InGaN/GaN based light-emitting diodes grown on maskless periodically grooved sapphire fabricated by wet chemical etching

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InGaN/GaN multiple quantum well (MQW) green and near ultraviolet (UV) light-emitting diodes (LEDs) were grown on maskless periodically grooved (MPG) sapphire by metal organic vapor phase epitaxy (MOCVD). The LEDs grown on MPG sapphire show better crystalline quality compared with those grown on planar sapphire. Meanwhile, the light output for LEDs grown on MPG sapphire show higher than those grown on planar sapphire. The improvement in the light intensity for green LED could be attributed to the enhancing external quantum efficiency (EQE) by adopting MPG sapphire. For UV LED grown on MPG sapphire, the enhancement is due to the combination of increasing internal quantum efficiency (IQE) by reducing threading dislocations and improving light extraction efficiency. The results show that the method adopting MPG sapphire will have potential application to develop high quality LEDs, especially in UV LEDs.

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Commercially available III-nitride light-emitting diodes (LEDs) are usually grown on sapphire, the mismatch in lattice constant and thermal expansion coefficient of the epitaxial layers and the substrate gives rise to high density of threading dislocations in the LED structures [1,2]. The high density dislocations compromise the device performance significantly. Now, commercially available blue/green LED using InGaN-based quantum wells has been realized [3,4], for ultraviolet(UV) LED, the performance of is found to be strongly affected by the dislocations, which is more sensitive to threading dislocations than green/blue one [5,6,7]. Therefore, reduce the dislocation density is an important issue for fabricating high-performance UV LEDs. The threading dislocations has been proved can be effectively eliminated by epitaxial lateral overgrowth (LEO) with SiO_2 mask patterned on as-grown GaN [8,9]. Although this technique can effectively improve the crystalline quality of the overgrown layer, there are complications of the mask-patterned growth that also increases the growth and process time. Additional mask-related drawbacks of LEO include chances of impurity contamination and stress-induced tilt in the overgrown layer [10,11]. The maskless and single-step overgrowth technique is more desirable in reducing dislocation density to improve the performance of optoelectronic devices, which has been employed by some researchers [12,13,14].

In this letter, InGaN/GaN multiple quantum well (MQW) green and UV LEDs were grown on maskless periodically grooved (MPG) sapphire, which was prepared standard photolithography and wet etching. The same structure was also grown in the planar sapphire under the same growing conditions for reference. High-resolution X-ray diffraction (HRXRD) was used to characterize the structural properties of the samples. Hot wet chemical etching was performed in a mixture of H_3PO_4/H_2SO_4 with a ratio of 3:1 at 280°C for 15 min reveal the density of threading dislocations. The morphology and distribution of etch pits was measured by atomic force microscopy (NanoScope □a-D3000 AFM). Temperature-dependent photoluminescence (PL) was used to estimate the internal quantum efficiency(IQE). The relative output power was measured by fixing a fiber optic cable coupled to an integrated sphere detector above the unpacked LED samples.

The InGaN/GaN MQW LEDs were grown on planar and patterned substrates by Axitron 2400G3HT MOCVD system. The MPG sapphire substrate was prepared by standard photolithography and wet chemical etching. Sapphire substrates were periodically patterned along $[11\bar{2}0]$ with 3-μm-wide SiO_2 strip and 3.5-μm-wide opening. Then, the patterned sapphire was etched in the solution of H_2SO4:H_3PO_4=3:1 followed by dipping in the solution of HF:H_2O =1:10 for removal of SiO_2. Meanwhile, planar sapphire was also loaded in the reactor to grow under the same conditions for reference. For simplicity, the green LEDs grown on planar and MPG sapphire were denoted as sample A and sample B, respectively, and another LEDs are UV structure denoted by sample C and sample D for simplicity. The green and UV LED have the same structures, the only difference is the In mole fraction of InGaN well layer. The films were deposited on them following by the standard two-step growth process, trimethylgallium (TMGa) and ammonia (NH_3) were used as precursors and with H_2 carrier gas. Biscyclopentadienyl magnesium (CP_2Mg) and Silane (SiH_4) were used as the P- and n-type doping sources, respectively. Low-temperature nucleation layer was deposited at 525°C. Then, the temperature was elevated to 1120°C to grow Si-doped n-type GaN buffer layer. The MQWs were composed of five periods of InGaN/GaN grown at 810 °C and 880 °C, respectively, and finally 150 nm p-type Mg-doped GaN capped. After thermal activation of P-type GaN at 700°C in an N_2 ambient by rapid thermal annealing(RTA). Top-emitting LEDs with a chip size of 300 μm × 300 μm were fabricated using standard photolithography and dry etch techniques. The standard Ni/Au and Ti/Al alloys were used as p- and n-type contacts, respectively.

Tabel.1 Measured GaN (0002) and (10$\bar{1}$2) ω scan curves from green and UV InGaN/GaN LEDs grown on different sapphire

Sample	FWHM (0002)	FWHM (10$\bar{1}$2)
Sample A	217 arc sec	278 arc sec
Sample B	188arc sec	208 arc sec
Sample C	221 arc sec	286 arc sec
Sample D	192 arc sec	214 arc sec

Fig.1 shows the schematic of fabrication procedure for MPG sapphire, which was prepared by standard photolithography and wet chemical etching. First, sapphire substrate was periodically patterned along [11$\bar{2}$0] with 3-μm-wide SiO_2 strip and 3.5-μm-wide opening. Then, the patterned sapphire was etched in the solution of H_2SO4:H_3PO_4=3:1 at 400 °C for 2h followed by dipping in the solution of HF:H_2O =1:10 at room temperature for removal of SiO_2.

Measured GaN (0002) and (10$\bar{1}$2) ω scan curves in HRXRD from the LEDs were shown in the table.1. The full-width at half-maximum (FWHM) is 217 arc sec and 188 arc sec for sample A and sample B in the (0002) diffraction while for sample C and sample D it is corresponding to 221 arc sec and 192 arc sec, respectively.

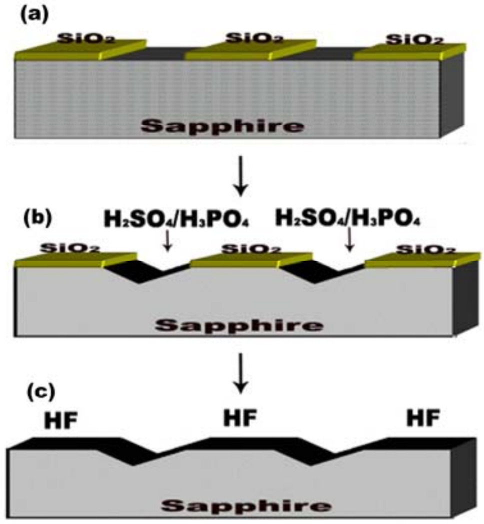

Fig. 1. A schematic of the procedure to prepare grooved sapphire by wet chemical etching. (a) Sapphire substrates were periodically patterned along [11$\bar{2}$0] with 3-μm-wide SiO_2 strip and 3.5-μm-wide opening. (b) Subsequently, the patterned sapphire was etched in the solution of H_2SO4:H_3PO_4=3:1 at 400 °C for 2h (c) Removal of SiO_2 in the solution of HF:H_2O =1:10 at room temperature.

For the asymmetric (10$\bar{1}$2) diffraction, the FWHM for sample A and sample B is 278 arc sec and 208 arc sec while for sample C and sample D it is corresponding to 286 arc sec and 214 arc sec respectively. The LEDs grown on MPG sapphire substrate show narrower FWHM than those grown on planar sapphire substrate for both symmetric and asymmetric diffraction. It is well accepted that the FWHM of the symmetric diffraction is primarily related to screw-type and mixed threading dislocations and the asymmetric FWHM reflects the information of all types of threading dislocations [16]. So it was inferred that lower density of threading dislocations were achieved for the LEDs grown on MPG sapphire.

Hot wet etching with mixed H_3PO_4/H_2SO_4 solutions was performed to reveal the dislocation distribution. The method using wet chemical etch combing with AFM has been proved is an effective technique to determine the density of defects propagating to the surface [17,18,19]. Typical AFM 3D images of the etched surface morphology of samples were showed in Fig. 2 with a measuring scale of 10×10 μm^2 for green LEDs and 20×20 μm^2 for UV LEDs respectively. The size of the etched pits is uniform attributed to the surface termination with threading dislocations. It is clearly seen that the amount of pits in the sample A is several times more than that of sample B, and also for the UV LED, the sample D show obvious less pits than that of sample C. Meanwhile, it was clearly seen that the pits were regularly spaced and arranged for the sample B and sample D, and most of the pits concentrated in the mesa region, in contrast, the wing region showed fewer etching pits. It was estimated the average dislocation density was approximately to 4.0×10^8 and 4.2×10^7 in the mesa and wing region for LEDs grown on MPG sapphire, respectively. Remarkable reduction of threading dislocations was achieved for the LEDs grown on MPG sapphire.

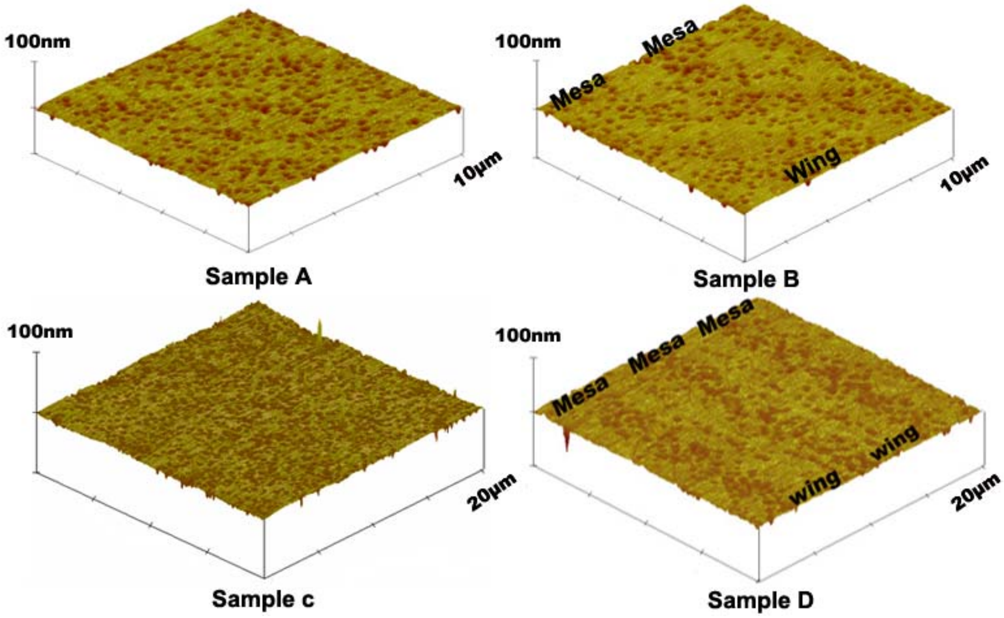

Fig.2. AFM 3D images of the etched surface morphology of samples with a measuring scale of 10×10 μm^2 for green LEDs and 20×20 μm^2 for UV LEDs respectively

Temperature-dependent PL spectra was carried out to estimate the internal quantum efficiency(η_{int}) of green and UV LEDs grown on different sapphires. The temperature dependences of the integrated PL intensities for green and UV LEDs grown on planar and MPG sapphire were shown in Fig.3. In general, The η_{int} can be regarded as 100% when neglecting the nonradiative recombination process[20,21]. The integrated PL intensities of all LEDs were nearly constant below 100 K and declined gradually with a further increase in temperature. In the case of green LEDs, the room temperature η_{int} values were about 14% and 16% for sample A and sample B respectively. No remarkable increase of η_{int} was found. For the UV LEDs, η_{int} values were about 3.8% and 10% for the sample C and Sample D respectively. Around 2.6 times improvement has been achieved for sample D.

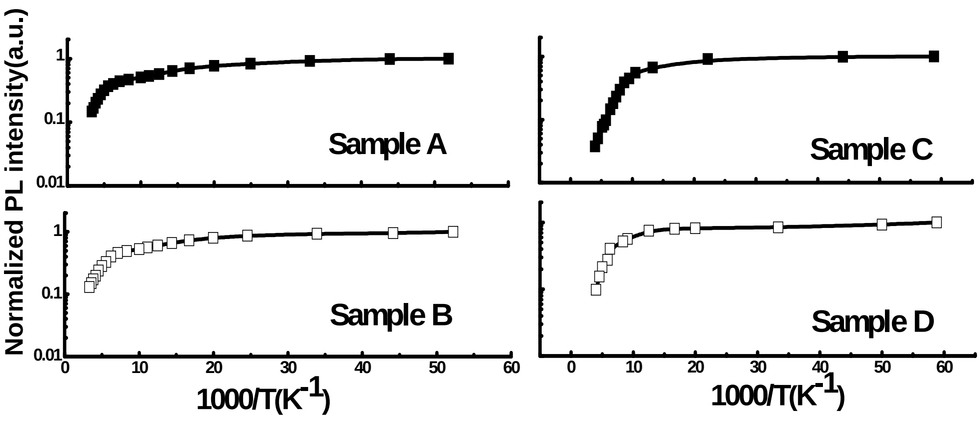

Fig.3. The temperature dependences of the integrated PL intensities for green and UV LEDs grown on planar and MPG sapphire.

Fig.4 shows the relative light output power of green and UV LEDs grown on different sapphire as the function of injection current. The output power intensity of all LEDs increases linearly with the injection current. The relative output powers for LEDs grown on MPG sapphire were drastically increased. Meanwhile, under the same injection current at 20mA, 1.2 times higher relative output power was achieved for sample B. For UV LED samples, sample D has 2.8 times higher relative output power than sample C.

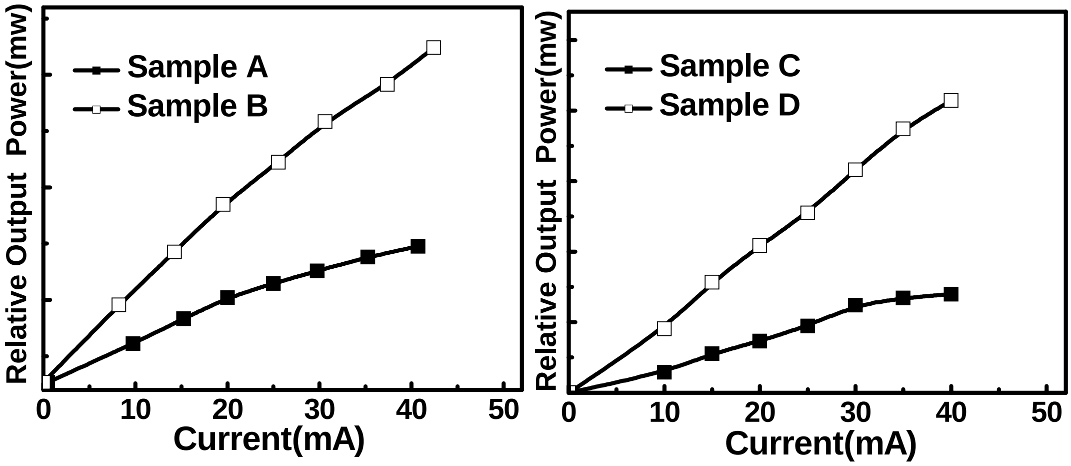

Fig.4. Relative light output power of green and UV LEDs grown on different sapphire as a function of injection current.

Fig. 5 shows the schematic diagram of improving extraction efficiency using MPG sapphire. Due to the refractive index of nitride films is higher than that of the sapphire substrate, most of the emission light from active layers propagates through the nitride films. The light generated in the active layer can exit into scatters the emission light from the active layer [22,23,24]. In this case, as compared to the normal sapphire substrate, the propagating light can more efficiently exit into the sapphire substrate. The MPG sapphire scatters some of the downward-directed emission back into the structure that would otherwise be lost through the substrate.

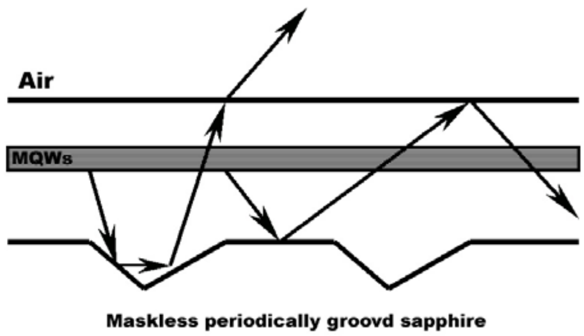

Fig.5. Schematic diagram of improving extraction efficiency of emission light of using MPG sapphire

In summery, green and UV InGaN/GaN MQW LEDs were grown on planar and MPG sapphire substrates. Remarkable reduction of threading dislocations was achieved for the LEDs grown on MPG sapphire. No obvious IQE improvement for the green LED grown on MPG sapphire from temperature-dependent photoluminescence measurements. However, the UV LED grown on MPG sapphire shows about 2.6 times higher IQE than that on the planar substrate. Meanwhile, at the same injection currents, the LEDs grown MPG sapphire exhibit much higher relative output power than those on planar substrates. Due to the insensitiveness to dislocations, the enhancement of green LED grown on MPG sapphire is mainly due to the increasing of light extraction by scattering from MPG sapphire. For UV LED grown on MPG sapphire, the enhancement could be attributed to the combination of increasing IQE and improving extraction efficiency by using MPG sapphire. The results show the method adopting MPG sapphire will have potential in high quality LEDs, especially in UV LEDs.

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