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Impurity resonant state p-doping layer for high-efficiency nitride-based light-emitting diodes

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Abstract

Impurity resonant state p-doping was recently proposed as an alternative to the commonly used p-GaN for high-efficiency nitride-based light-emitting diodes (LEDs) in order to address the issue of electron leakage and efficiency droop. We demonstrated that due to the effective acceptor ionization and reduction of the potential barrier for hole injection, a more symmetrical electron and hole injection and distribution could be achieved. Our experimental results revealed that the LEDs with this alternative p-type layer exhibited a higher quantum efficiency and reduced efficiency droop. We expect this approach to be equally applicable for deep-UV laser diodes and LEDs to replace the commonly used absorptive p-GaN layer.

Keywords: impurity resonant state p-doping, nitride, light-emitting diodes

(Some figures may appear in colour only in the online journal)

1. Introduction

Although sufficient n-type conduction was achieved in the early years of GaN growth, for decades achieving high p-type doping in nitrides has been shown to be extremely difficult. The situation results in serious asymmetry in carrier transport between electrons and holes, which hinders further improvement of nitride-based light-emitting devices [1–3]. It is well known that in GaN-based devices holes have a relatively low concentration and high effective mass compared with electrons. Hence, the low hole mobility makes hole transport from the p-type layer to the active region difficult.

This means that electrons will accumulate at the top-most quantum wells, resulting in carrier leakage and efficiency droop at high current density. For UV and deep-UV light-emitting diodes (LEDs), the injection of holes becomes even more difficult due to its higher acceptor ionization energy. The asymmetric carrier transport, arising from the poor conductivity of conventional p-GaN layers, has become a severe impediment for nitride-based devices, including both LEDs and lasers. An alternative strategy for achieving efficient p-type doping and hole injection is therefore highly desirable. By achieving highly p-doping layers, the excessive electrons will be exhausted by injecting more holes via radiative recombination. Consequently, both high quantum efficiency and low-efficiency droop can potentially be achieved.

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Compared with the common approach of increasing the barrier of the electron-blocking layer (EBL), it is a more promising solution to address the issues of asymmetric carrier transport in nitride-based LEDs [4].

However, it is well established that nitrides have an 'asymmetric' doping problem stemming from the electronic structure of the nitride materials [5–9], which is similar to other wide-band-gap semiconductors, for instance diamond and ZnO. As known, the valance band maximum (VBM) of nitrides is mainly composed of the deep 2*p* atomic orbital of nitrogen. Therefore, acceptors in GaN tend to exhibit high-ionization energies. Furthermore, other physical mechanisms, such as low dopant solubility of Mg, hydrogen passivation and self-compensation effect at high doping levels also make the design of highly p-doped nitrides more complicated [5–7]. Till now, the most effective p-type dopant for III-nitrides is still Mg. Unfortunately, the activation energy E_a of the Mg dopant in GaN is as high as 160–200 meV. For AlN materials, the activation energy can be even higher. Thus, only a small fraction of Mg can be ionized at room temperature. Various novel approaches have been developed to improve p-type doping in nitrides. Schubert *et al* and Kozodoy *et al* [10, 11] suggested a uniformly p-doped AlGaN/GaN superlattice (SL) to enhance the acceptor activation, with a considerable amount of follow-up effort along this line [12–15] and short-period SL for deep-UV laser diode structures [16, 17] Polyakov *et al* further showed that modulation doping only to the higher bandgap region could improve the carrier mobility and thus conductivity [18]. Simon *et al* [8] proposed that the built-in electronic polarization in a composition-graded $Al_xGa_{1-x}N$ layer can improve acceptor ionization. Recently, Gunning *et al* [9] proposed to lower the acceptor ionization energy by extremely high doping. Recently, co-doping was suggested as another method to address this issue [19–23], for instance, mutually passivated defect pair co-doping. Nevertheless, so far there is still no generally applicable effective p-type doping scheme for the nitride-based devices.

Besides achieving a high concentration, we are more concerned about applying such a p-type layer to improve the performance of nitride-based devices. Recently, we proposed an approach, referred to as impurity resonant state (IRS) p-doping [22], to achieve efficient p-type doping to overcome the fundamental issue of high activation energy and replace the conventional p-type GaN. Our approach is similar to the modulation doping method [18], but there is a subtle difference in the underlying physics (to be discussed later). In agreement with the theoretical results, InGaN/GaN LEDs with the IRS p-doping layer showed both higher quantum efficiency and reduced efficiency droop, compared with conventional structure with direct Mg-doped p-type GaN.

2. Experiment

InGaN/GaN LEDs with a conventional Mg-doped p-type GaN layer (labeled Structure I) and an IRS p-doping layer (labeled Structure II) were grown on (0001) patterned
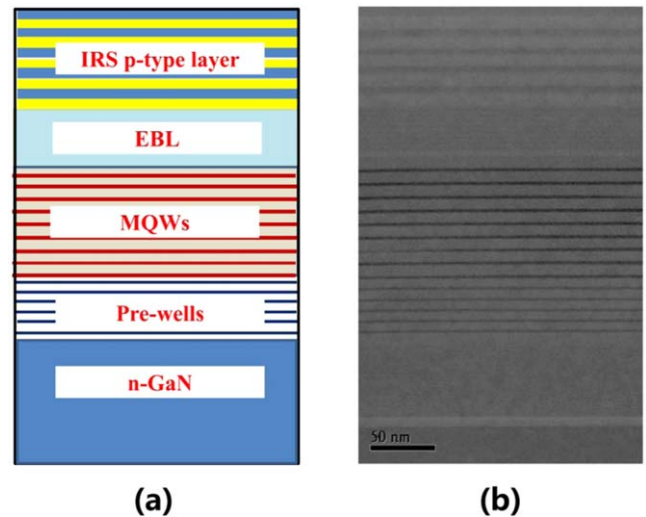

Figure 1. Device structure of an LED with an IRS p-doping layer. (a) Schematic structure, and (b) the corresponding TEM image.

sapphire substrate by a Veeco metal-organic chemical vapor deposition system. A 30 nm low-temperature GaN buffer layer was grown on a substrate at a growth temperature of 560 °C. After high-temperature annealing, 2 μm undoped GaN and Si doped n-GaN layers were grown at a temperature of 1150 °C followed by short-period InGaN/GaN SL as pre-strained layers. The active region consists of nine pairs of 7.5 nm GaN barriers and 3.0 nm undoped InGaN wells. AlGaN/GaN SLs were grown on the active region as an EBL. For Structure I, a 75 nm conventional Mg-doped p-type GaN layer was grown on the EBL as a p-type layer. For Structure II, a 75 nm $Al_{0.3}Ga_{0.7}N$(10 nm)/GaN (5 nm) SL (with five pairs) was used as the p-type layer where the only AlGaN layers were doped with Mg. The structure properties of LEDs were investigated by transmission electron microscopy (TEM).

3. Results and discussion

As illustrated in figure 1, for sample II the five periods of $Al_{0.3}Ga_{0.7}N$/GaN structure are clearly visible. Atomically sharp $Al_{0.3}Ga_{0.7}N$/GaN interfaces along the growth axis could be observed. Structure I and Structure II are identical, except for the p-type layer. Hall measurement was performed to examine the hole concentration of our IRS p-doping layer. In the present case, both bulk holes (delocalized in the GaN regions from thermal ionization) and parallel sheets of 2D hole gases (at the heterojunction interfaces from polarization effect) can be produced, simultaneously. As known, the conventional Hall-effect model offers no thickness information. Therefore, it is impossible to delineate 2D carrier gases and bulk carriers [11]. In this work, the two-carrier-species Hall-effect model used in our previous report was applied to quantitatively determine and delineate the contributions of bulk carriers and 2D carrier gases. The bulk hole concentration obtained by Hall measurement is 3.85×10^{18} cm^{-2}. At the same time, a certain amount of 2D hole gases will also

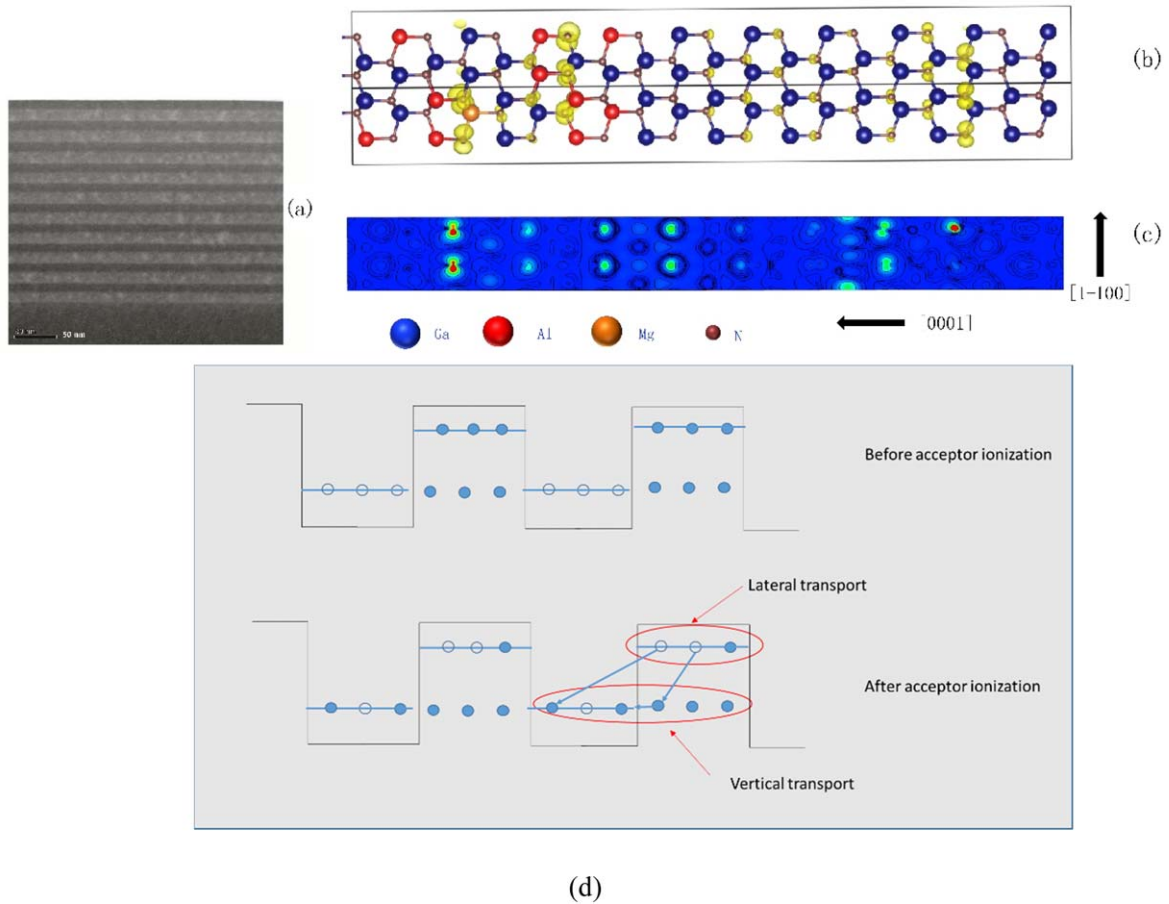**Figure 2.** Structure of the $Al_{0.3}Ga_{0.7}N$/GaN SL and charge distribution of Mg impurity states in a simulated $Al_{0.3}Ga_{0.7}N$/GaN SL. (a) TEM image of our $Al_{0.3}Ga_{0.7}N$/GaN structure for IRS state p-doping. Isosurface charge density plots of Mg impurity states at Γ point of $Al_{0.3}Ga_{0.7}N$/GaN, (b) atomic configuration and isosurface charge density of Mg impurity states in (11–20) plane, (c) isosurface charge density of Mg impurity states in m plane, and (d) a band diagram illustrating the IRS p-doping concept.

exist simultaneously at the $Al_{0.3}Ga_{0.7}N$/GaN interfaces due to the polarization effect. The underlying physics of IRS p-doping will be clarified later. Furthermore, it is worth pointing out that there is still no consensus about whether 2D holes contribute to the vertical direction transport and recombination for LEDs. This deserves further systematic analysis.

First-principles density-functional theory was used to calculate the electronic structure of the selectively doped AlGaN/GaN SL, using a projector-augmented-wave method with generalized gradient approximations implemented in the Vienna *ab initio* simulation package [24]. The charge density of the Mg impurity states was analyzed to clarify the underlying physical mechanism of the IRS doping. The details of the calculation procedure were described elsewhere [21, 25]. The $Al_{0.3}Ga_{0.7}N$/GaN SL structure was simulated by a $2 \times 2 \times 10$ supercell via randomly replacing 13 Ga atoms by Al atoms in $Al_{0.3}Ga_{0.7}N$ layer.

As expected, and illustrated in figure 2, the charge density is mainly accumulated at the Mg atoms. However, due to sharing the same t_{2p} symmetry, Mg impurity states and host N 2p states couple strongly with each other in the nitride matrix environment [26–28]. Thus, the Mg impurity states become delocalized to some extent due to sharing the characteristics

of N 2p orbitals. It could be observed in figure 2 that a significant amount of Mg impurity states was delocalized and distributed in both barriers ($Al_{0.3}Ga_{0.7}N$) and wells (GaN), although only the barriers were Mg doped. Now, the initially localized impurity states in the $Al_{0.3}Ga_{0.7}N$ barrier layers are below or close to the GaN VBM, and act as resonant states in the GaN layer. In this scenario, electrons at the VBM can easily transfer into the impurity states or band without any energy barrier, that is, now the acceptors are self-ionized. Therefore, effective p-type doping can be achieved. Furthermore, as analyzed in the previous reports, the polarization effect could also facilitate the ionization of the deep acceptors and produce a hole sheet, which further increases the hole concentration in the host nitrides [8, 29]. Here, we would like to point out that, even though the structure of IRS p-doping is similar to the p-type SLs, the underlying physics and acceptor ionization process are quite different.

'Superlattice-doping' proposed by Schubert *et al* [10] adopted uniform doping under the consideration that the tunneling of the valence electrons to the acceptor states in the AlGaN layer [30] increases the holes in the GaN layer solely generated by thermal excitation. Reality is more complicated than that, because the conventional hydrogenic mode is not applicable to the acceptor [31]. The acceptor impurity actually

has one empty state and five occupied states in the case of Mg on Ga [32]. Thus, the electrons of the occupied acceptor states are expected to compensate the acceptor states in the AlGaN layer, which will make this approach less effective. With this consideration, it would be better not to dope the GaN layers. Polyakov *et al* [18] suggested the modulation doping only in the AlGaN layer with the consideration that doing so could improve the hole mobility in the GaN layer. In either of these cases, the acceptor states in the barrier layers are considered not affected by the SL effect, because the acceptor Bohr radius is much smaller than the layer thickness. In our approach, when the SL layers are sufficiently thin, the acceptor impurity states are resonant states of the SL. Thus, they are not genuine localized states, but delocalized along the SL axis. The self-ionization of the acceptors will generate high-mobility holes in the SL that are not entirely confined in the GaN layers. Therefore, this can provide not only good lateral, but reasonably good vertical conductivity. The optimal design to achieve good vertical conductivity should have the acceptor impurity state of the barrier approximately aligned with the first quantum confined state of the well, that is, the valence band offset between the barrier and well should be somewhat larger than the acceptor binding energy. Our idea has indeed been experimentally validated, as described below.

The energy-band diagrams of the LEDs were investigated numerically with APSYS simulation software to gain a better understanding of the superior performance of the LED structure with the IRS p-doping layer. Most of the parameters used can be found in [33, 34]. Based on our Hall measurement, the hole concentrations and resistivities for Structure I and Structure II were found to be 3×10^{17} and 3.85×10^{18} cm^{-3}, 2.1 and 0.16 Ω.cm, respectively, showing major improvement in the hole density and conductivity. The achieved hole concentration is comparable to what has been reported with uniformly doped SLs [12, 15, 35, 36], but the conductivity has been improved [8, 9, 13, 16] (0.2 Ω.cm in 13. 6.Ω cm in 36, 0.8–10.5.Ω cm in [16], 0.6.Ω cm in [8], and 0.19 Ω.cm in [16], which reported the record hole concentration), even more than the previous modulation doping result [18].

Figure 3 shows the calculated hole distributions of Structure I and Structure II at an injection current of 350 mA. It can be observed that the hole concentration in the multiple quantum wells (MQWs) of Structure II is obviously increased, indicating the enhancement of the hole injection in the IRS doping LEDs. Such an increase should be attributed to: (i) more effective acceptor ionization by introducing IRS doping mechanism in the p-type barrier layer; (ii) the Al composition in the IRS p-doping layer pulls the effective valence band downwards, and results in the reduction of the potential barrier for hole injection [37]. Consequently, a high efficiency and less efficiency droop could be expected in the device.

To further demonstrate the advantage of the proposed structure, we randomly selected 20 pieces of conventional LEDs and the same number of LEDs with the designed p-type layer. Figure 4 shows the typical (averaged over the 20 LED
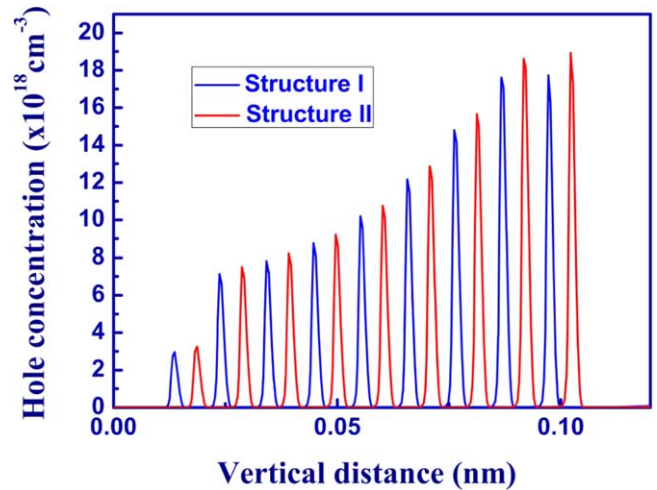

Figure 3. Hole concentration and distribution of LED structure with IRS p-doping layer and conventional p-type GaN layer at 35 A cm^{-2}. Curve of Structure I has been displaced to the left for clarity.
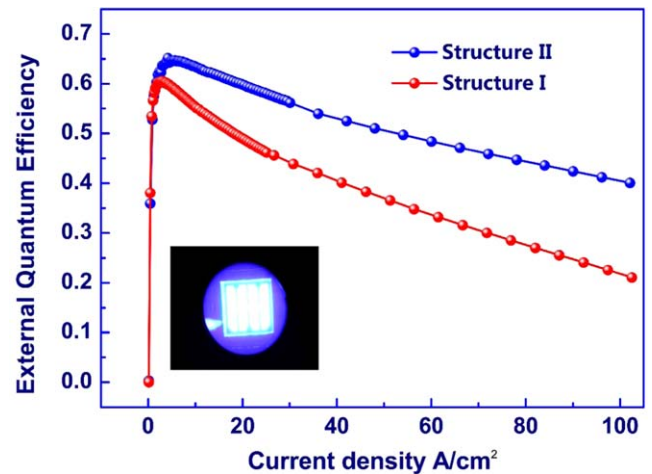

Figure 4. Measured EQE as a function of current for LEDs with different p-type layers.

chips) external quantum efficiency (EQE) as a function of current density. It can be observed that the LEDs with the IRS p-doping layer exhibit a higher efficiency (EQE of 57% @ 40 A cm^{-2}, 45% @ 100 A cm^{-2}) and less droop at high current, better than that of the conventional LEDs (EQE of 42% @ 40 A cm^{-2}, 24% @ 100 A cm^{-2}). We attribute the efficiency gain to our highly p-type layer via introducing the IRS mechanism, which facilitates a more symmetrical carrier injection. More holes are injected into the active layers and recombined with injected electrons, which increases the EQE and effectively suppresses the efficiency droop, especially at high injection. Figure 5 shows the measured *I–V* characteristics for LEDs with different p-type layers. Due to the more effective p-type doping, the LEDs also exhibit a lower operation voltage (3.88V @ 50 A cm^{-2}, 4.86V @ 100 A cm^{-2}) than the control LEDs (4.08V @ 50 A cm^{-2}, 5.06V @ 100 A cm^{-2}).
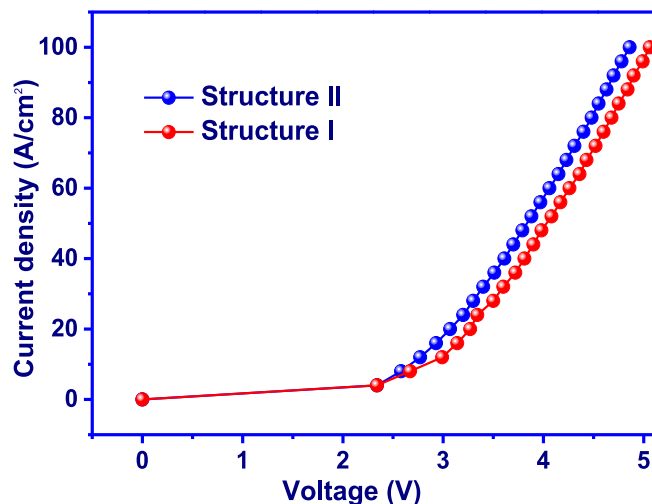
Figure 5. Measured *I–V* characteristics for LEDs with different p-type layers.

4. Conclusions

To conclude, the IRS p-doping was proposed and demonstrated as the p-type layer for high-efficiency nitride-based LEDs. Furthermore, we successfully demonstrated the advantage of the new p-type layer in high-power nitride-based light-emitting devices with reduced efficiency droop and enhanced overall efficiency simultaneously. We attributed such an improvement to better hole injection coming from the effective acceptor ionization and reduction of the band offset. We argued that it is a more promising solution to mitigate asymmetry carrier transport in nitride-based LEDs. By adjusting the Al composition of the IRS doping structure, we expect this approach to be equally applicable for deep-UV LEDs and LEDs to replace p-type nitrides, where efficient p-type doping is more difficult.

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