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Synthesis, characterization and photoluminescence of aluminium nitride nanopowders through an $AlCl_3$ aided CVD route

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Abstract

Single-phase AlN nanopowders, with average diameter of about 70 nm, were synthesized through an $AlCl_3$ aided CVD route; the formation process is also discussed in this paper. XRD and HRTEM revealed that the AlN nanopowders obtained are wurtzite structured with lattice constants of $a = 3.1114$ Å and $c = 4.9792$ Å. The photoluminescence spectrum showed that there is a deep-level blue luminescence band centred at 2.54 eV in AlN nanocrystals. This method is a simple and efficient way to synthesize AlN nanopowders.

1. Introduction

Aluminium nitride (AlN) has attracted great interest for a wide range of electronic and structural applications owing to its excellent properties, such as high thermal conductivity, excellent optical and dielectric properties, high mechanical strength and low expansion coefficient similar to silicon, corrosion resistance, non-toxic nature, useful piezoelectric properties, etc [1–3]. Conventionally, AlN is produced by direct reaction of aluminium with nitrogen (N_2) or ammonia (NH_3); or through the carbothermal reduction and nitridation of alumina [4, 5]. In past decades, various other preparation routes to synthesize AlN powders have been also developed, which mainly involve vapour phase reaction of ammonia with aluminium chloride ($AlCl_3$), aluminium fluoride, or tri-isobutyl aluminium [6–8] and thermal plasma processing [9, 10].

In recent years, the study of AlN nanopowders has become one of the hottest fields of AlN nanomaterials, because nanostructured AlN has the potential of unique properties

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in comparison with those of conventional micron-sized materials [11, 12]. In addition, the reported fabrication methods of AlN nanopowders are varied and somewhat different from the old ones. Chen *et al* [13] described chemically synthesized aluminium nitride nanopowders with 2-pyrrolidinones. Wang and his co-workers [14] obtained nanoscale AlN powders through a pulsed-discharge-aided laser ablation route. Another report concerned nano-sized AlN powders synthesized by electrical explosion of aluminium wire in nitrogen-containing gases [15], and single-phase AlN nanoparticles could be also synthesized at low temperatures using an ammonothermal route in an autoclave [16].

In the present work we report a simple and efficient way to synthesize AlN nanopowders: the raw materials used were Al powders and a small quantity of $AlCl_3$ as a promoter. The gas reactant was NH_3. Large-scale crystalline AlN nanopowders can be produced in this way. This is a promising way for producing commercial AlN nanopowders, because it is very practical and of low cost.

2. Experimental details

Pure aluminium powder (purity: 99.9%) (100–200 mesh) was put in an alumina boat, which then was placed at the centre of an alumina tube that was inserted in a horizontal tube furnace. On the upstream side of the tube, an alumina crucible loaded with $AlCl_3$ was placed in order to introduce $AlCl_3$ vapour into the reaction system. Prior to heating the system, N_2 gas (of 99.999% purity) at 100 sccm was let in for 1 h to expel the oxygen from the furnace. The temperature of the furnace central region was increased to 1200 °C at a rate of 30 °C min^{-1}, and held at this temperature for 2 h. When the temperature reached 500 °C, the N_2 flow was reduced to 20 sccm and NH_3 (purity: 99.999%) at 180 sccm was introduced into the system. At the cooling stage the NH_3 flow was shut off. After the furnace was cooled to room temperature, fine white powders were found in the boat.

The as-prepared products were characterized and analysed by x-ray diffraction (XRD) (Philips X'Pert Pro with Cu Kα radiation), field emission scanning electron microscopy (SEM) (JEOL JSM-6700F), and high-resolution transmission electron microscopy (HRTEM) (JEOL-2010). A photoluminescence (PL) spectrum was obtained using a LABRAM-HR Confocal Laser MicroRaman spectrometer at room temperature with the excitation wavelength of 325 nm.

3. Results and discussions

3.1. Characterization of the AlN nanopowders

Figure 1 shows an XRD pattern of the prepared nanopowders, which indicates that the products are the pure wurtzite structured AlN phase with lattice constants of $a = 3.1114$ Å and $c = 4.9792$ Å. Figure 2 is a SEM image of the AlN nanopowders obtained. The size distribution of the AlN nanopowders is shown in figure 3. It can be seen that the mean size of AlN nanopowders is about 70 nm.

Figure 4(a) is a TEM image, and figure 4(b) is a selected area electron diffraction (SAED) pattern of the AlN nanopowders, which show most nanopowders are crystal. The bigger particles have been well crystallized (as indicated in figure 5). Figure 5(a) is a HRTEM image of some bigger particles, and figure 5(b) is the partial enlarged image of the box in figure 5(a).

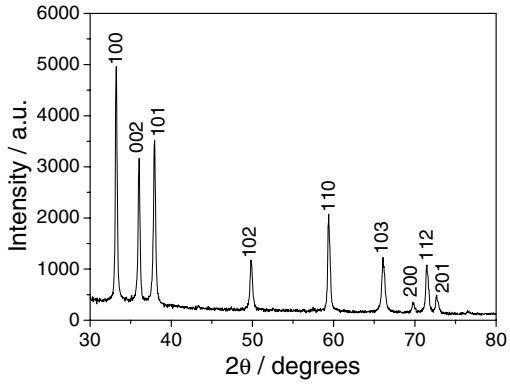

Figure 1. An XRD pattern of the prepared AlN nanopowders.

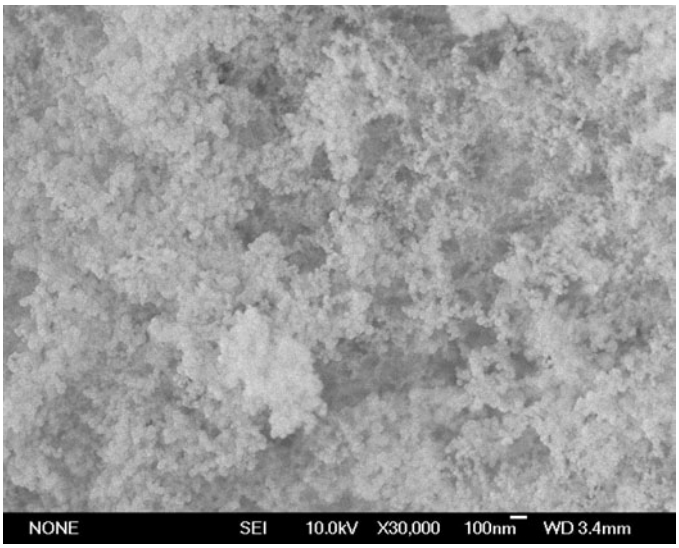

Figure 2. A SEM image of the AlN nanopowders obtained.

3.2. Formation process of the AlN nanopowders

According to Kato's study [17], the particle size may be controlled by the number of nuclei and the concentration ratio of the metal sources, and the number of nuclei formed then restricts the reaction temperature and the concentration of the reactant gases. In our work, the $AlCl_3$ used played an important role (a good promoter) in the nucleation stage of AlN nanopowders. At first, in the earlier heating stage, the $AlCl_3$ would evaporate (at about 180 °C) into gas and then react with NH_3 gas at lower temperatures:

$$AlCl_3(g) + NH_3(g) \rightarrow AlN(s) + 3HCl(g).$$

The above reaction was able to readily form a large number of precipitates of AlN nanoparticles, which served as the nuclei for AlN nanopowders. And subsequently, at elevated temperatures, the vaporized aluminium formed large numbers of active Al atoms and/or nanoclusters in the atmosphere, which reacted with plentiful active N atoms (decomposed by NH_3 at above 900 °C) or N_2 to form new AlN nuclei and precipitate on the former nuclei (generated at low

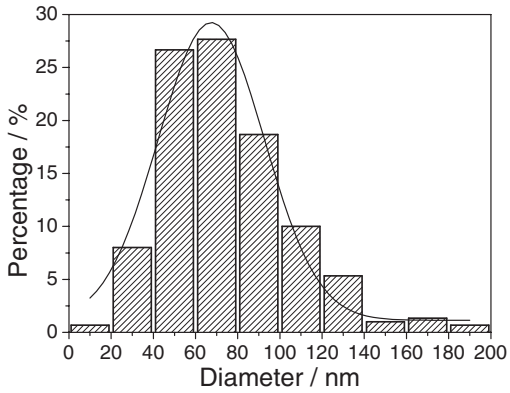

Figure 3. The size distribution of the AlN nanopowders.

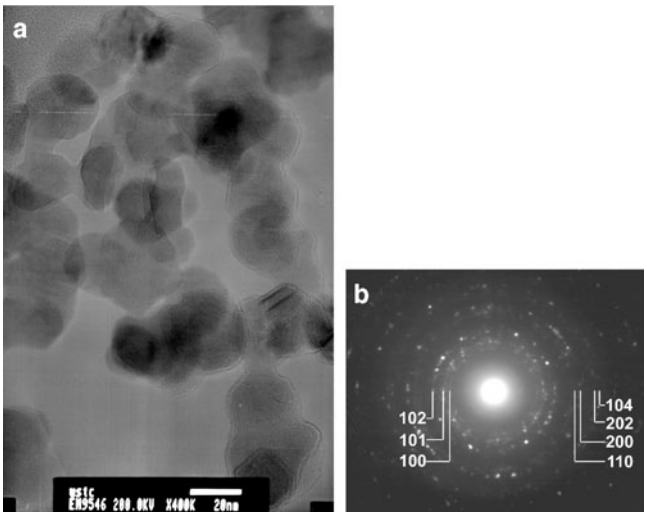

Figure 4. (a) A TEM image, and (b) a SAED pattern of the AlN nanopowders.

temperatures) to result in the growth of the AlN nanopowders. So some AlN nanopowders could become bigger in size.

In fact, the effect of $AlCl_3$ on the formation of AlN nanopowders was also confirmed by a comparative experiment, which was carried out in a similar condition but without $AlCl_3$ added, i.e., direct reaction of Al powder and NH_3/N_2 at 1200 °C. It was found that the yield of AlN nanopowders in this case was about 25% less than that with $AlCl_3$ (about 15 wt% $AlCl_3$ added). This proves that the $AlCl_3$ can efficiently promote the formation of AlN nanopowders. Therefore, the formation of AlN nanopowders in our work is regarded as an $AlCl_3$ assisted CVD process.

3.3. Photoluminescence of the AlN nanopowders

The photoluminescence (PL) measurements were carried out at room temperature at an excitation wavelength of 325 nm. A broad emission band (figure 6) is observed which ranges from 370 nm (3.35 eV) to 600 nm (2.07 eV), centred at 488 nm (2.54 eV), corresponding to

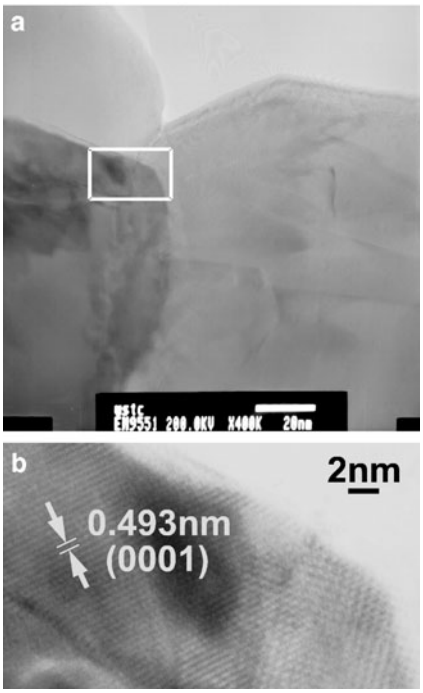

Figure 5. (a) A HRTEM image of some bigger particles, and (b) the partial enlarged image of the box in (a).

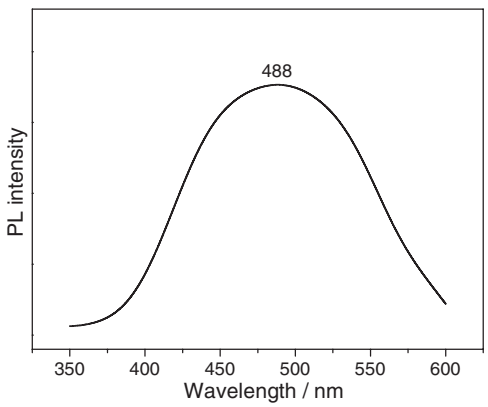

Figure 6. The PL spectrum of the synthesized AlN nanopowders with excitation wavelength of 325 nm.

the blue region. The PL mechanism of AlN materials have been extensively studied in the past decades; several authors [18–20] have explained the broad blue band of nanocrystalline AlN. The results suggested that the broad band originates from the vacancy of Al or O impurity, but no detailed information was given. Cox *et al* [21] have ascribed the band with a maximum at about 2.8 eV from nanocrystalline AlN to Al interstitials, whereas Youngman *et al* [22] proposed that a broad band at 2.7 and 3.8 eV from AlN single crystals grown under nitrogen-deficient conditions results from the vacancy of N. Pacesove and Jastrabik [23] indicated that the extremely broad band centred at 3.3 eV from AlN with oxygen of 1.53 wt% may originate

from O impurities. Cao *et al* [24] considered that the wide blue emission band (centred at 420 nm (2.95 eV)) from AlN nanopowders may be ascribed to the transition from the shallow level of V_N to the ground state of the deep level of the V_{Al}^{3-}–3 × O_N^+ defect complexes. It can be concluded that the defects are one of the key factors leading to the broadening of the width of the blue band. The present result in our work (the broad band with a peak at 2.54 eV) is supposed to be likely associated with the vacancies of N in the AlN nanopowder structure, because it is in agreement with the band structure calculations which predicted that the energy of the nitrogen vacancy lies deep within the band gap of AlN [25]. As a matter of fact, the exact PL mechanism of AlN nanopowders is not yet well understood, and warrants further investigation.

4. Conclusions

In conclusion, single-phase AlN nanopowders, with average diameters of about 70 nm, were synthesized through an $AlCl_3$ aided CVD route. XRD and HRTEM revealed that the AlN nanopowders obtained are wurtzite structured with lattice constants of $a = 3.1114$ Å and $c = 4.9792$ Å. The photoluminescence spectrum showed that there is a deep-level blue luminescence band centred at 2.54 eV in AlN nanocrystals. This method is a simple and efficient way to synthesize AlN nanopowders.

Acknowledgments

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