Growth of GaN on Nitriding TiN Buffer Layers

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The breakthrough of GaN epitaxial layer growth with mirror-like surface on the sapphire substrate using a MOCVD (metal organic chemical vapor deposition) technique was made by discovery of an AlN buffer layer prior to GaN deposition about 20 years ago. Since then, extensive efforts have been made to develop a conductive substrate for MOCVD grown GaN layers. In the present study, we explored a possibility of growing continuous, flat GaN layers on a metallic TiN buffer layer, and focused our experiments to investigate the effect of nitrogen contents of the TiN buffer layers on lateral growth of the GaN layers. It was concluded that nitrogen composition in the TiN buffer layers should be higher than that of stoichiometric TiN to grow smooth GaN layers. It was found that nitriding the TiN buffer layers after deposition enriched significantly the nitrogen content compared with increasing the ratio of $N_2$ to $N_2 + Ar$ ($N_2/(N_2 + Ar)$ ratio) during TiN deposition. Choice of the moderate $N_2/(N_2 + Ar)$ ratio during TiN deposition and nitriding the TiN buffer layers after TiN deposition were essential to grow continuous, flat GaN layers, since the reduction of the $N_2/(N_2 + Ar)$ ratio promoted few opening areas in the GaN layers.

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1. Introduction

GaN-based semiconductors with wide-band gaps have been used as the key elements for blue light-emitting diodes and laser diodes. Since the bulk GaN was not commercially available, conductive GaN layers are generally deposited on the rigid substrates. Currently, non-conductive sapphire was extensively used as the substrate. The lattice mismatch between GaN and sapphire is about 15% and thus buffer layers were needed for lateral growth of GaN on the sapphire substrate.¹ An AlN layer deposited at relatively low temperatures was found to be the best buffer layer, and the use of this buffer layer made it possible for growth of GaN with mirror surface.² Although the lattice mismatch between GaN and AlN is about 2.5%, the AlN buffer layers are believed to enhance GaN nucleation and growth due to relatively low AlN/GaN interface energy.³ Although GaN growth directly on nitrided sapphire was reported,⁴ the nitriding of sapphire would form a very thin AlN layer, and, thus, this is similar to form the AlN buffer layers on sapphire prior to GaN growth.

Although the growth technique of GaN with mirror-like surface was developed using the insulator AlN buffer layer, conductive substrates are desirable to increase the light emitting efficiency of the diodes.⁵ However, GaN growth on the conductive substrates such as Si, GaAs, and SiC has been extensively studied. Conductive SiC was successfully developed for the substrates of GaN layers, but the cost of the SiC wafers is extremely high. In order to achieve our goal to develop conductive substrates with relatively low cost, development of conductive buffer layers was challenged. In the present study, the application of transition metal nitrides as the conductive buffer layers was investigated. Among the transition metal nitrides, TiN was chosen, because TiN has the desirable properties such as low electrical resistivity ($\rho = 15-100 \mu\Omega\text{cm}$),⁷ NaCl type structure, a small lattice mismatch (about 6.2%) between GaN and TiN,⁸ and a high melting point of 2950°C (⁹ which is needed for the GaN growth at around 1000°C).¹⁰ TiN was reported to show an ohmic behavior for n-GaN.¹¹ In this experiment, we focused our attention to study an effect of nitrogen contents in the TiN buffer layers on the GaN growth mechanism. The TiN buffer layers with various nitrogen contents were grown by changing the flow ratio of $N_2$ to $N_2 + Ar$ (which is denoted as $N_2/(N_2 + Ar)$ ratio) during TiN deposition. Also, the effect of annealing the TiN layers at elevated temperature in NH₃ atmosphere prior to GaN deposition was studied on the GaN growth mechanism.

2. Experimental Procedures

Figure 1 shows a schematic illustration of sample preparation processes of sapphire/TiN/GaN, where a slash “/”

![Fig. 1 Flow chart of sample preparation processes and schematic illustrations of the thin film structures. (a) an as-deposited TiN layer on the sapphire substrate, (b) nitriding of the TiN layer, and (c) and (d) deposition of the GaN layers on the TiN buffer layers as shown in (a) and (b), respectively.](image-url)
sign means the deposition sequence. The 100–200 nm-thick TiN buffer layers were deposited on the (1102) sapphire at 600 °C in a radio frequency magnetron sputtering system [Fig. 1(a)]. The base pressure of the vacuum chamber was about $1 \times 10^{-7}$ Pa. The TiN$_{1+x}$ layers were prepared with the flow ratios of $N_2/(N_2+Ar)$ in the range of 5 and 40%. The background pressure of the vacuum chamber was kept to be about $4 \times 10^{-3}$ Pa during TiN growth. Some of the TiN$_{1+x}$ layers deposited on the sapphire substrates were exposed to NH$_3$ + H$_2$ mixed gas atmosphere at about 1000 °C, to enrich nitrogen content of the TiN$_{1+x+y}$ layers [Fig. 1(b)], which is called “nitriding” in this text. The GaN layers with about 2 µm-thickness were deposited simultaneously on both the TiN$_{1+x}$ and TiN$_{1+x+y}$ layers [Figs. 1(c) and (d), respectively] using a MOCVD (metal organic chemical vapor deposition) technique. These samples are denoted as Sample A and B, respectively. The surfaces of the as-deposited GaN layers were observed using a scanning electron microscope (SEM) and an atom force microscope (AFM). The microstructure of sapphire/TiN/GaN samples was analyzed by an X-ray diffraction (XRD) method.

3. Results and Discussion

Figure 2 shows SEM images of the GaN surface layers of Sample A (left) and Sample B (right). In Fig. 2(a), GaN of Sample A exhibits hexagons with bright contrast. The TiN$_{1+x}$ layer is not fully covered by these GaN hexagons and exhibits dark contrast in many grooves surrounded by the GaN hexagons. The area of the TiN$_{1+x}$ layer covered by the hexagons increases with increasing the $N_2/(N_2+Ar)$ ratios [Figs. 2(b) and (c)]. The growth of the continuous GaN layers is observed in Sample B [Figs. 2(d)–(f)]. The same mean thicknesses of the GaN layers of Sample A and B were measured to be about 2.0 ± 0.15 µm by a stylus surface profiler. However, in Sample A GaN hexagons with height of 3.4 ± 0.80 µm were locally observed.

Figure 3 shows surface roughness observed on the GaN surfaces of Sample A (a) and Sample B (b) as a function of $N_2/(N_2+Ar)$ ratios during TiN deposition. The surface roughness of the GaN layers of Sample B is smaller than that of Sample A. The distribution of the GaN surface roughness is also smaller in Sample B. These results indicate that nitrogen composition in the TiN buffer layers plays an
important role in growth of continuous, flat GaN layers.

Figure 4 shows a typical XRD profile of a sapphire/TiN/GaN sample. The TiN and GaN layers exhibit [111] and [0001] fiber textures, respectively. The orientation relationship among sapphire, TiN and GaN was determined using a transmission electron microscope:

\[
(11\overline{2}0)_{\text{Sapphire}} // (11\overline{1})_{\text{TiN}} // (0001)_{\text{GaN}}
\]

\[
(01\overline{1}0)_{\text{Sapphire}} // (1\overline{1}0)_{\text{TiN}} // (11\overline{2}0)_{\text{GaN}}.
\]

This epitaxial relationship was observed in all GaN samples prepared on the TiN buffer layers. Thus, the epitaxial structure does not influence the growth mechanism of continuous, flat GaN layers.

Figure 5(a) shows dependence of the \(N_2/(N_2 + Ar)\) ratios on the (111) plane spacing of the TiN buffer layers. The (111) spacing of the as-deposited TiN buffer layers has a wide scatter independent of the \(N_2/(N_2 + Ar)\) ratios. The (111) spacing of the TiN buffer layers annealed in Ar atmosphere does not have a strong dependence on the \(N_2/(N_2 + Ar)\) ratios and are similar to that estimated from the lattice parameter of stoichiometric bulk TiN. The lattice parameters of the nitrided TiN layers were found to be similar to that estimated from the lattice parameter of TiN with 53.7 at%N\(^9\), which corresponds to the upper limit of the nitrogen content of TiN. These results indicate that nitriding of the TiN buffer layers increased the nitrogen contents in the layers more efficiently compared with the TiN layers deposited in high \(N_2/(N_2 + Ar)\) ratio. Comparing Figs. 2 and 5, increasing the nitrogen contents in the TiN buffer layers plays an important role in the growth mechanism of the GaN layers. It is suggested that reduction of the TiN/GaN interfacial energy would be achieved when nitrogen contents of the TiN buffer layers become higher than 50 at%N. The similar result was obtained previously in AlN buffer layers.\(^9\) On the other hand, nitriding did not significantly reduce the grain size of TiN buffer layers and thus the growth mechanism of GaN layers cannot be explained by grain refining.

The lattice-mismatch between (0001)\(_{\text{GaN}}\) and (111)\(_{\text{stoichiometric TiN}}\) is about 6.2% and becomes large with increasing the nitrogen contents in the TiN buffer layers. The lattice-mismatch between GaN and TiN is larger than that of GaN and AlN and also that of GaN and SiC. Thus, a small lattice-mismatch may not be important for growth of continuous, flat GaN layers on the TiN buffer layers.

Figure 5(b) shows dependence of the \(N_2/(N_2 + Ar)\) ratios on half-value widths of (111)\(_{\text{TiN}}\) diffraction peaks of the TiN buffer layers. The half-value widths (\(\Delta\omega\)) of the (111)\(_{\text{TiN}}\) diffraction peaks increase with increasing the \(N_2/(N_2 + Ar)\) ratio. However, nitriding of the TiN layers after deposition provides a small change of the \(\Delta\omega\) value at a given \(N_2/(N_2 + Ar)\) ratio. This indicates that non-uniform strain introduced in the TiN buffer layers increases with increasing the \(N_2/(N_2 + Ar)\) ratios during TiN deposition.

Figure 6 shows a relationship of half-value widths between (0001)\(_{\text{GaN}}\) and (111)\(_{\text{TiN}}\) diffraction peaks. The narrower half-value width of (0001)\(_{\text{GaN}}\) was obtained when TiN with the narrower half-value width of (111)\(_{\text{TiN}}\) was used as the buffer layer. In order to obtain the continuous, flat GaN layers with small strain, the present result suggests that the \(N_2/(N_2 + Ar)\) ratios during TiN deposition should be kept as
small as possible and that the nitrogen content of the TiN buffer layer should be increased by the nitriding technique. However, few opening areas were observed in the GaN layers deposited even on the nitrided TiN buffer layers when the $N_2/(N_2 + Ar)$ ratio was reduced. Thus, choice of the moderate $N_2/(N_2 + Ar)$ ratio and nitriding of the TiN buffer layers are essential for continuous, flat GaN layer growth with small strain.

4. Conclusion

Growth of continuous, flat GaN layers was succeeded on the metallic TiN buffer layers. It was concluded that the nitrogen composition in the TiN buffer layers should be higher than that of stoichiometric TiN to grow smooth GaN layers. Nitriding of the TiN buffer layers after deposition enriched significantly the nitrogen content compared with increasing the $N_2/(N_2 + Ar)$ ratio during TiN deposition. Choice of the moderate $N_2/(N_2 + Ar)$ ratio during TiN deposition and nitriding of the TiN buffer layers are essential to grow continuous, flat GaN layers, since the reduction of the $N_2/(N_2 + Ar)$ ratio promoted few opening areas in the GaN layers.

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