STATUS OF ION IMPLANTATION DOPING AND ISOLATION OF III-V NITRIDES

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Ion implantation doping and isolation has played a critical role in the realization of high performance photonic and electronic devices in all mature semiconductor material systems. This is also expected to be the case for the binary III-V nitrides (InN, GaN, and AlN) and their alloys as the epitaxial material quality improves and more advanced device structures are fabricated. With this in mind, we review the status of implant doping and isolation of GaN and the ternary alloys AlGaN, InGaN, and InAlN. In particular, we reported on the successful n- and p-type doping of GaN by ion implantation of Mg+P and Si, respectively, and subsequent high temperature rapid thermal anneals in excess of 1000 °C.

In the area of implant isolation, N-implantation has been shown to compensate both n- and p-type GaN, N and O-implantation effectively compensates InAlN, and InGaN shows limited compensation with either N or O implantation.

INTRODUCTION

Ion implantation has been the foundation of most advanced electronic and, to a lesser extent, photonic devices in mature semiconductor materials systems such as silicon and gallium arsenide. The selective doping and isolation capabilities of ion implantation enables many high performance device structures. The III-V nitrides are far from a mature materials system, however, ion implantation has already been used successfully to achieve selective area doping and isolation. In this paper we review the status of ion implantation processing in the III-V nitrides.

In the early 70’s Jacques Pankove and co-workers used ion implantation to characterized the photoluminescence levels of an array of species in GaN [1]. In this work the levels of the common III-V semiconductor acceptors (C, Be, Mg, Zn, and Cd) were first determined as summarized in Table I. Mg was reported as having the shallowest acceptor level of ~240 meV with Zn, at ~ 580 meV, having the strongest luminescence intensity [2]. No electrical properties of the implanted species were reported. Although more recent measurements suggests the Mg ionization level is closer to 150 meV, Mg is still the shallowest acceptor reported as electrically active in GaN. Due to Mg’s relatively shallow ionization level (this level is still deep compared to acceptor levels in other III-V semiconductors such as GaAs or InP of ~25 meV), it has been employed for p-type doping of the bright GaN LEDs reported by Nichia [3].
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recently the only other implantation work on III-N material was Be and N implants in GaN and AlGaN to achieve donor compensation to enhance Schottky barrier formation [4,5].

**Table I**

Photoluminescence peak position, distance from the conduction band, and the rank order of luminescence intensity for GaN implanted with the species listed and annealed in NH$_3$ at 1050 °C for 1h (data from Jacques Pankove in ref. 1).

<table>
<thead>
<tr>
<th>species</th>
<th>peak position (eV)</th>
<th>(bandedge-peak) (meV)</th>
<th>rank order of PL intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>3.21</td>
<td>240</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>3.2</td>
<td>250</td>
<td>9</td>
</tr>
<tr>
<td>P</td>
<td>2.88</td>
<td>570</td>
<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>2.87</td>
<td>580</td>
<td>1</td>
</tr>
<tr>
<td>Cd</td>
<td>2.70</td>
<td>800</td>
<td>4</td>
</tr>
<tr>
<td>As</td>
<td>2.58</td>
<td>920</td>
<td>9</td>
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<td>1000</td>
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<tr>
<td>Be</td>
<td>2.16</td>
<td>1290</td>
<td>5</td>
</tr>
</tbody>
</table>

**IMPLANTATION ISOLATION**

With recent advancements in the growth of the III-V nitrides by MOCVD, MBE, and MOMBE it has been appropriate to re-examine the ion implantation characteristics of these materials. S. J. Pearton, et al. [6], first addressed the implant isolation of the In-containing nitrides (InN, InGaN, and InAlN) using F-implantation. They showed that, for the conditions studied, InN did not show significant compensation while the ternaries increased in sheet resistance by roughly an order of magnitude after a 500 °C anneal. Data for a more extensive study of In$_x$Ga$_{1-x}$N implant isolation for varying In-composition using N- and F-implantation is shown in Fig. 1 [7]. Three implant schedules were employed to vary the average ion concentration (N$_p$) in the InGaN layer from $5 \times 10^{18}$ cm$^{-3}$ (low), $5 \times 10^{19}$ cm$^{-3}$ (medium), to $5 \times 10^{20}$ cm$^{-3}$ (high). InN or the InGaN ternaries only realize a maximum of a 50 fold increase in sheet resistance independent of ion species after a 500 °C anneal. The damage levels created by N-implantation are estimated from the Arrhenius plot of Fig. 2 to be a maximum of 390 meV below the conduction band. The levels are seen to be high in the energy gap, not near midgap as is ideal for implant compensation. The position of the damage levels is analogous to the defect position reported for implant compensated n-type InP and InGaAs [8] but different from the midgap, damage-associated, states created in GaAs and AlGaAs [9,10].
InAlN, on the other hand, can be highly compensated with N- or O-implantation with over a three order-of-magnitude increase in sheet resistance after a 600 to 700 °C anneal while F-implantation produces only one order-of-magnitude increase in sheet resistance as seen in Fig 3 [6,11]. As seen in Fig. 4, the compensating level in InAlN is also high in the bandgap, although it is sufficiently deep to achieve highly compensated material. The enhanced compensation for N- and O-implantation in InAlN may result from a reduction in N-vacancies for N-implantation or the formation of an O-Al complex for O-implantation. An O-Al complex is thought to also be responsible for thermally stable implant isolation in O-implanted AlGaAs [9,10].

Fig 1: Sheet resistance versus anneal temperature for four compositions of \( \text{In}_{x}\text{Ga}_{1-x}\text{N} \) implanted with either \( ^{14}\text{N} \) or \( ^{19}\text{F} \) at one of three doses (low, medium, or high).

Fig 2: Arrhenius plot of the resistance/temperature product for as grown \( \text{InN} \) and \( \text{In}_{0.47}\text{Ga}_{0.53}\text{N} \) and three samples implanted with \( \text{N} \) at a base dose of \( 5 \times 10^{14} \text{ cm}^{-2} \) \( (N_p = 5 \times 10^{20} \text{ cm}^{-2}) \) and annealed at 500 or 600 °C. The estimated ionization level of the compensating defect is shown for each sample.

Fig 3: Sheet resistance versus anneal temperature for \( \text{In}_{0.75}\text{Al}_{0.25}\text{N} \) implanted with \( \text{O}, \text{N}_2 \), or \( \text{F} \) for a base dose of \( 5 \times 10^{13} \text{ cm}^{-2} \) (O and N) or \( 8 \times 10^{13} \text{ cm}^{-2} \) (F).
Fig 4: Arrenhius plot of the resistance/temperature product for In0.75Al0.25N implanted with a medium (N_p = 5x10^{19} \text{ cm}^{-3}) dose of N and a high (N_p = 5x10^{20} \text{ cm}^{-3}) dose of N or O and annealed at 600 °C. The estimated ionization energy of the compensating defect level is shown in the figure.

Fig 5: Sheet resistance versus anneal temperature for n- and p-type GaN implanted with N at energies of 50, 180, and 250 keV and corresponding doses of 2, 4, and 6x10^{13} \text{ cm}^{-2}.

For implant isolation of n-type GaN, S. C. Binari et al. [12], have used He implantation with the damage levels not annealing out until 800 °C. As seen in Fig. 5, N-implantation has also been shown to effectively compensate both p- and n-type GaN [13]. For n-type GaN the compensating damage anneals out starting at 850 °C while this does not occur until 950 °C for N-implanted p-type GaN. The defect level in this case is 0.8 to 0.9 eV below the conduction band, still not at midgap, but sufficient to realize a sheet resistance > 10^9 \Omega/\square.

**IMPLANTATION DOPING**

Recently ion implanted n- and p-type doping of GaN has been achieved for the first time with Si and Mg+P implants, respectively, and annealing at 1050 to 1100 °C [13]. Figure 6 shows the sheet resistance versus anneal temperature for the first demonstration of electrically active implant doping of GaN. Figure 7.a shows an Arrenhius plot of the carrier concentrations of the Mg+P and Si implanted samples annealed at 1100 °C from which ionization levels can be determined as 62 meV for the Si-sample and 170 meV for the Mg+P sample. Fig 7.b shows the Arrenhius plot of the resistance/temperature product which can also be used to estimate the ionization levels. In this case, the ionization level determined from fig. 7.b are 29 and 116 meV for Si and Mg, respectively, and are slightly
lower than those determined from the sheet carrier concentration of Fig. 7.a. There is still some debate as to the more correct approach to determine the ionization level in GaN due to the potential role of impurity band conduction [14]. Therefore, for completeness, both approaches are included here. For both approaches, the ionization levels for Si and Mg are in the range reported in the literature [15]. Based on the ionization levels of Fig. 7.a, ~93% activation of the Si as donors was achieved and ~100% activation of Mg as acceptors was achieved. The P co-implantation was found to be necessary to achieve p-type material with Mg implantation as evident in Fig. 6 where the Mg-only sample remains n-type and converges on the same sheet resistance as the unimplanted GaN for the 1100 °C anneal. The effect of the P co-implantation may be explained by a reduction of N-vacancies or an increase in Ga-vacancies leading to a higher probability of Mg occupying a Ga-site. P co-implantation has also been shown to be effective in enhancing activation and reducing diffusion for p-type implantation in GaAs [16]. A further study of the role of the co-implantation species on Mg activation is underway, however, based on work in other III-V semiconductors, other column V species such as N or As may also be effective in realizing p-type implantation doping. Work is also underway on the implantation properties of other acceptors such as C and Be as well as on the dose effects for Si implantation to study donor saturation.

**Fig 6:** Sheet resistance versus anneal temperature for GaN implanted with either Mg, Mg+P, Si, or unimplanted. The Mg+P sample is seen to become p-type after a 1050 °C anneal and the Si-implanted sample shows a sharp decrease in sheet resistance after a 1100 °C anneal.

**Fig. 7:** Arrhenius plot of the resistance/temperature product and the electron or hole concentration in Si and Mg+P implanted annealed at 1100 °C.
Further characterization of the implant activation anneal is shown for various Si implants in GaN in Fig. 8. The sheet resistance is seen to continue to decrease for anneals out to 1200 °C. An unimplanted sample annealed at 1100 °C remained highly resistive (ρs = 1x10^9 Ω/□). These results suggest that further work is needed to optimize the annealing time and temperature for implant activation in GaN, however, it seems clear that temperatures in excess of 1100 °C are required.

SURFACE DEGRADATION

As demonstrated in the previous section, high temperature annealing ≥ 1000 °C is required to activate dopants in GaN. Therefore is important to study the thermal degradation of the III-V nitrides.

A study of the effect of high temperature annealing on surface morphology using atomic force microscopy (AFM) and scanning electron microscopy (SEM) and chemical changes using Auger energy spectroscopy (AES) and energy dispersive analysis by x-ray (EDAX) of In-containing nitrides has been performed [17]. For In0.47Ga0.53N and In0.75Al0.25N the formation of In-droplets on the surface was observed by SEM with the chemical content confirmed by EDAX for 800 °C anneals. Fig. 9 is an SEM micrograph of a In0.47Ga0.53N after an 800 °C anneal showing the In-droplets.

Work on the thermal stability of GaN up to 1100 °C has shown morphology and luminescence improvements [18]. Using AFM to determine surface roughness, GaN samples annealed from 750 to 1100 °C were found to become smoother when annealed in Ar or N2 as shown in Fig. 10. In addition, both annealed samples showed stronger bandedge emission as compared to an as-grown sample. The sample annealed in N2 showed a reduced deep level emission level near 2.2 eV which is typically associated
with defect or impurity levels while the sample annealed in Ar showed an increase in the deep level emission. Although more structural and chemical analysis is required to understand the mechanism responsible for these changes, clearly rapid thermal annealing of GaN up to 1100 °C does not result in sample decomposition. This is consistent with the high activation energy of decomposition of 3.24 eV determined by Groh and co-workers for GaN annealed in vacuum [19].

**Fig. 10:** RMS roughness of GaN samples versus anneal temperature for samples annealed in Ar or N₂.

**CONCLUSION**

The status of ion implantation doping and isolation of GaN and the ternary III-V nitrides (AlGaN, InGaN, and InAlN) was reviewed. Successful p- and n-type implant doping as well as implant isolation has been demonstrated for GaN. Extensive studies of the implant isolation properties of InGaN and InAlN have shown InGaN to yield limited compensation while InAlN can be converted to a sheet resistance $\geq 1 \times 10^9 \, \Omega \cdot \square$. Thermal stability of In-containing nitrides has been shown to be limited to $\leq 900 \, ^\circ C$ while GaN can be annealed up to 1100 °C without degradation. Ion implantation is expected to play an important role in the realization of advanced devices fabricated in this material system as it has in all other mature semiconductor material systems.

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**References:**


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