Pre-treatment of low temperature GaN buffer layer deposited on AlN/Si substrate by hydride vapor phase epitaxy

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Abstract
We investigated the effects of pre-treatments of a low temperature GaN (LT-GaN) buffer layer on its properties, and of a thick GaN film to improve its qualities. Pre-treatment was performed by annealing the LT-GaN buffer layer under different conditions including different ambient gases (NH₃ and N₂) and temperatures. We found that the pre-treatments of LT-GaN strongly affected surface morphology, crystallinity and optical property of GaN. Crystallinity and optical property of the pre-treated LT-GaN were improved as compared with as-deposited LT-GaN buffer layer. Thick GaN layers with high quality were also obtained by pre-treatment of LT-GaN buffer layer. Surface roughness, morphology and chemistry of the pre-treated LT-GaN buffer layer and thick GaN film on AlN/Si substrate were examined by atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray photoemission spectroscopy (XPS) respectively. Optical characteristics and crystallinity of LT-GaN were measured by low temperature photoluminescence (PL), and X-ray diffractometry (XRD), respectively. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: LT-GaN buffer layer; Thick GaN layer

1. Introduction
GaN is one of the most attractive materials because of its potential applications to various devices such as light-emitting diodes (LEDs) and laser diodes (LDs) over the green to violet range and high temperature, high frequency electronic devices [1]. However, the large mismatch in the lattice constants and the thermal expansion coefficients between the GaN and substrate due to the lack of a suitable substrate make it very difficult to obtain a GaN layer with smooth surface morphology and good crystallinity [2]. In recent years, there has been renewed interest in the hydride vapor epitaxy (HVPE) method for the growth of thick GaN for freestanding GaN substrates [3]. HVPE has been widely used as a growth method for the growth of high-quality compound semiconductors epilayer at high growth rate [4]. Thick GaN growth by HVPE was usually carried out on sapphire substrates but we used silicon substrates instead of sapphire because Si has many advantages such as high quality, large size and low cost compared with sapphire [5,6]. However, high quality GaN films on silicon substrates have not been easily achieved because of large lattice mismatch and differences in thermal expansion coefficients between thick GaN and Si. Therefore, proper buffer layers for the GaN growth on Si substrate are highly desired. The characteristics of the GaN epilayers are strongly affected by the properties of the buffer layer [7]. Two-step growth with AlN or a low-temperature-grown GaN (LT-GaN) buffer layer is indispensable to the growth of GaN with flat surface and device quality. In this work, a double buffer layer consisting of the AlN and LT-GaN was employed.

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LT-GaN was grown by HVPE. In order to improve the properties of LT-GaN, pre-treatment of LT-GaN prior to thick GaN growth was carried out. In this paper, we investigate the effect of pre-treatment of LT-GaN buffer layer on the properties of LT-GaN and of the thick GaN layer. The LT-GaN was annealed under the different ambients at different temperatures.

2. Experimental

The growth of GaN layers was performed with an atmospheric vertical HVPE. The source materials for GaN are gallium trichloride (GaCl₃) and ammonia (NH₃). Detailed information on the growth system has been already published elsewhere [8]. A double-buffer layer consisting of AlN and LT-GaN was employed. The AlN layer was used as the first layer for the growth of thick GaN on Si substrate to reduce the difference in the thermal expansion coefficient and lattice mismatch between GaN and Si. An AlN thin layer of 850 Å was deposited on a Si(111) substrate by an RF sputtering system. Prior to the AlN deposition, the Si surface was degreased in TCE, acetone and methanol for 10 min, respectively, and then the surface oxide was removed in a buffered oxide etch BOE before loading the sample. RF sputtering was performed at the base pressure of 6 × 10⁻⁵ Pa, N₂ of 4 sccm, and Ar of 20 sccm. The plasma power was 300 W, typical chamber pressure was 1.33 Pa. The LT-GaN buffer layer as the second buffer layer was grown at 600 °C for 1 min with flow rate of GaCl₃, NH₃ and N₂, balance gas of 100 sccm, 1250 sccm, and 3500 sccm, respectively. To investigate effects of the pre-treatments of the LT-GaN buffer layer on the properties of thick GaN, the LT-GaN buffer layer was annealed under different conditions including different ambients, NH₃ and N₂, temperature. The LT-GaN grown on AlN/Si (111) was annealed at 925°C or 1000°C for 15 min.

The effects of pre-treatment of LT-GaN on the crystallinity, surface roughness, surface morphology and optical property were evaluated. The thick GaN was grown at 925°C for 10 min after annealing of LT-GaN. After stabilization of temperature, GaCl₃, NH₃ and the N₂ was transported into the chamber, and the bubbler temperature was 100°C. The carrier gas for GaCl₃ was N₂. Typical flow rates of NH₃ and balance gas, N₂ carrier gas were 1000 sccm, 2500 sccm and 100 sccm, respectively.

The surface roughness and morphology of the pre-treated LT-GaN buffer layer and thick GaN film on AlN/Si substrate were examined by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The optical characteristics of LT-GaN were measured by low temperature photoluminescence (PL) taken at 66 K where the 325 nm line of a cw He–Cd laser (3 mW) was used as an excitation source. The crystallinity and surface chemistry of LT-GaN were estimated by X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS) respectively.

3. Results and discussion

An optimized low temperature GaN layer (LT-GaN) on the AlN buffer layer was employed as the second buffer layer to improve the properties of thick GaN film. We previously investigated the effects of growth parameters such as temperature and deposition time on the surface roughness of LT-GaN buffer layer using AFM [8]. Deposition parameters were optimized and a minimum roughness of LT-GaN of 47.6 Å was obtained at 600°C for 1 min. The thickness of LT-GaN film was approximately 1 μm measured by SEM image. We examined the effects of pre-treatment of the LT-GaN buffer layer on the crystallinity of the LT-GaN buffer layer using XRD measurement. Fig. 1 shows an XRD spectrum of LT-GaN buffer layer deposited on AlN

![Fig. 1. XRD patterns from the LT-GaN annealed at 1000°C (a) and annealed at 925°C (b), under different conditions: A, as deposited; B, annealed at 1000°C under ambient N₂; C, annealed at 1000°C under ambient NH₃; D, annealed at 925°C under ambient NH₃; E, annealed at 925°C under ambient N₂.](image-url)
As shown in Fig. 1a, the XRD spectrum of sample C (annealed at 1000°C in the ambient NH₃) shows very large and sharp peaks at 2θ = 34.63°, 73.08° which are characteristic of the GaN (0002) and (0004) planes, respectively, compared with sample B (annealed at 1000°C under ambient N₂) and the sample A (as deposited). Fig. 1b shows similar results. However, the intensity of sample C annealed under ambient NH₃ at 1000°C was larger than that of sample D annealed at 925°C under NH₃ ambient. This result shows that the crystal quality of LT-GaN buffer layer was improved by annealing at high temperature. Especially under the NH₃ ambient, crystallinity of the LT-GaN layer annealed at 1000°C was significantly improved. These results may be attributed to the fact that NH₃ prevents nitrogen out diffusion from the LT-GaN layer more effectively due to resolvability of NH₃ is higher than N₂.

The effect of the LT-GaN buffer layer pre-treatment on the optical properties of LT-GaN was investigated by photoluminescence measurements at 66 K. Fig. 2 presents the low temperature PL spectra of the LT-GaN layer over the spectral range from 1.24 to 3.69 eV. Sample A (as-deposited) shows a broad yellow peak at 2.13 eV, which corresponds to deep levels, and many other peaks exist near the 2.13 eV are associated with other defects or impurities [9]. As shown in spectra of B and C, the peaks related to deep levels at 2.13 eV disappeared after annealing at high temperature. Sam-

Fig. 2. Photoluminescence spectra of LT-GaN at 66 K annealed at 1000°C (a) and annealed at 925°C (b), under different conditions: A, as deposited; B, annealed at 1000°C under ambient N₂; C, annealed at 1000°C under ambient NH₃; D, annealed at 925°C under ambient NH₃; E, annealed at 925°C under ambient N₂.

Fig. 3. Surface morphology of annealed LT-GaN and thick GaN grown: (a) the LT-GaN annealed under ambient NH₃ at 1000°C, (b) the LT-GaN annealed under ambient N₂ at 1000°C, (c) the thick GaN grown on (a), (d) the thick GaN grown on (b).
ple B (annealed at 1000°C under ambient N2) has a broad peak at 3.1 eV with tail at low energy side, while sample C (annealed at 1000°C under ambient NH3) has a strong emission peak at 3.3 eV attributed to the donor–acceptor pair [9,10]. However, sample D (annealed at 925°C under ambient NH3) did not show a strong peak like sample C, but sample D showed a little increase in intensity compared to sample E (annealed at 925°C under ambient N2). The PL spectra are in consistence with XRD results shown in Fig. 1. The quality of the LT-GaN buffer layer was improved by annealing under ambient NH3 at 925°C and 1000°C, resulting in the improvement of optical properties of LT-GaN.

In order to examine the changes in surface chemistry of the LT-GaN annealed under the different ambients, we used X-ray photoemission spectrometry focusing on Ga and N peak. However, there is no remarkable difference between the LT-GaN with NH3 pre-treatment and the LT-GaN with N2 pre-treatment at 925 and 1000°C.

The surface morphology of the LT-GaN buffer layer after annealing under NH3 and N2 ambients was examined. Fig. 3a,b shows the SEM image of the LT-GaN buffer layer surface annealed at 1000°C under ambient NH3 and N2, respectively. Surface of the LT-GaN annealed under ambient NH3 has cracks and protuberances. However, the surface of the LT-GaN treated with NH3 was clean and smooth. This result shows a similar trend to the XRD result. The smooth and clean surface of the LT-GaN annealed under NH3 ambient was due to the fact that NH3 prevent nitrogen evaporation from surface more effectively than N2 due to resolvability of NH3 is higher than N2.

To investigate the effect of pre-treatment of LT-GaN on the properties of thick GaN, thick GaN epilayers were grown on the pre-treated LT-GaN buffer layer (Fig. 3c,d). The thickness of thick GaN layer was 8 μm. As shown in Fig. 3c,d, the surface morphology of thick GaN grown on the LT-GaN annealed under ambient NH3 at 1000°C was improved compared with that of thick GaN on LT-GaN annealed under N2. The thick GaN on the LT-GaN annealed under N2 ambient has rough surface and cracks, but thick GaN grown on the LT-GaN buffer annealed under NH3 at 1000°C has a relatively smooth surface free from cracks.

Fig. 4 shows the XRD pattern of the thick GaN film grown on the LT-GaN grown on the LT-GaN annealed under different ambients at 1000°C. The spectrum of thick GaN grown on the LT-GaN annealed under N2 ambient shows the strong GaN(0002) peak with GaN(10̅10), GaN(10̅1̅), GaN(10̅13), and GaN(0004) peaks at 2θ = 34.64, 32.44, 36.99, 63.70 and 73.01, respectively. However, the spectrum of thick GaN grown on the LT-GaN annealed under NH3 ambient did not show GaN(10̅10), GaN(10̅1̅), and GaN(10̅13) peaks. Strong (0002) and (0004) peaks are observed. This result suggests that the crystallinity of thick GaN grown on the LT-GaN under NH3 treatment was improved compared with that of thick GaN on the LT-GaN annealed under N2.

4. Conclusions

The LT-GaN buffer layer was annealed under different ambients and at different temperatures. We found that the crystallinity, optical properties and surface morphology of the LT-GaN buffer layer annealed under NH3 ambient were improved compared with those of as-deposited and LT-GaN annealed under N2. We also confirm that improvement in the LT-GaN results in the improvement in thick GaN.

It may be due to the fact that NH3 effectively prevents nitrogen out diffusion due to the resolvability of NH3 which is higher than N2. Consequently, an improved high quality thick GaN layer with a smooth crack-free surface can be grown by pre-treatment of the LT-GaN buffer layer.

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