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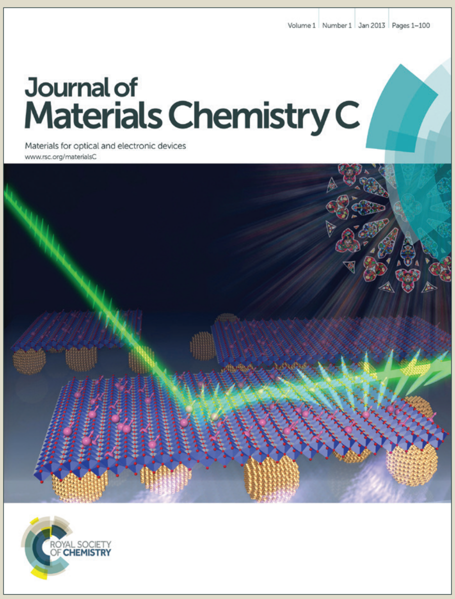

Epitaxial growth of GaN films on unconventional oxide substrates

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Abstract: GaN is a unique material with outstanding optoelectronic properties and is suitable for the application of light-emitting diodes (LEDs), laser diodes (LDs), high electron mobility transistors (HEMTs), *etc*. Usually, GaN films are grown on sapphire substrates. However, due to the relatively large lattice and thermal expansion coefficient mismatches between GaN and sapphire, to obtain high-performance and high-power GaN-based devices is still the pursuing target. In this regard, many researchers have tried hard to grow GaN films on unconventional oxide substrates other than sapphire, which share relatively small lattice and thermal expansion coefficient mismatches with GaN. This review focuses on the recent progress of the epitaxial growth of GaN films on unconventional oxide substrates. The perspectives for the epitaxial growth of GaN films on unconventional oxide substrates are also discussed.

1. Introduction

GaN and its related III-nitrides have been attracted remarkable interest due to their excellent properties, which make them possible for the applications in light-emitting diodes (LEDs), laser diodes (LDs), high electron mobility transistors (HEMTs), *etc*.[1-5] By now, GaN-based optoelectronic devices, particularly, LEDs prepared on sapphire substrates have already been commercialized.[6-8] However, Due to the relatively large mismatches in lattice parameters and thermal expansion coefficients between GaN and sapphire,[9-10] the formation of large stress and high dislocation density takes place in the as-grown GaN-based wafers, which deteriorates the performance of GaN-based optoelectronic devices, and hampers the further development of the devices. In order to circumvent this issue, researchers have tried hard to grow GaN films on unconventional oxide substrates other than sapphire, such as $MgAl_2O_4$, $LiGaO_2$, $LiAlO_2$, $LaAlO_3$, $LaSrAlTaO_6$(LSAT), ZnO, MgO, *etc*.[11-18] Compared with the sapphire substrates, these unconventional oxide substrates have superior properties in some aspects. On the one hand, they show very small lattice mismatch with GaN, which is good for the nucleation of GaN films during the initial growth and therefore benefits the growth of high crystalline quality GaN films. For example, the lattice mismatch between $LiGaO_2$ and GaN is as low as 0.9%, and that between LSAT and GaN is 1%. On the other hand, some oxide substrates, such as $LiGaO_2$(100), $LiAlO_2$(100), *etc*, are suitable for the preparation of nonpolar GaN-based devices. These nonpolar GaN-based devices are absent from the so-called quantum confined Stark effects (QCSEs) which cause the bending of the holes and electrons wave functions in the quantum wells, and lead to the increase of the radiative recombination efficiency ultimately.

In this work, we review on the recent progress of the epitaxial growth of GaN films on unconventional oxide substrates. The perspectives for the epitaxial growth of GaN films on unconventional oxide substrates are also discussed.

2. Epitaxial growth of GaN films on unconventional oxide substrates

2.1 $MgAl_2O_4$

$MgAl_2O_4$ is a crystal material which has a face-centered cubic unit cell with lattice parameter of 0.8083 nm and belongs to the *Fd3m* space group.[29] Fig. 1 illustrates the crystal structure of $MgAl_2O_4$. As shown in Table 1, $MgAl_2O_4$ has smaller mismatches in both lattice parameter and thermal expansion coefficient with GaN when compared with that of sapphire. The lattice mismatch between $MgAl_2O_4$ (111) and GaN (0002) is 9.5%,[29] which is smaller than that between GaN and sapphire (13.3%). The mismatch in thermal expansion coefficient between $MgAl_2O_4$ and GaN (12%) is also smaller than that between GaN and sapphire (34%).[30]

Table 1. Lattice parameters of unconventional oxide substrates and their epitaxial directions

Substrates	Lattice parameters a/nm	b/nm	c/nm	Epitaxial direction	Lattice mismatch %	Thermal mismatch %	Reference
GaN	0.3168	0.3168	0.5178	[0001]	0.0	0	11
α-Al_2O_3	0.4760	0.4760	1.2991	[0001]	13.3	27	11-12
LSAT	0.6312	0.6312	0.6312	[111]	1.0	3.6	13-15
$LiAlO_2$	0.5169	0.5169	0.6260	[010]	0.3	21.3	16-17
$LiGaO_2$	0.5402	0.6370	0.5007	[010]	0.2	16.6	18-20
$LaAlO_3$	0.3791	0.3791	0.3791	[1-10]	3	39.2	21
$MgAl_2O_4$	0.8083	0.8083	0.8083	[111]	9.0	37.9	22-23
MgO	0.4130	0.4130	0.4130	[110]	7	56.3	24-25
ZnO	0.3250	0.3250	0.5200	[0001]	0.4	7.6	26-28

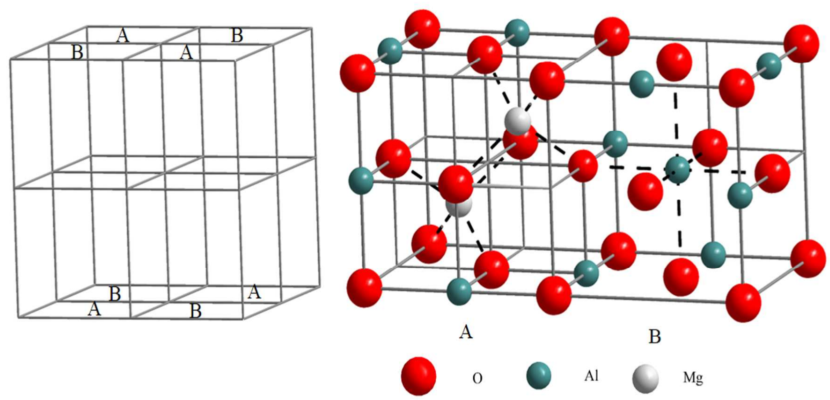


Fig. 1. The schematic diagram of the crystal structure of $MgAl_2O_4$.

Table 2. Thermal properties of substrates for GaN epitaxial growth.[29]

Materials	Thermal conductivity/ $W\cdot(m\cdot K)^{-1}$	Thermal expansion coefficient/ $10^{-6}\cdot K^{-1}$	Thermal stability
GaN	110	7.7	Good
Sapphire	46	7.5	Excellent
$MgAl_2O_4$	116	7.45	Medium

Another merit of $MgAl_2O_4$ substrate is its high thermal conductivity. As known, almost 70% of the input electric energy in LEDs would be eventually transferred into heat,[31] which leads to the rapid warming of LEDs and thereby reduces the chance of radiation recombination. Consequently, thermal conductivity of a substrate is of significance in determining the performance of LEDs. As for $MgAl_2O_4$ substrate, its thermal conductivity at room temperature is about 116 W/mK, which is about four times higher than that of sapphire, *i.e.* 33 W/mK.[29] In this regard, for the fabrication of high-power GaN-based LEDs, $MgAl_2O_4$ is undoubted to be a promising substrate. In addition, $MgAl_2O_4$ belongs to *F3dm* space group with (111) as its cleavage plane direction, and can be easily etched by chemicals, which gives advantages for the fabrication of free-standing GaN-based LEDs .[32]

As cubic $MgAl_2O_4$ has a spinel structure, both its (111) and (001) planes could be used for the epitaxial growth of α-GaN which has a hexagonal wurtzite structure, and β-GaN which has a cubic sphalerite structure, respectively.[33] However, researchers have demonstrated that there are many grains formed at the interface of β-GaN/ $MgAl_2O_4$ (001), and high density of stacking faults as well as microtwins going through the β-GaN, which greatly reduces the crystalline quality of GaN epitaxial layer.[33-34] Therefore, α-GaN is mainly grown on $MgAl_2O_4$ (111) substrate, and its properties are comparable to those of GaN grown on sapphire (0001) substrate.[35]

2.1.1 GaN films on $MgAl_2O_4$ substrate

However, there are still some problems for GaN epitaxy on $MgAl_2O_4$ substrates. As $MgAl_2O_4$ has high Mg partial pressure, when conducting the epitaxial growth of GaN on $MgAl_2O_4$ at high temperature, severe evaporation of Mg atoms will alter the crystalline structure of the substrate surface, and consequently enlarges the lattice mismatch between GaN and $MgAl_2O_4$. Meanwhile, these evaporated Mg atoms would easily react with Ga atoms and N plasma, resulting in severe interfacial layer. These problems make the subsequent epitaxial growth of GaN on $MgAl_2O_4$ substrate difficult. To solve these problems, various methods have been carried out.

2.1.1.1 Buffer layer

Though the lattice mismatch between GaN and $MgAl_2O_4$ is smaller than that between GaN and sapphire, it still reaches 9.5%, easily introducing defects into the GaN epitaxial layer. To alleviate this problem, low-temperature buffer layer, such as GaN, AlN and ZnO, is proposed for the growth of GaN on $MgAl_2O_4$.

In the 1990s, Kuramata and Yang *et al.* grow GaN epitaxial layers by metal organic chemical vapor deposition (MOCVD) on $MgAl_2O_4$ substrates.[33, 36] Low-temperature GaN buffer layer is firstly deposited at 550 ºC, followed by a 2.7 μm-thick GaN film grown at 1050 ºC. Characterization indicates that the thickness of buffer layer makes a great impact on the optical and electrical properties of as-grown GaN films. Within a suitable range of the buffer layer thickness, the crystalline quality of GaN films grown on $MgAl_2O_4$ substrate by MOCVD is comparable to that grown on sapphire substrate.[37]

It has been demonstrated that the growth of buffer layer is an effective approach to suppress the Mg diffusion. Especially, when the buffer layer is thick enough, *i.e.* more than 30 nm in practice, the diffusion of Mg atoms is limited within the buffer layer. In this way, the quality of GaN epitaxial films is greatly improved. Using this method, Kuramata *et al.* has achieved high-quality GaN films with very smooth surface on $MgAl_2O_4$ substrates, as shown in Fig. 2.[38]

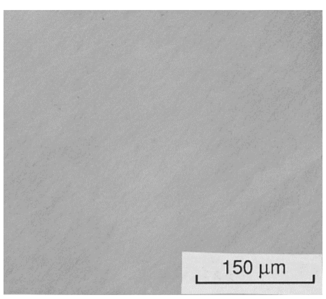


Fig. 2. The surface morphology of GaN films grown on $MgAl_2O_4$ substrates. Reprinted with permission from ref. 38. Copyright 1995 American Institute of Physics.

2.1.1.2 Surface treatment

As-received $MgAl_2O_4$ substrates often have many scratches or other defects on the surfaces,[30] which would produce negative effects on subsequent epitaxial growth of GaN. Therefore, prior to GaN deposition, surface treatment for $MgAl_2O_4$ substrates is required.

(1) Thermal annealing

Li *et al.* obtained the atomically flat surface of $MgAl_2O_4$ substrate by thermal annealing.[39] $MgAl_2O_4$ is annealed for 3 h at 1000 ºC in a box made from ceramic $MgAl_2O_4$. Fig. 3 shows the typical AFM image for the as-annealed $MgAl_2O_4$ surfaces, in which the step and terrace structure with a step height of 0.47 nm can be clearly observed. GaN film grown on the as-annealed substrate shows high crystalline quality, with the full widths at half maximum (FWHM) measured by X-ray rocking curves (XRCs) for GaN (0002) and GaN (10-10) equal to 0.21° and 0.37°, respectively.[30] It indicates that the interfacial reaction between GaN films and $MgAl_2O_4$ substrates is effectively suppressed by the application of annealing.

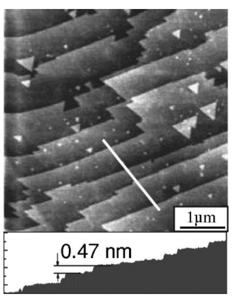


Fig. 3. AFM image for $MgAl_2O_4$ substrate annealed at 1000 ºC for 3 h. Reprinted with permission from ref. 39. Copyright 2006 American Institute of Physics.

(2) Thermal passivation

Thermal passivation for $MgAl_2O_4$ substrate in O_2 atmosphere will generate a surface layer of Al_2O_3. Meanwhile, it will remove the residual contamination on the surface. He *et al* proposed a simple interfacial engineering approach to improve the properties of GaN films.[29, 40] $MgAl_2O_4$ substrates are first treated by chemical etching with H_2SO_4:H_3PO_4 = 3:1 for 10 min at 90 ºC. Further thermal annealing for 3 h at 1000 ºC in O_2 ambient is then carried out to remove the residual contaminants. GaN films are grown on the as-prepared $MgAl_2O_4$ (111) by MOCVD after chemical etching and thermal passivation.[40] It shows that the Al_2O_3 buffer layer is formed in the interface of $MgAl_2O_4$ (111)/GaN via thermal passivation. Furthermore, this Al_2O_3 buffer layer remains stable during the following GaN deposition, which is primarily responsible for the epitaxial growth of high-quality single-crystalline GaN films on $MgAl_2O_4$(111) substrates.

2.1.1.3 PLD

Commonly, MOCVD and molecular beam epitaxy (MBE) are used for the epitaxial growth of GaN. However, the high growth temperature adopted in both techniques will cause interfacial reactions and result in an interfacial layer between GaN and $MgAl_2O_4$, which deteriorates the properties of the subsequently grown GaN. In this case, traditional MOCVD and MBE are not suitable for the epitaxial growth of high-quality GaN on $MgAl_2O_4$.[41-43] A low-temperature growth technique for GaN is urgently needed.

Pulsed laser deposition (PLD) has been proven to be a promising technique for the growth of high-quality GaN films even at low temperature. The pulsed laser supplies enough energy for the migration of precursors on the substrates, and thereby makes the films growth at low temperature possible.[44-48] In this regard, PLD technique is undoubtedly an effective approach for the low-temperature epitaxial growth.

Li *et al.* achieved the high-quality GaN films on $MgAl_2O_4$ (111) substrates at low temperature by PLD.[49, 50] XRC shows that the FWHM of GaN (0002) is only 0.07°, indicating the high crystalline quality of GaN epitaxial layer. Fig. 4 shows the AFM image of the as-grown GaN film. The root-mean-square (RMS) value of the surface is as small as 2.4 nm.[50] GaN grains are of 500 nm in diameter, and are starting the coalescence among each other, which verifies the two-dimensional growth of GaN at low temperature. Since the epitaxial growth is carried out at low temperature, the evaporation of Mg is effectively controlled at low temperature condition, and thereby the high-quality GaN films can be successively prepared.

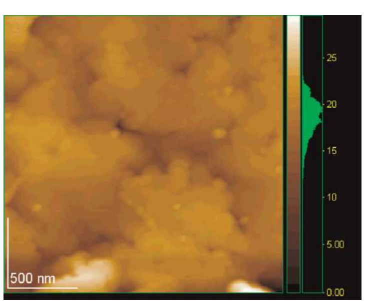


Fig. 4. AFM image of GaN films grown on $MgAl_2O_4$ (111) substrates by low-temperature PLD. Reprinted with permission from ref. 50. Copyright 2010 WILEY.

2.1.2 GaN-based devices on $MgAl_2O_4$ substrates

GaN-based LEDs on $MgAl_2O_4$ (111) substrates have been demonstrated by now. Low-pressure MOCVD is used to fabricate the high-brightness LEDs with InGaN/GaN multiple quantum wells (MQWs) on $MgAl_2O_4$.[51-52] Fig.5 shows the structure for these LEDs. It consists of a ten-periods InGaN/GaN MQWs, and the InGaN and GaN for each unit cell are 2.5 and 5 nm-thick. Ti/Al and Ni/Au are used as the n- and p-type contacts, respectively. Fig.6 shows the *I-V* characteristics of the LED. It presents an abrupt turn-on between 3 and 4 V with a total series resistance of about 15 Ω, which are comparable to those for the LEDs grown on sapphire or grown at atmospheric pressure by MOCVD.[41] The electroluminescence (EL) spectrum presents a strong band-edge emission peak at 395 nm with a linewidth of only 12 nm.[52]

Sun *et al.* used low pressure MOCVD to fabricate Mg-doped green LEDs on $MgAl_2O_4$ (111) substrates.[53] The *I-V* characteristics of these Mg-doped LEDs show a high turn-on voltage around 4.5 V, and the reverse leakage current is only 7 μA at the bias voltage of -10 V. The EL spectrum, as shown in Fig. 7, presents a smaller FWHM value of 60 nm, compared favorably to that of 30 nm reported by Nakamura.[54] According to the inset to Fig.7, the total output power reaches 200 μW at a forward current of 20 mA, which is translated to a conversion efficiency of 0.3%. These results verify the relatively high quality of GaN-based LEDs on $MgAl_2O_4$ (111) substrates. Nevertheless, to achieve high-efficiency LEDs on $MgAl_2O_4$ substrates, the crystalline qualities and surface morphologies of the as-grown epilayers need to be further improved. Therefore, future works should be focused on the optimization of the InGaN/GaN MQWs interface and design of the epilayer structure.

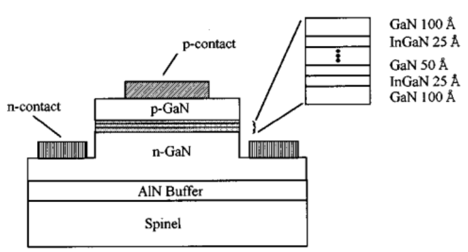


Fig. 5. The structure of LED chip grown on $MgAl_2O_4$ (111) substrates. Reprinted with permission from ref. 51. Copyright 1996 American Institute of Physics.

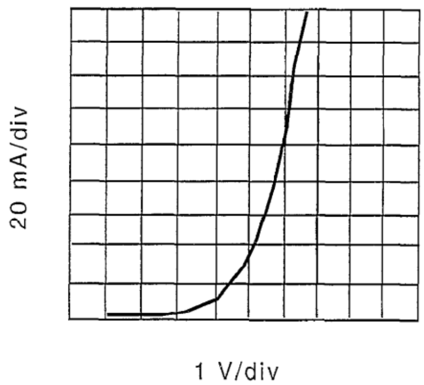


Fig. 6. *I-V* characteristics of the GaN-based LED. Reprinted with permission from ref. 52. Copyright 1997 ELSEVIER.

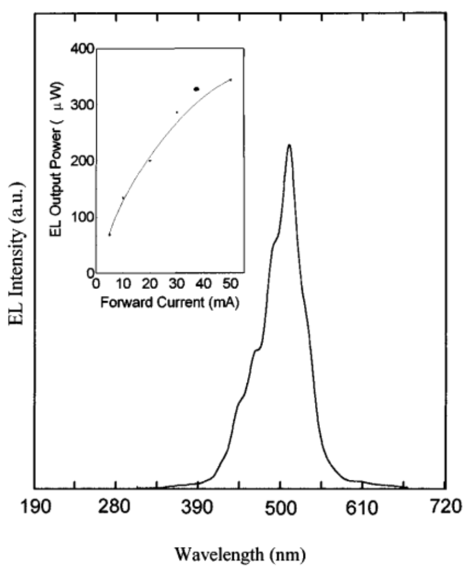


Fig. 7. EL spectrum of the green LED working at 20 mA. Reprinted with permission from ref. 53. Copyright 1997 American Institute of Physics.

2.2 LSAT

$La_{0.3}Sr_{1.7}AlTaO_6$ (LSAT) has a cubic unit cell with lattice parameter a = 0.7730 nm. LSAT is a mixed-perovskite crystal, which is another suitable substrate for the growth of GaN.[13, 55] On the one hand, the lattice parameters of GaN are close to that of LSAT (111) with a mismatch as low as 1%,[13, 56] as shown in Fig. 8,[57] which is beneficial for the nucleation of GaN films and reduces the formation of dislocations in the epilayers. On the other hand, the thermal expansion coefficient of

LSAT (111) is $5.8\times10^{-6}K^{-1}$ that is very close to that of GaN ($5.6\times10^{-6}K^{-1}$),[13, 56] which helps to alleviate strain accumulation in GaN films during cooling process. Furthermore, LSAT has a low phase transition temperature that is advantageous for achieving high-quality LSAT crystals free of twins.[58] In short, these properties make LSAT (111) a superior substrate for the epitaxial growth of high-quality GaN-based LED wafers.

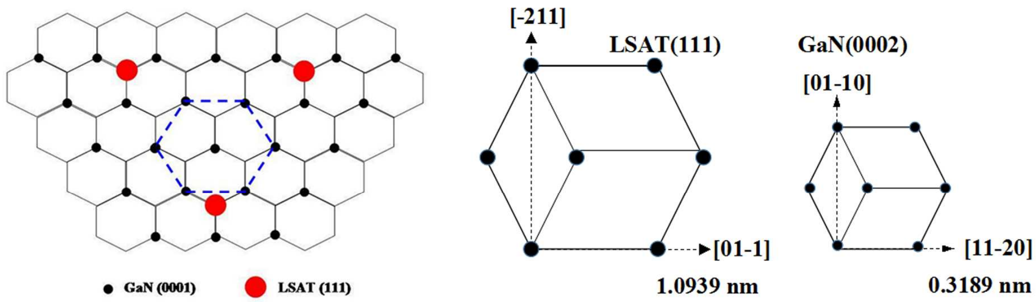


Fig. 8. Schematic diagram of in-plane relationship between LSAT (111) and GaN (0002). Reprinted with permission from ref. 47. Copyright 2014 Institute of Physics.

2.2.1 GaN films on LSAT substrates

Many researchers have tried hard to grow GaN films on LSAT substrates.[59-62] Sumiya *et al.* grew GaN films by MOCVD at high temperature of 1040 ºC,[59] which gives the FWHM value for GaN (0002) XRC of 1080 arcsec, revealing a very poor crystalline quality. Łukasiewicz *et al*. put much efforts to grow GaN films on LSAT substrates by MOCVD at lower temperature of 850 ºC.[62] Nevertheless, the crystalline quality of GaN films can be further improved, because these GaN films are grown under relatively high temperature by MOCVD. It is known that LSAT has high oxygen partial pressure,[47, 63] which would give rise to heavy evaporation of O atoms and then dramatic interfacial reactions, and significantly reduce the crystalline quality and damage surface morphology of GaN films during the high temperature growth. It has been reported by Li *et al.* that a low-temperature GaN buffer layer is an easy and effective way to solve this problem.[64] They employed MBE to grow GaN buffer layer on LSAT substrates with a low temperature of 500 ºC.[64] High-quality GaN films with *c*-plane oriented have been grown, and the FWHMs for GaN (0002) and GaN (10-12) are 198 and 400 arcsec, respectively. This is in striking contrast to that grown by

MOCVD. Meanwhile, very smooth GaN surface with a root-mean-square (RMS) of 1.2 nm and atomically abrupt interface have been obtained. These results indicate that high-quality GaN films have been grown on LSAT substrates by low-temperature MBE. The temperature dependence of crystalline quality, surface morphology, and interfacial properties of as-grown GaN films have also been reported.[64] They find that with the increase in growth temperature, the crystalline qualities, surface morphologies, and interfacial properties are gradually deteriorated, as shown in Figs. 9-11, Further study by reciprocal space map (RSM) indicates that the as-grown GaN film is found to be ~0.0094% tensile along its *a*-axis, and ~0.025% compressive along its *c*-axis,[57] suggesting that GaN films are almost fully relaxed. Furthermore, the surface roughness of GaN grown on LSAT at 500 °C is in the same level as the up-to-date results for device-ready GaN films grown on sapphire, SiC, and Si substrates using conventional high temperature growth techniques such as MOCVD, HVPE (hydride vapour phase epitaxy), PLD or MBE.[65-74] Evidently, low temperature GaN buffer layer is an effective way to achieve high-quality GaN films for GaN-based devices.

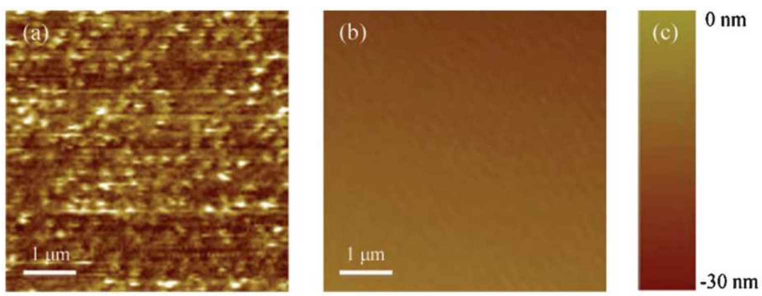
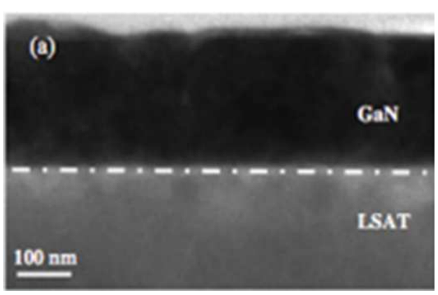


Fig. 9. AFM images of 300 nm-thick GaN films grown on LSAT substrates at (a) 750 °C, and (b) 500 °C. (c) is the color scale of the AFM images. Reprinted with permission from ref. 64. Copyright 2013 Royal Society of Chemistry.



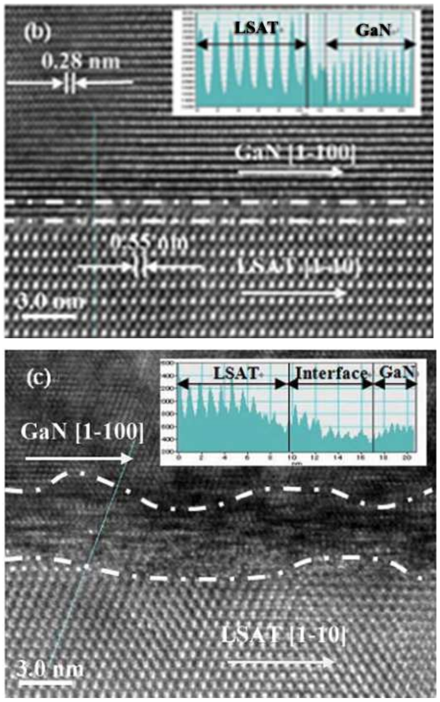
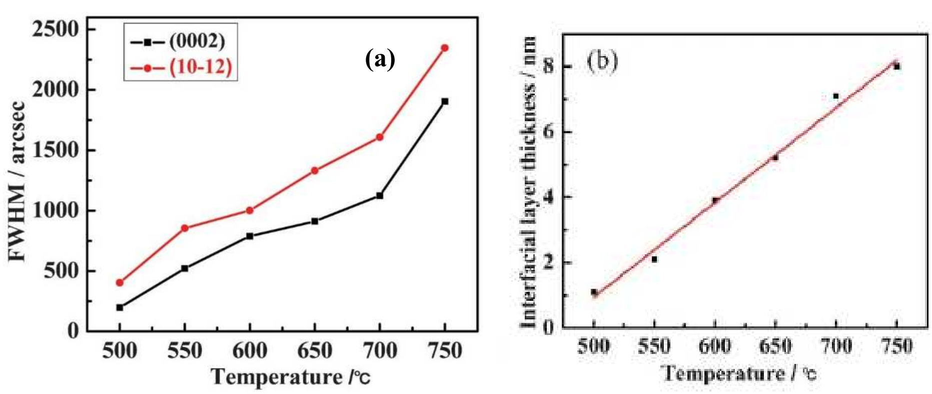


Fig. 10. The interfaces of GaN films grown on LSAT, (a) a bright field cross-section TEM image at low magnification for the interface between LSAT and GaN grown at 500 ^{o}C under the two-beam diffraction condition of g = [11-20], and (b) its HRTEM micrograph around the interfaces, and (c) HRTEM micrographs around the interfaces for GaN grown on LSAT at 750 ^{o}C. The interfaces exist between the dashed lines, and the lattice distance profiles across interfaces along the green thin solid lines are inserted in (b) and (c). Reprinted with permission from ref. 64. Copyright 2013 Royal Society of Chemistry.



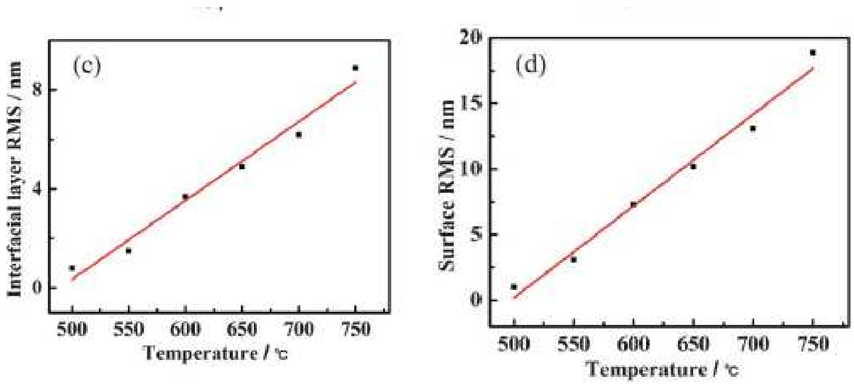


Fig. 11. The growth temperature dependencies of (a) FWHMs of XRCs for GaN (0002) and GaN (10-12), (b) the thickness and (c) the roughness of the interfacial layer between GaN and LSAT, as well as (d) the surface roughness of as-grown GaN. Reprinted with permission from ref. 64. Copyright 2013 Royal Society of Chemistry.

2.2.2 GaN-based devices on LSAT substrates

There is a great breakthrough in the fabrication of GaN-based LEDs on LSAT substrates since the high-quality GaN films have been prepared on LSAT by low-temperature MBE.[75] Li *et al.* tried hard to grow high-quality InGaN/GaN MQWs on LSAT substrates.[76] The as-grown InGaN/GaN MQWs reveal homogeneous and abrupt interfaces, as shown in Fig. 12. After achieving high-quality InGaN/GaN MQWs, GaN-based LEDs on LSAT have been successfully grown by low-temperature MBE. As shown in Fig. 13, the structure of this LED includes a 4000 nm-thick undoped GaN (u-GaN) buffer layer, a 3000 nm-thick Si-doped n-GaN layer, 7-periods MQWs ($In_{0.125}Ga_{0.875}N$ (3 nm)/GaN (12 nm)), a 20 nm-thick AlGaN electron barrier layer, and a 300 nm-thick Mg-doped *p*-GaN layer. The sharp and strong PL peak is observed at 445 nm with an FWHM of 24.0 nm. Meanwhile, there is an EL emission peak observed at 448 nm with an FWHM value of 22.6 nm collected at an injection current of 20 mA, Fig. 14b. This result is comparable with the commercial GaN-based LEDs on sapphire. The as-grown LED wafers were fabricated into LED chips with the size of 300 × 300 mm^2 by the standard procedure to further study their properties. It is believed that the better crystalline quality of epitaxial layers helps to improve internal quantum efficiency (IQE). Consequently, the light output for the LED on LSAT is larger than that on sapphire at the same injection current, and the forward voltages for LED chip on

LSAT is smaller than that on sapphire with the identical growth process and structure, as shown in Figs. 15a and b. Although the GaN-based LEDs on LSAT exhibits outstanding properties at low injection current, there is a relatively strong efficiency-droop effect with the further increase of injection current. As a result, further studies on the optimization of the growth conditions and the LED device structure should be carried out to improve the performance of LEDs on LSAT substrates.

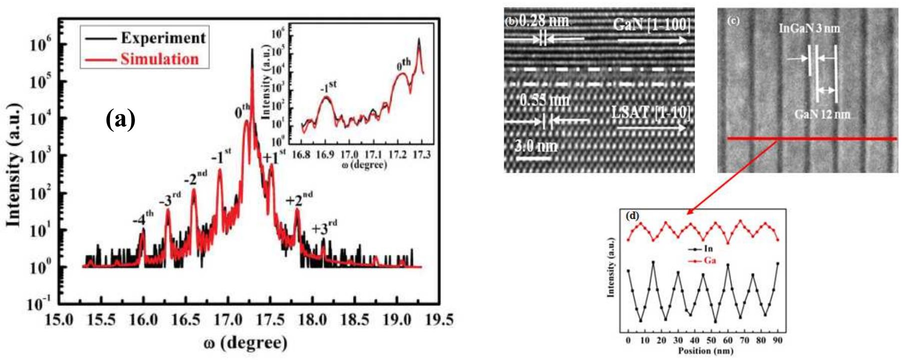


Fig. 12. (a) Typical HRXRD ω-2θ scan of the InGaN/GaN MQWs on LSAT (111) by a simulation using a genetic theory, cross-sectional HRTEM images for (b) GaN/LSAT hetero-interfaces, (c) InGaN/GaN MQWs, and (d) the signal intensity of Ga (red) and In (black) atoms obtained by EDS. Reprinted with permission from ref. 76. Copyright 2014 ELSEVIER.

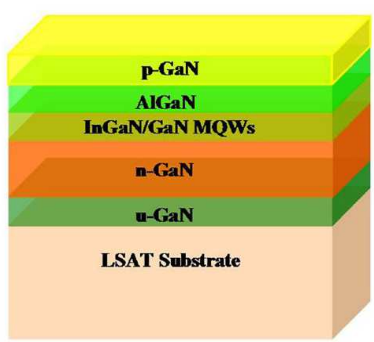


Fig. 13. The schematic structure of LED wafers on LSAT (111) substrates. Reprinted with permission from ref. 75. Copyright 2013 Royal Society of Chemistry.

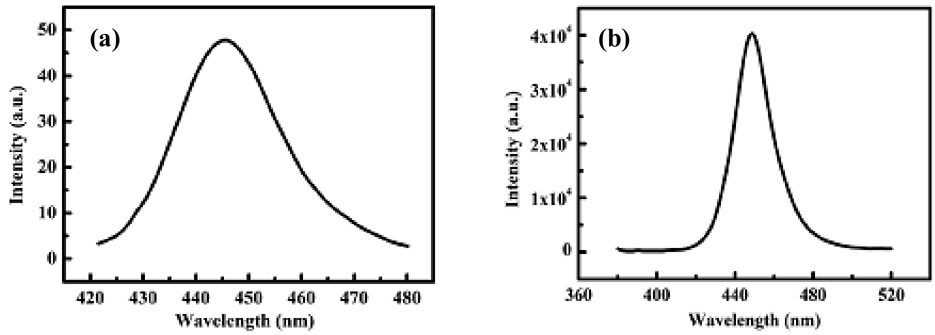


Fig. 14. Room temperature (a) PL and (b) EL spectrums of as-grown GaN-based LED wafers grown on LSAT substrates. Reprinted with permission from ref. 75. Copyright 2013 Royal Society of Chemistry.

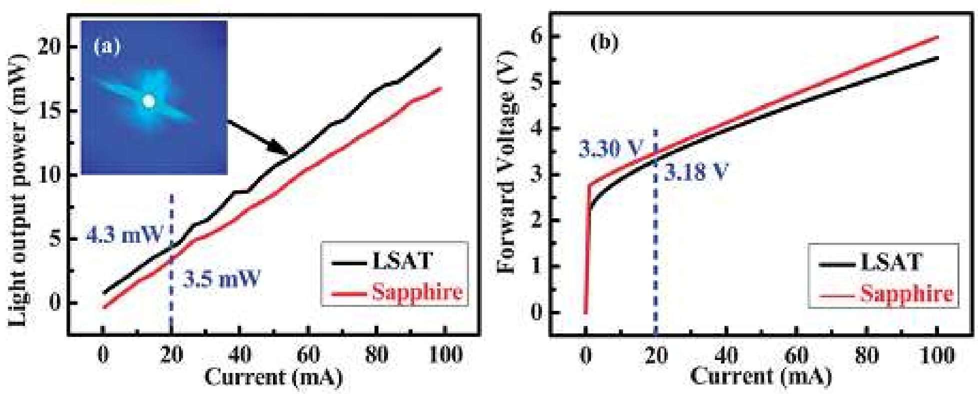


Fig. 15. (a) *L-I* and (b) *V-I* characteristics for LED chips with the size of 300 × 300 mm^2 on LSAT and sapphire substrates, respectively. The inset in (a) is the photograph of the LED device prepared on LSAT substrate working at an injection current of 20 mA. Reprinted with permission from ref. 75. Copyright 2013 Royal Society of Chemistry.

2.3 $LiAlO_2$

$LiAlO_2$ is tetragonal with cell dimensions a = 0. 5169 nm, c = 0.6267 nm, and the space group is assigned to $P4_12_12$. $LiAlO_2$ is another alternative for the epitaxial growth of GaN. Firstly, the lattice mismatch between $LiAlO_2$ and GaN is as low as 0.1%.[17] Secondly, the thermal expansion coefficients of $LiAlO_2$ is $7.1\times10^{-6}K^{-1}$,[17] which matches well with that of GaN ($5.59\times10^{-6}K^{-1}$).

Thirdly, $LiAlO_2$ also is a perfect candidate for the epitaxial growth of nonpolar *m*-plane GaN with a small lattice mismatch of 1.7%,[77] as illustrated in Fig. 16. This nonpolar *m*-plane GaN is free of internal polarization and is an important development tendency of achieving high-efficiency GaN-based LEDs.

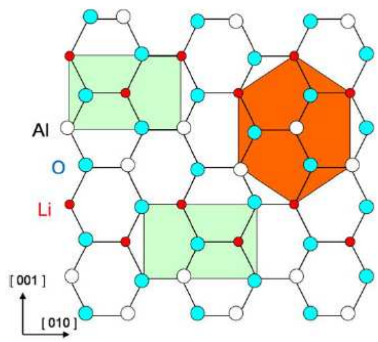


Fig. 16. The epitaxial relationship for GaN and $LiAlO_2$. The rectangles display nucleation sites of GaN (1-100), while hexagon presents nucleation sites for GaN (0001). Reprinted with permission from ref. 77. Copyright 2010 ELSEVIER.

2.3.1 GaN films on $LiAlO_2$ substrates

Due to the high equilibrium vapor pressure of Li of $LiAlO_2$, Li atoms easily diffuse to the substrate surface and thereby serious interfacial reactions may occur when growing GaN on $LiAlO_2$ at high temperature, which dramatically deteriorates the crystalline quality of GaN films. As mentioned above, various ways can be deployed to solve this problem. Among them, nitridation and buffer layer are the most common ways in MOCVD and MBE.[16, 78-81] Chou *et al.* has reported that the appropriate nitridation temperature for $LiAlO_2$ is at the range from 850 to 1000 ^{o}C by NH_3 plasma.[16] A three-step MOCVD process is employed to grow high-quality GaN, which reveals a 2 nm-thick interfacial layer and a striated surface morphology.[81] These results are much better than a highly anisotropic morphology grown by RF plasma-assisted MBE.[79] Some researchers have tried hard to grow nonpolar GaN on $LiAlO_2$ without growing buffer layer.[78, 80] Xu *et al.* deposit the *m*-plane GaN films on $LiAlO_2$(100) substrates by MOCVD with an FWHM for GaN(1-100) of 530 arcsec.[78] Later, this value is significantly improved to 112 arcsec by

Gerlach *et al.* using low-energy-ion-beam-assisted MBE.[80] This GaN film grown by low-energy-ion-beam-assisted MBE also shows flat and smooth surface morphology, with a RMS roughness value of 0.6 nm.

2.3.2 GaN-based devices on $LiAlO_2$ substrates

Researchers prepared InGaN/GaN MQWs on $LiAlO_2$.[82-85] It is found that surface segregation of In and compositional fluctuations in *m*-plane MQWs on $LiAlO_2$ leads to a redshift of PL spectrum.[82] Furthermore, comparative study reveals that optical polarization anisotropy in both *m*-plane and *c*-plane InGaN/GaN MQWs on $LiAlO_2$ is weakened but does not vanish.[83] It shall be noted that In concentration has a significant impact on the properties of MQWs. Mauder *et al.* report that PL peak wavelength for *m*-plane InGaN/GaN MQWs with different In concentrations grown on fully strained GaN/$LiAlO_2$, is stable at higher excitation intensity, as shown in Fig. 17-19.[84] The larger PL FWHM values and a pumping-induced PL peak shift towards higher energy would happen if more In is incorporated. The nonpolar *m*-plane InGaN/GaN MQWs LED have been grown on $LiAlO_2$(100) substrates by MOCVD after hard work.[86-87] Further investigation indicates that turn-on voltage of the nonpolar LED is from 1 to 3 V, which is mainly attributed to the high dislocation density of $LiAlO_2$(100) substrates, Fig. 20. Moreover, as illustrated in Fig. 21, EL peaks remain stable as the increase in injection current due to the absence of QCSEs. This result clearly demonstrates that nonpolar *m*-plane InGaN/GaN LEDs can be deposited on $LiAlO_2$(100) substrates. Although nonpolar *m*-plane InGaN/GaN LEDs have been obtained on $LiAlO_2$(100) substrates, the optoelectronic properties for the LEDs need to be further improved. Nevertheless, it opens up a bright prospect for the fabrication of high-efficiency nonpolar *m*-plane GaN-based LEDs on $LiAlO_2$(100) substrates.

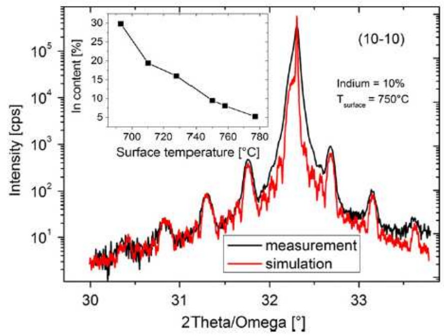


Fig. 17. HRXRD (10-10) 2θ-ω scan for an *m*-plane $In_{0.1}Ga_{0.9}N$/GaN MQWs. The inset shows the dependency of In content on surface temperature. Reprinted with permission from ref. 84. Copyright 2010 ELSEVIER.

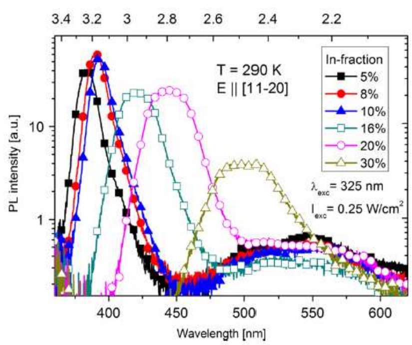


Fig. 18. Room temperature PL spectrum for *m*-plane InxGa1-xN/GaN MQWs. Only emission polarized in the [11-20] direction is displayed. Reprinted with permission from ref. 84. Copyright 2010 ELSEVIER.

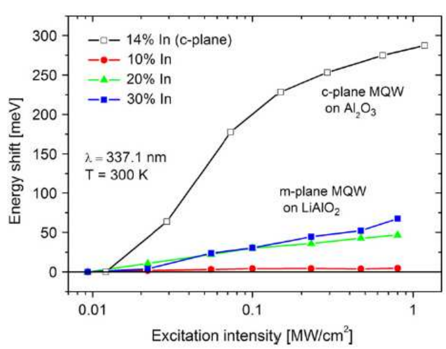


Fig. 19. Energy shift of *m*-plane $In_xGa_{1-x}N$/GaN MQWs structure with x=0.1, 0.2 and 0.3, respectively. The trend for a comparable *c*-plane structure with x=0.14 is also displayed as a reference. Reprinted with permission from ref. 84. Copyright 2010 ELSEVIER.

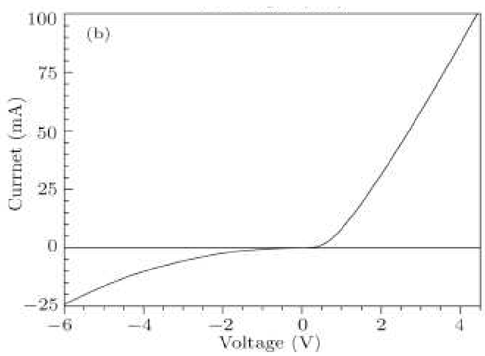


Fig. 20. *V-I* characteristics of nonpolar GaN-based LED grown on $LiAlO_2$(100). Reprinted with permission from ref. 87. Copyright 2008 Institute of Physics.

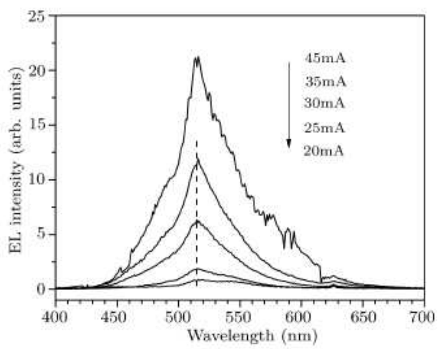


Fig. 21. Room temperature EL spectrums of nonpolar GaN-based LED grown on $LiAlO_2$(100) at different injection current. Reprinted with permission from ref. 87. Copyright 2008 Institute of Physics.

2.4 $LiGaO_2$

$LiGaO_2$ belongs to orthorhombic unit cell with dimensions a = 5.402 Å, b = 6.372 Å, and c = 5.007 Å, and its space group is $Pna2_1$.[88] Compared with sapphire substrate, $LiGaO_2$ substrate is superior for growth of high-quality GaN. Firstly, $LiGaO_2$(001) substrate has a small lattice mismatch with *c*-plane GaN of 0.2%, Fig. 22. Secondly, the (100) plane of $LiGaO_2$ substrate has an excellent lattice and structure match to GaN(1-100). The corresponding interface matching orientations are expected as $[001]_{LiGaO2} \parallel [11\text{-}20]_{GaN}$, only with a 0.1% mismatch, and $[010]_{LiGaO2} \parallel [0001]_{GaN}$ with 4.0% mismatch. Thirdly, the thermal expansion coefficient of $LiGaO_2$ matches well with that of GaN. It can be found that the [120] of $LiGaO_2$ is parallel to the [-12-10] of GaN. The thermal expansion coefficients for the $LiGaO_2$(100) plane are equal to 4.0×10^{-6} K^{-1} and 3.8×10^{-6} K^{-1} along its [010] and [120], respectively, while those for the GaN(1-100) plane are equal to 5.59×10^{-6} K^{-1} and 3.17×10^{-6} K^{-1} along its [-12-10] and [0001], respectively.) [89-90] Fourthly, $LiGaO_2$ can be easily etched by chemicals,[91] which makes the free-standing GaN films possible. The last but not the least, large scale $LiGaO_2$ single crystal can be obtained by Czochralski pulling method.[92] From the merits mentioned above, $LiGaO_2$ is no doubt an outstanding candidate for the epitaxial growth of GaN films.

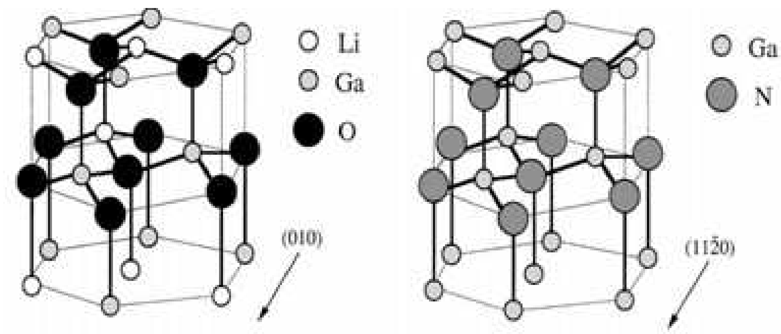


Fig. 22. The structure diagram of $LiGaO_2$ and GaN. Reprinted with permission from ref. 89. Copyright 2010 ELSEVIER.

2.4.1 GaN films on $LiGaO_2$ substrates

Since 1990s, growth of GaN films on $LiGaO_2$ substrates has been carried on for a long time.[93-101] In 1997, high-quality GaN on $LiGaO_2$ is successfully achieved by MBE with an FWHM for GaN (0002) of 260 arcsec.[95] In the same year, this FWHM value is sharply reduced to 103 arcsec.[97] Interestingly, this FWHM value is further decreased to 85 arcsec in the late two years.[98] As for MOCVD growth, the early FWHM value of GaN (0002) is 246 arcsec,[100] which is close to the result grown by MBE. By now, it is reported that the best GaN films on $LiGaO_2$ is produced by MOCVD with an FWHM for GaN (0002) of 46.7 arcsec and a RMS roughness value of 0.036 nm.[99]

However, as pointed out, as-grown GaN films suffer from both the formation of interfacial layers and the evaporation of Li atoms from the $LiGaO_2$ substrates during the initial high temperature growth by using MOCVD or MBE.[102-103] In order to overcome these problems, one of the best ways is to create a lithium gettering layer that effectively traps the lithium in the near-substrate region. It has been demonstrated that pure AlGaN or AlGaN/GaN superlattices can be used as the gettering layer.[104] Thanks to the effective suppression of the diffusion of Li atoms, a very high-quality GaN has been formed by MBE for the MSM photodiodes with a (004) FWHM value of 80 arcsec.[104] Because the heavy evaporation of Li atoms from the substrates is mainly caused by high growth temperature, low growth technology, for example, PLD, could be a superb way for synthesis of high-quality GaN on $LiGaO_2$.[105] It has been widely acceptable that high temperature annealing before growth can clean the residue on the substrate surfaces and lead to atomically flat surfaces, which is beneficial to the growth of high-quality GaN films. According to the characteristic of the diffusion of Li from $LiGaO_2$, Li *et al.* designed a novel thermal annealing way to suppress the diffusion of Li and to flatten the substrate surface,[106] finally obtain the atomically flat surfaces with a RMS roughness of 0.2 nm by annealing for 3h at 1050 ^oC. A comparative research reveals that the FWHM for the as-grown GaN (0002) by PLD on atomically flat $LiGaO_2$ surface is as low as 324 arcsec, which is much smaller than 1152 arcsec for GaN grown on the as-received $LiGaO_2$ surface with scratches. In 2010, Li *et al.* firstly reported on the high-quality nonpolar *m*-plane GaN on $LiGaO_2$(100) grown at low temperature by PLD with a dislocation density of ~10^{-8} cm^{-2}.[107] This work opens up a prospect for fabrication of high-quality nonpolar GaN-based devices on $LiGaO_2$ substrates. Meanwhile, Li *et al.* reported that high-quality nonpolar *a*-plane InN with a dislocation density of 3×10^{-9} cm^{-2} can be grown on $LiGaO_2$(001) substrates by PLD,[108] which opens up a new approach for high-efficiency nonpolar InN devices. These works from the group of Li *et al.* cause an increasing interest in growing nonpolar nitrides on $LiGaO_2$ substrates.[92, 109-111] Possibly, $LiGaO_2$ is an important candidate for synthesis of nonpolar III-nitride based devices in the near future.

2.4.2 GaN-based devices on $LiGaO_2$ substrates

The first device on $LiGaO_2$ substrates is MSM photodiodes reported in 2001.[104] Because the heavy evaporation of Li atoms has been successfully and effectively suppressed by the AlGaN/GaN superlattices, high-quality GaN with low dislocation density and low point defect density has been grown on $LiGaO_2$ by MBE.[104] Due to the high crystalline quality of GaN, the MSM photodiodes exhibit excellent electrical characteristics and are comparable to the best device that ever reported.[112] The free electron concentration in this structure is estimated at ~10^{13}-10^{14} cm^{-3} which is consistent with capacitance-voltage measurements on similar samples showing less than 10^{15} cm^{-3} by using the standard equations for flat-band voltage. Comparative study shows that there is essentially no degradation of the current-voltage characteristics for the two MSM devices before and after the devices were removed from the $LiGaO_2$ substrate and transferred to an oxidized silicon wafer.[104, 113]

As mentioned above, high-quality GaN films have also been successfully grown on $LiGaO_2$ by PLD at low temperature. However, since the growth rate of PLD is quite high, it is rather difficult for PLD to exactly control the very subtle thickness of InGaN/GaN MQWs. In order to solve this problem, the methodology by the combination of PLD and MBE, for the first time, is deployed by Li *et al.* to achieve high-quality nonpolar *m*-plane 7-periods InGaN/GaN MQWs on $LiGaO_2$(100) substrates.[114] High crystalline quality, abrupt and smooth InGaN/GaN interface are verified by HRXRD and HRTEM, as shown in Figs. 23 and 24. This nonpolar MQWs exhibit strong room temperature PL emission at 445 nm with an FWHM of 22.0 nm, Fig. 25, which is in the same level of the commercially available LEDs and semipolar InGaN/GaN LEDs.[75, 115-116] This work is considered as an important breakthrough by *Semiconductor Today* magazine,[117] firmly proving that high-efficiency nonpolar *m*-plane InGaN/GaN MQWs LED and related devices on a $LiGaO_2$ system are promising.

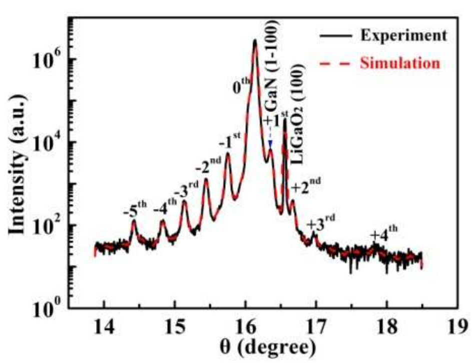


Fig. 23. Typical HRXRD ω-2θ scan of the InGaN/GaN MQWs grown on $LiGaO_2$(100) and its simulation curve using the genetic theory.

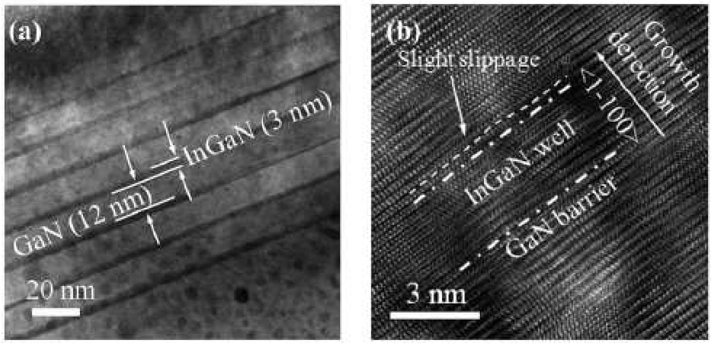


Fig. 24. (a) Cross-sectional TEM image of *m*-plane InGaN/GaN MQWs, and (b) its high magnification lattice image. Reprinted with permission from ref. 114. Copyright 2014 Royal Society of Chemistry.

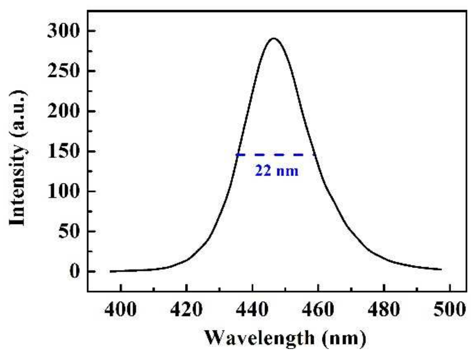


Fig. 25. Room temperature PL spectrum of nonpolar *m*-plane InGaN/GaN MQWs grown on the $LiGaO_2$ substrates. Reprinted with permission from ref. 114. Copyright 2014 Royal Society of Chemistry.

Later, high-quality nonpolar *m*-plane LEDs have been successfully grown on $LiGaO_2$(100) substrates by the combination of PLD and MBE technologies,[118] Fig. 26. Due to the absence of QCSE and high crystalline quality of GaN materials on $LiGaO_2$, the nonpolar LEDs exhibit excellent optoelectronic properties. It has been found that there is a slight blue shift in wavelength with the increase in current from 20 to 150 mA, Fig. 27a. Furthermore, as the current increases, the EL FWHM for GaN-based LED on $LiGaO_2$(100) substrate keeps constant, while that for GaN-based LEDs grown on *c*-plane sapphire substrate gradually increases, as shown in Fig. 27b. The as-grown LED wafers are fabricated into LED chips with the size of 300×300 mm^2 by the standard procedure to further study their properties. Ohmic contact between nonpolar *m*-plane p-GaN and p-electrodes and the low forward voltage have been obtained. The light output power (*L*) value for LED chips on $LiGaO_2$(100) is much better than that on *c*-plane sapphire, as shown in Fig. 28a. It can be noted that the best value of EQE for the LED chip on $LiGaO_2$(100) is 50.8%, Fig. 28b, which is comparable with the reported value of semipolar GaN-based LED chips grown on bulk GaN substrate.[119-122] Likewise, these excellent results can be attributed to the high crystalline quality of LEDs on $LiGaO_2$ and the absence of QCSE. In summary, this work clearly proves that the methodology by the combination of PLD and MBE is an effective approach to achieve high-quality nonpolar *m*-plane GaN-based LEDs on $LiGaO_2$(100) substrates. Furthermore, this methodology also can be widely used in the application of other chemically vulnerable substrates for the fabrication of GaN-based devices. Due to the successful and broaden applications of this new approach, this work is considered as a significant breakthrough by *Semiconductor Today* magazine.[123]

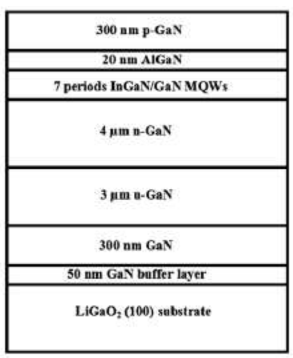


Fig. 26. The schematic structure of the GaN-based LED wafer om $LiGaO_2$(100) substrates. Reprinted with permission from ref. 118. Copyright 2014 Royal Society of Chemistry.

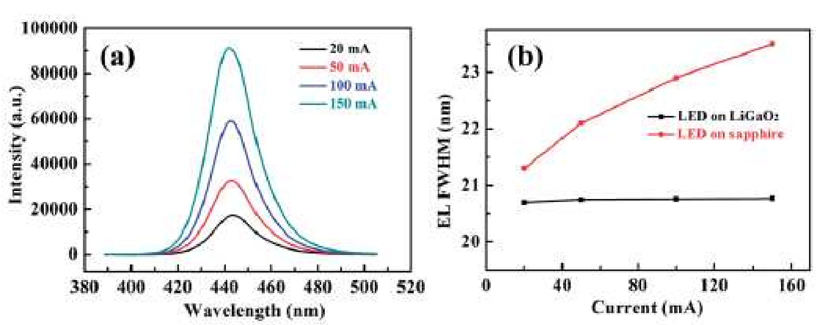


Fig. 27. (a) Room temperature EL of nonpolar *m*-plane GaN-based LEDs grown on $LiGaO_2$(100) substrates with various currents, and (b) the dependence of FWHM on current for GaN-based

LEDs grown on $LiGaO_2(100)$ and *c*-plane sapphire substrates. Reprinted with permission from ref. 118. Copyright 2014 Royal Society of Chemistry.

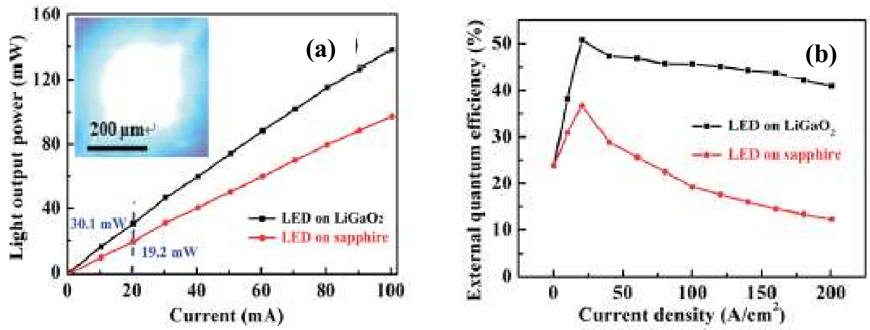


Fig. 28. (a) *L–I*, and (b) EQE–*I* characteristics of GaN-based LED chips with the size of 300×300 mm^2 on both $LiGaO_2(100)$ and *c*-plane sapphire substrates. The inset photograph in (a) is a lit-up LED on $LiGaO_2(100)$ substrate working at an injection current of 20 mA. Reprinted with permission from ref. 118. Copyright 2014 Royal Society of Chemistry.

2.5 $LaAlO_3$

$LaAlO_3$ (LAO) belongs to triangle phase with cell dimensions of a = 0.537 nm, b = 0.537 nm, c = 1.315 nm, which shows about 3% lattice mismatch with respect to *c*-plane GaN or *a*-plane GaN, as shown in Fig. 29a.[21] Furthermore, $LaAlO_3$ has perovskite-like structure (pseudo-cubic, a = 0.3791 nm) that matches well with nonpolar *m*-plane GaN with a lattice mismatch of about 4%.[124] With the melting point of about 2180 °C, the thermal stability under normal growth conditions makes it an excellent candidate for nitride growth.[125] Additionally, 2-inch large scale $LaAlO_3$ is commercially available with relatively low cost. Therefore, $LaAlO_3$ plays an important role in the epitaxial growth of GaN.

A 0.4 μm-thick GaN films has been deposited on $LaAlO_3(001)$ substrates for the first time by Lee *et al.* with RF plasma-assisted MBE.[126-127] Before the growth of GaN films, an AlN buffer layer is formed to reduce the lattice mismatch between GaN and $LaAlO_3$, which can be clearly observed by HRTEM, Fig. 29b. It is found by Ho *et al.* that ZnO buffer layer not only increases the crystalline quality of GaN films,[128] but also improves the surface morphologies of GaN films. Additionally, Li *et al.* find that high phase purity *m*-plane GaN films can be deposited on $LaAlO_3$

with smooth surface (RMS=1.2 nm) by PLD. [125] However, high-efficiency GaN-based devices prepared on $LaAlO_3$ substrates haven't been reported so far.

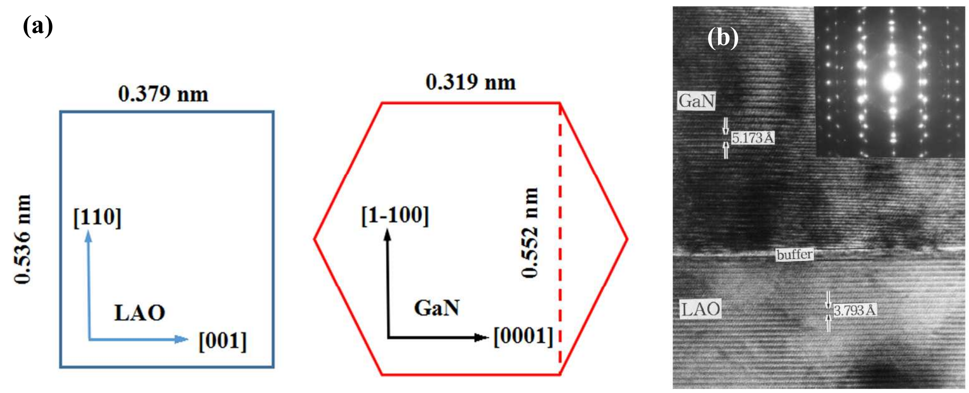


Fig. 29. (a) Illustration of in-plane relationship between GaN and LAO and (b) HRTEM lattice image of GaN and LAlO interface and the corresponding SAD pattern. Reprinted with permission from ref. 127. Copyright 2000 ELSEVIER.

3. Summary and prospect

In summary, unconventional oxide substrates share much smaller lattice and thermal expansion coefficient mismatches with GaN when compared with sapphire. Meanwhile, almost all of them can be easily etched by chemicals, which makes them superb for fabricating free-standing GaN substrates or vertical structural devices. Additionally, large scale unconventional oxide substrates have already been commercially available with relatively low cost. All those mentioned above lead to a conclusion that unconventional oxide substrates are of great significance in the future fabrication of high-quality GaN-based devices. To date, significant breakthroughs of growing high-quality GaN and GaN-based devices on unconventional oxides have been successfully achieved. On the one hand, thanks to the optimized growth condition and the development of growth technology, high-quality GaN films on unconventional oxide substrates have been grown by some common growth techniques, such as MOCVD or MBE. For example, free-standing GaN substrate with a (0002) FWHM of 46.7 arcsec and a RMS roughness of 0.036 nm has been grown by MOCVD. These breakthroughs of high-quality GaN provide a powerful force for the further development of highly-efficient GaN-based LED devices. On the other hand, the successful application of new technologies make high-quality GaN-based devices on unconventional oxide substrates possible. After effectively suppressing the heavy evaporation of oxide atoms by low temperature RF-MBE, high-quality LEDs on LSAT has been realized. A strong and sharp EL peak for this LED is observed at 448 nm with an FWHM of 22.6 nm at an inject current of 20 mA. Another important breakthrough is high-quality nonpolar *m*-plane LED grown on $LiGaO_2$(100) by the combination of PLD and MBE technologies. PLD is employed to grow GaN buffer layer at low temperature in order to effectively suppress the diffusion of Li atoms and the interfacial reactions. Subsequently, RF-MBE is introduced to fabricate nonpolar *m*-plane LEDs. Investigations of these nonpolar *m*-plane LEDs reveal the excellent optoelectronic properties. The EL peaks keep constant with the increase of injection current from 20 to 150 mA as well as stable EL FWHM values. After these LED wafers are made into chips by a standard process, the EQE for these nonpolar LEDs is as high as 50.8%, which is comparable to the reported value of a semipolar GaN-based LED chip grown on bulk GaN substrate. The combination of PLD and MBE technologies sheds light on the application of other types of thermally unstable substrates for the nitrides epitaxy and is believed to be an effective approach for the fabrication of high-efficiency nitride-based devices on unconventional substrates.

As a matter of fact, these breakthroughs of high-quality GaN films and GaN-based LEDs on the unconventional oxide substrates can be easily introduced to other GaN-based devices, such as laser diodes, solar cells, photoelectric detectors, field emission transistors, high electron mobility transistors, and so on, due to the fact that the structures of these GaN-based devices are similar to some extend. Hence, the achievements of high-quality of GaN films and GaN-based epilayers on the unconventional oxide substrates are of significant importance in promoting the development of the semiconductor devices.

However, there are still some obstacles to be overcome for the industrialization of GaN-based devices on unconventional oxide substrates. On the one hand, due to the inherent properties of unconventional oxide substrates, the unconventional oxide substrates are normally of small size. These are in striking contrast to the sapphire and Si substrates, which are of large size (more than 8 inches for Si substrates). Therefore, the technology of preparation of large-size unconventional oxide substrates must be further developed in order to meet the requirement of in the industrialization of GaN-based devices. On the other hand, the detailed mechanisms of GaN films grown on unconventional oxide substrates are not thoroughly studied, which is detrimental to achieve high-quality GaN-based epilayers. Furthermore, the optimized structure for GaN-based devices needs to be done to further enhance the performance of GaN-based devices on unconventional oxide substrates.

To conclude, we believe that with further advancement of growth technology, the quality of nitride materials and the performance of relevant devices on the unconventional oxide substrates will be further improved. Very possibly, these unconventional oxides will develop into mainstream commercial substrates for the fabrication of GaN-based devices.

Acknowledgements

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