Doping of III-nitride materials

CrossMark

Pietro Pampili[a,b], Peter J. Parbrook[a,b,*]

[a] Tyndall National Institute, University College Cork, Lee Maltings, Dyke Parade, Cork, Ireland
[b] School of Engineering, University College Cork, Western Road, Cork, Ireland

ARTICLE INFO

ABSTRACT

In this review paper we will report the current state of research regarding the doping of III-nitride materials and their alloys. GaN is a mature material with both n-type and p-type doping relatively well understood, and while n-GaN is easily achieved, p-type doping requires much more care. There are significant efforts to extend the composition range that can be controllably doped for AlGaInN alloys. This would allow application in shorter and longer wavelength optoelectronics as well as extending power electronic devices. It is found that doping of AlGaN and InGaN alloys with low-gallium-content has particular challenges, especially for p-materials and these issues are described.

1. Introduction

III-nitride materials, i.e. gallium nitride (GaN), indium nitride (InN) and aluminium nitride (AlN), along with their ternary and quaternary alloys, constitute one of the pre-eminent semiconductor systems both in research and industry. Their devices have now become part of our everyday life, such as blue light-emitting diodes (LEDs) that, if coupled with phosphors to obtain white light, can be found in background illumination of mobile phones and televisions, and in energy-saving light-bulbs [1,2]; or blue laser diodes (LDs) that power the high-definition Blu-ray players [3]. Furthermore, apart from these optoelectronic applications, III-nitride-based devices are starting to appear or are being investigated in an increasingy number of fields such as, for example, power [4] and high frequency [5] transistors, photovoltaic cells [6,7], and water-splitting devices [8].

The key achievement in the history of this system was the ability to control doping levels in a reliable way. In the early years of research, GaN and InN samples used to have a high unintentional n-type background, with free carriers concentrations up to 10^{20} and 10^{21} cm^{-3}, respectively [9–11]. It took time and substantial efforts in optimization of the growth techniques to be able to obtain a satisfactory material quality. This has led to material that is entirely depleted (semi-insulating) for GaN growth on c-plane [12], although in other orientations there remains a residual background in the range of 10^{17}–10^{18} cm^{-3} [13]; nevertheless these represent a sufficient basis for device fabrication. In addition to use of GaN and InN for visible optoelectronics, there is now substantial research in devices emitting at shorter wavelengths, down to the deep ultraviolet, and at this range, AlN and its alloys have received much more attention. In contrast to (In)GaN

materials, AlGaN with aluminium concentrations higher than 30% do not show any form of autodoping [9,10] and are very difficult to intentionally dope [14]. For years a few different groups have tried to improve the level of doping in increasingly high aluminium content materials, but it was only with Taniyasu and co-workers, who managed to demonstrate a pure AlN-based diode [15], that this material started to be considered as a useful semiconductor. At the moment deep ultraviolet LEDs with wavelength emission in the range of 250–350 nm are in production by companies such as SETi, Dowa, Crystal IS, and Nikkiso [16], but still good doping for ultraviolet-LEDs is challenging.

For all III-nitride materials, obtaining reasonably good p-doping has been a key issue for its development: for years scientists struggled to get any p-conductivity at all, until Amano and Akasaki [17] discovered that the reason for the poor results achieved with magnesium doping were due to the dopant passivation from hydrogen impurities, typically abundantly present in any MOVPE reactor, both as a carrier gas, and as a by-product of the cracking of the metalorganic precursors. They were also able to develop a technique to dissolve the Mg-H bonding and release the excess hydrogen that involved the use of low-energy electron-beam irradiation, but it was only with Nakamura that it was eventually possible to use a simple thermal annealing step in order to obtain the same result [18]. Both works contributed decisively to the award of the Nobel Prize in Physics 2014 to their authors [19]. Not unexpectedly the p-doping of high aluminium content materials has also proved a serious challenge, which is still subject of research.

In this review we examine the issues and current status of doping in III-Nitrides concentrating on the specific challenges that are particular to this system.

---

2. Growth and doping techniques

There are basically three different types of epitaxial techniques that can be used to produce monocrystalline III-nitride materials: Hydride Vapour Phase Epitaxy (HVPE), Metal-Organic Vapour Phase Epitaxy (MOVPE), and Molecular Beam Epitaxy (MBE). The first two are both chemical deposition methods that differ only in the mode of transport of the group-III elements to the reactor and resulting growth chemistry, while the latter is a vacuum technique in which the precursor atoms are evaporated and travel to the substrate as a "beam" due to the long mean free path for atom interaction in the growth chamber. A comprehensive analysis of the growth techniques of III-nitride materials is outside the scope of this article, and in this section we will only provide a brief description of the three methods, focusing in particular on the aspects that are relevant to doping. More details can be found in specific review papers such as [20,21] for HVPE, [20–22] for MOVPE, and [20,23] for MBE.

The first technique used to grow GaN was the HVPE, originally developed for silicon and germanium epitaxy, and afterwards for conventional III-V materials such as gallium arsenide (GaAs) and gallium phosphide (GaP). In HVPE growth, group-III atoms are brought into the reactor as halides (hence the name of *Halide Vapour Phase Epitaxy* sometimes used as a synonym), and group-V atoms are introduced as hydrides. In case of GaN growth, the halide precursor is usually in the form of gallium chloride, produced when pure metallic gallium, melted in a heated crucible, is exposed to hydrogen chloride. These molecules are then carried by a flow of hydrogen gas into the reactor where they react with ammonia, the nitrogen-carrying hydride, to form GaN with gaseous reaction by-products (H_2, HCl).

Using this technique at the RCA Laboratories in 1969, Markusa and Tietjen [24] were able to demonstrate, for the first time, the growth of monocrystalline GaN; and soon afterwards Pankove *et al.* [25] produced the first GaN-based LED. As a consequence of these results, several research groups in the US and in Japan built their own HVPE reactors and the approach became quite popular for a while. Nevertheless, few years later most of them, including RCA, eventually moved to the new emerging MOVPE method in the hope of better quality material, and HVPE was mostly abandoned. Nowadays, the modern versions of HVPE are still in use and, because of their fast growth-rate (typically 10—100 μm/h), they are particularly suitable for the growth of thick, high quality free-standing GaN substrates [26].

In MOVPE growth, the metal precursors are organic compounds such as trimethylgallium, trimethylaluminium and trimethylindium; while ammonia is still the nitrogen source. Within the reactor chamber, ammonia and precursors transported by a carrier gas (hydrogen or nitrogen) decompose because of the high temperature at which the substrate is kept (typically 1,000 °C or more). Group-III and nitrogen atoms are then adsorbed into the substrate and, some of them, are eventually incorporated into the epitaxial film. The chemical reactions involved in the process are more complicated than in HVPE and great care has to be taken, at reactor design level, to minimize any pre-reactions outside the substrate surface that might lead to the formation of non-volatile compounds. In the first years of development, MOVPE-grown films did not show any major improvement in quality compared with the HVPE system, but in 1986 Amano *et al.* [27] proposed the use of an AlN nucleation buffer-layer that significantly improved the crystalline quality and the uniformity of the subsequently grown GaN epilayers; in 1991 Nakamura [12] reported a similar approach using GaN buffer-layers. At the moment, virtually all MOVPE growths of III-nitride epilayers are based on some evolution of this approach, which consists of a high-temperature nitridation of the substrate with ammonia, a low-temperature deposition of a thin nucleation layer, followed by a high-temperature growth in which the increased mobility of the adsorbed adatoms contributes to a higher crystalline quality of the film [21,28,29]. If required, doping can be obtained during growth

by introducing into the reactor controlled amounts of dopant-containing gases, such as silane (SiH_4), disilane (Si_2H_6), or bis-cyclopentadienylmagnesium (Cp_2Mg) that undergo thermal dissociation and release the dopant species in the reactor chamber (i.e. silicon or magnesium, in these examples).

In MBE growth, group-III metal and dopant atoms come from high-purity solid sources contained in Knudsen effusion cells that, heated in high-vacuum chambers, produce a stream of non-interacting particles that impinge into the substrate, typically heated at around 800 °C, where they are adsorbed and, eventually, incorporated. The fluxes of the different atomic species can be controlled by varying the temperatures of the Knudsen cells, and can also be quickly stopped by means of mechanical shutters, a feature that allows MBE-grown devices to have structures with very sharp interfaces. Nitrogen, on the contrary, cannot be supplied through effusion cells, and must come from other sources in the form of reactive radicals able to be effectively incorporated into the epitaxial layer. The most widespread version of MBE is the so-called Plasma Assisted MBE in which the nitrogen radicals are produced by radio-frequency (RF) or electron cyclotron resonance (ECR) plasma sources [20,23]. Ammonia-based MBE systems also exist and have recently attracted considerable attention for the high quality of their materials [30]. They require more complex types of chamber in order to be able to maintain a high-vacuum level even with relatively large flows of ammonia, but they can take advantage from higher growth temperatures that are not only necessary to ensure the thermal cracking of the ammonia molecules, but are also beneficial to improve the quality of the epilayer.

In any type of III-nitride epitaxy, the major problem that hinders the quality of the epilayers is the lack of a suitable, low-cost substrate for homoepitaxy. Even though both GaN and AlN free-standing substrates do exist (produced using techniques such as ammonothermal crystal growth, sodium flux, physical vapour transport, and HVPE [26]), they are very expensive, usually available only in small sizes, and contain impurities that reduce their transparency in the visible. For deep ultraviolet emitters AlN is often proposed as a transparent quasi-homoepitaxial substrate, but impurity related transparency is an issue for this material also [31]. For this reason heteroepitaxy is widely employed, with sapphire, silicon, and silicon carbide being the most used substrates. However, notwithstanding the great deal of optimization in the growth techniques so far achieved, the large lattice mismatch between the substrates and the III-nitride materials inevitably lead to high dislocation concentrations that are not only detrimental to the optoelectronic device performance (they act as non-radiative recombination centres), but they also affect the quality of the doping, as we will see in the following sections.

III-nitride epilayers are grown much more easily with their hexagonal c-axis perpendicular to the substrate surface, but because of the presence of spontaneous and piezoelectric polarization fields along this direction, this causes the quantum wells typically used in optoelectronic devices, to be subjected to strong electric fields that bend their potential profiles and shift holes and electrons in opposite directions, greatly reducing the recombination efficiency. In order to overcome this issue different growth directions have also been studied, either with no polarization (nonpolar directions) or with reduced fields (semipolar directions) [13]. The resulting material often shows different electrical characteristics, if compared to polar epilayers subjected to the same doping conditions.

While the doping by ion implantation is a well-established technique routinely applied in the semiconductor industry, it has not so far gained widespread use in the III-nitride system because of the difficulty in reversing implant induced defects in those materials. The high-temperature annealing required for optimal activation of the implanted species, is usually of the order of two thirds of the melting temperature [32], which for both GaN and AlN would mean reaching temperatures of 1,500 °C or higher. Unfortunately, unless special conditions are put in place, GaN starts to decompose at 800 °C [33] and AlN at 1000 °C