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Preparation and characterization of AlN seeds for homogeneous growth

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Abstract: Large size AlN bulk crystal has been grown on SiC heterogeneous seed by physical vapor transport (PVT). The properties of AlN wafer were characterized by high resolution X-ray diffraction (HRXRD), Raman spectroscopy, etched method and atomic force microscope (AFM). Growth mechanism of AlN crystal grown on heterogeneous SiC seeds was proposed. Crystallization quality of AlN samples were improved with the growth process, which is associated with the growth mechanism. AlN single wafer has excellent crystallization quality, which is indicated by HRXRD showing the (0002), $(10\bar{1}2)$ XRD FWHM of 76.3, 52.5 arcsec, respectively. The surface of the AlN wafer is measured by AFM with a roughness of 0.15 nm, which is a promising seed for AlN homogeneous growth.

Key words: heterogeneous growth; AlN seeds; crystallization quality; characterization

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1. Introduction

AlN single crystal is a promising semiconductor material with the largest direct band gap, high breakdown voltage, good thermal conductivity, thermal stability and chemical stability. Compared with SiC substrate or sapphire substrate, AlN crystal has smaller mismatches with GaN and $Al_xGa_{1-x}N$ epitaxial layers in lattice structure and expansion coefficient, which can be an ideal substrate for GaN and $Al_xGa_{1-x}N$ based UV-C LED, high-voltage and high-power devices and solar-blind detections[1]. Based on low dislocation density AlN single crystal substrate, Crystal IS has developed two models (named as SMD and Optan) UVC-LEDs with maximum wavelength range of 250–280 nm and light output efficiencies of 5–10 mW and 0.5–4 mW[2], respectively. HexaTech Corporation is also devoted to the development of UV LEDs and Schottky diodes based on homemade high quality AlN substrates[3].

Method for preparing AlN single crystal mainly focused on physical vapor transport (PVT) due to high growth velocity and low dislocation density. In 1976, Slack *et al.* firstly developed sublimation technique and grew centimeter-scale AlN crystal in tapered tungsten crucible by spontaneous nucleation. Other research organizations[4–6] such as Erlangen University and IKZ have successively carried out spontaneous nucleation growth method to obtain high quality AlN grains. However, this growth method is often time-consuming due to the difficult in the optimization of crystal grains, the control of spontaneous nucleation number and the expansion speed in size.

Because SiC crystal has the same hexagonal structure and has a small mismatch in the a-axis lattice constant with AlN crystal, more and more scientists have paid more attention on SiC seeds for AlN growth. Otherwise, SiC crystal has other excellent features such as high melting point, highly stable and large size, which is an ideal seed for AlN growth. Nitride Crystal, LMU University and Erlangen University, etc.[7–9] had developed the growth on SiC seed. Nitride Crystal had announced the preparation of 2-inch AlN single crystal wafer. However, the crystal quality should be further improved and the impurities (such as silicon, carbon and oxygen) concentration should be decreased to make the optical absorption cutoff edge blue shift. Moreover, the cracks in the AlN single crystal should be solved due to the lattice and thermal mismatch when SiC seed is used in the growth. So AlN crystal grown on homogenous AlN seed has been put on the agenda, the prerequisite of which is the acquisition of AlN seed.

Generally, there are two ways to obtain AlN seed. One way for AlN seed is from AlN crystal ingots grown SiC seeds[10–12]. The second is from spontaneous nucleation and multiple expansions[9, 13]. Crystal IS, HexaTech, Crystal-N, etc. have grown 2 inch diameter AlN single crystal by homogenous AlN seed growth[14, 15]. It can be deduced that the growth method for AlN single crystal by PVT will eventually fall into homogenous growth. However, the quantities of AlN seed have limited the development of this technology. In order to obtain homogenous AlN seeds, experiment was carried out to grow AlN single crystals on SiC seed. Crystallization performance of AlN single crystal was investigated, and whether it can be used as AlN seed or not for homogenous growth was evaluated.

2. Experimental process

Crystal growth experiment was carried out in a self-made radio-frequency induction heating furnace. Before growth experiment, thermal field distribution of growth crucible was simulated, which could help us design the configuration of thermal zone and obtain moderate convex temperature distribution. In addition, the process of seed fixed was optimized

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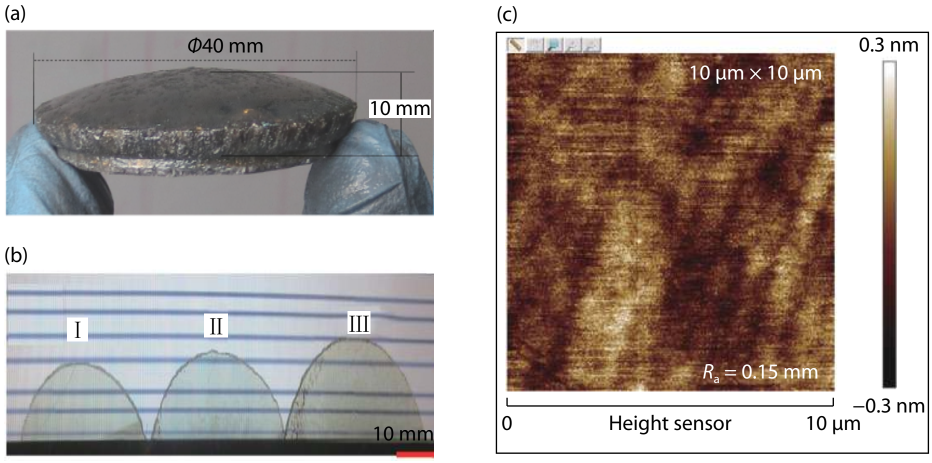

Fig. 1. (Color online) (a) AlN single crystal. (b) AlN samples. (c) R_a of AlN sample at area of 10 × 10 μm^2.

to reduce the probability of seed back-sublimation, while thermal zone structures (graphite, TaC crucible and felt insulation) was prepared strictly to increase used life and reduce the impurity in system. AlN polycrystalline source was placed at the bottom of TaC crucible, while self-made on-axis 4H-SiC seed was fixed on the crucible cap by glycosyl binder. Optimized parameters (supersaturation at the growth interface, growth temperature and growth pressures at different growth stage) were used in the growth process. Growth temperature was set at the range of 1830–2020 °C, while growth pressure at the range of 500–900 mbar, the distance between AlN polycrystalline source and SiC seed was 40 mm. Different growth strategies were used at different stages of AlN single crystal growth process by adjusting the relative positions of induction coil and crucible. For example, we adopted the strategy of lower seed temperature and higher pressure to suppress the deposition of SiC seed at the initial stage of growth. At the same time, a larger axial temperature gradient can accelerate the sublimation of AlN source and condensation on the SiC seed, which could further protect the integrity of SiC seed. Similarly, we adopted different growth parameters at the growth stages depending on the cognition of growth processes and growth experiences.

Crystallization performance of AlN wafers were characterized by delta-X type high resolution X-Ray diffractometer of Bruker corporation and HR800 type Raman spectroscopy at the wavelength from 100 to 1000 cm^{-1} in $X(Z\text{-}Z)Y$ direction using the 488 nm laser for excitation. Concentration and distribution of impurities such as silicon, carbon, and oxygen were measured by secondary ion mass spectrometry (SIMS). AlN wafer was placed in a KOH/NaOH melt for 3 min and the dislocation density was counted under a scanning electron microscopy (SEM). Roughness of AlN wafer was investigated by AFM.

3. Results and discussion

AlN crystal with diameter of about 40 mm and thickness of about 10 mm has been grown on SiC seed, as shown in Fig. 1(a). As-grown surface of AlN crystal is slightly convex with lots of hexagon tiny pits. No cracks are investigated in AlN crystal (shown in Fig. 1(a)) under bright light, when it is taken out of the furnace. However, there are two cracks in the wafers after the AlN crystal is sliced by the diamond wire with low slicing speed. The appearance of cracks may be due to the external force by the diamond wire or the internal force existed in the AlN single crystal which can't easily be detected. The two cracks exist in the slicing wafers without separation. However, the wafers are divided into three parts after polishing process, halves of which are shown in Fig. 1(b), named sample I, II, and III, respectively. Sample I is close to the growth surface, sample III is close to the AlN-SiC interface and sample II is between the above-mentioned two. Three samples were transparent and almost colorless with increasing diameters from 30 to 40 mm due to the thermal field distribution and convex growth. Roughness of AlN polished samples were at the level of 0.15 nm shown in Fig. 1(c).

Raman spectroscopy of AlN single crystal samples was shown in Fig. 2. It can be seen from Fig. 2(a) that the Raman peaks of three samples are located at the wavenumber of 247, 657 and 891 cm^{-1}, which are corresponded to E_2(low), E_2(high) and A_1(LO) phonon modes, indicating AlN samples are typical c-plane growth. Raman mapping mode were subjected to the samples (not shown here) indicating good uniformity of c-axis orientation. E_2 (high) phonon mode peaks of three samples in Fig. 2(b) are high-intensity and sharp, indicating good crystallization quality. Moreover, FWHM values of E_2 (high) phonon mode peak are gradually decreased from sample III to sample I, which means the improved crystallization quality during the growth process. However, the peak positions of E_2 (high) phonon mode in three samples are slightly lower than 657.4 cm^{-1}, which means tensile stress still exists in the samples. Compared with the peak position in sample I, the other two samples are modestly blue-shifted. It can be deduced that the tensile stress are gradually decreased during the growth process.

It can be seen from the HRXRD of AlN samples in Fig. 3 that diffraction curves of symmetrical (0002) plane and asymmetric $(10\bar{1}2)$ plane are sharp, narrow and good symmetry. FWHM values of (0002) and $(10\bar{1}2)$ diffraction curves gradually decrease from sample III to sample I, which means crystallization quality gradually increase with the growth process. In sample I, FWHM value of (0002) and $(10\bar{1}2)$ is 76.3 and 52.5 arcsec, respectively. Generally, FWHM value of (0002) plane in AlN single crystal grown on SiC heterogeneous seed is around 120 arcsec[16]. The lowest value of 13 arcsec for (0002) FWHM of AlN single crystal was reported grown on AlN homogeneous seeds[5]. So AlN samples grown in our ex-

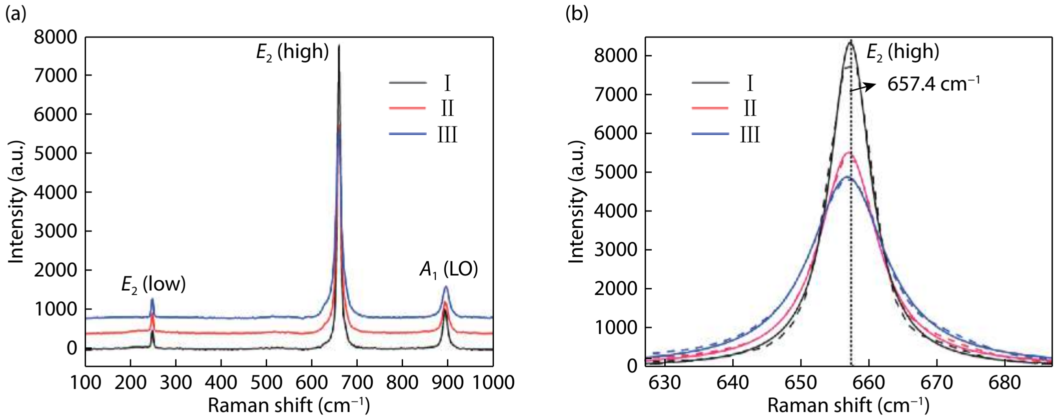

Fig. 2. (Color online) Raman spectrum of AlN samples. (a) Wavelength from 100 to 1000 nm. (b) Detailed E_2 (high) phone mode peaks.

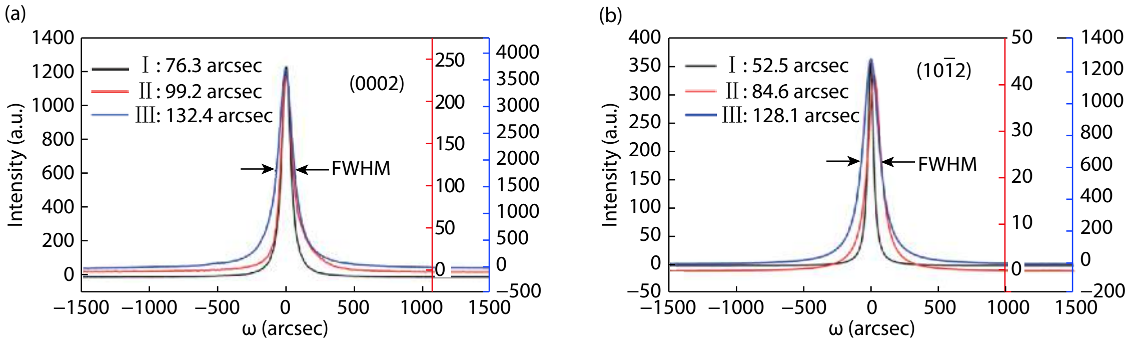

Fig. 3. (Color online) HRXRD of AlN samples (a) (0002) plane and (b) (10$\bar{1}$2) plane.

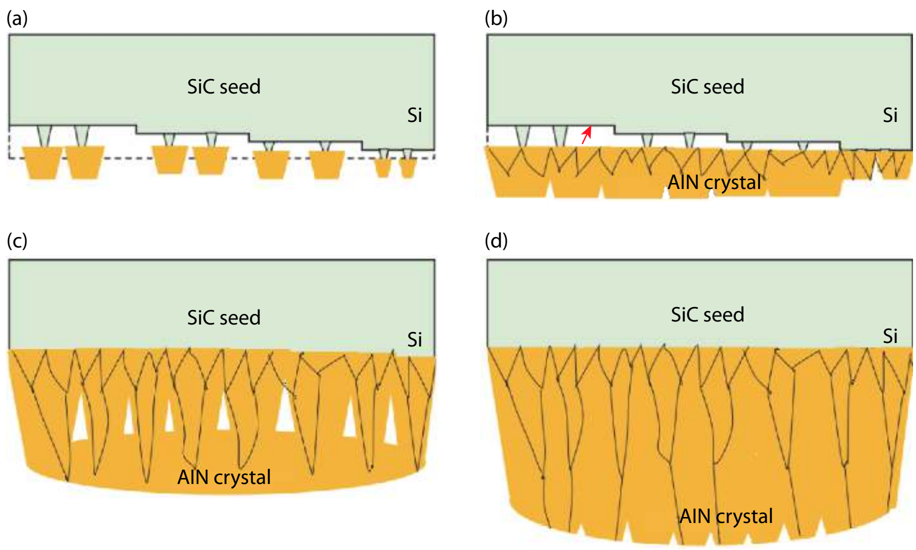

Fig. 4. (Color online) Schematic diagrams of AlN single crystal grown on Si-polar SiC seed. (a) SiC macroscopic steps and deposited AlN 3D islands. (b) AlN 3D islands lateral overgrowth and dislocation formation. (c, d) Cavity movement and dislocation "annihilation".

periment are believed to have high crystallization quality.

Crystallization performance of AlN samples improves with the growth process from the results of Raman and HRXRD measurements, which may be related with the growth mechanism of AlN crystals grown on SiC heterogeneous seeds, as shown in Fig. 4.

Because the Si-polar plane has the lowest corrosion rate[17], so the more stable Si-polar plane of SiC seed is used as the growth plane in our growth experiment. Defects like micropipes in SiC seed are etched faster and expanded laterally, finally forming SiC macroscopic steps. Pseudo-morphological AlN 3D islands has grown on SiC macroscopic steps randomly, which prevent the underneath SiC seed to further decompose remaining truncated SiC hexagonal pyramids (Fig. 4(a)). Next AlN 3D islands lateral overgrow on SiC hexagonal pyramids until they coalesce as shown in Fig. 4(b). Small-angle grain boundaries (SAGB) and threading dislocations (TD) are formed at the regions where AlN growth islands coalesce to a closed layer. Cavities (red arrows in Fig. 4(b)) at SiC–AlN interface are gradually filled by the "backward sublimation" due to temperature gradient of cavities, resulting the "cavity migration" (Fig. 4(c)) during the following

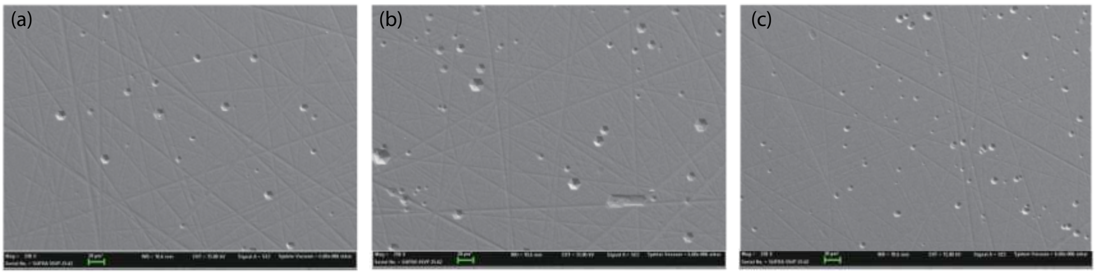

Fig. 5. SEM images of AlN samples etched in KOH/NaOH melt solution at 320 °C for 3 min. (a) Sample I. (b) Sample II. (c) Sample III.

growth until to the AlN growth surface (Fig. 4(d) and Fig. 1). Moreover, TD density gradually reduces with the thickness during the growth in <0001> direction[18], which is suggested to be dislocation annihilation by recombination driven by the dislocation strain fields and certain mobility of dislocations at moderate growth temperature in slightly convex growth.

In order to count the TD density, three AlN samples are etched in KOH/NaOH melt solution at 320 °C for 3 min, which are shown in Fig. 5. TD density decrease from 2.5×10^5 cm^{-2} of sample III to 6.5×10^4 cm^{-2} of Sample I for 250× magnification in SEM image, which is in coincident with dislocation "annihilation" in the growth mechanism of Fig. 4.

4. Conclusion

AlN single crystal with diameter of 40 mm has been grown on SiC heterogeneous seed. The growth mechanism on SiC seed include the following steps: SiC macroscopic steps formation, AlN 3D islands deposition, islands lateral overgrowth, dislocation formation, cavity movement and dislocation "annihilation", which can be used to account for the improved crystallization performance with AlN growth process. Sample I has high crystallization quality with (0002) and $(10\bar{1}2)$ XRD FWHM of 76.3 and 52.5 arcsec, respectively. The grown AlN crystal with high quality and flat surface ($R_a = 0.15$ nm) is a promising seed for homogeneous growth, which lays the foundation for the growth of large-sized and high-quality AlN single crystal.

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