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Structures of Tetra-needle Like ZnO Whisker During the Crystal Growth

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ABSTRACT: Zinc oxide whisker (ZnOw) with a shape of tetra-needle was prepared, and the structures during the crystal growth were studied by SEM images. The cross section of hexagonal of the product and the gradually converting profile from a trigonal through a pentagonal and finally to a hexagonal sectional profile was observed. The leg of the product was proved to be composed of a single crystal of Wurtzite structure by analysis of electron diffraction pattern. The theoretical prediction and experimental study gave the same results that the aspect ratio (lengths to radicals) of the whiskers could be adjusted by controlling the reaction conditions. The crystal form and lattice constants of the whiskers were determined by diffraction analyses of electron (TEM) and X-ray (XRD).

Key words: zinc oxide whisker, growing, structures, single crystals

1. INTRODUCTION

Zinc oxide whisker (abbreviated as ZnOw) is a single crystal with tetra-needle shape in micro-image. It possesses good comprehensive properties such as high strength, semiconductivity, wear resistance, vibration insulation, microwave absorption and antibacterial effect, and can be widely applied as both of functional and structural materials [1]. Several methods have been developed [2-4] for preparing and manufacturing this kind of crystal whisker. Almost all the efforts were concentrated on reducing the oxidation rate of material zinc that was pretreated to form a homogeneous and thin film of ZnO on the surface of zinc particle to prevent zinc vapor from spreading out and reacting with oxygen too fast, but the pretreatment process proved to be laborious and energy-consuming. Kitano *et al* [5] reported the preparation processes and the series of structures during the crystal whiskers' generation of the related method. An effective and convenient method, Gas Expanding Method, for preparation of the tetra-needle shaped ZnOw was reported by our laboratory [6-8]. In this paper, the series of structures of the crystal whiskers during their formation were studied.

2. EXPERIMENTAL

2.1 Preparation of ZnO whisker

The related zinc oxide whisker with a shape of tetra-needle was prepared by the Gas Expanding Method, which was invented by the previous study [6]. The reaction products or the intermediate samples were got from the reaction chamber when it was necessary.

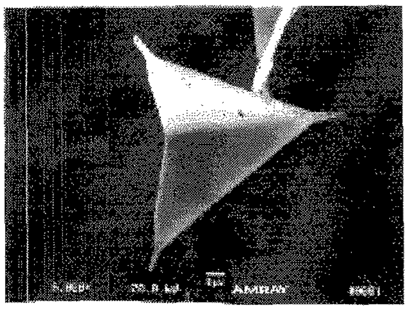
2.1 Structure studies of the product

The micro-morphologies and the related SEM images were taken on an Amary-1845 field emission scanning electron microscope. The X-ray diffraction analysis was performed using a system of DS=1°, SS=1°, RS=0.2 mm on a Rigaku-40 X-ray diffractometer at a scan rate of 0.030 °/s with a Cu K_α radiation at 40 kV and 20 mA. The electron diffraction analysis was carried out by an H-700 transmission electron microscope.

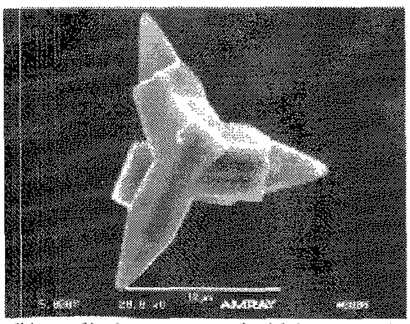
3. RESULTS AND DISCUSSIONS

3.1 Structures during the whisker growth

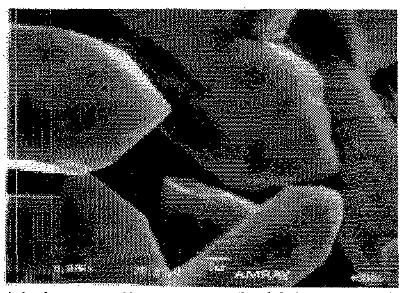
The structure of the tetra-needle like ZnOw consisted of a core and from which four needle-like crystalline bodies were generated. Accordingly, the growing process of ZnO whisker included the associated two stages. The growth rate of the crystal is one of the most important factors on preparing a single crystal, and generally the controlling to a slow growth is necessary. Since the growing process of the needle like crystalline body is based on the core crystal, a kind of zeolite with octahedral profile was used as the catalyst for inducing the formation of the core according to the successful method for preparation of tetra-needle like ZnO whisker [5]. It should be mentioned that in this work, no catalyst or other additives were used during the preparation. As a central core of the whisker, the structure with a configuration of tetrahedron was designed and prepared by controlling the oxidation process because the morphologies of ZnO crystals could be controlled through reaction conditions [9, 10]. As shown in Fig.1, the required crystal configurations were observed during the reaction process. It can be observed from this group of images that the shape and structure of the core, and the initial stage of the whisker growing differs from those reported in Kitano's report [5]. This can be explained by the catalyst or additive of zeolite used in the reported method and accordingly a different mechanism of the core growth.



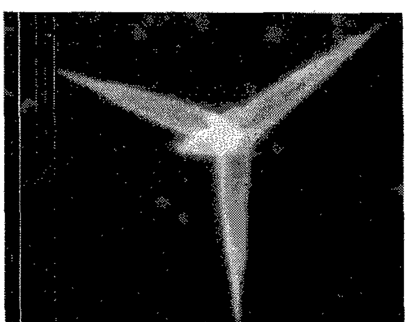
(a). central part of the whisker



(b). preliminary stage of whisker growth



(c). intermediate stage of whisker growth



d. later stage of whisker growth (800×)

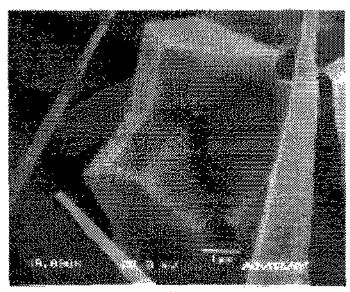
Fig. 1 SEM images during ZnOw growth

From Fig. 2, which gives the images of cross section of the needle part of the whisker, it can be found that it is a shape of hexahedron, which is in accordance with the observation of Kitano *et al* [5].

Fig. 2 The cross profile of ZnO whisker

From Fig. 3(a), it is obvious that the cross section of a needle crystal changes from a triangle at the base to a hexahedron at the later part of the whisker's leg, and the unequal edges pentagon image has been observed as shown in Fig. 3(b), which is in accordance with the imagination predicted by the report [5].

(a)



(b)

Fig. 3 The change process patterns of the cross section of the whisker's leg

A peculiar kind of whisker with an irregular configuration of cross sectional profile, shown in Fig. 4, was prepared by controlling the reaction condition and the raw materials of metallic zinc. During the process, metallic zinc with large size could not be heated and oxidized evenly, and the ZnO was supplied as the material for crystal growth unevenly. Beside this, the temperature during the reaction was also an important factor on the aspect ratio and cross profile of the whiskers.

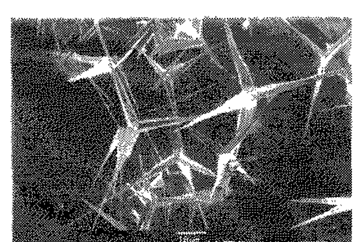
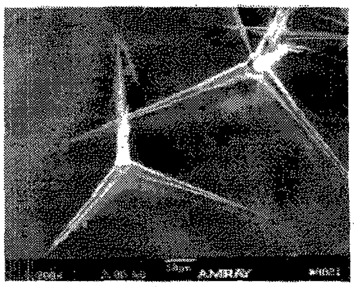


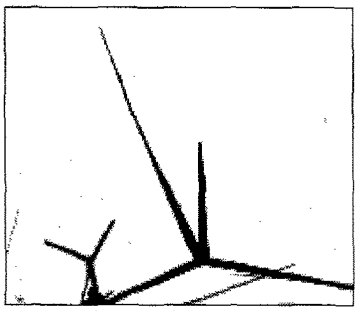
Fig. 4 Irregular cross profile legs of ZnO whiskers

3.2 The dimension and structure of the products

Fig. 5 gives the microstructure of the tetra-needle like ZnOw prepared in the above experiment.



(a) SEM



(b) TEM (1000×)

Fig.5 Images of electron microscope of ZnO whisker

Changing the reaction conditions or using different shape or size of the raw material can adjust the size of the products. The reaction rates of the core growth is less than that of the needles' generation [5, 11], so elevation of temperature is advantageous to the needle's growth according to the Arrhenius equation.

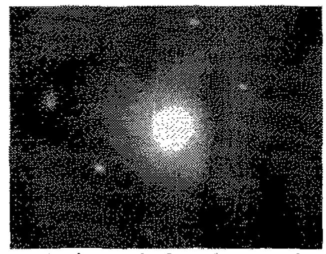
$$\ln k = -\frac{E}{RT} + B \qquad (1)$$

where k is the reaction constant, E is the activation energy of crystal process, R is the gas constant and B is a constant. It was proved by experiments that when all the reaction conditions fixed except the reaction temperature rose from 773 K to 1100 K, the average length of the crystal needles changed from 12 μm to 88 μm, and the average basal diameter changed from 2.6 μm to 1.8 μm. It was also found that structures with overgrowth of lamellae had formed as shown in Fig. 6 when the reaction temperature was over 1200 K. This phenomenon can be explained as that the boiling point of zinc is 1180 K, and a reaction in such a high temperature is no longer a Gas-Liquid but a Gas-Gas reaction. The quantity of ZnO for crystal growth was more than those of the core forming and the needles' growth.

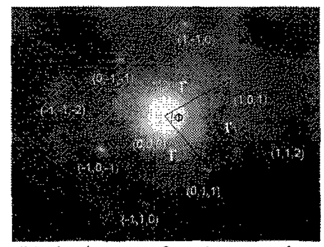
Fig. 6 SEM Image of ZnOw with overgrowth of lamella

3.3 Electron diffraction analysis

The single structure of the tetra-needle like ZnO whisker was analyzed by electron diffraction method, and the diffraction image was obtained as Fig. 7, which clearly indicated that the product had a single crystal character.



(a) the image before demarcation



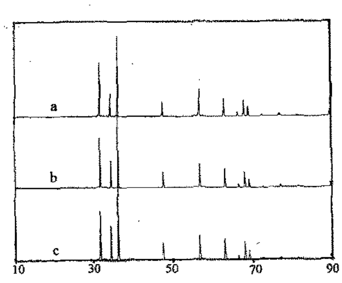
(b) the image after demarcation

Fig. 7 Electron diffraction image of ZnOw

According to the principles of the shortest border and the acute angle, r_1, r_2, r_3 and Φ (the inclination angle of r_1 and r_2) were selected and measured as: r_1=10.8, r_2=10.8, r_3=14.5, Φ=80.2°, r_2/r_1=1.000. Comparing the measured values of r_2/r_1 and Φ with the standard values of the tag file of crystal electron diffraction[12], it was proved that the model of the crystalline of the tetra-needle like ZnO whisker was *hcp*. The constant of the experimental camera is 26.8, from which the crystalline lattice constants of the ZnOw were calculated to be: a=3.2438Å, c=5.2873Å.

3.4 X ray diffraction analysis

The tetra-needle like ZnO whisker with average length of 120 μm and 13.3 μm respectively were subjected to the X-ray diffraction analysis and compared with commercial ZnO powder. The XRD patterns were given in Fig. 8.



a: ZnOw ($\bar{l} = 120\mu m, \bar{d} = 1.8\mu m$)

b: ZnOw ($\bar{l} = 13.3\mu m, \bar{d} = 2.1\mu m$)

c: ZnO Powder ($\bar{d} = 49\mu m$)

Fig. 8 XRD patterns of ZnOw and ZnO Powder

It can be observed that the XRD patterns have no obvious difference, which indicates that the three kind of ZnO belong to the same hexahedron structure. From the analysis, the lattice constants of ZnOw were calculated as: sample a: a=3.2491Å, c=5.2060Å; sample b: a=3.2468Å, c=5.2059Å, which coincided with the results of electron diffraction, Kitano's reports [5], and the standard card [12].

4. CONCLUSION

The tetra-needle like ZnOw was prepared using the metallic zinc as the material by Gas Expanding Method. As central core of the whisker, the structure with a configuration of tetrahedron was designed, prepared and observed by controlling the oxidation process. The cross section of ZnOw was gradually changed from a triangle at the base of the needle through a pentagonal and finally to a hexagonal profile. The size of the products was different as the reaction conditions changed and the shape or size of the raw material was different, and the structures with overgrowth of lamellae formed when the reaction temperature was over 1200 K. The crystal form of the whisker was *hcp* structure model, and the whiskers with different lengths of needles had similar lattice constants.

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