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

On-going work at NREL addresses order/disorder $Al_xIn_{1-x}P$ confinement structures, which are predicted to surpass the power-conversion efficiency of current materials used for red/amber LEDs as components of color-mixed LEDs.

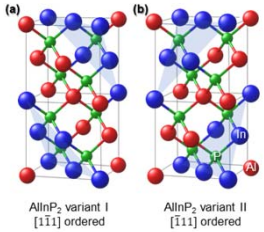

Fig. 1. CuPt-ordered variants in $AlInP_2$.

Strongly CuPt-ordered GaInP/GaAs [1] and GaInAs/InP [2] have been studied extensively. Less information is available on ordered AlInP/GaAs.

Lattice-mismatch for $Al_wIn_{1-w}P$/GaAs:

$$f_{AlInP} = (3.67\%)\cdot(1-w) + (-3.71\%)\cdot w$$

$Al_wIn_{1-w}P$/GaAs is lattice matched for w~0.5, but the bandgap is indirect for w>0.4 [3].

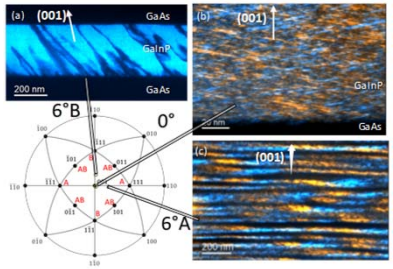

Fig. 2. (001) pole figure and ordered domain structure in $Ga_{0.52}In_{0.48}P$ (a) double-variant ordered/disordered SL; (a) single-variant ordered layer embedded in GaAs [■ variant-I, ■ variant-II, ■ disordered (or GaAs)].

Two ordered variants form during grown on exact (001) and [111]A offcut substrates. One ordered variant dominates for [111]B offcut substrates.

II. Experiment

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

A. Plasma-enhanced MOCVD (PE-MOCVD)

PE-MOCVD allows decomposition of precursors at low temps. [4] Plasma can be created by RF excitation at low pressures.

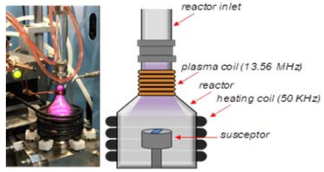

Fig. 3. PE-MOCVD growth at SDSMT: (a) photo; (b) diagram showing reactor inlet, coil for exciting plasma, quartz reactor, coil for heating susceptor, and graphite susceptor.

B. Lattice-mismatched heteroepitaxy

For LEDs, metamorphic GaInAs grades can be used to accommodate the mismatch of direct-gap AlInP compositions.

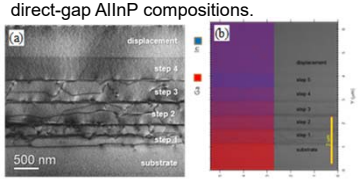

Fig. 4. Metamorphic GaInAs grades with displacement layers: (a) 220 dark-field image; (b) EDX map showing group-III composition.

C. TEM precession diffraction

Precession electron diffraction allows direct retrieval of structure factors for electron crystallography. A Buerger mask can be applied digitally to retain sharpness of the diffraction spots.

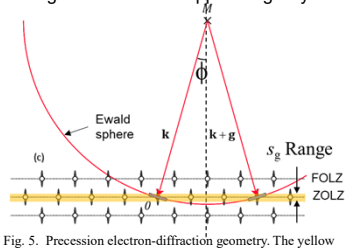

Fig. 5. Precession electron-diffraction geometry. The yellow band indicates a digitally applied Buerger mask.

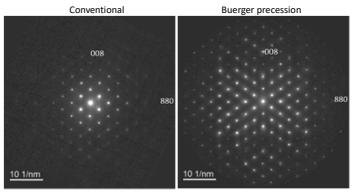

Fig. 6. Selected-area electron-diffraction patterns from Si: (left) conventional method (b) Buerger precession method (ϕ=30 mrad, s_gRange=0.02 1/nm.)

III. Preliminary Results

Initial growth experiments have studied PE-MOCVD to switch ordering on/off. TEM diffraction methods have been developed for order-parameter determination.

A. MOCVD/PE-MOCVD ordered/disordered $GaInP_2$

In early growth runs, we demonstrated the suppression of ordering in GaInP/GaAs by application of plasma.

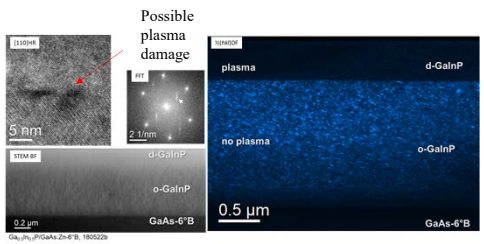

Fig. 7. TEM data from GaInP/GaAs film showing the use of PE-MOCVD to eliminate ordering.

Plasma activation used to eliminate ordering.

B. Epitaxial growth of $AlInP_2$

Further optimization of AlInP growth conditions is needed.

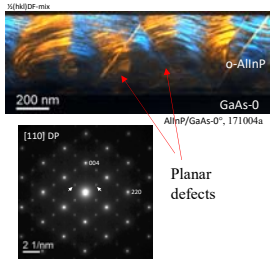

Fig. 8. TEM data from AlInP/GaAs heterostructures. Improvements are needed to grow high-quality AlInP layers. Nonetheless, strong double-variant ordering is obtained.

C. Analysis of TEM precession diffraction patterns

Correct structure factors for these alloys are needed to accurately determine order parameter by diffraction methods. Anion displacements resulting from cation ordering have been shown to have a significant effect. The displacement distances can be computed from the valence-force-field model.

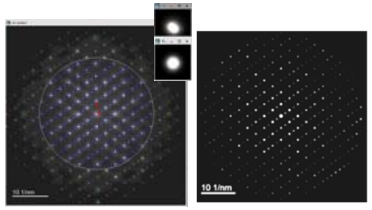

Fig. 9. PE-MOCVD from TMAl on TEM grid: (a) STEM bright-field; (b) SEM; (c) TEM lattice image; (d) electron-diffraction pattern consistent with fcc Al.

Automated measurement of electron-diffraction-spot intensities is used for refinement of simulated patterns.

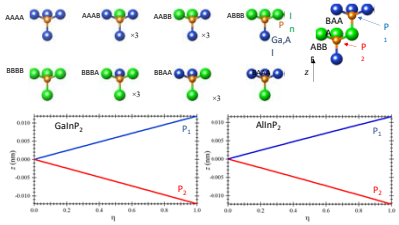

Fig. 10. VFF analysis gives a nearly linear variation of anion displacement with order parameter.

The mean anion displacement can be related to the order parameter η by weighing the displacement for all possible tetrahedral configurations by the probability of each configuration given a global value of η.

IV. Conclusions

We aim to create greater control of ordering, phase separation, and strain relaxation in III-Vs, through the use of non-equilibrium synthesis, for photovoltaic and solid-state lighting applications. Ordered/disordered structures synthesized by MOCVD/PE-MOCVD are currently under investigation by TEM precession diffraction. We intend to expand characterization of these materials using optical spectroscopy and high-resolution X-ray nano-diffraction methods using DOE facilities.

References:
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