IOP Conf. Series: Materials Science and Engineering **93** (2015) 012051 doi:10.1088/1757-899X/93/1/012051

The plasma dynamic synthesis of aluminum nitride in system with gaseous and solid precursors

I Shanenkov[1], A Sivkov[1], A Ivashutenko[1] and Yu Shanenkova[1]
[1] Institute of Power Engineering, Tomsk Polytechnic University,
Lenin av. 30, Tomsk, Russian Federation

E-mail: Swordi@list.ru

Abstract. Aluminum nitride is widely-used material for semiconductor devices and ceramics production. Despite the large number of known ways to obtain AlN powder, the problem of synthesizing high-purity and nanosized product is still urgent. This paper shows results on plasma dynamic synthesis of aluminum nitride using system based coaxial magneto plasma accelerator. The influence of using gaseous or solid precursors on such characteristics of the final product as phase content and particle size distribution was investigated. According to X-Ray diffractometry AlN phase content is increased in the case of use of solid nitrogen-containing precursor (melamine) in comparison with the use of gaseous nitrogen. The particle sizes distribution histograms are built in accordance with the data of bright-field TEM-images and shown in this paper. The most of particles are less than 100 nm in both experiment but there are some differences, depended on the precursor type, that are also described.

1. Introduction

Aluminum nitride was firstly synthesized in 1877, but only in the late of 20th century this material attracted the attention of scientists due to a number of its unique properties. High thermal conductivity, low dielectric constant, high thermal stability, non-toxic, high-mechanical strength make this material attractive for substrates of semiconductor devices and ceramics production.

But there are several known problems connected with the AlN applications [1]. The sintering process of AlN ceramics is sensitive to the presence of impurities in powder that impacts on the defects appearance. Also the high sintering temperature negatively influences on the obtaining of fully dense AlN. This temperature can be decreased by using powder with the smaller particles in order to increase the particle surface area. Thus, the key issue is how to obtain high-purity and nanosized powder [1-5].

There are many methods to synthesize aluminum nitride both in the form of thin films [6-12] and in the powdered form [12-16]. The synthesis by plasma methods has such advantages as the fast speed of reaction due to the high plasma temperature (~ 10^4 K), the possibility of obtaining ultrafine monocrystalline product due to the high cooling rate (> 10^6 K / s) and the possibility of using precursors without special pre-treatment [1]. The system based on coaxial magneto plasma accelerator can be used to obtain different ultrafine powders by varying energy and construction parameters with high efficiency [17-20].

This paper shows results on AlN synthesis in the discharge plasma jet generated by coaxial magneto plasma accelerator. The influence of both gaseous and solid precursors on the final product was investigated. Also particle size distribution, particles morphology and phase content were studied.

2. Experimental

Design and function of CMPA-based system were considered earlier [17]. In experiments the CMPA with aluminum central electrode and aluminum electrode-barrel was used. In order to initiate the discharge four Al wires (200 µm thickness) were stretched between electrodes. When the process was started and current, flowing through electrodes, increased, these wires exploded and the arc plasma discharge ignited. This plasma structure was accelerated by forces of conductive and inductive electrodynamics. Aluminum necessary for synthesis was accumulated from the central electrode and inner walls of electrode-barrel due to their electro erosion. Nitrogen was introduced into plasma by two ways: using the gaseous nitrogen atmosphere in the working chamber or using nitrogen-containing precursor put into the plasma formation zone. In the first case the aluminum-containing plasma was interacted with gaseous nitrogen in the second case the aluminum-nitrogen plasma flowed into the chamber space filled with argon atmosphere.

Two experiments were carried out in order to compare the influence of solid and gaseous precursors in this system on such synthesized powder characteristics as phase content, particle morphology, particle size distribution. In the first experiment the working chamber, preliminary evacuated, was filled with nitrogen (N_2) atmosphere at normal conditions. In the second experiment melamine ($C_3N_6H_6$) with the mass of 1 g was chosen as the solid nitrogen-containing precursor due to high nitrogen content and its low binding energy. The chamber was filled with argon atmosphere at normal conditions. Energy parameters of both experiments were as follows: charging voltage – 2.0 kV, charging capacity – 14.4 mF.

Synthesized powders were investigated using such methods as X-Ray diffractometry (XRD) and transmission electron microscopy (TEM). The XRD analysis was carried out using Shimadzu XRD7000S diffractometer with the counter monochromator Shimadzu CM-3121. The database PDF2+ and the software PowderCell 2.4 were used to provide respectively qualitative and quantitative analyses of XRD patterns. The TEM analysis was carried out using Philips CM 30 microscope. Particle size distribution histograms were built in the software ImageJ in accordance with the data of bright-field TEM-images.

3. Results and Discussions

Figure 1 shows XRD patterns of synthesized powders. The product obtained in the experiment with gaseous precursor (figure 1a) strongly differs from the product synthesized in the experiment with solid precursor (figure 1b). Both the main peaks ratio and the phase content noticeable change in dependence on the precursor changing. As for the experiment 1 the powder predominantly consists of aluminum phase with the small presence of hexagonal aluminum nitride (space group No. 186 P63mc). This small content of AlN phase can be explained by low reactivity of pure gaseous nitrogen due to high binding energy.

The powder synthesized in the second experiment also consists of hexagonal aluminum nitride and pure aluminum phases, but in this case there is a presence of Al_4C_3 and melamine in the final product. The quantitative analysis shows the increase of AlN phase content and decrease of pure aluminum. It seems natural due to the fact the energy parameters of experiments were the same but in the case of experiment with solid precursor the binding energy of nitrogen in melamine is less than that of gaseous nitrogen. The aluminum carbide formation can be explained by decomposition of precursor under the plasma influence. Free carbon ions, released after decomposition, react with aluminum, which present in excess, during the cooling down process. The appearance of melamine in the final product is unexpected but not unusual. After opening the system 0.2 g of unreacted melamine was found in the plasma formation zone.

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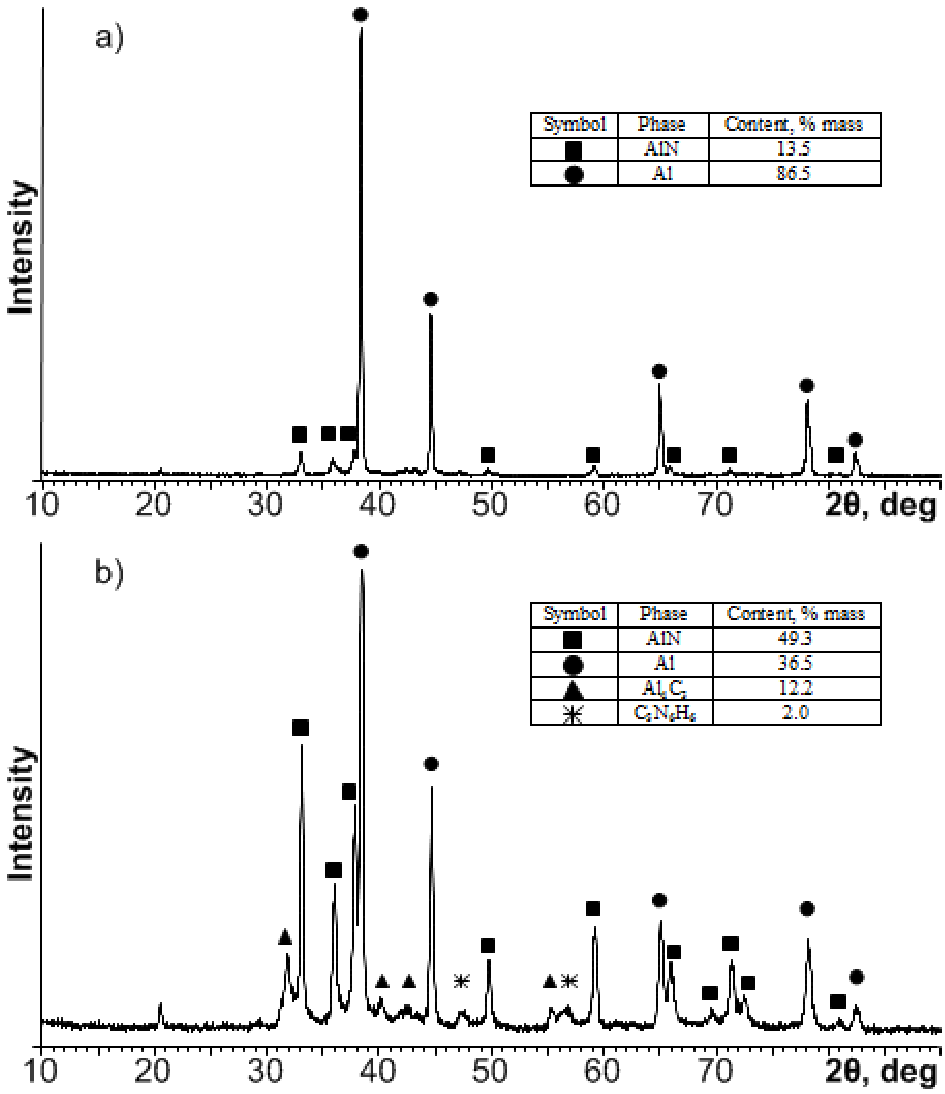

Figure 1. XRD-patterns of synthesized products: a) experiment with gaseous precursor; b) experiment with nitrogen-containing solid precursor.

Apparently due to its known dielectric properties the current flowed not through all volume and some part of melamine didn't convert into the plasma state. A small amount of unreacted precursor from this part could get into the final product that has given a reflection on the diffraction pattern.

The results of XRD analysis are confirmed by data of TEM analysis. Bright-field images of products synthesized in experiments with gaseous and solid precursors (figure 2a and 3a, respectively) are similar in terms of particle morphology. Both products have few clearly-seen types of objects: bright round particles, round particles with dark inclusions, well crystallized particles mostly in the form of hexagons and polygons and ultra-fine particles below 10 nm. The analysis of selected area electron diffractions (SAED), shown in figure 2b and 3b, allows confirming that products predominantly consist of pure aluminum and hexagonal aluminum nitride.

At displacement of the aperture in the area of different bright reflexes dark-field images were obtained. As it is seen in the figures 2c and 2d, obtained from reflexes of AlN in direction of [101] and [110], respectively, the particles with dark inclusions and hexagon particles are shone. The dark inclusions seem to be the regions doped with nitrogen. The round particles and hexagons are attributed to Al and AlN particles, respectively. This result is consistent with previous studies on the growth mechanism of AlN nanoparticles [1].

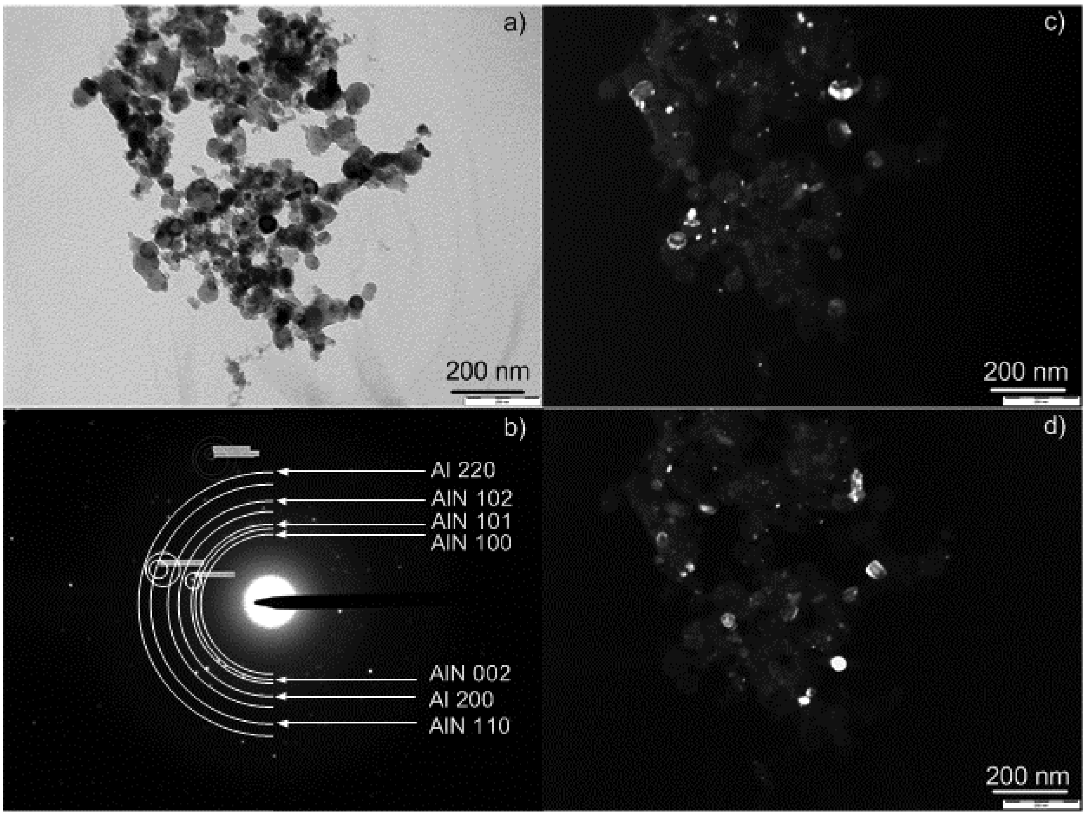

Figure 2. TEM-images of the product synthesized using gaseous precursor: a) bright-field image; SAED; c) dark-field image in the light of AlN reflex in direction [101]; d) dark-field image in the light of AlN reflex in direction [110].

The round Al particles react with the nitrogen in the plasma scope and form into hexagonal-shaped particles, and grain growth occurs by the reaction of nitrogen and Al crust on the surface of AlN particles. It should be noted the product synthesized in experiment one is predominantly consist of round objects attributed to Al that confirm the results of XRD analysis where the Al phase is dominant. In the case of experiment with solid precursor the dominant particles in the product are polygons and hexagons attributed to AlN phase. This result is also in a good agreement with XRD analysis data. Dark-filed images, obtained from reflexes of AlN phase in the direction of [100] and [102] (figure 3c and 3d, respectively) also show the luminescence of hexagons and locally-doped regions.

The visual comparison of bright-field images allows concluding that particles synthesized in experiments with solid precursor have larger sizes. This is confirmed by results of particle size distribution analysis, shown in figure 4. It is seen these histograms are different in terms of particle size maximums. The most of the particles in the product, synthesized in experiment with gaseous precursor, have sizes in the range of 20-80 nm. The particles in the product, obtained in experiment 2, have larger sizes in the range of 40-160 nm without noticeable maximum.

This result can be explained by features of melamine decomposition under the influence of plasma. Hydrogen, which is presented in melamine, is released in the current flow process. Its release increases the heat removal, that impacts on energy parameters of synthesis process. The voltage is increased and the level of current is limited. The limitation of current leads to decrease of plasma temperature and the cooling rate, respectively. The decrease of cooling rate results in increasing of particle sizes.

The decrease of current level due to hydrogen release also explains the presence of unreacted melamine in the plasma formation zone after carrying out the experiment. Thus, the effective

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conversion of melamine is important task to carry out experiments in this system in terms of increase of aluminum nitride content and decrease of impurity presence. There are several possible ways that can be realized in this system. The first way is to increase the energy parameters in order to increase the current level, but in this case the erosion of aluminum electrodes and its presence in final product will be also increased. The second way is to decrease the solid precursor mass at the same energy parameters. In this case there is a sense of using both solid nitrogen-containing precursor and nitrogen atmosphere with higher pressures. The third way is to use other solid nitrogen-containing precursors or their mix with melamine.

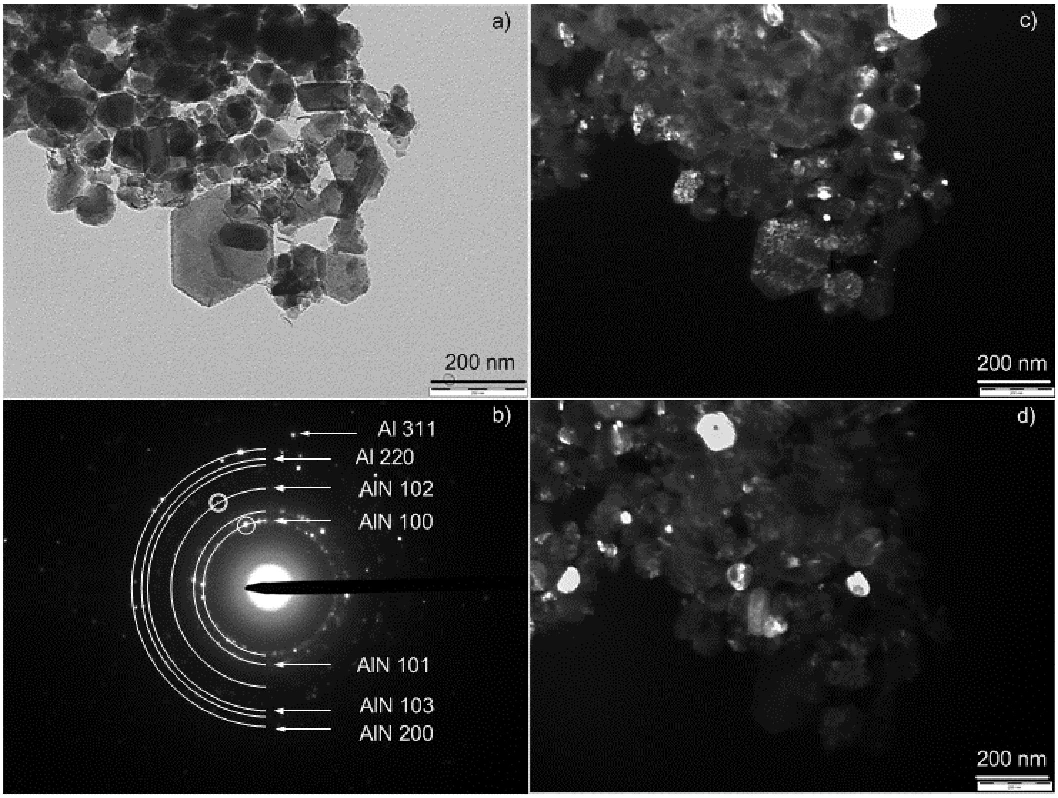

Figure 3. TEM-images of the product synthesized using solid precursor: a) bright-field image; SAED; c) dark-field image in the light of AlN reflex in direction [100]; d) dark-field image in the light of AlN reflex in direction [102].

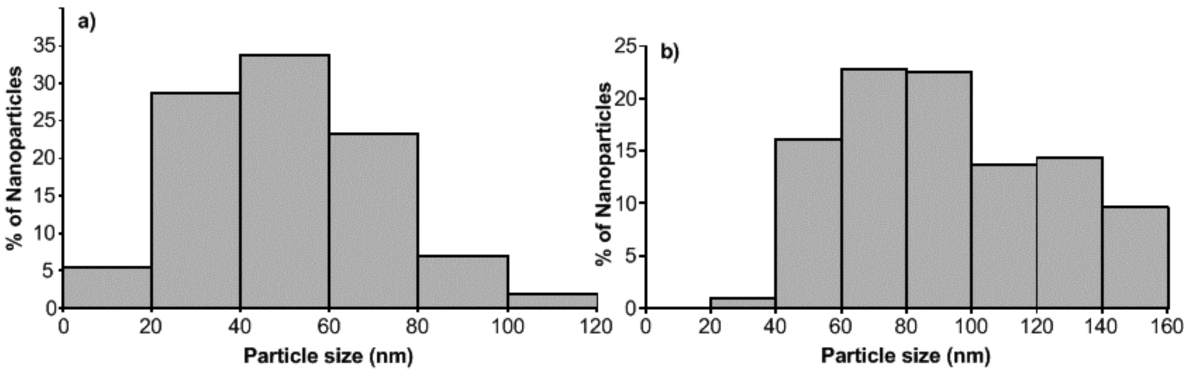

Figure 4. Particle size distribution histograms: a) experiment with gaseous precursor; b) experiment with solid precursor.

Conclusion

The synthesis of aluminum nitride can be realized using plasma dynamic method in the system based on coaxial magneto plasma accelerator. The influence of using solid and gaseous precursors on synthesized powders was investigated. According to XRD and TEM analyses the using of solid nitrogen-containing precursor (melamine) is preferable in terms of aluminum nitride content in the final product. But in this case the problem of impurities presence should be solved. Also the use of melamine influences on the particle size distribution aside increasing due to hydrogen presence. Thus the important task for further investigations in this system is to increase aluminum nitride content and decrease particle sizes.

Acknowledgements

This work was supported by the Russian Science Foundation (grant № 15-19-00049).

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