Plasma-Enhanced Atomic Layer Deposition of
III-Nitride Thin Films

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III-nitride compound semiconductors and their alloys have emerged as promising materials for a wide range of electronic and optoelectronic device applications. Although they possess very unique material properties individually, members of the III-nitride family with wurtzite crystal structure also exhibit direct band gaps, which cover a wide range with values of 6.2, 3.4, and 0.64 eV for AlN, GaN, and InN, respectively.[1] In this respect, ternary ($Al_xGa_{1-x}N$, $Al_xIn_{1-x}N$, $In_xGa_{1-x}N$) and quaternary alloys ($Al_xGa_yIn_{1-x-y}N$) of this family are particularly important since their bandgaps can easily be tuned by adjusting the alloy composition. With this motivation, III-nitride semiconductors and their alloys have been processed in the form of thin films and used for a variety of critical applications including UV optoelectronics (blue/violet light sources, UV/visible/solar-blind photodetectors), high-power and high-frequency electronics (field-effect transistors, high-electron mobility transistors), active and insulating layers in various devices such as photovoltaic solar cells and thin film transistors, chemical gas sensors, surface acoustic wave devices, and piezoelectric transducers.

Although high quality III-nitride thin films can be grown at high temperatures (> 1000 °C) with significant rates, deposition of these films on temperature-sensitive device layers and substrates (e.g., CMOS wafers, low-temperature compatible glass, flexible polymeric substrates) necessitates the adaptation of low-temperature methods such as atomic layer deposition (ALD). ALD is a special type of chemical vapor deposition, in which the substrate surface is exposed to sequential pulses of two or more precursors separated by purging periods. When compared to other low-temperature thin film deposition techniques, ALD stands out with its self-limiting growth mechanism, which enables the deposition of highly conformal thin films with sub-nanometer thickness control. Moreover, ternary or quaternary alloys can be deposited easily by ALD, where film composition is digitally controlled by the relative number of AlN, GaN, or InN sub-cycles. In this presentation, we will review our previous and current efforts on the development of plasma-enhanced ALD (PEALD) processes for III-nitrides together with the properties of resulting thin films.

It has been already shown that the thermal ALD of AlN using trimethylaluminum ($AlMe_3$) and ammonia ($NH_3$) is not possible since these two precursors react at temperatures where $AlMe_3$ self-decomposition takes place.[2] Therefore we lowered the deposition temperatures by activating $NH_3$ or $N_2/H_2$ through remote plasma and deposited polycrystalline wurtzite AlN thin films at temperatures ranging from 100-500 °C.[3] Deposition parameters were optimized for these processes to achieve true ALD conditions. ALD temperature windows were observed between 100-200 °C for both processes. Films deposited at 185 °C were carbon-free and had low oxygen concentrations (< 3 at.%) although 5N-purity $NH_3$, $N_2$, and $H_2$ gases were used without any further purification. Furthermore, these films were extremely smooth and showed good optical and electrical characteristics. We also demonstrated the conformality of $AlMe_3$-$NH_3$ plasma

process by fabricating AlN hollow nanofibers using electrospun Nylon 6,6 nanofibers as sacrificial templates.[4] Such high surface area AlN hollow nanofibers might potentially be used in high-temperature ambient chemical sensing applications.

Our initial efforts on depositing GaN thin films using trimethylgallium ($GaMe_3$) or triethylgallium ($GaEt_3$) with $NH_3$ plasma resulted in amorphous thin films with high oxygen concentrations (~20 at.%).[5] InN trials were even worse, trimethylindium ($InMe_3$)-$NH_3$ plasma and cyclopentadienylindium (CpIn)-$NH_3$ plasma processes both exhibited very low deposition rates and the resulting films had very high oxygen concentrations. Several experiments were carried out in order to determine the source of oxygen present in the films, and the most probable source was presumed as the O-containing impurities in $NH_3$ gas. However, this argument has failed when the same GaN and InN depositions were repeated with the purified process gases. The true source of oxygen contamination was found to result from the quartz tube of plasma source. Such plasma related oxygen contamination was also reported for GaN thin films grown by remote plasma enhanced chemical vapor deposition.[6]

When $N_2$ plasma was used instead of the $NH_3$ plasma, O concentration of GaN thin film deposited using $GaMe_3$ decreased to 4.5 at.%, whereas its C concentration increased to 9.1 at.%. We were able to deposit polycrystalline wurtzite GaN thin films with low O and C concentrations (4.7 and 4.2 at.%, respectively) at 190 °C by introducing 20 sccm $H_2$ in addition to 50 sccm $N_2$ during the third quarter of the plasma duration. When same approach was followed for the deposition of AlN using $AlMe_3$, O concentration of the film increased tremendously (i.e. ~47 at.%). This result suggests that in the presence of plasma related O contamination every precursor reacts differently with different types of N-containing plasma. In light of the foregoing, we decided to consider some alternative solutions including some modifications in the plasma source itself as well as search for alternative precursor materials. We will present our initial results within the context of this talk.

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