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Doping of III-nitride materials

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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.

Keywords

Gallium Nitride; Indium Nitride; Aluminium Nitride; Semiconductors; Doping; Conductivity

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 [34], mainly through nitrogen desorption and consequent formation of vacancies in the regions close to the surface. Ion implantation technique is particularly detrimental in optoelectronic devices where the introduced defects act as non-radiative centres, highly reducing or suppressing the luminescence [32]. On the contrary, some interesting applications of ion implantation in III-nitride-based transistors have been demonstrated [35-37], but considerably more optimization work is still needed. Further information about this topic can be found in the extensive review of Ronning *et al.* [32] and also in the section dedicated to implantation in the general review by Sheu and Chi [38].

3 GaN doping

3.1 Autodoping

As discussed above, the first GaN samples exhibited a background *n*-type doping of about 10^{20} cm^{-3} [9, 10]. Early work on GaN (e.g. [24, 39]), seemed to suggest that the impurity concentration was insufficient to account for the free carriers and, as a consequence, the background conductivity was assigned to some form of autodoping, and in particular to the nitrogen vacancy. The uncertainty in the experimental determination of impurity concentration was large, and experimental results could be interpreted differently but, despite the lack of a unequivocal experiment to prove or disprove this statement, for almost 25 years nitrogen vacancies were believed to be the cause of the background *n*-type conductivity.

This belief was later on justified by theoretical work based on a semi-empirical tight-binding approach [40, 41], which suggested that V_N would produce an s-like level containing two electrons below the conduction band edge, and a p-like level containing one electron above the conduction band edge. Because the p-like level would be resonant and its electron auto-ionized, it would decay to the conduction band edge, and cause *n*-type doping (one electron per vacancy). Moreover, the fact that at hydrostatic pressures exceeding 20 GPa the as-grown *n*-type samples showed a carrier freezeout was interpreted as the shifting of the V_N resonance level from the conduction band, down to the band gap under the effect of pressure [42, 43].

However Neugebauer and Van de Walle [44, 45], have pointed out that the tight-binding approach takes into account only nearest-neighbour interactions, whereas the extremely ionic character and the correspondingly small lattice constant of the group-III nitrides causes the second-nearest-neighbour interactions to play an important role. They focused their attention not only on the electronic structure of the defects and impurities, but also on their formation energies. To achieve that, they used a thermodynamic approach in which the equilibrium concentration *c* of an impurity can be expressed as:

$$c = N_{sites} N_{config} exp\left(-E^f/kT\right) \quad (1)$$

In which N_{sites} and N_{config} are the number of sites per unit volume in which the lattice allows defect incorporation and the number of possible equivalent configurations respectively; E^f is the formation energy, which ultimately expresses how likely the formation of that defect/impurity is; and finally, *k* and *T* are the Boltzmann constant and the absolute temperature.

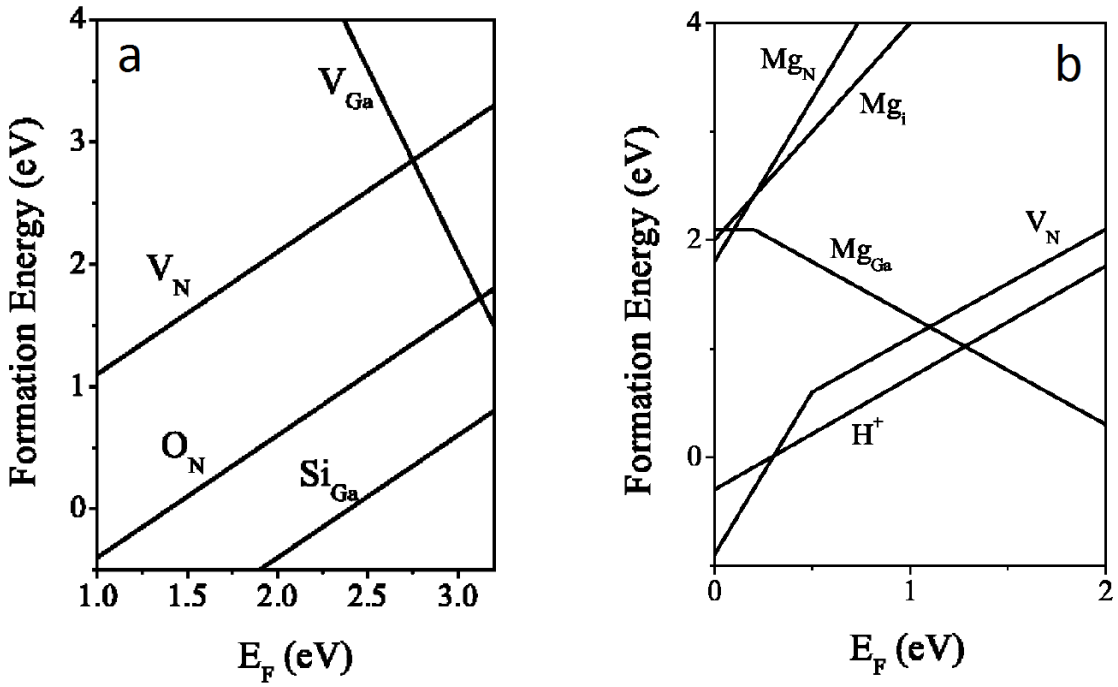

Figure 1. Formation energies for incorporation of impurities and defects during GaN growth, for *n*-type doping (a), and p-type doping (b). From [45].

Using this thermodynamic approach they suggested that formation energies are the most important parameter in determining the defect incorporation, even in non-equilibrium conditions such as during growth; their key results regarding *n*-type doping are summarized in figure 1. Even though V_N is indeed an effective donor if somehow introduced into the material (such as it happens, for example, in plasma treatment [46, 47] or, allegedly, during thermal annealing of Ti/Al-based metallization schemes [48]), it has a very high formation energy, much higher than Si_{Ga} (which is the most used way of intentionally *n*-dope GaN) and O_N which is hence the most likely cause of unintentional background doping in GaN. Another interesting result of this analysis is the fact that gallium vacancy V_{Ga}, which is an acceptor, has an increasingly reduced formation energy as we increase the *n*-doping and consequently the Fermi energy. This shows that the self-compensation that experimentally appears if we try to further increase the *n*-doping [49] is most likely due to gallium vacancy formation.

It is also important to point out that the freezeout of carriers at high hydrostatic pressures, and similarly in AlGaN alloys with high aluminium content, which was explained in term of nitrogen vacancies, can also be explained in term of shifting of the oxygen impurity from a shallow donor into a deep DX state [50], explanation that is perfectly consistent with their theory.

3.2 Intentional *n*-type doping

Generally speaking, *n*-doping can be achieved by substituting some of the atoms of the semiconductor with impurities having similar external electronic shell, but with one excess electron over above those required for bonding. In nitride materials, this can be done using group-IV atoms (such as C, Si and Ge) if incorporated as substitutions for cations; or using group-VI atoms (such as O, S and Se) when they substitute nitrogen.

Silicon is the most commonly used intentional *n*-dopant in group-III nitride materials, both in vacuum and vapour phase epitaxy. The amount of silicon introduced into the material during growth can be easily modulated either by direct control of the evaporated silicon flux from the effusion cell in MBE systems, or by varying the flow rate of the silicon-containing gases into the vapour phase reactor. Solubility of Si in GaN is high, of the order of 10^{20} cm^{-3}, and free carrier concentrations in the range from 10^{17} to 2×10^{19} cm^{-3} have been reported [51].

In particular, in vapour phase epitaxy, two main silicon containing gasses are normally used: silane (SiH_4) or disilane (Si_2H_6), with the first one being the most preferred choice. The reason for using disilane dates back to the 1980s when it was proposed as an alternative to silane for the doping of GaAs materials [52], because of its markedly higher reactivity. Silicon incorporation into GaAs by means of silane, was shown to be quite temperature dependent, leading to inefficient incorporation at low growth temperatures, and to substantial doping inhomogeneities resulting from any substrate temperature variation. As shown in figure 2, doping by means of disilane leads to an almost constant silicon incorporation into GaAs in the whole range of temperatures tested.

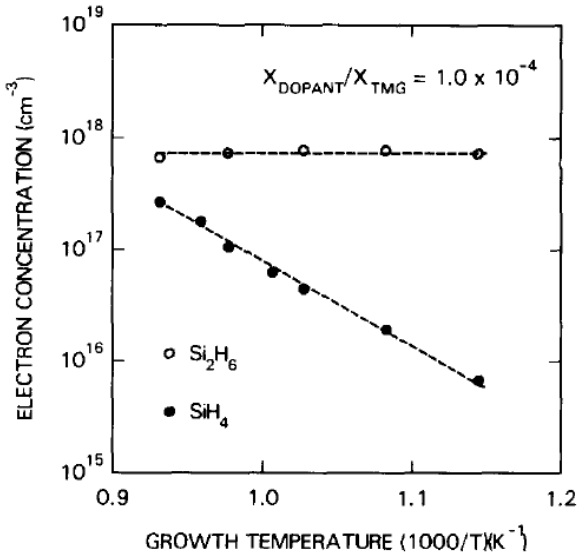

Figure 2. Comparison between silane and disilane incorporation in GaAs growth. From [52].

For GaN there are not many reports in literature that compare silane and disilane doping, apart from the review paper from Sheu and Chi [38], which basically indicates that both gases can be effectively used to induce the formation of free electrons and that in both cases their concentrations are linear with the molar flow rate. Nevertheless, disilane doping efficiency seems to be one order of magnitude lower than silane, even though it has to be noted that the two experiments were performed in different reactors and possibly different growth conditions (the data from Sheu and Chi about the use of disilane [38], were compared with those from Nakamura *et al.* who used silane [51]). Whatever the case here, given the higher growth temperatures required for GaN compared to GaAs it is not surprising that both provide an effective solution.

While silicon is an effective dopant for carrier concentrations up to about 10^{19} cm^{-3}, for higher values the quality of the material starts to degrade very quickly because of the build-up of tensile strain, which also limits the maximum thickness of the silicon-doped epilayer [53]. As proposed by Moram *et al.* [54], silicon is believed to "pin" the dislocations, preventing them from climbing and thus releasing the stress that occurs during growth. In order to explore the possibility of achieving higher doping levels, different dopants have also been investigated; early attempts with germanium [51] and selenium [55] have been reported using germane (GeH_4) and hydrogen selenide (H_2Se), respectively, as dopant-containing gases in MOVPE reactors. In the case of selenium, the free carrier concentration remained linear to only moderate doping level, followed by a sublinear rise of the free electron concentration; moreover, Hall-effect measurements indicated that the Se-doped material is highly compensated in the whole range of hydrogen selenide molar flow rate. For germanium doping the results were, on the contrary, encouraging with linear incorporation of dopants, and good surface morphology up to a free carrier concentration of 1×10^{19} cm^{-3}. Nevertheless, apart from a dopant incorporation ratio of about one order of magnitude lower, no differences were reported compared to silicon doping in this initial report [51]. However, more recent attempts by Fritze *et al.* [56], and by Kirste *et al.* [57] with improved growth conditions have proved to be successful in reaching a high *n*-type doping level up to 2.9×10^{20} cm^{-3}, with no sign of material degradation and mirror-like surfaces. This is particularly interesting because at this high level of free-carriers, surface plasma and bulk carrier plasma at infrared frequencies can be observed, which demonstrates the feasibility of GaN-based plasmonic detectors [57].

Starting from the late 1970s, doping of nonpolar and semipolar GaN has also been attempted, but it was not before 2000 that the first successful results were eventually reported [13]. The electron concentrations were not substantially different from those of standard polar epilayers, but the mobilities were often considerably lower as a result of the much higher defect concentrations typical of these materials [58]. Another interesting feature that has often been reported is the variation of

resistivity along different planar directions [59, 60]; because electrons have almost the same effective masses along these directions [61, 62], the observed behaviour has been often attributed to anisotropic scattering from defects. In particular, stacking faults (i.e. inclusions of few monolayers of zincblende-phase perpendicular to the c-direction) have been thought to be the most likely cause: due to the discontinuities in the polarization field they introduce, electrons that flow in the c-direction have to overcome band offsets, while those moving perpendicularly do not; a quantitative model based on this hypothesis has also been proposed by Konar *et al.* [63].

3.3 *p*-doping

In general terms, any substitutional impurity lacking of one electron compared to the atom it replaces can potentially be a shallow acceptor and induce *p*-type conductivity. This could be obtained, for example, by group-IIA and -IIB atoms (such as Be, Mg, Ca, Zn and Cd) on cation sites, or group-IV atoms on nitrogen sites. As discussed in the previous section, group-IV atoms can also act as shallow donors if incorporated on cation sites, and indeed the formation energies of the two configurations often favour the latter, as in the case of silicon and germanium that are always donors. The behaviour of carbon, on the other hand, is still not fully understood: according to Bogusławski *et al.* [64] it is an amphoteric impurity that can be incorporated either as a shallow acceptor in the C_N site and as a shallow donor in the C_{Ga} site, leading to self-compensation effects. However in a more recent theoretical study, Lyons *et al.* [65] have proposed that it is mostly incorporated in the C_N site, but in this configuration it actually acts as a very deep acceptor state. In any case, experimental evidence shows that carbon-doping of GaN makes the material highly resistive [66].

One of the earliest attempts to achieve *p*-GaN was at RCA Laboratories, whereby zinc (the standard choice for *p*-type doping of GaAs and GaP) and, later on, magnesium were used [67]. However, because of the unintentional hydrogen passivation of the acceptor impurities, which was only discovered and solved twenty years later [17, 18], they were only able to obtain highly resistive, compensated material. To overcome this, at that time mysterious, issue, the first GaN based LEDs ever demonstrated at RCA were in fact metal-insulator-semiconductor (m-i-s) junctions [25, 68, 69], which being majority carrier devices, require minority carrier tunnelling from the metal to produce some electro-luminescence.

After the aforementioned breakthroughs of Amano, Akasaki and Nakamura [17, 18], magnesium has become the acceptor impurity of choice for III-nitride materials. Nevertheless because of the high binding energy (which can be explained by the hydrogenic model as due to the higher effective mass of holes compared to electrons, and calculated to be around 200 meV) only about 1% of magnesium

atoms are ionized at room temperature. This means that in order to get a free carrier concentration of 10^{18} cm^{-3}, a Mg concentration of 10^{20} cm^{-3} would be required, but most likely because of solubility issues (competition with the formation of a Mg_3N_2 phase [45]), at this concentration, the hole mobility decreases substantially and the conductivity becomes poor [70].

However, to reduce this issue at least in the case of Plasma Assisted MBE growth, Burnham *et al.* [71] have proposed a new technique called Metal Modulated Epitaxy (MME). While it is known that a Ga-rich growth regime leads to degraded quality and formation of metal droplets, in standard N-rich conditions, Mg incorporations higher than $2—3.5 \times 10^{20}$ cm^{-3} are very difficult to achieve and can cause the onset of inversion domains [72, 73]. In the proposed MME technique, the growth happens in extremely Ga-rich conditions, but to prevent the formation of any droplets both Ga and Mg fluxes are modulated using the shutters with open and closed times in the order of 10 s each. Using this approach, Mg concentrations above 7×10^{20} cm^{-3} were obtained, leading to a hole concentration as high as 4.5×10^{18} cm^{-3}.

Apart from zinc and magnesium, beryllium is another possible acceptor candidate that has been extensively studied both experimentally [74-77] and theoretically [78, 79]. However, despite its calculated lower activation energy having apparently been confirmed by optical measurements, so far no reliable electrical data have been reported, and there are no accounts of Be-doping in actual devices. In two recent papers by Lyons *et al.* [80, 81], hybrid density functional calculations suggest that all common *p*-dopants in GaN exhibit features that are more typical of deep acceptors, such as neutral-charge states with highly localized holes. But whereas magnesium, having an ionization energy of 260 meV, can “accidentally” behave as a shallow acceptor, the calculated ionization energies of beryllium and zinc (550 meV and 460 meV, respectively) are too large to permit any *p*-type conductivity.

The difficulties in achieving a good *p*-doping are not unique to the III-nitride system, but seem to be a common problem also found in other wide-gap semiconductors; indeed quite a substantial body of literature is now available on the topic, both from a phenomenological point of view and from a more theoretical perspective (see, for example, [82-84] and references therein). The common idea behind these studies is that all semiconductor materials have a well-defined energy level, sometimes called stabilization-level, which can be seen as an average energy of all intrinsic defects. If, because of the doping, the Fermi level moves well above (or below) this stabilization-level, the formation energies of acceptor (or donor) intrinsic defects become so low that they inevitably appear and cause compensation. Such an issue is exemplified in the case of wide-gap II-VI semiconductors, where ZnO, ZnS, ZnSe are difficult to make *p*-type, whereas ZnTe cannot be made *n*-type [82]. For

the III-nitrides, the stabilization-level generally appears to be closer to the conduction band-edge and, as a consequence, *p*-type doping is usually harder to achieve.

As a possible way to overcome this limit, an approach based on co-doping with both acceptors and donors has also been investigated. Even though there is not widespread agreement about this method and its allegedly theoretical explanations, a few very interesting experimental results were reported for beryllium-oxygen [70, 85] and magnesium-oxygen [86, 87] co-doping. As expected, because the movement of the Fermi level during growth was considerably reduced and the incorporation energy of the dopants remained low (see figure 1b), the total amount of incorporated dopants was considerably higher compared to single acceptor doping. Quite surprisingly, though, the free hole concentration and the mobility were also noticeably improved, despite the compensation thus introduced. According to Katayama-Yoshida and co-workers [88-90], the explanation for this unexpected behaviour lies in the formation of Acceptor-Donor-Acceptor (ADA) complexes that cause the donor levels to rise and the acceptor levels to lower because of the energy splitting between the anti-bonding (donor) and bonding (acceptor) states within each complex. Moreover, the change of the scattering mechanism of the carriers from the long-range Coulomb interactions to the short range dipole scattering of the ADA complexes, was claimed to account for the increased carrier mobility.

In contrast to this explanation, Van de Walle *et al.* [79] performed a full first-principles analysis of the Be-O-Be complex and found that both the formation and the ionization energies of these complexes were not lower than those of isolated beryllium acceptors. They consequently concluded that the formation of ADA complexes does not seem to be a valid explanation of the experimentally observed *p*-conductivity [70, 85-87] in co-doped samples, and that other causes (e.g. surfactant effects due to the presence of donor atoms) should be investigated [45]. Further details on this topic can be found in the article by Korotkov *et al.* [91], which contains a full review of experimental reports and a comparison with the available theoretical explanations.

It should be noted that in recent years little effort has been made to develop a practical doping strategy using such a co-doping approach. The main problem seems to be the fact that the co-introduced donor species cannot usually be removed after growth, and consequently the advantages they bring in term of enhanced acceptor incorporation are counterbalanced by the reduction of free carriers through compensation. From this perspective, the unintentional hydrogen passivation of *p*-doped material in vapour phase epitaxy can be seen as the only fully successful example of co-doping. As shown in figure 1b, far from being detrimental, the compensation effects due to its presence not only pin the Fermi level and keep the formation energy of magnesium at a low level,

but also suppress the nitrogen vacancy formation, which in absence of hydrogen would have the lowest formation energy. But the uniqueness of this case is that, as opposed to oxygen, the loosely-bound hydrogen atoms can indeed be removed, as already discussed, either by low-energy electron irradiation or by thermal treatment.

Demonstrations of *p*-type doping have also been reported in nonpolar and semipolar GaN, and compared to polar materials. These consistently show a significant increase of the free-hole concentrations [58, 92, 93], which might be attributed to the fact that the formation of inversion domains, which limits the Mg concentration in polar material, is suppressed in nonpolar materials [92]. In addition, as in the case of *n*-type doping, an asymmetry in the conductivities along different planar directions has been reported [59, 92]. While some theoretical studies suggested that the effective masses of the free-holes might have quite large differences along different directions making their mobilities highly anisotropic [62, 94], other experimental studies contradict this hypothesis [61] and seem to suggest that, as in the case of *n*-type doping, scattering from stacking faults might be the most likely explanation [63, 95].

3.4 Other types of doping

Doping is usually intended to produce an increase of conductivity by modifying the amount of available free carriers; nevertheless, there are also other reasons for introducing controlled amount of impurities in a semiconductor.

For example in GaN-based high-electron-mobility transistors (HEMTs), it has been proved that even if the gate bias is high enough to prevent conduction in the channel, at high drain-source voltages, the current can nonetheless flow deep into the GaN buffer because of the poor carrier confinement due to residual free carriers present there, even at concentrations as low as 1.5×10^{16} cm^{-3} [96]. In order to prevent that, increasing the resistivity of the buffer by doping with iron [97, 98] or carbon [99, 100] has been proven to be an effective solution. However this kind of doping has also been claimed to induce a reduction in the power performance of devices under RF conditions compared to their DC characteristics, the so-called current-collapse [101, 102]. Simulation studies by Uren *et al.* [101] and by Verzellesi *et al.* [102] have shown that this issue depends on the microscopic mechanisms that control the conductivity in the buffer: if the Fermi level is pinned in the upper half of the band gap (such as for Fe-doping, or for C-doping with C_N-C_{Ga} self-compensation) the current-collapse will be significantly reduced. In contrast, if the Fermi level is pinned in the lower half of the band gap (such as for C-doping with a deep acceptor level) the device would become highly vulnerable to current-collapse. This because in the latter case the buffer would be *p*-type and hence isolated from the channel; as a consequence of being floating, large amounts of space charge could

be stored under the source or drain region junction, causing a dramatic increase in the on-state resistance.

Another interesting field of research regards the incorporation of rare-earth elements into solid hosts as a way to take advantage of their unique optical properties that can find application in many photonic devices such as LED and lasers, optical amplifiers, and optical storage systems [103]. In particular the use of erbium has received much attention because its intra-4*f* shell transition from the first excited state to the ground state produces 1.54 μm emission, which is within the minimum-loss window of silica-based fibres for optical communications. This emission is very stable because in rare-earth elements the outer 5*s* and 5*p* shells are completely filled and, consequently, electrons in the inner 4*f* shell are screened from interactions with the host. However the emission can nevertheless suffer from a thermal quench that may be severe in some host semiconductor materials. As pointed out by Favennec *et al.* [104], this quenching effect is much less pronounced in wide-gap material and, for this reason, the use of GaN as potential host has been extensively studied [105-108] and devices such as LEDs and optical amplifiers have been demonstrated [109-112].

However, due to the challenges in finding suitable growth precursors, rare-earth doping is mostly achieved by high-energy ion implantation. As a result, large concentrations of defects are typically introduced into the devices, which severely affect their performance, as already discussed in section 2. Apart from the general works of Ronning *et al.* [32], and Sheu and Chi [38], specific information on implantation damage in rare-earth doping can be found in the extensive review of Lorenz *et al.* [113].

4 AlN and AlGaN doping

4.1 *n*-doping

While most studies of doping have concentrated on GaN, there is a desire to extend the capabilities to wider-band-gap AlGaN. Early studies were just limited to aluminium concentrations of only few percent with the purpose of using these materials as cladding layers of electrically-injected blue laser diodes, and because of the large differences in band gap and refractive index between GaN and AlN, they were still able to provide sufficient optical confinement and were also relatively easy to grow and dope [114]. However, as already discussed, AlGaN materials with even fairly moderate (20—30%) aluminium concentrations were historically considered as insulating [9, 10, 14].

More recently, with the research moving towards shorter wavelength emitters, increasingly larger band gap cladding layers have become necessary. The first attempts to intentionally dope AlGaN

materials with an Al-concentration higher that 60% were undertaken, roughly in the same period, by Jiang and co-workers [115-117], and by Taniyasu and co-workers [49, 118]; in particular these latter two works led to the demonstration of the first working AlN-based light-emitting diode [15].

The main conclusions that Jiang and co-workers were able to draw from their experience, is that the presence of silicon atoms in the material initially just reduces the localization effects within the alloy, and only when the localization is sufficiently overcome (which was evaluated to happen at a silicon concentration of about 1×10^{18} cm^{-3}), does *n*-conductivity occur. They also conjectured that residual oxygen impurities could play an important role in the difficulties of achieving a reasonable level of doping, not only because of their DX transition, but also because, together with an high concentration of dislocations, oxygen can enhance the formation of cation vacancies that act as compensation centres [116]. For this reason they stressed the importance of achieving a good material quality as the key element that allowed them to obtain *n*-type conductivity in the whole composition range of the AlGaN alloy, up to pure AlN. They also reported some flattening in the dependence of the resistivity with temperature for the optimized materials with higher dopant concentrations, and they interpreted this as compatible with an onset of metallic behaviour due to a Mott transition. As a consequence of that, they concluded that this condition is favourable for a good conductivity, and they suggested increasing the dopant concentration as much as possible in order to push the material closer to the transition.

In contrast, Taniyasu and co-workers reported clear signs of self-compensation effects in their material and they thought this was the first cause of the difficulties in achieving a good doping level. Even though SIMS measurements revealed that the silicon incorporation was linear in the whole range of silane flow-rates examined, the room-temperature free-carrier density was at least one order of magnitude lower, and when the concentrations of incorporated atoms were 6×10^{19} cm^{-3} for $Al_{0.49}Ga_{0.51}N$, or 3×10^{19} cm^{-3} for pure AlN, the materials reached their maximum values of free carrier concentrations (4.5×10^{18} cm^{-3} and 9.5×10^{16} cm^{-3}, for $Al_{0.49}Ga_{0.51}N$ and AlN respectively). Any further attempt to increase the silane flow rate, led to a fully compensated and insulating material.

Both groups reported some estimation of the activation energies as a function of Al concentration, calculated from the Hall-effect measurements at different temperatures, which are shown in figure 3 and compared with the results from other works. These data were of fundamental importance in order to try to settle a controversy that is still very much on-going now, and that regards the origin of the increase of the activation energy for high-aluminium-content AlGaN alloys. One proposed reason of this behaviour only invokes the increase of the electron effective-masses and the decrease of the dielectric constant when shifting the AlGaN composition towards AlN. In a simple application

of the hydrogen-like model of the doping impurities, this would lead to a linear (or almost linear) increase of the activation energies from a few tens up to about 75—95 meV [119]. The other possible explanation involves a DX transition of the silicon dopant and a sudden, non-linear, increase of the binding energy. This latter hypothesis was firstly proposed by Bogusławski *et al.* [120] and by Park *et al.* [121] in 1997, and claimed to be experimentally proved by Zeisel *et al.* [122] making use of persistent photoconductivity measurements in 2000.

As shown in figure 3, the data from Jiang group [116] showed a clear linear trend (with only a slight deviation in the last datapoint), whereas Taniyasu *et al.* [49] reported a higher-than-linear increase of activation energy. Nevertheless, both teams concluded that their data supported the fact that silicon most likely remained a shallow donor in the whole alloy range, up to pure AlN. In particular Taniyasu proposed that their observed superlinear increase of the activation energy could be explained as due to the coexistence of shallow silicon donors and other deeper donors, possibly related to oxygen DX-levels.

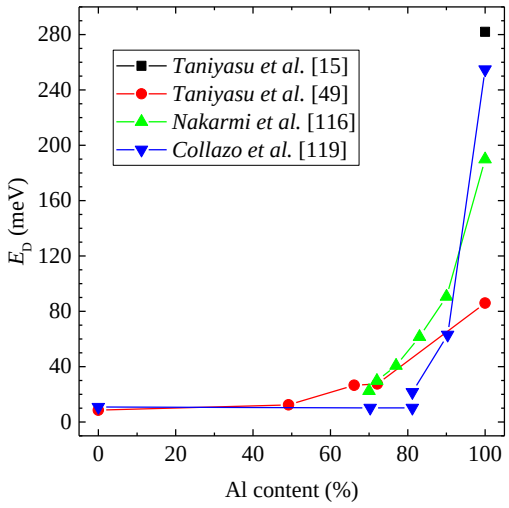

Figure 3. Comparison of the activation energies of silicon doped AlGaN material experimentally obtained by a few groups: [15, 49, 116, 119].

These conclusions were most likely influenced by Van de Walle and his co-workers, who, following the same approach already used for GaN, theoretically studied the doping of AlN and AlGaN. According to their results [123-125], the only type of defect that can influence the *n*-type doping is the aluminium vacancy, which is a compensating acceptor, and whose formation energy decreases with the increase of the Fermi level towards the conduction band. Moreover, in his 1998 paper [50], Van de Walle reported that according to his first-principles calculations, only oxygen, but not silicon, can undergo a DX transition in the whole range of AlGaN compositions. The reason for this claim is that silicon, contrary to oxygen, which is a nitrogen-substitution impurity, is almost exclusively

present as a cation substitution (either as Si_{Ga} or Si_{Al}) and hence, because of its position in the lattice and of the fact that in the DX state it would be negatively charged, the coulombic repulsion from its third-nearest-neighbour anion is able to suppress the DX formation. As a result they proposed that the difficulties in doping high-aluminium-content AlGaN could only be explained by the presence of a residual background of oxygen impurities that after the DX-transition become deep acceptors and, together with aluminium vacancies, heavily compensate the shallow silicon donors.

The controversy is still not conclusively settled, partially because Hall-effect measurements of the activation energy are quite scattered due to the fact that they are affected by screening effects and vary considerably with the free carrier concentration [126-128]. At the moment the most recent experimental works available in this area of research are those from Kakanakova-Georgieva's group [129, 130], who tested AlGaN materials having aluminium content higher than 63%, with a silicon concentration of 2×10^{18} cm^{-3}, specifically chosen because it is a high enough value to allow for some conductivity, but sufficiently low to avoid any degradation of the material quality. The concentrations of residual oxygen and carbon impurities measured with SIMS were at the detection limit of the equipment, i.e. 2×10^{17} cm^{-3}, one order of magnitude lower than silicon concentration, which excluded that they were able to cause any major compensation effects. Frequency dependent C–V measurements performed on this material for an aluminium composition higher that 79% seemed to prove that the silicon DX transition does indeed occur. Moreover electron paramagnetic resonance measurements showed that, starting from an aluminium concentration of 84%, two DX configurations of the Si donor are detectable: one with ionization energy remaining close to the shallow level, and the other one with energy increasing linearly and drastically with the Al content.

As already pointed out by Jiang and co-workers, the quality of the material has a profound impact on the outcomes of the doping, and this is true not only with respect to the concentrations of residual impurities, but also in term of the concentration of threading dislocations. From this perspective, it is particularly interesting the work of Collazo *et al.* [119] in which AlGaN thin films in the whole range from GaN to AlN were grown both on standard sapphire substrates and free-standing AlN single-crystal substrates. Up to an aluminium concentration of about 80%, the materials grown on the two substrates showed comparable results, both in term of carrier concentrations and mobilities. However, for higher aluminium concentrations, the resistivity of the materials grown on sapphire became significantly higher: up to 5 orders of magnitude for 90% aluminium concentration, and with no conduction at all for pure AlN. Hall-effect measurements indicated that this increase of resistivity is mostly due to the reduction of free carrier concentration rather than due to the decrease on mobility, which is nonetheless present.

It should be noted that for UV-LEDs the optimization of the *n*-doping is quite critical. For nearly all III-nitride optoelectronic devices the *n*-contact is placed to the side of the device requiring lateral conduction of electrons. For visible LEDs, GaN is fairly easily doped *n*-type and typical mobilities are around 200—300 $cm^2 V^{-1} s^{-1}$ [51]. Furthermore the resistance from the active region to the lateral *n*-contact can also be improved by simply making the *n*-GaN layer thicker. However for AlGaN, due to alloy scattering, typical *n*-type mobilities are about one order of magnitude lower, furthermore there is a degradation in AlGaN quality with thickness that is still poorly controlled [131]. Thus to minimize the device resistance the *n*-AlGaN layer must be carefully optimised.

To obtain such low resistivity of *n*-type material we have two conflicting requirements to achieve: a sufficiently high dopant concentration in order to push the material close to a metallic transition, and to ensure the dopant concentration is insufficient to lead to the onset of any major self-compensation effects. For AlGaN this trade-off is well summarized in the work of Mehnke *et al.* [132] where they report on the growth by MOVPE of *n*-AlGaN materials with aluminium concentrations higher than 80% with different doping conditions obtained by varying the silane flow rates into the reactor. Their results clearly show the existence of an optimum doping concentration expressed in term of the ratio between the partial pressure of silane gas over the sum of those of the metalorganic precursors (Si/III ratio). Moreover, the trade-off between the two conflicting requirements was shown to be increasingly difficult for higher aluminium compositions as the window of suitable doping conditions with no under or over-doping became considerably narrower, with a shift of the optimum condition towards reduced doping levels.

In our recent work [133] we have extended this analysis also including lower aluminium compositions (three series in total, with 50%, 60% and 85% aluminium concentrations), and we showed that the same trend is clearly present in our material and seems to be a general feature of MOVPE-grown AlGaN, independent of the particular growth conditions (see figure 4). On the other hand, the difference in the absolute values of the resistivities can be easily explained by the different dislocation concentrations due to the type of substrate used: i.e. patterned sapphire for lateral overgrowth in Kneissel's group approach, and AlN templates on standard sapphire in our work. By performing Hall-effect measurements, we were also able to show that close to the optimum conditions there is a range in which the resistivity stays almost stable due to the compensating effects of an increase in free carrier concentration and a simultaneous decrease in mobility, until the onset of self-compensation abruptly appears causing a drop in the carrier concentration.

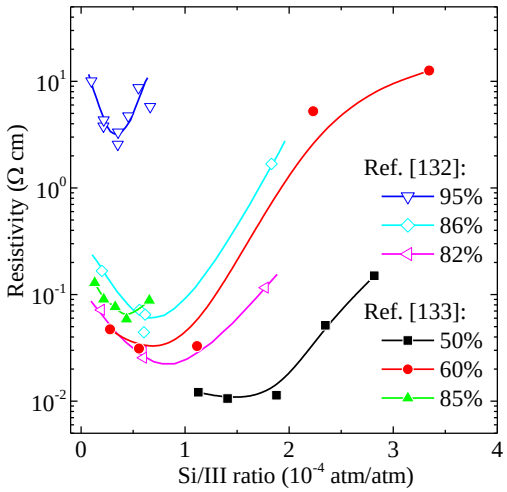

Figure 4. Variation of resistivity as a function of the Si/III ratio. Comparison between the results reported in [132] and [133].

Even though ultraviolet-LEDs based on nonpolar or semipolar AlGaN have already been demonstrated [134, 135], there are few systematic studies about doping of those materials. In recent work from our group [136], we have reported about *n*-type doping of semipolar (112-2) AlGaN with an aluminium concentration close to 50%, grown at different disilane flow rates. At the optimum doping conditions with a Si/III ratio of 2.3×10^{-4}, we measured a free-electron concentration of 1.2×10^{19} cm^{-3}; we also observed signs of anisotropy in the resistivity along different planar directions, as already reported for nonpolar GaN [59, 60].

4.2 *p*-doping

Compared to *n*-type, the *p*-doping of AlGaN materials has received much less attention in the last few years, and it is still considered quite challenging, especially in the high-aluminium-content range of the alloy. Obtaining satisfactory *p*-type epitaxial layers has proven to be so difficult that, at device level, some mitigation strategies had to be developed to in order to compensate for their low conductivity or poor contacts. For example in ultraviolet-LEDs it has become standard solution to grow a thin layer of about 10—50 nm of *p*-GaN in top of the *p*-AlGaN cladding layer [137-139]; notwithstanding its strong absorption at the emission wavelengths, which considerably reduces the light extraction efficiency, it is often the only way to achieve a reasonably good contact and ensure some hole injection into the device. More recently Rajan and co-workers at the Ohio State University have developed devices that make use of polarization-engineered tunnel junctions in order to reduce both absorption and electrical losses [140, 141].

Magnesium is practically the only dopant used and, according to first-principles calculations [125], it does not tend to form any AX deep level (which is the acceptor version of the donor DX-states).

Consequently any form of self-compensation would most likely be caused by the creation of nitrogen vacancies, whose formation energy is considerably lower in AlN than in GaN. Beryllium has also been considered as a possible acceptor because of its comparable (possibly lower) binding energy, but the calculations suggest that it may also be incorporated on interstitial sites, where it acts as a donor [125]. Very few experimental attempts were undertaken and, at present, it is hard to conclude whether or not it may be a suitable alternative.

As for the *n*-type material, the early reports of *p*-doping in AlGaN were aimed to obtain a suitable material for cladding layers and optical confinement in blue LDs. The attempted aluminium concentrations were limited to the range 8—15%, but a marked reduction of the free carrier concentrations was already noticeable, and was attributed to the increased activation energies of the dopants [142-144]. With the work of Li *et al.* [145], the alloy range was extended up to $Al_{0.3}Ga_{0.7}N$ and both Hall-effect and photo-luminescence (PL) measurements were performed from this alloy composition down to pure GaN. The activation energy as a function of the aluminium concentration was calculated by the variation of free-carrier concentrations and the PL intensity of the band-acceptor transition at different temperatures, and both methods gave the same results. In a later work from the same group, Nam *et al.* [146] for the first time reported magnesium doping of pure AlN. The material did not show any sign of conductivity, neither before nor after thermal annealing, but making use of the technique elaborated in [145], they were still able to optically estimate the Mg activation energy to be 510 meV, a value that fits well with calculations based on hydrogenic model (see [147] and reference therein). After careful optimization of the growth parameters, Taniyasu *et al.* [15] were eventually able to produce a conductive *p*-AlN material, with a free-hole concentration at room temperature in the order of 10^{10} cm^{-3} and an activation energy of 630 meV. Used as the *p*-cladding-layer in the first AlN-based LED, this material was able to effectively inject holes into the device as proved by a clear electro-luminescence peak at 210 nm.

Other studies of note include: Jeon *et al.* [148] who reported evidence of a marked self-compensation for a magnesium concentration higher than 3.5×10^{19} cm^{-3} for 30% aluminium-content and, more recently, Chakraborty *et al.* [149] and Kinoshita *et al.* [150] who focused on further optimizing the growth conditions, and the effect of Mg doping on $Al_{0.7}Ga_{0.3}N$ material. These two papers report rather different results. Chakraborty *et al.* have samples that are quite resistive at room temperature (about 10^4 Ω cm) and showed a strong reduction in resistivity with increasing temperature, consistent with a high acceptor binding energy as theoretically expected. In contrast Kinoshita *et al.* claim that under optimal conditions a room temperature resistivity of 50 Ω cm with a very low activation energy. This they attribute to a hopping conduction in the material, which might suggest that scope exists to improve doping through very careful growth optimization.

It is worth noticing that while ultraviolet-LEDs based on planar, very aluminium-rich AlGaN often have very high turn-on voltages, typically in the range 20—40V, Zhao *et al.* [151] have recently reported about high-efficiency AlN nanowire LEDs, with a turn-on voltage of only 6 V that appear to be only limited by the band gap of the material. According to the authors, the reasons for this substantial improvement can be partially ascribed to a more efficient Mg incorporation, achieved by controlling the nanowire growth rate, and partially to the N-polarity of the material that induces internal electrical fields able to favour hole injection.

Finally in discussing AlGaN doping there have been reports of using multilayer AlGaN super-lattices to improve the resistivity using polarisation effects [152]. Graded AlGaN layers can also be used in the c-plane to create so-called polarisation doped layers that have been shown to give good hole injection in a device [153].

5 InN and InGaN doping

With its narrow band gap close to 0.7 eV, InN is a very attractive material that can potentially extend the optoelectronic applications of III-nitride semiconductors to the near-infrared spectral range [154]. Its high electron mobility and large saturation velocity [155, 156] make InN also a very suitable material for high-speed electronics, and Tera-Hertz surface emission [157, 158].

Unfortunately, due to its low dissociation temperature and to the high lattice mismatch with any available substrate (e.g. 7%, 11%, 14% and 27% for Si, GaN, SiC and sapphire; respectively), it has proven to be very difficult to prepare. Early attempts to produce InN by means of RF sputtering (using nitrogen gas and a gallium target) were reported in 1972 by Hovel and Cuomo [159], but the material was polycrystalline and showed very low mobility. Using the best material available at the time, but still polycrystalline and obtained with a similar technique, Foley and Tansley [160] were able to measure its band gap and reported a value of 1.9 eV that, despite being about three times higher than the accepted value today, was believed to be true for very long time [161].

Moreover, apart from InGaN alloys with relatively small InN concentrations as typically used in quantum wells of blue LEDs, for many years any attempt to grow InN or high indium-content InGaN led to very high electron concentrations for nominally undoped material. This peculiar behaviour can be explained by the fact that the electron affinity of InN is quite high (about 5.8 eV) and, as a consequence of that, the Fermi stabilization-level lies well above the conduction-band minimum [82-84]. If the quality of the material is not good with a high concentration of intrinsic defects, the Fermi level moves to its stabilization-level and the material acquires a very strong *n*-type behaviour. This can also explain the band gap results of Foley and Tansley [160]: as the quality of their material was

relatively poor the position of the Fermi level above the conduction-band minimum caused the bottom part of the conduction-band to be completely filled with electrons inhibiting the absorption of low-energy photons, the so-called Burstein-Moss effect.

By using HVPE growth, Sato *et al.* [11] reported a better crystalline quality, but it was only with the use of MBE growth, whose lower growth temperature is much more suitable for InN, that the quality of the material could be improved considerably. After a growth optimization, Lu *et al.* [162] reported a free-electron concentration of $2—3 \times 10^{18}$ cm^{-3} and a mobility of 800 cm^2 V^{-1} s^{-1}. Using material of this quality, Davydov *et al.* [163] and Wu *et al.* [164] were independently able to measure the true value of the InN band gap.

More recently Wang *et al.* [165] were able to further optimize the growth conditions and reported a free electron concentration of 1.77×10^{17} cm^{-3} and a mobility of 3010 cm^2 V^{-1} s^{-1}, which is currently the best reported for planar InN. InN nanowires have also attracted a great deal of interest and showed very encouraging results [166]. Recently Zhao *et al.* [167] have characterized InN nanowires using an electrical nanoprobing technique and have reported free-electron concentrations as low as 10^{13} cm^{-3} and mobilities up to 12,000 cm^2 V^{-1} s^{-1}, close to the theoretical limit [155, 156].

Not unexpectedly, *p*-type doping has proven to be also very difficult to achieve, and even more difficult to be electrically measured as a high negative charge accumulation at the surfaces is always present and makes it almost impossible to perform a reliable Hall-effect measurement. For this reason the first demonstration of *p*-doping in InN by Jones et al. [168] was based only on indirect measurements. Even though the charge accumulation has been believed to be an intrinsic property of InN, Wu *et al.* [169] were able to show the absence of any Fermi level pinning in an *in-situ* cleaved nonpolar surface under ultra-high vacuum conditions, which may open interesting new possibilities towards the realization of InN devices.

Overall there is still much to understand concerning the doping of InN and very much indeed for InGaN alloy. If InGaN is to be used practically, in for example solar cells [170], then significant effort in this area will be required.

6 Summary

In this review, we have provided an overview of the historical background and the current issues of doping in III-nitride materials. While doping of GaN is now well understood and satisfactorily controlled in standard optoelectronic devices, there is still a great deal of research on-going to enhance the performance of advanced devices such as, for example, HEMTs, plasmonic sensors, or

optical amplifiers. In AlN and high-aluminium-content AlGaN, on the contrary, we have not fully understood how to achieve a satisfactory doping level and ultraviolet-LEDs still suffer from a reduced wall-plug efficiency due to the poor conductivity of their cladding layers. Finally, in InN and high-indium-content InGaN, reliable control of the doping is even more difficult. Even though *p*-doping has been demonstrated, and InN nanowires have shown very interesting electrical characteristics, there are still no commercial devices available based on In-rich InGaN.

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