Morphologies and growth mechanisms of aluminum nitride whiskers by SHS method—Part 2

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The high resolution electron microscopy was used to investigate the microstructure of AlN whiskers. The growth mechanisms of AlN whiskers were VLS and VS mechanism. The phenomenon of stacking fault was analyzed. Moreover, the growth mechanism of dendritic crystal was proposed.

1. Introduction
Historically, many growth mechanisms, such as screw dislocation mechanism, VLS mechanism [1, 2], were used to explain the growth mechanism of whiskers. There are various methods to synthesis AlN whiskers. The growth mechanisms of these AlN whiskers are VS [3–5], VLS [3–5], VTR [2], screw dislocation mechanism [4–6].

1.1. VS mechanism
Crystal growth by VS mechanism is associated with super saturation degree of atom in the gaseous phase. Whiskers are easy to grow under low supersaturation, while the material in gas phase nucleates evenly to produce powder under bigger supersaturation. It tends to produce tree shape and/or small round particle under middle supersaturation. The effect of impurity on whiskers' growth is not obvious.

1.2. VLS mechanism
The process is similar to the VLS process, invented in the early 1960s by Bell Laboratories for the production of high-quality SiC whiskers and detailed in Shyne [7] and Milewski [8]. In the VLS process, V stands for Vapor feed gases, L for Liquid catalyst, and S for Solid whisker, respectively. The presence of a liquid catalyst is what distinguish this mechanism from all other whisker growth mechanism. The role of catalyst is to form a liquid solution interface. Material is fed from the vapor through the liquid-vapor interface. The catalyst solution is a preferred site for deposition of feed from the vapor that cause the liquid to become supersaturated. Crystal growth occurs by precipitation from the supersaturated liquid at the solid-liquid interface. In VLS mechanism, the whiskers' growth is divided into two processes. The first is radial growth and unchangement of cross area, and the velocity is very fast. The second is whiskers thicken, and the velocity is determined by relative velocities between crystal side nucleation and crystal growth. The impurity and reactants form low co-melt Liquid-Solid interface. The material in the gaseous phase deposits on Liquid-Solid interface through the Vapor-Liquid interface to grow whiskers. Because high contain coefficient of the liquid phase supplies an intermediate state between gaseous phase and solid phase, the activation energy of VLS is several multiple lower than that of VS mechanism. In the course of whiskers' growth by VLS mechanism, the impurity plays important role. The liquid cools to form a round bead on the head of whiskers, which is important feature of VLS mechanism.

1.3. VTR mechanism
AlN whiskers are synthesized by CVD method [3], through VTR (vapor transaction reaction-chemical changes involved) mechanism. Al powder first gasifies and reacts with N_2, then nucleate. AlN is transported to wall to form AlN whiskers. In order to form whiskers, the reaction between Al and N_2 must take place on a substrate or droplets. So the growth mechanism is VLS and/or VS mechanism [2].

1.4. Screw dislocation
Historically, Frank proposed the screw dislocation. Screw dislocation mechanism has been considered as one of growth mechanism of whiskers. However, it is very difficult for vapor growth to examine the existence of screw dislocation through direct observing the whiskers' growth [9]. C. M. Drum [6] and Miao Weiguo [4] thought the screw dislocation mechanism is the growth mechanism of AlN whiskers fabricated by caborthermal method. Zhou Heping [5] observed the existence of the screw dislocation of AlN whiskers grown by sublimation recrystallization method.

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SHS method is a economic one. However, it is pity that growth mechanism of AlN whiskers grown through SHS method has not got detailed report. On account of the experiments' results of high-resolution microscope, the growth mechanisms of AlN whiskers were proposed.

2. Results and discussion

By using high-resolution microscope, the microstructures of AlN whiskers have been studied. The growth mechanisms of AlN whiskers are VLS and VS mechanism.

2.1. VLS mechanism

The observation of droplets at whisker tips (Fig. 1a) was evidence of VLS mechanism. The EDS (Fig. 1b) shows there are Al, N, O, Si and C five elements in the whiskers (The whiskers have been determined to be AlN whiskers by XRD method). In view of energy, it is easy to change the direction of whiskers' growth by the aid of droplet. So apart from droplets, kinking and branching, blade and needle structure can be found in the Fig. 1a.

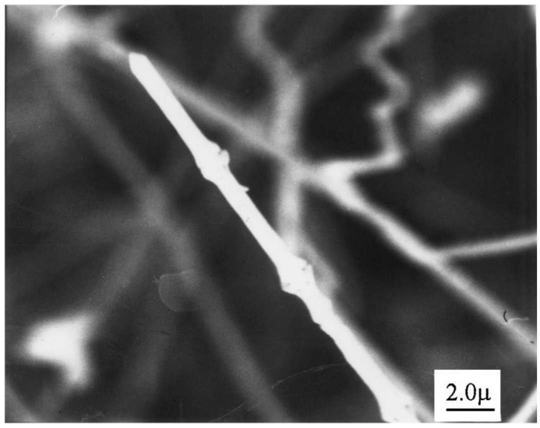
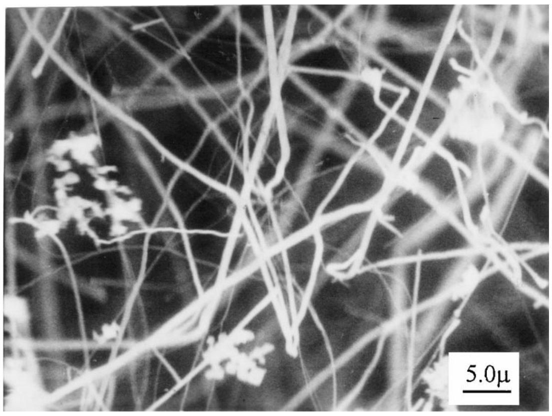
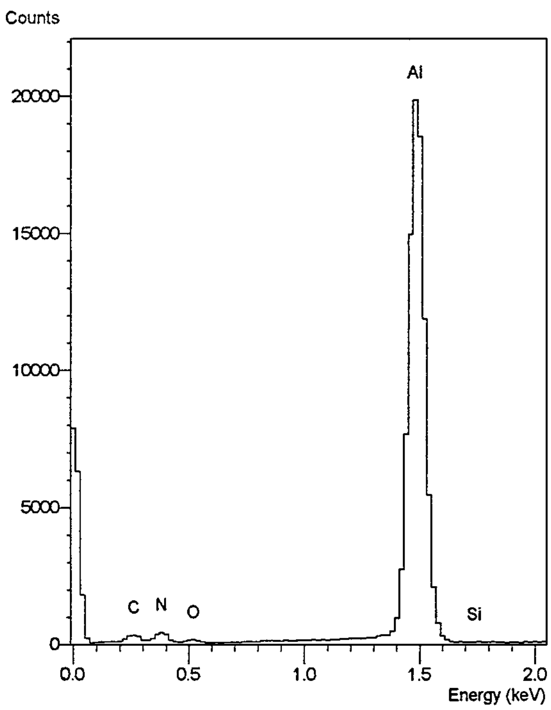


Figure 2 Smooth tip of AlN whiskers.



(a)



(b)

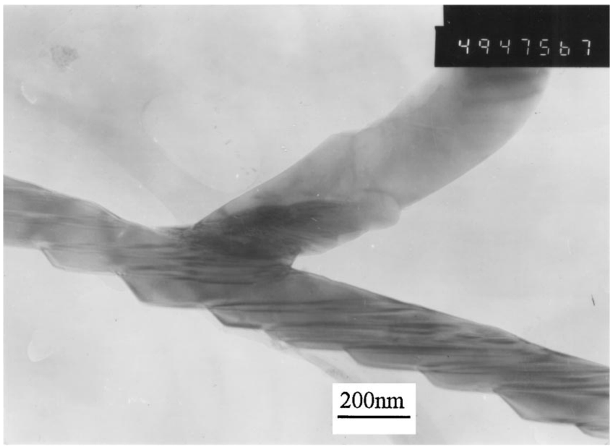
Figure 1 A liquid droplet on the tip of AlN whiskers (a) the EDS result of liquid droplet (b).

2.2. VS mechanism

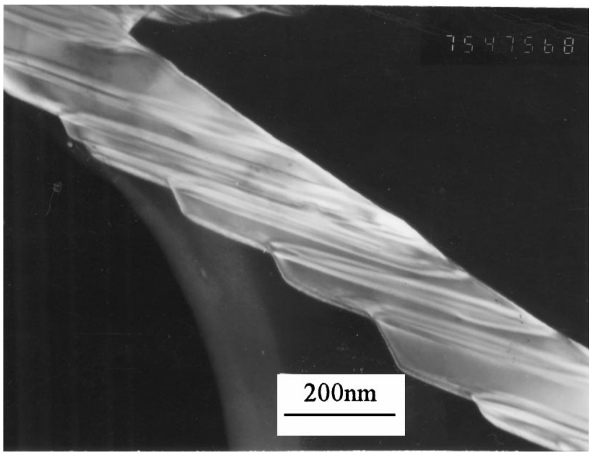
As for VS and VLS mechanism, they do not independent completely. At low temperature, the activation energy of VLS mechanism is lower than VS mechanism and it is easy for VLS mechanism to grow whiskers. While at high temperature, the function of VS mechanism is obvious.

One characteristic of AlN whiskers produced by carbothermal reaction is the lack of droplets at the whisker tips [3]. It may be explained by the evaporation of droplets, or a strong interaction between the substrate and the liquid catalyst. Here the droplets at the top of the whiskers (Fig. 1a) confirm VLS mechanism. However, the droplets were not observed in some whiskers. Smooth tips of AlN whiskers are shown in Fig. 2. According to Kato and Tamari [10], this phenomenon can be explained by the evaporation of the droplet. VLS can be transformed to the VS mechanism by this evaporation. So at the initial stage, whiskers are grown by the VLS mechanism, followed by VS mechanism because of the removal of droplets through evaporation at high temperature.

VS mechanism is also associated with the supersaturation closely. Fig. 3c, e, h (in paper 1) respectively show different morphologies at different supersaturation. The supersaturation of the reactant of 40 wt % Al is too low to grow whiskers. At higher supersaturation, the whiskers with needle type between 10 and 16 μm diameter (Fig. 3c in paper 1) can be grown. At rather higher supersaturation, minute multiple growth sites are activated on the substrate, and many smaller whiskers between 3 and 8 μm diameter (Fig. 3e in paper 1) can be grown. The excess supersaturation is sufficient to active secondary growth sites on the sides of the whisker, and then very small side branches between 1 and 3 μm (Fig. 3h in paper 1) diameter occur. The bright-field image and dark-field image of side branch are shown in Fig. 3. At the extreme high supersaturation, small fibrous clusters or dendritic crystal can be grown, as shown in Fig. 4a, b and c respectively.



(a)



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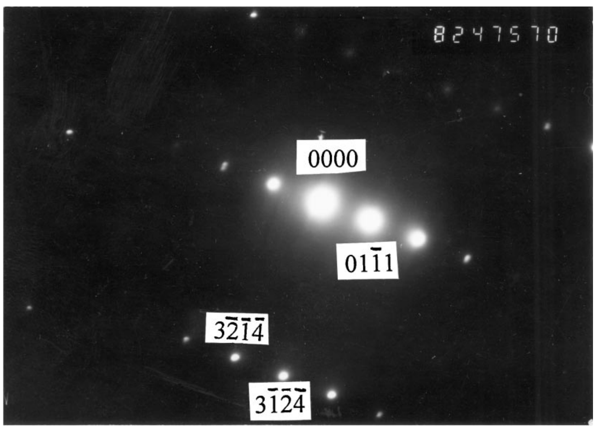
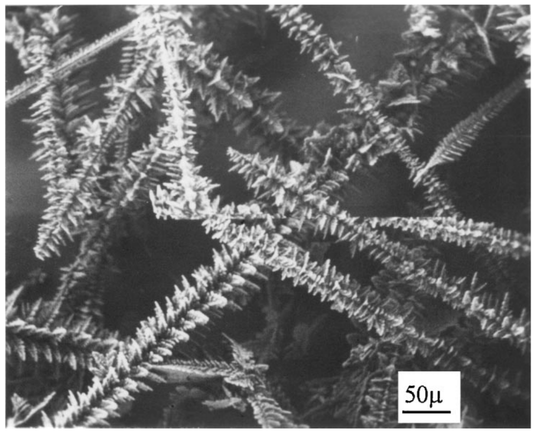


(c)

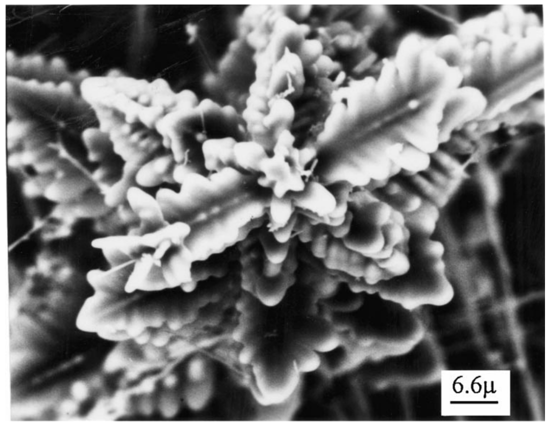
Figure 3 TEM morphology of growth bench of AlN whiskers (a) bright-field image (b) dark-field image (c) electron diffraction image.

2.3. Growth mechanism of dendritic crystal

At high supersaturation, the sublimation velocity is very big. Growth crystal face changes unsteady easily. In the higher supersaturation zone caused by fluctuation, the flange will occur on the crystal face because of fast growth. Latent heat at the tip of the flange dissipates easier than that of flank. The growth velocity at the tip of the flange is quicker than that of flank. The flange grows into very small crystal to form the trunk of dendritic crystal. The supersaturation interface between the trunk and surroundings is also unsteady, so the flange also occur on the flank to form branch. Every flank tip still extends and the side face of every flank can also form



(a)



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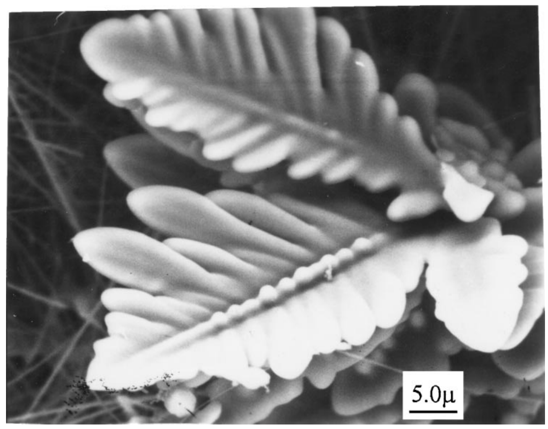


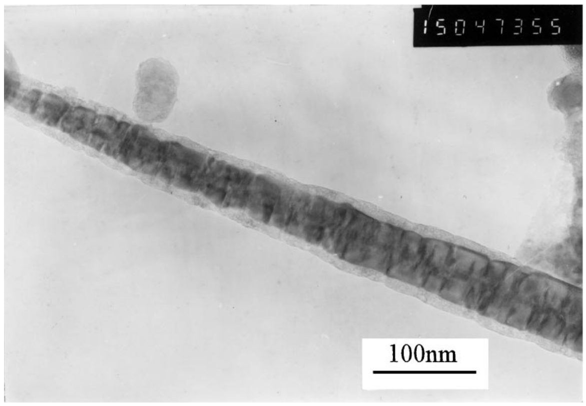
(c)

Figure 4 The SEM micrograph of dendritic crystal (a) low magnification (b) the tip of dendritic crystal (c) close-up of the tip.

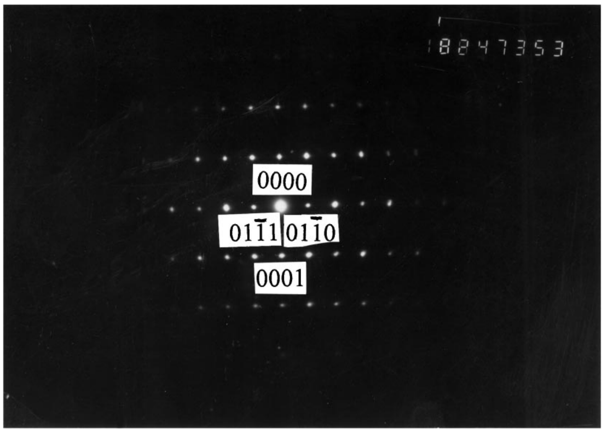
twice branch. This process continues to grow "branch-like" dendritic crystal.

2.4. Dislocation mechanism

The TEM micrograph and electron diffraction image of AlN whiskers are shown in Fig. 5a, b, c respectively. As for hexagonal structure crystal, the priority face of stacking fault is (0 0 0 1). From the high resolution image (Fig. 5c), the growth direction is (1 0 $\bar{1}$ 0) and there are many stacking faults. The face of stacking fault is (0 0 0 1). Above all, there are some screw dislocation and edge dislocation. However, unlike the screw dislocation mechanism reported in many references, the outcrop of screw dislocation cannot be found in AlN



(a)



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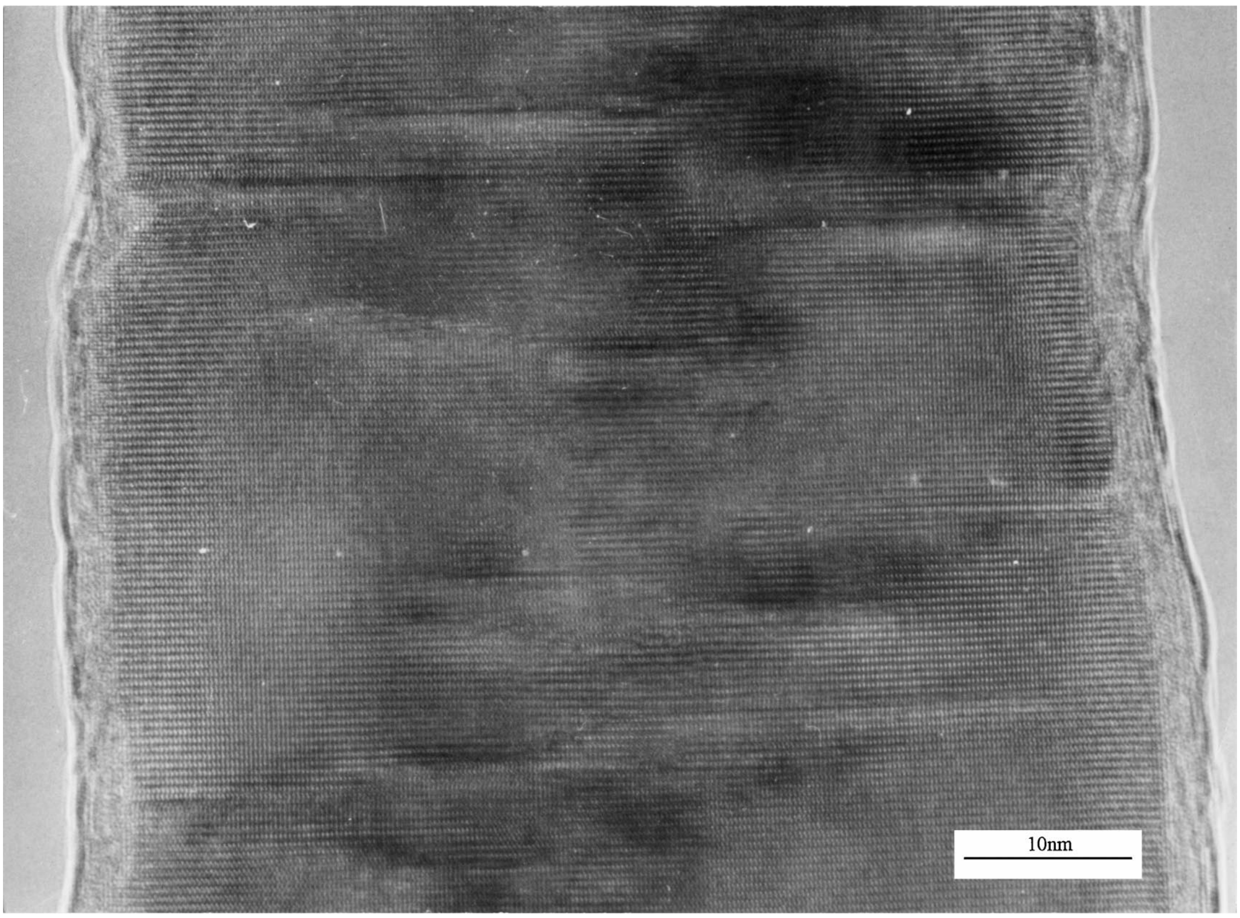
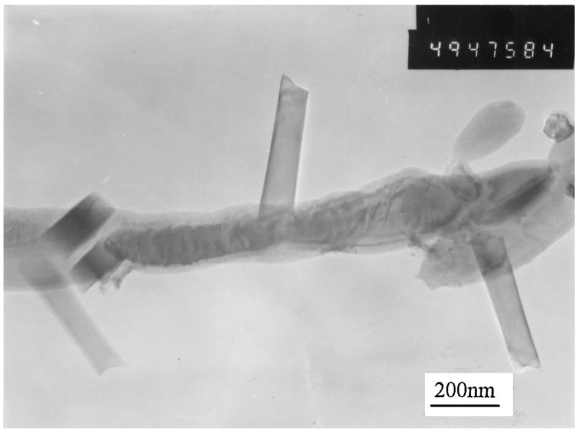
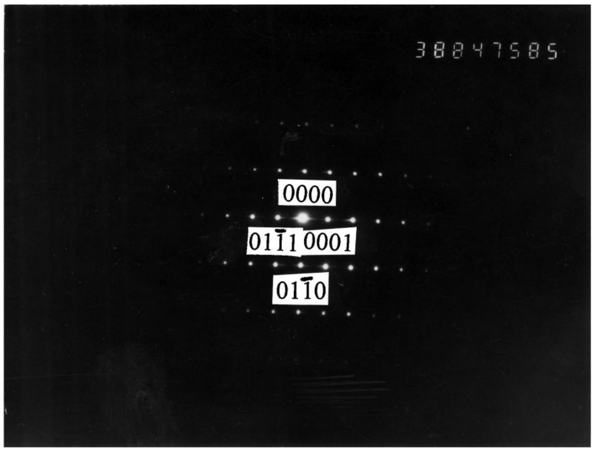


(c)

Figure 5 TEM micrograph of AlN whiskers (a), electron diffraction image (b) and high-resolution image.



(a)



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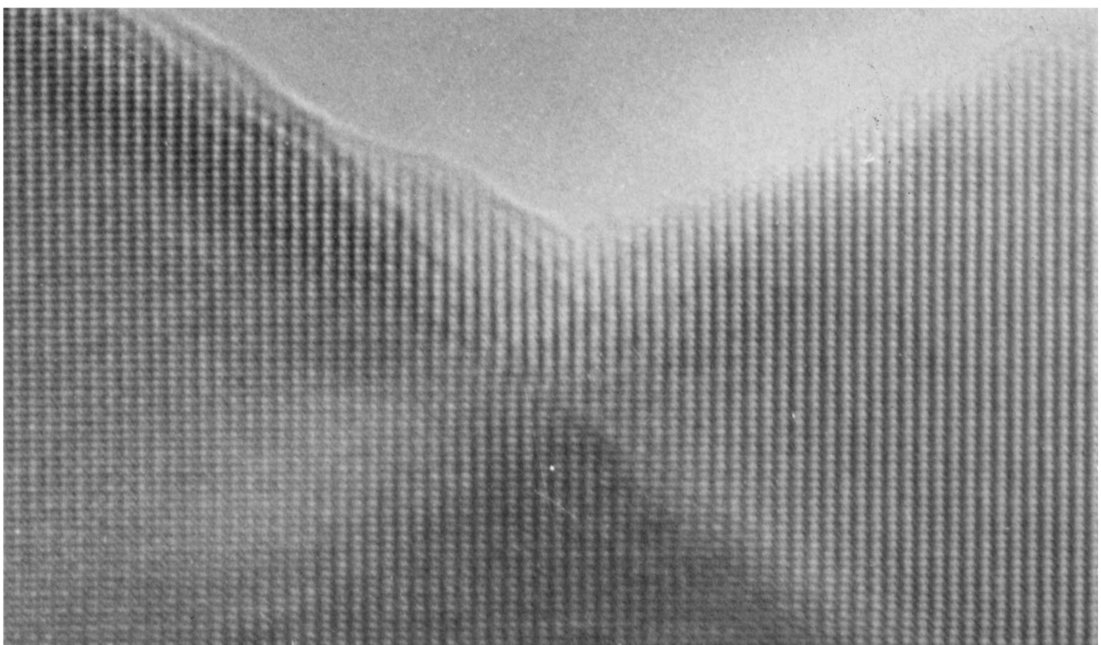

(c)

Figure 6 TEM micrograph of AlN whiskers by stopping growth (a), electron diffraction image (b) and high-resolution image.

whisker synthesized by SHS method. Does it move out during the growth process or are there other reasons? Moreover, the AlN whisker synthesized at regular condition is rather thick which is disadvantageous for electron microscope to observe. So the process must be designed to study the mechanism. The process is designed as follows: once the synthesizing process completed, the nitrogen gas must be given out immediately. The whiskers will stop growth and then are taken out to analysis their microstructure.

2.5. Stacking fault mechanism

The TEM micrograph and electron diffraction image of AlN whiskers of stopping growth are shown in Fig. 6a, b respectively. High resolution image is shown in Fig. 6c. From the electron diffraction image, the growth direction is $(1\,0\,\bar{1}\,0)$. The face of stacking faults is (0 0 0 1).

The facial cubic crystal is taken as an example to elaborate stacking fault mechanism. The stacking fault face of facial cubic crystal is {1 1 1}. The vector of stacking fault is $1/6\langle 1\,1\,2\rangle$ and $1/3\langle 1\,1\,1\rangle$. If the growth face is (1 1 1), stacking fault forms two kinds of sub-step on the outcrop of the growth face (1 1 1) : $1/3\delta(1\,1\,1\,1)$ height and $2/3\delta(1\,1\,1)$ height sub-step ($\delta(1\,1\,11)$ is the distance of crystal face (1 1 1)). The simple model is shown in Figs 7 and 8. There is $1/3\delta(1\,1\,1)$ height sub-step on the crystal growth face (1 1 1) of facial cubic crystal (Figs 7a and 8a). A layer atom is absorbed along the sub-step with $1/3\delta(1\,1\,1)$ height and sub-step of $2/3\delta(1\,1\,1)$ height is formed on the another side (Fig. 7b). At the certain growth condition, full-step rotates around the end of sub-step, the sub-step of $2/3\delta(1\,1\,1)$ height absorbs a layer atom to form another full-step. Then $1/3\delta(1\,1\,1)$ height sub-steps occur again (Fig. 7c). This process repeats alternatively and then step sources are formed on the outcrop of stacking fault (Fig. 7). Growth steps occur on the each side of stacking faults alternatively. When a pair of full-steps occurring on the each side of

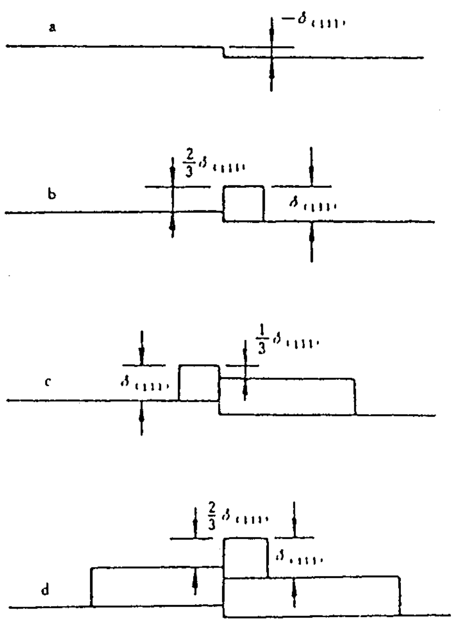

Figure 7 Sub-steps produced by stacking fault on the growth face (1 1 1) of facial cubic crystal and their growth mechanism.

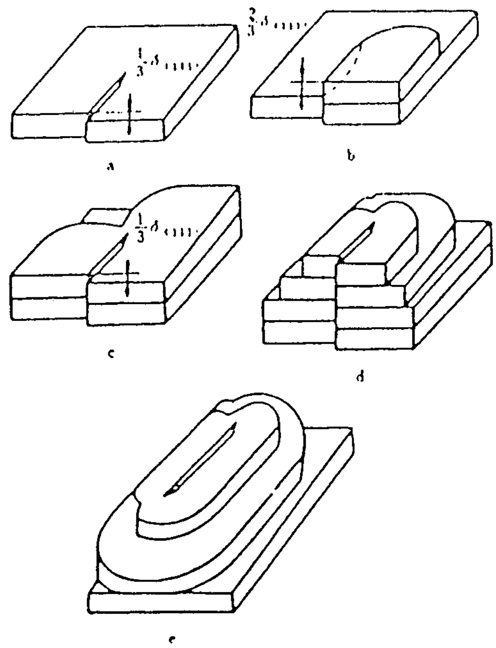

Figure 8 The step pattern of stacking fault mechanism.

stacking fault rotates along the end of sub-step, they encounter and destroy each other to form a new platform (Fig. 8c). This process repeats continually to form a growth dune on the outcrop of stacking fault (Fig. 8d). Two unwhole stacking faults crop out on growth face (1 1 1) to form growth dune (Fig. 8e).

The direct observation of Si crystal by the electron microscope and the original observation of $Ba(NO_3)_2$ by optical microscope have proved that the stacking fault is the priority mechanism of crystal growth [11]. Unfortunately the stacking fault mechanism of whiskers' growth has not been reported yet.

In the view of the stacking fault mechanism, unsymmetric molecular should rank on both sides of crystal along the crystal direction. However, from the high resolution image (Fig. 4c), stacking faults occur in some place and not everywhere. Some dislocations are also found in the whiskers, so these stacking faults may be from the decomposition of unwhole dislocations or the dissolve of some impurity. The second characteristic of stacking fault mechanism is the direction of the stacking faults and the crystal growth should be identical. The third characteristic is the stacking faults must be formed continuously, or else the crystal can not be grown. However, from the high resolution image (Fig. 5c), the direction of the stacking faults and the crystal growth is not identical. Moreover, there is a small amount of stacking faults only in the middle of whiskers. Whiskers can be also grown in the area of no stacking faults and no dislocation, which convincingly demonstrates the stacking fault mechanism is not the one of whisker growth. The stacking faults maybe result from the dissolve of some impurity, such as oxygen. Combining with Fig. 4c, the growth mechanism of AlN whiskers synthesized by SHS method is not stacking fault mechanism.

It is strange the dislocations were not found on the AlN whisker of stopping growth. Moreover, spiral reported in references [3–5] growth can not be observed.

3. Conclusions

By using the technology of SEM, TEM, EDS and HREM, the growth mechanism of AlN whiskers by SHS method has been proposed. These whiskers grew by the VLS and VS mechanism.

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