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Influences of nitridation and thermal annealing on GaN buffer layers and the property of subsequent GaN epilayers grown by MOCVD

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GaN epilayers were grown on sapphire substrates by metalorganic chemical vapor deposition using the two-step method. The surface morphology of the GaN buffer layer grown under various pregrowth and postgrowth treatments, such as nitridation duration, temperature-ramping rate and ambient during annealing, was analyzed by atomic force microscopy (AFM). It was found that the nitridation time and post-annealing parameters should be optimized in order to maintain the buffer layer with smooth surface for the GaN epitaxial growth. Lower ramping rate (<40^oC/min) and insufficient NH_3 flow will deteriorate the buffer-layer surface and yields large hexagonal three-dimensional islands. Under the optimum conditions developed by the AFM examinations, specular GaN epilayer with 25-nm-thick buffer layer can be obtained. The 25-K photoluminescence spectrum reveals a strong near-band-edge emission at 356.65 nm with a full width at half maximum of 13.1 meV.

1. Introduction

III-V nitride semiconductors are presently one of the most promising materials for optoelectronic devices operating in the visible-to-ultraviolet wavelength region [1]. Due to the chemical dissimilarity and large lattice mismatch between GaN and substrates (Si, GaAs, SiC, or sapphire, etc), growth of mirror GaN epilayers by metalorganic chemical vapor deposition (MOCVD) requires the use of two-step growth method. This method consists of a low-temperature (500-600°C) thin buffer-layer growth and a high-temperature (≥1000°C) over-layer deposition.

That is, the device-quality GaN epitaxial layer is grown at high temperature on the buffer layer annealed, during the heating process, to beyond 1000^oC. Therefore, the conditions of both buffer-layer pregrowth and annealing are very important for crystalline properties of the GaN epilayer. Although some investigations concerning the deposition conditions of the buffer layer have been reported recently [2-6], there is lack of a rule to follow to obtain high-quality GaN epilayers. In this study, a specially designed dual-flow horizontal MOCVD system was used to grow the GaN epilayers on sapphire substrates. The effects of process parameters, such as substrate nitridation, temperature-ramping rate and ambient during annealing, before and after GaN buffer layer growth on the overall quality of GaN epilayers were investigated. A rule to obtain mirror GaN epilayers on sapphire substrates is also presented.

2. Experimental

The experiments were carried out in a home-made dual-flow MOCVD reactor, as schematically shown in Fig. 1. The group V and group III sources are supplied separately into the chamber and mixed about 5 cm in front of the susceptor .

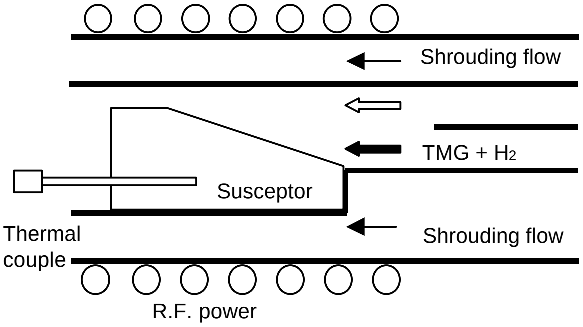


Fig.1. Schematic diagram of specially designed dual-flow MOCVD reactor.

This new dual-flow design can minimize the pre-reaction among the reactive gases. Trimethylgallium (TMGa) and ammonia (NH_3) were used for the column III and column V sources, respectively. Hydrogen was used as the carrier gas, and the N_2 gas was supplied into the column V source line to evaluate the effect of nitrogen incorporation. In this work, the (0001)-oriented sapphire wafer as the substrate.

After the degreasing process, the substrate was etched in a H_2SO_4: H_3PO_4: H_2O_2 =3: 1: 1 solution at 160^oC for 10 min. Prior to the GaN growth, the substrate was annealed in the H_2 ambient at 1000 ^oC for 10 min. Then the sapphire was annealed at 1000 ^oC in the NH_3/H_2 ambient with various nitridation time (0~50 min).

Following this treatment, the GaN buffer layer with 25 nm thickness was deposited at 600 ^oC under a V/III ratio of 3000. After the buffer-layer growth, the sample was ramped up to 1000 ^oC with various ramping rates and atmosphere. The timing chart of the growth sequence, growth process, flow rates of the source gases and related parameters are shown in Table 1.

Flow rate	Thermal cleaning	Nitridation Time	Buffer layer growth	Ramping annealing	High temp. annealing
H_2	2 slm				
NH_3		2 slm	0 ~ 4 slm		
TMGa			27.2 (µmole/min)		
N_2				0 ~ 4 slm	
Sub. Temp.	1000°C		600°C	annealing	1000°C
Time	6 min	0 ~ 50 min	115 sec	6 ~ 20 min	6 min

Table 1:Timing chart of the growth sequence, growth process, flow rates of the source gases and related parameters for GaN buffer layer growth.

The GaN buffer layers grown under various pregrowth treatments (such as nitridation duration) and annealed in various parameters (such as temperature-ramping rate and ambience) were analyzed by atomic force microscopy (AFM, PSI AutoProbe). Scanning electron microscope (SEM, JEOL 6400) was used to examine the overall surface morphology of the GaN epilayer. The optical quality of the epilayer was characterized by photoluminescence excited by a 325-nm He-Cd laser.

3. Results and Discussion

The substrate nitridation prior to the buffer-layer growth is known as a critical step in obtaining high-quality nitride materials. In an attempt to understand the determining factors of the GaN heteropitaxy, the nitridated sapphire surface and the GaN buffer-layer surface were examined by AFM. For comparison, the surface of the bare sapphire substrate is also measured and presents about 0.3 nm roughness. The nitridated surface roughness before and after the buffer-layer growth as a function of the nitridation time is shown in Fig. 2(a) and (b), respectively. It was found that the surface roughness for the nitridated substrates did not present an obvious change as compared with that of the bare sapphire, even for the nitridation duration of 50 min. However, after the buffer-layer growth, the surface roughness showed a strong dependence on the nitridation time. The optimum nitridation time seems to be 20 min in the present work, resulting in a flat buffer layer with 1.6 nm roughness. It has been reported that the nitridation process on the sapphire substrate forms the amorphous AlO_xN_{1-x} layer [7,8]. The nitridated layer could serve as the nucleation centers to aid the wetting of the successive nitride layer and to improve the surface morphology of the buffer layer. However, if the nitridation duration is too long, the amorphous nitridated layer becomes partially crystalline and results in the formation of high density of surface protrusions. As a consequence, the surface morphology of the GaN buffer layer becomes rough. In the present study, the protrusive nitridated surface was not observed even for long nitridation duration. However, a rough buffer-layer

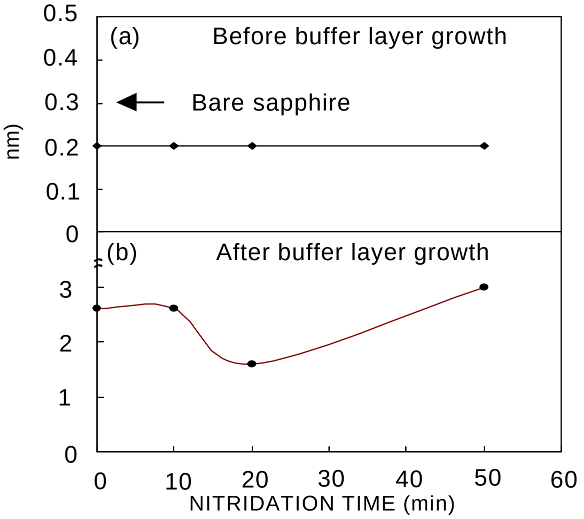


Fig.2. Influence of nitridation time on AFM surface roughness of sapphire substrate (a) before and (b) after GaN buffer layer growth.

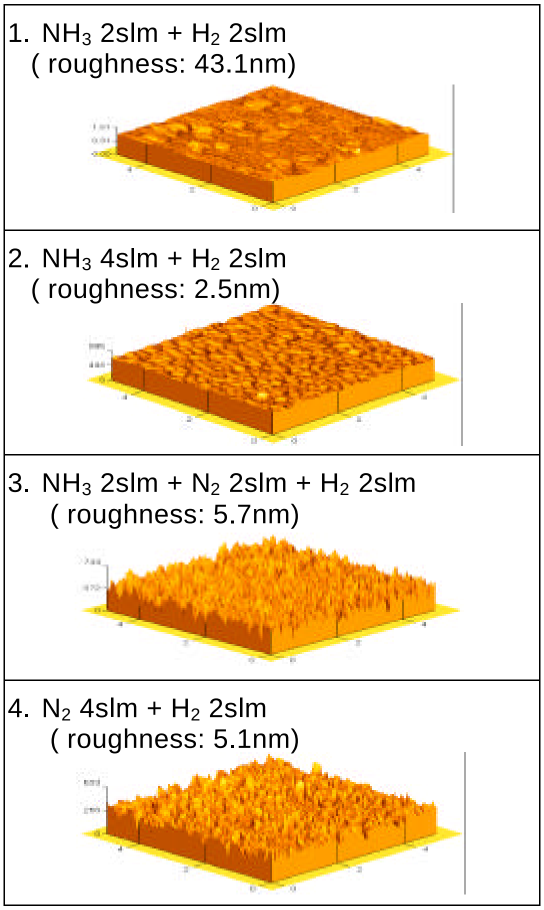


Fig.3. Surface morphology of GaN buffer layer annealed in various ambient. The annealing temperature used is 1000 °C with a temperature ramping rate of 40°C/min. The AFM image area is 5 μm × 5 μm.

surface was still obtained as the GaN buffer layer grown on the substrate treated by excessive nitridation time. This could be due to the fact that the AlO_xN_{1-x} layer was too thick and was ill-suited for the two-dimensional buffer-layer growth. The thickness and microstructure of AlO_xN_{1-x} for the nitridated sapphire substrate will be treated in detail at a latter point.

Although the smooth buffer layer can be obtained by a suitable nitridation duration, maintaining the smooth morphology till the growth of high-temperature GaN epilayers is important. Hence, the ambient effect on the surface morphology during the buffer layer annealed to 1000°C was investigated. Fig. 3 shows the morphology of the GaN buffer layer on sapphire annealed in various ambiences. Before annealing, the buffer-layer sample showed about 2.6 nm in roughness. It was found that the surface became very rough (roughness: 43.1 nm) as the buffer layer was annealed in a NH_3/H_2 (2/2 slm) ambient (Fig. 3(a)).

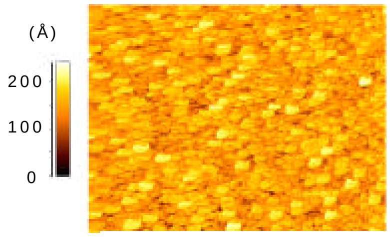
This means that the NH_3 flow rate of 2 slm can not suppress the desorption of the buffer-layer surface [9]. Apparently, this phenomenon can be improved as the NH_3 flow rate increases to 4 slm (Fig. 3(b)). The annealed buffer layer with 2.5 nm roughness can be obtained under the high NH_3 flow rate. In order to study the effect of N_2 incorporation, NH_3 was partially or totally replaced by N_2. The obtained surface morphologies are shown in Figs. 3(c) and (d), and present a roughness of 5.7 and 5.1 nm for partial and total N_2 anneal ambient, respectively. These results suggest that N_2 can be decomposed into atomic nitrogen. However, the efficiency of N_2 decomposition is still not high enough during the ramping duration. Thus the buffer layer presents rougher surface as compared with that of GaN sample annealed in the high-flow-rate NH_3 ambient.

To optimize the treatment condition during the buffer layer annealed to 1000°C, a series of GaN buffer-layer samples were subjected to different temperature ramping rates. Fig. 4 shows the AFM images of the as-deposited and annealed GaN buffer layer on sapphire. Increasing the ramping rate from 20 to 60°C/min, the grain size decreases and then increases. Because the higher ramping rates (>40°C/min) will shorten the annealing time, the grain size of the buffer layer could have no enough time to coarse. When the ramping rate was reduced to 40°C/min, the larger grain size would be grown at expense of the small grains through the process of clustering and recomposed GaN molecules.

On the other hand, the long annealing duration could induce the dramatic re-evaporation of the GaN buffer layer, resulting in the smaller grain size in the sample with the lower ramping rate of 20 °C/min. When the ramping time is optimized, the reconstructed surface takes place. The surface roughness of 2.5 nm can be maintained or improved for the sample with 40 °C/min ramping rate.

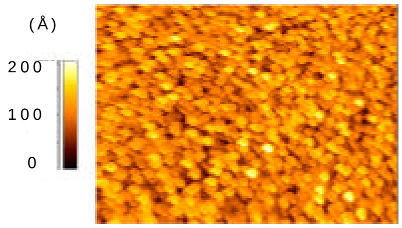
Based on the above results, the nitridation and thermal-annealing parameters are confirmed to be very important to obtain the very flat buffer-layer surface for the GaN epitaxial growth.

(a) As-deposited



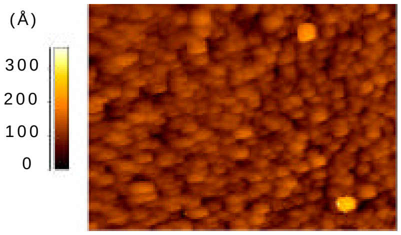
roughness: 2.6 nm

(b) Ramping rate: 20°C /min



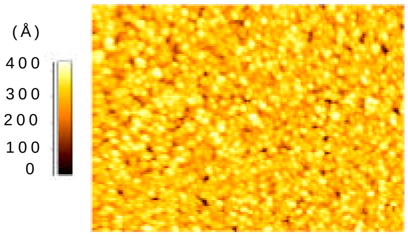
roughness: 2.5 nm

(c) Ramping rate: 40°C/min



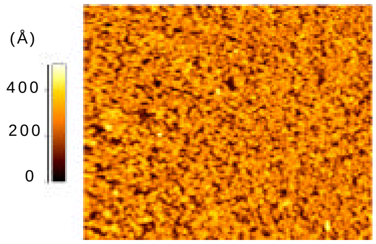
roughness: 2.5 nm

(d) Ramping rate: 50°C/min



roughness: 4.9 nm

(e) Ramping rate: 60°C/min



roughness: 7.8 nm

Fig. 4. AFM image for GaN buffer layer annealed with various temperature ramping rates. The annealing temperature used is 1000 °C with a NH_3 flow of 4 slm. The AFM image area is 5 μ m × 5 μ m.

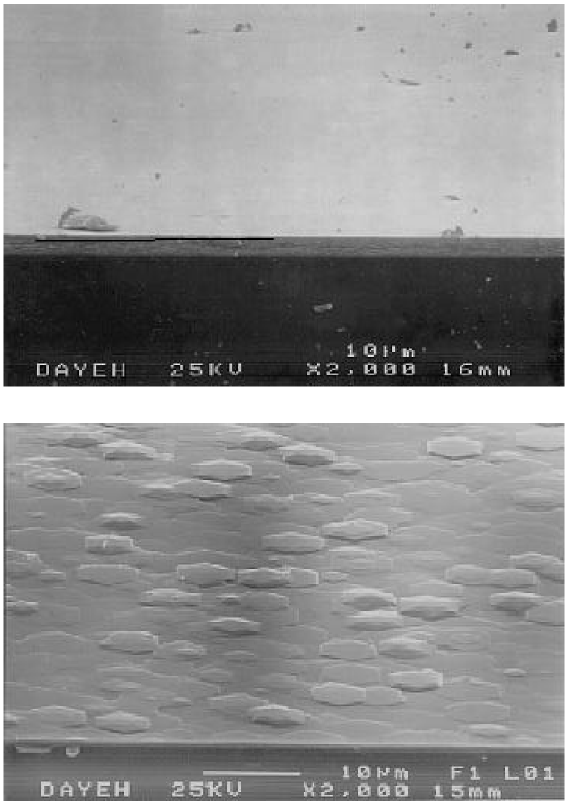


Fig.5. SEM surface morphology of GaN epilayer grown on buffer layer with roughness of (a) 2.5 nm and (b) 7.8 nm.

Under the optimum nitridation time (20 min) and temperature-ramping rate (40^{o}C/min) in the NH_3/H_2 (4/2 slm) ambient, specular GaN epilayers with 25-nm-thick buffer layer can be reproducibly obtained, see Fig. 5(a). For comparison, the GaN epilayers grown on the rough buffer layer (4.9 nm roughness before epilayer growth) is shown in Fig. 5(b).

Apparently, the GaN epilayer grown on a rough buffer layer yields large hexagonal three-dimensional islands. This indicates that the surface morphology of the GaN epilayer is strongly affected by the surface roughness before the GaN epitaxial growth. Further examination of the epilayer was performed by photoluminescence measurements. The mirror GaN epilayer shows a near-band-edge peak (25 K) centered at 356.65 nm with a full width at half maximum as narrow as 13.1 meV. More detailed studies of the structural and electrical properties are in progress and will be published in the near future.

4. Conclusions

An experimental guide using AFM to evaluate how to obtain a flat GaN epilayers is described. The roughness of GaN buffer layer was found to be highly sensitive to the nitridation duration. The surface morphology of the buffer layer during thermal annealing was affected by the temperature-ramping rate and annealing ambient.

In order to obtain the mirror GaN epilayer, the thermal annealing parameters before and after GaN buffer layer growth must be optimized simultaneously. Under the optimum parameters to maintain or improve the flat surface morphology before GaN epitaxial growth, superior surface morphology and optical properties of the GaN epilayer can be easily achieved.

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