Electrical and optical properties of Mg-doped $Al_{0.7}Ga_{0.3}N$ alloys

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Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayers ($\sim 1\ \mu m$) were grown on an AlN/sapphire template by metalorganic chemical vapor deposition and the electrical and optical properties of these epilayers were studied. For optimized Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayers, we have obtained a resistivity around $10^5\ \Omega\,cm$ at room temperature and confirmed *p*-type conduction at elevated temperatures (>700 K) with a resistivity of about 40 Ω cm at 800 K. From the temperature dependent Hall effect measurement, the activation energy of Mg acceptor is found to be around 400 meV for $Al_{0.7}Ga_{0.3}N$ alloy. The optimized Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayers have been incorporated into the deep-ultraviolet (UV) ($\lambda < 300$ nm) light-emitting diode (LED) structures as an electron blocking layer. An enhancement in the performance of the UV LEDs was obtained. LEDs with peak emission wavelengths at 280 nm were fabricated with a circular geometry (300 μm disk diameter). Output power reached 0.35 mW at 20 mA and 1.1 mW at 150 mA dc current. The importance of Mg-doped $Al_{0.7}Ga_{0.3}N$ alloys to suppress the long-wavelength emission components in deep-UV LEDs and the fundamental limit for achieving *p*-type Al-rich AlGaN alloys are also discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1879098]

Al-rich AlGaN alloys are ideal materials to realize deep-ultraviolet (UV) emitters with wavelengths shorter than 300 nm. Chip-scale solid-state UV emitters have many applications such as next-generation solid-state lighting, fluorescence detection of chemical and biological agents, water and air purification, medical research, and health care.[1] To achieve efficient deep-UV light emitting diodes (LEDs), highly conductive *p*-type and *n*-type Al-rich $Al_xGa_{1-x}N$ alloys ($x > 0.6$) are desired. It is difficult to grow high-quality Al-rich AlGaN alloys due to a large concentration of defects and dislocations. Conductivity also decreases with increasing Al content due to an increase in the ionization energy of the dopants, alloy scattering, and compensation effect from native defects. In terms of growth, controlling these defects and impurities are necessary to enhance the conductivity by reducing compensation. There has been impressive achievement for *n*-type conductivity control in $Al_xGa_{1-x}N$ epilayers with Si doping for $x \geqslant 0.7$.[2,3] A room-temperature resistivity of 0.0075 Ω cm for $x=0.7$ and 40 Ω cm for $x=1$ (AlN) have been obtained.[2] However, it is very difficult to achieve high *p*-type conductivity in AlGaN alloys due to the large activation energy of the Mg acceptor in AlGaN alloys. Enhancing *p*-type conductivity for AlGaN alloys is still one of the biggest challenges for the nitride community. We have reported *p*-type AlGaN for Al content up to 27% (Ref. 4) as well as optical properties and Mg energy level in the Mg-doped AlN epilayers.[5] From photoluminescence (PL) results, the Mg level in AlN was found to be around 0.5 eV. As the Mg levels in AlGaN deepen with increasing Al content, it is difficult to obtain sufficient free holes. To enhance the hole concentration, several methods have been proposed and explored, such as Mg delta doping,[6] short-period superlattice (SL) of AlGaN/GaN,[7] and modulation-doped AlGaN/GaN SL.[8] Due to the low conductivity of *p*-type AlGaN alloys, injection of holes is another problem in UV LEDs.

Recently, several groups have reported the achievement of deep-UV LEDs using AlGaN alloys.[9–14] In the UV LED structure, one of the crucial layers is the electron blocking layer. It plays an important role in blocking the electrons get into the *p*-layer region and thus enhances the carrier recombination in the active region and, hence, the emission efficiency. However, a low-quality blocking layer could introduce long-wavelength emission components in UV LEDs when injected electrons overflow to the *p* region. Furthermore, the quality of the electron blocking layer profoundly affects the hole injection into the active region. Understanding and improving the material quality and conductivity of Mg-doped AlGaN alloys are essential to improve the deep-UV LED performance.

In this letter, we report on the epitaxial growth, electrical, and optical properties of Mg-doped Al-rich $Al_xGa_{1-x}N$ epilayers for $x \sim 0.7$. The optimized growth condition of a Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayer was incorporated into the deep-UV ($\lambda = 280$ nm) LED structure as an electron blocking layer. The characteristics of the deep-UV LEDs with peak emissions at 280 nm and the fundamental properties of Mg-doped Al-rich AlGaN alloys are also discussed.

Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayers of thickness $\sim 1\ \mu m$ were grown on AlN/sapphire templates by metalorganic chemical vapor deposition (MOCVD). An AlN epilayer with a thickness of $\sim 0.5\ \mu m$ was first grown on a sapphire (0001) substrate and followed by the growth of a Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayer. The metalorganic sources used were trimethyl aluminum, trimethylgallium, and cyclopetadienyl magnesium for Al, Ga, and Mg, respectively. The samples were characterized by x-ray diffraction (XRD), deep-UV PL spectroscopy, and atomic force microscopy (AFM). No cracks were found on the samples as revealed by AFM images. XRD was used to determine the aluminum content and crystalline quality of the epilayers. PL spectroscopy was employed to investigate the optical properties of Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayers. The PL system consists of a frequency-quadrupled 100 fs Ti:Sapphire laser with an average power of 3 mW at 196 nm and repetition rate of 76 MHz. Mg concentration was determined by secondary ion mass spectroscopy. The epilayers have a Mg concentration of

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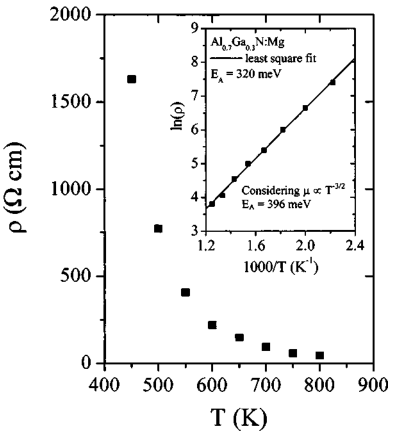

FIG. 1. Temperature variation of resistivity of a Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayer in the temperature range of 450–800 K. Inset is the semilog plot of ρ vs $1/T$. The solid line is the least-square fit of data with Eq. (1). The fitted value of E_A, the activation energy of Mg acceptor is 320 meV (396 meV) without (with) considering the variation of μ with T ($\mu \propto T^{-3/2}$).

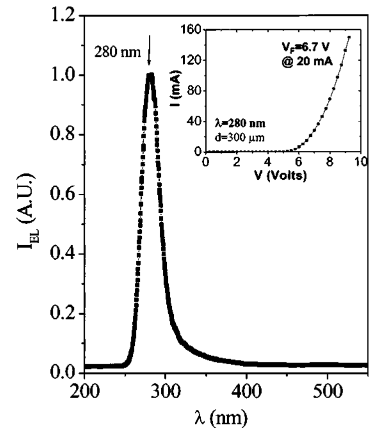

FIG. 2. EL spectrum of a disk shape (d=300 μm) deep-UV LED with peak emission at 280 nm under dc bias (I=40 mA). Inset is the I-V characteristic of the same 280 nm UV LED.

about 1.5×10^{20} cm^{-3}. Electrical properties of Mg-doped $Al_{0.7}Ga_{0.3}N$ alloys. were studied by the Hall effect measurement with a high-temperature capability (up to 900 K).

As-grown epilayers were highly resistive and postgrowth rapid thermal annealing was done to activate Mg acceptors. Ni/Au was used as contacts in the standard van der Pauw configuration for Hall effect measurements. The resistivity obtained at room temperature is about $10^5 \Omega$ cm (semi-insulating). Figure 1 shows the variation of resistivity with temperature in the range between 450 and 800 K of a typical Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayer. The resistivity decreases exponentially with increasing temperature. At high temperatures (>700 K), it consistently shows a signature of p-type conduction. At 800 K, the measured p-type resistivity is about 40 Ω cm. The activation energy of the Mg acceptor is first estimated by using the following equation:

$$\rho(T) = \rho_0 e^{E_A/kT}, \tag{1}$$

where $\rho(T)$ is the resistivity at temperature T, and E_A is the activation energy of the Mg acceptor. The inset of Fig. 1 shows the semilog plot of the resistivity versus $1/T$ ($\ln\rho$ versus $1/T$). The fitted value of E_A is about 320 meV. To obtain E_A more accurately, E_A is also estimated by including the temperature dependence of the mobility at high temperatures ($\mu \propto T^{-3/2}$). The fitted E_A value increased to 396 meV, which is close to the previously estimated value by extracting Mg levels between GaN and AlN.[6] With this result, we can now estimate the theoretical limit of the resistivity of Mg-doped Al-rich $Al_xGa_{1-x}N$ alloys.

Using the relations between free hole concentration (p), mobility (μ_p), and conductivity (σ), we have

$$p = N_a e^{-E_A/kT}, \quad \sigma = ep\mu_p, \quad \rho = \frac{1}{\sigma}, \tag{2}$$

$$\sigma(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N{:}Mg}) = ep(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N{:}Mg}) \times \mu_p(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N{:}Mg}), \tag{3}$$

where N_a is the Mg doping concentration. With experimental results, hole concentration can be estimated as (assuming the same doping concentration for GaN)

$$\begin{aligned} p(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N{:}Mg}) &= N_a \exp\left\{-\frac{E_A(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N{:}Mg})}{kT}\right\} \\ &= N_a \exp\left\{-\frac{E_A(\mathrm{GaN})}{kT}\right\}\cdot\exp\left\{-\frac{\Delta E_A}{kT}\right\} \\ &= p(\mathrm{GaN{:}Mg})\cdot\exp\left\{-\frac{\Delta E_A}{kT}\right\}, \end{aligned} \tag{4}$$

where $\Delta E_A = E_A(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N{:}Mg}) - E_A(\mathrm{GaN{:}Mg})$ is the Mg energy level difference between $Al_xGa_{1-x}N$ and GaN.

The hole mobility, μ_p, depends on its effective mass and alloy scattering. As alloy scattering increases with Al content, μ_p in $Al_{0.7}Ga_{0.3}N$:Mg is much smaller than that in GaN:Mg. The mobility of $Al_{0.7}Ga_{0.3}N$:Mg is estimated (from low Al content AlGaN:Mg)[4] in the range of (1–3)cm^2/V s,

$$\begin{aligned} \mu_p(\mathrm{Al}_{0.7}\mathrm{Ga}_{0.3}\mathrm{N{:}Mg}) &\approx (1\text{–}3)\mathrm{cm^2/V\,s} \\ &\approx (0.1\text{–}0.3)\mu_p(\mathrm{GaN{:}Mg}). \end{aligned} \tag{5}$$

Inserting Eqs. (4) and (5) into Eq. (3), the conductivity of Mg-doped $Al_{0.7}Ga_{0.3}N$ alloys is

$$\sigma(\mathrm{Al}_{0.7}\mathrm{G}_{0.3}\mathrm{N{:}Mg}) \approx (0.1\text{–}0.3)\sigma(\mathrm{GaN{:}Mg}) \times \exp\left\{-\frac{\Delta E_A}{kT}\right\}. \tag{6}$$

The resistivity of $Al_{0.7}Ga_{0.3}N$:Mg is thus

$$\rho(\mathrm{Al}_{0.7}\mathrm{Ga}_{0.3}\mathrm{N{:}Mg}) \approx (3\text{–}10)\rho(\mathrm{GaN{:}Mg})\exp\left\{\frac{\Delta E_A}{kT}\right\}. \tag{7}$$

Using typical values for p-GaN, E_A=160 meV and ρ =1 Ω cm (at room temperature), we have the room-temperature resistivity

$$\begin{aligned} \rho(\mathrm{Al}_{0.7}\mathrm{Ga}_{0.3}\mathrm{N{:}Mg}) &\approx (3\text{–}10)e^{236\ \mathrm{meV}/kT} \\ &\approx (3\text{–}10)e^{236\ \mathrm{meV}/25\ \mathrm{meV}} \\ &\approx (4\text{–}13)\times10^4\ \Omega\,\mathrm{cm}. \end{aligned} \tag{8}$$

Thus, ρ is in the range of $(4\text{–}13)\times10^4$ Ω cm (semi-insulating) at room temperature for Mg-doped $Al_{0.7}Ga_{0.3}N$ alloys. The resistivity we obtained for $Al_{0.7}Ga_{0.3}N$:Mg is in

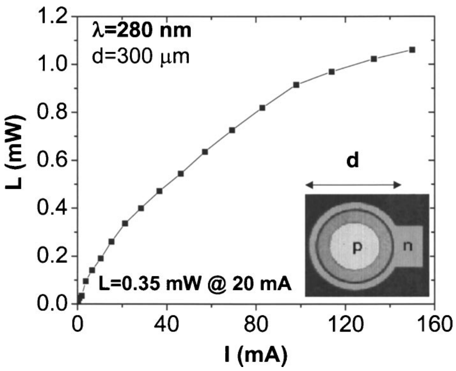

FIG. 3. (*L-I*) of a circular (d=300 μm) deep-UV LED (280 nm). Inset is an optical microscope image of the fabricated LED.

the range of the value estimated by Eq. (8). Taking into account of the hole mobility variation with temperature ($\mu_p \propto T^{-3/2}$), the resistivity of $Al_{0.7}Ga_{0.3}N$:Mg at 800 K is estimated from Eq. (8) to be in the range of (9–30) Ω cm as a lower limit, which is consistent with our measured value at 800 K (40 Ω cm).

Now, let us discuss the effect of this Mg-doped $Al_{0.7}Ga_{0.3}N$ electron blocking layer to the performance of UV LEDs. Typically, the thickness of the blocking layer is about 5–10 nm. For a standard size of 300 μm × 300 μm LED, the resistance of this layer is

$$R = \rho \frac{l}{A} = (4\text{–}13) \times 10^4 \Omega \text{ cm} \frac{(5\text{–}10) \text{ nm}}{300\ \mu\text{m} \times 300\ \mu\text{m}} \approx (22\text{–}130)\Omega. \qquad (9)$$

The voltage drop across this layer at 20 mA current (at forward bias V_f) is between 0.5–2.6 V. Although this electron blocking layer is semi-insulating at room temperature, the potential drop at this layer is still relatively small due to the fact that only a very thin layer (5–10 nm) is needed. This fact explains why the deep-UV LEDs are still performing reasonably well using high Al-content AlGaN:Mg as electron blocking layers.[9–14]

Resistance and PL spectra of the samples were carefully followed to optimize the growth condition. Before optimization, the spectra had dominant impurity emissions (not shown). By optimizing the growth condition (temperature, pressure, V/III ratio, etc.), the intensity of impurity emissions were suppressed and the resistance was reduced by more than two orders of magnitude.

The optimized Mg-doped $Al_{0.7}G_{0.3}N$ epilayer was incorporated into the deep-UV LED (λ < 300 nm) structure as an electron blocking layer. The deep-UV LEDs were grown on AlN/sapphire substrates by MOCVD. A high-quality epilayer of AlN was first grown on (0001) sapphire as a template. A highly conductive *n*-$Al_{0.7}Ga_{0.3}N$ layer of thickness 1.5 μm was then grown on this AlN/sapphire template, followed by AlGaN/AlGaN QW active region and the Mg-doped $Al_{0.7}Ga_{0.3}N$ electron blocking layer. The structure was then completed with *p*-AlGaN and *p*-GaN layers. LEDs were fabricated with a circular geometry. The fabrication procedure is explained elsewhere.[15]

Figure 2 shows the electroluminescence (EL) spectrum of a 280 nm deep-UV LED with a 300 μm diameter size under 40 mA dc current. The inset of Fig. 2 shows the current-voltage characteristic of 280 nm deep-UV LEDs. The forward voltage, V_F, of 6.7 V is observed at 20 mA current. We believe that with further optimization of *n*- and *p*-contact annealing, V_F can be further reduced.

Figure 3 shows the light-output power versus current (*L-I*) characteristic of the 280 nm deep-UV LEDs (with a 300 μm disk diameter). We have achieved an optical power output of 0.35 mW and a power density of 0.48 W/cm^2 at 20 mA (while the maximum optical power and power density are 1.1 mW and 1.5 W/cm^2, respectively). With the incorporation of the optimized growth condition of the electron blocking layer, we observed enhancement in the UV LED output power. The long-wavelength components were significantly reduced in the EL spectrum. We believe the improved material quality of the electron blocking layer played an important role in suppressing the long-wavelength components in the EL spectrum. Further improvement of the conductivity of the Mg-doped AlGaN epilayer is required to further enhance the efficiency and performance of deep-UV LEDs, especially when shorter-wavelength emission is required.

In summary, we have grown Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayers with improved quality by MOCVD. Electrical and optical properties of the epilayers were studied. We obtained a resistivity around 10^5Ω cm at 300 K and a *p*-type resistivity of about 40 Ω cm at 800 K. The energy level of Mg was estimated to be around 400 meV for $Al_{0.7}Ga_{0.3}N$ epilayer from the temperature dependence of the resistivity. The fundamental limit of *p*-type conductivity of Mg-doped Al-rich $Al_xGa_{1-x}N$ alloys was also addressed. The optimized Mg-doped $Al_{0.7}Ga_{0.3}N$ epilayer was incorporated into the deep-UV LED (280 nm) structure as electron blocking layers, which significantly improved the LED performance.

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