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Nanoporous AlN particle production from a solid-state metathesis reaction*

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This paper reports that nanoporous AlN particles are synthesized from solid-state metathesis reactions using $AlCl_3$ and Mg_3N_2 as reactants. The samples are characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction, high-resolution transmission electron microscopy (HRTEM), ultraviolet–visible (UV–vis) absorption spectroscopy and Raman spectroscopy. The results show that samples with walls 10 nm in thickness and pores between 10 nm and 100 nm in diameter were produced successfully from these reactions, and their band gap and vibration modes agree with those of AlN bulk crystal.

Keywords: nanoporous AlN, solid-state metathesis reaction
PACC: 6865, 8120L, 7280E

1. Introduction

Because of the many pores that form in them, porous semiconductors exhibit many new interesting properties,[1] for example, a reinforced intensity of photoluminescence, an increased quantum efficiency of photoresponse and a reinforced strength of optical secondary harmonic generation. Thus porous semiconductors will have many potential applications in advanced microelectronics, sensors, interfacial structures and catalysis.[2]

Among porous semiconductors, wide bandgap semiconductors such as GaN, AlN, ZnO, SiC and BN etc are expected to enable novel technologies in optoelectronics, magnetism, catalysis and bio-sensors due to their unique properties, including efficient luminescence, high surface area and size-selective adsorption.[3,4] However, the difficulty in applying nanoporous materials is that current methods to produce them do not fully understand the pore-forming mechanism and cannot effectively control their morphology; furthermore they lack a good synthetic procedure to produce nanoporous IIIA-nitride semiconductors with a high specific surface area and a well defined nanopore size.[4]

In this paper, a simple approach—the solid-state metathesis reaction—was introduced to produce nanoporous AlN particles, and some optical properties of the nanoporous AlN samples were also explored.

2. Experiments

The reaction to produce nanoporous AlN particles is

$$AlCl_3 + Mg_3N_2 \rightarrow AlN + MgCl_2,$$

where $AlCl_3$ is an aluminum source and Mg_3N_2 is a nitride source. The experimental procedure is as follows: a stoichiometric mixture of reactants $AlCl_3$ and Mg_3N_2 was ground together with an agate mortar and pestle, and then the mixture was transferred to a sealed container (all of the reactants were analytical reagents and all manipulations were carried out in a nitrogen-filled glove-box). Then the container was heated up to a temperature above 750 °C and maintained at that temperature for two hours in an electrical furnace. After the container cooled down to room temperature, the reaction products were removed from the container, and washed and filtered three times with 0.1 M HCl to remove the byproducts, and then washed and filtered with de-ionized water. Finally the remainder, a gray–white powder, was dried at 80 °C for two hours in a vacuum drying chamber. The gray–white powder was collected for characterization.

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In order to characterize the samples, an x-ray diffraction (XRD) analysis was carried out with a Rigaku Damx X-ray diffractometer with a Cu Ka radiation with a scanning speed of 10°/min. Transmission electron microscopy (TEM) images and selected area electron diffraction patterns were taken on a JEM-200CX TEM. High-resolution HRTEM images were taken on a JEM-3010 HRTEM.

The optical properties of the samples were characterized by UV–vis absorption spectroscopy and Raman spectroscopy. The UV–vis absorption spectrum was obtained on the UV-2501PC spectrophotometer and the Raman spectrum was recorded on Lab-RAM HR800 by using an Ar^+ ion laser as excitation source.

3. Results and discussion

Figure 1 shows an XRD pattern of the samples. From the location of the peaks, the samples can be identified as hexagonal AlN. The Miller indices of the peaks are marked in the figure.

Figures 2 and 3 are a TEM image and an HRTEM image of the AlN samples, respectively. From the two

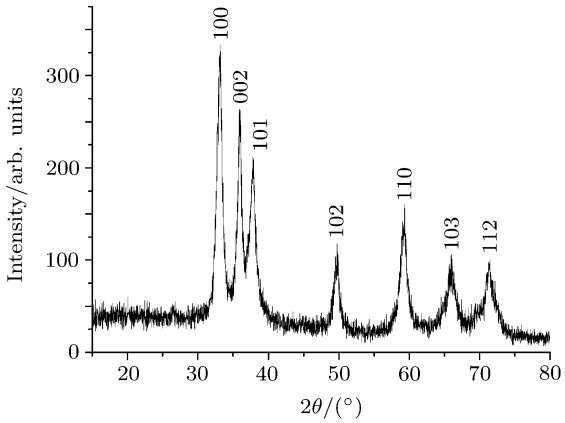


Fig.1. X-ray diffraction patterns of AlN samples.

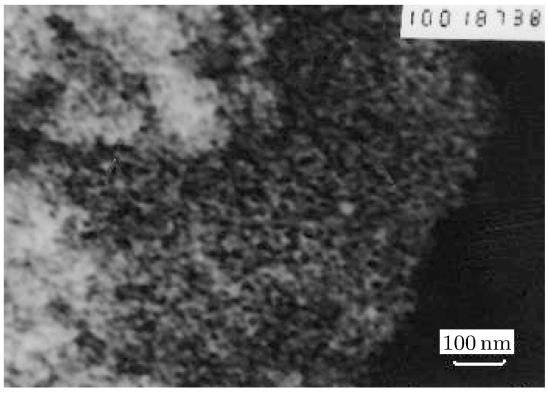


Fig.2. A TEM image of the AlN samples.

TEM images, it can be seen that the morphology of the AlN samples has a honeycomb structure, and the pore diameter varies from 10 nm to 100 nm with 10 nm wall thickness. Comparing the pore diameter with the wall thickness, we can anticipate that the porous AlN particles would have a high value of specific surface area.

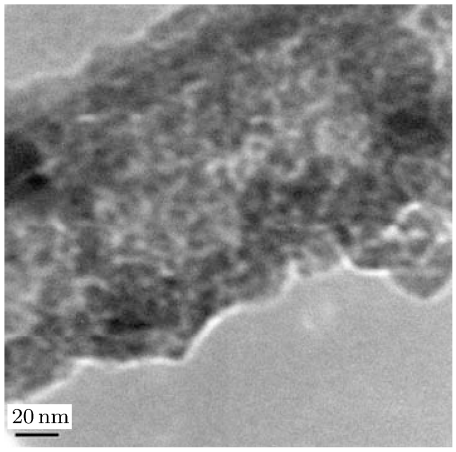


Fig.3. An HRTEM image of the AlN samples.

Figure 4 is a selected area electron diffraction pattern of the AlN samples. The electron diffraction pattern shows a set of rings, which means that the crystallographic orientations of the nanoporous AlN particles are random. The rings from innermost to outermost can be assigned to the (100), (101), (102), (110), (112) and (201) planes of hexagonal wurtzite AlN.

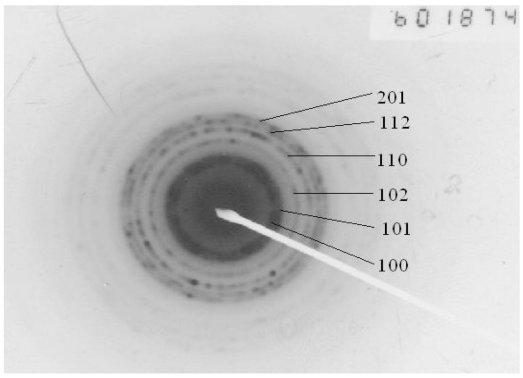


Fig.4. Electron diffraction pattern of the nanoporous AlN particles .

The UV–vis absorption spectrum of the samples is shown in Fig.5. There is an obvious knee of absorption edge at a wavelength of about 200 nm (6.2 eV) in the figure. This knee is caused by the optical transition of the first excitonic state of AlN,[5] so the data at 6.2 eV can be considered as the band gap of AlN

samples,[5] which is in accordance with that of AlN bulk crystal.

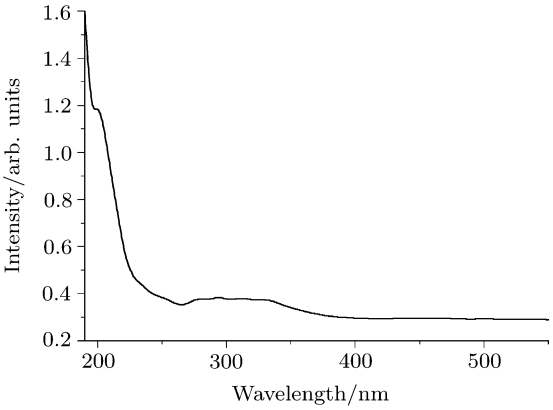


Fig.5. A UV–vis absorption spectrum of the samples.

The Raman spectrum of the AlN samples is shown in Fig.6. There are five peaks in the figure, centred at 615 cm^{-1}, 656 cm^{-1}, 670 cm^{-1}, 898 cm^{-1} and 912 cm^{-1} respectively, which is in agreement with the results for AlN crystal.[6] The peaks presented at 615 cm^{-1}, 656 cm^{-1}, 670 cm^{-1} correspond to the A1(TO), E2(high) and E1(TO) modes respectively, and two broad peaks at around 898 cm^{-1} and 912 cm^{-1} are resulted from the modes of A1(LO) and E1(LO).

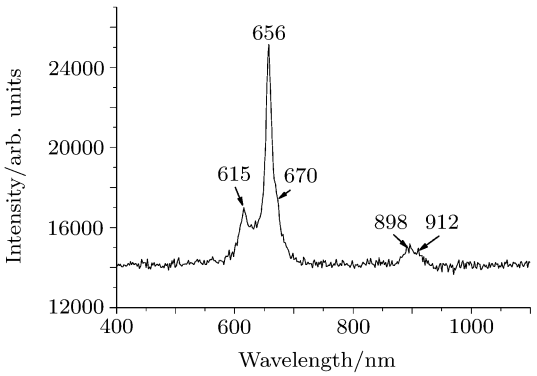


Fig.6. A Raman spectrum of the samples.

Our experiments finds that in order to obtain nanoporous AlN materials from a metathesis reaction, the properties of the reactants and/or the resultants must satisfy the following requirement: a eutectic solution cannot be generated from the mixture of the AlN with the reactants and/or the resultants. Otherwise, other morphologies of AlN apart from the nanoporous morphology can be obtained. For example, using Li_3N as a nitride source and $AlCl_3$ as an aluminum source, we cannot generate nanoporous AlN because a eutectic solution is generated from the mixture of AlN, LiCl and Li_3N.[7–9] The TEM image of the AlN samples synthesized from the reaction of Li_3N and $AlCl_3$ is shown in Fig.7. From the image, it can be seen that the samples were composed of irregular and regular nanoparticles without containing nanopores.

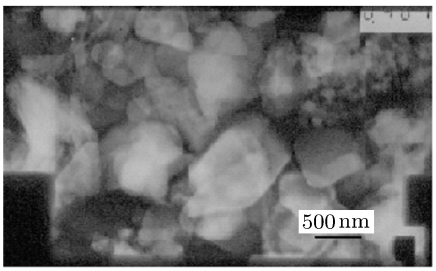


Fig.7. TEM image of AlN samples synthesized from the reaction of Li_3N and $AlCl_3$.

4. Conclusion

Nanoporous AlN particles with walls 10 nm in thickness and pores between 10 nm and 100 nm in diameter were produced successfully from a solid-state metathesis reaction using $AlCl_3$ and Mg_3N_2 as reactants. In order to obtain nanoporous AlN from the reaction, the reactants and/or the resultants must satisfy the requirement that a eutectic solution cannot be generated from the mixture of the AlN with the reactants and/or the resultants.

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