ISSN 1027-4510, Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques, 2009, Vol. 3, No. 3, pp. 460–463. © Pleiades Publishing, Ltd., 2009.
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Analysis of the Local Atomic Structure of Aluminum Nitride Nanoparticles

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Received June 23, 2008

Abstract—The structure of synthesized AlN nanoparticles was studied based on the theoretical analysis of X-ray absorption spectra near the *K*-absorption edge of aluminum. The method of full multiple scattering and finite difference method were used for theoretical calculations. The set of phases being present in nanoparticles and concentrations of different phases are determined. It turned out that besides cubic and hexagonal AlN phases the pure Al metal phase is present in synthesized objects.

DOI: 10.1134/S1027451009030215

INTRODUCTION

Aluminum nitride is the wide band gap semiconductor. This material possesses interesting tribological, electronic, and unique mechanical properties. AlN is used in current technology basically due to its high heat conductivity and small coefficient of thermal expansion [1]. At room temperature AlN crystallizes into the wurtzite phase. Previously both cubic and wurtzite phases were observed for nanosized AlN samples [2]. At the moment, there is no data in the literature on macroscopic AlN samples with the cubic sphalerite-type structure.

The AlN nanosized objects, whose properties could be changed according to the synthesis parameters, are of great interest. The atomic structure of nanotubes or nanoparticles differs usually from the structure of crystals or thin films due to reduction of symmetry and/or extremely unstable synthesis. Both the wurtzite and cubic phases of aluminum nitride find application in various areas of technology, in particular, in such exotic devices as electroacoustic systems [3], etc.

EXPERIMENTAL

AlN nanoparticles have been grown in the dc-arc plasma [4]. According to electron microscopy data, the average diameter of particles is 100 nm (Fig. 1). The preliminary structure analysis has been carried out using an X-ray diffractometer [5]. Spectra of X-ray absorption near the *K* edge of aluminum have been measured at the BESSY II (Germany) and DAFNE-Light (Italy) synchrotron radiation sources for a more accurate analysis. The spectrum of high purity (99.9%) aluminum nitride powder was used as the model spectrum. X-ray absorption spectra were measured in the transmission mode; the energy resolution was 10^3; and the aluminum foil was used for energy calibration. The analysis of the dimensions and distribution of the obtained nanoparticles was carried out using a FEI scanning electron microscope with a spatial resolution better than 10 nm.

CALCULATION PROCEDURE

The full multiple scattering method (realized in the feff 8.2 program complex [6, 7]) and the finite difference technique (realized in the FDMNES2007 program complex [8]) were used for theoretical calculations of X-ray absorption near edge spectra (XANES). The

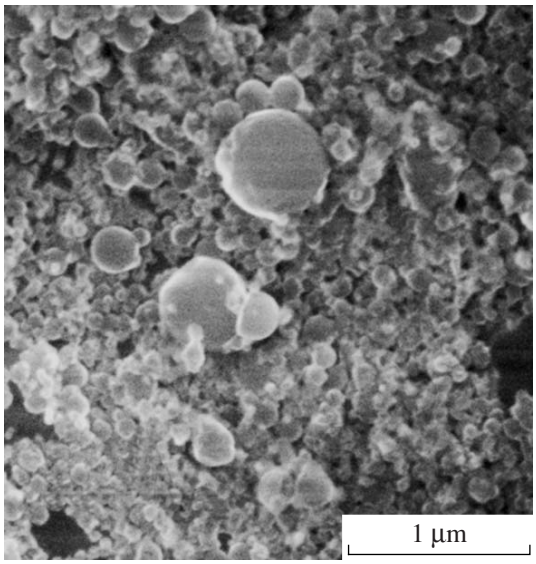

Fig. 1. Photograph of synthesized AlN samples obtained with a scanning electron microscope.

method of full multiple scattering assumes that the thin structure of an absorption spectrum can be described as the result of an interference of the outgoing photoelectron wave with the wave, which has come back after the single or multiple scattering by surrounding atoms. However, because of features of the calculation, it imposes the restriction on the form of potential, the so-called muffin-tin approximation, in which all space is partitioned into two areas: nonoverlapping spheres around all of the atoms and the region between them. It is supposed that the potential possesses a spherical symmetry in the spherical region around each atom. The value of the potential is set being constant outside these regions (between muffin-tin spheres) [7]. The finite difference method determines the values of an electron wave function of the final state at the set three-dimensional mesh after photon absorption. It is reached by the finite difference solution of the Schrodinger equation on this mesh. Having determined the wave function of the final state without restrictions on the form of potential, we can calculate the spectrum of X-ray absorption using the Fermi golden rule for the cross-section

$$\mu \sim \sum_f \left|\langle \Psi_f | \boldsymbol{p} \cdot \boldsymbol{A}(\boldsymbol{r}) | \Psi_i \rangle\right|^2 \delta(E_f - E_i - \hbar\omega),$$

where Ψ_f is the wave function of the final state of the electron; Ψ_i is the wave function of the initial state of the electron; $\boldsymbol{p}$ is the operator of the electron's momentum; and $\boldsymbol{A(r)}$ is the vector potential of the incident electromagnetic wave. The presence of a delta function provides the law of conservation of energy, i.e., the sum of energies of the initial state and of the incident photon is equal to the energy of the final state. The summation is carried out over all final states Ψ_f, into which an internal atomic electron can pass at the absorption of incident photons.

However, in the latter method the potential is not self-consistent and the calculations require greater computer resources.

RESULTS AND DISCUSSION

The particles with an average diameter of 100 nm (Fig. 1) have been formed as a result of synthesis. According to the X-ray diffraction data, AlN both in the wurtzite phase (average estimations of lattice parameters: $a = 3.11$ Å, $c = 4.98$ Å, and $u = 0.382$ Å) and in the cubic phase (sphalerite structure, lattice parameter $a = 4.439$ Å) are present in the formed material in comparable amounts [5]. Spectra of X-ray absorption near the Al *K*-edge in the AlN powder with a wurtzite structure and in AlN nanoparticles are presented in Fig. 2. Energy positions of the basic maxima in the spectra are presented in the table. Because the samples of AlN nanoparticles are nanostructured, the usual X-ray diffraction is unsuitable for the accurate quantitative analysis of their phase composition. On the contrary, the cross-section of near edge X-ray absorption is very sensitive to the local environment of an absorbing atom. Spectra of absorption near the *K*-edge of aluminum containing information on the local environment of aluminum atoms being considerably different in different AlN phases have been investigated. For example, the first coordination sphere of the aluminum atom in the AlN with the NaCl-type structure contains six nitrogen atoms located at the octahedron vertexes and the one in the AlN with a wurtzite structure, four nitrogen atoms located at the tetrahedron vertexes. Significant differences in the local environment of aluminum atoms in the second coordination sphere are observed for AlN with wurtzite and sphalerite structures.

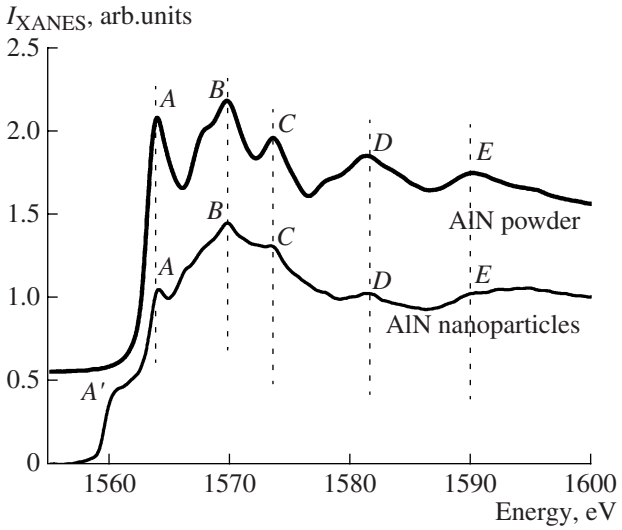

Fig. 2. The absorption spectrum near Al *K*-edge in the AlN powder (99.9% of hexagonal phase) and in the synthesized nanoparticles.

Account for the non-muffin-tin effects is important for the theoretical calculation of the Al *K*-edge in the AlN with the wurtzite structure. Consequently, the finite difference method, which is not imposing any restrictions on the potential, describes better the experimental spectrum (Fig. 3). The finite difference method and the method of full multiple scattering yield similar results for the AlN cubic structure with the NaCl-type lattice being in good agreement with the experiment. Cubic AlN, but with the sphalerite lattice, is unstable in macroscopical amounts and, consequently, there is no experimental absorption spectrum near the *K*-edge of aluminum for it. It was necessary to select the adequate theoretical method of calculation. It turned out that both approaches, the method of multiple scattering with muffin-tin potential and the finite difference method,

Energy position of basic maxima in the spectra of X-ray absorption near Al *K*-edge in AlN powder and AlN nanoparticles

Peak designation	*A*'	*A*	*B*	*C*	*D*	*E*
Energy position, eV	1560.5	1564	1570	1573.5	1581.5	1590

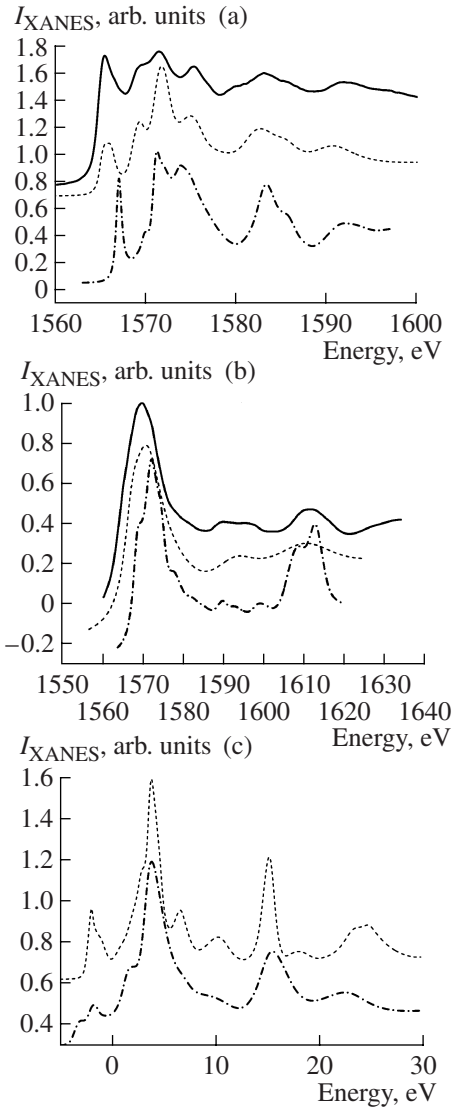

Fig. 3. Absorption spectra near Al *K*-edge for different modifications of AlN: (a) wurtzite structure, (b) NaCl-type structure, and (c) sphalerite structure. In each plot (top-down) the solid line represents the experiment; the dotted line, the calculation by the method of full multiple scattering; the chain line, the calculation by the finite difference method. It is not possible to obtain the experimental spectrum at the bottom plot for the AlN sphalerite structure because this modification is unstable in macroscopical samples.

yield similar results (Fig. 3). Therefore, one may state that the spectrum of the AlN phase with the sphalerite structure has been simulated correctly.

The main distinction of spectra of AlN nanoparticles and powder is the pre-edge feature *A'* in the spectrum of nanoparticles (Fig. 2). Appearance of a prepeak corresponds to the formation of new free electronic levels below the Fermi level of AlN with the wurtzite structure (the upper plot in Fig. 2). Calculations show that the appearance of these levels cannot be explained by the presence of additional cubic phase of AlN. Simulation

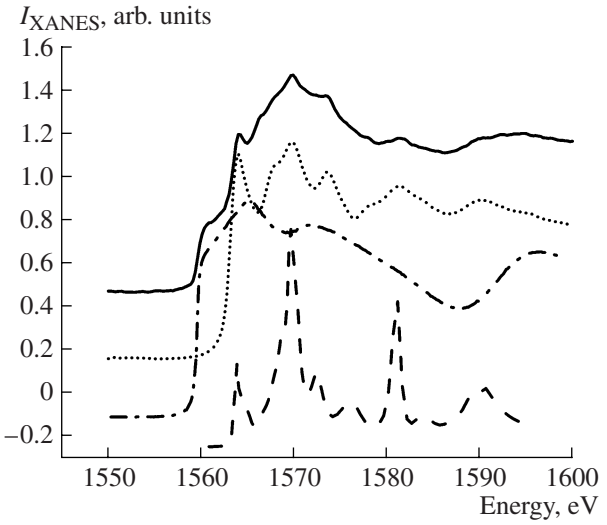

Fig. 4. Absorption spectra near Al *K*-edge in the synthesized nanoparticles (upper solid line), in the AlN powder (wurtzite structure) (dotted line), in the pure aluminum (fcc lattice) (chain line), in the AlN sphalerite structure (dashed line).

of the spectra of X-ray absorption for AlN in different phases with variation of lattice parameters in the range of 10% of their true value shows that the appearance of these levels cannot be explained also by the expected change in lattice parameters of AlN in nanoparticles. We have assumed that new free levels correspond to metal aluminum, which is formed during the synthesis of nanoparticles (Fig. 4). The purpose of the further reasonings is the confirmation of this hypothesis.

Figure 5 shows the spectra superposition for three phases and the spectrum of nanoparticles. The least deviation between spectra has been achieved for the following concentration of phases: 40% metal Al, 30% AlN with a wurtzite structure, 30% AlN with a sphalerite structure. However, the question is still open, how are different phases distributed in nanoparticles? There are several variants:

(i) Nanoparticles have a hexagonal or cubic structure depending on the size and nanoparticles of pure aluminum are present separately.

(ii) Two phases are present simultaneously inside one large nanoparticle and nanoparticles of pure aluminum are present separately.

(iii) Three phases are present simultaneously inside one large nanoparticle.

It is impossible now to answer this question explicitly. However, it would be possible to determine not only the composition of the synthesized mixture of nanoparticles and the structure of each phase, but also the mutual distribution of phases after carrying out further investigations using the focused electron beam of resolving power for obtaining the spectra of electron diffraction.

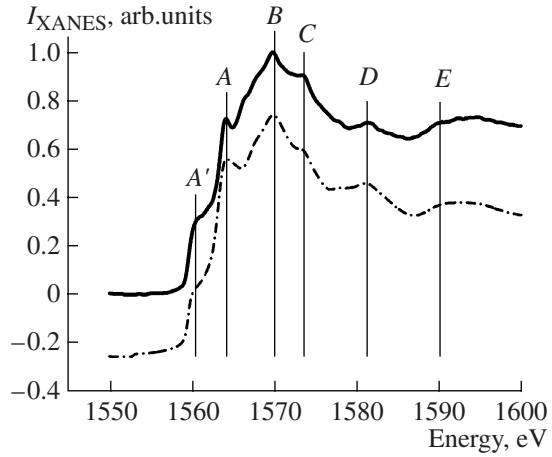

Fig. 5. Absorption spectrum near Al *K*-edge in the synthesized nanoparticles (solid line) and the mixture of absorption spectra from three phases: 40% pure aluminum, 30% AlN with the wurtzite structure, and 30% AlN with the sphalerite structure.

CONCLUSIONS

The synthesized nanosized samples of aluminum nitride have been investigated. Based on the theoretical analysis of X-ray absorption spectra and diffraction data, the conclusions on the composition of synthesized objects have been drawn: 40% pure aluminum, 30% AlN with the wurtzite structure (a = 3.110 Å, c = 4.980 Å, and u = 0.3821 Å), and 30% AlN with the cubic sphalerite structure (a = 4.439 Å). Since the nanoparticles were large enough, the noticeable change in the lattice parameters, as compared with the macroscopical samples, was not observed. The question on the distribution of these phases in the synthesized nanoparticles is still open.

ACKNOWLEDGMENTS

Authors are grateful to V. Ya. Shklover (OOO Systemy dlya mikroskopii i analiza) for the help in investigation of samples with electron microscope. This work was supported by the Ministry of Education and Sciences (grant RNP 2.1.1.5932).

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