The effects of sapphire nitridation on GaN growth by metalorganic chemical vapour deposition*

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In situ optical reflectivity measurements are employed to monitor the GaN epilayer growth process above a low-temperature GaN buffer layer on a *c*-plane sapphire substrate by metalorganic chemical vapour deposition. It is found that the lateral growth of the GaN islands and their coalescence are promoted in the initial growth stage if optimized nitridation time and temperature are selected when the substrate is pre-exposed to ammonia. As confirmed by atomic force microscopy observations, the quality of the GaN epilayers is closely dependent on the surface morphology of the nitridated buffer layer, especially grain size and nucleation density.

Keywords: X-ray diffraction, metalorganic chemical vapour deposition, nitrides

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1. Introduction

GaN is one of the most promising materials for optoelectronic devices.[1−3] One of the major obstacles for high-quality GaN growth is the lack of a suitable large-area lattice-matched substrate, although attempts to epitaxially grow III–V nitrides on sapphire have been made using metalorganic chemical vapour deposition (MOCVD) since the late 1960s.[4−9] It is known that a buffer layer grown at low temperature promotes the two-dimensional growth of subsequent high-temperature GaN epilayers, while the high interfacial energy between GaN and sapphire often results in three-dimensional growth.[10] It was reported that the initial nitridation of sapphire substrates, which probably results in the formation of a thin AlN layer on the sapphire substrates, has an influence on the structural and electrical properties of the buffer layers and the subsequent thick GaN epilayers.[11−15] However, the effect of the initial nitridation of the sapphire substrate needs to be explained more accurately. In this paper, we investigate the differences between epilayer growing processes under different sapphire substrate nitridation conditions using *in situ* optical reflectivity measurements. In addition, the optimum conditions for nitridation are searched for indirectly by evaluating the structural and electrical properties of a thick GaN grown on a buffer layer at high temperature.[11,16]

2. Experimental procedure

The GaN epilayers with low-temperature GaN buffer layers were grown on *c*-plane sapphire substrate by MOCVD. Ammonia, trimethylgallium and trimethylaluminium were used as the N, Ga, and Al sources, respectively. H_2 was used as the carrier gas. The substrates used in this experiment were (0001) sapphire substrates which were degreased in an organic solvent and thermally cleaned in H_2 gas flow at 1080 °C. Then sapphire substrates were nitri-

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dated by NH_3 gas at different temperatures (520 °C–850 °C) for different time lengths (0–30 min). The low-temperature GaN buffer layer with fixed thickness was deposited on the sapphire substrate. Finally, the substrate temperature was raised to 1040 °C to grow a 2-μm thick GaN layer. Double crystal X-ray diffraction was performed on a Rigaku SLX-1AL X-ray diffractometer to obtain the full width at half maximum (FWHM) of the ω-scan rocking curve. A Hall measurement was carried out using an indium contact, and the surface morphology was examined by atomic force microscopy (AFM).

3. Results and discussion

Figure 1 shows the traces of *in situ* optical reflectivity measured from four GaN epilayers grown on a GaN buffer layer with different nitridation times at the same temperature (520 °C) during the initial nitridation of the sapphire substrate. The nitridation times of the sapphire substrate used in the growth of samples A, B, C, and D were 0, 3, 10, and 30 min, respectively. As shown in Fig. 1, four traces (a, b, c, and d) are divided into three parts corresponding to the three growth stages of the GaN deposit on the low-temperature GaN buffer layer as follows: (i) the thermal treatment and the nitridation of the sapphire substrate, (ii) the low-temperature GaN buffer layer deposition and the annealing process, and (iii) the growth of the GaN epilayers. The differences between samples B and C are noticeable. In the initial growth of sample C, whose sapphire substrate is nitridated for 10 min (Fig. 1(c)), the surface of the GaN layer becomes rough and the intensity of the *in situ* optical reflectivity decreases. Afterwards, the surface of the GaN layer turns optically smoother step by step, which means that the lateral growth and the coalescence of the GaN islands occurs. Finally, the quasi-two-dimensional growth of the GaN layer appears. An oscillation of the reflectivity intensity with large and equal amplitude is well observed. However, the growth procedure of sample B, whose sapphire substrate is nitridated for only 3 min, exhibits a different kind of trace in Fig. 1(b). The surface roughing process of the GaN layer experiences a shorter time, and then it enters into the stage of lateral growth right away. The quasi-two-dimensional growth of the GaN layer also emerges soon after. It is found that the quality of sample C is somewhat better than that of sample B, as revealed by the XRD and electron mobility characterization results, which are shown in Table 1. Actually, the results of samples A, B, C, and D displayed in Table 1 indicate that the quality of the GaN epilayer, i.e. the data of the FWHM of the X-ray ω-scan rocking curve for the (0002) and ($10\bar{1}2$) planes and the electron mobility, is dependent on the initial nitridation time of the sapphire substrate. In particular, whether the initial nitridation of the sapphire substrate exists largely affects the GaN layer quality. It implies that an appropriate initial nitridation time of the sapphire substrate tends to promote the lateral growth of the GaN islands, thereby improving the quality of the GaN epilayers.

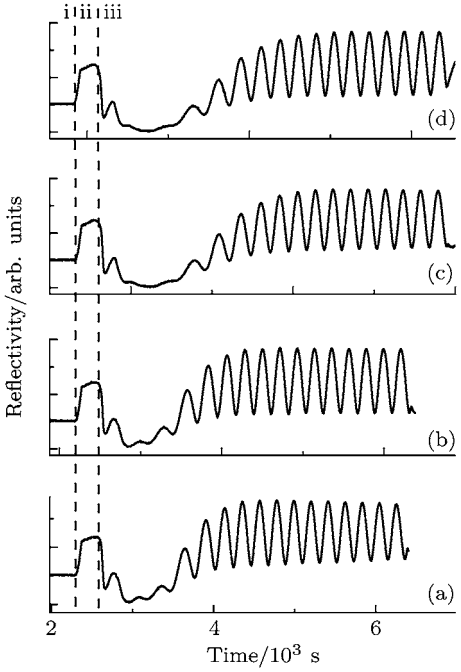


Fig. 1. Traces of *in situ* optical reflectivity measurements for the three stages in the whole growth process of GaN epilayers on a low-temperature GaN buffer layer with different nitridation times: (a) 0, (b) 3, (c) 10, and (d) 30 min.

It is found that not only the initial nitridation time, but also the nitridation temperature, has an effect on the quality of the GaN epilayer. The five traces of *in situ* optical reflectivity measured from GaN epilayer growth on a low-temperature GaN buffer layer with different nitridation temperatures, i.e. 520, 600, 650, 700, and 850 °C, for samples C, E, F, G, and H, respectively, are shown in Fig. 2, where the dashed line marks the beginning of GaN epilayer growth. For the five samples, the same 10 min nitridation time of the sapphire substrate is used, and the growth conditions of the GaN epilayers are almost the same except for the nitridation temperature of the sapphire substrate.

Table 1. The growth conditions and characterization results of the GaN samples.

Sample	Nitridation time/min	Nitridation temperature/°C	X-ray FWHM (arcsec) (0002)	X-ray FWHM (arcsec) $(10\bar{1}2)$	Mobility/$cm^2 \cdot V^{-1} \cdot s^{-1}$
A	0	520	385	410	570
B	3	520	335	356	580
C	10	520	295	353	603
D	30	520	338	367	569
E	10	600	295	346	565
F	10	650	280	335	592
G	10	700	346	364	363
H	10	850	385	454	340

It can be seen from Fig. 2 that many differences exist in the reflectivity curves measured during the initial stage of the growth process of the GaN epilayers. The obvious lateral growth of the GaN islands is observed in the growth processes for samples C, E, and F, as shown in Fig. 2(a), (b), and (c), but is stopped in samples G and H as shown in Fig. 2(d) and (e), indicating that in the latter two curves the nitridation temperature is too high, which leads to a stop in the coalescence of the GaN islands and quasi-two-dimensional growth. In this case, the quality of the GaN epilayers becomes very poor. The FWHM of X-ray ω-scan rocking curves

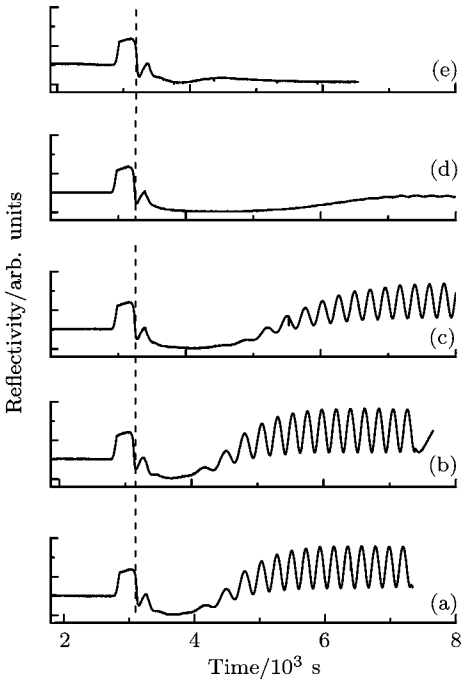


Fig. 2. Traces of *in situ* optical reflectivity measurements for the whole growth process of GaN epilayers on low-temperature GaN buffer layer, with the same 10 min nitridation time and different nitridation temperatures: (a) 520 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 850 °C. The dashed line marks out the beginning of the growth of GaN epilayers.

and the electron mobility of five samples, C, E, F, G, and H, are shown in Table 1. It is found that the narrowest FWHM of the X-ray ω-scan rocking curve and the mobility that is almost at its highest are observed for sample F. The optimal nitridation temperature of the sapphire substrate is thus around 650 °C. Too high or too low a temperature will lead to a deterioration in the quality of the GaN epilayers.

In order to clarify the physical mechanism for the effect of the GaN buffer layer on the quality of the GaN layers, three GaN buffer layers, a, b and c, with growth stopped just before the growth of the high-temperature GaN epilayer (as indicated by the dashed line in Fig. 2) are prepared and examined by AFM. These GaN buffer layers are grown under the same growth conditions as those used for samples C, F and H, i.e. 520 °C and 10 min for sample a, 650 °C and 10 min for sample b, and 850 °C and 10 min for sample c. The surface morphologies of these GaN buffer layers are quite different, as shown in Fig. 3(a)–(c), where sample a has a smaller grain size and a higher nucleus density than samples b and c, which leads to a quicker coalescence of the GaN islands in the initial growth stage, as shown in Fig. 2(a). Then, many dislocations will form and go through the GaN epilayers, and the film quality will deteriorate. On the other hand, for a GaN buffer layer such as sample b, which has a larger grain size and lower nuclei density, the quality of the deposited GaN epilayer becomes better, since the lateral growth and the coalescence of the GaN islands will be promoted, leading to an increased volume of defect-free columnar domains and an improved crystal quality. Of course when the GaN buffer layer has too large a grain size and too low a nuclei density, it will take too long a time to laterally grow the GaN islands, and so the quality of the GaN epilayers will become poor. This is the case in sample c. In fact, Sumiya and Fuke[17] also reported that by

increasing the nitridation temperature of the sapphire substrate too much, the surface morphology of the GaN layer may transform from smooth to hexagonal-faceted. Therefore, both nitridation time and nitridation temperature need to be optimized to gain the best GaN epilayer quality.

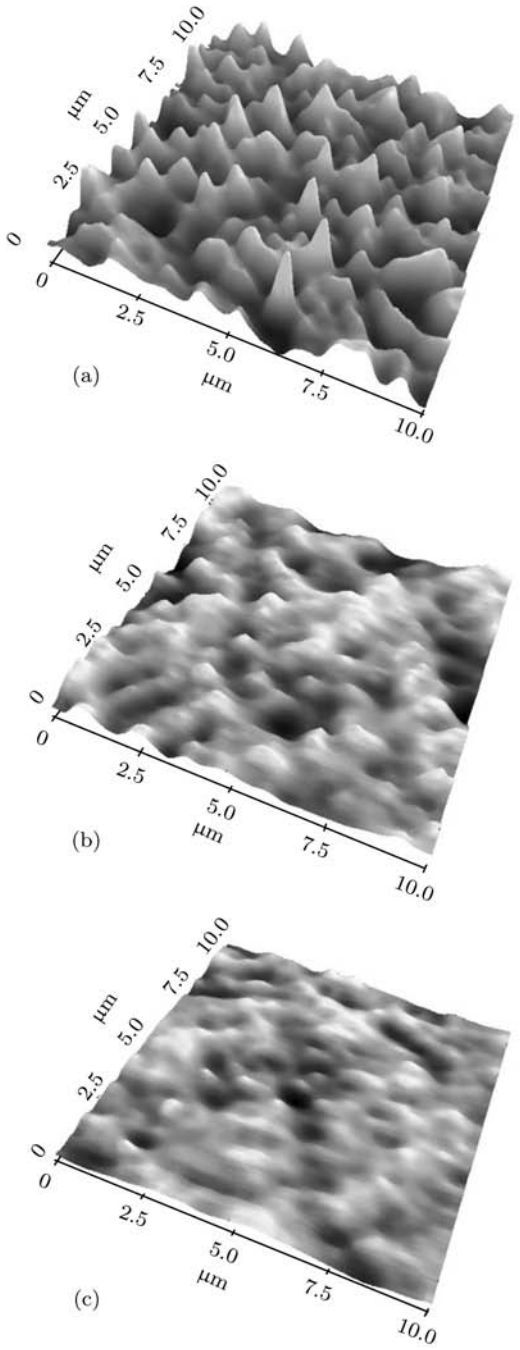


Fig. 3. AFM images of the surface morphology of GaN buffer layers for samples E (a), F (b), and H (c).

4. Summary

We investigated the effect of the initial nitridation of a sapphire substrate on the growth of GaN epilayers via a low-temperature GaN buffer layer by MOCVD. The traces of *in situ* optical reflectivity measurements reveal that the initial stage of the growth process of the GaN epilayers is affected prominently by nitridation time and nitridation temperature. The quality of the GaN epilayers is strongly dependent on the grain size and the nucleation density of the GaN buffer layer after the annealing treatment stage of the growth process. High-quality GaN epilayers can be deposited on GaN buffer layers only when optimized initial nitridation conditions are selected.

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