

Investigation of molecular co-doping for low ionization energy p-type centers in (Ga,Al)N

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ABSTRACT

This work initiates an investigation of molecular co-doping to produce p-type centers in (Ga,Al)N with ionization energies lower than Mg. Dopant complexes can be formed between a doubly ionized acceptor such as (Cu, Li or Ag) and a singly ionized donor (silicon). Ion implantation of Cu, Li and Ag into silicon doped GaN films grown by Metalorganic Chemical Vapor Deposition (MOCVD) has been performed. Secondary ion mass spectroscopy (SIMS) data confirmed the simulated depth profile. High resolution X-ray diffraction and Raman spectroscopy were used to characterize the crystalline damage and subsequent recovery upon anneal. A complete recovery was observed after high temperature (700-900°C) annealing. Low temperature (6K) photoluminescence (PL) for Cu-implanted GaN showed bands identified with crystalline lattice damage due to the Cu-implantation. The annealed samples showed recovery of standard crystalline GaN features. Additional donor-acceptor pair features are observed below 3.35 eV indicating the existence of an acceptor state.

INTRODUCTION

GaN (and its alloys with Indium and Aluminum) has become the dominant material system for the fabrication of light emitting diodes operating in the blue and ultra-violet ranges. One of the major obstacles to overcome for the development of electronics using GaN-based materials is the lack of a good p-type dopant. Once Nakamura^{1,2} showed that Mg could be used as an acceptor, GaN was rapidly developed into a commercial product—blue LEDs. However, Mg as a dopant is far from ideal. Mg is an acceptor in GaN residing between 180 meV to 250 meV from the valence band edge making ionization difficult at room temperature.^{3,4} This problem is greater at shorter wavelengths, and higher aluminum concentrations, due to a further deepening of this center. Thus Mg is only used because no other alternative exists. By solving this problem, it would be possible to make not just more efficient blue (and UV) LEDs, but it would also make possible improved high current injection devices, such as blue and UV lasers.

The use of dopant complexes or molecular co-dopants, has been investigated towards the goal of improving p-type doping in GaN. Katayama-Yoshida and Yamamoto^{5,6} have suggested that co-doping of certain elements might create more shallow-lying acceptor states, based on theoretical models and simulations of co-doped materials. Their work implies that multiple co-dopants might preferentially form complexes which themselves lie closer to the band edges and are thus more efficiently ionized. Specifically, some researchers have observed evidence for

enhancement of p-type doping in GaAs when doped with both Si and Cu.⁷ Others have noted that co-doping silicon with both Se and B causes a decrease in the ionization energy of the selenium donor compared with singly ionized selenium by itself⁸. Selenium as a singly ionized dopant which resides 0.3 eV from the conduction band, but when boron is incorporated into the silicon lattice, it forms a complex with Se and the ionization energy is lowered to 0.2 eV. These researchers hypothesize that the Coulombic attraction of doubly ionized Se attracts the positively charged boron acceptor and that together they form a complex with lower single donor energy. The equivalent band diagram for acceptors in GaN is depicted in Figure 1. For this work on GaN there are a number of acceptors which, determined by their (valence) electron configuration, are potential doubly ionized acceptors. These elements and the possible corresponding singly ionized donors are listed in Table I. The type I donors are from column 4A of the periodic table and can, in principal, be amphoteric dopants in III-Nitride materials. The type II donors are from column 6A of the periodic table and are non-amphoteric dopants.

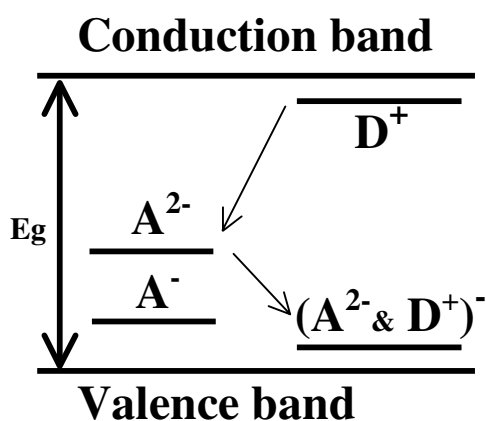


Figure 1. A schematic depiction of singly ionized acceptor (A^{-}), doubly ionized acceptor (A^{2-}), a singly ionized donor (D^{+}), and a complex formed by the attraction of the latter two states ($A^{2-} & D^{+}$). By forming a complex, the doubly ionized acceptor can create an energy level below that of the original singly ionized acceptor, and thus enhance the ionization efficiency of the p-type dopant.

Table I. Potential elements for co-doping in GaN.

Category	Acceptor	Donor
I	<u>Li</u> , Na, K, <u>Cu</u> , <u>Ag</u> , Au	<u>Si</u> , Ge, Pb, Sn
II	<u>Li</u> , Na, K, <u>Cu</u> , <u>Ag</u> , Au	O, S, Se, Te

EXPERIMENTAL DETAILS

For the initial testing of molecular co-doping in GaN, silicon was chosen as the most common n-type dopant. Cu was the initial acceptor material, followed by Li and Ag, which are still under investigation. The GaN films were deposited on sapphire wafers using metal-organic chemical vapor deposition (MOCVD). The gallium source was TMGa and silane was used as the source for silicon dopant. The carrier gases included ammonia and nitrogen. The films are approximately 2 μm thick and doped uniformly throughout with silicon at a level of $1.8 \times 10^{18} \text{ cm}^{-3}$ or $3.8 \times 10^{18} \text{ cm}^{-3}$, unless stated otherwise. After film deposition, ^{63}Cu ions were implanted into the films both at room temperature and at 375°C . The dosage level was $3.4 \times 10^{13} \text{ cm}^{-2}$, and the

implant energy was 280 keV. Based on the implant simulation and secondary ion mass spectroscopy, the Cu had a peak implantation concentration of $3 \times 10^{18} \text{ cm}^{-3}$ at a depth of 100 nm and a full width at half max of $\sim 90 \text{ nm}$. After implantation, the samples were annealed using an AET rapid thermal annealing unit at 600°C , 700°C and at 900°C for 2 minutes under N_2 ambient to enable recovery from the damage caused by the implantation. This paper focuses on the data obtained from the Cu-implanted films.

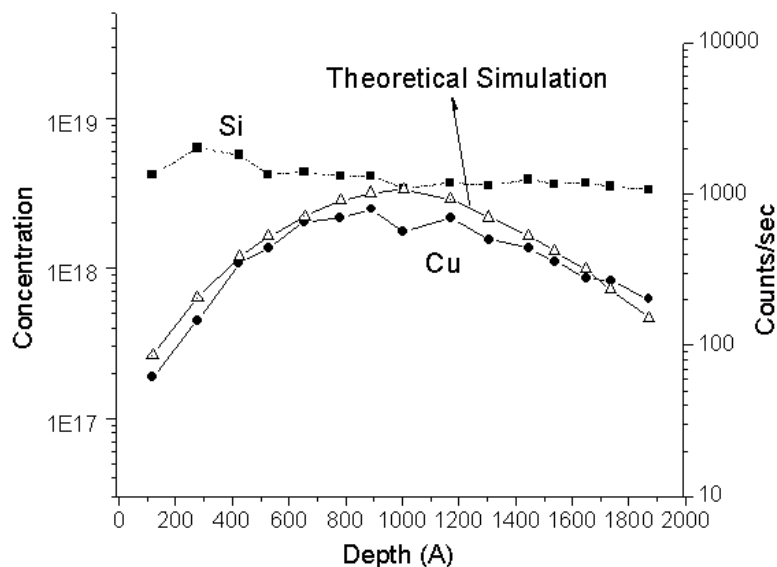


Figure 2. Secondary Ion Mass Spectrometry of a film of GaN:Si, implanted with Cu.

A second series of films, grown at 1050°C using TMGa as a source gas and 200 ppm SiH_4 as the doping source, were grown in a reactor with a modified injection system. This second set of films was doped with silicon to $\sim 1.5 \times 10^{19} \text{ cm}^{-3}$. These films were then ion implanted with Ag and Li at doses of $1 \times 10^{15} \text{ cm}^{-2}$ and $1 \times 10^{16} \text{ cm}^{-2}$ at energies of 60 keV (Li) and 200 keV (Ag) at room temperature and 7° off-axis to avoid channeling. These samples were annealed, also in a rapid thermal annealing unit, in N_2 for 5 minutes at 850°C to recover from implant-damage to the lattice.

X-ray diffraction (XRD) measurements were performed on a Philips X'pert MRD triple-axis diffractometer equipped with a four bounce Ge (022) monochromator and a Cu sealed anode. 2θ - Ω scans were carried out on the (0004) planes of the samples prior to implantation, after implantation, and after annealing. Photoluminescence spectra were taken at room temperature and 6K for the as-grown, as-implanted, and annealed samples.

RESULTS AND DISCUSSION

X-ray diffraction was used to confirm the healing of implant-damage after annealing as shown in Figure 3. After implantation and XRD measurements, the films were rapidly annealed at 700°C and at 900°C for 2 minutes in nitrogen, as noted above, to remove lattice damage caused by the implantation. The post-implant films exhibited an additional, subsidiary band at $\sim 0.43^\circ$ below the GaN (0004) peak. Similar peaks were also observed for the Li and Ag implants. Annealing successfully removed the subsidiary peak of the GaN (0004) peak for all the samples. This removal indicates the removal of the lattice damage. Raman spectroscopy confirmed the same results regarding lattice damage and recovery.

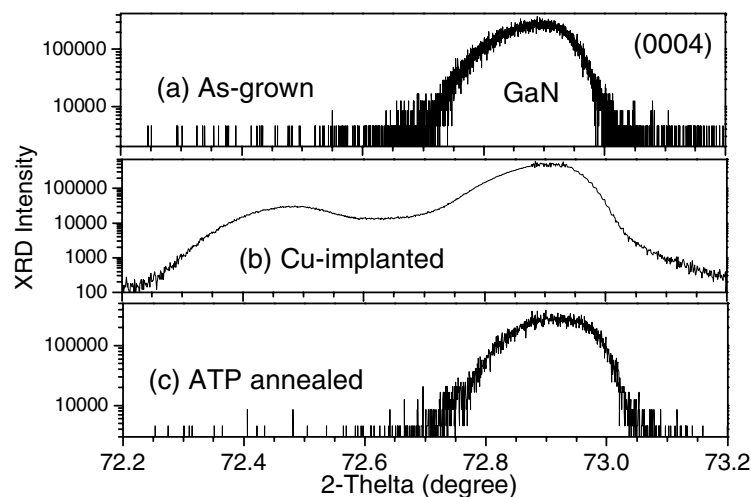


Figure 3. X-ray diffraction of as-grown, implanted, and annealed samples. The anneal was at 700°C, for 1 minute in N₂. Complete elimination of the subsidiary peak at 72.43° is interpreted as removal of most of the implantation damage to the GaN lattice. Similar results were observed for Li and Ag implanted samples and at annealing temperatures from 700-900°C.

A study of the low temperature photoluminescence (PL) of these samples was undertaken to determine whether bands similar to those commonly observed for acceptor states such as Mg could be observed. PL spectra were taken at room temperature (298 K) and at 6 K. Figure 4 shows the PL spectra for the as-grown, implanted, and annealed films at 6 K. The first observation is that there is little difference between the 700°C and 900°C annealed films. Thus future studies will only need to anneal ion implanted films at 700°C. PL spectra were also taken for both the room temperature ion implanted and the 375°C implanted samples (not shown here). The differences in these spectra are exceedingly minor and indicate that room temperature ion implantation followed by anneal is sufficient to remove structural damage to the GaN lattice. The as-implanted sample has a very broad structural defect band from ~3.2 eV down to 2.6 eV. This band disappears upon anneal, indicating the removal of implant damage.

Beside the near bandedge emission dominated by silicon bound excitons, the emission band around 3.29 eV is the most remarkable feature in the as-grown and the annealed samples. The zero phonon line (ZPL) peaks at 3.29 eV and is followed by two longitudinal-optic (LO) phonon replicas at 3.197 eV and 3.107 eV, respectively. This peak is attributed to transitions involving Si dopants. For the as-grown sample it is believed that the donor acceptor pair transition (DAP) is facilitated by the amphoteric character of the silicon since silicon can also reside in an acceptor state for concentrations typically greater than 10¹⁸ cm⁻³. This assignment was not confirmed through the use of by excitation density-resolved PL. We note that the DAP ZPL consists of at least two different peaks caused by different acceptors and donors. Here, a pronounced difference is observed for the as-grown and the implanted samples. After copper implantation and annealing, a second peak of the ZPL is observed redshifted by 10 meV in comparison to that of the as-grown sample. Assuming the same donor state contributing to the DAP as in the as-grown sample and the respective conduction band to acceptor transition⁹, the binding energy for this acceptor transition is thus estimated to be approximately 200 meV.

Bright excitonic emission, the lack of blue emission band and the strong reduction of the intensity of the yellow luminescence band indicate a good crystalline quality as well as a low compensation grade in the p-doped samples after the implantation and annealing procedure.

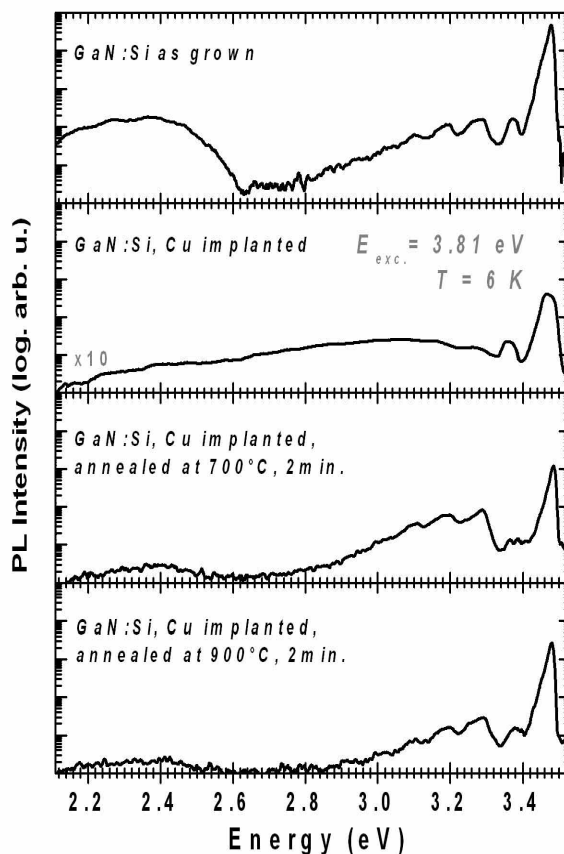


Figure 4. Photoluminescence spectra from 2.1 eV to 3.5 eV. Annealed and as-grown samples have quite similar spectra. The as-implanted sample has a very broad structural defect band from ~3.2 eV down to 2.6 eV which disappears upon anneal. The intensities of the spectra are normalized to the maximum of the as-implanted sample. For the sake of clarity, the intensity of the implanted sample was magnified by a factor of ten.

Scratch diodes were also constructed to see if the dopant complexes were electrically active. This was achieved by placing a top contact on the top epilayer that should show p-type conductivity and ‘scratching’ down to the thick n-type underlying the implanted region. It is expected to easily form a good ohmic contact to the heavily doped n-type material. The implantation profile shown for Cu sample in Figure 2 shows that the surface of the implanted sample will likely maintain its n-type character with any p-complexes underneath. The initial measurements were inconclusive. The Cu and Ag implanted samples showed no evidence of a diode function. The Li-implanted samples did show some evidence for rectification for lower

implantation concentrations possibly due to the diffusion of Li to the surface, but this result was not duplicated for higher implantation concentrations. Additional measurements are now being conducted on diodes that are being fabricated after etching away the surface n-type layer.

CONCLUSION

Copper ion implantation into heteroepitaxially grown Si-doped GaN films on sapphire substrates causes lattice damage as seen by XRD and PL. This damage can be recovered upon a 2 minute anneal in N₂ at a temperature of 700°C. Annealed films were measured with low temperature photoluminescence at 6 K. Peaks associated with broad defects were observed for the as-implanted sample. The annealed sample has peaks similar to the as-grown sample. These peaks are associated with donor-acceptor pair and conduction band-acceptor transitions and place an acceptor at ~200 meV from the band edge.

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REFERENCES

1. S. Nakamura, M. Seino, and T. Mukai, *Japanese Journal of Applied Physics, Part 2 (Letters)* **30**, L1708 (1991).
2. S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, *Japanese Journal of Applied Physics, Part 2 (Letters)* **31**, L139 (1992).
3. Y. Nakano and T. Jimbo, *physica status solidi c* **1**, 438 (2002).
4. J. K. Sheu and G. C. Chi, *Journal of Physics: Condensed Matter* **14**, R657 (2002).
5. H. Katayama-Yoshida, T. Nishimatsu, T. Yamamoto, and N. Orita, *Journal of Physics: Condensed Matter* **13**, 8901-14 (2001).
6. T. Yamamoto and H. Katayama-Yoshida, *Materials Science Forum* **258-263**, pt.2, 1185 (1997).
7. K.H. Schoenbach, V.K. Lakdawala, R. Germer, S.T. Ko, *Journal of Applied Physics* **63**, 2460 (1988).
- 8 H. R. Vydyanath, J. S. Lorenzo, and F. A. Kroger, F.A., *Journal of Applied Physics* **49**, 5928 (1978).
- 9 J. Jayapalan, B. J. Skromme, R. P. Vaudo, and V. M. Phanse, *Applied Physics Letters*, **73**, 1188 (1998).