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Growth-Mode Control in Sublimation Epitaxy of AlN

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2H-AlN layers were grown on 6H-SiC substrates by sublimation epitaxy. In the growth of AlN, AlN powder and 6H-SiC (0001) Si-face 3.5° off-oriented toward $<11\bar{2}0>$ substrates were set in a graphite crucible as the source and the substrate, respectively. The crucible was heated by an inductively coupled RF generator. Additionally, a Ta sheet was placed in the reaction space in order to suppress the reaction of N_2 with C. The growth of 2H-AlN on 6H-SiC was confirmed by X-ray diffraction and Raman scattering. At pressures of 1.0×10^5 Pa and 0.4 Pa, epitaxial layers were grown by step-flow growth without sub-grains and three-dimensional growth with sub-grains, respectively.

1. Introduction

The group III nitride semiconductors have been expected and developed for applications of high frequency, high power or optical devices with low loss. The lattice mismatch between AlN (a=3.11 Å) and GaN (a=3.18 Å) is small, and AlN has high thermal conductivity (2.2 W/cm·K) and a high thermal stability. AlN is promising as a GaN substrate which is a typical material for group III nitride semiconductors.

Among many polytypes of SiC, 2H-SiC has the widest band gap and the highest electron mobility.[1] Taking into account that 4H- and 6H-SiC can be obtained on the same polytype substrate by step-controlled epitaxy,[2] 2H-SiC growth is expected on a 2H polytype substrate. 2H-AlN is promising as a substrate for the growth of 2H-SiC with a small lattice mismatch.

In order to grow AlN crystal, many methods have been proposed. Generally, AlN crystal is grown by metal-organic chemical vapor deposition (MOCVD)[3] or molecular beam epitaxy (MBE)[4] on various substrates. However, in these methods, the growth rate is very low for the bulk crystal growth. On the other hand, a high growth rate can be obtained with hydride vapor phase epitaxy (HVPE).[5] However, in this method, a special exhaust system to remove ammonia (NH_3) is required and the process for crystal growth is very difficult because of the use of many species of gas. The bulk crystal of AlN can be obtained by the sublimation method.[6] The sublimation method has been used for the growth of the SiC bulk crystal with a high growth rate and high quality and it has a simple process.[7]

In this work, the sublimation epitaxy of 2H-AlN was carried out. In order to obtain high-quality AlN crystal, it is important to control both the initial nucleation on the substrate and the growth mode. In this paper, the sublimation growth of 2H-AlN and the control of the growth mode are described.

2. Experiment

The setup for the AlN sublimation growth was the same as that for the SiC sublimation growth.[7] The schematic image of the setup and a crucible are shown in Fig. 1. A graphite crucible as a growth cell was heated by a RF generator at a frequency of 36 kHz. The temperature of the crucible was measured by a pyrometer. N_2 was used as an ambient gas. AlN powder and 6H-SiC (0001) Si-face 3.5° off-oriented toward $<11\bar{2}0>$ substrates were used as the source material and the substrate, respectively. Growth under two conditions was carried out. One was at the growth temperature of 1850°C and the growth pressure, i.e., the ambient gas pressure, of 1.0×10^5 Pa (condition *A*); the other was at 1750°C and 0.4 Pa (condition *B*). The distance between the substrate and the source was 1.0 mm. In the growth of SiC by the sublimation method, a Ta sheet is placed to absorb excess C from the

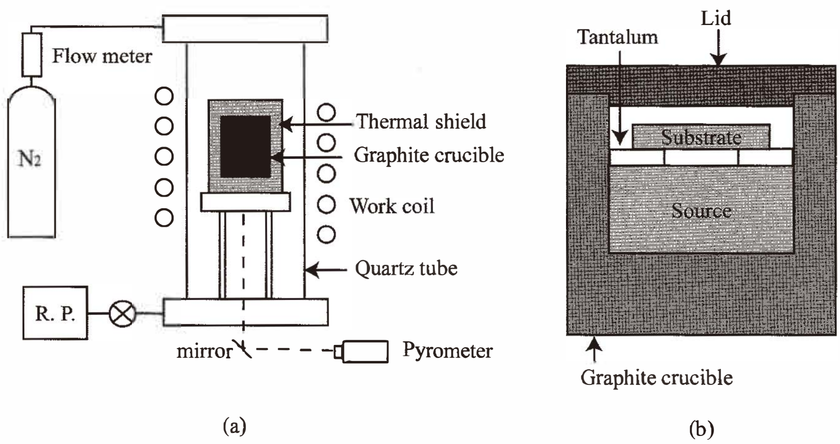

Fig. 1. Schematic image of (a) the setup and (b) crucible.

graphite crucible, which leads to high-quality crystals.[8] In this AlN growth, a Ta sheet was also placed in the graphite crucible in order to absorb excess C, in order to suppress the reaction of N_2 with C.

Figure 2 shows the temperature and pressure diagram during the crystal growth under condition *B*. Before the growth, a reaction tube including the crucible was purged with N_2 gas three times in order to remove residual gases such as oxygen from the tube. Next, the graphite crucible was heated from room temperature to 1750°C. During the heating process, the pressure of the ambient gas was maintained at 1.0×10^5 Pa. When crystal growth was carried out at the reduced pressure of 0.4 Pa (condition *B*), the pressure was reduced after heating the crucible. After the growth, the pressure was increased to 1.0×10^5 Pa and the temperature was reduced to room temperature. The grown layers were characterized by observation using an optical microscope, Raman scattering and X-ray diffraction (XRD).

3. Result and discussion

Figure 3 shows Raman spectra of the grown layers. The peaks at 248, 657 and 890 cm^{-1} in the figure are assigned to E_2(low), E_2(high) and A_1(LO) modes of 2H-AlN, respectively.[9] Peaks at 767 and 789 cm^{-1} are due to the E_{2T} mode of the 6H-SiC substrate.[10] The 2H-AlN signal becomes stronger with increasing the film thickness. These results confirm the growth of 2H-AlN on 6H-SiC substrates by sublimation epitaxy.

Figures 4(a) and 4(b) show optical microscope images of epitaxial layers grown for 2 and 12 h, respectively, under condition *A*. Under this growth condition, the growth rate was measured to be about 2.0 μm/h. Many hexagonal steps directed to $<11\bar{2}0>$ are observed in Fig. 4(a). Since the substrates have an off-axis angle toward $<11\bar{2}0>$, atomic

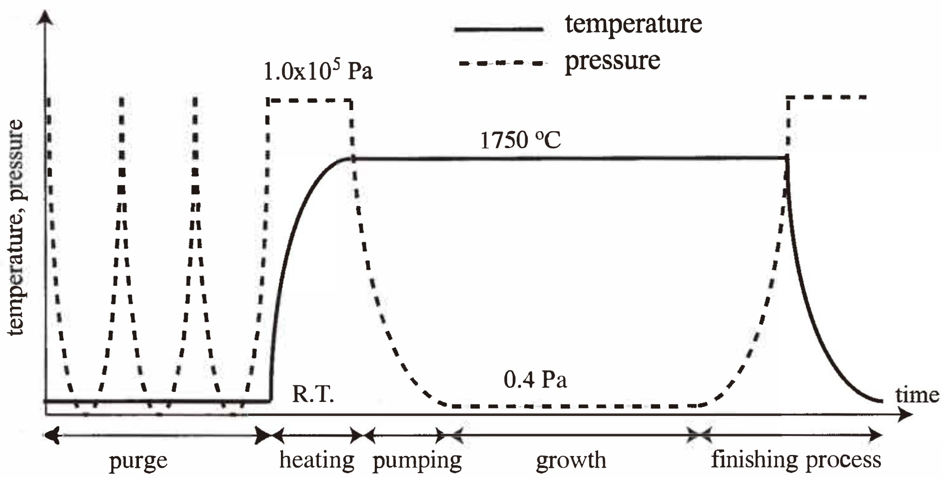

Fig.2. Temperature and pressure diagram during sublimation process under condition *B*.

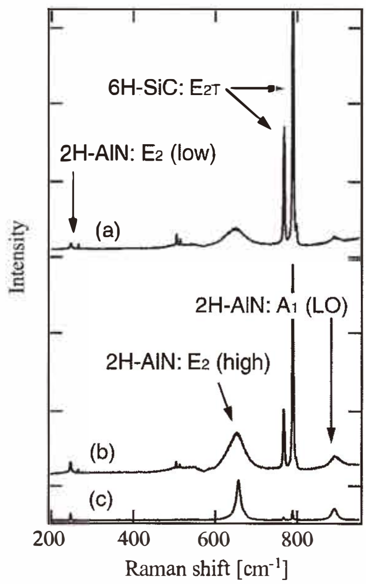

Fig. 3. Raman spectra of grown layers. (a) 2 h growth (2.0 μm thick) and (b) 12 h growth (15 μm thick) under the condition *A* and (c) 8 h growth (25 μm thick) under condition *B*.

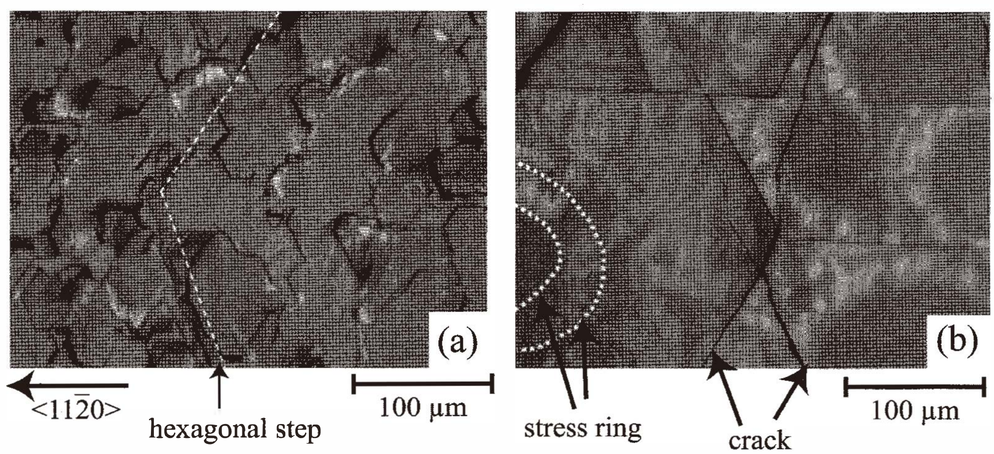

Fig. 4. Optical microscope images of epitaxial layers grown under condition *A* for (a) 2 h and (b) 12 h.

steps exist directed to $<11\bar{2}0>$. In this case, the growth direction is along $<11\bar{2}0>$. Figure 5 shows the schematic image of the step-flow growth. Under this growth condition, crystal growth proceeds under the step-flow growth.[2] No step is observed at the layer grown for 12 h [Fig. 4(b)]. It seems that as crystal growth proceeds, the hexagonal steps are bunched. On the thick epitaxial layer shown in Fig. 4(b), cracks and stress rings are observed.

Figure 6 shows the XRD rocking curve of the epitaxial layer grown under condition *A* for 12 h. The X-ray target was copper (CuKα: 0.155 nm). The resolution of ω was

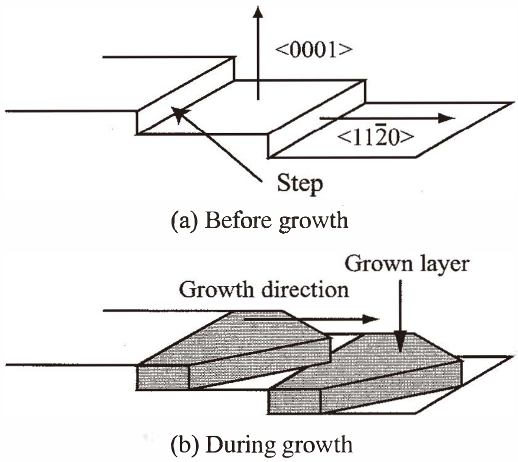

Fig. 5. Schematic image of the step-flow growth.

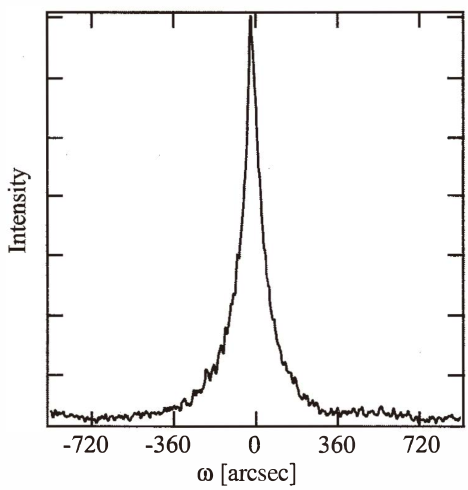

Fig. 6. XRD rocking curve around (0002) reflection from the AlN layer grown under condition *A* for 12 h.

achieved to be 7.2 arcsec by using a four-crystal monochromator. To obtain the rocking curve, (0002) reflection was used. The size of the measured area was 1.0 mm×1.0 mm. The rocking curve shows a single peak with a full-width at half maximum (FWHM) of 82.8 arcsec. This indicates that the AlN layer consists of a single grain without any sub-grains. The step-flow growth of AlN results in the exclusion of sub-grains.

Figures 7(a), 7(b) and 7(c) show optical microscope images of epitaxial layers grown for 1, 6 and 8 h under condition *B*. Under this condition, the growth rate was measured to be about 6.0 μm/h. Many hexagonal islands are observed at the layer grown for 1 h, indicating three-dimensional nucleation growth [Fig. 7(a)]. As crystal growth proceeds, the islands coalesce with each other, followed by enlargement of the hexagonal islands [Fig. 7(b)]. Finally, the islands coalesce completely and the surface becomes smooth [Fig. 7(c)]. A smaller number of cracks is observed in this layer than in the layer shown in Fig. 4(b). The suppression of cracks is probably due to the relaxation of stress caused by the sub-grain boundaries.

Figure 8 shows the XRD rocking curve of the epitaxial layer grown under condition *B* for 8 h. This rocking curve was obtained under the same conditions as for Fig. 6. Three peaks are observed in this rocking curve. Since the thickness of this layer was 52.8 μm, these signals did not originate from the SiC substrate but from the AlN layer. The three peaks indicate the existence of sub-grains in this layer. The three-dimensional growth

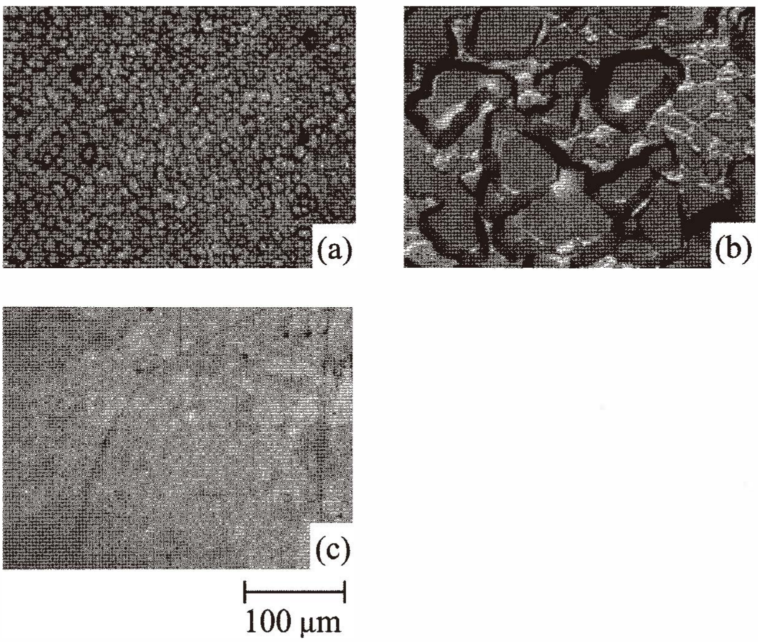

Fig. 7. Optical microscope images of epitaxial layers grown under condition *B* for (a) 1 h, (b) 6 h and (c) 8 h.

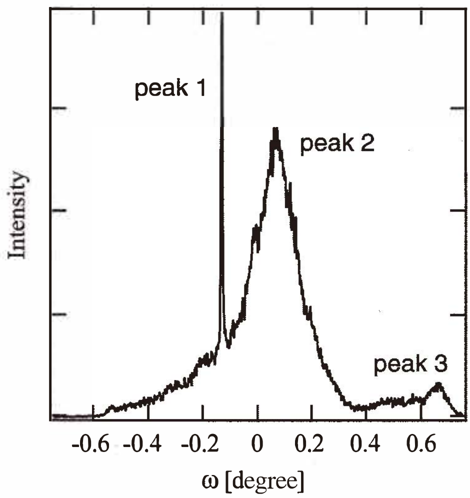

Fig. 8. XRD rocking curve around (0002) reflection from the AlN layer grown under condition *B* for 8 h.

under condition *B* as shown in Fig. 7(a) presumably leads to the formation of sub-grains. The FWHM of peak 2 shown in Fig. 8 is evaluated to be 634 arcsec which is inferior to that shown in Fig. 6, indicating the existence of many sub-grains in this layer.

Step-flow growth occurred under condition *A* and three-dimensional growth occurred under condition *B*. The main difference between these conditions is the pressure of the ambient gas. The growth rate under condition *B*, 6.0 μm/h, is three times higher than that under condition *A*, 2.0 μm/h. In the growth of SiC, step-flow growth occurs with the growth rate of even 50 μm/h.[8] Therefore, it is considered that the difference of the growth rate does not affect the growth mode.

A simulation involving Al vapor flow in the sublimation growth of AlN was reported by Karpov *et al.* [11] The result of the vapor flow in the sublimation growth of AlN is shown in Fig. 9. When the vapor pressure of Al is lower than the pressure of the ambient gas, the vapor flow is directed from the source and the substrate. In this case, the Al concentration gradually increased from the source to the substrate. Al atoms are successively adsorbed and migrate to kink sites on the substrate surface. These Al atoms react with N_2 molecules. Finally, the growth of stoichiometric AlN occurs under step-flow growth as shown in Fig. 10. Under condition *A*, the vapor pressure of Al is calculated to be 1.4×10^4 Pa which is lower than the pressure of the ambient gas, 1.0×10^5 Pa. Therefore, this model agrees with condition *A*.

In contrast, when the vapor pressure of Al is higher than the pressure of the ambient gas, Al vapor sublimated from not only the source but also the substrate surface can easily escape from the crucible through the gap between the lid and the bottom parts of the crucible. This gap is made necessarily and structurally. In this case, Al vapor uniformly distributes over the growth cell as shown in Fig. 9. Al atoms which are adsorbed on the

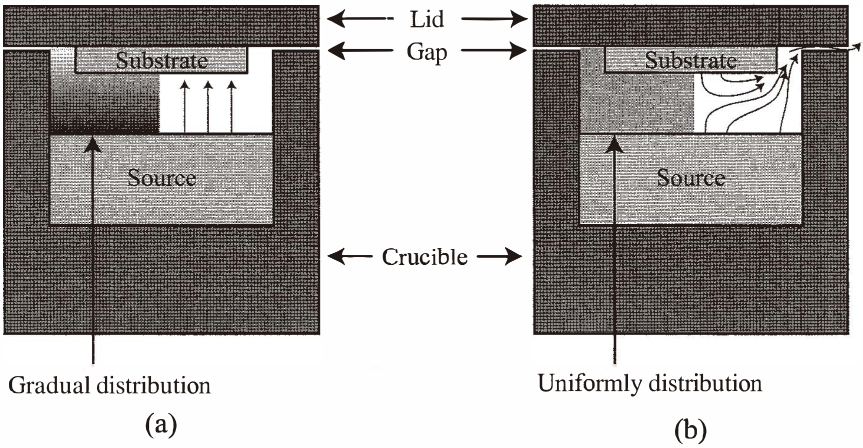

Fig. 9. Streamlines of gas flow (right) and Al concentration (left) under (a) condition *A* and (b) condition *B*. The color gradation from white to black indicates the increase of Al concentration.

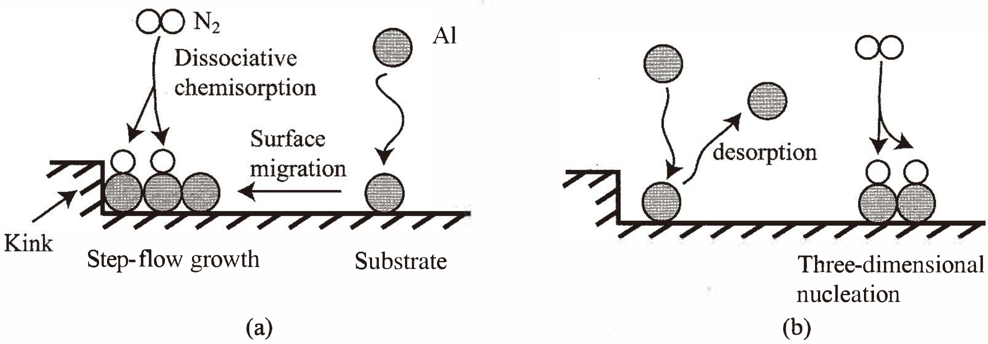

Fig. 10. Growth model of the sublimation growth of AlN. (a) condition *A* and (b) condition *B*.

substrate surface are easily desorbed before migrating to kink sites. A small amount of Al atoms which are adsorbed on the substrate surface react with N_2 molecule. In this case, because Al atoms cannot migrate to kink sites on the substrate surface, crystal growth proceeds in three-dimensional growth as shown in Fig.10. In condition *B*, the vapor pressure of Al is calculated to be 9.3×10^3 Pa which is higher than the pressure of the ambient gas, 0.4 Pa. Therefore, this model agrees with condition *B*.

In our case, in the growth under atmospheric pressure (condition *A*), crystal growth proceeded in step-flow growth mode. In contrast, in the growth at the reduced pressure (condition *B*), Al vapor easily escaped from the growth cell. Therefore, three-dimensional growth occurred under condition *B*. Control of the growth mode can be achieved by changing the growth pressure.

4. Conclusion

Thick 2H-AlN layers (3.0–25.0 μm) were grown on 6H-SiC by sublimation epitaxy with the growth rate of 2–6 μm/h. Raman spectra confirmed the growth of 2H-AlN on 6H-SiC substrates. In the growth under atmospheric pressure (condition *A*), crystal growth proceeded in the step-flow mode. Sub-grains were not observed in the epitaxial layer grown under condition *A*. On the other hand, in the growth under the reduced pressure (condition *B*), crystal growth proceeded in the three-dimensional mode. Sub-grains exist in the epitaxial layer grown under condition *B*. The growth mode of AlN can be controlled by the growth pressure.

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