NON-EQUILIBRIUM SYNTHESIS OF SEMICONDUCTOR ALLOYS FOR ENERGY APPLICATIONS

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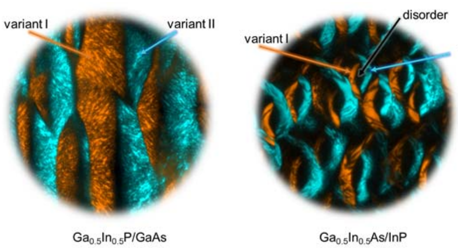
Overview: We are exploring the synthesis under equilibrium/non-equilibrium conditions of semiconductor alloys critical to SSL to impose top-down influence on the formation of atomic-scale microstructures.

I. Introduction

Red and amber LEDs based on ordered/disordered (*o/d*) $Al_xIn_{1-x}P$ confinement structures show excellent power-conversion efficiency compared to current materials. These components are needed for improved color-mixed LEDs.

A. Ordering in lattice-matched III-V alloys

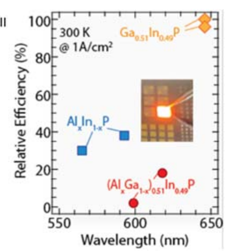
Strongly CuPt-ordered, pseudomorphic GaInP/GaAs [1] and GaInAs/InP [2] have been studied extensively. The most direct evidence of ordering has come from TEM studies.



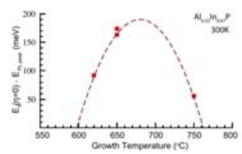
An intricate domain structure is observed in double-variant CuPt-B ordering in GaInP and GaInAs. (Samples courtesy NREL.)

B. Ordered, metamorphic AlInP/GaAs for LEDs

$Al_xIn_{1-x}P$ (x<0.4) also shows ordering and has a direct bandgap that is suitable for LEDs. But growth on GaAs requires metamorphic grades, complicating fabrication. Nonetheless, order/disorder AlInP LEDs have shown promising results.



The bandgap reduction for ordered AlInP is exceptionally large (~180 meV), although the ordering strength is limited by the alloy stochiometry.



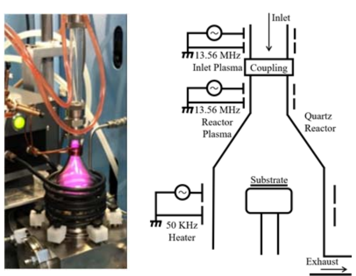
LEDs using lattice-mismatched AlInP show good relative efficiencies, and at shorter wavelengths, compared to lattice-matched GaInP and AlGaInP.

II. Experiment

This study aims to control ordering using non-equilibrium synthesis and characterize ordered/disordered microstructures.

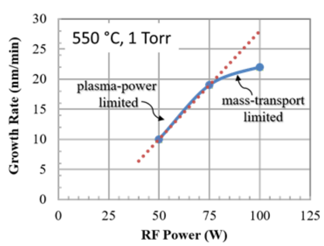
A. Plasma-enhanced MOCVD (PE-MOCVD) crystal growth

Plasma is created by RF excitation at low pressures.



PE-MOCVD growth at SDSMT.

The RF power can be used to activate growth, with other parameters held constant, which could be used for growth of abrupt heterointerfaces, for example.

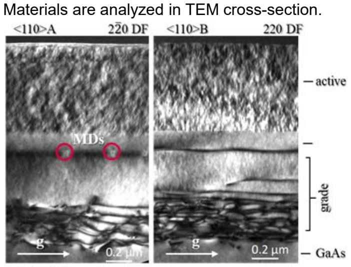


GaAs growth rate vs. RF power using PE-MOCVD.

B. TEM microstructural characterization

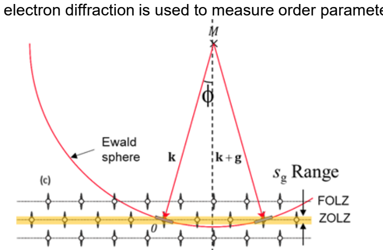
TEM is being used to study ordering, strain relaxation, and compositional inhomogeneity in metamorphic AlInP layers.

Materials are analyzed in TEM cross-section.



Structures grown at MicroLink show good suppression of the threading of dislocations into the LED active region.

Precession electron diffraction is used to measure order parameter.



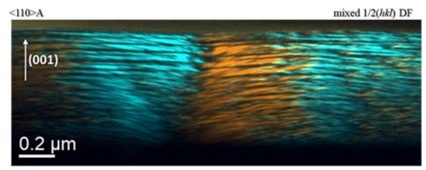
The electron beam is precessed about the optical axis to limit dynamical diffraction effects.

III. Results

Device-quality heterostructures are grown at MicroLink. Despite low defect densities, some challenges remain towards materials optimization.

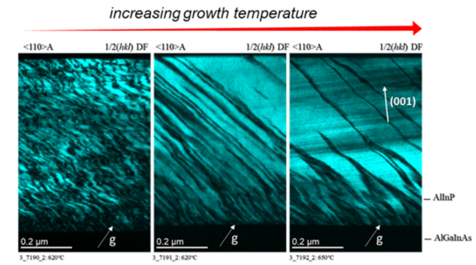
A. Microstructures of metamorphic AlInP

Double-variant ordering appears to be the most promising for devices. However, the ordered domain structure is heavily influenced by composition modulation, which leads to spontaneous *o/d* superlattice formation.



Double-variant ordered, metamorphic AlInP layer showing dark bands that arise from spontaneous composition modulation.

Antiphase boundaries (APBs) are evident in single-variant ordered AlInP. The APB structure varies with growth temperature.

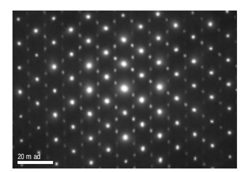


Single-variant ordered AlInP shows APBs. As the phase domain size increases, composition modulation becomes visible

B. Electron-precession diffraction for analysis of ordering

We have measured the order parameter, *S*, in a large collection of samples, using the precession method. We are also studying other diffraction signatures of ordering, such as high-order Laue zone (HOLZ) superstructure spots.

Precession allows measurement of a large number of diffracted intensities that would unavailable using standard selected-area diffraction.

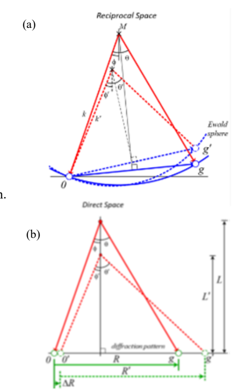


The measured intensities are fit using a MatLab simulation.

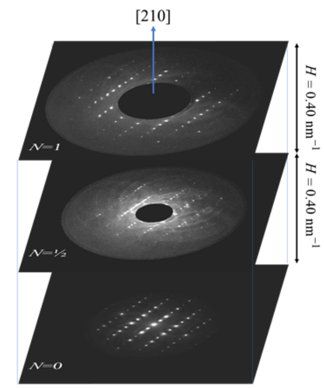
Sample	Tg (°C)	V/III ratio	S_{total} (S_1+S_2)
3_7721_1	620	150	0.27 (0.15+0.12)
3_7722_1	620	225	0.32 (0.15+0.17)
3_7723_1	620	300	0.18 (0.098+0.082)
3_7833_1	650	150	0.14 (0.074+0.065)
3_7834_1	650	225	0.245 (0.234+0.011)
3_7835_1	650	300	0.205 (0.097+0.108)

The order parameter is taken as the sum of order parameters measured for the two variants.

Corrections are made for distortions that arise from optical effects. Without these corrections, the HOLZ spot positions change with beam tilt.



The beam tilt in reciprocal space gives a shift in direct space.



After applying corrections, each precession series can be used to reconstruct HOLZ layers for the crystal.

IV. Conclusions

We are exploring the use of PE-MOCVD to gain greater control of microstructure in metamorphic, ordered AlInP for solid-state lighting. Towards that end, we have gathered extensive information on the challenges met in growing these heterostructures by conventional MOCVD, such as phase separation and incomplete ordering. Precession diffraction provides a way to quantify ordering strength, with few free parameters, and can be applied to electron-diffraction tomography to reconstruct an entire reciprocal-space volume for a crystal under investigation.

References:

[1] T. M. Christian, et al., *J. Appl. Phys.* 114, 74505.
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Acknowledgement:

This work was supported by the U. S. Dept. of Energy-EPSCoR through Award #DE-SC0019430, DOE-EPSCoR State/National Laboratory Partnership.