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Morphologies and growth mechanisms of aluminium nitride whiskers

WEI-GUO MIAO, YIN WU, HE-PING ZHOU
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Morphologies of AlN whiskers grown by the vapour–liquid–solid mechanism (VLS) were investigated. Several types of whisker structures, such as growth hill, wavy, crossed and stack structures, were found due to the variation of growth conditions. Growth mechanisms and orientations of AlN whiskers were also studied. Besides preferential crystallographic planes, several other planes were found to be growth layers due to the perturbation of the AlN lattice change caused by dissolution of oxygen. A screw dislocation growth mechanism was clearly confirmed. An oblique growth mechanism was found in this work, which may be the result of two processes: the vapour–liquid–solid process and dissolution of oxygen.

1. Introduction

Aluminium nitride (AlN) has a high thermal conductivity, low dielectric constant and high electrical resistivity. Its thermal expansion coefficient matches well with that of silicon. All these factors make it a promising material for passivation and dielectric layers in semiconductor devices, as well as for electric substrates [1, 2]. Thermal conductivity is the most important property of AlN substrate. The theoretical value of the thermal conductivity of AlN was predicted to be 319 $W m^{-1} K^{-1}$ at room temperature, which is a big advantage over Al_2O_3. However, Slack [3] pointed that oxygen, dissolved in the AlN lattice, created aluminium vacancies which effectively lower thermal conductivity. On the other hand, densifying pure AlN is difficult owing to its high melting point and strong covalent bonding . Usually Y_2O_3 is doped as a sintering aid. It may react with Al_2O_3, precipitating Y–Al–O compounds such as $YAlO_3$, $Y_3Al_5O_{12}$ and $Y_4Al_2O_9$ in grain boundaries, and then increases the thermal conductivity by decreasing the oxygen content in AlN grains [4]. However, a high sintering temperature (more than 1800 °C) is still required to achieve satisfactory results.

By considering the successful application of polymer–ceramic composite in transducers [5], it is thought that the composite may be another promising substrate. For example, AlN in a powder or sintered grain form, has been added as filler for polymer and glass compounds, to increase the heat-transfer properties of these materials. Also, AlN fibres or whiskers have been used to optimize the thermal properties of electronic-packaging application [6]. Polymer-whiskers may be selected as a promising substrate, which combines advantages of polymer and ceramic substrates. SiC whisker could be a candidate for this composite because it has been extensively studied for the past decade and it has an excellent thermal characteristic, but it would be detrimental to the advantage of the polymer substrate because of its high dielectric loss. So this avenue was abandoned, and AlN whisker was chosen instead. Compared with SiC, AlN whisker has not been widely investigated, especially the fabrication method. However, owing to its high thermal and electrical quality, it has attracted much interest and we choose it as an ideal material for a composite substrate. To apply AlN whisker commercially, it is necessary to produce it by an economic means, rather than vapour–solid (VS) and chemical vapour deposition (CVD) methods, which have been reported previously [7, 8]. Caceres and Schmid [9] have recently fabricated AlN whisker by an innovative way – the vapour–liquid–solid (VLS) process – in which AlN whiskers were fabricated by carbothermal nitridation of alumina with the aid of droplets formed by a catalyst. Compared with other whisker-producing techniques, VLS provides an effective way to produce high-quality whiskers. In this work, AlN whiskers were also successfully produced by a similar method.

Historically, several mechanisms were broached to explain the growth of whiskers, such as the axial screw dislocation mechanism [10], the vapour–liquid–solid (VLS) mechanism [11], and others [12]. The axial screw dislocation mechanism was originated by Frank [10], who postulated the presence of an axial screw dislocation, but examination of this theory by direct observation has generally been extremely difficult [13]. VLS mechanism was initiated by Wagner and Ellis, by which whiskers were grown from the droplets formed by the catalyst [11]. Usually, the axial screw dislocation and VLS mechanisms are considered to be two different processes. However, according to Kato [14] and our observation, the VLS process may transform to the vapour–solid (VS) process (which forms the basis of the axial screw dislocation) at high temperature. Under this condition, the axial screw

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dislocation mechanism may be involved, thus very interesting results would be obtained due to the combination of these two processes. In this work, the morphologies and growth mechanisms of AlN whiskers grown by VLS process were studied.

2. Experimental procedure

Alumina, carbon (mole ratio $C:Al_2O_3 = 6$) and a small amount of catalyst, were mixed together by wet grinding for 48 h. Recarburizing coke was used as a source of carbon. The mixture was dried and placed in a graphite tube. The carbothermal reduction was carried out in a graphite furnace at 1800 °C for 4 h with flowing high-purity nitrogen.

Obtained whiskers were identified by X-ray diffraction (XRD). The morphologies of these whiskers were investigated by optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM, H800, Hitachi Corporation). Electron diffraction was applied to determine the whisker-growth direction.

3. Results and discussion

3.1. Morphologies of AlN whiskers

AlN whiskers were formed at the original powder bed and around the wall of the graphite tube. Fig. 1 shows the morphology of wool-like whiskers. The diameters of these whiskers are in a range between 0.1 and 1μm, and the lengths are of the order of milli metres. Fig. 2 shows whiskers with tetragonal cross-section. From the bottom of these whiskers, it can be clearly seen that these whiskers have originated from the bottom crystals.

Optical microscopy shows some whiskers with growth hills (Fig. 3). It is considered that an isolated screw dislocation source of constant strength located at the origin, provides a boundary condition which determines the successive shapes of the growth hills [15]. Fig. 3 shows that the hills have grown from the contaminated areas, but not from the clean areas. So the distribution of these hills is greatly affected by the impurities. One characteristic of AlN whiskers produced by carbothermal reaction is the lack of droplets at the whisker tips [9]. It may be explained by the evaporation of droplets [14], or a strong interaction between the substrate and the liquid catalyst [16]. Here the hill structure provides strong evidence to confirm that the whiskers were fabricated by a VLS mechanism. This conclusion is supported by the droplets at the top of the hills. The diameter of the whisker and the heights of the hills are seen to be lowered with increasing of distance from the whisker bottom. This phenomenon can be explained by the evaporation of the droplet. According to Kato and Tamari [14], VLS can be transformed to the VS mechanism by this evaporation effect. Very interesting results ensued

Figure 1 Scanning electron micrograph of wool-like AlN whiskers.

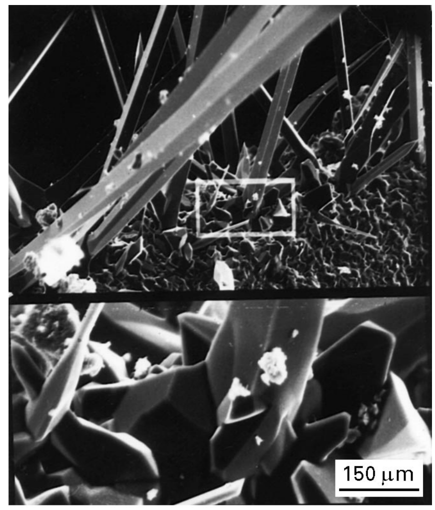

Figure 2 Scanning electron micrograph of whiskers grown from the bottom crystals.

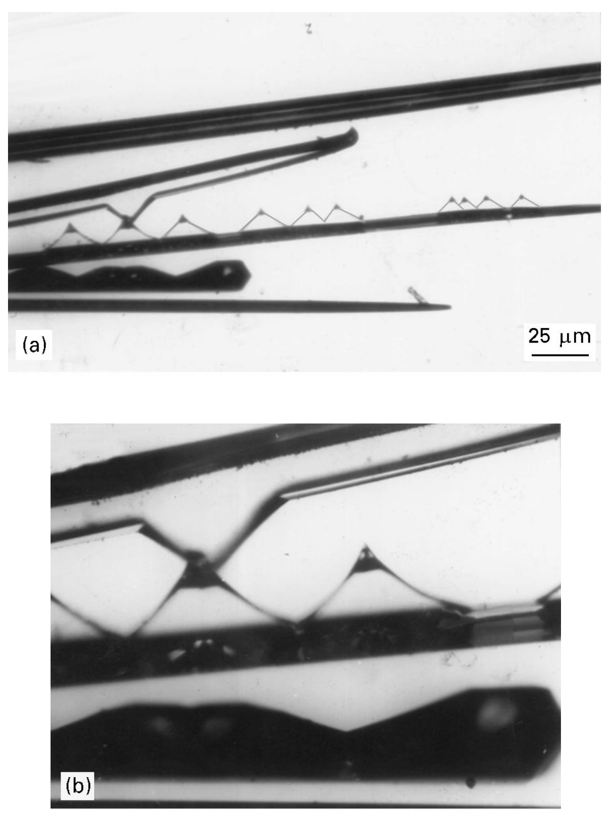

Figure 3 Optical micrograph of whiskers with growth hills. The droplets at the top of the hills strongly confirm the VLS mechanism.

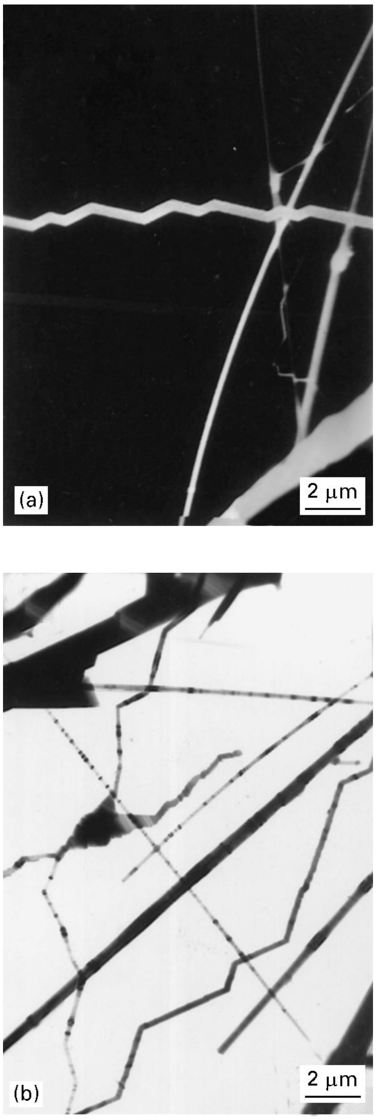

Figure 4 AlN whiskers with wavy structures. (a) Wavy angle 141°, (b) wavy angle 130°.

with this effect, which will be extensively discussed later.

Fig. 4 shows AlN whiskers with wavy structures. The wavy structure is so ordered that the neighbouring edges form an angle of 141° (Fig. 4a) and 130° (Fig. 4b). Because equivalent planes have the same possibilities of growth at equivalent directions, these wavy structures were formed with the aid of growth-condition fluctuation.

Whiskers grown by the axial screw dislocation mechanism can be observed in Figs. 5 and 6. This mechanism will be discussed later. Fig. 6 is now of greatest concern. It is rather surprising that the axis of the whisker grown by screw dislocation can change to another direction. As discussed previously, it is possible that the whisker axis can change to another direction, as for the whiskers in Fig. 4. But with the existence of axial screw dislocation, the twist strain caused by the turning direction is so high that it is unusual for the axis direction to change [17]. One possible explanation is that the turning process could be realized with the aid of droplets.

Fig. 7 shows two whiskers crossing each other. This structure is caused by the encountering of these two

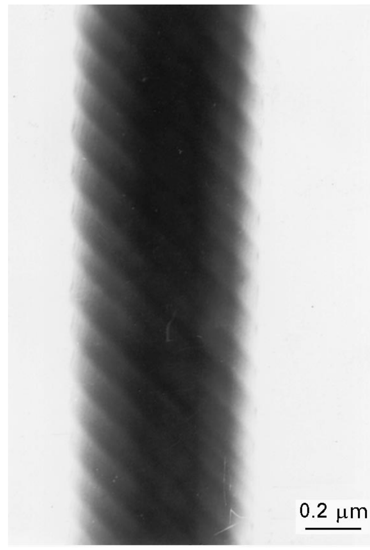

Figure 5 Transmission electron micrograph of a whisker grown by the axial screw dislocation mechanism.

Figure 6 Transmission electron micrograph of a whisker with the axial screw dislocation turning to another direction.

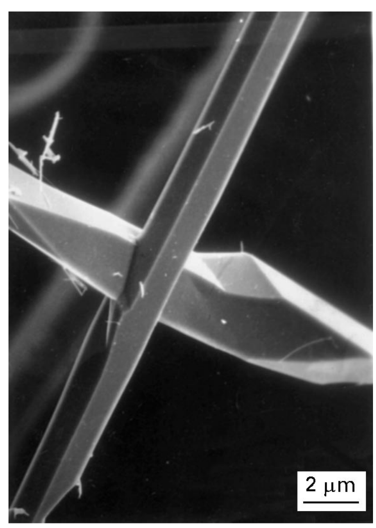

Figure 7 Two whiskers crossing each other, which had no impact on each other's growth.

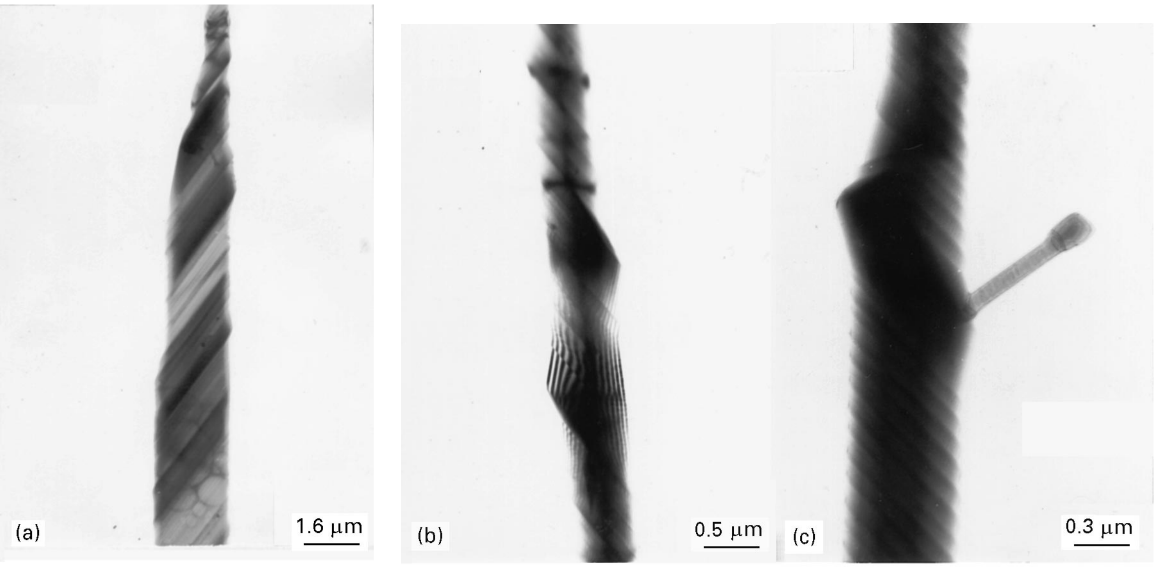

Figure 8 Transmission electron micrographs of whiskers with secondary thickening structure. (a) Normal secondary thickening structure. (b) Knuckles distributed along the whisker. (c) Secondary nucleation caused by impurities at the knuckle.

whiskers at the growth stage. The initial stage of this structure can be observed in Fig. 3 – two growth hills meeting each other. As in the propagation of two independent wavy structures, these two whiskers did not influence each other's growth process, and thus this crossed structure was formed.

Fig. 8 shows whiskers with secondary thickening structures. This structure is caused by layer growth, in which the initial leader is followed by a succession of secondary growth layers [18]. Sometimes knuckles were found in the secondary thickening structure, as shown in Fig. 8b and c. It is interesting to see that the knuckles are homogeneously distributed along the whisker (Fig. 8b), which may indicate that some secondary thickening structures are formed during the whisker growth process, not in the later stage. The secondary thickening structure may result from the secondary nucleation caused by impurities or changes of the growth conditions, as shown in Fig. 8c [19]. A change in the droplet′s size may also contribute to this effect [15].

Although most AlN whiskers were formed by the growth of atomic layers, there are still some whiskers which were formed by stacking of the AlN single crystals. This stack structure can be clearly observed in Fig. 9. Single crystals of AlN were joined face-to-face and grew without a special direction, thus forming the stack structure. Another kind of stack structure is shown in Fig. 10. The AlN crystals are so small that the whisker diameter is only about 0.2 μm. Electron diffraction shows that this whisker is polycrystal. It is surprising that this whisker has a texture structure to some extent, which was observed by the brightness variation of the diffraction ring. It can be considered that impurity, flowing nitrogen and variation of temperature may contribute to this stack structure. The whisker growth was interfered by the fluctuation of growth conditions. Thus the growth direction would be changed by this influence.

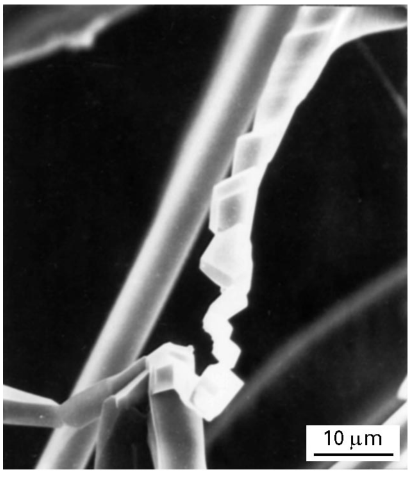

Figure 9 Stack structure of AlN single crystals joined face-to-face without a special direction.

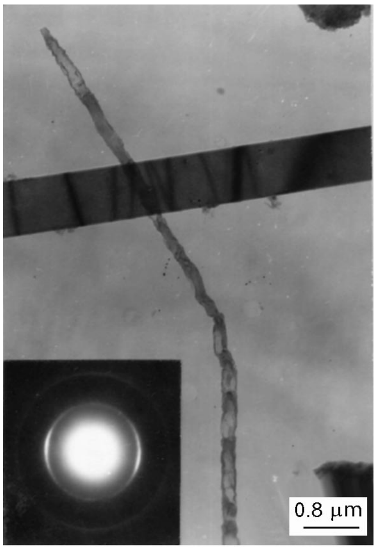

Figure 10 Brightness variation of the diffraction ring shows the whisker has a texture to some extent.

3.2. Growth mechanisms of AlN whiskers

3.2.1. Growth planes of AlN whiskers

Aluminium nitride has a hexagonal wurtzite structure ($c/a = 1.60$). The $\{\bar{1}\,2\,\bar{1}\,0\}$ and $\{1\,0\,\bar{1}\,0\}$ planes are more densely packed than are the $\{0\,0\,0\,1\}$ planes [20]. Whiskers with these three kinds of plane as growth layers were reported in other papers [9, 13, 21] and in the present work. For example, Fig. 11 shows a whisker with an axis normal to $(\bar{1}\,2\bar{1}\,0)$. There are still other kinds of growth planes, such as $(1\,0\,\bar{1}\,1)$, which was reported by Caceres and Schmid [9]. Fig. 12 shows a whisker with growth plane $(1\,0\,\bar{1}\,3)$. Whiskers with a $(1\,0\,\bar{1}\,2)$ growth layer (Fig. 13) will be discussed later. So, besides preferential crystallographic planes, several other growth layers do exist in AlN whiskers. These kinds of growth may be the results of oxygen dissolution in the AlN lattice, which causes the change of the AlN lattice parameter and then alters the crystallinity of AlN [22].

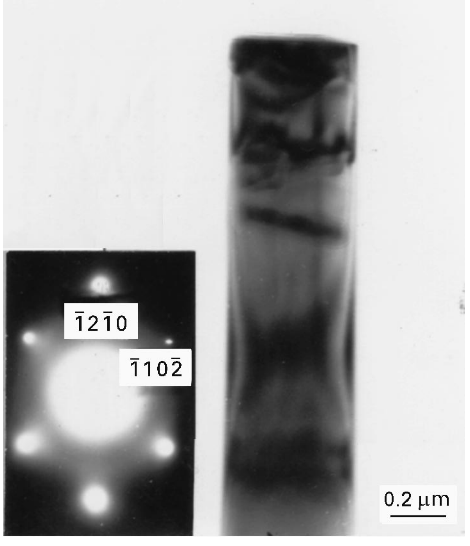

Figure 11 Transmission electron micrograph of a whisker with its axis normal to $(\bar{1}\,2\,\bar{1}\,0)$.

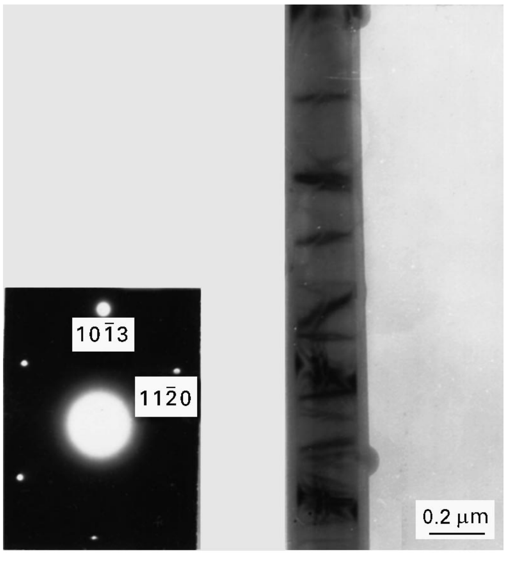

Figure 12 Transmission electron micrograph of a whisker with growth layer $(1\,0\,\bar{1}\,3)$.

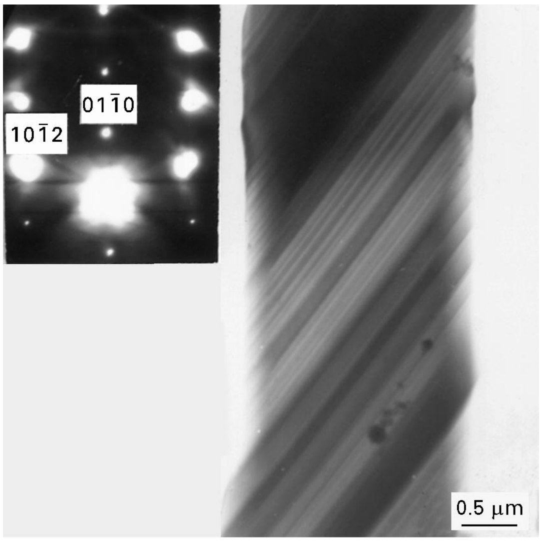

Figure 13 Transmission electron micrograph of a whisker grown by axial screw dislocation, with growth layer $(1\,0\,\bar{1}\,2)$.

3.2.2. Whiskers grown by axial screw dislocation

Fig. 13 shows an AlN whisker with axial screw dislocation; the image matches the model of Frank well. The helical growth layer is determined to be $(1\,0\,\bar{1}\,2)$, and the fibre axis (or Burgers vector) is 38° away from the growth layer. The helical growth layers are clearly observed due to the large height of the steps, which is the result of the VLS process. In the original screw dislocation model, the height of the step is small due to the low supersaturation of AlN vapour. But according to the VLS process, a droplet appears at the tip of the whisker, and the AlN in the droplet is so supersaturated that solid AlN precipitates from the droplet on to the substrate [23]. Using this process, the growth step is high, up to about 200 nm. Because the step height measured in terms of the number of displaced atomic layers is a direct measurement of the local Burgers vector, $\boldsymbol{b}$, and the strain energy of a dislocation is proportional to $\boldsymbol{b}^2$, these high steps are very uncommon for whiskers. Although various things remain unknown about how this phenomenon is formed, it does provide a prominent structure to satisfy our needs – to observe directly the axial screw growth mechanism, thus strongly supporting Frank's theory. Another string-like whisker (Fig. 14) also confirms the existence of axial screw dislocations in some AlN whiskers.

3.2.3. Whiskers grown by an oblique growth mechanism

Fig. 15 shows another interesting filamentary form of AlN. The selected-area diffraction pattern shows that the spots have satellites. This feature confirms the presence of planar defects such as stacking faults in this whisker. The growth layer was determined to be $(0\,0\,0\,1)$, which is very common for wurtzite structure. But it is interesting that the growth layer glides a distance after climbing a step. This distance was determined to be about 40 nm, and caused the fibre axis to

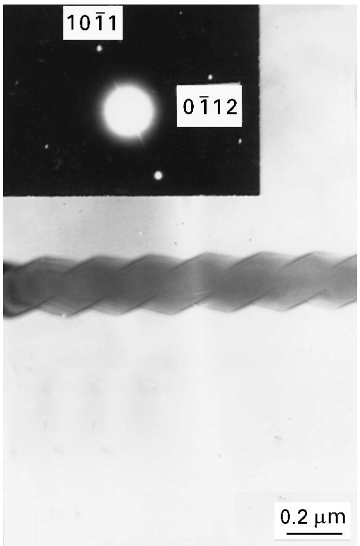

Figure 14 A string-like whisker confirming the existence of axial screw dislocation.

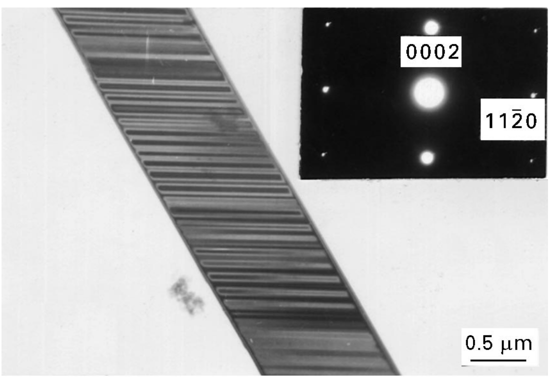

Figure 15 Stair-structure whisker, showing that oblique growth may be another growth mechanism for AlN whiskers.

move 31° away from the [0 0 0 1] direction. This effect is termed the glide or oblique growth mechanism. If there was no glide effect, the growth direction would be along [0 0 0 1], but because of this glide effect, AlN whiskers fabricated by the VLS process have no fibre axis normal to the (0 0 0 1) plane. This phenomenon is rather surprising in view of the fact that (0 0 0 1) is known to be the preferential crystallographic plane for HCP crystals [9].

Fig. 16 shows a whisker with two parts, both of which have equivalent growth layers $\{1 0 \bar{1} 2\}$. Clearly, the lower part was originated by the combination of a screw dislocation and oblique growth mechanisms, the morphology of which is quite different from the upper part, which is only the result of screw dislocation growth. The oblique growth mechanism has been reported in the films due to the size effect [24], but has not been found in whiskers. Because the VLS process is involved in the whisker growth, the droplet's surface tension may be one of the causes of this effect. The surface tension may provide a force to pull the droplet to the edge and form the stair structure. However, there exists another question: why are the glide directions the same? The other cause may contribute to the

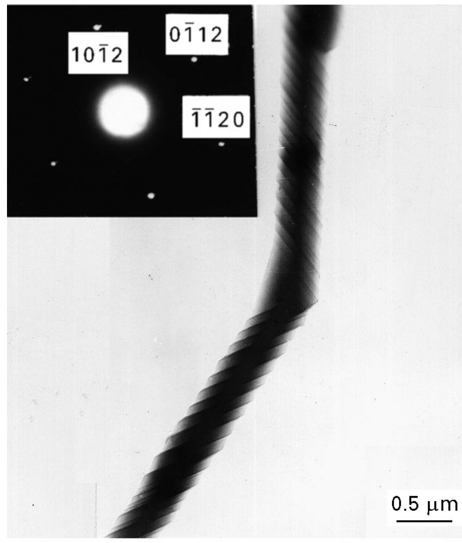

Figure 16 Two parts of a whisker with an equivalent growth layer $\{1 0 \bar{1} 2\}$. They have different morphologies due to the oblique growth involved in the lower part.

oxygen dissolved in the AlN lattice, which would produce lattice defects, such as stacking faults and inversion domains [25]; these defects would influence the crystallinity of AlN to some extent. Further investigation is required to examine this mechanism.

4. Conclusions

1. Morphologies of AlN whiskers grown by the VLS mechanism were observed. Whiskers with growth hills were formed due to the impurities. The whisker axis could turn to another direction to form a wavy structure. With the aid of droplets, whiskers with axial screw dislocations could change to another direction, which is unstable from the energy point of view. Owing to space limitation and fluctuation of the growth conditions, whisker growth was influenced, and thus crossed and stack structures were formed. A secondary thickening structure was also found in this work.

2. Although $\{\bar{1} 2 \bar{1} 0\}$, $\{1 0 \bar{1} 0\}$ and $\{0 0 0 1\}$ planes are theoretically densely packed in wurtzite structure, other growth layers were also found in AlN whiskers, which may be the results of crystallinity change caused by oxygen dissolution in the AlN lattice.

3. Owing to the liquid involved in the screw growth process, whiskers grown by axial screw dislocation were clearly observed.

4. By considering the stair-structure whisker, the oblique growth mechanism was studied. This mechanism postulated the existence of a force which causes the growth layer to glide after climbing a step. This force may originate from the VLS process and lattice distortion caused by oxygen incorporation.

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