

N- and P- type Doping in Al-rich AlGa_N and AlN

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Attaining a high conductivity in both p-type and n-type Al-rich AlGa_N epitaxial films is necessary for highly efficient deep-UV emitters. While reliable n-type conductivity has been demonstrated in Al_xGa_{1-x}N up to $x < 0.8$, achieving a reasonable p-type conductivity is a challenge even in Ga-rich AlGa_N films. As one increases the x in Al_xGa_{1-x}N, several point defects and charge compensators appear in the epitaxial film. This report reviews recent observations on doping, conductivity, point defect control of Al-rich AlGa_N films. Discussions on activation energy, state-of-the-art epitaxial material quality, contact formation and surface treatments are also presented.

I. Introduction

III-nitride ultra-wide bandgap semiconductors deep-UV emitters are promising for applications like water purification, laser surgery, communication, etc (1). Interestingly, these semiconductors also offer a higher Baliga figure of merit (BFOM) than SiC and GaN based power devices (2). For highly efficient III-nitride deep-UV emitters, a high conductivity is required in both n-type and p-type AlGa_N epitaxial layers. As of now, a high free carrier concentration in n-GaN and n-Al_xGa_{1-x}N ($x < 0.8$) has already been demonstrated (3-5). However, achieving a high conductivity in Al-rich n- Al_xGa_{1-x}N ($x > 0.8$) and p-Al_xGa_{1-x}N ($0 \leq x \leq 1$) is still a major concern. Moreover, the carriers suffer from significant scattering in Al-rich n-AlGa_N and p-AlGa_N films resulting in lower mobilities. Thus, conductivity in Al-rich n-AlGa_N and p-AlGa_N films is much lower than desired.

This paper describes the materials consideration to develop highly conductive n-type and p-type Al-rich AlGa_N epitaxial layers on sapphire and single crystalline AlN substrates. Section II highlights the current status of Al-rich n-AlGa_N and n-AlN epitaxial layers grown using metalorganic chemical vapor deposition (MOCVD) technique. A discussion is presented on point defect control that can be used to enhance the conductivity by reducing the compensating defects in Al-rich n-AlGa_N epitaxial films. Along with in-situ doping, a discussion on ion-implantation for n-type doping of Al-rich AlGa_N and AlN is also presented. Section III presents the recent reports of doping and activation efficiency in Al rich p-AlGa_N films. A discussion on alternate growth techniques (such as

superlattices and graded p-AlGa_N layers) to achieve a high free hole concentration in Al-rich p-AlGa_N layers are also presented in this review.

II. N-type doping of Al-rich AlGa_N and AlN films

Si is primarily used as the n-type dopant source for all III-nitride epitaxial films. Si typically shows a very low activation energy (E_a) in GaN and Ga-rich AlGa_N (6,7). As a result, carrier density in the range of $\sim 10^{19} \text{ cm}^{-3}$ can be obtained in GaN and Ga-rich n-AlGa_N films. However, Si donor E_a shows a steady rise when the Al mole fraction in AlGa_N goes beyond 0.80 (3). Unfortunately, Si dopants in Al-rich n-AlGa_N undergoes a DX transition with increasing Al composition (8). Si DX-centers act as acceptor-type compensating point defects which is detrimental for the free electron concentration. Moreover, Si doping also shows a “knee behavior” in resistivity with doping (9). At high Si doping levels, self-compensation reduces the free charge in the Al-rich n-AlGa_N epitaxial films. Recently, Harris *et. al.* has reported the formation of $V_{\text{Al}} + n\text{Si}_{\text{Al}}$ complex in highly doped AlN which act as charge compensator to free electrons (10). On the other hand, at low Si doping (below the knee), carbon and vacancy-oxygen complex compensate the free electron concentration. Thus, there exists a trade-off between different compensating species due to Si doping in Al-rich AlGa_N films.

TABLE I. Recent reports on free carrier concentration and resistivity in Al-rich n-AlGa_N films.

x in n-Al _x Ga _{1-x} N	n (cm ⁻³)	ρ ($\Omega\cdot\text{cm}$)	TDD (cm ⁻²)	Substrate	Reference
0.70	$\sim 1.3 \times 10^{19}$	~ 0.0088	10^3 - 10^4	AlN	(8)
0.70	$\sim 1.3 \times 10^{19}$	~ 0.018	Low 10^{10}	Sapphire	(8)
0.70	$\sim 2.2 \times 10^{18}$	~ 0.168	Mid 10^{10}	Sapphire	(8)
0.85	$\sim 2.7 \times 10^{18}$	~ 0.05	5×10^8	Sapphire	(9)
0.96	$\sim 3.5 \times 10^{16}$	~ 4.087	5×10^8	Sapphire	(9)

Control of compensating point defects is also necessary to achieve a high free carrier concentration in Al-rich n-AlGa_N films. Recently, Bryan *et. al.* has shown that the compensating point defect incorporation is a strong function of the threading dislocation density (TDD) in the Al-rich n-AlGa_N film (8). The reduction in point defects in the epitaxial layer also leads to a higher carrier mobility by lowering the charged dislocation scattering. Traditionally, AlGa_N films grown on sapphire substrate suffer from high TDD due to the lattice mismatch. So far, the lowest TDD ($< 10^4 \text{ cm}^{-2}$) has been achieved by growing Al-rich n-AlGa_N on single crystal AlN substrate. A significantly lower TDD in the Al-rich n-AlGa_N film grown on AlN substrate resulted in orders of magnitude higher free carrier concentration compared to films grown on foreign substrate. However, growth of Al-rich n-AlGa_N on foreign substrate using a low TDD template has been shown to significantly enhance the free carrier concentration. Although controlling the TDD in the epitaxial films allows to achieve a very high free carrier concentration, however, a superior mobility offered by low TDD AlN substrate results in a better conductivity (8). Furthermore, a tensile strain leads to cracking in heteroepitaxial AlGa_N layers, whereas homoepitaxial AlN grown on AlN substrates are typically crack-free (11). Thus, growth of Al-rich n-AlGa_N films on single crystal AlN substrate is still the preferred choice to obtain

very high conductivity. Table I highlights some of the recent reports on free carrier concentration and low resistivity obtained in Al-rich n-AlGaN films.

Ion implantation is another technique that can be used to dope AlGaN and AlN films. Some of the previous works on Si ion-implantation to AlGaN has been focused to enhance the contact formation in high electron mobility transistors (HEMTs) (12-14). In a previous attempt, Kanechika *et. al.* has reported a free carrier concentration and E_a of $8.8 \times 10^{15} \text{ cm}^{-3}$ and 294 meV, respectively in Si-implanted AlN grown on sapphire substrate (15). The hetero-epitaxial AlN film grown on sapphire substrate already suffers from a high TDD, and the observed high E_a can be due to the presence of point defects incorporated during growth, and after implantation. However, it should be noted that a lower TDD in the epitaxial film influences a better point defect control. Thus, studies are necessary to understand the Si ion-implantation in AlN homoepitaxial films grown on single crystalline AlN substrates.

It should be noted that Al-rich n-AlGaN films grown on foreign substrates offer a better ohmic contact formation (at low bias voltages) (4,16). A higher TDD in n-AlGaN films allows a significant Frenkel-Poole trap assisted tunneling (FP-TAT) at low bias voltages. However, a lower TDD restricts the FP-TAT current in Al-rich n-AlGaN grown on single crystal AlN substrates. To facilitate a better contact formation to n-AlGaN grown on AlN substrates, RIE surface treatment resulting in a defective surface can enhance the FP-TAT current (4). Moreover, metallization schemes such as V/Al-based contacts outperforms the traditionally used Ti/Al-based metallization schemes by orders of magnitude in Al-rich n-AlGaN films (2,17). All these results point toward the research required to understand the point defect control, growth of high quality epitaxial films, understanding the contact formation mechanisms etc. in Al-rich n-AlGaN films for future deep-UV emitters.

III. Doping and contact analysis of Al-rich p-AlGaN

Achieving high free hole concentration in p-GaN or p-AlGaN has been a major issue for decades. Mg is the only known acceptor impurity source that can be effectively incorporated in GaN and AlGaN films. A free hole concentration in the order of mid 10^{17} cm^{-3} is achievable in p-GaN films grown on sapphire substrates using MOCVD (18). The value of E_a for p-GaN grown on foreign substrates using MOCVD typically lies in the range of 120-180 meV. On the other hand, nearly an order of magnitude higher free hole concentration can be achieved in p-GaN films grown on AlN substrates (19). Mg doped GaN films grown on single crystal AlN substrate show reduction in incorporation of nitrogen vacancies acting as free hole compensator. The availability of higher free carrier concentration screens the Coulombic potential thereby reducing the E_a (20). Thus, E_a less than 100 meV is achievable in p-GaN grown on single crystal AlN substrates (19). However, Mg acceptor activation energy in $\text{p-Al}_x\text{Ga}_{1-x}\text{N}$ is believed to increase monotonically from ~160 meV to 500 meV when x increases from 0 to 1 (21). Contrary to this, recent studies indicate that E_a of acceptors in p-AlGaN bulk films is lower than predicted previously. Kinoshita *et. al.* has reported an E_a of 47-72 meV in $\text{p-Al}_{0.7}\text{Ga}_{0.3}\text{N}$ grown on sapphire substrate (21). Surface treatment was also observed to be effective for p-AlGaN. Chen *et. al.* has reported a free hole concentration of $3.26 \times 10^{17} \text{ cm}^{-3}$ in uniformly

doped $\text{p-Al}_{0.4}\text{Ga}_{0.6}\text{N}$, which increased to $4.75 \times 10^{18} \text{ cm}^{-3}$ by using In surfactants and Mg delta-doping scheme (22).

Apart from bulk p-AlGaN growth, several alternative approaches have also been developed to achieve a high free hole concentration in p-AlGaN. Among them, superlattice structures have been under investigation from several research groups. A short-period superlattice consists of several thin p-AlGaN films with alternating Al mole fraction. Consequently, the periodic oscillations of the valence band of p-AlGaN layers leads to regions where the Mg energy level is much closer to the Fermi-level (23). Consequently, the effective E_a is reduced, and the superlattice p-AlGaN films show a significantly higher free hole concentration compared to the bulk p-AlGaN films having equivalent Al mole fraction. A free hole concentration in the order of 10^{18} cm^{-3} has been reported for Al-rich p-AlGaN superlattices (24,25). Polarization doping schemes have also been used to obtain very high free hole density in p-AlGaN. In polarization doping scheme, a graded p-AlGaN film is grown which yields in the presence of polarization induced 3D charges. Thus, the resultant p-AlGaN film is degenerate of free carriers. Simon *et. al.* has reported a free hole concentration of $\sim 2 \times 10^{18} \text{ cm}^{-3}$ in graded p- $\text{Al}_x\text{Ga}_{1-x}\text{N}$ film grown on sapphire substrate (graded from $x = 0$ to $x = 0.3$) (26). More recently, Dalmau *et. al.* obtained a free hole concentration of $4.5 \times 10^{18} \text{ cm}^{-3}$ in p- $\text{Al}_x\text{Ga}_{1-x}\text{N}$ grown on single crystalline AlN substrates using a grading from $x = 1$ to $x = 0.36$ (27).

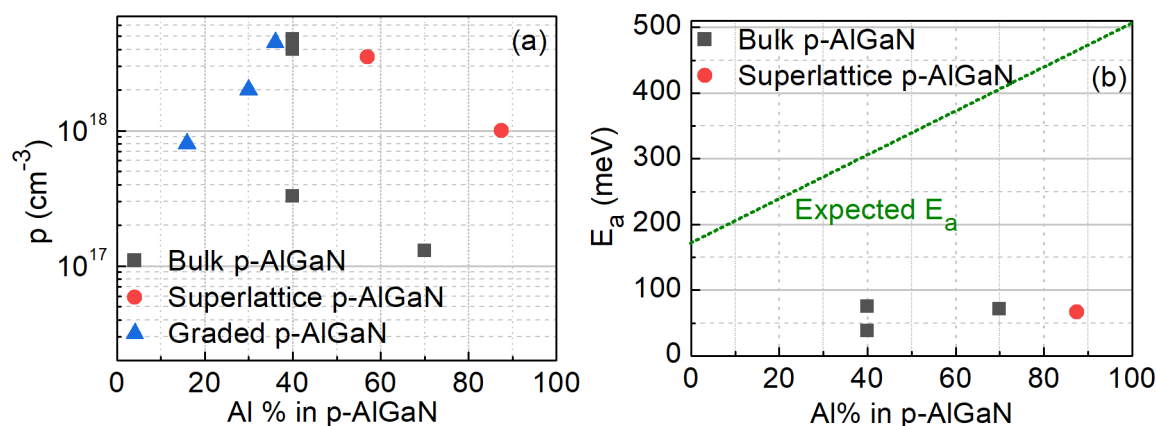


Figure 1. Recent reports on (a) free hole concentration, p , and (b) E_a , in Al-rich p-AlGaN epitaxial layers (21-27).

Figure 1 summarizes some of the recent reports on free hole concentration (p) and E_a observed in p-AlGaN. As observed in Figure 1 (a), free hole concentration (p) in the range of mid- 10^{18} cm^{-3} has already been achieved in bulk p-AlGaN film, p-AlGaN superlattices and graded p-AlGaN layers. This also means that a relatively poor conductivity observed in p-AlGaN is solely due to poor hole mobility. For lateral power devices, low hole mobility can be detrimental to the switching speed. However, for the case of vertical and/or quasi-vertical LEDs or laser diodes, sufficient number of holes can be injected into the active region with the help of vertical electric field. Considering Mg activation efficiency, the reported E_a in p-AlGaN (for both bulk and superlattices) are much lower than the expected

E_a for p-AlGa_{0.9}N, as shown in Figure 1 (b). Interestingly, the E_a observed for p-AlGa_{0.9}N is even lower than p-GaN. Kinoshita *et. al.* has attributed the low E_a in Al-rich p-AlGa_{0.9}N to hole hopping or impurity band conduction mechanism (21). However, further studies are necessary to understand the influence of point defects in the incorporation of compensators (such as hydrogen, nitrogen vacancies, etc.) in Al-rich p-AlGa_{0.9}N films.

IV. Conclusions

In conclusion, this paper provides a brief review of current status of doping in Al-rich AlGa_{0.9}N films grown on foreign and native substrates. Identification of different vacancy-complexes are necessary to understand the charge compensators in Al-rich n-AlGa_{0.9}N films. Control of point defects by lowering the threading dislocation density increases the free carrier concentration in the Al-rich n-AlGa_{0.9}N films. On the other hand, Al-rich p-AlGa_{0.9}N films has been shown to offer a high free hole concentration and significantly lower acceptor activation energy. All these points highlight the efforts made to realize high conductivity in both n-type and p-type Al-rich AlGa_{0.9}N films. With advancement in availability of single crystal AlN substrates, high performance vertical and/or quasi-vertical Al-rich AlGa_{0.9}N devices like LEDs and laser diodes can be realized in the near future.

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