Influence of free-standing GaN substrate on ultraviolet light-emitting-diodes by atmospheric-pressure metal-organic chemical vapor deposition

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ABSTRACT

We reported the influence of free-standing (FS) GaN substrate on ultraviolet light-emitting-diodes (UV LEDs) by atmospheric-pressure metal-organic chemical vapor deposition (APMOCVD). The Raman spectrum shows the in-plane compressive stress of the GaN epitaxial structures grown on FS GaN substrate. Besides, the Raman spectrum reveals the relation between the crystal quality and the carrier localization degree in multi-quantum wells (MQWs). High resolution X-ray diffraction (HRXRD) analysis results show that the $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ MQWs grown on FS GaN substrate has higher indium mole fraction than sapphire at the same growth conditions. The higher indium incorporation is corresponding with the red-shift 6 nm (387 nm) of the room temperature photoluminescence (PL) peak. The full widths at half maximum (FWHM) of omega-scan rocking curve in (002) and (102) reflectance on FS GaN substrate (83 arcsec and 77 arcsec) are narrower than UV LEDs grown on sapphire (288 arcsec and 446 arcsec). This superior quality may attribute to homoepitaxial growth structure and better strain relaxation in the FS GaN substrate. An anomalous temperature behavior of PL in UV LEDs designated as an S-shaped peak position dependence and W-shaped linewidth dependence indicate that exciton/carrier motion occurs via photon-assisted tunneling through localized states, what results in incomplete thermalization of localized excitons at low temperature. The Gaussian broadening parameters of carrier localization is about 16.98 meV from the temperature dependent photoluminescence (TDPL) measurement. The saturation temperature from the TDPL linewidth of UV LEDs on FS GaN substrate at about 175 K represents a crossover from a nonthermalized to thermalized energy distribution of excitons.

Keywords: FS GaN substrate, UV LEDs, APMOCVD, InGaN/AlGaN MQWs, HRXRD, Raman, PL

1. INTRODUCTION

The GaN-based devices on bulk GaN substrate with large area have been become available recently because of recent progress in production of thick free-standing GaN (FS GaN) layers grown by hydride vapor phase epitaxy (HVPE). A variety of optoelectronic devices such as UV-blue-green light-emitting diodes (LEDs) [1-3], laser diodes [4-5], and ultraviolet avalanche photodiodes [6] have reported. The homoepitaxially grown LEDs also benefit from the relatively lower defect density of FS GaN substrate than sapphire, therefore are suitable for high current operation. However, InGaN-based UV LEDs tend to be less efficient as the emission wavelength decreases. It is well known that high efficiency radiative recombination in dislocated blue and green InGaN/GaN multiple quantum wells (MQWs) LEDs has been attributed mainly to the localized states due to indium phase separation or fluctuation in the wells.[7-8] For UV LEDs, the InN mole fraction in MQWs is lower than blue and green LEDs. Since phase separation does not occur at low Indium composition, it is proposed that less localized states lead to lower internal quantum efficiency (IQE) of the UV LEDs.

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The InGaN-based UV LEDs existed large biaxial stress due to large lattice mismatch and thermal expansion coefficient incompatibility between GaN and sapphire, resulting in a large piezoelectric field along the c-plane orientation, thus forming the quantum confined Stark effect (QCSE), resulting in the reduction in IQE of InGaN-based UV LEDs.[9] The properties comparison of grown GaN-based UV LEDs on FS GaN and sapphire was shown in Table I.

Table I. Comparison of grown GaN-based UV LEDs on FS GaN and sapphire

substrate	FS GaN [10]	Sapphire
Lattice mismatch	Lattice match	13%
Thermal expansion coefficient	$5.45x10^{-6}/K$	$7.50x10^{-6}/K$
Thermal conductivity	1.3 W/cm K	0.35 W/cm K
Defect density	$3 \times 10^6/cm^2$	$10^8 \sim 10^9/cm^2$
Raman spectrum (E_2)	567.2 /cm	569.0 /cm
XRD FWHM of (002) GaN	83 arcsec	288 arcsec
XRD FWHM of (102) GaN	77 arcsec	446 arcsec
RTPL peak of UVLED	387nm (3.20eV)	381nm (3.25eV)

In this study, we investigate the influence of free-standing (FS) GaN substrate on ultraviolet light-emitting-diodes (UV LEDs). These UV LEDs structure were grown on FS GaN substrate and GaN/sapphire template at the same growth conditions by atmospheric-pressure metal-organic chemical vapor deposition (APMOCVD). We achieve a deeper understanding and relationship from the structural and optical characteristics of grown UV LEDs on FS GaN substrate and GaN/sapphire template.

2. EXPERIMENT

The 300-μm-thick FS GaN substrates were produced using the hydride vapor phase epitaxy (HVPE) technique. The substrates were provided by SUMITOMO ELECTRIC INDUSTRIES, LTD [10]. For direct comparisons, an optimized low temperature 20-nm-thick GaN buffer layer and a 2-μm-thick undoped GaN epilayer were also grown on 2 inch (0001) c-plane Sapphire substrates. The 380 nm UV LEDs structure with $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ MQWs were grown on 2 inch c-plane FS GaN substrate and on 2-μm-thick GaN templates on c-plane sapphire at the same growth conditions by atmospheric-pressure metal-organic chemical vapor deposition (SR4000) system. The MO compounds of TMGa, TMIn, TMAl and gaseous NH3 were employed as the reactant source materials for Ga, In, Al, and N, respectively, and H_2 and N_2 were used as carrier gases. Silane (SiH_4) and biscyclopentadienyl magnesium (Cp_2Mg) were used as n-type and p-type dopants. Then the epitaxial structures of InGaN/AlGaN MQWs UV LEDs comprise a 2.5-μm-thick *n*-GaN epilayer, a ten-period $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ multi-QW (MQWs) active layer at 830℃, a 15-nm-thick Mg-doped $Al_{0.3}Ga_{0.7}N$ electron blocking layer (EBL) at 1050℃, a 11-nm-thick Mg-doped $Al_{0.11}Ga_{0.89}N$ EBL at 1050℃ and a 5.5-nm-thick *p*+-GaN contact layer at 1030℃ on FS GaN substrate and GaN template. The thickness of the $In_{0.025}Ga_{0.975}N$ well and $Al_{0.08}Ga_{0.92}N$ barrier in the active layer were around 2.5 and 12.5 nm, respectively.

The 380 nm UV LEDs samples using $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ MQWs grown on FS GaN substrate and GaN template were analyzed by high resolution X-ray diffraction (HRXRD D8) method using Cu $K\alpha 1$ (λ=1.54056 A) as source. The room temperature (RT) Raman scattering was used to analyze the strain state of InGaN/AlGaN MQWs. The optical properties were investigated by temperature dependent PL measurements, which were excited with the 325 nm line of a He–Cd laser at excitation power densities of 20 mW.

3. RESULTS AND DISCUSSION

In wurtzite GaN films, the FWHM of the (002) rocking curve was associated with the density of screw or mix dislocations, while the FWHM of the (102) rocking curve was affected by all dislocations. [11] Figure 1 (a) shows that the HRXRD pattern for the (0002) reflection from grown UV LEDs with $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ MQWs on FS GaN substrate and GaN template. The strongest peak is due to the GaN layer. The Spectra clearly shows high-order MQW diffraction peaks with the fourth-order satellite peak still being observable, indicating good epilayer periodicity. Besides, the MQW period can be determined from the positions of the MQW satellite peaks. UV LEDs with In$_{0.025}$Ga$_{0.975}$N/Al$_{0.08}$Ga$_{0.92}$N MQWs on FS GaN substrate compare to UV LEDs with In$_{0.025}$Ga$_{0.975}$N/Al$_{0.08}$Ga$_{0.92}$N MQWs on GaN template, and we find more compressive strain on GaN substrates than on GaN templates. Although the zero-order satellite peak of the InGaN wells is merged into the main peak in both the spectra, several satellites peaks from -4 to +2 can be clearly distinguished. It exhibits high crystal quality and good structure interfaces for homo-epitaxial UV LEDs on GaN substrate. The FWHM of rocking curve of UV LEDs in (002) and (102) reflectance on FS GaN substrate (83 arcsec and 77 arcsec) were narrower than In$_{0.025}$Ga$_{0.975}$N/Al$_{0.08}$Ga$_{0.92}$N MQWs grown on GaN template (288 arcsec and 446 arcsec) from Fig. 1 (b).

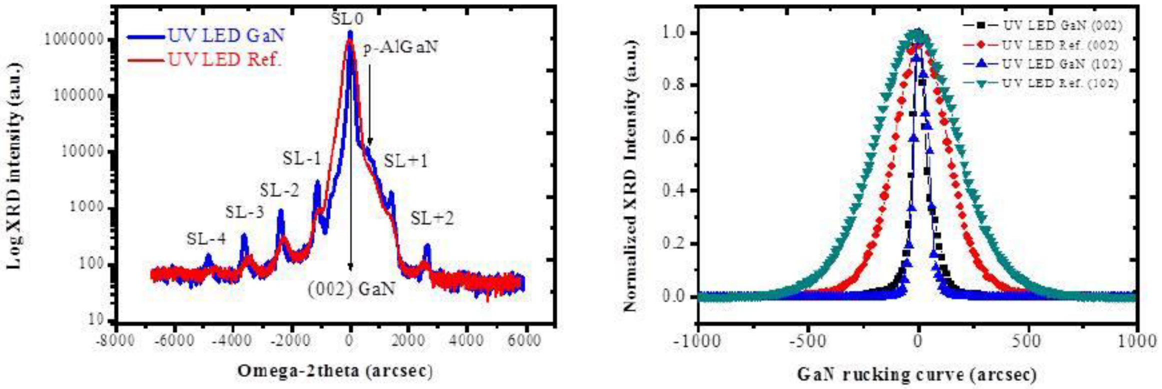

Figure 1.shows the (a) (002), (102) GaN rucking curve and (b) (002) omega-2theta scan of grown GaN-based UV LEDs on FS-GaN substrate and sapphire.

In addition to estimate FWHM of rucking curve by HRXRD, another important feature to estimate is the internal stress of the epitaxial GaN film since the different of lattice mismatch at FS GaN substraye and sapphire that potentially alleviate the built-in stress. To analyze the residual strain in the GaN films, Raman backscattering measurements were performed at room temperature.

Fig. 2 shows the Raman spectrum for GaN-based UV LEDs grown on FS GaN substrate and GaN template. The Raman shift peaks of E2 (high) mode for GaN epitaxial layer grown on FS GaN substrate and GaN template are located at around 567.2 and 569.0 cm^{-1}, respectively. The in-plane compressive stress σ for GaN-based UV LEDs is estimated to decrease from 1.121 to 0.307 GPa on FS GaN substrate by using the following equation as $\boldsymbol{\Delta\omega = \omega_{E2} - \omega_0 = C\sigma}$ [12], where $\boldsymbol{\Delta\omega}$ is the Raman shift peak difference between the strained GaN epitaxial layer ω_{E2} and the unstrained GaN epitaxial layer ω_0 (566.5 cm^{-1}), and C is the biaxial strain coefficient, which is 2.25 cm^{-1}/GPa. Thus grown UV LEDs on FS GaN substrate can release strain in MQWs, consequently we can expect that the GaN-based UV LEDs grown on FS GaN substrate have weaker quantum-confined Stark effect (QCSE) [13] and higher IQE.

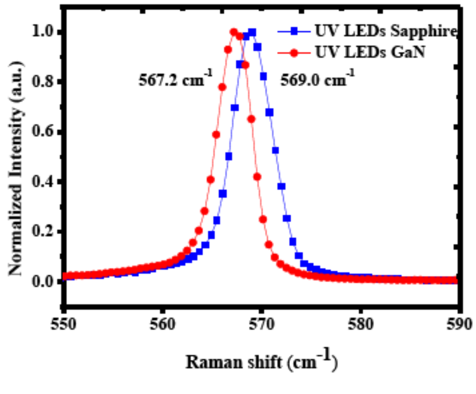

Figure 2.shows the Raman spectrum of grown GaN-based UV LEDs on FS GaN and sapphire

Fig. 3 shows the PL spectra for GaN-based UV LEDs on FS GaN substrate and GaN template in the temperature range from 25 K to 300 K and excitation power densities of 20 mW. We obtain that the higher indium incorporation for UV LEDs on FS GaN substrates is corresponding with the red shift 6nm of the PL emission peak at 300 K. Higher indium mole fraction is in the UV LEDs grown on FS GaN substrate due to the strain relaxation in the GaN substrate. An anomalous temperature behavior of PL in group-III nitride structures designated as an S-shaped peak position dependence and W-shaped linewidth dependence that shown in Fig. 3 and Fig. 4 indicate that exciton/carrier motion occurs via photon-assisted tunneling (hopping) through localized states, what results in incomplete thermalization of localized excitons at low temperature. Fig. 3 exhibits a S-shaped temperature dependence of the emission energy of the PL peak and could be fitted by the Varshni empirical formula as $\mathbf{E_g = E_g(0) - \alpha T^2/(T+\beta) - \sigma^2/K_BT}$ where $E_g(0)$ is the bandgap at 0 K, α and β are Varshni's thermal coefficients, K_B is the Boltzmann constant, and σ is the Gaussian broadening parameter. The deviation of the PL peak position from the Varshni's characteristics is considered due to the thermal broadening of carrier distribution, the delocalization of carriers, the dissociation of the excitons, and the piezoelectric field intensity with temperature change. Thus, the Gaussian broadening parameters of $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ MQWs grown on FS GaN substrate and GaN template were determined as 16.98 and 15.59 meV, respectively. The Gaussian broadening parameter can be seen as an indication of order degree of InGaN/GaN MQWs. [14] We find that the carrier localization degree of the UV LEDs grown on FS GaN substrate was larger than UV LEDs on GaN template.

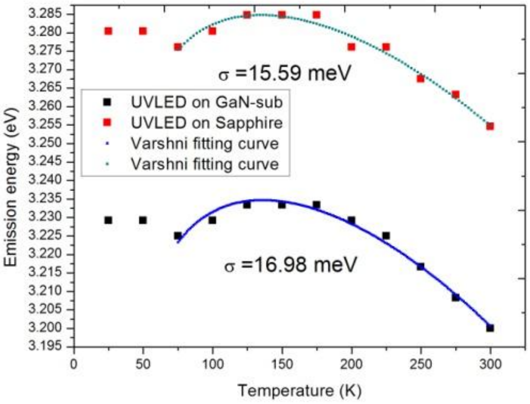

Figure 3 shows the emission energy of the grown GaN-based UV LEDs on FS GaN and sapphire by TDPL.

Fig. 4 shows a W-shaped temperature dependence of the FWHM of the PL band with a characteristic kink at about 175 K and 150 K separately. The W-shaped temperature behavior of the linewidth is known to be a signature of exciton hopping over randomly dispersed localized states with a crossover from a nonthermalized to a thermalized distribution function of the excitons. From Kazlauskas's simulation results show that the dispersion of the localized states within the In-rich clusters and the cluster distribution in average localization energy might be roughly estimated as $\boldsymbol{\sigma} = 2k_BT_S$ and $\boldsymbol{\Gamma} = \sqrt{(\boldsymbol{\Gamma}_S^2/\ln 4 - \boldsymbol{\sigma}^2)}$, respectively. [15] Here T_S is a saturation temperature of the linewidth and Γ_S is the experimental linewidth above the saturation temperature. So the $\boldsymbol{\sigma}$ and $\boldsymbol{\Gamma}$ of the UVLEDs grown $In_{0.025}Ga_{0.975}N/Al_{0.08}Ga_{0.92}N$ MQWs on FS GaN substrate were 30 meV and 50 meV at 175K. And the $\boldsymbol{\sigma}$ and $\boldsymbol{\Gamma}$ of the UVLEDs on GaN template were 26 meV and 46 meV at 150K. The dispersion of the carrier localized states of the UV LEDs grown on FS GaN substrate was larger than UV LEDs on GaN template. We attributed the results to the better thermal conductivity of FS GaN substrate than sapphire.

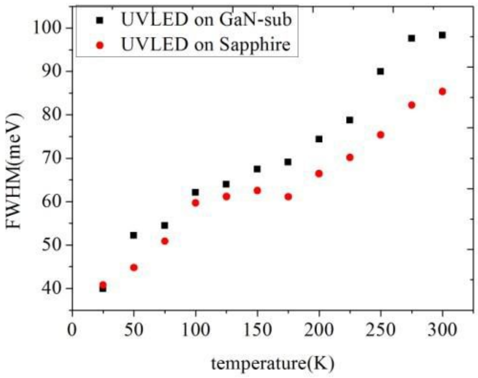

Figure 4 shows the FWHM of the grown GaN-based UV LEDs on FS GaN and sapphire by TDPL.

4. SUMMARY

We systematically report the structural and optical characteristics of UV LEDs grown on FS GaN substrate by APMOCVD. Comparison of grown GaN-based UV LEDs on FS GaN and sapphire is shown in Table I. HRXRD and Raman spectrum measurement results show that the $\mathrm{In}_{0.025}\mathrm{Ga}_{0.975}\mathrm{N}/\mathrm{Al}_{0.08}\mathrm{Ga}_{0.92}\mathrm{N}$ UV LEDs on FS GaN substrate have better crystal quality and larger strain release than sapphire. HRXRD and PL measurement results show that grown UV LEDs on FS GaN substrate have higher indium mole fraction (red-shift 6 nm) and the higher Intensity than sapphire at the same growth conditions. The $\mathrm{In}_{0.025}\mathrm{Ga}_{0.975}\mathrm{N}/\mathrm{Al}_{0.08}\mathrm{Ga}_{0.92}\mathrm{N}$ UV LEDs grown on FS GaN substrate exhibit the better carrier localization effect and the dispersion of carrier localized states than sapphire from TDPL measurement.

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