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Solution growth of AlN single crystal on sapphire using multi-component solvent designed by thermodynamic calculation

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Abstract

We realized AlN single crystal growth on sapphire using the multi-component solvent. Based the thermodynamic calculation, we designed solvent composition and experimental configuration, and successfully obtained the AlN single crystal with relatively high crystallinity.

1. Introduction

Aluminum nitride (AlN) has a potential for the next-generation power device materials as well as substrate materials for AlGaN-based ultraviolet light emitting devices due to its wide bandgap and high thermal conductivity [1,2]. For the growth of AlN single crystal, various kinds of growth method was attempted such as sublimation growth and hydride vapor phase epitaxy (HVPE) [3,4]. In order to grow high-quality AlN single crystal, we focused on solution growth method. Solution growth is expected to grow high-quality crystals because the growth proceeds near the thermal equilibrium [5]. In the solution growth of AlN, nitrogen gas is dissolved into Al-containing solvent at the high temperature position and AlN single crystal grows on the substrate which is located in the low temperature position [6]. In the present study, we carried out thermodynamic calculation to design the solvent composition and growth configuration, and finally obtained AlN single crystal on a sapphire substrate.

2. Design of experimental configuration

Figure 1 shows the schematic illustration of the AlN solution growth. When we consider the thermal equilibrium between atmospheric nitrogen gas and the solvent, the equilibrium nitrogen concentration for nitrogen gas (x_{N2}) can be defined. Similarly when we consider the thermal equilibrium between AlN and the solvent, the equilibrium nitrogen concentration for AlN (x_{AlN}) can also be defined. When the value of x_{N2} is larger than that of x_{AlN}, the concentration of nitrogen is supersaturated to the AlN crystal. On the other hand, when the value of x_{N2} is smaller than that of x_{AlN} the nitrogen concentration is undersaturated to AlN. At the surface of the solvent where nitrogen gas dissolved into the solvent, it is necessary to suppress the crystallization of AlN. Therefore we should keep $x_{N2} < x_{AlN}$ near the solvent surface. On the other hand, near the substrate where AlN single crystal grow, it is necessary to keep

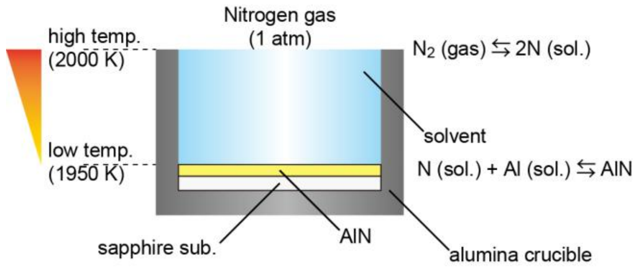

Figure 1: Schematic illustration of the AlN solution growth.

supersaturated condition ($x_{N2} > x_{AlN}$). Thus we must control x_{N2} and x_{AlN} in the solvent.

For the solution growth of AlN, the solvent with large values of x_{N2} and x_{AlN} is preferable. In order to increase the values of x_{N2} and x_{AlN}, we should chose the elements with large negative interaction parameters with nitrogen and aluminum in the solution. From the thermodynamic assessments, we revealed that Cr and Fe is suitable solvent materials for AlN solution growth.

Furthermore, in order to determine the solvent composition, we carried out thermodynamic calculation. Figure 2 shows the temperature dependence of the assessed values of x_{N2} and x_{AlN} for the Fe-15at%Cr-3at %Al solvent. In this solvent, the value of x_{N2} is larger than that of x_{AlN} above

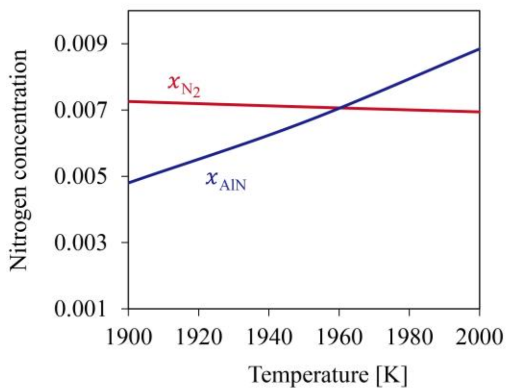

Figure 2: Temperature dependence of the values of x_{N2} and x_{AlN} for the Fe-15at%Cr-3at %Al solvent.

1960 K and the value of x_{N2} is smaller than that of x_{AlN} below 1960 K. Thus it is expected that the crystallization in the solvent surface is suppressed and AlN crystal would grow on the substrate when we set the temperature of solvent surface at 2000 K and the temperature of substrate at 1950 K.

3. Experimental procedure

AlN solution growth was carried out in a radio frequency-heated hot-zone furnace. The solvent with the composition of Fe-15at%Cr-3at%Al was used for the growth. The solvent was placed in an alumina crucible and kept in a vertical temperature gradient under a N_2 gas flow for 10 hours. The alumina crucible had an inner diameter of 14 mm and was 17.5 mm high. A sapphire (0001) crystal (φ 13 mm) were used as the substrate. We set the temperature of solvent surface at 2000 K and the temperature of substrate at 1950 K. In that case, the solution is expected to be supersaturated to AlN only near the substrate.

Grown crystal was evaluated by optical microscopy, Raman spectroscopy, scanning electron microscopy (SEM), and X-ray rocking curve (XRC) measurement.

4. Results and discussion

Figure 3 shows the optical microscopy image of the grown crystal. At the point (A), a Raman spectrum which is characteristic of AlN was obtained, while a Raman spectrum which is characteristic of sapphire was obtained at the point (B). This indicates that AlN crystal grew on a sapphire substrate. The coverage ratio of AlN crystal was about 65%. From the confocal microscopy measurements, the average thickness of the grown crystal is about 0.64 μm. From the X-ray diffraction measurement, the heteroepitaxial relation of $(0001)_{sapphire}//(0001)_{AlN}$ was confirmed. The full width at half maximum (FWHM) of XRCs for tilt components were 370 arcsec. The present FWHM value is larger than that of the crystal grown by HVPE on sapphire (127 arcsec) [7]. However, among the reported solution growth AlN crystals on sapphire, the FWHM value is smallest to our knowledge [6,8]. Note that the crystallization of AlN was hardly observed except for on the sapphire substrate. This indicates that this growth configuration can suppress the unintentional crystallization and achieve long-term stable growth. Although the grown crystal had relatively high crystallinity, the growth rate was as low as 0.06 μm in the present study. In order to increase growth rate, we further searched the suitable solvent and growth configuration, and we achieved the growth rate up to 200 μm/h for now.

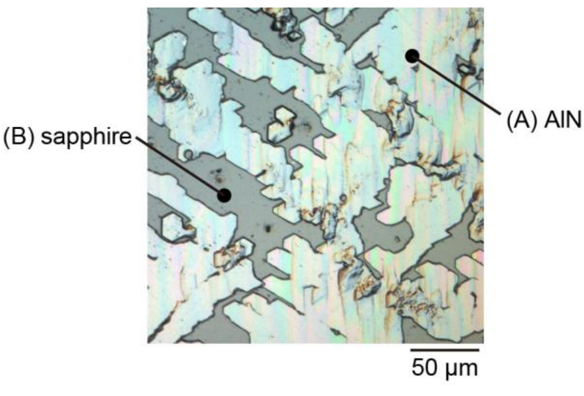

Figure 3: Differential interference contrast microscopy image of the grown crystal.

5. Conclusion

By using Fe-15at%Cr-3at%Al solvent, which was designed based on the thermodynamic calculation, we achieved the heteroepitaxial growth of AlN on (0001) sapphire. The FWHM of XRCs for tilt components were 370 arcsec.

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