Beryllium Doped \( p \)-type GaN Grown by Metal-Organic Chemical Vapor Deposition

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Abstract: The authors report on the growth of Be-doped \( p \)-type GaN epilayers by metal-organic chemical vapor deposition (MOCVD). The electrical and optical properties of the Be-doped GaN epilayers were studied by Hall-effect measurements and photoluminescence (PL) spectroscopy. The PL spectra of Be-doped GaN epilayers exhibited two emission lines at 3.36 and 2.71 eV, which were absent in undoped epilayers. The transition at 3.36 eV was assigned to the transition of free electrons to the neutral Be acceptor, Be\textsuperscript{0}. The transition at 2.71 eV was assigned to the transition of electrons bound to deep level donors to the Be\textsuperscript{0} acceptors. Three independent measurements: (a) resistivity vs. temperature, (b) PL peak positions between Be doped and undoped GaN and (c) activation energy of 2.71 eV transition all indicate that the Be energy level is between 120 and 140 meV above the valence band. This is about 20-40 meV shallower than the Mg energy level (160 meV) in GaN. It is thus concluded that Be could be an excellent acceptor dopant in nitride materials.

Keywords: Be-doped GaN; \( p \)-type, MOCVD epitaxial growth.

Introduction

Group III nitride semiconductors [1, 2], especially Gallium Nitride (GaN), have successfully been employed to realize blue-green light-emitting diodes, blue laser diodes [3, 4] and ultra violet light sources and detectors [5, 6]. Controllable and efficient doping is one of the most important issues for the development of these devices. For \( n \)-type doping of nitrides, silicon can be successfully used as dopant and carrier concentrations exceeding \( 5 \times 10^{20} \) cm\(^{-3} \) can be achieved [7]. For \( p \)-type doping, magnesium (Mg) is the acceptor of choice. It can be incorporated in concentrations up to \( 10^{20} \) cm\(^{-3} \); however, because of its large ionization energy (~160 meV), the resulting room-temperature hole concentration is only about \( 10^{18} \) cm\(^{-3} \); i.e., only about 1% of Mg atoms are ionized at room temperature. Increasing the Mg concentration beyond \( 10^{20} \) cm\(^{-3} \) leads to saturation and a decrease in the hole concentration [8]. The limited conductivity of \( p \)-type doped layers impedes progress in device applications. Therefore, it is desirable to find an alternative acceptor. Beryllium has a low theoretical activation energy of about 60 meV [9], making it a promising candidate for \( p \)-type doping in GaN. In spite of the promising theoretical predictions, practical realization of this idea is very difficult. The main problem with the use of Be as a dopant in GaN is that it is easily incorporated on interstitial sites, where it acts as a donor [10, 11].

Experimentally, Be doping of GaN in molecular beam epitaxy has been reported by various groups [12, 13]. Another technique for Be incorporation that has been attempted is ion implantation [14, 15]. Characterization was mostly by optical spectroscopy measurement. A photoluminescence (PL)
peak just below the band edge of GaN was observed and attributed to Be related transition. Assuming that this PL line results from a Be acceptor, an acceptor energy level can be extracted. However, these results in a wide range of values, ranging from 90 to 250 meV, depending on the assumptions made in the analysis [16]. To the best of our knowledge, there have not been any reports on the growth of Be doped GaN using MOCVD.

**Experiment**

Be doped GaN epilayers were grown on the c-plane (001) of Al₂O₃ substrates by MOCVD. The growth temperature and pressure were 1080 °C and 70 Torr, respectively. Trimethylgallium (TMGa) and blue ammonia were used as sources for gallium and nitrogen. C_{10}H_{14}O₄Be was used as the Be source. A 2 µm insulating undoped GaN epilayer was grown to serve as a template, followed by the growth of a 0.5 µm Be doped GaN epilayer. X-ray diffraction (XRD) was used to determine crystalline quality, while atomic force microscopy (AFM) was used to study the surface morphology. Variable temperature Hall effect measurement (Standard Van der Pauw) was utilized to assess the electrical properties and PL spectroscopy was employed to investigate the optical properties. The deep UV PL spectroscopy system consists of a frequency quadrupled 100 femtosecond Ti: Sapphire laser with an average power of 3 mW, a repetition rate of 76 MHz at 196 nm and a 1.3 m monochromator with a detection capability ranging from 185 to 800 nm [17].

**Results and Discussion**

The surface morphology of the Be doped GaN epilayers is relatively rough with a root mean square (RMS) surface roughness of about 6 nm for a 10 µm x 10 µm area, in contrast to the smooth surface of undoped GaN epilayers which have an RMS value of less than 1.5 nm. The (002) peak of Be doped GaN epilayers has a rocking curve full width at half maximum of about 450 arcsec. As grown Be doped GaN epilayers were highly resistive, post growth rapid thermal annealing was done to activate Be acceptors. The annealing conditions were the same as those for Mg acceptor activation (920 °C for 12 seconds under N₂ ambient). Ni/Au was used to make ohmic contacts in the standard Van der Pauw configuration for Hall-effect measurements. Fig. 1 shows the Be and oxygen concentration profiles as measured by secondary ion mass spectrometry (SIMS) for the sample with Be source flow rate of 175 ml/min. The result indicates a Be dopant concentration of about 2 x 10¹⁹ cm⁻³ in the epilayer. The Be dopant concentration was on the order of 10¹⁸ cm⁻³ as determined by linear extrapolation from samples measured by SIMS. Oxygen concentration was in the order of 10¹⁸ cm⁻³ and has a negative effect on the material quality and surface morphology. Hall effect measurements indicate the formation of a p-type GaN epilayer by Be doping. The resistivity obtained at room temperature is about 3.7 Ω.cm. Variable temperature Hall-effect measurements were attempted to probe the electrical properties of Be doped GaN epilayers. Fig. 2 shows the Arrhenius plot of the resistivity (ρ) of Be doped GaN epilayers. The resistivity decreases with increasing temperature from 3.7 Ω.cm at 300 K to 2.7 Ω.cm at 600 K. The solid line is the least squares fit of data to the following equation:

$$\rho(T) = \rho_0 \left[1 + e^{(-E_a/kT)}\right]^{-1}$$  \hspace{1cm} (1)

where $\rho(T)$ is the resistivity at temperature $T$, $E_a$ is the activation energy and $k$ is the Boltzmann constant. The fitted value of the activation energy ($E_a$) is 118 ± 4 meV.

The average values of hole concentration and mobility at room temperature are ~ 1.7 x 10¹⁸ cm⁻³ and 1.3 cm²/V.s, respectively. The measured values of hole concentration and mobility were fluctuating, so we were not able to use the hole concentration to directly evaluate the activation energy. This fluctuation could be related to the relatively high resistivity of the materials and the unoptimized annealing conditions of the materials and the contacts. More studies are needed to optimize material and annealing conditions for materials and contacts. The small reduction in resistivity between 300 K and 600 K indicates that the materials are highly compensated. This compensation could be due to oxygen molecules in the Be source.
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![Graph](image)

FIG. 1. Oxygen and beryllium dopant concentration profiles in GaN epilayer with Be source flow rate of 175 ml/min, as probed by SIMS (performed by Charles Evans and Associate).

![Graph](image)

FIG. 2. The Arrhenius plot of resistivity ($\rho$) between 300 and 600 K for the Be doped GaN epilayers. The solid line is the least-square fit of data with Eq. (1). The fitted value of the activation energy ($E_A$) for Be is $118 \pm 4$ meV.

Low temperature (10 K) PL spectra of Be-doped and undoped GaN epilayers are shown in Fig. 3. The PL spectrum of undoped GaN exhibits a strong band-edge emission at 3.48 eV due to the donor bound exciton ($I_{2}$) transition [18]. The band gap of GaN at 10 K is around 3.505 eV [18, 19]. The PL spectrum of Be-doped GaN comprises a band-edge transition at 3.36 eV, which is assigned to the transition of free electrons to neutral Be acceptors ($Be^0$). A peak at 3.35 eV was observed in Be implanted GaN and assigned to the transition of the same free electrons to neutral Be$^0$ recombination [20]. Our assignment determines the energy level of Be acceptors in GaN to be $E_A \sim 3.505$ eV $- 3.36$ eV = 0.145 eV, which agrees with the value estimated from the temperature dependence of resistivity discussed above. An additional Be related emission line at 2.71 eV was also observed and is believed to be a donor-acceptor-pair (DAP) transition involving deep level donor and Be acceptor. The broad width of the 2.71 eV emission line is a typical characteristic of DAP transitions involving deep level impurity.

![Graph](image)

FIG. 3. PL spectra of (a) undoped and (b) Be-doped GaN epilayers measured at 10 K.
Fig. 4 shows the temperature dependence of the 2.71 eV emission line in the Be-doped GaN epilayer measured from 10 to 240 K. The thermal quenching of the 2.71 eV transition is due to the dissociation of the neutral Be acceptor, which is shallower than the energy level of the donor involved. Fig. 5 shows the Arrhenius plot of the 2.71 eV emission intensity in Be-doped GaN. The solid line is the least-squares fit of the data with the equation:

\[
I_{eml}(T) = I_0 \left[ 1 + Ce^{-\frac{E_o}{kT}} \right]^{-1}
\]

where \( I_{eml}(T) \) and \( I_0 \) are the integrated PL intensity at temperature \( T \) and 0 K and \( E_o \) is the activation energy of PL emission intensity. The fitted value of the activation energy \( E_o \) is 126 meV. This value is close to the activation energy determined from the temperature dependent resistivity measurement. All these results indicate that the energy level of Be is between 120 and 145 meV and is about 20-40 meV shallower than that of Mg in GaN.

**Conclusion**

Be-doped GaN epilayers were grown by MOCVD and their optical and electrical properties were probed. It was confirmed from Hall measurement that these epilayers are \( p \)-type. The activation energy of Be acceptors was deduced to be between 120 and 145 meV from Hall-effect measurement, direct comparison of band-edge transitions and activation energy of DAP transition. The energy level of Be is about 20-40 meV shallower than the Mg level in GaN. These results thus suggest that Be could be an excellent candidate as a \( p \)-type dopant in GaN. Additional improvements in material quality, doping conditions and annealing parameters of materials and contacts would further enhance the material conductivity.
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References


[17] http://www2.ece.ttu.edu/nanophotonics

