Wet etching and infrared absorption of AlN bulk single crystals

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Abstract: The defects and the lattice perfection of an AlN (0001) single crystal grown by the physical vapor transport (PVT) method were investigated by wet etching, X-ray diffraction (XRD), and infrared absorption, respectively. A regular hexagonal etch pit density (EPD) of about 4000 cm^{-2} is observed on the (0001) Al surface of an AlN single crystal. The EPD exhibits a line array along the slip direction of the wurtzite structure, indicating a quite large thermal stress born by the crystal in the growth process. The XRD full width at half maximum (FWHM) of the single crystal is 35 arcsec, suggesting a good lattice perfection. Pronounced infrared absorption peaks are observed at wave numbers of 1790, 1850, 2000, and 3000 cm^{-1}, respectively. These absorptions might relate to impurities O, C, Si and their complexes in AlN single crystals.

Key words: AlN; PVT; etching; defects
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1. Introduction

AlN is a direct band gap semiconductor with a large band gap (6.2 eV), high thermal stability and conductivity[1, 2]. Recently, GaN and AlGaN, representatives of III-nitrides materials, are being widely used in the fabrication of optoelectronic and new high power electronic devices. However, due to the thermal and lattice mismatch with traditional substrates, the epitaxy material contains a large dislocation density (10^6–10^{10} cm^{-2}) and many defects, which limits the lifetime and performance of devices[3–5]. AlN matches well with GaN and Al-rich AlGaN, making it an ideal substrate for GaN and their ternary compounds[6]. In this case, a low defect density and a good lattice perfection of the AlN single crystal are a prerequisite for the fabrication of high quality III-nitrides. Thus, it is necessary to investigate defects and their formation mechanism in AlN single crystals.

Wet chemical etching is a reliable and simple technique to analyze defects and the dislocation density in single crystals. This method is also being widely used to characterize dislocations in AlN single crystals. Zhuang *et al.* have shown that an anisotropic-selective etching of AlN was well performed in molten NaOH–KOH at a temperature ranging from 170 to 360 °C[7]. It was proven by Bickermann later[8]. A free nucleated single crystal is an ideal material for wet chemical etching. Due to its high quality, its low dislocation density and defects, it is easy to identify its surface structure. However, due to different surface kinetics of etching on different facets, the dislocation density and defects at each facet will vary a lot[9,10]. In the meantime, the etching condition will also be more strict because of the high quality of the crystal. Only at a higher temperature (300–400 °C) and a longer etching time, can AlN be etched.

In this paper, experimental results of dislocation etching and X-ray diffraction (XRD) of an AlN single crystal grown in our laboratory are presented. In addition, impurities and related defects in the AlN single crystal are characterized by infrared absorption. The formation mechanism of the defects is discussed based on the results.

2. Experimental procedure

The AlN single crystal samples used in the experiment were grown by a physical vapor transport (PVT) method in our laboratory. High purity AlN powder was first sintered at about 2000 °C for 30–40 h to remove the high concentration of oxygen in the raw material. Then the sintered AlN material was placed in a tungsten crucible for the PVT single crystal growth using a tungsten mesh heater furnace manufactured by Suzhou Advanced Rare Metal Co, Ltd. The details of the PVT growth can be found in Ref. [11]. An AlN crystal boule with a diameter of about 40 mm was obtained after a growth at 2200 °C for 40 h. A lot of AlN single crystal grains with natural smooth hexagonal surfaces are formed in the boule. The surface can be identified as the (0001) Al face of the AlN single crystal by referring to the reported results in Ref. [11]. It is used directly as a sample for the wet etching since the (0001) Al surface can give clear and reliable results of the etching pit dislocation density[12]. Sample wafers with a size of $5 \times 10 \times 0.6$ mm^3 were sliced from the boule and polished on both sides for the XRD and infrared absorption measurement.

Prior to etching, the sample wafer was ultrasonic cleaned in acetone for 5 min, washed with alcohol and deionized water, and dried. Then the wafer was dipped into molten NaOH–KOH contained in a silver crucible for 3 min. The temperature of the molten NaOH–KOH was 300–400 °C. After a continual etching of about 20 min, clear, regular hexagonal etch pits were observed on the (0001) Al face. The etch pits of the sam-

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Fig. 1. Etching pits on a naturally formed (0001) Al surface of an AlN single crystal.

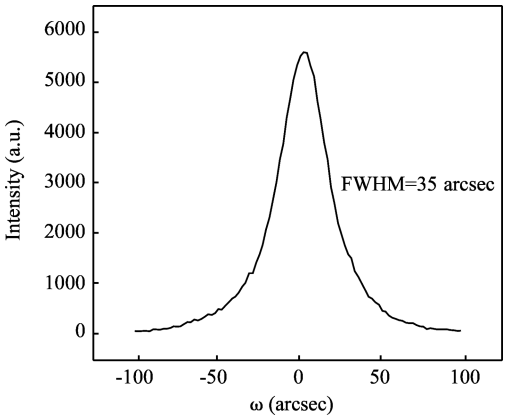

Fig. 2. XRD (0002) rocking curve of an AlN single crystal sample.

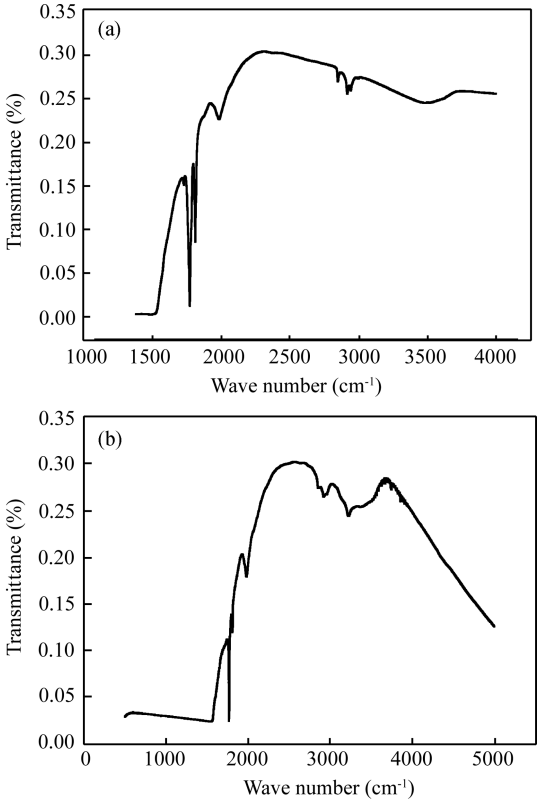

Fig. 3. Infrared absorption spectra of two AlN single crystal samples.

ple were examined and counted by using an Olympus X40 optical microscope. XRD and the infrared absorption were measured by using a Bede D/max-RB X-ray diffractometer (Japan, Rigaku, D/max-RB) and FTIR-120.

3. Results and discussion

A typical optical microscopy photography of the etched (0001) Al surface is shown in Fig. 1. Regular hexagonal pyramids with different sizes were visible on the surface. Since the sample is obtained in its natural as-grown state, its surface is not as flat as a polished face. Residual growth steps are also observed on the surface, as shown in Fig. 1. This fact reflects that the (0001) Al face nucleates and grows up via a two dimensional step-flow growth mode under the present growth condition. This is in agreement with the reported results of Bickermann *et al.*[8], in which (0001) AlN with the (0001) Al face is easily formed at a growth temperature of 2000 °C. It is also noted that most of the etching pits are formed in several parallel lines. The line is in parallel with one of the sides of the hexagonal, suggesting a direction along $(1\bar{1}00)$, which is the lattice glide system direction of an AlN single crystal[13]. This implies a large thermal stress acting on the single crystal grain during the AlN single crystal growth. The thermal stress is larger that the critical resolved slip stress of the AlN lattice and the dislocations are generated by the cooling of the single crystal. Since the AlN crystal boule consists of a large quantity of grains with different orientations, the thermal stress comes most likely from the mechanical anisotropy of the grain. A lot of small pits are also observed on the etched surface, and these pits are not due to dislocations since their sizes do not change with increasing etching time. It is possible that the pits are micro hole defects formed during the PVT AlN growth process.

The etch pit density (EPD) of the dislocations on the (0001) Al face of the AlN single crystal is counted to be 4000 cm^{-2}. As shown in Fig. 2, the XRD rocking curve of the AlN single crystal has a full width at half maximum (FWHM) of 35 arcsec, indicating a good quality of the AlN single crystal.

Infrared absorption spectra in the wave number range of 1500–4000 cm^{-1} of two AlN samples are shown in Fig. 3. Absorption peaks around 1790, 1850, 2000, and 3000 cm^{-1} are clearly observed. Localized vibrational modes (LVM) is a very powerful tool to identify impurities in semiconductors. The approximation formula of LVM is described as $w_{\mathrm{Loc}}^2 = A(\frac{1}{m_{\mathrm{i}}} + \frac{1}{\beta m_{\mathrm{nn}}})$, where w_{Loc} is the frequency of the vibrational mode, A and β are model-adjust parameters, m_{i} is the mass of the impurity atom, and m_{nn} is the mass of the atom adjacent to the impurity. Thus, the LVM of an impurity atom in III–V compounds are similar to each other. We can estimate the infrared absorption of impurities in AlN by a comparison with the results of other III–V compounds. Song *et al.* first reported a 715 cm^{-1} infrared absorption peak in GaAs to be related to O impurities[15]. The study of the GaN optical absorption shows that the oxygen will form donors and results in infrared absorption[14]. Since the adjustment parameters of

LVM in AlN are undefined constants, the absorption peak of O is estimated to be higher than that of GaAs. It has been shown that oxygen enters the AlN lattice and forms structure as Al_2O_3, not as AlO[14]. Pastrnak found that the main absorption of oxygen was between 3.5 and 5.5 eV in AlN[14]. By using the formula $\sigma = 1303\sqrt{\frac{k}{\mu}}$ (k is bonding force, $\mu = \frac{m_1+m_2}{m_1 m_2}$, m_1 and m_2 is the mass of the atoms), the infrared LVM absorption peak of Al_2O_3 material is calculated to be at about 1600 cm^{-1}. However, considering the influence of the adjacent atom, the bonding force between Al and O in AlN will be weaker than that of Al_2O_3; so the absorption peak will be higher than 1600 cm^{-1}. Thus, the absorption peak in AlN at 1790 cm^{-1} might be related to oxygen.

Oxygen is a major residual impurity with a quite high concentration in AlN[16–19]. It negatively influences the properties and the structure quality of an AlN single crystal[19–21]. With a high content of O in AlN, $(AlN)_m(Al_2O_3)$ compounds are formed, and irregular crystallization and a large number of defects and dislocations are generated. After a high temperature sinter treatment for more than 30 h, the oxygen content in AlN decreases significantly. However, an oxygen concentration of 10^{18}–10^{19} cm^{-3} still exists in the AlN single crystal due to the strong affinity between oxygen and aluminum.

Absorption peaks at 1850 and 2000 cm^{-1} might be caused by carbon and silicon in AlN, respectively. The LVM absorption of C and Si in GaN is between 450 and 1500 cm^{-1}[22]. Hence, the absorption frequency of these impurities in AlN will be higher. Besides, carbon–hydrogen and silicon–hydrogen complexes possess characteristic LVM frequencies of more than 1500 cm^{-1}. Typically, the absorption of silicon–hydrogen varies in three absorption bands: (a) the stretching band between 2000 and 2090 cm^{-1}, (b) the bending band between 840 and 890 cm^{-1}, and (c) the wagging band around 640 cm^{-1}. It is not surprising that C and Si are detected in AlN because they are also very common residual impurity in AlN single crystal grown by the PVT method. Unlike oxygen, the two impurities might increase the electrical conductivity of the AlN by substituting Al sites and acting as shallow donors. However, the doping efficiency of AlN is very low and it is still difficult to obtain n type AlN with good electrical conductivity so far[23]. Due to the low activation ratio of donor impurities in AlN, it is estimated that at least a concentration as high as 10^{20} cm^{-3} of Si has to be incorporated in AlN to cause a change of the material from an insulator to a semiconductor. Thus the residual Si and C have a negligible influence on the electrical property of our AlN sample and it is still an insulator with an electrical resistance of 10^9–10^{13} Ω·cm. In our recent study, after a concentration of 10^{19} cm^{-3} Si was implanted in the AlN single crystal, the material was still an insulator.

The essence of the 3000 cm^{-1} absorption peak is still unclear. It might be caused by complex defects but its structure was unknown. Reports[24, 25] show that carbon–hydrogen has a LVM infrared absorption at 2853, 2923, and 2956 cm^{-1}, related to CH, CH_2, CH_3 in GaN and SiC, respectively. Recently, computer simulations were used to help to analyze and build a theoretical model of the complex defect[26]. According to the simulation results of Qulian *et al.*[27], the two defect systems of oxygen impurities (V_{Al}–O_N–3N and V_{Al}–$2O_N$–2N, V_{Al}: aluminum vacancy, O_N: oxygen antisite) have an energy gap of about 0.56 eV. The energy of the absorption peak observed is 0.37 eV. This might give us some clue as to the structure of the complex defects. It is possibly caused by the transition of two oxygen-related defect systems, other impurities, or even more complex system.

4. Conclusion

A self-nucleated PVT AlN single crystal experiences a large thermal stress in the growth process, resulting in lattice slip and the formation of dislocation line arrays. The existence of oxygen, carbon, silicon and their complex defects in the AlN single crystal are evidenced by infrared absorption. It is necessary to optimize the raw material treatment technique to further reduce the impurity content in the AlN single crystal.

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