

Role of Carbon in n-type Bulk GaN Crystals

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Commercially available gallium nitride (GaN) wafers are today prepared from crystals grown by halide vapor phase epitaxy (HVPE) and ammonothermal technologies. Both highly conductive (n-type) and semi-insulating (SI) GaN are present on the market. Two-inch n-type HVPE-GaN is doped with silicon (Si), germanium (Ge), or their co-doping [1], while 2-inch ammonothermal GaN (Am-GaN) contains oxygen (O) at the level of 10^{19} cm^{-3} [2]. All these wafers show a similar concentration of free carriers (electrons), regardless of the dopant used. There are two significant differences between the ammonothermal and HVPE technologies: growth rate and purity of grown GaN. HVPE crystals can be grown 100 times faster in each crystallographic direction and they are of much higher purity. Concentrations of the main donors: Si and O, are usually lower than 10^{17} cm^{-3} . The most commonly detected acceptor impurity is iron (Fe). All these impurities come from elements of both the growth zone of the reactor (often quartz) and the gas lines. In the HVPE technology the presence of hydrochloride (HCl) is responsible for a corrosive environment. Halide vapor phase epitaxy reactors are carbon-free unless some graphite elements are intentionally introduced. Therefore, in comparison to metal-organic vapor phase epitaxy (MOVPE), which relies on carbon-containing metalorganics as gallium (Ga) precursor, HVPE can be a carbon-free growth process. It is well known that for MOVPE-GaN layers the compensation of donors by carbon (C) is observed at low concentration of donors. This leads to a drastic reduction in the carrier mobility, called a mobility collapse. Carbon acts as a trap for minority holes as well as a compensator for majority electrons.

Due to electronic applications the C impurity in GaN is mainly analyzed as a trap in thin n-type epitaxial nitride layers of low conductivity grown by MOVPE and HVPE. Carbon-doped HVPE-GaN bulk crystals, in turn, are SI with resistivity exceeding $10^8 \text{ }\Omega\text{cm}$ at room temperature [1]. The detailed analysis of C in bulk HVPE-GaN showed that it can be self-compensated. The compensation ratio depends on the C concentration and for high concentrations ($>10^{19} \text{ cm}^{-3}$) the compensation can even reach 1 [2]. The role of carbon in n-type bulk HVPE-GaN has not yet been examined. Therefore, in this paper HVPE-GaN crystals co-doped with Si and C are studied. The assumption was to grow and examine HVPE-GaN strongly doped with Si (with the doping level kept constant) and to increase the C concentration. It was also assumed that the C concentration should not exceed the Si concentration and, thus, the crystallized HVPE-GaN had to always be highly conductive (n-type). The morphology, structural quality and growth rate of the co-doped crystals were analyzed. Secondary ion mass spectrometry (SIMS) was applied for determining the concentrations of all the impurities. Optical and electrical properties of the new-crystallized co-doped HVPE-GaN were examined, analyzed and described basing on Raman spectroscopy (RS), photoluminescence (PL), and Hall van der Pauw measurements.

[1] Iwinska M. et al., Highly resistive C-doped hydride vapor phase epitaxy-GaN grown on ammonothermally crystallized GaN seeds, *Appl Phys Express*. 2017;10(1): 011003.

[2] Piotrkowski R., et al., Self-compensation of carbon in HVPE-GaN:C, *Appl Phys Lett*. 2020; 117(1); 012106