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Highly Mg-doped GaN thin film grown by RF plasma-assisted molecular beam epitaxy

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In this paper, we present the study of the electrical, structural and optical properties of p-type GaN grown on sapphire by RF plasma-assisted molecular beam epitaxy (RF-MBE). Hall effect measurement shows that the film was highly doped with carrier concentration of 6.58 x 10^{18}cm^{-3}. X-ray diffraction (XRD) measurement reveals that the GaN was epitaxially grown on sapphire substrate. For the photoluminescence (PL) measurement, a sharp and intense peak at 363.8 nm indicates that the sample is of high optical quality. The presence of the peak at 658.4 cm^{-1} in Raman measurement confirmed that our p-type GaN sample was highly doped with Mg. Low resistance ohmic contacts on p-type GaN utilizing Ni/Ag metallization were fabricated and characterized. A good ohmic contact with a specific contact resistance as low as 8.5 x 10^{-3} Ω cm^2 was achieved without any annealing treatments.

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1. Introduction

III-V nitride compound semiconductors have received much attention for use in optoelectronic devices such as light emitting diodes (LEDs) and laser diodes (LDs). Most of the research groups working on GaN based material have concentrated on the metalorganic chemical vapor deposition (MOCVD) growth technique. However, the turn on voltage of MOCVD grown laser diode is 28V due to high contact resistance of p-GaN layer [1]. The main advantages of molecular beam epitaxy (MBE) over MOCVD for GaN growth are precise control thickness and composition, low temperature growth and high p-type doping concentration [2]. However, slow growth rate of MBE is the main disadvantage compared with other growth techniques. In this work, we are using sapphire as a substrate because sapphire has been most commonly utilized as substrate in III-nitrides growth mainly due to its wide availability and good crystalline quality for epitaxial layer growth, etc. Furthermore, the optical transparency of sapphire is beneficial in back-illuminated detectors and LED's for lack of absorption.

P-type doping is one of the critical issues in growth of III-nitride semiconductors. It is conventionally achieved by using magnesium as the only appropriate p-type impurity. In metalorganic vapor phase epitaxy (MOVPE), thermal annealing is commonly employed to activate the Mg acceptors, which is aimed at destroying the magnesium-hydrogen complexes formed in course of epitaxy. In contrast, there is no necessity to activate the Mg acceptors in III-nitride materials grown by molecular beam epitaxy (MBE) utilizing both activated nitrogen and ammonia as the group-V precursors. In the latter case, the achievable hole concentration is largely controlled by Mg incorporation during growth that is experimentally found to depend on the growth conditions, temperature and V/III ratio. The case of p-type doping is much more complicated than that of n-type doping. Achieving a high hole concentration with Mg as the dopant is still not an easy task. Neugebauer and Van de Walle [3] commented that the determining factor is the solubility of Mg in GaN, which is limited by competition between incorporation of Mg atoms and formation of Mg_3N_2. However, it is possible to obtain a high quality GaN with a specular surface, a low residual carrier concentration and high carrier mobility if the nucleation layers are used to overcome the large mismatch between GaN and sapphire [4].

Providing a low-resistance ohmic contact on p-GaN has been a challenge for years. Especially blue laser diodes require low contact resistances, preferably values below 10^{-4} Ωcm^2. The problem to obtain a low resistance and thermally stable ohmic contacts to p-GaN is the low carrier density of the Mg-doped GaN epilayer and the intrinsic nature of the p-GaN layer [5, 6]. Various metallization schemes along with surface preparation methods, metal deposition techniques, and annealing processes have been investigated in order to enhance the performance of contacts on p-type GaN. Single layer and multilayer metallization schemes based on metals with high work functions (Ni, Pt, Pd, Au) have been investigated for ohmic contact formation on p-GaN [7–11] however silver (Ag) is rarely as a metal contact on p-GaN [11].

In this work, a study of the structural, electrical and optical characteristics of these epitaxial p-type GaN thin films were carried out using Hall effect measurement, high resolution X-ray diffraction (XRD), photoluminescence (PL) and Raman spectroscopy. We also report the low contact resistance for Ni/Ag bi-layer ohmic contacts on p-type GaN.

2. Experimental method

The growth was carried out in a RF plasma-assisted molecular beam epitaxy (RF-MBE) system. The active nitrogen was supplied by RF plasma source while conventional effusion cells were used for Ga and Mg. The nitrogen flux was adjusted by varying the RF power input to the plasma. The substrate temperature was measured with a pyrometer. The c plane sapphire wafer was used as substrate. The sapphire wafer was metallized on the back surface in the interest of radiative heating and reliable temperature measurement. After being loaded into the growth chamber, the substrate was thermally cleaned at a substrate temperature (Ts) of 930ºC for 20 min, and then nitridation was carried out at Ts = 200◦C for 45 min. In order to improve the quality of GaN, nitridation of sapphire become a key feature of MBE-grown nitrides on sapphire. It is usually used before the deposition of AlN buffer layer. During the nitridation, N atoms will replace O atoms and a thin AlN layer is formed with an epitaxial relationship of AlN/Al_2O_3. This process results in the formation of a relaxed AlN thin buffer layer [12]. The thin AlN buffer layer may act as a substrate fixing the polarity of the subsequent deposition of GaN layers [13]. Before p-type GaN deposition, a thin AlN buffer layer is grown at substrate temperature of 743ºC. Subsequently, GaN layer was grown at substrate temperature of 761ºC, followed by *in situ* doping using Mg. The growth was monitored by RHEED which displayed a streaky pattern characteristic of two-dimensional surface.

For the electrical characterization of contact resistances on p-type GaN, the transmission line model (TLM) was utilized. In this experiment, only one wafer was used and it was divided into several small pieces to minimize possible variability between different growth runs. The characteristics of ohmic contacts are strongly influenced by the condition of the semiconductor surface prior to the metallization. For III-V semiconductors, a few nanometers thin oxide layer grows rapidly on the surface when exposed to air. Hence, prior to the metal deposition, the p-type GaN film was cleaned by aqua regia solution to remove the native oxide on the surface. The contact metal schemes, consisting of Ni/Ag were deposited using thermal evaporation.

Scanning electron microscopy (SEM) was used to observe the cross section of the sample. The Van der Pauw method was used for room temperature Hall effect measurements. Indium ball was used to fabricate ohmic contacts for electrical measurements. The structural and optical properties of the grown layers were examined by using high-resolution X-ray diffraction, photoluminescence (PL) and Raman scattering. PL measurements were performed at room temperature by using Jobin Yvon HR800UV system with 325nm He-Cd laser as excitation source while Raman scattering experiments were carried out at room temperature by using Jobin Yvon LabRam HR system with air-cooled 514.5nm Argon laser source operating at 10mW. The current-voltage (I-V) measurements were performed with a Kiethley High-voltage-source-measure-unit model 237. The specific contact resistance (referred to as ρ_c) was determined by a five-point measurement in a voltage range between -0.5 and 0.5 V.

3. Results and discussion

Fig. 1 shows the SEM cross section of the p-type GaN. As seen in the figure, the AlN buffer layer and p-type GaN layer are clearly seen. The thickness of the p-GaN and AlN buffer layer are 681nm and 261nm respectively. Result from Hall effect measurement shows that we obtained a p-type carrier concentration of GaN as high as 6.59×10^{18} cm^{-3}. This is about two orders of magnitude higher than the typical reported values. From the literature, the common hole carrier concentrations are mostly found in the range of 1×10^{16} cm^{-3} - 2×10^{17} cm^{-3} [14].

Fig. 2 shows the 2θ XRD spectra of the sample. The XRD measurement shows that the heterostructure of III-nitrides were epitaxially grown on sapphire. It can be seen from the presence of the peak at 34.521º which is identified as wurtzite GaN (002) diffraction, and three peaks at 35.998º, 72.844º and 76.351º, which correspond to AlN (002), GaN (004) and AlN (004) respectively. The peak at 41.670º is from the sapphire substrate (006). The position and relative intensity of the peaks are clearly compiled in Table 1. The XRD spectra indicate that no sign of cubic phase GaN are found within the detection limit of the XRD, so it is comfirmed that our samples possessed hexagonal structure.

Fig. 3 shows a PL spectrum measured for the p-GaN sample. As reported by F.A. Ponce [15], the intensity of the near band-edge PL emission of GaN is indicative of its high optical quality. From this figure, the sample exhibits the intense and sharp peak at 362.2 nm, which is attributed to the band edge emission of GaN, indicating that the grown p-GaN thin films are of high optical quality. There are also two weak broad bands at 369.5, 391.4 nm, which could be related to the shallow donor-acceptor pair (DAP) transitions. The increase of the Mg atomic concentration will lead to deepening of the donor-acceptor pair (DAP) transitions (3.17eV) and the disappearance of the band-edge luminescence [16].

Raman spectroscopy has been used to investigate the low-wavelength phonons in GaN in order to obtain information on the crystalline quality of the layers. The crystalline structure of wurtize-type GaN is described by the space group C_{6v}^{4} with two formula units per primitive cell. The broad band micro–Raman spectra of the p-GaN are shown in Fig. 4. The sample show a peak at 147.1 cm^{-1}, which corresponds to E_2(low) mode of GaN. Peaks at 568.4 cm^{-1} and 736.5 cm^{-1} are probably due to E_2(high) and A1(LO) modes respectively. The presence of a LO mode in the spectrum indicates a high crystalline quality of the sample [17]. Furthermore, the result confirmed that our sample has a high carrier concentration. This can be seen from the presence of the peak at 658.4 cm^{-1}. The ~657 cm^{-1} peak is assigned to the local vibrational mode (LVM) for the Mg-N bond because the mode intensity is almost proportional to the hole density and the frequency agrees with an estimate from the optical mode frequency of GaN (~560 cm^{-1}), obtained by considering the difference in reduced mass between the Mg-N and Ga-N pairs [18]. It is found that our sample has native p-type character [19] so it is not surprising that the ~657 cm^{-1} peak was observed in our sample.

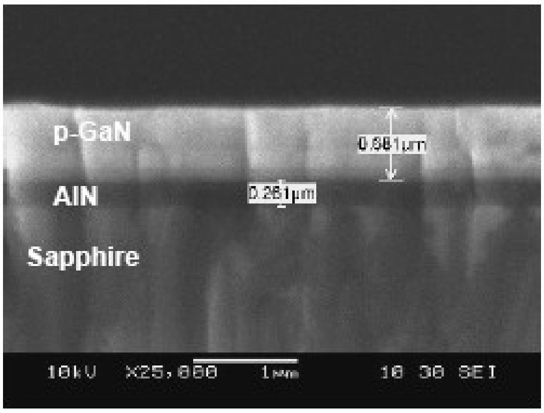

Fig.1 SEM cross section of p-type GaN..

Table 1. The 2θ XRD spectra of different crystal planes and their relative intensity.

2θ peak position (°)	Crystal Plane	Rel. Intensity (%)
34.521	GaN (002)	100.00
35.998	AlN (002)	7.09
41.670	Sapphire (006)	23.12
72.844	GaN (004)	3.13
76.351	AlN (004)	0.16

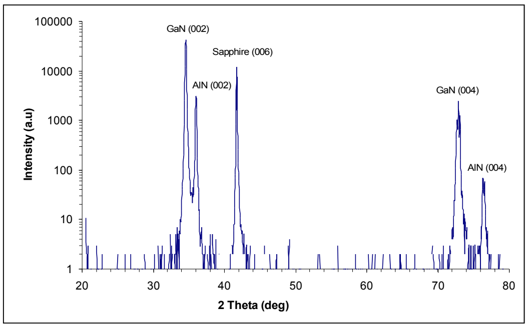

Fig. 2. XRD spectra of the p-GaN.

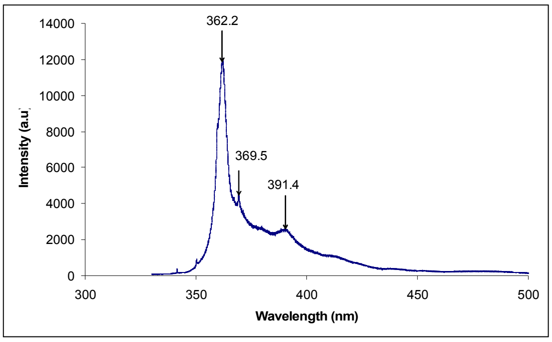

Fig. 3. PL spectra of the p-GaN.

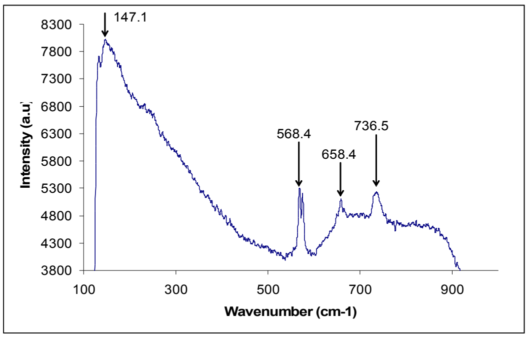

Fig. 4. Room temperature micro-Raman spectra of p-GaN.

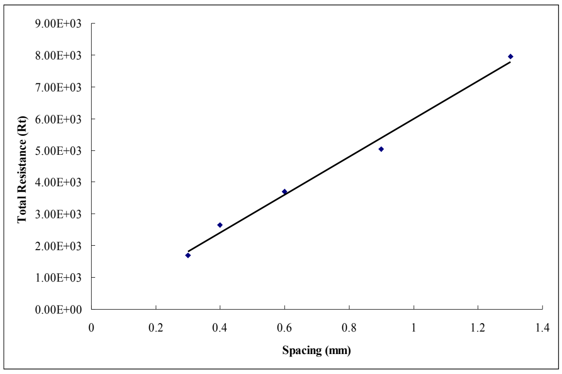

Fig. 5. Plot of measured total resistance (R_T) against the contact pad spacing.

From literature review, Ni is the most commonly used ohmic metallization for p-GaN but the metal combination of Ni/Ag for low resistance contact on p-GaN is rarely used. In this work, Ni/Ag was used as ohmic contacts for p-GaN because Ag has a good electrical resistivity (1.59×10^{-6} Ωcm) and thermal conductivity (1 cal/cm-s-°C) [20]; it can form electrically superior contacts to p-GaN than Ni/Au and has higher reflectivy than Al [21]. Z. Hassan *et al* [22] has successfully used Ni/Ag as ohmic contacts for p-GaN with a specific contact resistance as low as 9.9×10^{-2} Ωcm^2 when annealed at 700°C in nitrogen ambient. To determine the specific contact resistance (ρ_c), data on the total resistance (R_T) were plotted as a linear function of pad spacing in Fig. 5. Measurements show that the specific contact resistance ρ_c of Ni/Ag is 8.5×10^{-3} Ωcm^2 without any annealing treatments. The low ρ_c may be attributed to the high carrier concentration of our samples. This work demonstrates that the Ni/Ag contact scheme should be very useful in fabricating high performance optoelectronic devices.

4. Conclusion

In conclusion, the growth of high carrier concentration p-GaN thin film on sapphire has been obtained by plasma-assisted molecular beam epitaxy. Results of Hall effect measurement revealed that our sample has a high carrier concentration of 6.58×10^{18} cm^{-3}. The sharp and intense peak at 362.2 nm in PL measurement indicates that the sample is of high optical quality. In addition, the presence of a peak at 658 cm^{-1} in Raman results confirmed that our sample was highly doped. A good Ni/Ag ohmic contact with a specific contact resistance of 8.50×10^{3} Ωcm^2 was obtained.

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