Structure and Optical Properties of AlN Crystals Grown by Metal Nitride Vapor Phase Epitaxy with Different V/III Ratios

Luxiao Xie, Hui Zhang, Xinjian Xie, Endong Wang, Xiangyu Lin, Yuxuan Song, Guodong Liu, and Guifeng Chen*

ABSTRACT: The epitaxial aluminum nitride (AlN) crystals were grown on c-plane sapphire using high-temperature metal nitride vapor phase epitaxy at the source materials’ different molar flow ratios (V/III ratios). The effects of various V/III ratios on the surface morphology, crystalline quality, material straining, and optical properties of heteroepitaxial AlN thin films were studied using X-ray diffraction, scanning electron microscopy, Raman spectroscopy, and photoluminescence (PL). With the increase in the V/III ratio from 1473 to 7367, the substrate surface underwent changes that vary from whiskers to three-dimensional island structures, two-dimensional layered stack structures, and stacked sheet structures. Additionally, due to the presence of nanoscale pits on the substrate surface, almost all samples were tensile stressers. The PL spectra demonstrated the defect luminescence of the epitaxial films, indicating that nitrogen vacancies and oxygen impurities were the samples’ main defects.

INTRODUCTION

Compared with other group III nitride compounds, aluminum nitride (AlN) provides important physical properties for applications in optoelectronic devices. Some of these properties are the wide band gap, high thermal conductivity, high volume resistivity, low dielectric constant, strong breakdown field, and good chemical stability. AlN has a large direct band gap of about 6.2 eV, which allows it to have a broad application prospect in deep ultraviolet light-emitting diodes (UV-LEDs) and vacuum UV photodetectors. However, the low surface migration of Al atoms and lattice and thermal mismatch with the substrate, the growth of high-quality, thick, and crack-free AlN is currently facing great challenges.

As an important growth process parameter, the V/III ratio has been widely studied. For instance, Zhao et al. confirmed that the quality of the GaN epitaxial layer grown on an AlN buffer layer at low temperature can be improved by reducing the V/III ratio at the beginning of growth. Imura et al. reported that the growth rate of each crystal surface was changed by controlling the V/III ratio during the growth process, which resulted in the change in the macromorphology of the crystal and the annihilation of the screw dislocation, consequently enhancing the crystallinity of AlN. To increase the quality of thin epitaxial AlN layers grown at high temperature, Claude et al. conducted an investigative study on the effect of the V/III ratio in the gas phase, from 1.5 to 15, on the growth rate, surface morphology, roughness, and crystalline quality. Therefore, studying the relationship between the V/III ratio, the AlN structure, and optical properties is of great significance for controlling the physical properties of AlN, eventually obtaining higher quality AlN thin films. Compared with the traditional hydride vapor phase epitaxy and physical vapor transport methods, the metal nitride vapor phase epitaxy (MNVPE) method has the advantages of both methods: good UV transmittance and environmental friendliness. However, the relationship between AlN thin films prepared by the MNVPE method and the V/III ratio has been rarely reported.

In this paper, the epitaxial AlN crystals were grown on a 2 inch c-plane sapphire using high-temperature MNVPE at different V/III ratios.

EXPERIMENTAL SECTION

The MNVPE setup consists of a rotating graphite subsector heated by induction in a vertical water-cooled cold-wall reactor working at low pressure. The investigated samples were grown on a c-plane sapphire substrate. N2 (purity 5 N) and high-purity aluminum particles (purity 5 N) were used as N and Al sources, respectively. Between them, Ar gas (purity 5 N) was used as the carrier gas for Al vapor. As shown in Figure 1, the AlN crystals were prepared by a two-step process: the first step was depositing the buffer layer on the sapphire substrate for 10
min at 1200 °C, where the N₂ flow rate is 3 standard liter per minute (SLM) and the Ar flow rate is 45 standard cubic centimeter per minute (SCCM); the second step was growing the AlN crystals on the thin buffer layer for 3 h at 1550 °C, for which the gas flow and the specific growth parameters are shown in Table 1. The V/III ratio was obtained by calculating the molar flow ratio between N₂ gas and Al vapor. The Al vapor pressure at a certain temperature was calculated using the formula:

$$\log P(\text{Pa}) = -16.45 \times 10^3 / T(\text{K}) + 12.36$$

$$- 1.023 \log T(\text{K})$$

An X-ray diffractometer (Bruker D8 Discover, Germany) was used to identify crystal phases. The surface morphology of the samples was analyzed by field emission scanning electron microscopy (SEM). Raman spectra were collected at room temperature using a LabRAM-HR evolution confocal Raman spectrometer equipped with a high-resolution charge-coupled detector (CCD). Photoluminescence (PL) was also measured using a LabRAM-HR evolutionary confocal Raman spectrometer manufactured by HORIBA. The PL excitation source was a 325 nm laser beam from a helium-cadmium laser.

**DISCUSSION**

The full X-ray diffraction (XRD) patterns of the as-grown AlN crystals are shown in Figure 2. As demonstrated in the figure, no Al signal or any other impurities were detected for all samples besides the peaks for the AlN wurtzite structure [space group: P6₃mc (186)] and the sapphire substrate. When the V/III ratio was 1473, the XRD pattern exhibited multiple peaks corresponding to the crystallographic planes of (100), (002), (101), (102), (110), and (200) of AlN. The (100) plane had the highest intensity and the most dominant orientation. As the V/III ratio increased to 1573, with the exception of the sapphire substrate, only the (100) and (002) crystallographic planes of AlN remained; the (002) peak started becoming the dominant orientation. As the V/III ratio increased to 2210 and 4420, the (002) peak became the only orientation. It is well known that the full width at half-maximum (fwhm) value of the (002) plane is closely related to the density of screw dislocations; additionally, the fwhm value of the (102) plane is directly correlated to the density of edge dislocations in the XRD ω-scan rocking curves.

Figure 3 shows the plan-view and cross-sectional images of AlN layers grown at various V/III ratios ranging from 1473 to 2210.
When the ratio was 1473, there were a lot of densely distributed whiskers on sample S1’s surface. Due to their different orientations, this observation is consistent with the XRD patterns. When the V/III ratio increased to 1573, the whiskers disappeared and a three-dimensional island structure began to appear, but it does not close completely. As the V/III ratios continuously increased to 2210 and 4420, the surface was composed of a large number of hexagonal two-dimensional layers. However, as the ratio continuously increased to 7736, the two-dimensional layered structures were replaced by a large number of stacked sheet structures. As shown in all cross-sectional images of grown AlN layers, there are a large number of pits on the substrate surface; this is because the sapphire substrate was thermally decomposed to form a large number of pits at a nanometer depth in the N2 atmosphere.

Table 2. Position and fwhm of the $E_2$ (high) Mode and Residual Stress in AlN Crystals

| sample | $E_2$ (high) (cm$^{-1}$) | fwhm (cm$^{-1}$) | residual stress (MPa) |
|--------|--------------------------|-----------------|----------------------|
| S1     | 656.88                   | 4.43            | −141                 |
| S2     | 656.02                   | 13.74           | −373                 |
| S3     | 657.47                   | 15.22           | 19                   |
| S4     | 656.47                   | 70.60           | 19                   |
| S5     | 657.00                   | 15.22           | −108                 |

Figure 4. Plan-view and cross-sectional SEM images: (a,b) sample S1; (c,d) sample S2; (e,f) sample S3; (g,h) sample S4; and (i,j) sample S5.

Figure 5. Normalized Raman spectra of the AlN $E_2$ (high) phonon mode.

Figure 6. Room-temperature PL spectra of the as-grown AlN films: (a) PL spectra of samples at the different /III ratios and (b) PL spectra of samples S2 and S3 untreated and cleaned with HF.

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Figure 5 shows the normalized Raman spectra of the AlN E2 (high) phonon mode. Lughi and Clarke\textsuperscript{12} reported that the fwhm of E2 (high) in AlN is related to the phonon lifetime. Scattering caused by point defects, interface and stress gradients, and different orientations of crystals will shorten the phonon lifetime and increase the fwhm of Raman spectra. Therefore, the fwhm of E2 (high) can be used to characterize the crystal quality of AlN. As shown in Table 2, the fwhm of the E2 (high) phonon mode in the AlN films was calculated. The fwhm of the E2 (high) phonon mode of S1 is 4.43 cm\(^{-1}\), which is lower than that of the AlN bulk.\textsuperscript{13} This is because the whiskers have fewer defects and are closer to a perfect crystal. Additionally, the E2 (high) peak of AlN with a hexagonal wurtzite structure is especially sensitive to stress.\textsuperscript{14,15} It was reported that lattice mismatches, thermal mismatches, and grain polymerization will produce different stresses.\textsuperscript{16–18} The lattice mismatch ratio between AlN and the sapphire substrate is 13%, which causes compressive stress. The thermal expansion coefficient of AlN is much smaller than that of the sapphire substrate. During the sample cooling process, the sapphire crystal lattice’s shrinkage is stronger than that of the AlN crystal lattice, resulting in compressive stress. The grain agglomeration process during the growth or annealing process would generate a certain amount of tensile stress. As shown in Figure 4, the frequency shift of the E2 (high) phonon mode of AlN in the unstressed state is seen at 657.4 cm\(^{-1}\),\textsuperscript{19} where the vertical line represents the peak position of the E2 (high) phonon mode in the unstressed state. The in-plane compressive stress can be calculated using the following equation:\textsuperscript{20}

\[ \Delta \omega = k\sigma_{xx} \]

where \(\Delta \omega\) is the Raman shift of the E2 (high) peak with respect to unstressed AlN and \(k\) is the biaxial strain coefficient, 3.7 cm\(^{-1}\)/GPa. The residual stresses in the samples were roughly calculated and are listed in Table 2. Except for the samples S3 and S4 (which are almost in a stress-free state), the E2 (high) phonon mode of all samples is the blue shift of the wavelength, indicating that there is tensile stress in the samples. The existence of pits on the substrate surface of all samples releases most of the compressive stress caused by lattice mismatch and the thermal stress generated in the cooling process. Thus, the tensile stress generated in the process of grain agglomeration becomes the main source of stress. Combined with the above SEM surface analysis results, the excessive V/III ratio leads to a further grain agglomeration process, resulting in the increase in tensile stress to 108 MPa when the V/III ratio is 7367.

The room-temperature PL of samples is shown in Figure 6a. There was a weak peak centered at 374 nm (3.32 eV), a sharp peak centered at about 400 nm (3.10 eV), and a broad band ranging from 510 to 540 nm centered at about 525 nm (2.36 eV). The near-band-edge recombination\textsuperscript{21} is beyond the range of measurement and will not be discussed here. In recent decades, the luminescence properties of AlN have been studied extensively. The literature suggests that these broad luminescence bands are attributed to the formation of complexes between the nitrogen vacancy (VN) and oxygen (O) impurities or DX-like shallow donors.\textsuperscript{22–27} The S1 sample has the lowest luminescence intensity because it has more perfect crystals and fewer defects in the morphology of the whiskers. When the V/III ratio increased to 1573, the surface morphology of the sample began changing from a whisker to a film. The luminescence intensity also increased sharply, which was caused by the deterioration in crystal integrity caused by the film, the existence...
of a large number of aluminum vacancies, and other related defects. Herein, the $V_{\text{N}}$ and luminescence intensity decreased as the V/III ratio continuously increased to 7367. It is important to note that the broad band ranging from 510 to 540 nm disappeared at a V/III ratio of 4420, presumably due to the decrease in oxygen concentration.\(^{29,30}\)

To investigate the effect of oxygen impurity on PL spectra, the S2 and S3 samples were rinsed with HF solution for 1 h. As shown in Figure 6b, the intensity of the luminescence bands decreased significantly after being washed with the HF solution, even the weak peak centered at 374 nm disappeared. The HF solution can dissolve and wash away the oxides and other impurities on the surface of the samples. However, internal defects are not affected by this process. This phenomenon indicates that oxide- or hydrocarbon-related nonradiative recombination centers on the film surface play an important role in these luminescence peaks.\(^{30,31}\) Additionally, as apparent in Figure 7a–c, there is a significant $V_{\text{N}}$ in the AlN epilayer. Compared with Figure 7d, the O concentration appears to be significantly higher than that of other impurities, which is consistent with previous results.

### RESULTS

The AlN crystals were grown on sapphire by MNVPE at different V/III ratios. When the V/III ratio was low, AlN whiskers appeared on the surface of the substrate. At this time, there were multiple planes of mainly (100), and the whisker had excellent crystal quality and low PL intensity due to its crystal integrity and fewer defects. With the increase in the ratio to 1573, the plane of (002) became the dominant orientation. The substrate surface was replaced by three-dimensional islands that were not completely closed, and the PL emission intensity increased sharply. When the ratio continuously increased to 2210 and 4420, (002) became the only orientation, and the substrate surface was composed of two-dimensional layered structures. When the ratio reached 7367, the two-dimensional layered structures were replaced by a large number of sheets stacked together, and the luminescence intensity significantly decreased. Additionally, a large number of nanoscale pits on the substrate surface effectively released the thermal stress during cooling. They also released the compressive stress caused by lattice mismatch, turning the tensile stress caused by grain extrusion during crystal formation into the main source of stress for all samples. In summary, the appropriate V/III ratio can determine the quality and surface morphology of crystals and even affect their properties. The above research rules have a certain guiding significance for high-quality AlN crystal materials.

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