Materials Letters 128 (2014) 156–159

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Combustion synthesis of AlN nanowhiskers with different metallic catalysts

Zhongqi Shi[a,*], Changjian Zhao[a], Hailong Wang[b], Guanjun Qiao[a], Hongjie Wang[a]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
[b] Advanced Energy Storage Materials and Devices Lab, School of Physics Electrical Information Engineering, Ningxia University, Yinchuan 750021, China

ARTICLE INFO

Article history:
Received 15 February 2014
Accepted 22 April 2014
Available online 30 April 2014

Keywords:
Combustion synthesis
Aluminum nitride
Nanoparticles
Powder technology

ABSTRACT

AlN nanowhiskers were successfully fabricated via combustion synthesis route in the presence of different metallic catalysts (Ni, Cu or Fe). FESEM and HRTEM images show that the nanowhiskers, which are single-crystalline hexagonal wurtzite AlN growing along the [001] direction, have diameters in the range of 130–200 nm and lengths in several micrometers. The effects of metallic catalysts on the growth of AlN nanowhiskers were discussed. It was found that metallic catalysts could not only promote the growth of nanowhiskers by vapor–liquid–solid mechanism, but also able to dominate the morphologies of the products.

1. Introduction

AlN is an important III–V semiconductor material, which has attracted great attention owing to many advantages including high thermal conductivity, high electrical resistance, wide band gap, low dielectric constant, and low thermal expansion coefficient, etc. [1]. AlN can be used as electronic substrates, IC packaging materials, heat sinks and field-emission devices [2,3]. Recently, one-dimensional (1D) nanostructured AlN has shown attractive possibilities for use in a number of new applications, such as field emitters, flexible pulse-wave sensors, optoelectronic and micro-electronic devices [4–7]. Many efforts have been devoted to synthesis 1D AlN nanosturctures, including arc-discharge, chemical vapor deposition, carbothermal reduction and nitridation, as well as other chemical routes [8–12]. However, these methods usually require high temperature, substrates, or long-term production cycle. Therefore, it is imperative to further exploit new synthetic routes for preparation of 1D AlN nanostructures.

Combustion synthesis (CS, also known as self-propagating high temperature synthesis or SHS), is considered as an promising synthesis route to fabricate 1D AlN nanostructures due to its low processing cost, high energy efficiency and short reaction period compared with conventional synthesis methods [13–17]. Generally, the addition of ammonium halides (NH_4X, X = F, Cl, Br and I) is crucial for the synthesis of AlN nanowhiskers by CS [14–17]. However, these additives can decompose into NH_3 and HX during the CS process, which could lead to the equipment corrosion and environment pollution. In this work, metallic catalysts (Ni, Cu or Fe) were used to promote the growth of AlN nanowhiskers in the CS process, and the effects of catalysts on the morphology of the products were also investigated.

2. Experimental procedure

The synthesis experiments were carried out in a combustion chamber, as schematically shown in Fig. S1. The experimental procedure is illustrated in Fig. S2. In a typical experimental procedure, Al powders (> 99.9%, ~23 μm) and AlN diluent powders (> 99.9%, ~0.5 μm) were mixed with a molar ratio of 4:6, and 5 wt% of metal (Ni (> 99.7%, ~45 μm), Fe (> 99.8%, ~55 μm) or Cu (> 99.9%, ~40 μm)) powders were added as catalyst. The powders were mixed in a mortar for 10 min. Then, 50 g of the mixture was poured into a porous graphite container and ignited under a 1.0 MPa nitrogen gas atmosphere. The combustion temperature and combustion rate were measured by two W–Re thermocouples (one at the middle and the other near the top surface) at a fixed distance of 30 mm. The obtained products were analyzed by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM) equipped with energy dispersive spectrometer (EDS).

3. Results and discussion

Table 1 shows the combustion temperatures and rates for the synthesis of AlN with Ni, Fe and Cu catalysts. After the combustion

* Corresponding author. Tel.: +86 29 82667942; fax: +86 29 82663453.
E-mail address: zhongqishi@mail.xjtu.edu.cn (Z. Shi).

http://dx.doi.org/10.1016/j.matlet.2014.04.147
0167-577X/

reactions were triggered, the combustion temperatures for all of these mixtures rapidly increased to just above 2000 °C and without significant differences, which were much higher than the melting points of Al (660 °C) and metallic catalysts (Table 1). However, the combustion rate for the Cu added sample was 0.72 mm s^{-1}, which was slower than that of Ni or Fe added samples (1.62 and 1.67 mm s^{-1}, respectively). The difference of the combustion rates should be caused by the different melting points of the catalysts. In the present CS process, the Al powders were molten and gradually vaporized to react with nitrogen, and then transformed into AlN gaseous clusters. With the temperature increase, the molten catalysts hindered the nitrogen gas infiltration, and therefore suppressed the nitridation of Al. Since the melting point of Cu is much lower than that of Ni or Fe, the combustion rate for the Cu added sample was the slowest.

Table 1
Physical properties of the metallic catalysts, and combustion temperatures and rates for the synthesis of AlN with different catalysts.

Samples with different catalysts	Melting point of catalyst (°C) [18]	Viscosity of molten catalyst (mPa S) [19]	Combustion temperature (°C)	Combustion rate (mm s^{-1})
Ni	1455	4.5–6.4	2037	1.62
Fe	1535	6.92	2045	1.67
Cu	1084	4.34	2030	0.72

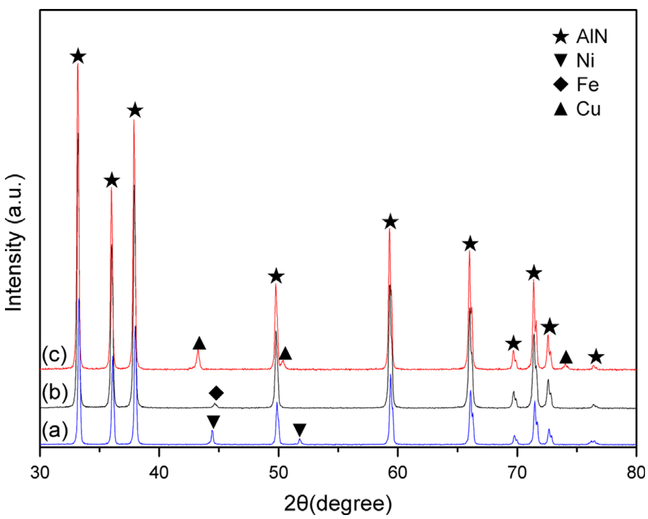

Fig. 1. XRD patterns of the as-synthesized products with different metallic catalysts: (a) Ni, (b) Fe and (c) Cu.

Fig. 1 shows XRD patterns of the as-synthesized products with different metallic catalysts. All the products are almost pure AlN (hexagonal wurtzite structure, JCPDS no. 25–1133) with a trace amount of impurities (Ni, Fe or Cu), indicating that all Al was converted to AlN, and metallic catalysts did not involved in the reactions. The sharp diffraction peaks indicate the good crystallinity of the products.

Fig. 2 shows the morphologies of the AlN fabricated with Ni catalyst. Fig. 2(a) is a low-magnification SEM image which clearly shows that the product is composed of a large amount of AlN nanowhiskers and some agglomerated AlN particles (gray contrast). SEM images with higher magnification show that the nanowhiskers are ~160 nm in diameter and ~4 μm in length (Fig. 2(b)), and the agglomerated AlN particles are bonded together by Ni catalyst where many nanowhiskers grow on (Fig. S3). Some droplets can be observed (noted by arrows in Fig. 2(b)) which indicates that the nanowhiskers are grown by vapor–liquid–solid (VLS) mechanism. Fig. 2(c) shows the TEM image of a typical AlN nanowhisker with a diameter of 130 nm. Considering the XRD peaks of Ni in Fig. 1(a) and the EDS spectrum in Fig. 2(d), the component of the droplet is metallic Ni. It can be confirmed that the growth of AlN nanowhiskers is promoted by the Ni droplets. Metallic Ni droplets have been reported to act as a catalyst by continually absorbing AlN vapor (or clusters) to form a solid-solution compound, and then precipitating

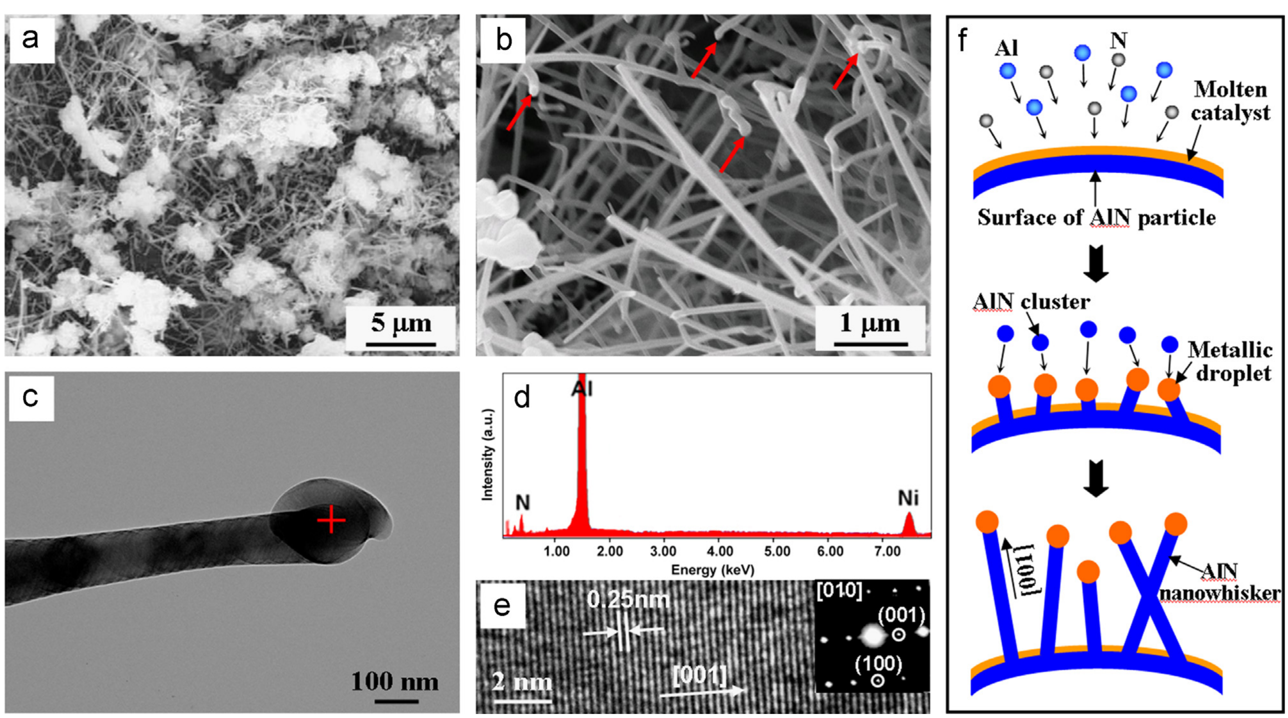

Fig. 2. (a) A low-magnification FESEM image of the as-synthesized AlN product with the addition of Ni catalyst; (b) high-magnification FESEM image of the as-synthesized AlN nanowhiskers; (c) TEM image of a typical AlN nanowhiskers and (d) EDS spectrum of the Ni droplet at the end of the nanowhiskers; (e) corresponding HRTEM image and SAED pattern of the nanowhisker; and (f) schematic illustration of the growth mechanism for the nanowhiskers.