Low temperature buffer growth to improve hydride vapor phase epitaxy of GaN

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Abstract

Two-step growth of hydride vapor phase epitaxy (HVPE) was optimized to grow high-quality, thick GaN film on the (0001) sapphire substrate using ammonia, chlorinated gallium and nitrogen carrier gas. Chlorinated Ga and NH₃ were used to grow GaN-buffer layers at a temperature range of 550–650°C for 1 to 7 min. The main growth of approximately 30 µm thick GaN film was performed at 1125°C for 30 min. Surface roughness after the low temperature buffer growth was measured by atomic force microscopy (AFM), and its effect on thick GaN film was characterized by double crystal X-ray diffractometry (DCXRD) and electron microscopy techniques (SEM and TEM). Direct correlation between AFM roughness (in terms of the RMS value) of the buffer layer surface and crystalline quality of the GaN film was observed. It is suggested that the smooth surface of low temperature grown GaN is critical in obtaining good quality GaN film in HVPE. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: GaN; GaN-buffer; HVPE; Surface roughness

1. Introduction

GaN-based material is dominating the light emitting diodes (LEDs) with a blue to green light, and laser diodes (LDs) utilizing an InGaN single quantum well (SQW) or a multi-quantum well (MQW) were already demonstrated [1–3]. Heteroepitaxial growth on sapphire or SiC is mainly employed to produce these devices. However, the defect density in a GaN film is as high as approximately 10⁶ cm⁻². Even though blue LEDs based on the high dislocation density material are highly efficient, dislocation need to be significantly reduced for LDs, because the efficiency and lifetime of the optical devices negatively depends on the defect density in the GaN film. Recent developments by Nam et al. [4] and Usui et al. [5] have demonstrated that a dislocation density of about 10⁵ cm⁻² could be obtained by utilizing the lateral over growth (LOG) technique. Another route of interest is to use a GaN bulk single crystal as a substrate to achieve homoepitaxial growth [6].

Hydride vapor phase epitaxy (HVPE) [7], sublimation [8] and high pressure [9] methods have been employed to obtain a GaN bulk single crystal. Among these methods, the HVPE process is the most suitable to grow thick GaN because of its high growth rate. Nonetheless, a thick HVPE GaN film grown on a sapphire contains large amount of defects and cracks could occur to relieve a stress, which makes the crystalline quality of a homoepitaxial GaN layer worse. One method of reducing misfit dislocations or grown-in defects in GaN is to use a buffer layer before the main growth of GaN film [10]. In this study, a two-step HVPE growth of GaN film has been investigated, which consists of low temperature GaN-buffer growth followed by a growth of GaN-film at high temperatures, and the effect of buffer growth condition on the epitaxial GaN film by the HPVE method is analyzed.

2. Experimental

A conventional HVPE system with a horizontal reactor was used to grow GaN-buffer layers and GaN-films on Al₂O₃ (0001) substrates. Chlorinated Ga and NH₃
Fig. 1. The surface roughness of GaN-buffer layer with various growth time at 550°C

(Solkatronic, 99.999%) with a stream of N₂ (99.999%) carrier gas were source materials for Ga and N, respectively. Premixed HCl gas (Solkatronic, 10% HCl with N₂) was reacted with metallic gallium (Aldrich, 99.999%). Sapphire substrate was degreased, cleaned and rinsed in TCE, ACE, MeOH and deionized water for 10 min, respectively. H₂SO₄:H₃PO₄ (3:1) solution, HF (10%) were used for etching. A two-step growth method was employed, that is, a GaN-buffer growth at 550–650°C followed by the GaN film growth at 1125°C. Flow rates of 10% HCl, NH₃, and N₂ during the two steps were 50, 850 and 3000 sccm, respectively.

The surface morphology after the buffer growth was observed by atomic force microscopy (AFM) with a scanning frequency of 4 Hz. Three different measurements were obtained on a scanning area of 0.5 × 0.5 μm. The crystal and optical quality of the GaN films were analyzed by double crystal X-ray diffraction (DCXRD) and photoluminescence (PL) measurements, respectively. The PL spectra were obtained at 16K using a He–Cd laser (λ = 325 nm). The grown surface and thickness of the GaN films were observed by a scanning electron microscope (SEM). Cross-sectional transmission electron microscopy (X-TEM) was performed to identify crystalline defects in the HVPE GaN films. Utilizing a low-angle ion milling technique, large and thin area in the X-TEM specimens could be analyzed.

3. Results and discussion

After the buffer growth step, the samples were cooled down to room temperature, and the root mean square (RMS) value and the average roughness were estimated by AFM. The surface roughness (in terms of an average RMS value) of the sapphire substrate after GaN-buffer growth at 550°C is shown in Fig. 1 as a function of the reaction time. The roughness decreases initially to a minimum value, and then increases to a higher value with reaction time. The data in Fig. 1 exhibits a minimum roughness of 15 Å after 4 min of reaction. Even though a maximum value of 600 Å after 6 min is represented, the measured RMS values fluctuated rather significantly due to spike formation as the buffer growth time was longer than 6 min. A similar behavior was observed at 600 and 650°C, too. The current result is similar to the case of MOCVD reaction where trimethylgallium (TMG) was used for the GaN-buffer growth either on sapphire and 6H–SiC substrates [11] and to the case of nitridation treatment [12]. Uchida et
al. [13] analyzed that the formation of 3-D hillocks had deteriorated the roughness of the Al₂O₃ (0001) surfaces after a prolonged pre-treatment reaction.

The surface morphology of buffer layers seems to affect the surface quality of the thick GaN films grown by the present HVPE method. It is demonstrated in Fig. 2, where SEM micrographs of GaN films grown at 1125°C for 30 min are compared. It needs to be noticed that the surface quality in Fig. 2(b) is superior than others, where about 30 μm thick GaN-film was grown on a sample with minimum RMS roughness after 4 min buffer treatment at 550°C. Even for the case of GaN-buffer growth at 600 or 650°C, an exactly similar trend was observed. This implies that there is a correlation between the surface roughness of the low temperature buffer layer and the HVPE GaN film grown at high temperatures. That is, a smooth buffer layer promotes a large 2-D nucleation and lateral growth of GaN during the HVPE process. DCXRD measurement and X-TEM observation provided further proofs.

XRD spectra showed that the HVPE GaN films exhibited an epitaxial relationship of GaN (0002)∥ Al₂O₃ (0001). The full width at half maximum (FWHM) values of the DCXRD GaN (0002) peaks were determined and they are given in Fig. 3 as a function of the buffer growth time at 550 (●) and 600°C (●). Unfilled circles in Fig. 3 correspond to GaN films without pretreatment of buffer growth. The FWHM value decreases initially to minimum values of 767 and 555 arcs at 550 and 600°C, respectively, and then increases afterwards to higher values. The buffer growth time for the minimum of FWHM values is observed from the specimen with lowest RMS roughness after the pretreatment. As far as the current data is concerned, it is clear that the crystalline quality (in terms of X-ray measurement) is the best when GaN film was grown on the smoothest sapphire surface. Now the defect structure in X-TEM micrographs is discussed. Fig. 4(a, b) are cross-sectional TEM pictures near the interfaces of HVPE GaN films without and with 4 min of buffer growth at 600°C, respectively. They are bright field images at a zone axis of [1010] GaN. They are qualitatively similar in the following aspects. The dislocation density is very high at the interface and gradually decreases with the film thickness. The defects are mostly threading dislocations growing perpendicular to (0001) GaN, and lots of stacking faults, which are parallel to (0001)GaN, exist next to the highly defected region. At the top region the amount of threading dislocation was the same in both cases, and the threading dislocation was identified to be \( b = \frac{1}{3}[1120]a \). However, the density of misfit dislocations at the interface is much higher in Fig. 4(a) than in Fig. 4(b), and a detail analysis revealed that the stacking fault-like contrast in Fig. 4(b) was another type of dislocation. Its identity is not clear at present. Current authors consider that a GaN-buffer layer has reduced the formation of misfit dislocations at the early stage of growing, because the buffer zone has somewhat relaxed the lattice mismatch between GaN and sapphire substrate. Dissociation of threading dislocations into stacking faults due to internal stress and a strong possibility of its elimination by crossing of opposite sense vectors could be visualized. The detail mechanism of the annihilation of threading dislocations needs further analysis.

The RMS value after GaN-buffer growth was considered as a guideline to optimize the two-step HVPE process and its usefulness was analyzed by measuring low temperature PL spectra. The optimum reaction time for the first step of buffer growth was determined to be 3–5 min at 550–650°C, and GaN films were grown at 1125°C for 30 min. From the optimized GaN

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Fig. 4. The BF image of interface between thick GaN film and substrate by X-TEM: (a) without GaN-buffer layer; (b) with GaN-buffer layer.
films, a pronounced PL peak at 16 K was observed at 3.47 eV, which corresponds to the bound exciton peak. The FWHM values of the PL peak was 11.0–17.3 meV for three samples. Current observations are comparable to that of Molnar et al. [14], who reported a FWHM value of 2.42 meV at 2 K.

4. Summary and conclusion

AFM was used to study the role of GaN-buffer growth on an Al₂O₃ (0001) substrate in improving the GaN film grown by a HVPE process. From the observation that a smooth surface always produced the best DCXRD data and a specular GaN film, the optimum GaN-buffer growth condition be the case when the surface roughness (in terms of RMS values) is minimum. It has been concluded that a smooth surface after GaN-buffer growth is desirable because it relaxes the lattice mismatch and promotes 2-D nucleation and lateral growth during the HVPE. Based on the analysis a two-step method to grow GaN film by HVPE has been suggested. The optimum condition for the first step of GaN-buffer growth was at 550–650°C for 3–5 min in the present study. The usefulness of the two-step method has been demonstrated by successfully growing good GaN films exhibiting an excellent PL behavior at 16 K. GaN films with FWHM of 11.0–17.3 meV at 356.7 nm PL peak were grown.

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References