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INFLUENCES OF IONS DOPING ON MICRO MORPHOLOGY OF AlN NANOWIRE

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AlN ceramics with special crystal structure, showed many excellent characteristics, such as thermal conductivity, low dielectric constant, electric insulating reliability, non-toxic, heat expansion coefficient and silicon matching. In this paper, the effects of reaction temperature, reaction time and the addition of metal additives on the micro morphology of AlN nanowires were studied. XRD results showed when reaction temperature at 450 ℃, with holding time was 24 hours，hexagonal AlN can be synthesized. SEM results revealed that the crystal boundary of AlN grew well without reunion phenomenon, and the particle size was 70-100 nm around. TEM results showed that the surface of AlN nanowires was smooth without attachments and it presented long linear crisscross state. More important was that the addition of the metal catalyst can change the morphology of AlN. It showed the addition of Mg can make the formation of AlN nanowires, and the addition of Zn can allow AlN to generate nanorods.

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1. Introduction

Aluminum nitride (AlN) was a kind of important IIIA nitride which was covalent compounds and belonged hexagonal system. It was not only an excellent structural material, but also a special functional material. AlN with high resistivity, low dielectric constant, high thermal conductivity, low thermal expansion coefficient and high mechanical strength, was used as packaging materials for high temperature and high power electronic devices, heat radiating material for high power device and integrated circuit, substrate material for semiconductor device and additive or reinforcing agent of composite material, etc[1-4]. Therefore, AlN in the field of high performance requirements such as electronic, metallurgy, chemical and functional ceramics had broad application prospects and a wide range of market.

At present, the AlN powder which prepared by carbothermal reduction method[5], accounted for a large proportion of international market, almost more than 70 %, but this method existed many problems, such as low reactivity of alumina, alumina and carbon difficult to mix uniform, long reaction time, reaction temperature higher, resulting in high cost of AlN preparation. Due to the large aspect ratio, one dimensional nano materials have the advantages of high thermal performance, mechanical properties, electrical properties and optical properties.

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This passage used solid-phase metathesis method to synthesize AlN nanowires under low temperature. The experiment using anhydrous aluminum chloride and sodium azide as raw materials with low price. The effects of different conditions on the micro morphology of AlN were discussed by adjusting the reaction temperature, reaction time and the addition of metal additives.

2. Materials and Methods

2.1 Materials

Aluminum chloride ($AlCl_3$, AR) was purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Sodium azide (NaN_3, AR) was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd., China. Magnesium powder and zinc powder were Tianjin Kaitong Chemical Reagent Co. Ltd., China. All chemicals were of analytical reagent and used directly without further purification.

2.2 Preparation

In this experiment, aluminum chloride and sodium azide were used as raw materials, and the complex decomposition reaction occurred in the reaction vessel under a certain temperature. The chemical reaction was as follows, .

2.3 Characterization

The phase of the product was identified by X-ray diffraction (XRD, Rigaku D/max-2200, Japan) with Cu-Kα radiation. Morphological features of the samples were observed using field emission scanning electron microscopy (FE-SEM, Philip Sirion200, Holland) and transmission electron microscopy (TEM, JEOL JEM2100, Japan). Photoluminescence (PL, Shimadzu RF-5301PC, Japan) spectra were measured at room temperature using a 150 W xenon lamp as the excitation source. The composition of the prepared samples were further tested by fourier transform infrared spectroscopy (FTIR, Bruker EQUINOX55, Germany).

3. Result and discussion

3.1 Phase and Morphology Characterization

To determine the phase purity of the samples, XRD measurements for the synthesized products were conducted. Fig, 1 showed the XRD patterns of the powders which prepared by experiment.

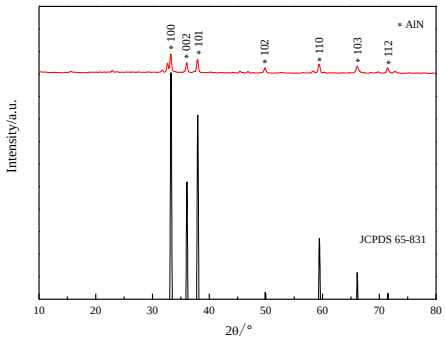

Fig. 1. XRD patterns of the powders prepared by experiment

The test sample was prepared under 450 ^{o}C sintering 24 h. From the pattern, the characteristic diffraction peaks of the sample diffraction pattern can be well corresponded to the 65-831 card in the JCPDS. The product can be identified as AlN, which belongs to the structure of the six wurtzite structure. By the Scherrer formula, the average grain size was 57.5 nm, a=3.111 Å, C=4.980 Å. Because the grain size of the product was too small and the test speed was fast, the diffraction peak intensity was low.

Fig. 2 was the morphology images of the prepared powder under 450 ^{o}C sintering 8 h. Fig, 2a was SEM image and figure 2b was TEM image of local of AlN nanowires.

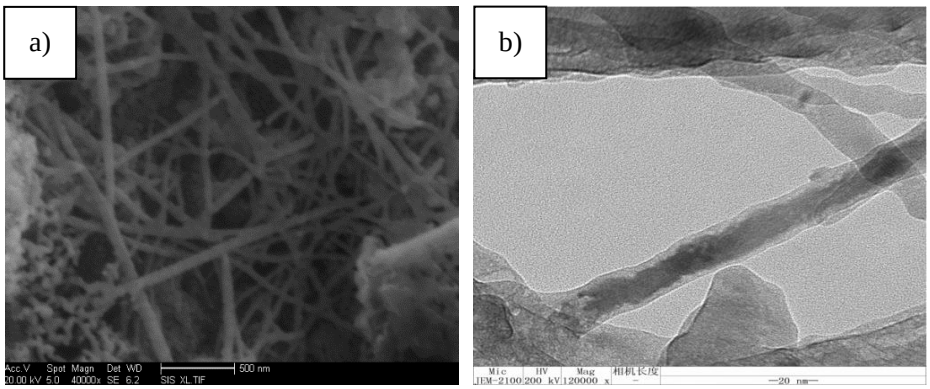

Fig. 2. a). SEM image of AlN nanowire; b) TEM image of local of AlN nanowire

Seen from Fig. 2a, the crystallinity of the AlN was better, the morphology as staggered distribution of nanowires. There were slight links between the line and the line, but no agglomeration. The diameter of AlN nanowires was about 70-100 nm, the length more than 1 μm. From figure 2b, the surface of the nanowire was relatively smooth, basically no other attachments, and the thickness was relatively uniform.

3.2 Structural Analysis

Fig. 3 was the photoluminescence (PL) spectrum of AlN, which prepared under 450 ^{o}C sintering 8 h. The test was completed at room temperature and excitation wavelength was 290 nm. The existence of crystal defects was analyzed through this spectrum.

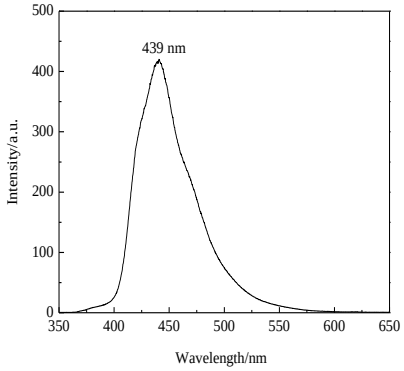

Fig. 3. Photoluminescence spectrum of AlN nanowire

By the above PL spectrum, a wide emission spectrum located from 350 nm to 550 nm, and a strong emission peak at 439 nm, corresponding to AlN band gap of 2.95 eV[6,7], attributed to nitrogen vacancy.

Fig. 4 was the infrared spectrum of AlN samples, preparation using KBr compression method.

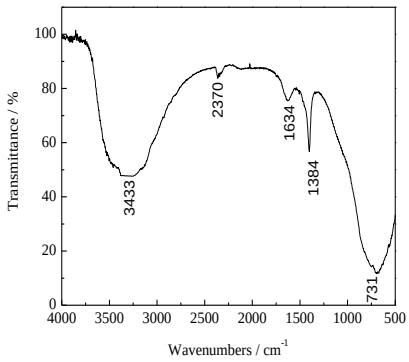

Fig. 4. Infrared spectrum of AlN nanowire

From Fig. 4, it is clear that a strong wide absorption band was located at 731cm^{-1} . There are a number of other peaks, which located at 1384, 1634, 2370 and 3433 cm^{-1}. According to the literature, the absorption peak of 1384 cm^{-1} was attributed to the infrared absorption of $(AlN)_2$[41]. Absorption peaks at 1634 and 3433 cm^{-1} were caused by the adsorption of H_2O on the surface of AlN and KBr crystals. 2370 cm^{-1} is the CO_2 in the infrared cavity, while it can be compensated by the atmosphere. The absorption peak of 731 cm^{-1} is in agreement with the infrared absorption of nano AlN single crystal. The infrared absorption band is basically the same as the frequency of the optical vibrational mode of the infrared active of AlN single crystal. It can be determinately attributed to the Al-N bond in the AlN crystal, which difference may be derived from the crystal lattice.

3.3 Effect of reaction temperature and time on morphology

Fig 5a/b was the SEM images of the prepared AlN under 500/550 ^{o}C sintering 24 h. By

observing, AlN nanowires were not got in these temperatures. AlN which were prepared showed granularly, furthermore smaller particles aggregate and grow into larger particles. Smaller particles of the remainder were reunited and adhered to the surface of the larger particles and the gap between them. The average particle size was over ten microns. When the reaction temperature rises to 550 ^{o}C with the growth of particles, most of the AlN particles have been massive, the remaining small particles attached to the surface of the block AlN (as shown in Figure 5b). The phenomenon of agglomeration was more obvious with the increase of reaction temperature.

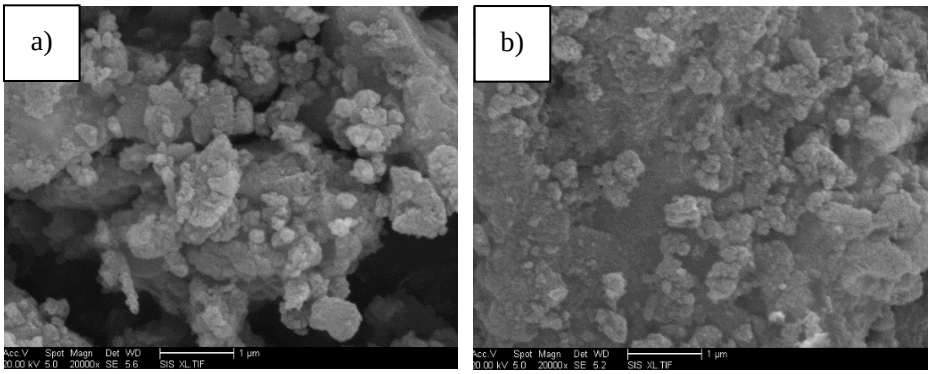

Fig. 5. SEM images of AlN powders with different reaction temperatures: a) 500 ^{o}C; b) 550^{o}C

Fig. 6a/b was the SEM images of the prepared AlN sintering 12/24 h under 450 ^{o}C. Contrasted Fig. 2a, with the extension of reaction time, the preparation of AlN changed from linear to granular, and the average size of the particles in the reaction 24 h reached micron level.

The reason for this change was that, when the reaction temperature and reaction time increased, the energy available to the AlN crystal nucleus grow more and more, to make the particles grow up and even happen. Therefore, to obtain a good morphology of AlN nanowires, it was appropriate to control the reaction conditions can provide the growth energy.

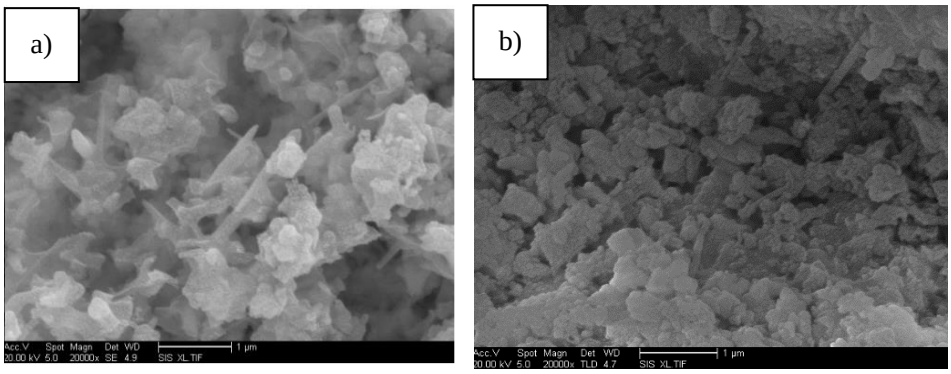

Fig. 6. SEM images of AlN powders with different reaction times: a) 12h; b) 24h

3.4 Effect of metal ions on morphology

Fig. 7a/b was the SEM images of the AlN added metal ion of Mg or Zn under 450 ℃ sintering 8 h.

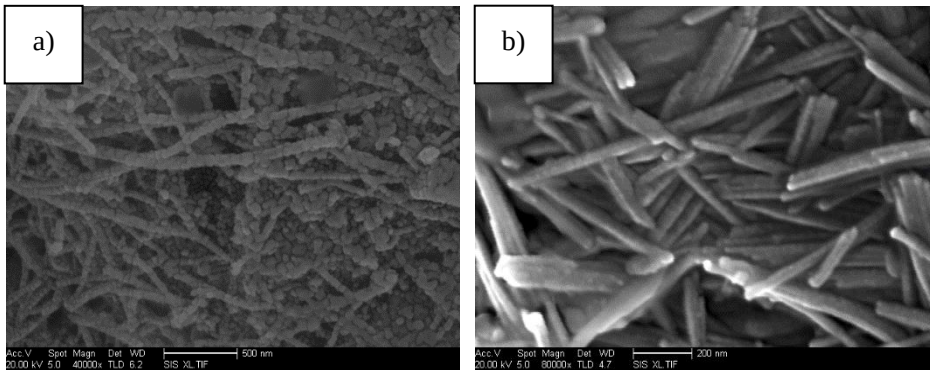

Fig. 7. SEM images of AlN nanowire added different metal ion: a) Mg; b) Zn

Form Fig. 7a, AlN added metal additives Mg showed linear, and agglomeration phenomenon was not obvious, and the nanowires showed a uniform dispersion, of which average diameter was less than 100 nm. Form figure 7b, AlN added metal additives Zn showed rodlike, of which average diameter was about 50 nm. This showed that the addition of metal additives can not only change the particle size of the powder, but also can change the shape of the nano materials.

Fig. 8a was the SEM images of the AlN not added metal ion of Mg under 450 ℃ sintering 8 h, but figure 8b added.

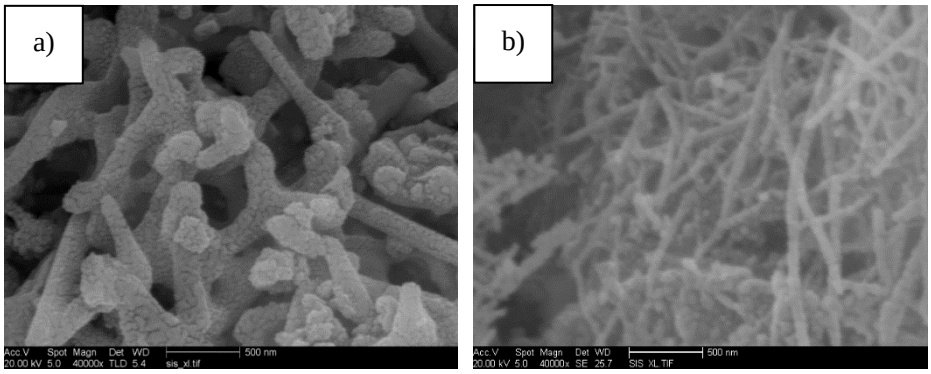

Fig. 8. SEM images of AlN nanowire: a) react without addictive; b) addictive Mg

To contrast two images, after adding magnesium powder, AlN nanowires became thinner and longer which were prepared under the same reaction time and temperature. This was because that the reaction activity of the reactants was enhanced by magnesium, leading to the generation of nanowires in advance. It was concluded that the addition of additives has positive effect on the formation of AlN nanowires.

4. Conclusions

AlN nanowires were successfully synthesized at 450 ^{o}C and the reaction temperature was 8h. The diameter of AlN nanowires was about 70-100 nm, and the length was more than 1 μm. The

emission peak appeared at the wavelength of 439 nm in the photoluminescence spectrum, corresponding to the band gap of AlN which was 2.95 eV. The increase of reaction temperature and time all made the AlN obtained from the linear transformation to granular. The AlN powders added with magnesium showed linear, and the diameter was smaller than without of the metal ions. The AlN powder with the addition of zinc showed rodlike.

Acknowledgment

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