PVT growth of AlN single crystals with the diameter from nano- to centi-meter level
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Abstract. Physical vapor transport (PVT) is the most successful and widely used approach for bulk aluminum nitride (AlN) single crystals. During the process of PVT growing AlN crystals, crucible materials, the growth setup, and the growth parameters (e.g., temperature distribution, growth pressure) are crucial. This work proposes a detailed study on the PVT growth of single AlN crystals with sizes ranging from nanometers to centimeters. AlN crystals with different sizes are grown by spontaneous nucleation. Furthermore, it discusses and contrasts the growth conditions and mechanisms of AlN crystals with different sizes. The structural and optical properties of the AlN crystals are also involved.

1. Introduction
Aluminum nitride (AlN), gallium nitride (GaN), silicon carbide (SiC), diamond, and other wide-band gap semiconductor materials are often referred to as third-generation semiconductor materials. Compared to first-generation and second-generation semiconductor materials, the third generation is characterized by high breakdown field strength, high thermal conductivity, high electron saturation velocity, and high resistance to radiation; they are suitable for the production of high-frequency, anti-radiation, large power, and high-temperature semiconductor devices. AlN, a typical representative of this group, has the widest direct band gap of 6.2 eV as well as excellent electrical, optical, mechanical, and piezoelectric properties. The properties make AlN as one of the best choices for electronic and optoelectronic applications. For example, AlN is a promising material for deep-ultraviolet (DUV) solid-state light-emitting diodes (LEDs) and laser diodes (LDs). AlN LEDs with a wavelength of 210 nanometers have been made successfully [1,2].

There is no natural occurrence of AlN as a mineral. Since AlN powder was first synthesized in 1862 by molten aluminum in nitride atmosphere, the first AlN single crystal (Φ0.03 mm×0.3 mm) was obtained in 1956 and AlN crystal bullets were grown in 1976. [3] Due to a very high melting point and a very large dissociation pressure at the melting point, AlN crystals are hardly grown from the melt at normal pressure condition. Over the past several decades, physical vapor transport (PVT – also named the sublimation-recondensation method) has been proved to be the most successful and widely used approach for bulk AlN crystals growth [4,5,6]. Now the maximum size of AlN single crystal grown in laboratory is about 1 inch in diameter [4,7]. Moreover, high quality AlN nanocrystals can be also obtained by PVT [8]. However, the contrastive research on the PVT growth of AlN crystals with different sizes is absent. The study of AlN crystal-growth technology remains a hot topic of solid state physics in the near future.

In this work, a detailed study was proposed on the PVT growth of AlN single crystals with size range from nano- to centi- metre. The growth conditions and mechanism of AlN crystals with different sizes were also discussed contrastively. Finally, attention was also paid to investigate the structural and optical properties of AlN crystals.

2. Experimental procedure
The growth experiments were performed by the PVT technique. The resistance-heated furnace was operated with a high purity nitrogen atmosphere (99.999%) at 90-120 kPa. AlN powder source usually begins to sublimate at the temperature of 1850 °C. [3] During the growth, the species gaseous of AlN or Al and N2 from the source located at the hotter bottom of the crucible sublimated and re-condensate on the crucible lid where the temperature is relatively lower. This process is really that the overall reaction AlN(s) = Al(g) + ½N2 is run in the forward (sublimation) direction at the source, and in the reverse (recondensation) direction at the top of the crucible. To achieve high quality bulk AlN crystals with fast growth rates (>200 μm/h), high temperature are required [9,10]. The upper limit of growth temperature is about 2500 °C, when the Al vapor pressure reaches 1 atm [11]. The induction heating unit as shown as Figure 1 included a main heater and a top heater which heated on sublimation zone and crystalline zone, respectively. A vertical thermal gradient was established by the two heaters. The temperatures of two zones were measured and controlled separately by infrared two-color pyrometers on the body and the lid of the crucible. Growth experiments were carried out in a tungsten crucible. The high purity tungsten was also used for the resistance heater and the thermal shield. AlN polycrystals, which had been grown by
commercially available AlN powder, were employed as the AlN source and resublimed for 4 hours at 1850-1900 °C prior to the use for achieving the highest possible degree of purification.

Figure 1 Scheme of the induction heating unit mainly composed of tungsten

The suitable growth temperature and the temperature gradient between the crystallization and the sublimation zone (i.e. the crucible lid and body) were investigated to restrain preferential growth AlN crystals along the c-axis orientation and controlled by the top heater and the main heater. However, a high temperature usually results in too many defects in product, since the thermal equilibrium concentration of point defects increases with rising growth temperature.[7,12] During the cooling, an auxiliary annealing process with optimal is employed to reduce the defects. X-ray diffraction (XRD) with Cu Kα radiation on a Philips x-ray diffractometer at 45 kV and 40 mA. Moreover, the Energy Dispersive Spectrometer (EDS) were employed to investigate the composition of AlN crystals

3. Results and discussion

The sublimation-recondensation process of AlN can be described by the simple reaction: AlN(s) = Al(g) + ½N₂. In fact, the PVT growth of AlN crystal includes following five sub-processes: (a) sublimation of the AlN source, (b) mass transfer of the vapor species, (c) adsorption of the vapor species on the substrate surface, (d) diffusion and nucleation on the surface, (e) desorption[9]. The sublimation behavior of AlN, which is well described with experimentally and calculationally relevant curves, is mainly related to growth temperature (usually above 1850°C) and vapor pressure (80-120 kPa) [3,4]. The gas phase transport and the adsorption mechanisms of the vapor species has been also discussed intensively [9,10,11]. Diffusion is the main mass transport model for the growth species. Gaseous Al and N₂ are as the main species during the growth, while possible vapor species like metastable AlₓN (g) (x = 2,3,4) can be almost excluded [13]. The growth experiments are usually performed with a high purity nitrogen atmosphere at 80-120 kPa, which exceeds multiple times above the partial pressure. However, a nitrogen molecule has the strong binding energy. Thus sticking coefficients of gaseous N₂ (αN₂), which are much less than one, are introduced to model correct during the description of the adsorption behavior and surface reactions [14]. Higher temperatures lead to enhance values of αN₂ and surface diffusion of the adatoms, which are better for improving structural quality of the AlN crystals. The maximal temperature of AlN crystals PVT growth is lower than the decomposition point about 2430 °C at 100 kPa nitrogen [15].

Considering these factors, the growth rate of crystalline AlN, or V_G, can be expressed in Eq(1). [10,11,13]

\[
V_G = \frac{M_{AlN} D_{sub} \Delta H}{T_0 R} e^{(\frac{\Delta S}{R}) - (\frac{\Delta H}{RT}) \frac{\Delta T}{\Delta d}} = \frac{k}{P_T^{\delta T^{1/2}}} \frac{\exp(\frac{\Delta S}{R}) - \exp(\frac{\Delta H}{RT}) \frac{\Delta T}{\Delta d}}{\Delta d}
\]

where k is a constant; \( \Delta S \) and \( \Delta H \) represent entropy and enthalpy of sublimation, respectively; R is the universal gas constant; PT is the pressure when the local gas phase temperature is T; \( \delta \) is the distance from the source to the substrate surface; and \( \Delta T \) is the temperature difference between the crystallization and sublimation zones. The equation shows that \( \Delta T \) constitutes a key factor in the growth rate V_G, especially when T and P are determined. It is obtained that the common temperature range for the AlN source and the nucleation zone is about 2050-2320°C, which provides sufficient surface mobility and mass transport. [16]

During the early stages of growth, self-nucleation and the subsequent growth of millimeter-sized freestanding crystals dominate the growth process. It can be seen in Figure 3 that the AlN crystal pattern changes from nanometer-sized (in diameter) whiskers to micrometer-sized needles to millimeter-sized, perfect, well-faceted hexagonal prisms as the growth temperature increases from 1850 °C to 2200 °C. AlN crystal growth demonstrates a strong anisotropy and preferential behavior along the c-axis. However, this habit decreases as the temperature increases. With increasing temperature, polycrystalline AlN boules, shown in Figure 3, rather than single crystals are produced on the tungsten substrate because of the absence
of seeds. The majority of crystallies are (0001) oriented, but some are twisted and tilted against each other by several degrees. This creates the opportunity to develop new techniques to grow bulk AlN crystals.

![SEM photos of AlN crystals](image)

**Figure 2 SEM photos of AlN crystals with the diameter from (a) nano- to (d) milli-meter level**

During growth, proper process conditions lead to low nucleation densities and high growth rates. Numerical simulations of the thermal field and supersaturation can determine the optimal parameters. The local supersaturation relative to thermal equilibrium can be defined as [17]

\[ S = \frac{p_{Al} - p_{N_2}}{K(T)} - 1 \]  

where \( p_{Al} \) is the gaseous Al pressure, \( p_{N_2} \) is the gaseous \( N_2 \) pressure, and \( K(T) \) is the equilibrium constant. Excessively low supersaturation leads to very low growth rates, and excessively high supersaturation results in defective densities and high-density nucleation points that cause the polycrystallization of AlN. Supersaturation values in the range of 0.25 < S < 0.3 have proven to be suitable for growing separate freestanding AlN crystals with appreciable size and high structural quality [5]. At a constant ambient pressure in a given growth setup, the variable process parameters are the growth temperature and the temperature difference between crystallization and the sublimation zone. Due to the high vapor pressures of Al and \( N_2 \) at temperatures of 2050-2320°C, the temperature gradients must be maintained at 5-20 °C/cm.

![Optical photos of AlN single crystal](image)

**Figure 4 Optical photos of AlN single crystal with the diameter from (a) milli- to (b) centi-meter level**

The crystal growth was composed of three main sub-processes: (a) heating-up, (b) holding, and (c) cooling. According to the traditional growth model where the temperature of the crystallization zone is higher than that of the sublimation zone during the heating-up process, or \( \Delta T < 0 \), the AlN polycrystals form on the tungsten lid, as shown in Figure 3. Hexagonal AlN single crystals in <0001> orientation form at a growth temperature of 2,250 °C, with a temperature difference of \( \Delta T \) of positive 20-50 °C during sub-processes (a) and (c). Maintaining the proper values of \( \Delta T \) before growth can help avoid too much crystallization on the substrate, where conditions are close to thermal equilibrium and only a few detached AlN single crystals grow, as shown in Figure 4 (b) (c), and recrystallize in sub-process (c). Transparent yellow or amber crystallites roughly grow in <0001> orientation, with excellent hexagonal morphology. By optimizing experimental parameters, a single AlN crystal has grown to a maximum diameter of 22 mm, as shown in the dash-dotted frame in Figure 4(c).

Strong spontaneous and piezoelectric polarization fields affect AlN crystals and other structures grown in the polar c-axis direction. AlN has an anisotropic emission pattern where light is barely emitted from the c-
plane and is emitted preferentially from the a-plane. The a-plane emission intensity is estimated to be 25 times higher than that of the c-plane. Therefore, controlling growth direction is the most effective and directive method to grow nonpolar plane AlN crystals. During sub-process (b) of AlN crystal growth, M-plane AlN single crystals can also form on the tungsten lid when the temperature difference is negative 10-40 °C. Reducing the values of $\Delta T$ and other parameters allows M-plane AlN crystals to grow easily. Figures 4 (b) and (d) show C-plane and M-plane AlN single crystals with $\Delta T$ values of 30 °C and 15 °C, and growth temperatures of 2200-2250 °C. The $\omega/2\theta$ XRD data of the sample (Figure 4 (d)) has only a sharp diffraction peak for wurtzite (100), indicating the growth of M-plane surface-oriented AlN crystals with a size of about 1cm. The full width at half maximum (FWHM) of the symmetric x-ray rocking curve (XRC) is about 300 arcsec. Figure 5 shows the cathodoluminescence (CL) spectra of AlN crystals from a low temperature of 8 K to room temperature or 300 K, over a narrow spectral range of 190-230nm. Free exciton (FX) emission peaks in the near band-edge emissions spectra shift from 206 nm to 210 nm.

4. Conclusions

AlN single crystals with the diameter from nano- to centi-meter level have been grown by PVT. During the growth, the optimized temperature range for the AlN source and the nucleation zone, about 2050-2320°C. The size of AlN crystal increases as the temperature increases. The temperature difference between the crystallization and sublimation zones ($\Delta T$) is crucial to grow AlN single crystal. Maintaining the proper values of $\Delta T$ before growth can help avoid too much crystallization on the substrate and also affect growth direction from C-plane to M-plane. With the CL spectra at 8–300 K with 15 KV excitation, AlN crystal FX emission peaks in the near band-edge emissions spectra shift from 206 nm to 210 nm.

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