

Auger electron spectroscopy of boron nitride whiskers produced in optical furnace without catalysts

L. L. Sartinska, V. V. Stonis^{*}, A. A. Frolov

^{*}Kurdyumov Institute for Metal Physics of NASU, Kiev, Ukraine

Results of Auger electron spectroscopy (AES) investigations of boron nitride whiskers produced in optical furnace without catalysts as well boron and initial h-BN for comparison are presented. The Auger process was initiated by exposing the sample to a beam of high energy electrons 3 keV.

Research of surface of solids is important for many fields in electronics, at direct transformation of thermal, solar and chemical energy to electric, in catalysis and other, where the purity of the produced materials and chemical state of atoms has the special value in a near-surface layer.

Auger electron spectroscopy is a very powerful surface analytical technique that has found applications in many fields of solid-state physics and chemistry. Several phenomena such as adsorption, desorption, surface segregation from the bulk, measurement of diffusion coefficients, and catalytic activity of surfaces have been investigated using AES [1, 2]. The basic advantages of this technique are its high sensitivity for chemical analysis in the 0,55- to 2 Å region near the surface, a rapid data acquisition speed, its ability to detect all elements above helium, and its capability of high-spatial resolution. The high-spatial resolution is achieved because the specimen is excited by an electron beam that can be focused into a fine probe. It was developed in the 1960s, when ultra-high vacuum technology became commercially available [3].

Filamentary structures of BN, produced in an optical furnace in the atmosphere of nitrogen [4—6] due to its structural peculiarities can differ by the chemical state not only surface layer of atoms in a homogeneous and perfect enough area of the surface from the chemical state of the second and subsequent near-surface layers but also by the chemical state of imperfect inhomogeneous area of polycrystalline surface of whiskers. Thus, study of power spectrums of Auger-electrons for definition of element composition of solids and chemical state of atoms of surface of BN whiskers can considerably extend the notion about our produced structures.

It is known that almost any solid can be analyzed by AES. Our powder samples were analyzed as there were and the analysis was done in high vacuum. A pure aluminum (SIGMA-ALDRICH, 99%, particle size <75 μm) was added to every sample for better estimation and for the removal of superficial charge of the probed dielectric objects.

Boron nitride whiskers were selected for investigations. They were produced in optical furnace without catalysts on the surface of compacted samples of the initial powders. A quartz chamber was used for the process. Heating of the surface of initial powders was done in a furnace of high intensity optical energy in the flow of dried and purified nitrogen. The optical furnace involves three xenon tubes centered in the focus of three ellipsoidal reflectors.

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A diameter of the light spot is 10 mm. The calculated value of the density of the light flux energy in the focal zone is about $E = 0,7 \cdot 10^4 \text{ kW/m}^2$ that corresponds $\sim 2000 \text{ K}$ [3—5].

For comparison the initial powders of platelet-like fine-grained boron nitride (Chempur, CH070802) have been used. These powders are h-BN textured on 002 with impurity of B_2O_3 . A diameter of platelets of boron nitride is $\sim 0,6\text{--}1,0 \text{ }\mu\text{m}$ and thickness — $\sim 0,1 \text{ }\mu\text{m}$. Detail description of origin powders and experimental presented in [4].

The Auger process was initiated by creation of a core hole carried out by exposing the sample to a beam of high energy electrons 3 keV (beam current — 120, 180, 200 μA ; modulation — 1—2 eV; time constant — 3 sec; sensitivity — 50—100 μmV ; scanning time — 1000 sec; energy rate — 500 eV). The high energy electrons had sufficient energy to ionize proper levels of the lighter elements, and higher core levels of the heavier elements. In general, since the initial ionisation is non-selective and the initial hole may therefore be in various shells, there will be many possible Auger transitions for a given element — some weak, some strong in intensity. AES is based upon the measurement of the kinetic energies of the emitted electrons. Each element in a sample being studied will give rise to a characteristic spectrum of peaks at various kinetic energies.

It is known that the number of detected Auger electrons varies with topography. Topographical corrections can be made only by comparing the intensities of different elements in the same spectrum, because the effect of topography is the same for all elements. So, intensities of our investigated elements which enter into the composition of powders can vary from table data (table) of the flat surfaces of materials in solid state.

Semiquantitative calculations from differential Auger spectrum of the surface of boron powders (fig. 1) demonstrated that boron powders have $\sim 58\%$ boron, 22% carbon and 20% oxygen. The AES peaks involving valence electrons carry significant information about the chemical state of the surface. The chemical effect may appear as a simple peak shift, a change in peak shape, or both. The peak of carbon is shifted. It's mean the presence BC or Al_4C_3 on the surface. Oxygen is in adsorbed layer. Differential Auger spectrums (fig. 2) from different parts of the upper layer of the surface of boron powders have noise-like signals. However these spectrums also have shown the clear carbon and oxygen peaks. These peaks are shifted, there are changes in their shapes and their intensities. So, powders of boron and alumina have a lot of oxygen and carbon on their surfaces, which can be components of different compounds such as BC or Al_4C_3 , CO, CO_2 and so on.

Kinetic energy and AES transition of B, C, N, O, Al

N	Elements	AES transition	Kinetic energy of AES transition, eV
1	Boron	KLL	179
2	Carbon	KLL	272
3	Nitrogen	KLL	379
4	Oxygen	KLL	508
5	Aluminum	LMM	68

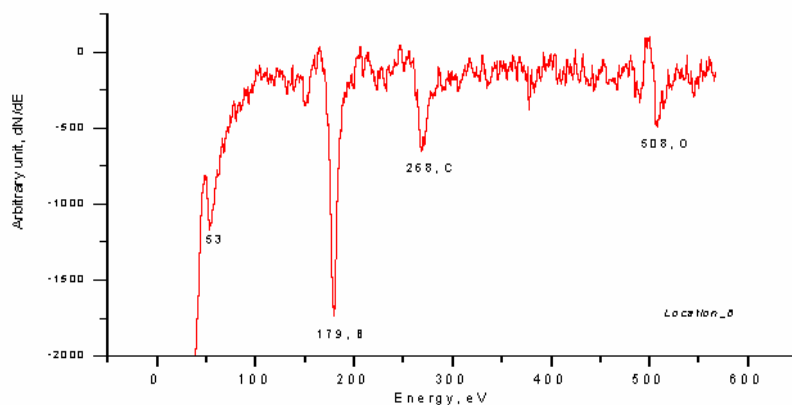


Fig. 1. Differential Auger spectrum of the upper layer of the surface of boron powders.

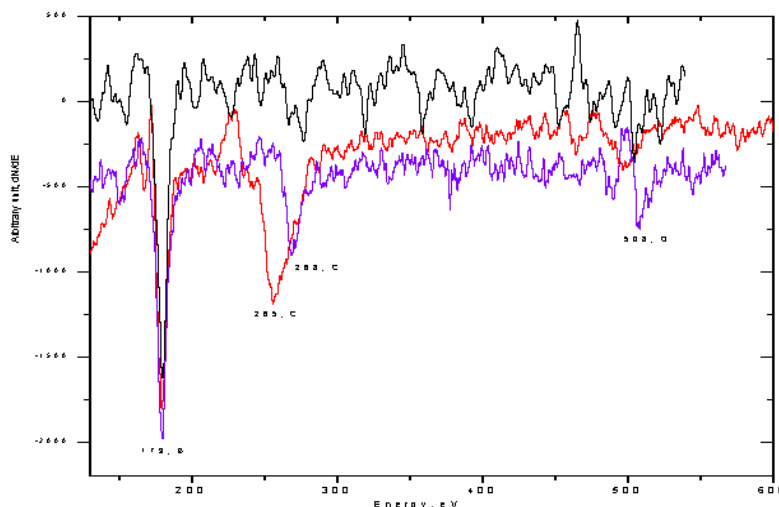


Fig. 2. Differential Auger spectra of the upper layer of the surface of boron powders in different points.

Auger-spectroscopy of the initial plate-like fine-grained powders of h-BN with the impurities of B_2O_3 has confirmed the results of X-ray diffraction analysis [1—3] about the presence of enough large amount of oxygen in initial powder of BN (fig. 3). Semiquantitative calculations from differential Auger spectrum of the surface of boron nitride powders have demonstrate that upper layer of h-BN have ~15% carbon, 20% oxygen, 31% boron, 34% nitrogen. Oxygen content is the same like in boron, but it's mean that its content is increased, because there is nitrogen in composition. Carbon content decreased. It is, perhaps, because of the method of h-BN powders production that effect also on a lack of nitrogen in their stoichiometric composition in the surface layer.

There are far less oxygen in whiskers from BN and in the pure boron. Presence of plenty amount of carbon on the surface of whiskers in comparison to initial boron nitride it is possible to explain by over activity to adsorption of hydrocarbons and CO from an atmosphere. Appearance of the divided peak of the boron in initial h-BN and in whiskers from BN in comparison to the pure boron nitride indicates the effect of nitrogen on the change of electronic boron structure.

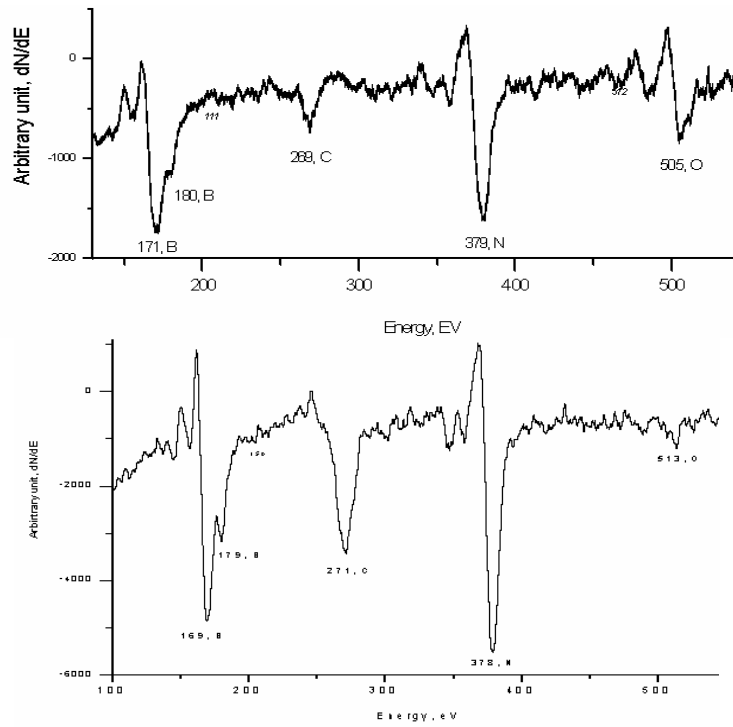


Fig. 3. Differential Auger spectrum of the upper layer of the surface of boron nitride powders (a) and nitride whiskers (b).

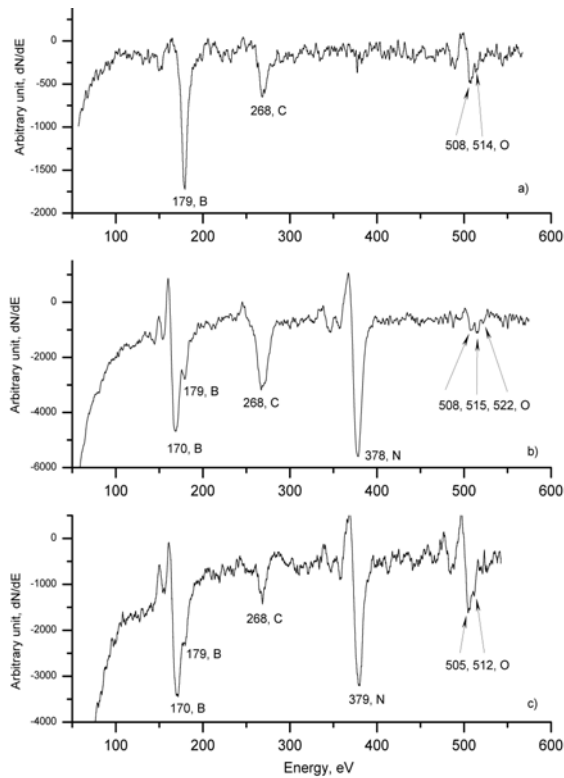


Fig. 4. Auger electron spectra: a — boron; b — whiskers from boron nitride; c — initial powder of h-BN.

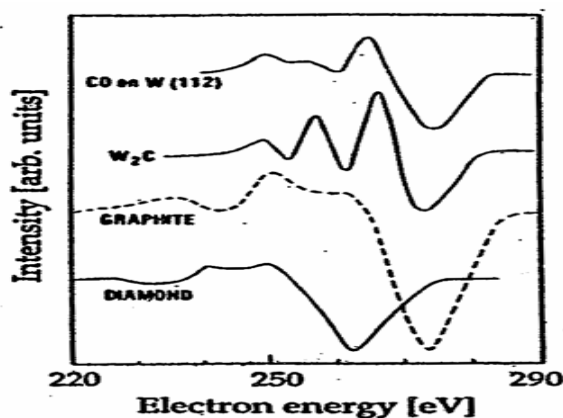


Fig. 5. Auger electron spectra of carbon from CO on W, W_2C , graphite and diamond [7].

Comparing obtained differential Auger spectrums (fig. 4) with Auger electron spectra of carbon from CO on W, W_2C , graphite and diamond [6] (fig. 5) it's possible to make some explanations of shifting, shapes changes and change of intensities of main peaks in boron and BN powders and also BN whiskers. Shifting of boron peaks in BN powders and whiskers demonstrates close-packed arrangement of these structures, which results in lowering of electronic levels like in diamond (fig. 5). Moreover, close-packed arrangement of BN whiskers structure gives rise to appearance additive peak in boron due to deeper electronic levels splitting (fig. 4, b). Smooth peaks of oxygen in BN whiskers like from CO on W (fig. 5) can give evidence of its adsorption state.

So, the Auger Electron Spectroscopy research indicates difference in electronic structures of pure boron and boron in h-BN and in BN whiskers. Presence of nitrogen results in lowering of electronic levels and appearance additive peak in boron due to deeper electronic levels splitting. Catalyst-free transformation of h-BN in optical furnace reduces oxygen content in material. We acknowledge support of STCU project No. 4133.

1. Lander J. Auger peaks in the energy spectra of secondary electrons from various materials // *Phys. Rev.* — 1953. — **91**, 1382.
2. Kai Siegbahn. Electron spectroscopy for Atoms, Molecules and Condensed Matter. Nobel lecture, 8 December, 1981. Nobel lectures. World Scientific. — 1995. — **1**, No. 26. — P. 63.
3. Harris L. A. Analysis of materials by electron-excited Auger electrons // *J. Appl. Phys.* — 1968. — **39**. — P. 1428.
4. Frolov A. A., Sartinska L. L., Koval' A. Yu., Danilenko N. A. Using of optical furnace for producing of nanostructure boron nitride. *Nanostructure materials science.* — 2008. — No. 2—4. — C. 115—120 (in Russian).
5. Sartinska L. L., Frolov A. A., Koval' A. Yu. et al. Transformation of Fine-grained Graphite Boron Nitride Induced by Concentrated Light Energy. *Materials Chemistry and Physics.* — 2008. — **109**. — P. 20—25.
6. Frolov A. A., Andrievskaya E. P., Sartinska L. L. // *Internat. conf. "Modern Materials Science: Achievements & Problems"*, Proceedings, 26—30 Sept. 2005. Kyiv, Ukraine, 174—175pp. (in Russian).
7. Czanderna A. W. "Methods of Surface Analysis", Elsevier Scientific Publishing Company, Amsterdam. — 1975. — **19**.