Hydrogen in Gallium Nitride Grown by MOCVD

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Hydrogen is an impurity in many semiconductors which exhibits very complex behaviour because of its high diffusivity and chemical reactivity. The ability of atomic hydrogen to passivate or compensate both shallow and deep defects and to induce extended defects has a large influence on the mechanical and optoelectronic properties of several semiconductor materials [1]. The development and commercialisation of light emitting diodes and semiconductor lasers operating in the infrared, red and green regions of the optical spectrum have generated much interest in materials capable of extending the operation of these devices into the blue and ultraviolet regions. The hexagonal III–IV nitrides AlN, GaN and InN are materials for application at such energies. These materials have several advantages, including direct bandgaps for high efficiency in optoelectronic devices, high radiation hardness, and complete solubility among the binary compounds. Currently, metalorganic chemical vapour deposition (MOCVD) seems to be the most advanced technique for producing these semiconductor devices on sapphire substrates, although molecular beam epitaxy (MBE) is catching up with the implementation of new nitrogen plasma sources. In the MOVCD process, the hybrides and metalorganic compounds used as precursors and the molecular hydrogen used as a transport gas are possible sources for hydrogen incorporation in group–III nitrides. Hydrogen can influence the chemical reaction mechanism in the gas phase by changing the reaction temperature of the metalorganic compounds or the concentration of reaction products. Hydrogen at the surface of the growing film can influence the growth rate and the structural properties. In order to obtain a basic understanding of the role of hydrogen in GaN, the possible sources and the influence of hydrogen on the chemical reaction mechanism in the gas phase and the growth of GaN need to be discussed. Especially, the determination and manipulation of the hydrogen concentration in GaN is necessary to estimate the influence of hydrogen on the properties of GaN.

The deposition of epitaxial GaN layers by MOCVD has been carried out using mixtures of triethylgallium (TEG) and ammonia (NH_3) in the presence of N_2 and H_2 in a temperature range from 650 to 1100° C [2]. Molecular hydrogen and nitrogen cause a decrease of the necessary deposition temperature for the decomposition reaction of the precursors from typically more than 900 $°C$ down to about 300 $°C$ [3].

In order to get exact information about the stoichiometry and the incorporated impurities and doping elements, the total concentration of Ga, N, H, C and Mg was determined by elastic recoil detection (ERD). The measurements were performed with the arrangement for ERD analysis at the Munich tandem accelerator described in Refs. [4,5]. With the help of ERD measurements, the stoichiometry of the samples was confirmed to be Ga/N = 1.00 ± 0.02. Within the accuracy of the measurement, the nitrogen concentration of $4.4\times10^{22}\,\mathrm{cm}^{-3}$ is not influenced by the substrate temperature (Fig. 1). The total hydrogen and carbon content decreases exponentially from 2×10^{21} to $3\times10^{19}\,\mathrm{cm}^{-3}$ and from 1.4×10^{21} to $2\times10^{18}\,\mathrm{cm}^{-3}$, respectively, when the substrate temperature is changed from 650 to 1100° C. This is caused by a more efficient desorption of hydrocarbons from the GaN surface during the growth and a, reduced effective surface (with increasing crystallite size) at higher substrate temperatures [2].

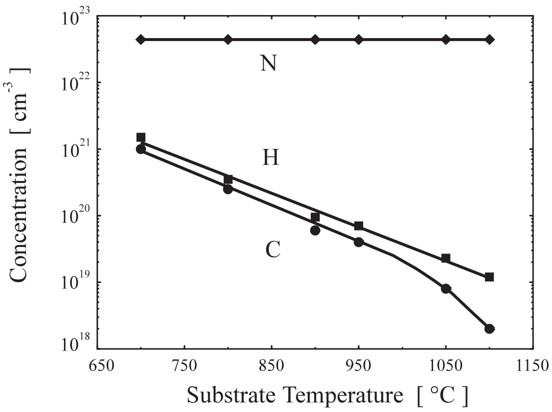

Fig. 1: Concentration of N, H and C determined by ERD

Hydrogen in Mg–doped GaN

As–grown GaN is commonly n–type conductive and p–type conductivity has been more difficult to obtain. It could be demonstrated that the activation of Mg–acceptors can be achieved by thermal annealing in the temperature range of 600 to 775 $°C$, and that the annealing step is reversible by hydrogenation using a hydrogen plasma for temperatures above 500 $°C$ [6]. Based on these observations, it has been suggested that hydrogen plays a cruical role in passivating the Mg–acceptors and there are hints from theoretival calculations of incorporated Mg:H complexes. ERD measurements of two Mg–doped GaN samples revealed Mg concentrations of 2.5×10^{19} and $6.6\times10^{19}\,\mathrm{cm}^{-3}$ with a corresponding hydrogen content of 2.7×10^{19} and $7.8\times10^{19}\,\mathrm{cm}^{-3}$, respectively. Finally, thermal desorption measurements revealed that the hydrogen loss from the GaN:Mg samples occurs in the same temperature range as the activation of acceptor levels, indicating that hydrogen is responsible for the passivation of acceptor levels in GaN [2].

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