Mg–Ga liquid metal ion source for implantation doping of GaN

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A magnesium liquid metal ion source was investigated for *p*-type doping of GaN. The metal is an alloy composed of 33.3% Mg and 66.7% Ga. The source type is a direct heating needle source with a spring-type reservoir, which is constructed using tungsten wire and a ceramic tube. The source has been tested and characterized in a NanoFab 150 focused ion beam (FIB) system. A typical source lifetime was 250 μA h. Mg^+ ion implantation of GaN thin films has been performed at different energies between 30 and 100 keV for doses ranging from 5×10^{13} to 1×10^{15} cm^{-2}. After Mg^+ FIB implantation, samples were annealed at 1100 °C in N_2 ambient. Low temperature photoluminescence with a He–Cd laser of 325 nm exhibited the donor—acceptor recombination peak, which was enhanced by the activated magnesium ions. © *2001 American Vacuum Society.*
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I. INTRODUCTION

Since gallium nitride (GaN) was revealed as a wide and direct band gap semiconductor,[1] enormous work has been done to realize its predicted advantages in devices. High-quality single crystal films were obtained and *p*-type GaN was also realized by different approaches.[2,3] Magnesium is the most promising species *p*-type dopant. Mg ion implantation of GaN thin film and Mg acceptor associated energy levels have being studied by many groups.[4–9] Various device prototypes were designed and GaN based light emitting diodes (LEDs) are commercially available. Ion implantation of Mg and Si has also been used to manufacture a GaN blue LED.[10] However, the nature of Mg doping and the method of incorporating Mg into GaN are far from clear.

Focused ion beam (FIB) is well known for its capability in the field of microfabrication. As a maskless direct writing instrument, a FIB provides great flexibility for fabricating prototypes of novel optoelectronic devices. Magnesium liquid metal ion source (LMIS) is a critical part to make a FIB a powerful tool in GaN research. Nevertheless, to the best of our knowledge, no Mg LMIS has been reported to date. Magnesium is an alkaline metal with moderate melting point and high vapor pressure. Compared to the LMIS working vacuum environment (10^{-7} Torr), the Mg vapor pressure is 3 Torr at its melting point (~650 °C). Therefore a pure metal ion source of magnesium is impossible. However, alloying Mg with other metals can substantially reduce the melting point with a concomitant reduction in vapor pressure. Gallium is well known for its low melting point, while its vapor pressure is surprisingly low at high temperature. We have selected an alloy containing 33.3% Mg and 66.7% Ga (Ga_2Mg) for its rich magnesium component and very low melting point (285 °C, see Fig. 1, Mg–Ga phase diagram[11]). At this temperature the vapor pressure of magnesium is below 10^{-4} Torr.

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II. EXPERIMENT

The source structure used in this study is the needle-reservoir type. The reasons for choosing this source type are ease of fabrication and stable operation. An aluminum oxide rod was used as supporting and insulating material. Tungsten was selected to form the emitter and spring-shaped reservoir because of its high melting point and stiffness. The needle was ground and polished mechanically until the radius of the apex was approximately 10 μm. The sources and the alloys were then tested in a test station. Detailed source and test station design were reported elsewhere.[12]

A mixture of gallium and magnesium chunks with an atomic ratio of 2:1 was placed in a molybdenum crucible, which was supported by a tungsten coil in the center of the test station chamber. The tungsten coil also served as a heating element, able to heat the crucible to temperatures above 1800 °C. After the chamber was pumped down to below 10^{-7} Torr, the crucible temperature was raised very slowly to prevent severe evaporation of Mg. During the process, the temperature of the molten alloy was closely controlled between its melting point (285 °C) and 350 °C for up to 4 h to ensure adequate mixing and to reduce loss of magnesium. The tungsten source structure was preheated to incandescent temperature to clean off organics and oxide. Then the temperature was lowered down to the crucible temperature and the source was dipped into the melt for wetting and loading the alloy, 2 min is sufficient for source loading when good wetting occurs. By applying appropriate extracting voltage and heating current, the loaded source was preliminarily tested *in situ*.

Next, the magnesium source was transferred into a NanoFab 150 FIB system. With high voltage capability up to 150 kV, the two-lens FIB system incorporates an $E\times B$ mass separator with a sensitivity of $m/\Delta m=50$. The Mg–Ga source was positioned 3.5 mm upstream of a Wehnelt electrode with an aperture of 3 mm in diameter. The extractor electrode was positioned 25 mm downstream of the Wehnelt electrode, which has an aperture of 1.85 mm in diameter. The extractor voltage V_E is applied between the extractor elec-

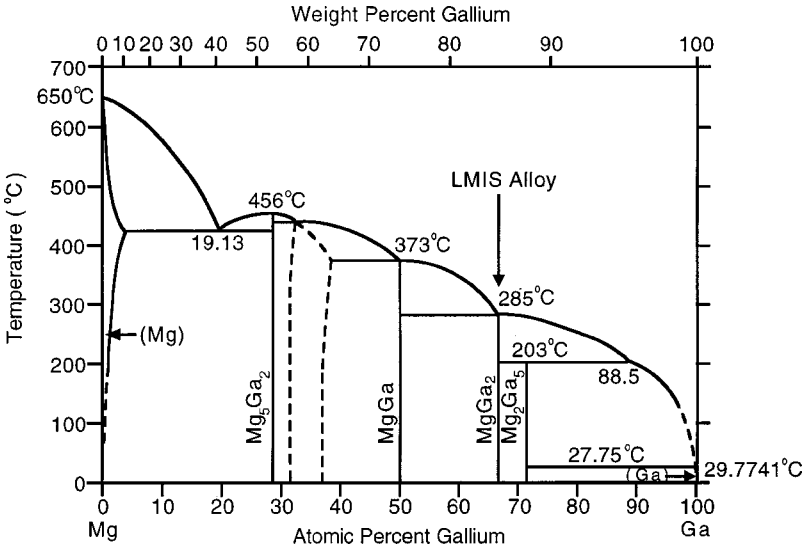

FIG. 1. Magnesium–gallium phase diagram.

trode and the source. The Wehnelt electrode was biased at positive 1.1 kV relative to the source. An automatic source stabilization program is used to maintain steady emission by adjusting the Wehnelt electrode voltage. The target current was periodically collected by a Faraday cup in the target chamber and measured by an external picoammeter. During the experiment, the total acceleration voltage was maintained at 30 kV.

The implanted magnesium dopant was activated by rapid thermal treatment in an AG Associates Heatpulse 410 rapid thermal processor (RTP) at 1000 °C for 15 s in nitrogen.

The photoluminescence (PL) of the sample was investigated by pumping with a He–Cd laser emitting 15 mW at 325 nm. An Acton Research Corp. SpectraPro–500 monochromator with a PD439 photomultiplier tube (PMT) was utilized to detect the dispersed luminescence. A Princeton Applied Research 124A lock-in amplifier with an optical chopper was used to amplify the signals from the PMT. During the PL measurement, the sample is cooled in a MMR R2300 Joule-Thomson type refrigerator with a K-20 temperature controller. With nitrogen as the cooling gas the temperature can be lowered down to 77 K. PL intensity was measured at different temperatures.

III. RESULTS AND DISCUSSION

Figure 2 shows the mass spectrum of a Mg–Ga LMIS. The spectrum was obtained by sweeping the electric field of the $E \times B$ filter from 0 to 80 V while the magnetic field was driven by a direct current of 0.75 A. The voltage was then converted to the mass/charge (m/q) ratio. The mass spectrum was obtained while the source was operated with the extractor voltage set at 7.4 kV and a total ion emission current of 30 μA. For a newly made source, Mg took approximately 16% of the total beam current. The ion beam components associated with the three main magnesium isotopes ^{24}Mg, ^{25}Mg, and ^{26}Mg can be distinguished by utilizing the system's mass filtering resolution (Fig. 3). ^{24}Mg is the predominant species. This reflects the isotope distribution in the natural abundance of Mg.

Controlling the magnesium vapor pressure was the key issue during the whole process. To form binary alloys, the conventional approach is to melt the elements separately, then mix the liquid metals. However, it is impossible to melt magnesium under vacuum environment before it sublimes. Our method was to heat the mixture of the two elements between 285 and 350 °C. The melting point of gallium is 29.774 °C. At the temperature mentioned above, Ga is in liquid form. This gave a chance that solid Mg could be dissolved into molten Ga. The process took several hours before a uniform mixture was formed. In this temperature range the

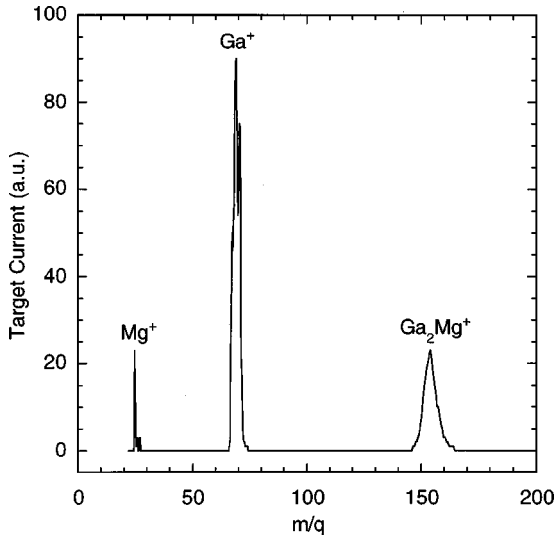

FIG. 2. Mass spectrum of the Mg–Ga LMIS. The operation conditions were as follows: heating current was 3.2 A, extractor voltage was 12 kV, intermediate acceleration voltage was 30 kV and Mg^+ target current was 100 pA.

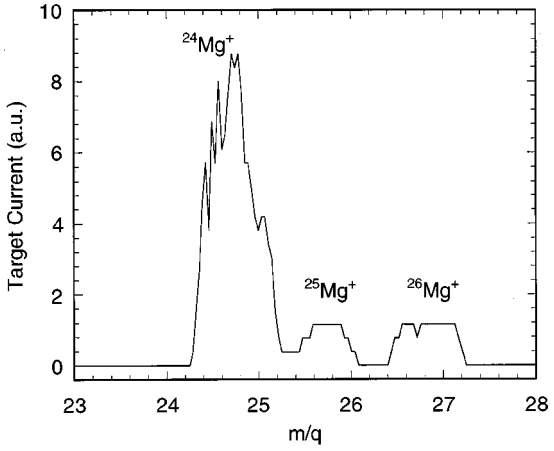

FIG. 3. Mass spectrum of Mg isotopes present in Mg–Ga LMIS. ^{24}Mg, ^{25}Mg, and ^{26}Mg can be distinguished by utilizing the FIB system mass filter.

vapor pressure of Mg is around 10^{-4} Torr. The loss of Mg would not be significant.

The Mg/Ga alloy system is very sensitive to the presence of oxygen even at room temperature. In the process of loading the source in the test station and operating the source in the FIB, a thorough outgassing step was required. The raw $MgGa_2$ alloy is porous and has a rough surface that contains a large amount of oxygen. With rising temperature, the absorbed O_2 tends to react with the alloy. Thus the heating procedure needs to be done very carefully and very slowly. Even with these measures, some oxidation of different degrees always occurred. For example, after loading the alloy the source needed to be transferred from the test station into the FIB system. A slight oxidation occurs during this step and the oxygen absorbed on the alloy surface could lead to further oxidation at elevated temperature. Therefore outgassing of the source was necessary before full operation.

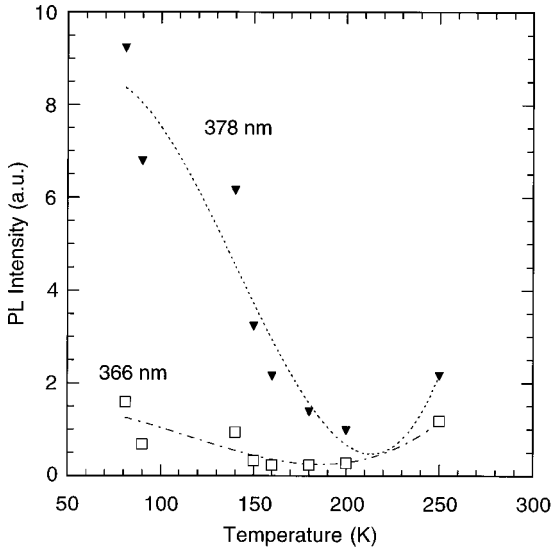

FIG. 4. PL intensity vs temperature. 366 nm is band edge emission and 378 nm is from Mg associated donor–acceptor pair recombination.

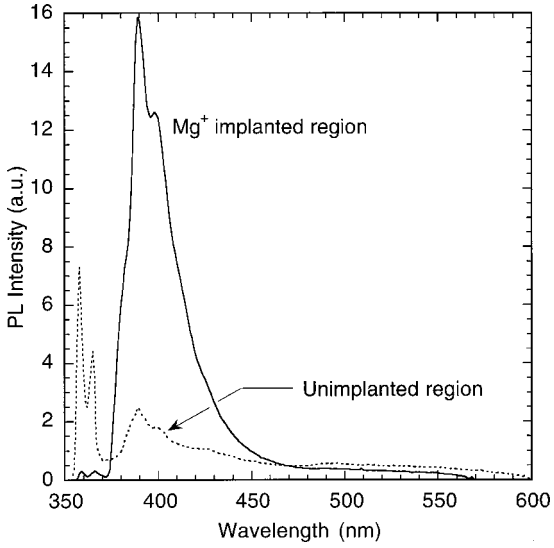

FIG. 5. PL from the Mg^+ implanted region (solid line) and unimplanted area (dotted line) at 81 K.

While stable emission from the Mg–Ga LMIS has been attained, operation with appropriate controlling factors is still of concern, not only because Mg tends to be depleted from the source alloy though evaporation but also, since Ga has a lower ionization potential (5.9993 eV) than that of Mg (7.646 24 eV), a single species ion beam (pure Ga^+ beam) can occur. We optimized the operating conditions experimentally. The source heating current was tuned to 4.4 A for the best combination of heating and controlling the Mg vapor pressure. Before applying the heating current the base vacuum in ion column was typically at 1.2×10^{-7} Torr. During ion source operation the pressure increased only slightly, to 1.4×10^{-7} Torr. This indicated that the vapor pressure of the alloy under this heating condition did not significantly deteriorate the background pressure. The extractor voltage was between 7000 and 8000 V for sufficient emission current. The typical source lifetime is 250 μA h with the longest lifetime achieved to date being 540 μA h.

GaN shows strong yellow band PL emission at room temperature. As the measurement temperature is reduced, the yellow band emission intensity is gradually reduced while

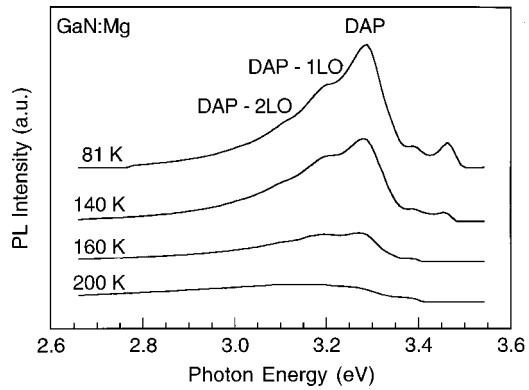

FIG. 6. Energy levels associated with Mg acceptors at selected temperatures.

band edge emission and emission from Mg-associated donor–acceptor levels become dominant (Fig. 4). Figure 5 shows PL spectra obtained at 81 K. The dotted line is the emission from the unimplanted area. Peaks at 358 and 366 nm are associated with GaN near band edge emission. In the ion implanted region, strong deep blue/purple emission at 377 and 388 nm was detected. Figure 6 shows energy levels associated with Mg acceptors at selected temperatures. Peaks at 3.28 and 3.19 eV and a shoulder at 3.12 eV correspond to shallow donor–acceptor pair (DAP) transitions. DAP is the zero phonon donor–acceptor pair transition. DAP-1LO and DAP-2LO are the first and second phonon replicas.[7] No deep level donor to shallow Mg acceptor recombination was observed. At temperatures above ~200 K, these peaks are greatly reduced and the GaN yellow band dominates the PL spectrum. Because defects produced by ion implantation were not entirely removed by the annealing process, the band edge emission was not very strong.

IV. CONCLUSION

Mg–Ga liquid alloy ion sources with lifetimes of 250 μA h were fabricated. The source was tested in our high voltage focused ion beam system and Mg ion implantation of GaN thin film has been performed. Low temperature PL measurement has revealed magnesium acceptor levels. In conclusion we have shown that Mg, which is the standard *p*-type dopant for GaN, can be introduced by FIB implantation.

ACKNOWLEDGMENT

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