Influence of high-temperature processing on the surface properties of bulk AlN substrates

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Deep-level luminescence at 3.3 eV related to the presence of Al vacancies (V_{Al}) was observed in room temperature photoluminescence (RT-PL) spectra of homoepitaxial AlN layers grown at 1450 °C by hydride vapor-phase epitaxy (HVPE) and cooled to RT in a mixture of H_2 and N_2 with added NH_3 . However, this luminescence disappeared after removing the near surface layer of AlN by polishing. In addition, the deep-level luminescence was not observed when the post-growth cooling of AlN was conducted without NH_3 . Secondary ion mass spectrometry (SIMS) studies revealed that although the point defect

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density of the interior of the AlN layers remained low, the near surface layer cooled in the presence of NH_3 was contaminated by Si impurities due to both suppression of the surface decomposition by the added NH_3 and volatilization of Si by decomposition of the quartz reactor walls at high temperatures. The deep-level luminescence reappeared after the polished AlN wafers were heated in presence of NH_3 at temperatures above 1400 °C. The surface contamination by Si is thought to generate V_{Al} near the surface by lowering their formation energy due to the Fermi level effect, resulting in deep-level luminescence at 3.3 eV caused by the shallow donor (Si) to V_{Al} transition.

Keywords: A1. Impurities, A2. Point defects, A3. Hydride vapor phase epitaxy, B1. Nitrides, B1. Quartz, B2. Semiconducting aluminum compounds

1. Introduction

Bulk AlN substrates with low dislocation density and UV-C optical transparency are needed for the fabrication of high performance AlGaIn-based UV-C light emitting diodes (LEDs) [1,2]. In addition, conductive AlN substrates are crucial for the exploitation of the high bandgap energy of AlN (~6 eV) in power electronic devices [3,4]. Therefore, there have been many reports on the preparation of bulk AlN substrates by physical vapor transport (PVT) [5-8] and hydride vapor-phase epitaxy (HVPE) [9,10].

It is widely known that AlN boules with low dislocation density ($< 10^4 \text{ cm}^{-2}$) can be grown by PVT [5,11,12]. However, the generation of unwanted optical absorption bands below the bandgap due to the introduction of various impurities (C, O, Si), Al vacancies (V_{Al}), and their complexes limits the utility of this material [7,8,12-14]. On the other hand, HVPE can produce high-purity bulk AlN substrates with UV-C optical transparency [10]. However, one serious problem with HVPE is the generation of cracks and dislocations in AlN layers grown heteroepitaxially on foreign substrates such as SiC or sapphire because of lattice and thermal expansion mismatches between the AlN and the substrate [9,15-19].

In a previous study, our group has demonstrated the preparation of the first practical bulk AlN substrates from thick AlN layers grown homoepitaxially on PVT-AlN substrates by HVPE [10]. This approach allowed the preparation of high-purity bulk AlN substrates with both low dislocation density and excellent UV-C optical transparency. UV-C LEDs with a long lifetime and a high output power were successfully fabricated on these HVPE-AlN substrates [2,20]. However, AlN substrates were prepared from thick, HVPE-grown AlN layers through removal of the PVT-AlN substrate and subsequent polishing to remove surface roughness generated during the HVPE growth. A similar hybrid approach was taken for HVPE growth of GaN on high quality but low purity ammonothermal GaN substrates [21]. In HVPE of GaN, it is known that the top GaN surface is frequently contaminated with O and Si

impurities, although there is no such contamination inside the grown layers [22]. Therefore, similar surface contamination could be expected in the HVPE of AlN. However, to our knowledge, the impurity contamination of the AlN crystal surfaces grown by any method has not been investigated comprehensively. As in the case of boron contamination [23], understanding the role of all impurities involved may lead to improved growth process for bulk AlN substrates. In this study, the mechanism of unintentional contamination of the AlN surface during post-growth cooling and pre-growth heating, and the influence of this contamination on the optical properties is investigated.

2. Experimental details

A high-temperature HVPE system composed of an atmospheric pressure horizontal hot-wall quartz reactor and a local heating susceptor was used [10]. AlN was grown at 1450 °C on chemo-mechanically polished Al-polar surfaces of PVT-AlN(0001) substrates produced by HexaTech (dislocation density $< 10^3 \text{ cm}^{-2}$) using AlCl_3 and NH_3 (Super Ammonia, Taiyo Nippon Sanso) as precursors. AlCl_3 was generated in the upstream region of the reactor, which was maintained at 500 °C by introducing HCl gas over 6N-grade Al pellets [24]. A gas mixture of H_2 and N_2 (mole fraction of hydrogen $F^\circ = 0.70$) was used as a carrier gas. The input partial pressures of AlCl_3 and NH_3 during AlN growth were 4.0×10^{-4} and 1.6×10^{-3} atm, respectively, which gave an AlN growth rate of 25 $\mu\text{m/h}$. The total gas flow rate was fixed at 10 slm.

First, the effect of the flowing gas during the post-growth cooling process on the properties of the as-grown AlN surface was investigated. A 200- μm -thick homoepitaxial layer was grown at 1450 °C and then cooled to room temperature (RT) at a rate of 5 °C/min in an H_2/N_2 carrier gas with added NH_3 (input partial pressure: 1.6×10^{-3} atm) to prevent decomposition of the AlN surface [25]. For comparison, another sample was prepared with

the same procedure, but the post-growth cooling was performed without the NH_3 addition.

Second, the surface contamination of HVPE-grown AlN layers heated in an H_2/N_2 carrier gas with and without the NH_3 supply was investigated. For this purpose, HVPE-AlN layers were grown at 1450 °C on PVT-AlN substrates as described above, but the substrates were cooled to RT without the NH_3 supply to expose the AlN surface to the H_2 etching. Then, the substrates were heated again to 1450 °C in the carrier gas with or without NH_3 (input partial pressure of NH_3 : 1.6×10^{-3} atm), and the growth of several- μm -thick AlN layers was performed again to form an HVPE-AlN/HVPE-AlN “interface”.

Third, the influence of the heat treatment atmosphere and temperature was investigated using HVPE-AlN substrates prepared from HVPE-grown layers with optical-grade polishing of the surface. The substrates were heated to temperatures of 1350-1450 °C in the carrier gas with and without the NH_3 supply (input partial pressure of NH_3 : 1.6×10^{-3} atm). The substrates were maintained at each temperature for 1 min and then cooled to RT at a rate of 5 °C/min.

The optical properties of the AlN surfaces were evaluated by RT photoluminescence (RT-PL) using a pulsed ArF excimer laser ($\lambda = 193$ nm) operated at 10 Hz. The surface morphology of the HVPE-grown layers was investigated by tapping-mode atomic force microscopy (AFM). The type and concentration of impurities at the HVPE-AlN/HVPE-AlN interface were examined by secondary ion mass spectrometry (SIMS). Thermodynamic analysis of the decomposition of the quartz glass reactor walls was also performed to elucidate the mechanism of AlN surface contamination.

3. Results and discussion

RT-PL spectra of thick homoepitaxial AlN layers cooled from 1450 °C to RT in the carrier gas with and without the NH_3 supply are shown in Fig. 1. Irrespective of the NH_3 supply

during the post-growth cooling or surface finish, a near band-edge (NBE) emission was observed at 5.94 eV. In addition, high-resolution X-ray diffraction ω -rocking curves of the symmetric (0002) and skew-symmetric (1011) reflections of these layers showed narrow full width at half maximum (FWHM) values of about 20 and 30 arcsec, respectively; these values were similar to those of the PVT-AlN substrates used in this study. It was found that as-grown AlN layers cooled with added NH₃ showed an intense and broad deep-level luminescence centered around 3.3 eV (Fig. 1(a)). This deep-level luminescence almost disappeared after 40 μ m of the surface was removed by polishing (Fig. 1(b)). It has been reported that the deep-level luminescence of AlN around 3.3 eV was due to the recombination of shallow donors and V_{Al} or a related V_{Al} complex with oxygen or silicon [26-28]. This suggested that additional point defects were introduced/generated near the top surface of the AlN layer during the post-growth cooling in the carrier gas with added NH₃, however, the depth to which these point defects were introduced has not been investigated. Furthermore, it was found that insignificant deep-level luminescence was observed for as-grown AlN surfaces that underwent post-growth cooling without the NH₃ addition (Fig. 1(c)). The underlying mechanism for these observations will be examined in the following paragraphs.

Fig. 2 shows AFM images of as-grown surfaces of the AlN layers shown in Figs. 1(a) and 1(c), i.e., cooled to RT in the carrier gas with and without the NH₃ supply, respectively. The AlN layer cooled with added NH₃ (Fig. 2(a)) had a smoother surface than the sample cooled without added NH₃ (Fig. 2(b)). The root-mean-square roughness (R_{rms}) values of these surfaces were 0.20 and 0.35 nm, respectively. These results indicated that the surface was roughened during the cooling in the carrier gas without the NH₃ supply due to the following equilibrium reaction:

where n is an integer between 0 and 3. We have reported previously that heating of AlN in

flowing H_2 caused appreciable etching of AlN at temperatures above 1200 °C, however, the addition of NH_3 into the flowing H_2 prevented this etching even at 1400 °C, due to the shift of the equilibrium reaction (1) to the left [25]. Therefore, the AFM image shown in Fig. 2(a) depicts a surface that was preserved after the AlN growth at 1450 °C, whereas Fig. 2(b) shows a surface that was etched by H_2 during post-growth cooling. A comparison of these results with those shown in Fig. 1 suggests that it is likely that the contamination and introduction of V_{Al} or related complexes at the AlN surface occur when NH_3 is added to the carrier gas during post-growth cooling because the addition of NH_3 stabilizes the AlN surface. On the contrary, the contamination and introduction of V_{Al} is absent when post-growth cooling is performed in the carrier gas without the NH_3 supply and the surface is continuously etched by H_2 . Using the rate of AlN etching by H_2 reported in Ref. 25, the etch depth of the AlN surface during post-growth cooling from 1450 °C to RT without added NH_3 was estimated to be roughly 120 nm, indicating that the point defects introduced/generated during the post-growth cooling with added NH_3 were no deeper than the etch depth estimate.

The influence of the NH_3 addition to the carrier gas during high-temperature processing on AlN surface contamination was investigated by analyzing the HVPE-AlN/HVPE-AlN “interfaces”. Fig. 3 shows SIMS depth profiles of O and Si near the interfaces formed by growing AlN layers on HVPE-AlN layers heated to 1450 °C with and without the NH_3 supply in the carrier gas. The concentrations of other impurities (H, B, C, and Cl) did not show fluctuations at either interface and were similar to those reported in Ref. 10. The O and Si concentrations were higher at the interface: the peak concentrations of O at interfaces prepared with and without an NH_3 supply were similar (4×10^{18} atoms/cm³), whereas the Si concentration at the interface was higher when the HVPE-AlN was heated in a carrier gas with the added NH_3 ($[Si] = 5 \times 10^{18}$ atoms/cm³) than when the HVPE-AlN was heated without NH_3 ($[Si] = 1.5 \times 10^{17}$ atoms/cm³). The contamination of the interface (AlN surface

before regrowth) by O and Si was attributed to the decomposition of the quartz glass reactor walls at high temperatures during AlN heating (cooling) before (after) HVPE growth by an analogous process responsible for the contamination of GaN surfaces [22]. This process will be thermodynamically assessed in the next paragraph. Because the formation energy of V_{Al} or related complexes at the AlN surface is drastically lowered by contamination of the AlN surface with relatively shallow donors (Si) due to the Fermi level effect [29,30], the deep-level luminescence centered around 3.3 eV, and shown in Fig. 1, most likely originated from the introduction of V_{Al} or related complexes due to the accumulation of Si contamination at the surface because the added NH_3 stabilized the AlN surface during the high temperature processing.

In order to further clarify the mechanism of AlN surface contamination, thermodynamic analysis of the decomposition of the quartz glass reactor walls of the HVPE system was performed. Here, an analysis of the reactions between the quartz glass (SiO_2) and H_2 in the carrier gas is described. The following two simultaneous reactions are considered:

The decomposition of SiO_2 into gaseous SiO and O_2 was not included because the equilibrium constant of that reaction is negligible. The following five gaseous species are thought to be present in the HVPE reactor: SiH_4 , SiO , H_2O , H_2 , and N_2 . The respective equilibrium equations for reactions (2) and (3) are

$$K_2(T) = \frac{P_{SiH_4} \cdot P_{H_2O}^2}{P_{H_2}^4}, \quad (4)$$

$$K_3(T) = \frac{P_{SiO} \cdot P_{H_2O}}{P_{H_2}}, \quad (5)$$

where the $K_i(T)$'s represent the temperature-dependent equilibrium constants, which can be

calculated from thermochemical tables [31] and the P_i 's are the equilibrium partial pressures of the gaseous species over the quartz reactor walls. The activity of SiO_2 is assumed to be 1.

The equilibrium constants were fitted to the functions:

$$\log_{10} K_2(T) = 13.0 - 2.45 \times 10^4 / T - 4.28 \cdot \log_{10} T, \quad (6)$$

$$\log_{10} K_3(T) = 20.5 - 3.01 \times 10^4 / T - 2.90 \cdot \log_{10} T. \quad (7)$$

The total pressure in the HVPE reactor (P_{tot}) is constant, giving the following equation:

$$P_{\text{tot}} = P_{\text{H}_2}^{\circ} + P_{\text{N}_2}^{\circ} = P_{\text{SiH}_4} + P_{\text{SiO}} + P_{\text{H}_2\text{O}} + P_{\text{H}_2} + P_{\text{N}_2}, \quad (8)$$

where $P_{\text{H}_2}^{\circ}$ and $P_{\text{N}_2}^{\circ}$ represent the input partial pressures of H_2 and N_2 , respectively. As the number of hydrogen and nitrogen atoms in the reactor is constant, the following constraint is obtained:

$$F^{\circ} = \frac{P_{\text{H}_2}^{\circ}}{P_{\text{H}_2}^{\circ} + P_{\text{N}_2}^{\circ}} = \frac{2P_{\text{SiH}_4} + P_{\text{H}_2\text{O}} + P_{\text{H}_2}}{2P_{\text{SiH}_4} + P_{\text{H}_2\text{O}} + P_{\text{H}_2} + P_{\text{N}_2}}. \quad (9)$$

Furthermore, the stoichiometric relationship associated with the SiO_2 decomposition gives

$$P_{\text{SiH}_4} + P_{\text{SiO}} = \frac{1}{2}(P_{\text{SiO}} + P_{\text{H}_2\text{O}}). \quad (10)$$

The equilibrium partial pressures of the gaseous species in the HVPE reactor can be calculated by solving a set of simultaneous equations (4), (5), (8)-(10).

The calculated equilibrium partial pressures of the gaseous species over the quartz glass reactor walls as a function of temperature are shown in Fig. 4. A mixed carrier gas of H_2 and N_2 with a mole fraction of hydrogen $F^{\circ} = P_{\text{H}_2}^{\circ} / (P_{\text{H}_2}^{\circ} + P_{\text{N}_2}^{\circ}) = 0.70$ is introduced into the atmospheric-pressure system. It can be seen that the equilibrium partial pressures of SiO and H_2O increase with increasing temperature. For example, at 1450 °C, these partial pressures reach 5.7×10^{-4} and 5.7×10^{-4} atm, respectively. Note that the vapor pressure of SiO [32] is higher than the equilibrium partial pressure of SiO , which may indicate an enhanced

decomposition of the quartz walls. Nevertheless, the calculated equilibrium partial pressure of SiO is comparable to that of AlCl₃ during the AlN growth and is thus a likely source of surface contamination. Based on their studies with Ar carrier gas, Usikov et al. suggested a reaction between the quartz walls and NH₃ as the source of Si and O contamination of the GaN surfaces [22], however, reactions of SiO₂ with H₂ are still present due to the pyrolysis of NH₃ even if the carrier gas contains no H₂ [33]. Therefore, the contamination of the AlN surface by Si during cooling (heating) in the carrier gas with added NH₃ is thought to be due to both etching of the quartz glass reactor walls by H₂ and suppression of the AlN surface etching by the added NH₃, as shown in Fig. 3.

Finally, the influence of heat-treatment temperature on deep-level luminescence was investigated. Specifically, surface contamination with Si and V_{Al} or related complexes formation on the AlN surface were examined. Fig. 5 shows RT-PL spectra of polished HVPE-AlN substrates before and after 1 min of heat treatment at 1350, 1400, and 1450 °C in the carrier gas with and without added NH₃. Although the PL spectra of AlN substrates heated to 1350 °C with and without added NH₃ were almost identical to that of the original AlN substrate, the deep-level luminescence appeared at a similar position to that observed for the as-grown HVPE-AlN layers cooled in the carrier gas with added NH₃ when the AlN was heat-treated at or above 1400 °C with added NH₃. In contrast, the deep-level luminescence was not observed for any temperature when the heat treatment was performed without NH₃. Because the equilibrium partial pressures of SiO at 1350 and 1450 °C do not differ significantly, as shown in Fig. 4, the rapid increase in the deep-level luminescence intensity of AlN heated at or above 1400 °C with added NH₃ indicates the onset of Si diffusion and the introduction of V_{Al} at temperatures above 1400 °C. Therefore, when AlN substrates are heated to more than 1400 °C, special attention should be paid to the flowing gas, surface etching/contamination, and possible generation of Al vacancies at the surface.

4. Conclusions

The origin of deep-level luminescence around 3.3 eV in RT-PL spectra of homoepitaxial AlN layers grown by HVPE on PVT-AlN substrates at 1450 °C was investigated. The deep-level luminescence was observed when the AlN layers were cooled in presence of NH₃, but the luminescence disappeared after surface polishing or when the AlN layers were cooled without NH₃. It was found that the surface contamination by Si volatilized from the quartz reactor walls by H₂ was greatly increased when etching of the AlN surface was suppressed by added NH₃. Si contamination of the AlN surface led to the introduction of compensating V_{Al} or related complexes at high temperatures via the Fermi level effect, and the recombination of the shallow donor (Si) and V_{Al} resulted in an emission at 3.3 eV. Heating of polished HVPE-AlN substrates that did not feature deep-level luminescence revealed that the necessary conditions for the reappearance of this luminescence were a temperature > 1400 °C and presence of NH₃ in the carrier gas.

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Figure captions

Fig. 1. RT-PL spectra of thick homoepitaxial AlN layers cooled from 1450 °C to RT after HVPE growth (a), (b) with and (c) without NH₃ added to a mixed carrier gas of H₂ and N₂. Spectra (a) and (c) were obtained from as-grown surfaces of 200-μm-thick AlN layers. Spectrum (b) was obtained from the same sample as (a) but with 40 μm of the surface polished to optical grade before the PL measurement.

Fig. 2. AFM images ($2 \times 2 \mu\text{m}^2$) of the as-grown surfaces of HVPE-AlN layers cooled from 1450 °C to RT in a mixed carrier gas of H₂ and N₂: (a) with added NH₃ and (b) without added NH₃.

Fig. 3. SIMS depth profiles of O and Si at the HVPE-AlN/HVPE-AlN interface. HVPE-AlN layers grown at 1450 °C and cooled to RT without added NH₃ were used for the growth of AlN: (a) with added NH₃ and (b) without added NH₃ in a mixed carrier gas of H₂ and N₂ while increasing the temperature to 1450 °C for AlN growth.

Fig. 4. Equilibrium partial pressures of gaseous species over quartz glass reactor walls as a function of temperature when a mixed carrier gas of H₂ and N₂ ($\text{H}_2/\text{N}_2 = 7/3$) is introduced into the atmospheric-pressure reactor. The vapor pressure of SiO, $P_{\text{SiO}}^{\text{V}}$, is also shown as a dashed line.

Fig. 5. RT-PL spectra of surface-polished HVPE-AlN substrates obtained before and after 1 min of heat treatment at temperatures of 1350-1450 °C in a mixed carrier gas of H₂ and N₂: (a) with added NH₃ and (b) without added NH₃ during the entire heat treatment process.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.