Title

Single Crystal Growth of Aluminum Nitride on 6H-SiC substrates by an open-system sublimation method

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Abstract

Single crystalline aluminum nitride (AlN) has successfully been grown on 6H-SiC (0001) substrates by sublimation using an open-system crucible at 2273 K within 30 hrs. The thickness of the AlN single crystal layer is about 1 mm. The dislocation density in the vicinity of the crystal surface has been calculated to be less than 10^7 cm^{-2} from transmission electron microscopy observation and etch pit density measurement of the crystal. Single crystal growth of AlN has been carried out by varying supersaturation of Al vapor and employing on-axis and off-axis SiC substrates. Supersaturation of Al vapor has critically influenced the crystalline quality and morphology, while it has not affected the growth rate so much. Thus, precise control of supersaturation is a key to ensuring the quality of AlN single crystals. The quality of the crystals grown on off-axis SiC substrates is superior to that grown on on-axis SiC substrates. Moreover, the quality has been improved as the thickness of the crystals has increased.

Keywords

A2. Growth from vapor; A2. Single crystal growth; B1. Aluminum nitride

1. Introduction

Aluminum Nitride (AlN) is characterized by its extra-wide band gap energy (6.28 eV) [1] that is the largest among semiconductors and has superior properties of electric breakdown field ($1.17 \times 10^7 \text{ V cm}^{-1}$) [2], electron mobility ($1100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [2], and thermal conductivity ($3.4 \text{ W cm}^{-1} \text{ K}^{-1}$) [3]. Therefore, AlN-based III-nitride semiconductors are expected to be used as energy-saving, high-voltage, and high RF power electronic devices.

AlN is a direct semiconductor, suitable for light emitting devices. Recently, AlN-based light-emitting diodes (LED) with wavelengths of the deep-ultraviolet (DUV) region were demonstrated [4, 5]. Therefore, AlN-based DUV LEDs and laser diodes (LD) will go into practical use in the near future. DUV LEDs are expected to grow in use for general illumination, decomposition and sterilization of chemicals containing hazardous substances, and LDs for micromachining and medical treatments.

It is necessary to grow epitaxial layers with high crystalline quality to take advantage of the excellent potential of AlN-based semiconductors. Single crystalline AlN substrates are desirable for this purpose because substrates for the epitaxial layers must have good lattice matching with AlN-based semiconductors. However, so far, few reports have been published on semiconductor-grade AlN substrates [6, 7].

At atmospheric pressure, AlN does not melt but sublimes by heating. Consequently, AlN crystal growth with Al-nitrogen melt cannot be carried out at the pressure. Growth techniques of AlN single crystals are listed as follows: liquid phase epitaxy with the flux method [8, 9], hydride vapor phase epitaxy [10-12], nitridation of sapphire [13, 14], and so on. The sublimation method [15-21] is the most promising technique for the production of AlN crystals among them because the method has been established for the growth of bulk SiC with high-crystalline quality [22, 23], and the growth rate is relatively high compared to those by other methods. This method is used in a quasi-closed crucible, where sublimates from the source material placed in the hotter zone of the crucible are transferred to the colder zone by diffusion to achieve seeded crystal growth. For AlN, the following chemical reaction formulas are applied to the sublimation of the source and the crystal growth, respectively.

As shown in eq. (2), the AlN growth reaction involves nitrogen gas, N_2 . Thus, we employed an open-system crucible to introduce N_2 into the crucible. For a closed-system sublimation method, AlN is crystallized from sublimates based on a stoichiometric Al/ N_2 ratio from the source material. However, the ratio of Al to N_2

cannot be changed. On the other hand, for an open system, the ratio can be changed by controlling the sublimation rate of the source and the N₂ flow rate. The open system needs relatively higher consumption of the source material compared to the closed system [24], but the former system helps understand the effects of parameters on crystal growth and provides extended degrees of freedom in the selection of growth conditions. Once a single crystal growth condition is established, it is possible to control the parameters for a high degree of reproducibility.

This paper presents the results of single crystal growth of AlN on SiC substrates by sublimation with an open-system crucible. The aim of this study is growing high quality AlN single crystals employing this method. For this goal, we have investigated the effects of the Al vapor supersaturation calculated from an Al/N₂ ratio in gas phase and the on-axis and off-axis SiC substrates on the morphology and crystalline quality of AlN crystals.

2. Experimental procedure

2.1. Control of supersaturation in AlN sublimation growth

According to the Gibbs' phase rule, when the reaction (2) is in equilibrium, the degree of freedom is unity under the condition that the temperature and the ambient pressure are constant. The degree of freedom is either an Al partial pressure or N₂ partial pressure, and then one is automatically fixed when the other is determined. Thus, only the supersaturation of Al vapor of the reaction (2) is considered here.

The supersaturation of chemical species of i , σ_i is defined as follows:

$$\sigma_i = \frac{P_i - P_{i,e}}{P_{i,e}} \quad (3)$$

where P_i is the actual partial pressure of i , and $P_{i,e}$ the equilibrium partial pressure of i .

The equilibrium Al partial pressure, $P_{Al,e}$ of the reaction (2) is represented by the following equation:

$$P_{Al,e} = P_{N_2}^{-1/2} \exp\left(\frac{\Delta G_{(3)}^\circ}{RT_G}\right) \quad (4)$$

where $\Delta G_{(3)}^\circ$ is the standard Gibbs energy change of the reaction (2), P_i is the partial pressure of species of i , R is the gas constant, and T_G is the crystal growth temperature. Since P_{Al} and P_{N_2} are controlled by the sublimation rate of the AlN source and the flow rate of N₂, σ_{Al} is obtained from the eq. (3). Then, to change σ_{Al} , AlN

crystals are grown while the sublimation rate of AlN is fixed by keeping the source temperature constant and controlling the N₂ flow rate into the crucible. By extrapolating the data from [25], $\Delta G_{(3)}^\circ$ at a crystal growth temperature of 2273 K is obtained.

2.2. Crystal growth method and evaluation

AlN crystals have been grown in an RF-induction furnace with a graphite crucible. Si-face, on-axis and off-axis (0001) 6H-SiC substrates are employed as seed crystals.

Figure 1 illustrates the scheme of the open-system crucible used for sublimation growth of AlN. AlN powder in a graphite container is set at the bottom of the crucible. SiC substrates are fixed on a graphite susceptor, which is held by the crucible lid. The crucible is heated to an predetermined temperature, and the sublimates from the source are mixed with N₂ through an inlet into the crucible using a mass flow controller. The gas mixture is then transported to the SiC seed and condensed to form AlN crystals. The exhaust gas is flown out of the crucible through the outlet.

Growth and sublimation temperatures are controlled by monitoring temperatures on the back of the susceptor and on the bottom of the crucible by dual-color infrared pyrometers, respectively. Crystal growth is performed at 2273 K for 1.5~30 h. The ambient pressure is kept constant by using a pressure controller with a butterfly valve.

The surface and cross section of the grown crystals are observed with optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The crystalline quality is evaluated by X-ray rocking curves (XRCs) of AlN (0002) and (10 $\bar{1}$ 0) using the CuK α line. The dislocation density is obtained by measurements of the number of dislocations in cross-sectional TEM images and etched pits with NaOH-KOH melt.

3. Results and Discussion

3.1. Single crystal growth of AlN on-axis 6H-SiC substrates

The conditions for sublimation growth are shown in Table 1. Here, on-axis 6H-SiC substrates with the size of 5 mm $\times$ 5 mm $\times$ 0.38 mm were used. Figure 2 shows OM and SEM images of SiC surfaces after AlN crystals were grown under $\sigma_{\text{Al}} = 0.079 \sim 1.1$ at 2273 K for 1.5 h. Polycrystalline grains were grown at σ_{Al} exceeding 1.1. Transparent-colorless layers with smooth surfaces were obtained in the range of σ_{Al} from 0.23 to 0.71. For σ_{Al} below 0.079, the AlN layer grew partially on the surface of

the SiC substrate. The regions without being covered with AlN are carbonized. From this result, it is shown that morphology of AlN grown on the substrates highly depend on σ_{Al} .

As shown in Fig. 2, cracks appeared in growth layers and ran in a certain direction. These cracks were generated during the cooling process because of the difference between the two thermal expansion coefficients of AlN and SiC.

Table 2 shows the full-width at half-maximum (FWHM) of the XRCs of the AlN (0002) and (10 $\bar{1}$ 0) measured on the AlN layers grown at $\sigma_{\text{Al}} = 0.23 \sim 0.71$ at 2273 K for 1.5 h. The values of FWHM depended on σ_{Al} , and the narrowest peaks of the (0002) and (10 $\bar{1}$ 0) are 650 arcsec and 180 arcsec, respectively. From these results, it is found that the crystalline quality improves when the supersaturation of the Al is lowered within the range where AlN single crystals can be obtained.

Figure 3 shows an OM image of a cross section of the AlN layer grown on SiC under $\sigma_{\text{Al}} = 0.23$ at 2273 K for 1.5 h. This figure illustrates that the thickness of the layer is 50 μm , which results in a growth rate of 35 $\mu\text{m h}^{-1}$ under the condition. From cross-sectional observation of the layers grown in a σ_{Al} range of 0.23 to 0.71, the single crystal thickness of each of the layers has been found to be almost 50 μm . This result indicates that the effects of σ_{Al} on the growth rate are little. As shown in Fig. 2, the range of the Al supersaturation is narrow when AlN single crystals grow on SiC substrates at 2273 K. Therefore, it is considered that the Al supersaturation has little effect on the growth rate of single crystalline AlN under this condition.

Figure 4 shows a TEM image of the cross section surface of the AlN/SiC interface of the sample. The interface is sharp and clearly separated. Consequently, the solid-state reaction rate between AlN and SiC has been found to be very low even at a high temperature of 2273 K. From this result, it is expected that the thickness of AlN grown on SiC at the temperature is proportional to the time.

3.2. Crystalline quality of AlN grown on off-axis 6H-SiC substrates

Figure 5 shows an OM image of the surface of AlN grown on off-axis SiC under $\sigma_{\text{Al}} = 0.23$ at 2273 K for 1.5 h. The growth mode is step flow along the $[11\bar{2}0]$ direction and the crystallites grow from the steps introduced by formation of off-axis angle. Cracks appeared in a certain direction in this sample as well. From the result of the cross-sectional observation, it is found that the thickness of the layer is 50 μm , the same as that of the layer grown on the on-axis SiC substrate under the same conditions.

FWHM of the XRCs of AlN (0002) and (10 $\bar{1}$ 0) taken from the sample,

shown in table 2, were 540 arcsec and 160 arcsec, respectively, which were narrower than that of the crystals grown on the on-axis SiC. Accordingly, this result indicates that using the use of the off-axis SiC substrates improves the quality of the crystals. The reason for the improvement of the crystalline quality using off-axis substrates is presumably that the growth mode is step flow from the initial stage, so the crystallographic orientation is uniform.

3.3. Crystal growth of millimeter-sized AlN and measurement of dislocation density

Figure 6 shows the appearance and the fracture of AlN grown on off-axis SiC with a surface area of $10 \times 10 \text{ mm}^2$ under $\sigma_{\text{Al}} = 0.23$ at 2273 K for 30 h. Amber-colored transparent AlN crystals grew on SiC, and the thickness exceeded 1 mm. The thickness is in good agreement with the value estimated from the growth rate and time under this condition. Although single crystalline AlN with a thickness exceeding 1 mm was obtained, cracks still appeared. In order to prevent cracks, AlN single crystals on SiC substrates need to grow thicker, so that they can endure the stress originated from the difference between the two thermal expansion coefficients of AlN and SiC. The amber coloration of AlN crystals has been found to be caused by the incorporation of oxygen into the crystals [20]. The oxygen partial pressure in the growth system needs to be reduced, for example, by setting oxygen removable substances in the crucible.

Figure 7 shows TEM images of cross sections of the AlN growth layer presented in Fig. 6(b). It is recognized that black dots and black lines extending to the growth direction exist in the AlN layer in Fig. 7(a) and (b). The dots are dislocation loops, and the lines are edge or screw dislocations. The dislocation density was calculated by dividing of the total number of dislocations by TEM image areas. In the calculation, black dots on the AlN/SiC interface, which are misfit dislocations, were excluded. The results of the dislocation density are presented in table 3. The dislocation density in the vicinity of the surface wasn't obtained by TEM observation. Then, the surface of the sample was etched with eutectic NaOH-KOH melt after polishing, and the etch pit density was measured. Wet chemical etching was performed at 350°C for 90 sec by referring to [26, 27]. Figure 8 shows an SEM image of the surface after etching. The etch pit density was calculated to be $1.5 \times 10^6 \text{ cm}^{-2}$.

Based on these findings, it is understood that the dislocation density decreases as the thickness of the AlN layer increases. Although the chemical composition analysis of dislocation parts and non-dislocation parts was carried out with energy dispersive X-ray spectroscopy, there was no remarkable difference in the chemical composition of the both parts. Accordingly, we consider that the factor responsible for the generation of

the dislocation is not due to incorporation of impurities, but a strain caused by a misfit between AlN and SiC. As the thickness of AlN increases, the strain become relaxed, and for that reason, crystalline quality increases.

4. Conclusions

Single crystals of AlN have been grown on 6H-SiC substrates by sublimation using an open crucible. Transparent AlN single crystals have been obtained on SiC substrates by controlling the supersaturation of Al vapor. The crystalline quality and morphology depends on the supersaturation of Al, however the growth rate has been affected little by the supersaturation. Although the growth rate of $35 \mu\text{m h}^{-1}$ has been obtained this time, it is by an order of magnitude lower than that obtained by sublimation in a report [21]. For the production of AlN crystals, the growth rate needs to be improved by closely investigating the effects of the experimental conditions. On-axis and off-axis SiC were used as substrates. In comparison of the crystalline quality by using both of off-axis and on-axis substrates, crystals of better quality have been obtained when off-axis SiC substrates were used. Both of them have almost the same growth rate. The solid-state reaction rate between AlN and SiC has been very low, even at a high temperature of 2273 K because the interface of the AlN/SiC has been clearly separated after the AlN crystal growth. Single crystalline AlN with a thickness exceeding 1 mm with a dislocation density less than 10^7 cm^{-2} has been grown on SiC of a 10 mm square. From cross-sectional observation, it has been found that the crystalline quality can be improved by thickening the crystal layer. Therefore, this result shows the possibility that high-quality AlN substrates useful for electronic/opt-electronic devices can be produced by growing bulk crystals employing this growth technique for controlling the Al vapor supersaturation in an open crucible.

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References

- [1] J. C. Rojo, L. J. Schowalter, K. Morgan, D. I. Florescu, F. H. Pollak, B. Raghothamachar, M. Dudley, Mater. Sci. Res. Soc. Symp. Proc., 680E, (2001) E2.1.1
- [2] T. P. Cho, Mater. Sci. Forum, 338/342, (2000) 1155

- [3] P. B. Perry, R.F. Ruz, Appl. Phys. Lett., 33, (1978) 319
- [4] Y. Taniyasu, M. Kasu, T. Makimoto, Nature, 441 (2006) 325
- [5] M. Asif Khan, M. Shatalov, H. P. Maruska, H. M. Wang, E. Kuokstis, Jpn. J. Appl. Phys. 44 (2005) 7191
- [6] R. T. Bondokov, K. E. Morgan, G. A. Slack, L. J. Schowalter, Mater. Res. Soc. Symp. Proc. 955E (2007) 0955-I03-08
- [7] Y. N. Makarov, O.V. Avdeev, I.S. Barash, D.S. Bazarevskiy, T.Yu. Chemekova, E.N. Mokhov, S.S. Nagalyuk, A.D. Roenkov, A.S. Segal, Y. A. Vodakov, M.G. Ramm, S. Davis, G. Humnic, H. Helava, J. Crystal Growth, 310 (2008) 881
- [8] D. I. Florescu, V. M. Asnin, F. H. Pollak, Compound Semicond. 7 (2001) 62
- [9] K. Kamei, Y. Shirai, T. Tanaka, N. Okada, A. Yauchi, H. Amano, Phys. Stat. Sol. (c), 4 (2007) 2211
- [10] O. Y. Ledyayev, I. Nikitina, A. Zubrilov, M. Mynbaeva, Y. Melnik, V. Dmitriev, Phys. Stat. Sol. (c), 0 (2002) 474
- [11] Y. Kumagai, T. Yamane, A. Koukitu, J. Crystal Growth, 281 (2005) 62
- [12] Y. Liu, T. Tanabe, H. Miyake, K. Hiramatsu, T. Shibata, M. Tanaka, Physica Status Solidi (c), 3 (2006) 1479
- [13] S. Hirai, M. Ozawa, H. Katayama, Y. Uemura, Mater. Trans. JIM 56 (1992) 541
- [14] W. Nakao, H. Fukuyama, J. Crystal Growth, 259 (2003) 302
- [15] G. A. Slack, T. F. McNelly, J. Crystal Growth, 34 (1976) 243
- [16] G. A. Slack, T. F. McNelly, J. Crystal Growth, 42 (1977) 560
- [17] P. M. Dryburgh, J. Crystal Growth, 94 (1989) 23
- [18] R. Schlessler, Z. Sitar, J. Crystal Growth, 234 (2002) 349
- [19] J. H. Edgar, L. Liu, B. Liu, D. Zhuang, J. Chaudhuri, M. Kuball, S. Rajasingam, J. Crystal Growth, 246 (2002) 187
- [20] B. M. Epelbaum, C. Seitz, A. Magerl, M. Bickermann, A. Winnacker, J. Crystal Growth, 265 (2004) 577
- [21] E. N. Mokhov, O. V. Avdeev, I. S. Barash, T. Yu. Chemekova, A. D. Roenkov, A. S. Segal, A. A. Wolfson, Yu. N. Makarov, b, M. G. Ramm, H. Helava, J. Crystal Growth, 281 (2005) 93
- [22] St. G. Müller, R. C. Glass, H. M. Hobgood, V. F. Tsvetkov, M. Brady, D. Henshall, D. Malta, R. Singh, J. Palmour and C. H. Carter Jr., Materials Science and Engineering B, 80 (2001) 327
- [23] N. Ohtani, T. Fujimoto, M. Katsuno, T. Aigo, H. Yashiro, J. Crystal Growth, 237-239 (2002) 1180
- [24] A. S. Segal, S. Yu. karpov, Yu. N. Makarov, E. N. Mokhov, A. D. Reonkov, M. G.

- Ramm, Yu. A. Vodakov, J. Crystal Growth, 211 (2000) 68
- [25] I. Barin, G. Platzki, Thermochemical Data of Pure Substances, Vch Verlagsgesellschaft MbH, Weinheim, 1997, p. 18, p. 42
- [26] D. Zhuang, J. H. Edgar, B. Strojek, J. Chaudhuri, Z. Rek, J. Crystal Growth, 262 (2004) 89
- [27] M. Bickermann, S. Schmidt, B. M. Epelbaum, P. Heimann, S. Nagata, A. Winnacker, J. Crystal Growth, 300 (2007) 299

Figure captions

Fig. 1. Schematic illustration of a crucible

Fig. 2. OM and SEM images of surface morphology of AlN grown on on-axis SiC substrates

(SEM images are magnification of the center in OM images.)

Fig. 3. OM image of a cross section of the AlN growth layer on SiC under $\sigma_{Al} = 0.23$ at 2273 K for 1.5 h

(SiC of the upper part was used to prevent the edge of the AlN layer from inclining under polishing.)

Fig. 4. TEM image showing a cross section of AlN/ SiC interface of the AlN growth layer on SiC under $\sigma_{Al} = 0.23$ at 2273 K for 1.5 h.

Fig. 5. OM image of the surface of AlN grown on 6H-SiC(0001) with off-axis toward $[11\bar{2}0]$ under $\sigma_{Al} = 0.23$ at 2273 K for 1.5 h

Fig. 6. Stereo microscope images of AlN grown on off-axis SiC with an area of $10 \times 10 \text{ mm}^2$ under $\sigma_{Al} = 0.23$ at 2273 K for 30 h

Fig. 7. Cross-sectional TEM images of the sample shown in Fig. 6

Fig. 8. SEM image of the sample shown in Fig. 6, which surface is etched with NaOH-KOH at 350°C for 90 sec.

Tables

Table 1. Conditions for sublimation growth of AlN

Table 2. FWHM of XRCs measured on AlN growth layers on SiC

Table 3. Dislocation density calculated from cross-sectional TEM images shown in Fig.

Table 1
Conditions for sublimation growth of AlN

No.	Flow rate of N ₂ / sccm	Al fraction in gas phase in crucible	Supersaturation of Al(g), σ_{Al}
1	30	0.14	1.1
2	40	0.11	0.71
3	50	0.092	0.43
4	60	0.078	0.23
5	70	0.068	0.079

Table 2

FWHM of XRCs measured on AlN growth layers on SiC

No.	SiC substrate	σ_{Al}	(0002) reflection/ arcsec	(10 $\bar{1}$ 0) reflection/ arcsec
2	on-axis	0.71	1580	440
3	on-axis	0.43	900	320
4	on-axis	0.23	650	180
6	off-axis	0.23	540	160

Table 3

Dislocation density calculated from cross-sectional TEM images shown in Fig. 7

Measurement area	AlN/ SiC interface	Middle of AlN layer	Surface of AlN layer
Number of dislocations	33	19	0
Dislocation density/ cm ⁻²	9.4×10^7	3.7×10^7	—

Figure(s)

Fig. 1. Schematic illustration of a crucible

No.	1	2	3	4	5
σ_{Al}	1.1	0.71	0.43	0.23	0.079
OM
SEM

Fig. 2. OM and SEM images of surface morphology of AlN grown on on-axis SiC substrates (SEM images are magnification of the center in OM images.)

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(a) appearance

(b) fracture

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