Friday Morning, November 14, 2014

Electronic Materials and Processing
Room: 311 - Session EM+EN-FrM

Nitrides for LED and PV Device Applications
Moderator: Nikolaus Dietz, Georgia State University

9:00am **EM+EN-FrM3 The Capricious Effect of Heating on the Surface Photovoltage in Si-doped GaN**, ***Joy McNamara***, *K.L. Phumisithikul, A.A. Baski, M.A. Reshchikov*, Virginia Commonwealth University

Surface photovoltage (SPV) studies on gallium nitride (GaN) thin films have recently revealed much information, including the band bending at the surface, the effect of polarity on the surface potential, the role of the surface oxide layer, and many other surface related behaviors. By using the Kelvin probe method, the surface potential of GaN can be measured in respect to a vibrating metal probe. To investigate the SPV behavior of both n- and p-type GaN, several experimental conditions have been varied, such as ambient or temperature. It is expected from a thermionic model that the surface band bending decreases immediately under ultraviolet (UV) illumination with the intensity used in these measurements. This results in the production of an immediate increase in the SPV signal as measured by the Kelvin probe. In recent studies on GaN thin films grown by metal organic chemical vapor deposition (MOCVD) and doped with silicon (concentration of ~10^{19} cm^{-3}), we observed an effect of heating on the transient SPV behavior due to the history of sample preparation. For the first group of samples, a very fast rise of the SPV signal by 0.7 eV was observed at room temperature under UV illumination in vacuum, after the samples were initially exposed to air. However, after heating these samples to 600 K in vacuum before taking measurements at room temperature, the fast SPV component decreased to 0.2 eV, while a slow, logarithmic-in-time increase was observed for longer times of UV exposure, with a maximum SPV signal of only 0.4 eV after 30 min. For the second group of samples, the heating in vacuum caused the magnitude of the initial fast SPV in vacuum to be much smaller (0.7 eV after air exposure and 0.3 eV after heating), but without a slow, logarithmic-in-time increase. The SPV behavior could be reversed by UV illumination in air at room temperature. Interestingly, similar SPV behavior has also been observed in ZnO films. The reversible heating effect is preliminarily explained by assuming that the presence of an oxide layer either inhibits or allows the transfer of UV-induced charge carriers between the bulk and surface states, depending on the conditions of the measurement.

9:20am **EM+EN-FrM4 Atomic Layer Deposition of III-Nitride Alloys using Hollow-Cathode Plasma Source for Post-CMOS Processing and 3D Integration**, *C. Ozgit-Akgun, A. Haider,* ***AliKemal Okyay***, *N. Biyikli*, Bilkent University, Turkey

Plasma-assisted atomic layer deposition (PA-ALD) is a cyclic, low-temperature thin film deposition method, in which the substrate surface is exposed to sequential pulses of precursor molecules and plasma species separated by evacuation and/or purging periods. When compared to other techniques, ALD stands out with its self-limiting growth mechanism, which enables the deposition of highly uniform and conformal thin films with sub-angstrom thickness control. These features make PA-ALD a promising and alternative technique for the low-temperature deposition of III-nitrides and their alloys in post-CMOS processing and 3D integration technology.

In our previous reports on the PA-ALD of polycrystalline wurtzite AlN thin films at temperatures ranging from 100-500 °C using trimethlyaluminum as the Al precursor, films deposited at temperatures within the ALD window (100–200 °C for both NH_3 and N_2/H_2 processes) were C-free and had relatively low O concentrations (<3 at.%). Our initial efforts for depositing GaN thin films, however, resulted in amorphous thin films with high O concentrations (~20 at.%). Following experiments revealed the source of this O contamination as the quartz tube of the inductively coupled RF-plasma source itself. In view of these circumstances, the choice of N-containing plasma gas (N_2, N_2/H_2 or NH_3) determined the severity of O incorporation into the deposited AlN and GaN thin films.As an effort to completely avoid this contamination problem, we integrated a stainless steel hollow-cathode plasma (HCP) source to the ALD system, and thereby reported on hollow cathode PA-ALD (HCPA-ALD) of nanocrystalline AlN and GaN thin films with low impurity concentrations at 200 °C using trimethylmetal precursors.Within the scope of the same study, $Al_xGa_{1-x}N$ thin films were also deposited via digital alloying, where alloy composition was determined by the relative number of AlN and GaN subcycles in the main HCPA-ALD cycle.

In this presentation, we will review our recent efforts on the development of low-temperature HCPA-ALD processes for III-nitride alloys including GaN, InN, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$ thin films. In-detail materials characterization results including structural, optical and electrical properties as well as potential device architectures for post-CMOS processing and 3D integration will be presented and discussed.

9:40am **EM+EN-FrM5 Development of Nitride Nanorod Light-emitting Diode Array**, *C.G. Tu, C.H. Liao, Y.F. Yao, C.Y. Su, H.S. Chen, W.H. Chen, C. Hsieh, H.T. Chen, Y.W. Kiang,* ***Chih-Chung Yang***, National Taiwan University, Taiwan, Republic of China **INVITED**

With the nano-imprint lithography and the pulsed growth mode of metalorganic chemical vapor deposition, a regularly-patterned, c-axis nitride nanorod (NR) light-emitting diode (LED) array of uniform geometry with m-plane core-shell InGaN/GaN quantum wells (QWs) is formed. To grow an NR with uniform cross-sectional size, in the pulsed growth mode, the sources of groups III and V are switched on and off alternatively with fixed supply durations. By growing a p-i-n core-shell structure, an InGaN/GaN QW NR LED array can be fabricated by depositing a conformal layer of GaZnO on the NRs for serving as the transparent conductor. The electrical property of such an LED array is comparable with that of a conventional planar LED. Besides, by varying the supply duration of group III source (TMGa) in the pulsed growth process, the NR cross section can be tapered for growing another section of NR of a different cross-sectional size. Based on this growth technique, a multiple-section GaN NR of changing cross-sectional size can be obtained. When InGaN/GaN QWs are deposited on the sidewalls of the NR, the indium contents and QW thicknesses are different in different sections of different cross-sectional sizes due to different strain relaxation conditions. In this situation, the emission wavelengths of the QWs from different sections are different, leading to the multiple-color emission of such an NR array. Such an emission behavior can be used for fabricating a phosphor-free white-light LED.

10:40am **EM+EN-FrM8 Trends in Production Scale MOCVD Equipment for Nitride Semiconductors**, ***Alexander Gurary***, Veeco Instruments, Inc. **INVITED**

Metalorganic Chemical Vapor Deposition (MOCVD) is a technology of choice for large scale production of GaN based LED and Power Electronic devices. For the last 20 years MOCVD equipment evolved from small R&D oriented deposition systems (three 50 mm wafers per run) to large industrial cluster type systems (two hundred sixteen 50 mm wafers per run) with very sophisticated in-situ devices and process control. Evolution of the production scale MOCVD equipment is driven by one major goal – Cost of Ownership (CoO) reduction. Industry is achieving this goal utilizing several trends:

Migration from R&D to production requirements. GaN MOCVD systems started as an R&D tool. Further development of these systems is the path from universality and flexibility typical for R&D tools to stability and simplicity required for production environment.

Increasing batch size. This is the most obvious way to improve CoO as the cost to manufacture system with two times more wafers per run is less than the factor of two. All major MOCVD equipment companies follow this trend and release new larger batch systems every 3-5 years. One of the most important questions for scaling up is the limit of this trend.

Move from the single reactor system to the cluster and increase level of automation. Majority of modern MOCVD systems migrated from the single reactor to the cluster type multi-reactor design with central loading module and wafer carrier transfer robot.

Increasing role of the in-situ devices for wafer parameters measurement and control. Evolution of in-situ devices for production system includes the following sequence: thermocouple - conventional pyrometer – reflectometer - emissivity compensated pyrometer - deflectometer (wafer bow measurements). There is also a trend for more sophisticated control methods that move from PID to predictive and model based algorithms.

Increased wafer carrier complexity. The wafer carrier is a unique component of MOCVD system that to a large degree defines system yield. Complexity of the wafer carriers is constantly increasing with the goal to improve deposition uniformity. Wafer carriers are a subject of majority MOCVD equipment patents.

Increased role of process modeling. Troubleshooting and process optimization in production environment exclude “trial and error” approach and require good computational models for flow dynamic and process chemistry that are fine-tuned based on experimental data.

In this presentation we will describe above trends in detail and make an attempt to predict next steps in the development of the equipment for large scale production of GaN based materials.

11:20am **EM+EN-FrM10 Growth of GaN on Sapphire, Si (111), and Ge/Si (111) using a Pulsed Electron Beam Deposition (PED) Process**, ***Nazmul Arefin***, University of Oklahoma, *M.H. Kane*, Texas A&M University, *K. Hossain*, Amethyst Research Inc, *B.N. Pritchett*, Oklahoma Geological Survey, *M.B. Johnson*, *P.J. McCann*, University of Oklahoma

This presentation will describe results recently obtained with pulsed electron beam deposition (PED) of GaN on sapphire, silicon (111), and 2 nm germanium coated silicon (111) substrates. The PED technique is potentially useful for growth of III-nitrides at lower substrate temperatures, a capability that can allow use of new buffer layer materials, introduction of chemically dissimilar lattice-matched materials, and help solve wafer bowing and cracking problems during growth. The introduction of this technique could lead to improvements in device quality and fabrication of vertical LED structures. In this study, GaN was deposited on sapphire at a substrate temperature of 750°C, and on silicon (111) and Ge/Si (111) at 600°C in a UHP N_2 (15 mTorr) environment (without any surface pre-treatment such as pre-nitridation). A high power electron gun pulse (Neocera, Inc) was used to ablate the GaN target (1" dia. x 0.250" thick, 99.99% pure) stationed at 5 cm vertical distance from the substrate. The electron pulses were generated at 15KV, 0.3 J/pulse at 1 Hz for initial few nm of growth, and then increase to a 3 Hz pulse rate. Scanning Electron Microcopy (SEM), X-ray Diffraction (XRD), Rutherford backscattering, and optical absorption characterization were performed. SEM imaging confirms a rough surface morphology with the presence of 30 nm to 300 nm scaled GaN crystallites (for the GaN/Sapphire sample) while smaller but more coalesced crystallites of 30-50 nm size is observed for GaN/Si (111) and GaN/Ge/Si (111) samples. The average film thickness is 350 nm for the samples, yielding a growth rate of 0.16 angstrom/pulse. From SEM, it appeared that high aspect ratio filament structures have grown over the crystallites. XRD θ–2θ scans from $2\theta = 0°$ to $2\theta = 70°$ on the GaN on sapphire showed only two other peaks, besides the peaks from the sapphire, near $2\theta = 34.6°$. The peaks near $2\theta = 34.6°$ consist of a stronger peak at 34.668° and a much weaker peak at 36.903°. These peaks correspond to the (0002) and (10-11) orientations for GaN, respectively. XRD θ–2θ scans from $2\theta = 0°$ to $2\theta = 70°$ on the GaN on Si (111) and GaN on Ge/Si (111) samples show presence of only polar GaN (0002) peak at 34.7° besides the Si (111) peak at $2\theta = 28.5°$. The XRD results clearly show that the deposited GaN material is not polycrystalline. Optical absorption spectroscopy over a 1.2 eV to 6.2 eV spectral range, for the GaN/Sapphire sample, showed an abrupt absorption edge at 3.4 eV, a clear indication of interband transitions in binary GaN. These results confirm that our PED-grown GaN is highly *c*-axis oriented and suitable for the initial growth of GaN on various substrate materials.

11:40am **EM+EN-FrM11 Growth Template Impact on the Properties of InN Epilayers Grown by High-Pressure CVD**, ***Sampath Gamage***, *M.K.I. Senevirathna*, Georgia State University, *H. Babar*, *I.T. Ferguson*, University of North Carolina at Charlotte, *R. Collazo*, North Carolina State University, *N. Dietz*, Georgia State University

The unique optical and electrical properties of InN and related ternary InGaN alloys make the material system attractive for various optoelectronic device applications, including but not limited to high-speed electronics, photovoltaic solar cells, or light emitting devices. Even though progress has been made in establishing the base properties of the binaries InN and GaN, the growth of high-quality InN and indium-rich ternary InGaN epilayers and heterotructures is an open challenge. In previous work, we demonstrated the stabilization of InN and InGaN epilayers utilizing superatmospheric MOCVD (also denoted as HPCVD) to suppress the decomposition at higher growth temperatures.

In this contribution, we explored the influence of the growth templates (e.g. sapphire substrates, micrometer-scale patterned AlN/sapphire templates, and/or patterned GaN/AlN/sapphire) on the properties of bulk InN epilayers, keeping the reactor pressure constant at 8bar (15bar) as well as the III/V precursor ratio. The growth temperature was optimized in the range of 800°C to 900°C based on Raman E_2(high) mode evolution. The various templates are assumed to introduce different strain fields during the initial nucleation process, affecting the extended defect generation and propagation processes. To assess this effect on the bulk properties of thick InN epilayers, Raman spectroscopy [e.g. E_2(high) and A_1(LO) mode analysis], XRD rocking and ω-2θ scans and photoluminescence (PL) spectroscopy where performed to analyze the crystallinity as well as the extended defect and point defect densities in these layers. The free carrier concentrations in these epilayers and the mobility was determined by FTIR spectra analysis as well as Raman A_1(LO) fitting.

Authors Index

Bold page numbers indicate the presenter