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Materials

Growth and microstructure of AlN whiskers and dendrites

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Abstract: AlN whiskers or dendrites were synthesized with a sublimation-recrystallization method by using Al, AlN powders and some additives as raw materials. Whiskers with different sizes that featured high purity and good crystallinity were obtained by controlling temperature and gas supersaturation in the reaction container. The whiskers were described as long and straight single crystals of approximately 1-30 μm in diameter by the centimeter range in length. However, AlN dendrites were about 1 mm in diameter by 0.5 cm in length, and showed an obviously preferential growth orientation, *i.e.*, perpendicular to $[2\bar{1}\bar{1}1]$ and $[10\bar{1}1]$ planes. It is concluded that the whiskers or dendrites grow *via* the vapor-solid mechanism.

Key words: aluminum nitride; whiskers; dendrites; sublimation-recrystallization method

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Aluminum nitride (AlN) is considered an ideal material for semiconductor substrate applications. It combines properties such as high thermal conductivity, low thermal expansion coefficient, high electrical resistivity, and excellent dielectric properties, which make it an effective heat sink or heat-dissipating medium [1]. However, these properties depend critically on material purity, *e.g.*, the thermal conductivity is greatly influenced by impurities, especially oxygen impurities [2]. So far, the thermal conductivity of AlN ceramics is far lower than its theoretical value (319 W/(m·K)). Whiskers are one-dimensional single crystals with perfect crystallinity and free of defects in their structure, and their strength and modulus approach the theoretical value of perfect crystals. The commercial high-purity AlN whiskers can be used as reinforced phase in structural composites and also as functional unit in functional composites.

Since AlN whiskers were accidentally discovered by Kohn [3], some researches were carried out [4,5]. However, the fabrication was still in an experimental stage up to now. AlN whiskers were not commercially available on a large scale. The main reason lies in the high cost and low purity of AlN whiskers. In this paper, AlN whiskers were synthesized with a sublimation-recrystallization method by using suitable additives, and its microstructure was investigated.

1 Experimental

The starting materials used in this study were commercial Al and AlN powders. The Al powders (99.9%Al) were passed through a 260 mesh sieve and the AlN powders (containing 33%N) had a particle size less than 2 μm. Some additives were added. The fully mixed powders were placed on multilayered plates in a reactor. The reactor was put into a furnace with nitrogen atmosphere and controllable nitrogen pressure. The synthesis temperature was in a range of 1750-1950℃ and hold for 3 h.

The phases of the samples were identified by an X-ray diffraction (XRD) with CuK_{α}. The whiskers were observed by a scanning electron microscopy (SEM) and an electron probe X-ray microanalyzer (EPMA).

2 Results and discussion

Whiskers are single-crystal fibers or filaments with a high aspect ratio. Growth characteristics not only depend on their crystallinity, but also to a large extent on external growing conditions. By varying the proc-

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essing parameters such as reaction temperature, time, species and quantity of additives, and gas flow rate, the quantity and quality of whiskers can be controlled [6].

A large amount of white wooly materials were formed on the multilayer plates in the reactor under suitable processing conditions. XRD patterns of the collected specimens were identified as AlN. A large number of long and straight whiskers obtained at 1750 ℃ were observed by EPMA in **figure 1**(a). Typical energy dispersive spectrum analysis of the AlN whiskers was shown in figure 1(b). Chemical analysis showed strong aluminum and nitrogen peaks (the peak of Cu was that of substrate), no oxygen and other impurity peaks were observed. It was illustrated that the products were of high-purity AlN whiskers with a diameter of approximately 1-30 μm by a length in the centimeter range. The whiskers featured rhombic needle-shaped structures. Most of whiskers were prisms with smooth surfaces, and a little were with serrate-shaped surfaces. Spiral growth patterns could be clearly seen under a high resolution SEM shown in **figure 2**(a).

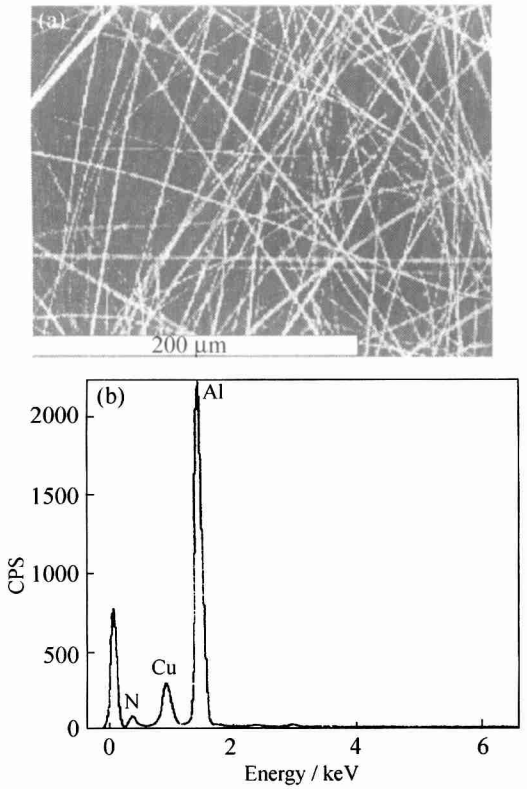

Figure 1 EPMA image of AlN whiskers obtained at 1750 ℃ (a) and their EDS (b).

The morphology of the whiskers with a diameter of approximately 20 μm by a length in the centimeter range obtained at 1850℃ were showed in figure 2 (b). The whiskers were prisms with smooth surfaces. It is obvious that the diameter of AlN whiskers increases with the increase of temperature.

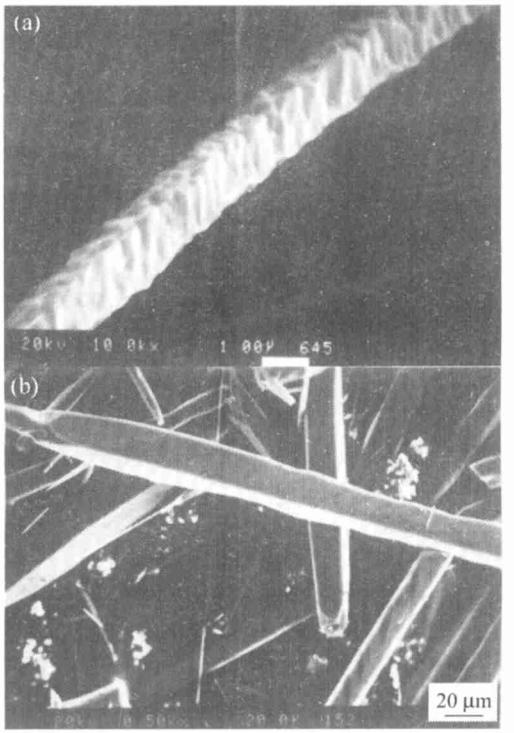

Figure 2 SEM micrograph of AlN whiskers at 1750℃ (a) and 1850℃ (b), respectively.

As the temperature and gaseous supersaturation increased, the whiskers grew from one-dimensional to multi-dimensional structures and then dendritic spikes of AlN were formed. **Figure 3** shows the dendritic spikes of AlN obtained at 1900℃ with a diameter of approximately 1 mm by a length of 0.5 cm. The dendritic spikes of AlN were white and transparent. Most of them were hexagonal needle-shaped prisms. The product was proved to be single phase AlN by the XRD patterns in **figure 4**. The intensity of diffraction peaks showed drastic difference from the standard value in AlN card (JCPDS). The obviously preferential growth orientation was observed. The diffraction peaks were identified to be strong orientation along $[2\bar{1}\bar{1}1]$ and $[10\bar{1}1]$, *i.e.*, the growing planes were

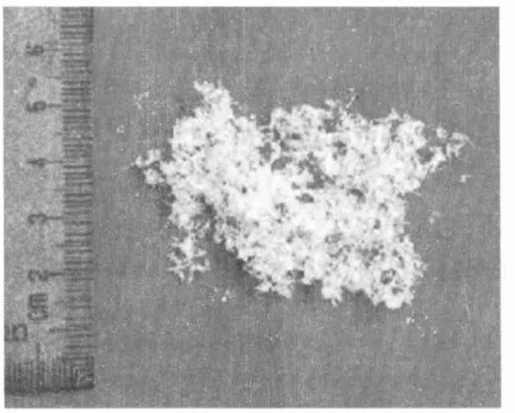

Figure 3 Dendritic spike of AlN at 1900℃.

perpendicular to [2$\bar{1}\bar{1}$1] and [10$\bar{1}$1] planes.

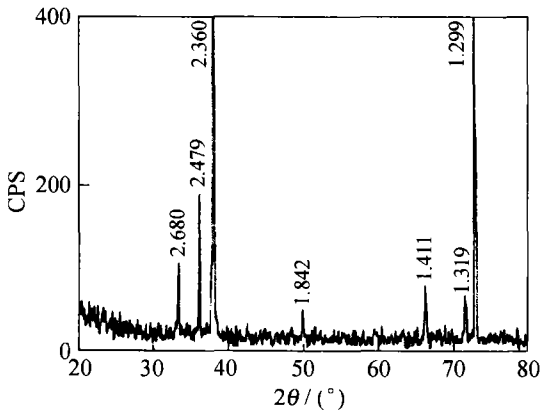

Figure 4 XRD pattern of dendritic spikes of AlN.

The formation of whiskers consists of two processes: nucleation and growth. AlN whiskers grew *via* sublimation-recrystallization of gaseous AlN. It is suggested that these whiskers grew by the VS mechanism, *i.e.*, they grew by "vapor-solid" nucleation and growth. The temperature and gaseous supersaturation are two important factors for the growth of whiskers in the vapor-solid mechanism. In our experimental system, high-purity AlN whiskers were synthesized at lower temperatures. On the one hand, the starting powders consisting of Al and AlN powders were nitridated in nitrogen atmosphere. The nitridated product of Al is nanocrystalline AlN with high activity [7]. AlN nanocrystallines can be vaporized at a lower temperature than normal AlN powders. On the other hand, suitable additives can promote vaporization of AlN at a lower temperature than that of its sublimation. The gaseous supersaturation of AlN was effected by the species and quantity of the additives in the reactor. The AlN whiskers with good crystallization can be obtained with a moderate gaseous supersaturation of AlN. If the gaseous supersaturation of AlN was too high, the vaporized nuclei cluster with some molecules aggregative should be absorbed on the surface of nuclei, and then the dendritic spikes of AlN were formed.

3 Conclusions

Whiskers with different sizes were obtained by controlling temperature and gas supersaturation in the reaction container. The whiskers were described as long and straight single crystals of approximately 1-30 μm in diameter by a centimeter range in length. They featured high purity and good crystallinity. If the gaseous supersaturation of AlN is relatively high, the dendritic spike of AlN is formed. AlN dendrites were 1 mm in diameter and 0.5 cm in length. The microstructures were hexagonal spikes and showed an obviously preferential growth orientation, *i.e.*, perpendicular to [2$\bar{1}\bar{1}$1] and [10$\bar{1}$1] planes. As a result, the whiskers or dendrites grow *via* the vapor-solid mechanism.

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