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Characteristics of InGaN/AlGaN light-emitting diodes on sapphire substrates

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We report characteristics and degradation of an InGaN/AlGaN double-heterostructure light-emitting diode (LED) grown by metalorganic chemical vapor deposition on a sapphire substrate. The InGaN/AlGaN LED exhibited an optical output power of 0.17 mW, an external quantum efficiency of 0.2%, a peak emission wavelength at 440 nm with a full width at half-maximum of 63 nm, and a stable operation up to 3000 h under 30 mA dc operation at 30 °C. However, the InGaN/AlGaN LED showed electrical and optical degradations under high injected current density and high ambient temperature. Electroluminescence, electron-beam-induced current and cathodoluminescence observations showed that the degraded InGaN/AlGaN LED exhibited formation and propagation of dark regions, which act as nonradiative recombination centers. The values of the degradation rate were determined to be 1.1×10⁻³, 1.9×10⁻³, and 3.9×10⁻³ h⁻¹ under the injected current density of 100 A/cm², and 1.6×10⁻², 3.6×10⁻², and 8×10⁻² h⁻¹ under 200 A/cm² at ambient temperatures of 30, 50, and 80 °C, respectively. The activation energy of degradation was also determined to be 0.23–0.25 eV. The degradation of electrical and optical characteristics was caused by the growth of dark regions. It was also observed that GaN-based LEDs on sapphire substrates have longer lifetime than the ZnSe-based LED, but shorter than the AlGaAs and InGaAsP LEDs. © 1997 American Institute of Physics. [S0021-8979(97)06423-2]

I. INTRODUCTION

GaN- and ZnSe-based compound semiconductors, which are candidates for applications such as high-density optical data storage and full-color displays, have attracted much attention because of their large direct band gap at room temperature. These materials are appropriate for short-wavelength light-emitting diodes (LEDs) and laser diodes. In the past few years, high-efficiency blue and green LEDs have been developed using ZnSe- and GaN-based materials.¹,² High-brightness GaN-based LEDs have been commercially available and are about 100 times brighter than SiC-based LEDs.³ Ever since the achievement of continuous-wave (cw) operation of GaN-based laser diodes,⁴ recent degradation studies have been focused mainly on the 300 K stable operation of laser diodes. One of the main problems encountered in epitaxial growth of GaN is a lack of a suitable substrate that matches the GaN lattice constant and thermal expansion coefficient. Sapphire has hexagonal symmetry with lattice constants of a = 4.758 Å and c = 12.991 Å. The lattice constants of GaN are a = 3.189 Å and c = 5.185 Å. However, sapphire is, to date, the most commonly used substrate because it allows the epitaxial growth of the GaN layer, providing the growth of a buffer layer at low temperature.

Dislocations acting as nonradiative recombination centers cause limitation of stable operation for optical devices under high injected current density and ambient temperature. For example, a GaAs-based laser diode on a Si substrate, which involves differences of lattice constants and thermal expansion coefficients between GaAs and Si materials, suffers from a rapid degradation due to high dislocation density (>10⁶ cm⁻²) and large tensile stress (~10⁸ dyn/cm²) in the active region. We have shown that rapid degradations in electrical and optical characteristics of AlGaAs/GaAs single quantum well laser diodes on Si substrates are caused by the formation of dark-line defects (DLDs) during high injected current density.⁴

Room-temperature characteristics of ZnSe-based LEDs and laser diodes have been reported. Eason et al.⁵ reported ZnCdSe/ZnSe blue LEDs on ZnSe substrates with an external quantum efficiency (ηe) of 1.3% and an emission peak wavelength at 489 nm, and a ZnTeSe/ZnSe green LED with the ηe of 5.3% and a peak wavelength of 512 nm at the injected dc current of 10 mA. They obtained the exponential lifetimes of the ZnTeSe/ZnSe green LEDs at 675 h at the injected current density of 15 A/cm² and 350 h at 50 A/cm², corresponding to the half-intensity lifetimes of 468 and 243 h, respectively. Nakayama et al.¹ reported ZnCdSe/ZnSSe LEDs on GaAs substrates, showing ηe of 2.8%, a half-intensity lifetime of 1000 h at 10 mA dc current and an emission peak wavelength of 486 nm. Taniguchi et al.⁶ also reported the ZnSe-based laser diode with a lifetime of 101.5 h under 1 mW constant output power in cw operation at 20 °C. Guha et al.⁷ reported that major degradation in II–VI blue-green light-emitting devices occurred due to microstructural changes such as the formation of dark spots, ⟨100⟩ DLDs and dark patches, which act as nonradiative recombination centers. Hua et al.⁸ also reported that formation of

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dislocation networks in quantum well regions by climb motion of dislocations degraded the characteristics of II–VI blue-green laser diodes during current injection, which was similar to dislocation network formation in degraded AlGaAs/GaAs double-heterostructure (DH) laser diodes. Although the LED shows stable operation, the laser diodes degrades quickly due to high injected current density. Thus, the reliability of optical devices depends on the generation and propagation of dark regions under high injected current density.

On the other hand, the progress in the GaN-based LEDs and laser diodes is remarkable. Nakamura et al. fabricated high-efficiency InGaN/AlGaN LEDs with a wavelength of 450 nm and $\eta_\text{eff}$ of 2.7% at 20 mA. Lester et al. reported that the high density of dislocations ($2 - 10^{10}$ cm$^{-2}$) in GaN-based LEDs on sapphire substrates do not act as efficient minority carrier recombination sites in comparison to other III–V materials. However, the reliability of the GaN-based optical devices, in particular the laser diode, is a key issue because the reliability of the GaN-based LED strongly depends on the injected current density and ambient temperature. Nakamura reported a GaN-based laser diode with a lifetime of 35 h under 1.5 mW constant output power in cw operation at room temperature. The relationship between the operating current and aging time is very similar to those of the GaAs-based laser diodes on Si (Ref. 11) and ZnSe-based laser diodes. This suggests that the optical degradation mechanism of GaN-based laser diodes relates to the dark defects acting as nonradiative recombination centers.

In this study, we report the characteristics and degradation of InGaN/AlGaN LEDs on sapphire substrates. We estimated the degradation rate and activation energy of degradation, and observed the formation and propagation of dark regions. The degradation characteristics of the GaN-based LED are also compared with those of ZnSe-, GaAs-, and InP-based LEDs.

II. EXPERIMENT

Samples were grown on sapphire substrates with (0001) orientation (c face) by metalorganic chemical vapor deposition (MOCVD) at atmospheric pressure using a modified two-step growth technique. After the substrate was heated at 1050 °C in a hydrogen ambient, the InGaN/AlGaN DH was grown. Trimethylaluminum (TMA), trimethylgallium (TMG), trimethylindium (TMI), ammonia (NH$_3$), monosilane (SiH$_4$), bis-cyclopentadienyl magnesium (Cp$_2$Mg)$_2$, and diethylzinc (DEZ) were used as Al, Ga, In, N, Si, Mg, and Zn sources, respectively. Figure 1 shows the schematic cross-sectional structure of the InGaN/AlGaN LED on a sapphire substrate. The structure consists of the following growth sequence: a 25 nm thick GaN buffer layer at 500 °C, a 4 µm thick n-GaN layer at 1020 °C; a 150 nm thick n-$\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$ layer at 1020 °C, a 50 nm thick In$_{0.06}\text{Ga}_{0.94}\text{N}$ layer at 780 °C, a 150 nm thick p-$\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$ layer at 1020 °C, and a 350 nm thick p-type GaN cap layer at 1020 °C. In order to increase the output power from the InGaN/AlGaN LED, codoping with both Si and Zn was used in the InGaN active layer. Thermal annealing in N$_2$ ambient was performed to obtain p-type GaN and AlGaN layers at 750 °C for 30 min. After the growth, the sample was partially etched until the n-GaN layer was exposed. The Ohmic electrodes of Ni/Au and Ti/Al were formed by vacuum evaporation on the p- and n-GaN layers, respectively.

The LED chips were mounted on copper headers to evaluate the device characteristics. Aging tests were performed under various dc current densities and ambient temperatures. Optical degradation studies were carried out by electroluminescence (EL), electron-beam-induced current (EBIC), and cathodoluminescence (CL) methods. To study the formation and propagation of nonradiative recombination centers, the measurements of EL, EBIC, and CL were carried out by passing the light exiting from the top surface through the thin Ni pad of the InGaN/AlGaN LED. The degraded samples were also studied by CL at an accelerating voltage of 20 kV.

III. RESULTS AND DISCUSSION

The InGaN/AlGaN LED exhibited a forward turn-on voltage between 3.5 and 4.0 V at a forward current of 1 mA, and a reverse voltage of 11 V at a reverse current of 0.1 mA. Figure 2 shows the light output power-injected current $(L-I)$ characteristic of InGaN/AlGaN LED on the sapphire substrate under dc operation at 30 °C. The light output power increased linearly with increasing current, and saturated at a high injected current level probably due to heating. The inset of Fig. 2 shows an aging result of the LED under a constant current density of 60 A/cm$^2$ at 30 °C. We confirmed the stable operation up to 3000 h under this aging condition. Osinski et al. also reported stable operation of Nichia GaN-based LEDs under relatively low current conditions. As discussed in the following text, however, the GaN-based LED
exhibited electrical and optical degradations under high injected current density and ambient temperature. The emission spectra at various dc currents are shown in Fig. 3. For low injected current, an impurity related broad spontaneous emission was observed around 443 nm. As the injected current increases, the emission intensity of 443 nm increases and a new emission is observed at 380 nm. Fabry–Perot fringes with a spacing of 7 nm are clearly observed, as shown in Fig. 3. The fringe spacing agrees with the calculated value based on the total epitaxial layer thickness. The presence of these Fabry–Perot fringes indicates the high quality of interfaces and thickness uniformity of our samples. The InGaN/AlGaN LED exhibited an optical output power of 0.17 mW, $\eta_c$ of 0.2%, and a peak emission spectrum at about 440 nm with a full width at half-maximum (FWHM) of 63 nm at the injected current density of 60 A/cm$^2$ (30 mA). To investigate degradation, accelerated aging tests were carried out under the injected current densities of 100 and 200 A/cm$^2$ at ambient temperatures of 30, 50, and 80 °C. We studied the degradation to the half-intensity device lifetime, defined as the time at which the optical output power decreases to 50% of its initial value. The half-intensity lifetimes were 656.7, 365.7, and 170 h for 100 A/cm$^2$ and 43.3, 19.3, and 8.6 h for 200 A/cm$^2$ at the ambient temperatures of 30, 50, and 80 °C, respectively. The output power $P$ can be expressed by

$$P = P_0 \cdot \exp(-\beta t),$$  

where $P_0$, $\beta$, $t$ are the initial output power, the degradation rate, and operating time, respectively. The degradation rate depends on the device temperature, and is given by

$$\beta = \beta_0 \cdot \exp(-E_a/kT),$$

where $\beta_0$, $E_a$, $T$, and $k$ are a constant, the activation energy of degradation, the device temperature, and Boltzmann’s constant, respectively. The values of $\beta$ were estimated to be $1.1 \times 10^{-3}$, $1.9 \times 10^{-3}$, and $3.9 \times 10^{-3}$ h$^{-1}$ under 100 A/cm$^2$, and $1.6 \times 10^{-2}$, $3.6 \times 10^{-2}$, and $8 \times 10^{-2}$ h$^{-1}$ under 200 A/cm$^2$ at the ambient temperatures of 30, 50, and 80 °C, respectively.

Figure 4 shows a comparison of the temperature dependence of the degradation rate and half-intensity lifetime for the InGaN/AlGaN LED on sapphire, InGaAsP/InP, and AlGaAs LEDs. It has been reported that the activation energy $E_a$ and the value of $\beta_0$ were 1.0 eV and $1.84 \times 10^7$ h$^{-1}$ for an InGaAsP LED (Ref. 17) at 8 kA/cm$^2$, and 0.57 eV and 93 h$^{-1}$ for an AlGaAs LED (Ref. 18) at 10 kA/cm$^2$. The values of $E_a$ and $\beta_0$ for the InGaN/AlGaN LED were determined to be 0.23 eV and 7 h$^{-1}$ at 100 A/cm$^2$, 0.25 eV, and 270 h$^{-1}$ at 200 A/cm$^2$, respectively. In spite of the low injected current densities, these values were much smaller than the values for the InGaAsP and AlGaAs LEDs. In comparison with the InGaAsP and AlGaAs LEDs, the InGaN/AlGaN LED on sapphire has a problem with reliability even at a lower injected current density. We have already reported the dependence of the injected current density on the output power for InGaN/AlGaN LEDs on sapphire.\(^{10}\) The InGaN/AlGaN LED showed stable operation under relatively low injected current densities. However, the output power from the LED decreased rapidly under high injected current densities. As shown in the previous report,\(^{10}\) the output power and the external quantum efficiency measured at 60 A/cm$^2$ (30 mA) were initially 0.17 mW and 0.2%, and 0.07 mW and 0.08% after the aging test at 280 A/cm$^2$ for 24
Thus, the output power from the InGaN/AlGaN LED decreases during the aging test under higher injected current densities and ambient temperatures.

In order to study the optical degradation process, EBIC and CL observations were carried out on the InGaN/AlGaN LED. Figure 5 shows the EBIC image of the InGaN/AlGaN LED on the sapphire substrate before degradation. As shown in Fig. 5, the faint dark spots were initially observed, which indicate preexisting defects in the structure since they act as nonradiative recombination centers. The preexisting dark spot density obtained from EBIC measurement was estimated to be $3 \times 10^7 \text{ cm}^{-2}$ for the InGaN/AlGaN LED. Lester et al.\textsuperscript{9} reported that a GaN-based LED on sapphire contained a dislocation density as high as $2 \times 10^{10} \text{ cm}^{-2}$ by use of transmission electron microscopy. However, the optical characteristics of the device relate to the nonradiative recombination centers. We reported that the EL and EBIC observations showed the growth of dark regions with the aging test.\textsuperscript{10} The CL measurement was also carried out for the degraded InGaN/AlGaN LED, which was the same sample as shown in Fig. 3(c) of Ref. 10. Figure 6 shows the CL image of the degraded LED aged under 400 A/cm$^2$ for 310 h at 30 °C. The CL image shows the dark spots and a crescent-shaped dark patch, which correspond to those of the EL and EBIC images reported in Ref. 10. The CL image indicates the nonradiative recombination centers in the active region. It is known that the energy of the Al–N bond is 2.88 eV/bond, whereas it is 2.24 and 1.93 eV/bond for the Ga–N and In–N bonds, respectively. The dark areas in the InGaN active region of the InGaN/AlGaN LED are likely due to the weak strength of the In–N bond.\textsuperscript{19}

Figure 7 shows the variation of operating voltage as a function of aging time for an InGaN/AlGaN LED. The operating voltage increased with the coefficients of 5 and 385 mV/h under the injected current densities of 400 and 500 A/cm$^2$, respectively. The growth rates of dark spots were also estimated to be 0.02–0.04 μm/h under 400 A/cm$^2$ and 1.2 μm/h under 500 A/cm$^2$ from the EL observations of the progressive stages of degradation. Thus, there is a strong relation between the growth of dark spots and the increase in operating voltage. The InGaN/AlGaN LED also showed degradation of current–voltage ($I$–$V$) characteristics under the aging test. The forward current at 1.0 V increased from 9.4 × 10$^{-10}$ A at the initial stage to $1.8 \times 10^{-8}$ A after the aging test at 400 A/cm$^2$ for 250 h. The reverse current at 1.0 V also increased from $2.6 \times 10^{-9}$ A at the initial stage to $2.9 \times 10^{-8}$ A after the aging test under 400 A/cm$^2$ for 250 h. The degraded devices showed a softness in both the forward and reverse $I$–$V$ characteristics. These results indicate that
the growth of dark regions in the $p-n$ junction causes the leakage current in the $I-V$ characteristics. The degraded $I-V$ characteristics are thought to be caused by the defect-assisted impurity diffusion during the aging process.\textsuperscript{4,20}

Figure 8 shows the dependence of the half-intensity lifetime on the injected current density for InGaN/AlGaN LEDs on sapphire from this study together with the experimental data for the ZnCdSe/ZnSSe LED on GaAs (Ref. 1) and ZnTeSe/ZnSe LED on ZnSe.\textsuperscript{5} The half-intensity lifetimes measured at 30 °C were 656.7, 43.3, and 24.3 h for the InGaN/AlGaN LED operating under the injected current densities of 100, 200, and 280 A/cm$^2$, respectively. A strong dependence on the injected current density was observed in both GaN- and ZnSe-based LEDs. Similar degradation in laser diodes, where very high injected current density is required for the lasing oscillation, has been reported. For example, the GaN-based laser diode\textsuperscript{3} with a threshold current density of 3.6 kA/cm$^2$ operated for 35 h at room temperature. However, the half-intensity lifetime of the GaN-based LED is longer than those of the ZnSe-based LEDs, which indicates that the GaN-based material is more suitable for the short-wavelength laser diode.

IV. CONCLUSIONS

The InGaN/AlGaN LED on sapphire grown by MOCVD exhibited an optical output power of 0.17 mW, external quantum efficiency of 0.2%, and a peak emitting spectrum at 440 nm with a FWHM of 63 nm under 30 mA dc operation at 30 °C. Although the InGaN/AlGaN LED showed stable operation up to 3000 h under low injected current density, the electrical and optical characteristics were degraded under high injected current density and ambient temperature. The EL, EBIC, and CL measurements revealed the formation and propagation of dark spots and a crescent-shaped dark patch in the degraded LED. The degradation under high injected current density and ambient temperature has been caused by the formation of dark regions, which act as nonradiative recombination centers.

The reduction of dislocation density by uses of thermal cycle annealing, strained layer superlattice, and selective area growth is necessary to improve the reliability of GaN-based laser diodes on sapphire.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7}
\caption{Variation of operating voltage as a function of aging time for the InGaN/AlGaN LED on sapphire. The aging tests were performed under 400 and 500 A/cm$^2$ at 30 °C.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8}
\caption{Dependence of the half-intensity lifetime on injected current density for the InGaN/AlGaN LED on sapphire. For comparison, data at 27 °C for a ZnCdSe/ZnSSe LED (Ref. 1) on GaAs and ZnTeSe/ZnSe LED (Ref. 5) on ZnSe are also plotted.}
\end{figure}

\begin{thebibliography}{10}
\end{thebibliography}
19 W. A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980).