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Preparation of nano-porous AlN micro-rods

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In this paper, nano-porous AlN micro-rods were prepared and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emett-Teller (BET) method of nitrogen adsorption at low temperature, UV-via absorption spectrometry and Raman spectrometry. The SEM images and TEM images showed that the AlN samples were micro-size rods with pores in their surfaces evenly. The length of the rod was in the range of a few microns to tens of micron, the diameter of the rods was about one micron, the diameter of the pore was about hundreds of nanometer and the wall thickness of the pore about tens of nanometer. The BET surface area of the sample was 41.424 m^2/g. The optical spectra showed that the optical properties of the AlN samples almost agreed with that of AlN bulk or film.

porous AlN micro-rods, preparation

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1 Introduction

Porous semiconductors have many interesting properties such as unique optical, electrical, mechanical and magnetic properties, which are distinct from those of the bulk materials and make them have many applications, for example fabrication of enhanced devices for advanced microelectronics, sensors, interfacial structures and catalysis [1]. Among these materials, wide band-gap porous materials (SiC, GaN, AlN, ZnO, BN, etc.) are especially important because of some of their particular properties, including band gap shift, efficient luminescence, high surface area, and size-selective adsorption [2]. Some methods, for example, photoelectrochemical etching [3], plasms etching [4], supra-molecular self-assembly [5, 6], precursor pyrolysis [7] and focused ion beams milling [8], have been introduced to prepare the porous semiconductor materials. However, for the porous IIIA nitrides, most of the papers were concerned about the two shapes: porous film and/or porous bulk; only a few papers presented to prepare the other porous shapes [1, 9–13]. In the paper, one of the porous AlN materials, porous AlN micro-rods, was produced successfully at the temperature of 850°C through the nitridation of Al plates and Mg strips, and the rods were characterized by XRD, TEM, SEM, N_2-adsorption isotherms, UV-via absorption spectrometry and Raman spectrometry.

2 Experimental

The processes of synthesizing porous AlN micro-rod were as follows: 1 g aluminum plates with purity of 99.5% and thickness of 1 mm and 1 g magnesium thin strips with purity of 99% and thickness of 0.5 mm were weighed, respectively. The plates and strips were put into a stainless steel

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crucible with an aluminum plate and a magnesium strip alternatively then the crucible was put into a vacuum furnace. After the pressure in the furnace was lowed down to 0.01 atm, nitrogen with a purity of 99.999% was filled into it till the pressure was up to 0.5 atm, then the pressure was kept. Heated to 850°C and maintained at the temperature for 15 h, the crucible was cooled down to room temperature, and then the products were cleaned and filtered by 0.1 M hydrochloric acid to remove the residual aluminum, magnesium and the products Mg_2N_3. Finally, the remainder, grey powders, was dried at 120°C for 4 h in a vacuum drying chamber and collected for characterization.

In order to characterize the products, an X-ray diffraction (XRD) analysis was carried out with a Rigaku Damx X-ray diffractometer with a Cu $K\alpha_1$ radiation with a scanning speed of 10°/min. Transmission electron microscopy (TEM) images were obtained on a JEM-3010 transmission electron microscope. Scanning electron microscopy images were recorded on a JSM-7000F field emission microscope. N_2 adsorption isotherms were taken on a Coulter SA 3100 surface area and pore size analyzer at 77 K. The optical properties of the samples were characterized by UV-transmission spectroscopy and Raman spectroscopy. The UV-vis transmission spectra were gotten on the UV-2501PC spectrophotometer and the Raman spectra were taken on Lab-RAM HR800 by using an Ar^+ ion laser as excitation source.

3 Results and discussion

3.1 Structure and morphology of the samples

Figure 1 is the XRD patterns of the rods. In the patterns, all the peaks can be indexed according to the hexagonal wurtzite AlN with lattice constants a=0.311 nm and c=0.498 nm and the Mill index of all the peaks are marked in the figure respectively. It can be seen that except the diffraction peaks corresponding to the hexagonal wurtzite AlN, there are no other obvious diffraction peaks in the XRD patterns, indicating that the main part of the sample is AlN and the content of impurity is low.

Figure 2 is TEM images of the samples. The shape of samples is rod and there are some grey regions or dark lines in the images of the AlN rods, as shown by the arrows. The grey regions correspond to the pores in the surfaces of AlN rods, and the dark lines are resulted from the walls of pores. In order to verify more intuitively the porous structure in the AlN micro-rods, SEM images were obtained through a JSM-7000F field emission microscope. Figure 3 and its inset are SEM images of the AlN samples. It can be seen clearly that the AlN samples consist of many micro-rods, the length of the rods varies from several microns to tens of micron, the diameter of the rods is about one micron, there are many pores in the rods, and the pores are evenly distributed on the whole surfaces. The diameter of the pores is about hundreds of nano-meters and the wall thickness of the pores is about tens of nanometer.

The BET surface area of the AlN samples is 41.424 m^2/g. Through calculation, for the micro-rods, their specific surface area can be formulated as $2(h+r)/(r\times h\times\rho)$ m^2/g, where

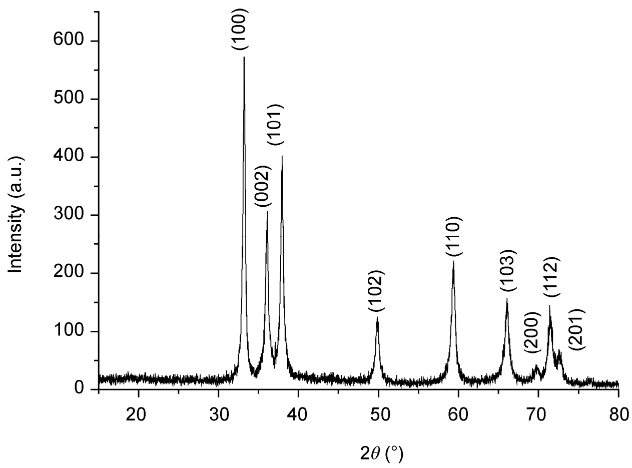

Figure 1 The X-ray diffraction patterns of the samples.

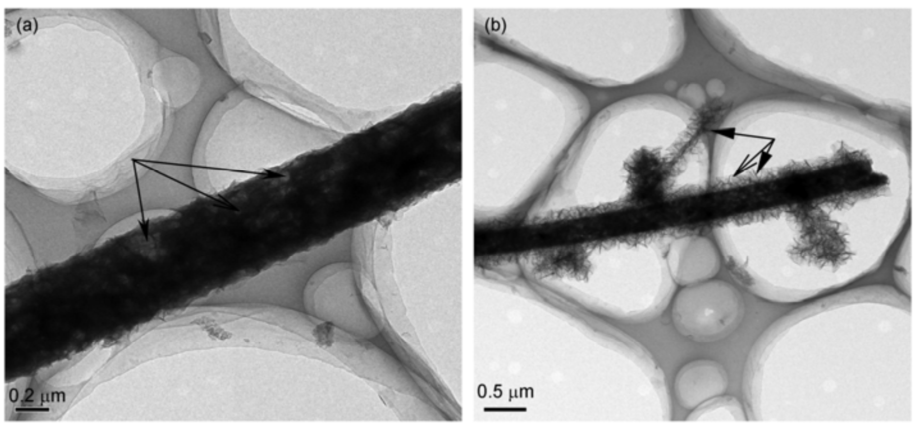

Figure 2 TEM images of the AlN samples.

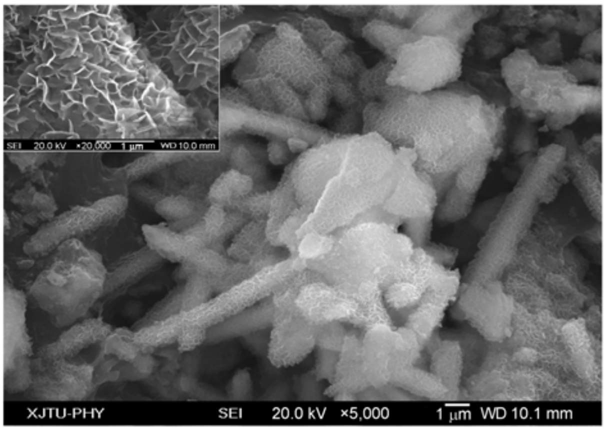

Figure 3 SEM images of the AlN samples.

"r" is the radius of the micro-rods, "h" represents the height of the micro-rods, and "ρ" is the density of the samples (for AlN, its value is 3.23 g/cm^3). Thus we can conclude that for the AlN micro-rod with "r" equal to 0.5 microns and "h" equal to 2 microns, its value of specific surface area is about 1.5 m^2/g. From the SEM image of the AlN samples in Figure 3, it can be concluded that the value of "r" of AlN micro-rod samples is about 0.5 microns, and the height of the AlN micro-rods is larger than 2 microns, so the increment of the measured specific surface area is attributed to the formation of pores in the surfaces of AlN micro-rods.

3.2 Optical properties of the samples

The UV-vis absorption spectrum of the samples is shown in Figure 4. There is an obvious shoulder in the figure around 200 nm, which is the result of the optical transition of the first excitonic state of AlN [14]. So the band gap of the AlN samples is about 6.2 eV, approximately equal to that of bulk crystal AlN. However, limited by the performance of UV-2501PC spectrophotometer, we can't more accurately define the optical properties of the AlN samples.

Figure 5 is a Raman spectrum of the AlN samples, where the three sharp peaks, centered at the 613, 657.7 and 897 cm^{-1}, respectively can be attributed to the modes of A_1(TO), E_2(high) and A_1(LO), respectively, the knee at 672 cm^{-1} comes from the mode of E_1(TO), and the shoulder peak around 910 cm^{-1} corresponds to the mode of E_1(LO). The Raman spectrum of the samples is nearly consistent with that of AlN film and bulk [15, 16].

3.3 The growth mechanism of porous AlN micro-rods

Wang have suggested that AlN grows to be cylindrical grains through a vapor-liquid-solid (VLS) mechanism in a direct nitridation of the Al melts when magnesium exists [17]. In the temperature of 850°C, the Al plates are melted, so the AlN rods will be obtained in a direct nitridation of Al plates. But different from Wang, at the temperature of

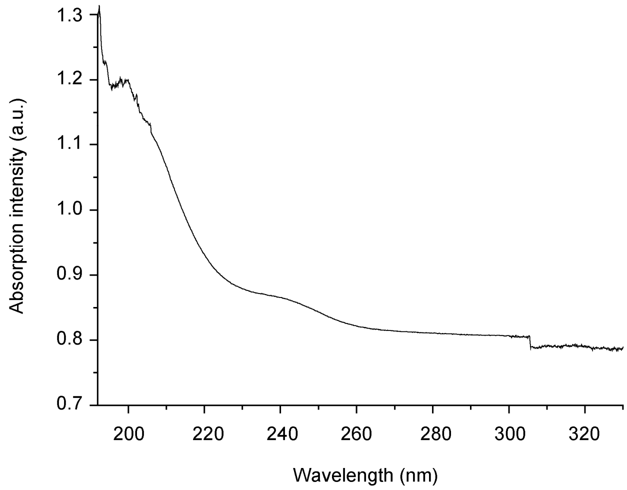

Figure 4 UV-vis absorption spectrum of the samples.

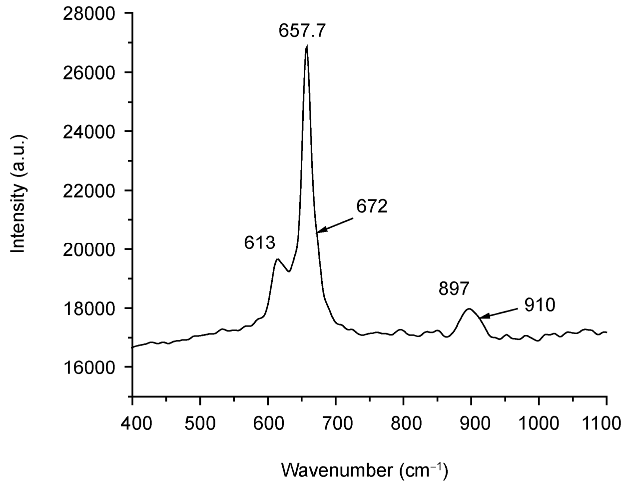

Figure 5 Raman spectrum of the samples.

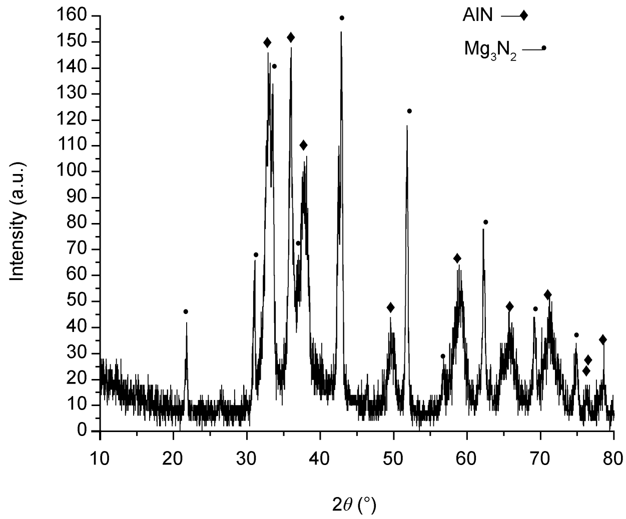

Figure 6 The X-ray diffraction patterns of the products produced by heating the Al plates and Mg strips at 850°C for 10 h (not cleaned by hydrochloric).

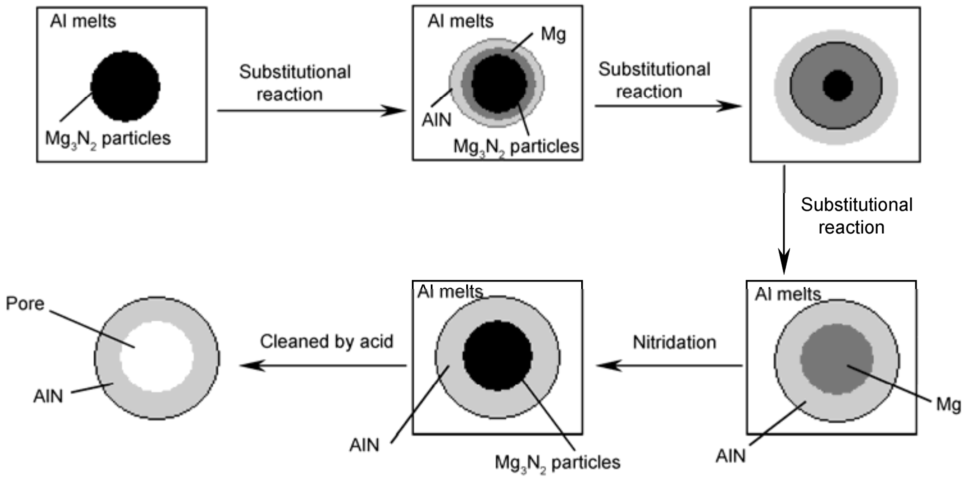

Figure 7 Illustration of pores formation in AlN rods.

850°C, most of magnesium were nitridized into Mg_3N_2 particles and were still in the Al melts, other than disappeared from the melts and deposited on the wall of the crucible. Figure 6 is the XRD patterns of the products not cleaned by hydrochloric. All the peaks were marked in the figure. It can be seen that there are many Mg_3N_2 in the products, indicating that the magnesium was not disappeared from the Al melts. According to He [18], when Mg_3N_2 was in the Al melts, it would be advantageous to the formation of AlN through the substitutional reaction:

$$2Al+Mg_3N_2 \rightarrow 2AlN+3Mg$$

Thus, the processes of pores formation in AlN rods can be illustrated in Figure 7.

4 Conclusion

The porous AlN micro-rods were prepared through the aluminum plates and magnesium strips. The length of the rods is in the range of a few microns to tens of micron, and the diameter of the rods is about one micron. The pores were distributed evenly on the surfaces of the AlN micro-rods, the diameter of the pores is about hundreds of nano-meter and the wall thickness of the pores is about tens of nanometer. The BET surface area of the porous AlN micro-rods is 41.424 m^2/g. The optical properties of the AlN samples are essentially in accordance with that of AlN film or bulk crystal.

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