Deposition of thin layers containing Ga, C and N by sequential pulses of Trimethylgallium and Ammonia

Gallium nitride (GaN) is a semiconductor with broad applications in the (opto-)electronic industry. State-of-the-art fabrication of GaN demands a nanometer-level control over layer thickness, which can be achieved with atomic layer deposition (ALD). Introducing carbon (C) into GaN layers, similar to introducing C into BN [1] or as a dopant in GaN [2], can facilitate control over material properties such as the band-gap and resistivity, respectively. In this work, we report on our results obtained from thermal deposition of layers, containing varying concentration of gallium (Ga), carbon (C) and nitrogen (N), from trimethylgallium (TMG) and ammonia (NH₃) precursors. The precursors were sequentially introduced in a pulsed mode, i.e., without mixing them.

The layers of 6 - 16 nm in thickness, were deposited in a home-built reactor, between temperatures of 400 – 600 °C and pressure of 0.02 mbar, on 4-inch Si(111) wafers. Growth was monitored in-situ with spectroscopic ellipsometry (SE). Ex-situ characterization was performed with X-ray photoelectron spectroscopy (XPS) for the layer composition, grazing incidence X-ray diffraction (GIXRD) for crystallinity, and scanning-electron microscopy (SEM) for thickness.

Depositions on bare Si wafers, for 1200 cycles, resulted in only 3 - 4 nm-thick carbon-rich films, containing traces of gallium and no incorporation of nitrogen, irrespective of the deposition temperature (400 – 600 °C) and precursor pulse durations. An AlN buffer layer was found to be essential for depositing films containing Ga, C and N. The buffer layer was deposited on Si(111) by thermal ALD at 350 °C in the same reactor prior to the deposition of the Ga-C-N layers, and without vacuum break. The ratio between the Ga-, C- and N-contents, correspondingly to the layer growth rate, was found to be strongly dependent on the buffer layer thickness, the deposition temperature and the precursor pulse durations. For example, a thicker buffer layer increased the Ga-content, while a lower deposition temperature decreased the C-content. Tuning these parameters, we deposited C-rich layers [11 at.% Ga, 67 at.% C, 22 at.% N] at 0.005 nm/cycle, Ga-rich layers [58 at.% Ga, 21 at.% C, 21 at.% N] at 0.018 nm/cycle, C-deficient layers [49 at.% Ga, 5 at.% C, 46 at.% N] at 0.003 nm/cycle, and layers with roughly equal composition of the three elements [34 at.% Ga, 36 at.% C, 30 at.% N] at 0.006 nm/cycle.

The layer thicknesses were extracted in real-time (and verified with SEM) by in-situ SE using a Cauchy-Urbach optical model; while their optical constants were extracted using a Kramers-Kronig consistent B-spline optical model. The refractive index was found to increase, while the band-gap was found to decrease, for layers rich in carbon. GIXRD revealed that the AlN buffer layer was polycrystalline and wurtzitic, while the Ga-C-N top-layer had a peak located in close vicinity to the theoretical (10 1 0) peak of h-GaN, at 32.4 degrees.

Our work on Ga-C-N layers shows similarities with B-C-N materials, which are extensively investigated nowadays for their foreseen properties [1,3]. In our presentation, we will show further details regarding the deposition and characterization of the Ga-C-N layers, the function of the AlN buffer layer, as well as discuss about hot-wire activated ALD as a novel deposition technique for Ga-C-N and GaN materials.