Polar dependence of impurity incorporation and yellow luminescence in GaN films grown by metal-organic chemical vapor deposition


a Key Lab of Wide Band-Gap Semiconductor Technology, School of Microelectronics, Xidian University, Xi'an 710071, China
b School of Electronic & Mechanical Engineering, Xidian University, Xi'an 710071, China

1. Introduction

Gallium nitride and its alloys with indium and aluminum nitride are very attractive materials especially due to their wide range of applications in electronic and opto-electronic devices. A majority of conventional GaN devices are grown with respect to the c-plane. The polarization fields in multiple quantum well structures along the polar c-axis cause a significant band bending and thus give rise to the spatial separation of electrons and holes. This situation leads to a reduced optical emission efficiency of light-emitting diodes (LEDs) as well as an undesirable redshift in the emission spectra from the quantum wells [1]. The problem can be avoided by growing GaN in nonpolar orientations, in which the electric field can also be reduced by growing in semipolar orientations, in which the c-axis is at an acute angle to the growth plane [2]. So recently there have been considerable interests in the growth of nonpolar and semipolar gallium nitride based on epitaxial films, heterostructures and devices [3–8]. The polar properties of GaN make the behaviors of the different polar directions distinct, especially when there is impurity incorporated. Furthermore, the impurity related emission is an important deep-level phenomenon in GaN. For example, the origin of the well-known yellow luminescence (YL) band centered at 2.2–2.3 eV in the luminescence spectra of GaN is associated with the impurities and complexes [9–11]. However, the influence of the polar direction on impurity incorporation and luminescence properties is lacking. In fact, by comparing the luminescence properties between different polar directions, GaN will probably be helpful to further study the intrinsic mechanism of impurity incorporation and YL band in GaN from a different view.

In this study we investigated how unintentional incorporation of O, C, and Si impurities into polar (0 0 0 1), nonpolar (1 1 2 0) and semipolar (1 1 2 2) GaN by a combination of the atom bonding structure and the origin direction of the impurities. Furthermore, it has been found that there is a stronger yellow luminescence (YL) in GaN with higher concentration of carbon, suggesting that C-involved defects are originally responsible for the YL.

2. Experimental procedure

The polar (0 0 0 1), nonpolar (1 1 2 0) and semipolar (1 1 2 2) GaN samples used in this study were grown on c-, r- and m-plane sapphire substrates, respectively, by MOCVD. Hydrogen was used as the carrier gas and triethylgallium, trimethylaluminium and ammonia (NH3) were used as source compounds. Prior to the growth, nitridation treatment was carried out at 1020 °C in NH3 for 5 min to suppress the formation of mixed phase (1 0 1 3) grains and consistently obtain semipolar (1 1 2 2) GaN on the m-plane sapphire. The growth process of the nonpolar (1 1 2 0) and semipolar (1 1 2 2) GaN was initiated by a low temperature AlN (20 nm) nucleation layer, followed by a high-temperature AlN
(100 nm) and high-temperature AlN (8 nm)/AlGaN (12 nm) SLs with five periods. In the epitaxial growth stage, the pressure was kept at 40 Torr and the flow rates were kept constant at 1020 °C for all the samples. The growth process of the polar c-plane GaN is nearly the same as the nonpolar GaN except that it is without SLs. Secondary ion mass spectroscopy (SIMS) analysis was performed on all samples. To avoid ambiguities related to the variations in the measurement conditions for impurities, the following detection limits were used: carbon $2 \times 10^{16}$ cm$^{-3}$; oxygen $2 \times 10^{16}$ cm$^{-3}$; and silicon $1 \times 10^{16}$ cm$^{-3}$.

3. Results and discussion

The concentrations of oxygen, carbon and silicon impurities, measured by SIMS, for different planes are shown in Fig. 1. The concentration of silicon in both GaN layers is very low, close to detection limits. While there is a very clear distinction between the polar, nonpolar and semipolar face samples, the concentration of oxygen in the semipolar sample was at least six times higher than that of oxygen in the polar sample, and the concentration of carbon in the polar sample was at least 10 times higher than that of carbon in the semipolar sample, which was about $2 \times 10^{16}$ cm$^{-3}$, close to the detection limit in SIMS experiments. It should be noted that the semipolar GaN is N-polar [12,13]. Oxygen and carbon have shown different trends in the semipolar and polar GaN. Fichtenbaum et al. [14] predicted that for the Ga-face, oxygen atoms impinging on a group V site will form only a single bond to the Ga surface atoms. On the N-face, an atom impinging on a group V site will form 3 bonds to the Ga surface atoms, leading to a stronger bonding of oxygen atoms on the N-face surface. Therefore, the N-face GaN has more oxygen. However, it was difficult to explain the carbon incorporation on different misorientations. The difference in oxygen and carbon incorporation between the different planes can be explained by the surface bonding structure and the origin orientation of the impurities.

It should be noted that oxygen comes from decomposition of the “downside” sapphire, and the carbon incorporation most likely stems from decomposition of Ga precursor molecule, namely it is from the “upside”. Because the semipolar GaN is N-polar, we use the standard N-polar configuration to represent the entire semipolar GaN. For oxygen and carbon, it is well known that under n-type conditions the energetically, by far, the most stable site is $\text{Co}_3$ and $\text{O}_3$ [10]. For the polar Ga-face GaN, oxygen atom from the bottom attempts to replace N to form $\text{O}_3$, however, every time there is a bigger gallium atom giving an effective protection to the upper N. In comparison with the Ga-face condition, the N-face GaN did not have a protection for N as shown in Fig. 2(b). Simultaneously for the condition of carbon, in the polar Ga-face GaN as shown in Fig. 2(a), there was no protection for the N atom due to replacement of carbon; furthermore, even if there is a Ga atom to bond the surface of the N atom, the N atoms under Ga adlayer are exposed to the carbon all the same, and there is another chance for replacement. In contrast, as shown in Fig. 2(b), the carbon cannot penetrate the topmost Ga easily, so the N-face GaN films contained significantly higher concentrations of oxygen; however, demonstrated lower levels of carbon can be explained. In order to further identify the model, the analysis of the nonpolar a-plane GaN is considered and shown in Fig. 2(c). Based on the principle mentioned above, there is no protection effect of the Ga and N atoms being free of the attack of the oxygen and carbon atoms, so the nonpolar GaN must have the highest concentrations of oxygen and carbon. This is consistent with the SIMS result shown in Fig. 1.

For further discussion, we examine the optical properties of these different polar samples. The 325 nm He–Cd laser was used to perform the PL measurement and laser’s output power was set constantly to be 10 mW. Fig. 3 shows the PL spectra at 300 K for the GaN obtained from the different plane sapphires. As shown in Fig. 3, it can be found that different polar GaNs have significant differences in YL intensity. The defect-related YL emission is an important deep-level phenomenon in GaN. However, the origin of
the deep acceptors responsible for YL is still not identified [9,10,15,16]. First, the gallium vacancies (VGa)-involved defects, such as VGa–ON complex, are regarded as the candidate of the deep acceptors to enhance the YL band by some authors [9,15,17]. Second, several other experimental groups also attributed the YL band to carbon impurity or a complex involving carbon [18–20]. Third, some authors suggest that the yellow luminescence is related to the edge dislocation density [21,22].

We have investigated the possible factors that could contribute to the intensity of YL. First, high resolution X-ray diffraction (HRXRD) measurements were carried out to gain further insight into the relation between edge dislocations and YL in GaN. Fig. 4 shows the full width at half maximum (FWHM) at the (1 0 2) plane of c-plane sample as 0.18°, but that of the a-plane and semipolar (1 1 2 2) GaN as 0.4° and 0.58°, respectively. It has been reported that the densities of edge dislocation including edge component of mixed dislocation are indirectly represented by the XRD FWHM at the (1 0 2) planes [23]. This implies that the c-plane must have the lowest density of edge dislocation, but the results have shown that the c-plane GaN has a much stronger YL than the semipolar (1 1 2 2) GaN. The result of XRD and PL indicates that edge dislocation has less effect on YL than GaN. Moreover, it is likely that the impurity related defect could play an important role in YL emission. As shown in Fig. 1, it can be found that the semipolar (1 1 2 2) GaN has a high oxygen intensity, but YL of the semipolar (1 1 2 2) GaN has a much weaker one. These indicate that the VGa–ON complex is not responsible for YL in HR-GaN. Xu et al. have also found that the high resistance GaN free of VGa–involved defects has a very strong YL and is proved by mono-energetic positron annihilation spectroscopy. So there must be another origin of YL. As shown in Fig. 5, it can be found that the YL intensity increases with increase in carbon concentration in different polar GaN samples. These indicate that carbon does enhance YL in as-grown GaN. In the metal-organic precursors, for example, the metal source of the trimethylgallium, Ga(CH3)3, is inevitable to introduce carbon impurities into GaN epilayers. Furthermore, in previous studies of hydride metal-organic vapor phase GaN epilayers, we found that YL is very weak even in the nonpolar a-plane GaN. We believe that it is ascribed to the lack of carbon. Specifically, Wright [24] has proved that carbon-involved defects have suitable deep levels for producing YL. All of this is consistent with our observations of the relation between carbon concentration and PL intensity. So we believe that carbon and carbon-involved defects are the origins of the deep-levels accounting for YL in the as-grown GaN.

4. Conclusions

In summary, we have grown the polar (0 0 0 1), nonpolar (1 1 2 0) and semipolar (1 1 2 2) GaN on the c-, a- and m-plane sapphire by MOCVD, respectively. Through SIMS analysis, the different polar directions of GaN growth and the origin directions are found to be responsible for differences in impurity incorporation. In addition, it can be found that the YL intensity increases with increase in carbon concentration in different polar GaN samples, suggesting that C-involved defects are originally responsible for the YL in GaN.

Acknowledgements

This work was supported by the National Key Science and Technology Special Project (Grant no.2008ZX01002-002), the Major Program and State Key Program of National Natural Science Foundation of China (Grant nos. 60890191 and 60736033) and the Chinese Advance Research Program of Science and Technology (Grant nos. 51308040301, 51308030102, 51311050112 and 51323030207).

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