, faculty and staff) and external users (commercial industry) through the previously established CHTM User Facility. Researchers from the groups of four different PIs are currently using the tool. Mr. Douglas Wozniak and Dr. Tito Busani are responsible for training new users on the equipment and insuring the correct usage of the equipment. Users must also undergo the radiation training procedure mandated by UNM. The X-ray diffractometer was inspected by the UNM radiation officer on January 4, 2019. The instrument passed the inspection and a signed copy of the system acceptance test is shown in Figure 6.

Figure 5(a). December 20th 2018: PANalytical field engineers working on the installation of the XRD instrument

Figure 5(b). January 4th 2019: The XRD instrument installed and ready for users.

PANalytical
SYSTEM ACCEPTANCE TEST (SAT) FORM
And Software List

Company Name: University of New Mexico

City and State: Albuquerque

Instrument: Empyrean Serial #: 208479 DY1909

Customer Name (printed): Tito Busani

CSE Name (printed): Vladimir Finegersh

Software Name	Part Number	Version	License Number
Data Collector	9430 032 40921	6.0a	1907737494
High score Plus	9430 032 42921	4.8	856587445998604173
PAN-ICSD	9430 032 13921	4.0	
Epitaxy	9430 032 14921	4.5a	222164601784918204
Xpert Refelectivity	9430 032 17921	1.4	
Xper Smoothfit	9430 032 16921		
XRD2D SCAN	9430 032 23921	6.1	
PAN Viewer	9430 032 40921	1.3a	190773494

Event	Date	PANalytical Signature	Customer Signature
System Acceptance Training Complete	01/04/2019	V. [signature] CSE	[signature]
Installation Manager Review			

Sales Order Number (from the weekly Installation Report):

Comments: PAN Viewer delivered version 1.3, not installed because of glitches according to CM-1275. Will install 1.3a version as soon as it is released.

The CSE and customer sign and date this form after completion of System Acceptance Test and basic customer training. This form must be accompanied by the appropriate XRF, XRD or SEMI checklist. (Note - not all instruments and/or upgrades have System Acceptance Tests or checklists). This form indicates that the system is capable of being calibrated, measuring samples and producing results. By signing this form, the customer and CSE certify that the system is operational and ready for "First Use" by the customer. Please note that "First Use" does not necessarily mean it is ready to analyze the customer's samples. Basic training is an introduction to the software. Not all aspects of the software are covered. Normally, additional training by an Application Specialist is required before the instrument can be used to its fullest. If additional training has been purchased, a voucher for on-site or remote training by an Application Specialist will be given to the customer after this form is signed.

This SAT form should be immediately emailed to Dave Reed as soon as it is signed.

Revised June 20, 2014

Figure 6. Signed copy of the system acceptance test after inspection by the radiation officer.

A timeline for the specification, acquisition, installation, and training process is shown below:

- Award date: Sept 5th 2017
- Grant was processed by UNM 3 months later (due to an internal processing delay)
- Bidding started in March 2018
- April 10th UNM purchasing department completed the first round of the bidding process and requested PANalytical to provide, for the stage 2 bidding process, the a *tool performance verification and technical presentation.*
- May 21st UNM purchasing department provided a letter of award to Malvern PANalytical for the XRD
- UNM issued a PO for the purchase of the XRD on June 13, 2018
- The system was delivered on December 12, 2018
- The system installation was completed and the tool was certified on January 4, 2019 (see Figures 5 and 6)

4. Examples of Research Supported

The system was successfully installed and qualified by January 4, 2019. Although the system has only been online for three months, it is already being used to support important epitaxial growth activities at CHTM. Summaries of two projects already supported by the system are given below.

XRD Measurements of III-N Materials

Prof. Feezell's group is using the newly installed X-ray diffractometer to supports projects on GaN-based materials, including high-speed optoelectronics, nanostructure-based electronics, VCSELs, and vertical power electronics. We performed rocking curve measurements using the Empyrean X-ray diffractometer on our sample labeled 150727PL. We are able to analyze and quantify the quality, strain, epi-layers and quantum well thicknesses and chemical composition using different types of measurements like omega, omega-2theta, and reciprocal space mapping. The measurements can also be tailored towards obtaining the most accurate data, depending on the structure's growth orientation (polar *c*-plane, non-polar *m*-plane, or even semipolar). The data can be analyzed in the commercial software using batch routines developed by PANalytical. Additionally, we can directly fit the experimental measurements to our model that can be built and simulated, in order to obtain the most accurate thickness and composition values.

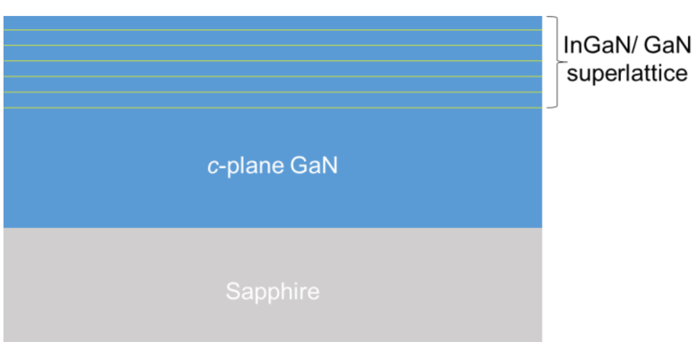


Figure 7. The epitaxial structure of the sample 150727PL.

Our sample was comprised of a GaN template grown on *c*-plane sapphire using MOCVD. The epilayers on the GaN substrate consisted of a 6 period InGaN/GaN superlattice, as shown in Figure 7. The sample was mounted on the diffractometer so that the $[10\bar{1}0]$ direction of the sapphire substrate was aligned along the goniometer axis. The reflections of GaN obtained under these conditions are 002, 004, 006, etc., thereby strengthening the epitaxial relationship between GaN and sapphire. The following show the rocking curve (Figure 8) and reciprocal space map measurements (Figure 9) obtained on the sample described in Figure 7.

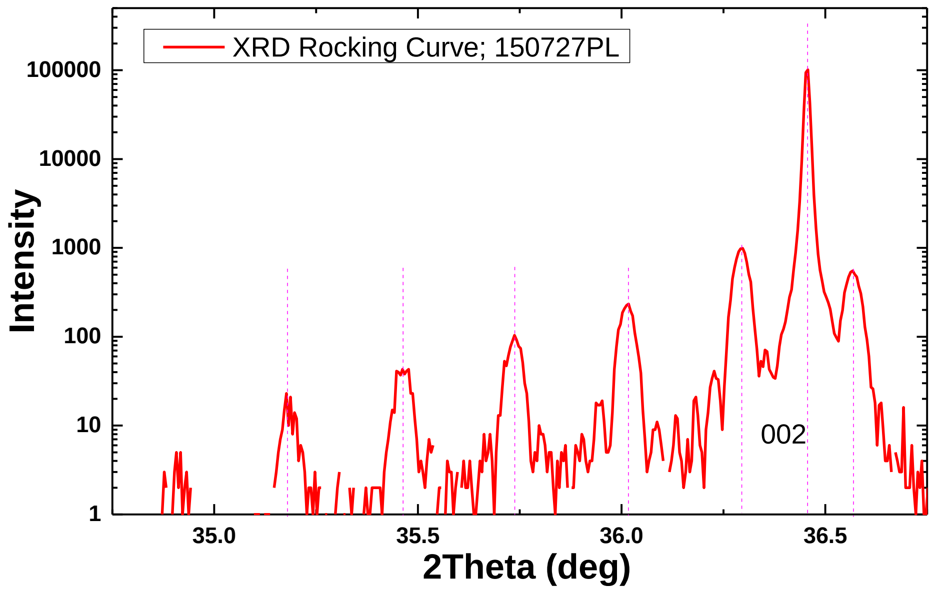


Figure 8. The X-ray rocking curve measurement of the sample labeled 150727PL on the PANalytical Empyrean diffractometer

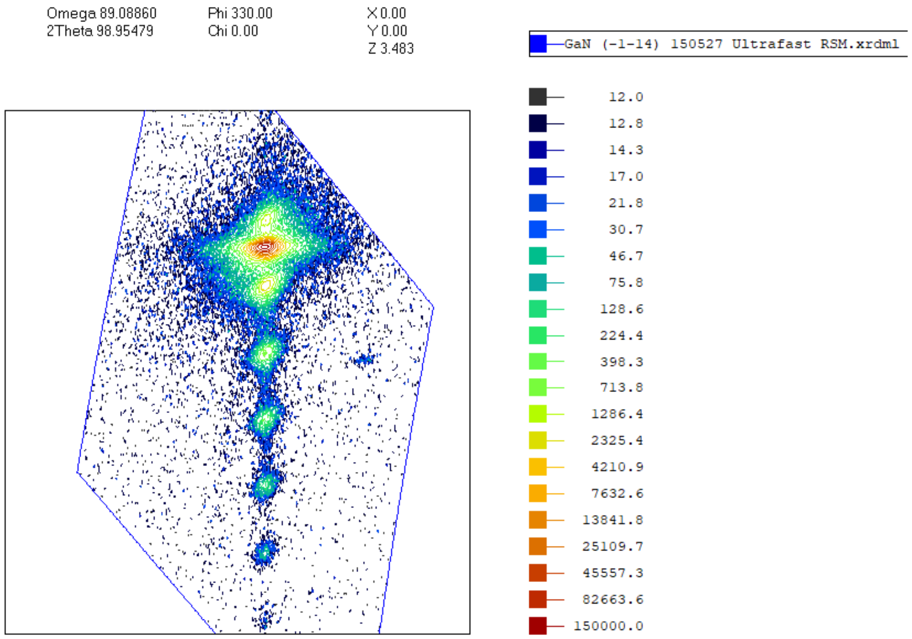


Figure 9. The ultrafast reciprocal space map performed on 150727PL, indicative of strained epitaxial superlattice InGaN layers sandwiched between GaN layers.

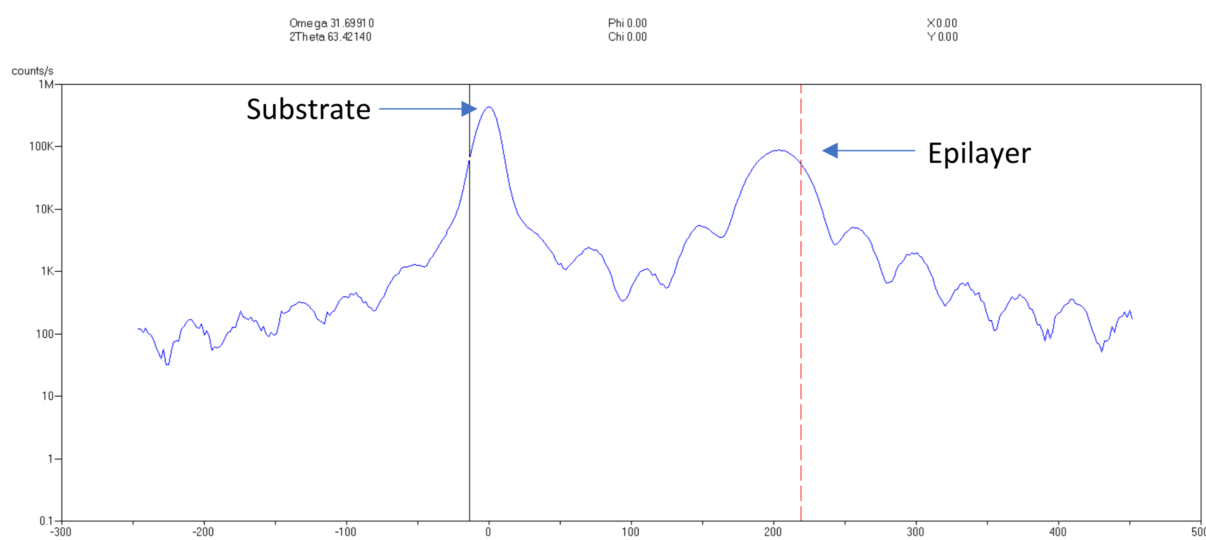
The measurements described above are used to calibrate growth rate and alloy composition for quantum well layers, cladding layers, electron blocking layers, and n-type and p-type GaN layers in a variety of devices grown by Prof. Feezell's group. Knowledge of the growth rate and alloy composition is critical to enable accurately designed optoelectronic and electronic devices. Prof. Feezell's group is using the X-ray diffractometer on a regular basis. The X-ray diffractometer is supporting projects sponsored by Army Research Labs (ARL), Air Force Research Labs (AFRL), Defense Threats Reduction Agency (DTRA), National Science Foundation (NSF), and Advanced Research Projects Agency Energy (ARPA-E).

<u>XRD Measurements of III-As and III-Sb Materials</u>

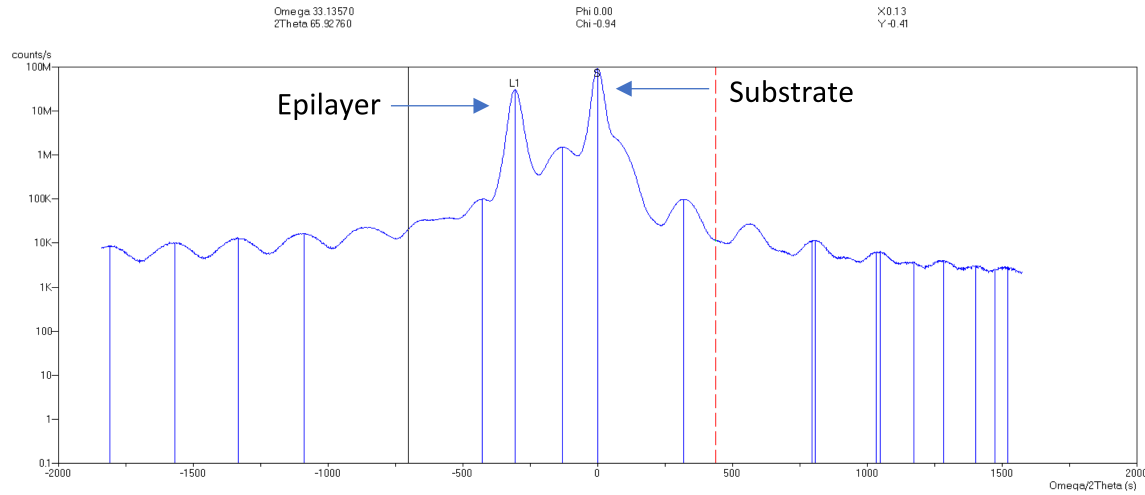
Dr. Ganesh Balakrishnan's group at CHTM uses molecular beam epitaxy (MBE) for thin-film epitaxial growth of group III-arsenide, antimonide, and phosphide semiconductor compounds. We are part of multiple JTO, AFOSR and NSF-funded projects for growth and characterization of a variety of devices including high-power lasers, saturable absorbers, solar cells and detectors. Additionally, we also supply III-V epitaxial material for a number of small businesses, national laboratories and universities. In order to verify the quality of epitaxial material and achieve device specifications, Dr. Balakrishnan's group extensively uses XRD. The new Empyrean XRD system has been instrumental in characterizing our MBE-grown samples. We use XRD to characterize a wide range of epitaxial properties including composition, thickness, superlattice periods, relaxation, wafer uniformity and dislocation densities. Below we point out a few recent results from the Empyrean XRD system:

1) Composition and thickness:

For growths that contain ternary, quarternary, or quinary III-V compounds, XRD is used to verify the exact composition. The compositions of these compounds determine lattice-matching or other device specifications. For example, Figure 10 below shows a symmetric <004> ω-2θ scan for InGaAs grown on InP (a) and AlGaAs grown on GaAs (b). The peak separation between the epilayer and the substrate (at 0) can be used to calculate the exact compositions of the alloys.



(a)



(b)

Figure 10. <004> ω-2θ scan for 0.5 µm InGaAs grown on InP (a) and AlGaAs grown on GaAs (b).

The epilayer thickness can be calculated using the fringe thickness in both cases. Additionally, the PANalytical Epitaxy® software can be used to fit these plots to calculate composition and thicknesses. The calculated results are shown in Figure 11 below for InGaAs grown on InP. (targeted composition: $In_{0.53}Ga_{0.47}As$; targeted thickness: 0.5µm)

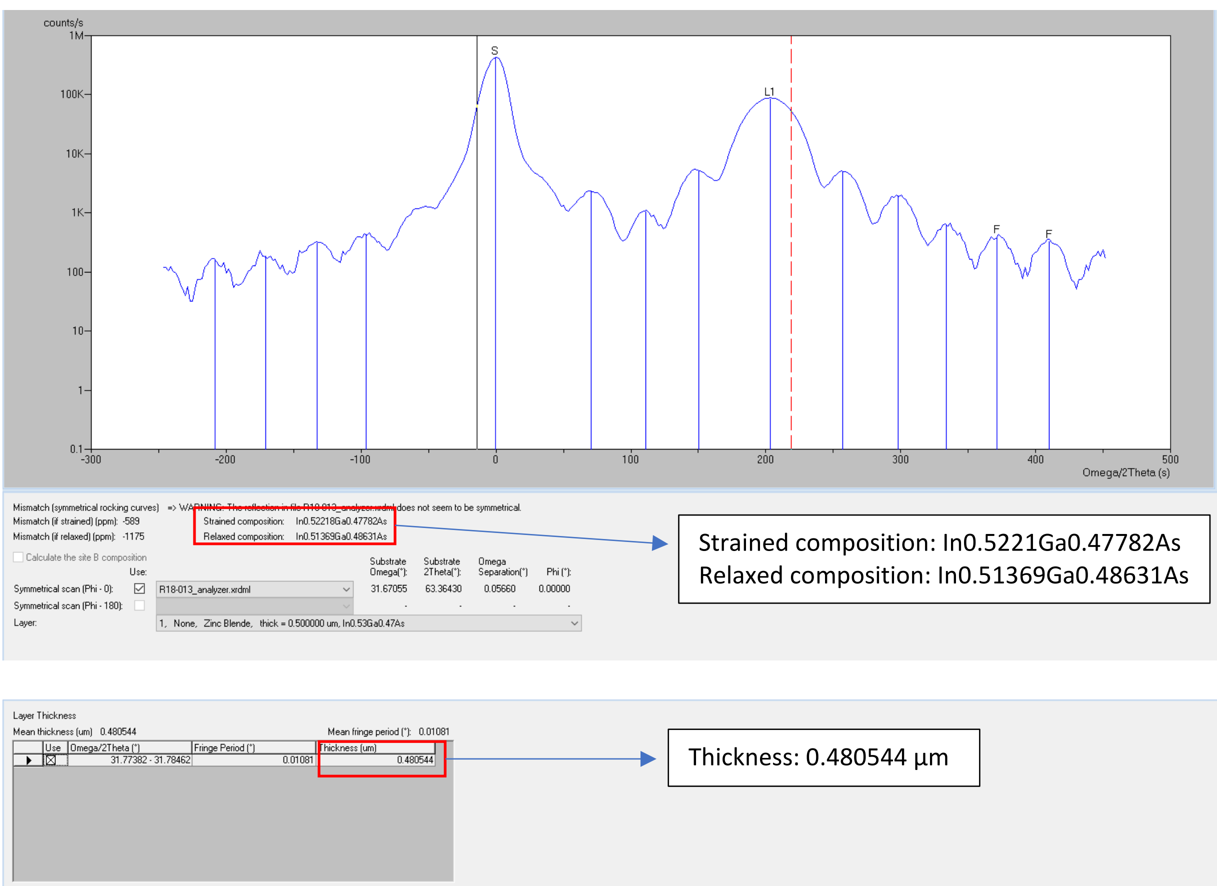


Figure 11: Calculation results on Epitaxy® for InGaAs grown on InP.

2) Relaxation and defects:

The Emyprean XRD is equipped with a 3D PIXcel detector which is capable of doing rapid reciprocal space mapping (RSM) and rocking curve measurements for thin-films. RSMs can be used to calculate relaxation and other structural information. Figure 12 below shows a symmetrical (004) RSM for InGaAs (almost lattice-matched) grown on InP.

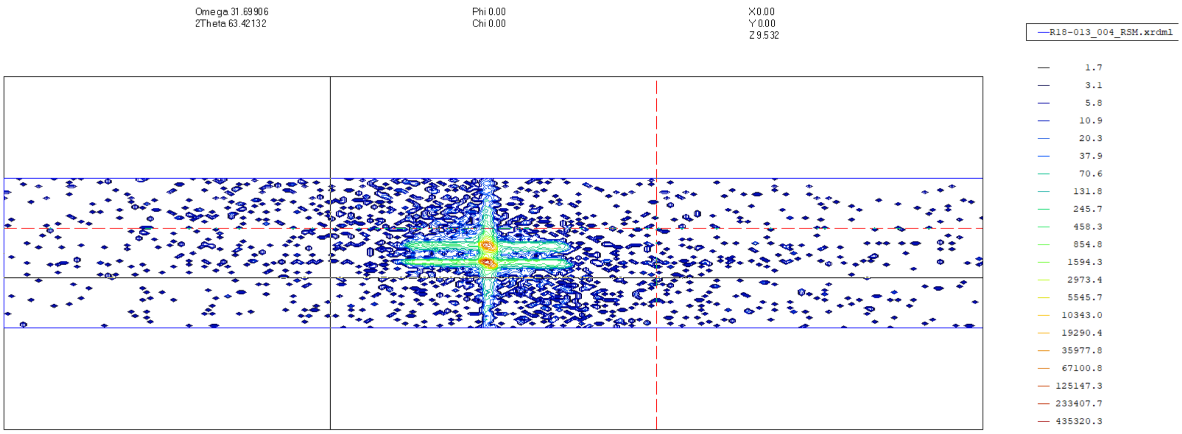


Figure 12: <004> symmetrical RSM for 0.5μm of InGaAs grown on InP.

RSMs are more valuable in figuring out relaxation values in highly mismatched films (not shown here). We can also use rocking curve analysis in mismatched films to calculate threading dislocation densities.

3) Wafer mapping:

The 5-axis stage available on the Emyprean XRD enables wafer mapping for up to 3” diameter areas. This measures the XRD scans at multiple points on the wafer and provides insight into the uniformity of growth and temperature profiles over the sample. Figure 13 below shows an example of a 25-point wafer map for a strained layer superlattice (InAsSb/InAs SLS) grown on GaSb. Here, the superlattice thickness can be calculated from the separation between satellite peaks.

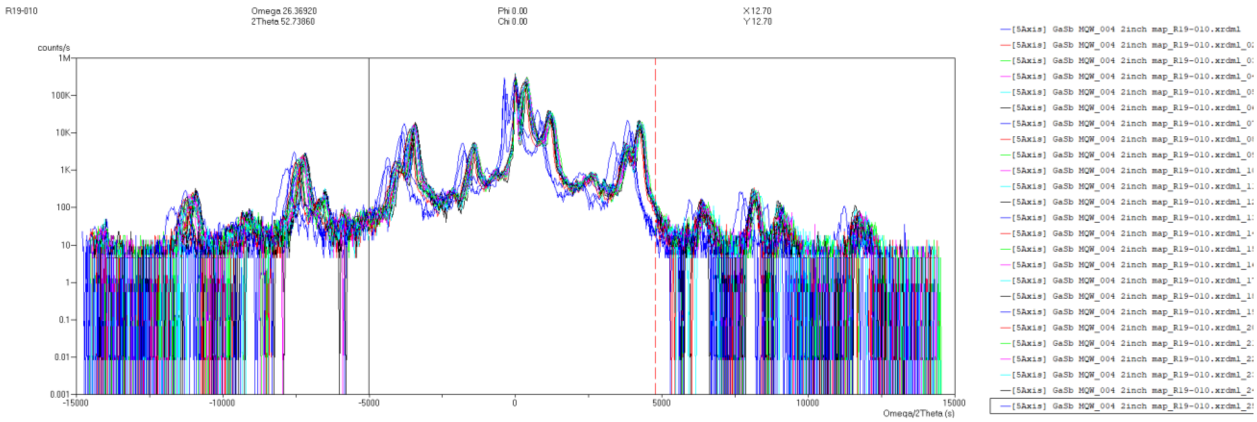


Figure 13: 25-point wafer map of a InAs/InAsSb SLS grown on GaSb.

In the near future, we envision using the XRD for a range of other things including:

- Rocking curve analysis for threading dislocation densities
- X-ray reflectometry (XRR) for measuring interface and surface roughness
- Wafer curvature and defect density measurements

5. Summary

In summary, we have specified, ordered, installed, and qualified a new PANalytical Empyrean X-ray diffractometer at the Center for High Technology Materials. The tool us currently being used to support a variety of DoD project under the supervision of several PIs at CHTM. In the future, we expect the internal user base of the tool to expand greatly and that the tool will also support users from Air Force Research Labs and the commercial sector.