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Preparation of a Freestanding AIN Substrate from a Thick AIN Layer Grown by Hydride Vapor Phase Epitaxy on a Bulk AIN Substrate Prepared by Physical Vapor Transport

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The structural and optical quality of a freestanding AIN substrate prepared from a thick AIN layer grown by hydride vapor phase epitaxy (HVPE) on a bulk (0001)AIN substrate prepared by physical vapor transport (PVT) were investigated. The prepared HVPE-AIN substrate was crack- and stress-free. High-resolution X-ray diffraction ω -rocking curves of symmetric (0002) and skew-symmetric (1011) reflections had small full widths at half maximum (FWHMs) of 31 and 32 arcsec, respectively. Deep-ultraviolet optical transparency of the HVPE-AIN substrate was higher than that of the PVT-AIN substrate, which was related to lower concentrations of C, O impurities, and AI vacancy. © 2012 The Japan Society of Applied Physics

ingle-crystal AlN possesses a wide direct bandgap of about 6 eV, a high thermal conductivity, and lattice and thermal parameters that are closely matched with those of high-Al-content $Al_xGa_{1-x}N$ alloys. Therefore, bulk AlN substrates with low dislocation densities are required to fabricate high-performance $Al_xGa_{1-x}N$ -based deep-UV optoelectronic devices designed to emit deep-UV light through the substrate.

A promising method for growing bulk AlN crystals is sublimation–recondensation, which is also known as physical vapor transport (PVT).^{1–4)} This method can be used to grow AlN with low dislocation densities of less than 10^4 cm^{-2} at a high growth rate of over $100 \,\mu\text{m/h}$. However, significant decrease of optical transparency at photon energies below the bandgap is generally observed, which is thought to be caused by the presence of Al vacancies (V_{Al}), substitutional impurities, and their complexes.^{3–5}

Another promising method for preparing bulk AlN crystals is growing a thick AlN layer by hydride vapor phase epitaxy (HVPE) on foreign substrates such as SiC or sapphire and then separating the AlN layer.^{6,7)} Freestanding AlN substrates showing a steep optical transmission cutoff near the band edge have been reported. However, owing to different lattice parameters and thermal expansion coefficients between AlN and the foreign substrates, generation of high densities of dislocations (>10⁷ cm⁻²) and cracks is a severe problem. Therefore, use of AlN substrates prepared by sublimation–recondensation (hereafter, PVT-AlN substrates) as starting substrates becomes one of choices in the preparation of freestanding AlN substrates by HVPE with deep-UV transparency and low dislocation densities.

Recently, 20–30-µm-thick AlN layers have been grown by HVPE on PVT-AlN substrates.^{8,9)} However, to the best of our knowledge, no freestanding AlN substrates have been prepared from thick HVPE layers grown on PVT-AlN substrates. In this study, a freestanding AlN substrate is prepared from a thick AlN layer grown by HVPE on a PVT-AlN substrate and its properties are investigated. A homebuilt atmospheric-pressure hot-wall HVPE system⁷⁾ was used. An AlN substrate was locally heated by a heating susceptor made of a graphite element coated with pyrolytic boron nitride. The source gases were AlCl₃ and NH₃. AlCl₃ was generated in the upstream of the reactor by introducing HCl gas over high-purity Al metal (6N grade) maintained at 500 °C. AlCl₃ and NH₃ were separately introduced to the AlN substrate using a mixture of H₂ and N₂ (H₂/N₂ = 7/3) with a dew point of -110 °C as the carrier gas. The total gas flow rate was 10,000 sccm throughout the entire procedure.

A 540-µm-thick (0001)AlN substrate obtained by cutting a 10-mm-diameter circular PVT-AlN substrate^{2,10} with a dislocation density of $10^2 - 10^3$ cm⁻² into four was used. The Al-polar surface of the substrate was subjected to chemical mechanical polishing (CMP) for subsequent HVPE of AlN. Prior to being set on the heating susceptor, wet chemical etching of the substrate was performed.¹¹⁾ The substrate was then heated at 1450 °C in a gas flow consisting of the carrier gas with added NH₃ (Taiyo Nippon Sanso Super Ammonia, input partial pressure: 1.6×10^{-3} atm) in order to eliminate the surface aluminum hydroxide. After that, a 200-µm-thick AlN layer was grown at 1450 °C with AlCl₃ and NH₃ input partial pressures of 4.0×10^{-4} and 1.6×10^{-3} atm, respectively. The growth rate under these conditions was $25 \,\mu$ m/h. The substrate was subsequently cooled to room temperature (RT) while NH₃ was supplied. Finally, the PVT-AlN substrate was removed by mechanical polishing, and both sides of the HVPE layer were subjected to optical polishing to prepare a freestanding HVPE-AlN substrate.

The structural quality of AlN was characterized by Nomarski differential interference contrast (NDIC) microscopy, Raman spectroscopy, and high-resolution X-ray diffraction (HRXRD). The optical quality of AlN was characterized by optical transmittance. Secondary ion mass spectrometry (SIMS) was used to measure impurity concentration in AlN.

Figure 1 shows an NDIC microscopy image of the AlN layer grown by HVPE on the PVT-AlN substrate. The surface is very smooth and does not contain any pits or cracks. The macrostep array observed is thought to be

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Fig. 1. NDIC microscopy image of 200- μ m-thick AlN layer grown by HVPE on a PVT-AlN substrate.

formed due to the misorientation of the PVT-AlN substrate and/or thickness fluctuations in the HVPE layer. Raman spectroscopy measurements were performed at RT in the $z(x, x + y)\overline{z}$ backscattering geometry using 532 nm solidstate laser excitation. E₂ (high) phonon modes of both the PVT-AlN substrate and the HVPE-grown AlN layer were observed at 657.5 cm⁻¹ (the spectrometer was calibrated using a Ne lamp). The position of the E₂ (high) mode is sensitive to stress; it is 657.4 ± 0.2 cm⁻¹ for stress-free AlN.¹²) Thus, this result clearly demonstrates that both the PVT-AlN substrate and AlN layer grown on it by HVPE are stress free.

A freestanding AlN substrate $(3 \times 3 \times 0.114 \text{ mm}^3)$ was prepared from the HVPE-grown layer by removal of the PVT-AlN substrate, both sides optical polishing, and cutting. (Hereafter, the prepared freestanding substrate is called the HVPE-AlN substrate). In the preparation process, 40 and 46 µm of the top and bottom surfaces of the HVPE-grown layer were respectively worn away. Figure 2 shows photographs of the PVT-AlN substrate used in this study and the prepared HVPE-AlN substrate. Although the PVT-AlN substrate is amber in color, the HVPE-AlN substrate is water-clear with no macrocracks.

Figure 3 shows HRXRD ω -rocking curves of the symmetric (0002) and skew-symmetric (1011) reflections of the PVT- and HVPE-AlN substrates. The rocking curves were measured in the double-axis configuration using a Cu K α_1 X-ray source with a beam size of $1.2 \times 12 \text{ mm}^2$. For both reflections, PVT- and HVPE-AlN substrates exhibit single symmetric peaks, which indicate no mosaic structures with low-angle grain boundaries in AlN. The (0002) and $(10\overline{1}1)$ reflections of the PVT-AlN substrate have full widths at half maximum (FWHMs) of 15 and 30 arcsec, respectively; those of the HVPE-AlN substrate are similar being 31 and 32 arcsec, respectively. The reason for the slight increase in the FWHM of the (0002) reflection of the HVPE-AlN substrate is the bending of the substrate when it was attached to the sample stage of HRXRD. These results indicate that the HVPE-AlN substrate has a high structural quality and that no dislocations were generated at the PVT-AlN substrate/HVPE layer interface.

The lattice parameters of the PVT- and HVPE-AlN substrates at RT were also obtained by the Fewster method.¹³⁾ Lattice parameters were determined by HRXRD $2\theta-\omega$ scans of the (0006) and (1015) reflections performed in the tripleaxis configuration with a Ge(220) analyzer crystal in front of



Fig. 2. Photographs of AlN substrates: (a) PVT-AlN substrate used for HVPE growth and (b) HVPE-AlN substrate prepared from HVPE layer grown on PVT-AlN substrate.



Fig. 3. HRXRD ω -rocking curves of PVT- and HVPE-AlN substrates: (a) symmetric (0002) and (b) skew-symmetric (1011) reflections.

the detector (no corrections for refraction were performed). The lattice parameters of the PVT-AlN substrate were a = 3.1111 Å and c = 4.9809 Å and those of the HVPE-AlN substrate were a = 3.1111 Å and c = 4.9808 Å. The lattice parameters of the PVT- and HVPE-AlN substrates are almost identical. These results reveal that the HVPE layer grew without any distortion on the PVT-AlN substrate, which is consistent with the Raman results presented above.

The optical quality of the PVT- and HVPE-AlN substrates was assessed at RT in air using a double-beam spectrophotometer (JASCO V-7300; photometric range: 0–8.0 Abs) at normal incidence to the AlN substrates with 1-mmdiameter aperture plate. Since reflectance spectra were not available, external optical transmission spectra of the AlN



Fig. 4. External optical transmission spectra of PVT- and HVPE-AlN substrates measured at RT in air. Substrates of the same thickness and surface polish state were used.

substrates including reflection losses were obtained from the ratio of transmitted light intensity I and incident light intensity I_0 simply as I/I_0 . Here, I is influenced by thickness and surface polish state of an AlN substrate. Therefore, a PVT-AlN substrate with the same thickness as the HVPE-AlN substrate and with both sides optical-polished surfaces was prepared for comparing external optical transmittance of the PVT- and HVPE-AIN substrates. The results are shown in Fig. 4. Although the PVT- and HVPE-AlN substrates had similar structural qualities, their external optical transmission spectra were different. The PVT-AlN substrate had below-bandgap optical absorption bands at about 250-290, 340, and 450 nm. Although there is still discussion, these absorption bands are attributed to presence of substitutional carbon impurity (C_N), presence of isolated V_{Al}, and the transition from V_{Al} to substitutional oxygen impurity (O_N), respectively.^{3,5)} In contrast, although the HVPE-AlN substrate still had a weak optical absorption band at 450 nm, it had larger external optical transmittance than the PVT-AlN substrate at the wavelengths below 600 nm, and showed a steep optical transmission cutoff at 206.5 nm (6.00 eV). The external optical transmittance in the deep-UV range of 220-300 nm was above 63%, which suggests that the HVPE-AlN substrate is a promising candidate as a substrate for fabricating deep-UV optoelectronic devices on it.

To obtain further information, impurity concentrations in the PVT- and HVPE-AlN substrates were measured by SIMS; results are listed in Table I. The PVT-AlN substrate contains large quantities of C, O, and Si impurities; of these, C has the highest concentration. In contrast, the impurity concentrations of C, O, and Si in the HVPE-AlN substrate become remarkably lower. In particular, the C and O concentrations were below the background levels of the SIMS system. Therefore, it is understood that the decrease of

 Table I. Impurity concentrations in PVT- and HVPE-AlN substrates (atoms/cm³) measured by SIMS. The B concentration in the PVT-AlN substrate was not measured.

	Н	В	С	0	Si	Cl
PVT-AlN	${<}5\times10^{17}$		3×10^{19}	2×10^{19}	5×10^{18}	$<3 \times 10^{14}$
HVPE-AlN	$<5 imes 10^{17}$	$5 imes 10^{15}$	$<\!2 imes 10^{17}$	$< 4 \times 10^{17}$	2×10^{17}	1×10^{15}

the below-bandgap optical absorption bands of the HVPE-AlN substrate, in other words, increase of external optical transmittance of the HVPE-AlN substrate, is brought about by the lower concentrations of C, O impurities, and V_{Al} in the HVPE-AlN substrate.

In summary, a 114-µm-thick freestanding AlN substrate was prepared from an HVPE layer grown on a PVT-AlN substrate. The prepared HVPE-AlN substrate was waterclear and free of stress and cracks. HRXRD ω -rocking curves of the symmetric (0002) and skew-symmetric (1011) reflections of the HVPE-AlN substrate showed single symmetric peaks with FWHMs of 31 and 32 arcsec, respectively. The HVPE-AlN substrate had larger external optical transmittance in the deep-UV range than the PVT-AlN substrate, which was brought about by the lower concentrations of C, O impurities, and V_{Al} in the HVPE-AlN substrate.

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