

## Semiconductors

### Room 321/322 - Session SC-TuA

#### Compound Semiconductor Growth and Processing

Moderator: P.I. Cohen, University of Minnesota

2:00pm **SC-TuA1 Complex Formation between Magnesocene (MgCp@sub 2@) and NH@sub 3@: Origin of the "Memory Effect", G.T. Wang, J.R. Creighton**, Sandia National Laboratories

Magnesocene (MgCp@sub 2@) is a common Mg precursor for the p-type doping of Group III nitride semiconductor materials. Unfortunately, difficulties remain with controlling the incorporation of Mg during MOCVD film growth, which often exhibits poorly understood memory effects. While the formation of a reaction product between magnesocene and ammonia has been previously speculated, one has never been experimentally isolated or identified. We have spectroscopically observed and identified, for the first time, the adducts formed between magnesocene and ammonia. Density functional theory (DFT) quantum chemistry calculations have also been performed on the system to determine the structures and energetics of the reaction products. It was found that ammonia can form complexes with magnesocene in both 1:1 and 2:1 ratios, i.e. NH@sub 3@:MgCp@sub 2@ and 2NH@sub 3@:MgCp@sub 2@, via NH@sub 3@ attack of the positively charged Mg center of MgCp@sub 2@. Adduct formation is reversible and the 1:1 and 2:1 products can be converted to one another by varying the NH@sub 3@ partial pressure. Both adducts are condensable at room temperature and their formation is the probable origin of the magnesium memory effects that have been observed during MOCVD of III-Nitride materials. Improved understanding of the equilibrium between condensed phase adducts, gas phase adducts, and precursors should allow for reactor and processing adjustments that reduce or eliminate the memory effects. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

2:20pm **SC-TuA2 Real-time Optical Monitoring of Gas Phase Kinetics in InN Vapor Phase Epitaxy at Elevated Pressures, N. Dietz, V. Woods**, Georgia State University

Understanding the kinetics of nucleation and coalescence of heteroepitaxial thin films is a crucial step in controlling a chemical vapor deposition process, since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. The initial nucleation process also defines the film quality during the later stages of film growth. The growth of emerging materials heterostructures such as InN or indium-rich GaIn<sub>1-x</sub>N requires deposition methods operating at high vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition experiments. The extension of chemical vapor deposition (CVD) to elevated pressure is also necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. The here presented research focuses on the base material InN and addresses the real-time optical monitoring of gas phase- and surface chemistry processes during high pressure (100 bar) CVD of InN. The high pressure CVD reactor has integrated optical diagnostics to monitor in real-time gas flow dynamics, gas-phase decomposition kinetics, and the film growth process itself. These experimental data are of crucial importance to provide (a) input parameter for process models and simulation codes, and (b) establish growth parameter sets needed for analysis and control of chemical vapor deposition at elevated pressure. Data are presented for the optical methods of real-time process monitoring to analyze the initial stages of heteroepitaxy and steady-state growth in the different pressure ranges.

2:40pm **SC-TuA3 Chemical Complexities of AlGaInN MOCVD, J.R. Creighton, G.T. Wang, M.E. Coltrin, W.G. Breiland**, Sandia National Laboratories

INVITED

We have used a variety of experimental techniques to investigate possible sources of the parasitic chemical reactions that occur during AlGaInN MOCVD. Growth rates for GaN, AlGaIn, and InGaIn were measured over a wide range of reactor conditions and compared to reactive flow simulations in order to test possible parasitic chemical reaction mechanisms. All of our results indicate that the parasitic chemical reactions require high temperatures and occur in the boundary layer near the

growing surface. These reactions ultimately lead to the formation of nanoparticles, which we have recently observed using in situ laser light scattering. Thermophoresis keeps the nanoparticles from reaching the surface, so the material tied-up in nanoparticles cannot participate in the thin film deposition process. In the case of AlN, the particle size was determined to be 48 nm, and the particle density was in the range of 10<sup>10</sup> to 10<sup>11</sup> cm<sup>-3</sup>. At these densities a significant fraction (20% or more) of the input Al is converted into nanoparticles. We have also directly examined precursor chemistry in the 30-300°C range using in situ FTIR. All three commonly used group-III precursors form adducts with ammonia, but this reaction is entirely reversible for trimethylgallium and trimethylindium. In this temperature range only trimethylaluminum reacts irreversibly with ammonia, evolving methane and forming the expected (CH<sub>3</sub>)<sub>3</sub>Al-NH<sub>3</sub> product. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.)

3:20pm **SC-TuA5 Ab initio Prediction of the Gas-Phase Precursors for AlN Sublimation Growth@footnote 1@, Y. Li, D.W. Brenner**, North Carolina State University

A free energy model using input from ab initio calculations is used to predict the concentration and saturation state (with respect to the growing crystal) of 16 Al@sub n@N@sub m@ species under conditions typical of AlN sublimation growth. The calculations predict that Al and N@sub 2@ are the dominant species, in agreement with available experimental measurements. However, our calculations predict that the N@sub 2@ molecule is undersaturated and therefore is not likely a growth precursor. Instead, our model predicts that Al@sub 2@N, Al@sub 3@N, and Al@sub 4@N, while in much smaller concentrations than N@sub 4@, are supersaturated and therefore are the source of nitrogen to the growing crystal. This prediction is in stark contrast to assumptions made in prior growth models, and may help explain why very small sticking coefficients had to be assumed for N@sub 2@ in prior modeling studies to match experimental growth rates. @FootnoteText@ @footnote 1@ Funded by the Office of Naval Research through MURI contract N00014-01-1-0302.

3:40pm **SC-TuA6 Reflectance Interferometry During III-V Nitride Growth, Much More than a Growth Rate Monitor, C.R. Eddy, Jr., R.T. Holm, R.L. Henry, J.C. Culbertson**, Naval Research Laboratory

The application of laser interferometry to the monitoring of wide bandgap semiconductor nitride growth has expanded considerably in recent years. At present, a rapidly growing number of III-V nitride growth systems, MBE and MOCVD alike, employ some version of the technique to monitor growth rates. But growth rate monitoring makes use of a small subset of the useful information the technique affords. In this paper, we discuss the application and interpretation of laser interferometry in the MOCVD growth of gallium nitride and aluminum gallium nitride thin films that employ AlN nucleation layers. We employ a 543.5 nm HeNe laser, lock-in amplifier, and ratiometer (to normalize out laser fluctuations) to monitor growth in a simple vertical tube reactor that is rf heated. In this application, the technique has proven useful as a monitor of not only the thickness, but also the quality of the material grown. Further, the technique can help identify drifts in the process from run to run and within a given run. We will comment on the usefulness of the technique in monitoring surface and interface roughness, film stoichiometry (for ternaries) and thickness uniformity. Finally, we will highlight specific examples where the technique has proven useful in troubleshooting growth irregularities.

4:00pm **SC-TuA7 Real-time Diagnostics of OMCVD Epitaxy with an Integrated Rotating-compensator/Rotating-sample Polarimeter, K.F. Flock, S.J. Kim, M. Asar, D.E. Aspnes**, North Carolina State University

We obtain new insights on III-V epitaxy and heteroepitaxy with a rotating-compensator/rotating-sample ellipsometer/polarimeter for diagnostics and control of organometallic chemical vapor deposition (OMCVD). The system obtains up to 5 1024-pixel spectra per second from 230 to 840 nm, allowing the p- and s-polarized reflectances and the complex reflectance ratio to be determined from the dc, 2@omega@t, and 4@omega@t components of the transmitted intensity. In addition the optical anisotropy follows from the 10@omega@t component, and alignment parameters from the @omega@t and 3@omega@t components, providing the maximum amount of sample information obtainable from optical data over the available spectral range. Rotating-compensator operation eliminates the serious shortcoming of older, rotating-analyzer and -polarizer designs associated with the loss of phase information when the phases of the complex reflectance ratios are near 0 or 180 degrees. The anisotropy data

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returns surface-chemical information through their spectral dependences. We relate these non-normal-incidence anisotropy spectra to RDS data obtained at normal incidence by numerical analysis of the system transfer function. This combination of capabilities allows OMCVD growth processes to be studied in greater detail, especially when combined with a recently developed algorithm for simultaneously determining the thickness and dielectric function of films in the Å thickness range. For example we follow the growth of nm thick layers of Ga on (001)GaAs substrates, and track the connection between surface reconstruction and film growth. The relatively short data-acquisition time also allows us to follow growth under highly nonequilibrium "burst" conditions, which appear to be necessary to establish uniform layers of some III-V materials on chemically different substrates.

**4:20pm SC-TuA8 GaN Nucleation Layer Evolution on Sapphire, D.D. Koleske, J.J. Figiel, M.E. Coltrin, A.A. Allerman, K.C. Cross, C.C. Mitchell, M.J. Russell, Sandia National Laboratories**

For UV, blue, green and eventually white light LEDs, GaN is most often grown on low-cost sapphire substrates. To improve the GaN epitaxial quality and reduce dislocations, a low temperature GaN nucleation layer (NL) is first deposited prior to high temperature (T) GaN growth. Despite the progress in the MOCVD growth of GaN, details of the NL and high temperature growth evolution are not well understood. In this presentation the GaN NL evolution as it is annealed from low to high T will be investigated using optical reflectance and AFM measurements of stopped growth runs. During the anneal, the NL morphology changes from a continuous 30 nm thick layer composed of 20 nm sized grains to a discontinuous layer that contains large grains approaching 500 nm in width to 180 nm in height. Further annealing of the NL causes a decrease in the size of these large grains. Since only NH@sub 3@ and H@sub 2@ are flowing during the NL annealing, the growth of the large GaN grains is explained by partial decomposition of the NL@footnote 1@ and redeposition of the Ga atoms on the growing grains through a gas phase desorption and readsorption mechanism rather than a surface diffusion mechanism. Evidence for this mechanism is obtained from the height-height correlation functions@footnote 2@ measured from the AFM images of the annealed nucleation layers as well as direct measurements of the GaN NL decomposition kinetics using optical reflectance@footnote 1@. Based on details of the decomposition kinetics and NL roughening, fits to the optical reflectance waveform will be presented. Contributions of the surface diffusion, bulk diffusion, and desorption/readsorption mechanisms to the overall GaN NL morphology will also be discussed along with guidance as to when the NL achieves optimal morphology for further GaN growth at high T. @FootnoteText@ @footnote 1@D. D. Koleske, et al., Appl. Phys. Lett 82, 1170 (2003). @footnote 2@Tong and Williams, Annu. Rev. Phys. Chem. 45, 401 (1994).

**4:40pm SC-TuA9 Investigations of Plasma Etching and Contact Processing on AlGaN Alloys Containing 0 to 50% Al, K.H.A. Bogart, A.J. Fischer, M.H. Crawford, D.D. Koleske, A.A. Allerman, R.J. Shul, D.E. Peebles, Sandia National Laboratories; I. Adesida, University of Illinois at Urbana Champaign; S. Jones, Sandia National Laboratories; D. Selvanathan, University of Illinois at Urbana Champaign; K.W. Fullmer, F. Jalali, Sandia National Laboratories**

AlGaN alloys are suitable for a variety of light emitting devices including LEDs and laser diodes as well as electronic devices such as high electron mobility transistors. Deep UV (<300 nm) LEDs have important applications as UV light sources for chemical-biological sensors, non-line-of-sight optical communications, and UV curing. Optical performance near 300 nm requires Al stoichiometry of 0.25 to 0.5, or more. The difficulty of forming high-quality ohmic contacts to n-type AlGaN materials increases with increasing percent Al due to the difficulty in effectively doping high %Al AlGaN. We performed a series of experiments to study the effects of several contact processing steps on the resultant material and device characteristics for AlGaN alloys with the percent Al ranging from 0 to 50%. For example, during LED device processing, plasma etching of the p-type material and the active material is done in order to access the underlying-n-type material for contact formation. We determined the effect of percent Al in AlGaN alloys on the surface roughness, etching rates, and resist selectivity, as a function of plasma etch method (ICP vs. RIE) and etching parameters such as substrate bias voltage. We also varied the pre-metallization surface treatments using dry plasma etching and wet chemical (BOE and HCl) etching. We evaporated metal contacts of either TiAlNiAu or TiAlMoAu and determined metal adhesion and specific contact resistance as a function of percent Al (0 to 50%). Annealing studies were also performed on materials after the contact deposition. Surface analysis

by XPS, performed before and after plasma etching showed striking stoichiometric differences between the as-grown alloy and the etched surface. The composition of the metal-AlGaN interface was also investigated by XPS. The results from all of these studies will be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

**5:00pm SC-TuA10 Morphological Evolution of GaAs Surface during Damage-free Etching, S.H. Lee, H.P. Gillis, UCLA**

GaAs was etched in Cl@sub 2@/H@sub 2@/Ar plasmas both with ion and electron enhancement. Since bombardment with higher energy ions induces structural damage, electron bombardment and low-energy ion bombardment were used to prevent etch-induced damage. Damage was checked with XRD which shows peak broadening after etching when structural damage is induced on a surface or in a sub-surface layer. XRD peak broadening was seen in high-energy ion bombardment, but not in electron or low-energy ion bombardment. In order to study the competition between the thermal reaction and the electron enhanced reaction, temperature and bias for samples were varied as etching parameters. SEM images and AFM images were obtained and compared for the samples etched at different conditions. Under the damage-free etching conditions morphology development was followed by measuring etch rate, surface roughness, skewness, and autocorrelation function (ACF) for surface roughness. The evolution of ACF was interpreted by scaling theory. Chemical and bombardment effects were explained based on the scaling theory. Morphological evolution steps and a key effect that determines surface morphology during etching were revealed from this study, and a way to control surface smoothness during dry etching was found.

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