Photoluminescence studies of GaN epilayer–nanocrystals grown on γ -LiAlO₂ substrate

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Abstract

We report the optical studies of the properties of *M*-plane GaN/*c*-plane GaN nanocrystal heterostructure on γ -LiAlO₂ substrate grown by plasma-assisted molecular beam epitaxy. In this structure, in addition to the *M*-plane epilayer, nanocrystals grown in *c*-direction could also be observed in the step edges of the *M*-plane GaN terraces and the hexagonal basis of the γ -LiAlO₂ substrate. X-ray diffraction (XRD) with peaks at $2\theta = 32.295^\circ$, 34.680° and 34.505° are attributed to the *M*-plane GaN, LiAlO₂ and *c*-plane GaN, respectively. Two peaks were observed in the photoluminescence spectra at low temperature. The peak at 3.33 to 3.35 eV is attributed to the emission from *c*-plane GaN nanocrystals and the peak at 3.50 eV is attributed to the emission from *M*-plane GaN epilayers. The relative intensity of these peaks is position-dependent. In the area with higher concentration of the GaN nanocrystals the emission for the nanocrystals is stronger and vice versa. Cathodoluminescence shows that the emission peak at 3.33–3.35 eV is originated from the nanocrystals GaN.

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Gallium nitride (GaN) is the popular material for the fabrication of semiconductor devices, such as blue light-emitting diodes (LED), blue laser diodes (LD), and polarization-sensitive photo-detectors (PSPDs) [1–5]. In standard heterostructures, such as GaN/AlGaN quantum well (QW), the crystal growth direction is along *c*-axis [0001] and the associated surface is called *c*-plane. The *c*-plane crystal has build-in large piezoelectric and pyroelectric field across the hetero-interface [6]. This strong field tilts the band structure at the interface, resulting in the low efficiency of the photoluminescence. Structures grown along any direction perpendicular to [0001], like [11 $\bar{1}$ 00] which is called *M*-plane, are free of both piezoelectrical and pyroelectrical polarization. *M*-plane GaN provides a flat band structure at the interface, resulting in a high efficiency

of photoluminescence [2]. In addition, since *c*-axis of GaN lies in the non-polar plane, it provides a controllable light polarization for the application of PSPDs due to the reduced in-plane symmetry and the large in-plane anisotropic strain [7,8].

Sapphire has been the most used substrate for the growth of GaN. Because of the lattice mismatch between GaN/sapphire is very large, and GaN grown on sapphire has high density of defects [9]. Recently, the growth of *M*-plane GaN on γ -LiAlO₂ has been proposed [10–12]. The GaN/LiAlO₂ system shows a smaller lattice mismatch GaN [11 $\bar{1}$ 00]||LiAlO₂[010]~0.3% and GaN[11 $\bar{2}$ 0]||LiAlO₂[001]~1.7% [13]. The thermal expansion coefficients (TECs) α_a (along *a*-axis) and α_c (along *c*-axis) of GaN are 5.59×10^{-6} and $3.17 \times 10^{-6} \text{ K}^{-1}$. The TECs of LiAlO₂ are 7.1×10^{-6} and $15 \times 10^{-6} \text{ K}^{-1}$, respectively [14,15]. The anisotropic thermal expansion difference results in a strain release for GaN in [11 $\bar{2}$ 0] direction when the sample was

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cooled down from growth temperature [16]. However, the compressive stress along $[1\bar{1}00]$ is still there and it causes the bandgap of GaN grown on γ -LiAlO₂ to increase over the energy gap of bulk GaN.

The samples were grown on the γ -LiAlO₂ substrate by radio-frequency plasma-assisted molecular beam epitaxy (MBE) system. The growth of Ga-adsorption was performed with a standard effusion cell for Ga evaporation, and an rf-plasma cell was used to provide N₂-plasma source for the GaN growth. Prior to the growth, the substrate in the MBE chamber was out-gassed for 20 min at 700 °C. Then, the γ -LiAlO₂ substrate was exposed to the N₂-plasma flux 10 min for nitridation at 500 °C, under the conditions that the N₂-plasma power was set to 500 W and the N₂ flow rate was preserved in 1.00 sccm. Thereafter, the GaN buffer layer was grown at 500 °C. During the growth of GaN epilayers, the N₂ flow rate was varied from 0.63 to 0.75 sccm, while the N/Ga flux ratio was changed from about 15 to 37, measured by a flux monitor. The growth

temperature for the epilayers was set in the range between 500 and 600 °C and the growth rate achieved was about 0.4 $\mu\text{m}/\text{h}$. The growth condition of the sample is keeping GaN epilayer growth for 2 h and changing GaN buffer layer growth time from 6 min (sample A) to 10 min (sample B). The samples are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), continuous wave photoluminescence (PL), and cathodoluminescence (CL). Continuous wave PL spectra at 10 K are recorded using the 325 nm line of a He–Cd laser. CL measurements are performed at room temperature in the SEM.

The SEM images of sample A are shown in Figs. 1(a) and (b), the SEM images of sample B are shown in Figs. 1(c) and (d), where Figs. 1(a) and (c) are the images of the central area and Figs. 1(b) and (d) are the images of the border area. In the SEM images, there are two types of GaN. One type is terrace-like GaN, the other is hexagonal nanocrystal GaN. The terrace-like GaN is *M*-plane GaN, and the hexagonal nanocrystal GaN is *c*-plane GaN. The

Fig. 1. The SEM morphologies for sample A at the (a) central area and (b) at the border area and the SEM morphologies for sample B at the (c) central area and (d) at the border area.

c-plane GaN nanocrystals were self-assembled at the step-edges of *M*-plane GaN. There are two kinds of formations for the self-assembled nanocrystals: one is nucleated on the hexagonal basis of γ -LiAlO₂ and the other is transformed from *M*-plane terraces GaN. From the SEM image, we found that the diameter of the nanocrystals varies from 100 to 400 nm and the density of nanocrystals depends on growth condition and on the position of the samples. The results of θ – 2θ XRD for samples A and B were obtained (not shown here). The reflection peaks at $2\theta = 32.295^\circ$ and 34.680° are attributed to reflection from *M*-plane GaN ($1\bar{1}00$), and LAO (200), respectively. In addition, a reflection peak at $2\theta = 34.505^\circ$ is also observed and is attributed to the reflection from *c*-plane GaN (0002). From these results we know that both samples A and B contain *M*-plane terrace and *c*-plane nanocrystal GaN.

PL measurements at 10 K were performed on samples A and B and the results were shown in Figs. 2(a)–(d). Figs. 2(a) and (c) are taken with the laser focus on the central area of the samples. And Figs. 2(b) and (d) are taken with the laser focus on the border of the samples. In Fig. 2(a), in addition to the weak laser-plasma line at 2.8 eV, there are two main peaks in the spectra: one is the strong peak at 3.33–3.35 eV (*C* transition), and the other is the weak peak at 3.5 eV (*M* transition).

The *M* transition is attributed to the donor bound exciton from *M*-plane GaN [16]. Compared to relaxed bulk GaN [17], this transition was blueshifted, providing evidence of the rather large compressive stress along $[1\bar{1}00]$ direction in *M*-plane film. The *C* transition has a peak and a shoulder. The peak is at 3.26 eV and the shoulder is located at 90 meV below the main peak, and is

the one LO phonon replica of the main peak. The peaks of *C* transitions did not shift with changing temperature or laser power and is attributed to the donor bound exciton from *c*-plane GaN. In Fig. 2(b), the spectrum also shows two main peaks at *C* transition and *M* transition. But the *M* transition in Fig. 2(b) (border area) has stronger intensity than that in Fig. 2(a) (central area). This result agrees with the SEM images in Figs. 1(a) and (b) (sample A). The SEM images show that the density of nanocrystals in the central area is higher than that in the border area. In Fig. 2(c), which has a thicker buffer layer, the relative intensity of *M*-peak vs *C*-peak is higher than the sample with thinner buffer layer. Indicating there is more *M*-plane GaN in this sample. For the boarder of this sample, as could be seen in Fig. 2(d), the intensity of *M* transition is even stronger than the intensity of *C* transition. These results also agree with the SEM images in Figs. 1(c) and (d) (sample B). In the border area of sample B, the density of *M*-plane GaN (rectangular form) is higher than the density of *c*-plane GaN (hexagonal nanocrystal form). The results suggest that thicker buffer layers favor the formation of *M*-plane GaN. In order to prove that *C* transition is the donor bound exciton from *c*-plane GaN, we performed CL measurement. Fig. 3(a) shows a plane view SEM image of sample B at room temperature. The CL map at the wavelength of *c*-plane (at about 3.35 eV) recorded at room temperature is shown in Fig. 3(b). The emission does indeed occur from the nanocrystals GaN.

In conclusion, the *M*-plane GaN and the nanocrystal *c*-plane GaN grown simultaneously on γ -LiAlO₂ substrate by plasma-assisted MBE were studied. From the SEM

Fig. 2. PL spectra at 10 K for sample A at the central area (a) and at the border area (b); for sample B at the central area (c) and at the border area (d).

Fig. 3. (a) Room-temperature plane-view SEM micrograph of sample B and (b) CL map obtained from the same region, detected at the wavelength of the *C*-plane (3.35 eV).

images, we learned that the nanocrystals were self-assembled at the step-edges of *M*-plane GaN epilayers. The concentration of the nanocrystals is position-dependent. In PL measurement, two peaks at *C* transition and *M* transition were observed and they were attributed to the emission from *M*-plane GaN terrace and the GaN nanocrystals, respectively. The relative intensity of these peaks is also position-dependent and is consistent with the

results obtained from SEM measurement. In the CL measurement it was found the emission at 3.35 eV was resulting from the nanocrystal GaN. The successful growth of self-assembled nanocrystals in *M*-plane GaN terrace provides an opportunity for the fabrication of GaN/AlGaN hetero-nanocrystal devices for optoelectronic and spintronic application.

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