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Annealing of an AlN buffer layer in N₂–CO for growth of a high-quality AlN film on sapphire

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Abstract

The annealing of an AlN buffer layer in a carbon-saturated N₂–CO gas on a sapphire substrate was investigated. The crystal quality of the buffer layer was significantly improved by annealing at 1650–1700 °C. An AlN buffer layer with a thickness of 300 nm was grown by metallocorganic vapor phase epitaxy (MOVPE), and was annealed at 1700 °C for 1 h. We fabricated a 2-µm-thick AlN layer on the annealed AlN buffer layer by MOVPE. The full widths at half maximum of the (0002)- and (1012)-plane X-ray rocking curves were 16 and 154 arcsec, respectively, and the threading dislocation density was 4.7 x 10⁶ cm⁻².

Table 1. Annealing condition of AlN buffer on sapphire using N₂–CO gas mixture

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>N₂ (atm)</th>
<th>CO (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>1550</td>
<td>0.85</td>
<td>0.15</td>
</tr>
<tr>
<td>1600</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>1650</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>1700</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>1750</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The annealing temperature was varied from 1500 to 1750 °C for 10 min during the annealing. In order to prevent desorption of the AlN layer, the partial pressure of N₂ was chosen to be 5–15% rich of the phase equilibrium condition of AlN+C and Al₂O₃+C. For annealing with partial pressures of N₂: 0.9 atm and CO: 0.1 atm at 1700 °C, the surface of AlN buffer layers became rough because of the Al₂O₃ decomposition from the interface of the AlN layer and the sapphire substrate.

Finally, high-temperature (HT) AlN layers with a thickness of HT = 2 µm were grown on the AlN buffer layers in a H₂–N₂ mixture at HT = 1450 °C under 30 Torr by the MOVPE. The growth rate of the HT-AlN layers was 1 µm/h. The crystalline quality of the AlN was characterized by X-ray diffraction analysis with asymmetric Ge(220) and symmetric Ge(440) monochromators and transmission electron microscopy (TEM), and the surface morphology was examined by atomic force microscopy (AFM).

Figure 1 shows AFM images of the AlN buffer layers with TBuf = 200, 300, and 1000 nm grown at TBuf = 1150 °C before and after annealing at TAnneal = 1650 °C. The root-mean-square (RMS) surface roughness of the AlN buffer layers increases as the thickness AlN increases. After annealing the AlN buffer layers, the surface morphologies were markedly changed, and the RMS values were improved. The surfaces of the AlN buffer layers with a thickness of 300 nm or less were smooth. In particular, the RMS value of the annealed AlN buffer layer with TBuf = 300 nm (e) was 0.49 nm, and...
atomic steps were observed on its surface. However, the surface of the AlN buffer layer with \( t_{\text{Buf}} = 1000 \) nm was rough even after annealing.

The full widths at half maximum (FWHMs) of the (0002)- and (10\( \bar{1} \)2)-plane X-ray rocking curves (XRCs) using an asymmetric Ge(220) monochromator for the AlN buffer layers with thicknesses of 100–1000 nm, which were grown at \( T_{\text{Buf}} = 1150 \) °C and annealed at \( T_{\text{An}} = 1650 \) °C, are shown in Figs. 2(a) and 2(b), respectively. Compared with those for the samples before annealing, the FWHMs of the XRCs for the samples after annealing were significantly decreased. This indicates that the crystalline quality of AlN was improved by annealing. The minimum FWHM of the (0002)-plane XRC was obtained in the sample with \( t_{\text{Buf}} = 300 \) nm and gradually increased with increasing \( t_{\text{Buf}} \). The FWHMs of the (0002)- and (10\( \bar{1} \)2)-plane XRCs for the sample with \( t_{\text{Buf}} = 300 \) nm were 68 and 421 arcsec, respectively.

Figure 3 shows AFM images of the AlN buffer layers with \( t_{\text{Buf}} = 300 \) nm grown at \( T_{\text{Buf}} = 1150 \) °C before and after annealing at \( T_{\text{An}} = 1500–1700 \) °C. The surface of the AlN buffer layer without annealing was observed to have small grains, and the RMS value was 3.1 nm. After annealing at temperatures above 1500 °C, the RMS value markedly decreased with increasing annealing temperature. The RMS value for the AlN buffer layers after annealing at \( T_{\text{An}} = 1650 \) °C was 0.49 nm. Figure 4 shows the FWHMs of the (a) (0002)- and (b) (10\( \bar{1} \)2)-plane XRCs for the AlN buffer layers after annealing at various temperatures. The dotted line shows the FWHM of the XRC for the AlN buffer layer before annealing. The FWHM of the (0002)-plane XRC decreased after annealing but increased at temperatures above 1650 °C. The FWHM of the (10\( \bar{1} \)2) plane XRC monotonically decreased with increasing annealing temperature up to 1700 °C but increased at 1750 °C. For the AlN buffer layer annealed at 1750 °C, the FWHMs of the (0002)- and (10\( \bar{1} \)2)-plane XRCs increased, and the surface became rough owing to the decomposition of AlN. It was considered that the surface roughness was caused by the thermal decomposition of the AlN buffer layer during annealing. This phenomenon has also been observed in AlN films formed by the thermal nitridation of sapphire substrates.14,19) It was found that the mechanism of crystal quality improvement was related to solid-phase reactions at annealing temperatures of 1500–1600 °C from the AFM images shown in Fig. 3 and cross-sectional TEM observations. Figure 5 shows the TEM micrographs of the AlN buffer layer on sapphire annealed at 1500 and 1550 °C. In the AlN layer annealed at 1500 °C, inverted cone-shaped domains were observed as shown in Fig. 5(a).9) The domains are in contact with one another. After annealing at 1550 °C, the AlN layer has changed to have a two-layer structure, as shown in Fig. 5(b). The boundary between the upper and the lower layers is rather flat in parts but bends in a zig-zag manner. It was confirmed that the zig-zag boundary propagates transversely in the whole area of the AlN layer. Evaluating the mutual similarity in the microstructures between Figs. 5(a) and 5(b), the upper layer seems to be formed by coalescence of the inverted cone-shaped domains. It is considered that
domain boundaries can be eliminated by the lateral growth and mutual coalescence of domains even if boundaries penetrate vertically up to the top surface. This finding will be reported elsewhere.

After annealing at 1700 °C for 1 h, a MOVPE-grown AlN buffer layer with \( t_{\text{Buf}} = 300 \text{ nm} \) at \( T_{\text{Buf}} = 1200 \text{ °C} \), we also grew an AlN film (HT-AlN) with a thickness of 2 \( \mu \text{m} \) on the annealed AlN buffer layer at 1450 °C by MOVPE. The FWHMs of the (0002)- and (1012)-plane XRCs using a symmetric Ge(440) monochromator were 16 and 154 arcsec, respectively. Figures 5(a) and 5(b) show dark-field cross-sectional TEM images of AlN under the two-beam condition with \( g = 0002 \) and \( g = 1100 \). The thickness of the TEM specimen is about 100 nm. No type-\( a+c \) or type-\( e \) dislocations can be observed in (a). Type-\( a \) dislocations can be observed in (b), and their density is estimated to be \( 5 \times 10^8 \text{ cm}^{-2} \).

In conclusion, we have clarified the effects of annealing in a carbon-saturated \( N_2-\text{CO} \) mixture on AlN buffer layers grown on sapphire substrates. The morphology and RMS value of the AlN buffer layer surface markedly changed after annealing at temperatures above 1500 °C. The FWHMs of the (1012)-plane XRCs for the AlN buffer layers significantly
decreased with increasing annealing temperature up to 1700 °C. However, for the AlN buffer layers after annealing at 1750 °C, the FWHMs of the (0002)- and (10\overline{1}2)-plane XRCs increased and the surface was rough.

A high-quality AlN layer was successfully grown on the annealed AlN buffer layer on a sapphire substrate by MOVPE. The FWHMs of the (0002)- and (10\overline{1}2)-plane XRCs were 16 and 154 arcsec, respectively. Most of the threading dislocations were of type-\(a\), and their density was \(4.7 \times 10^8 \text{ cm}^{-2}\).

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