Regularities of electronic structure transformations in nanomaterials with decreasing their characteristic size

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Abstract. The set of nanomaterials (PbS equiaxial nanocrystals, ZnO films and whiskers, Ag films in TiAlN/Ag nanolaminate multilayer coatings) was studied in a wide range of characteristic sizes. Parameters of their electronic structure as functions of the characteristic size of the nanosystems were analyzed using X-ray photoelectron spectroscopy (XPS) and High resolution electrons energy losses spectroscopy (HREELS) methods. There were determined critical sizes manifesting transition to nanostate. Basing on dependences of donor and acceptor XPS lines size shifts, the two-stage mechanism of electronic structure transformations is proposed: the electronic structure starts to transform below $D_0$ due to surface/volume atoms ratio growth while $D_q$ is associated with preferred role of quantum effects in solids.

1. Introduction

During last decades nanomaterials are attracting attention of science and industries due to their properties sharply distinguished from traditional “bulk” materials. Specific properties of such small objects are obviously connected to growing role of free surface or interfaces with decreasing their characteristic dimensions firstly due to growth of surface energy in the system and secondly through radical transformations of electronic structure and consequently properties due to quantum phenomena. The limit cases of such systems are 2D materials possessing only surface: graphene and carbon nanotubes as well as dichalcogenides of transitional metals, MoS$_2$ or TiSe$_2$ for example.

According to ISO [1] and IUPAC [2] definitions, the “nanomaterials” term means materials with structure elements with size 100 nm and below at least in one dimension. Such round number rightfully raises doubts in its physical signification. So this research was aimed to study systematically regularities of electronic structure transformations in various materials (metals, semiconductors) with decreasing their size.

2. Materials and methods

There were studied equiaxial PbS nanocrystals, ZnO films and whiskers, Ag layers in TiAlN/Ag coatings. Characteristic dimensions of these systems determined by SEM or STEM were in range from several hundred to units of nanometers.

The electronic structure was investigated using ESCALAB MK2 (VG) spectrometer with hemispherical energy analyzer. The samples surface was cleaned by one of two standard ways: Ar$^+$ ions etching at vacuum $10^{-5}$ Pa, accelerating voltage 8 kV, ion current 20 $\mu$A either heating in vacuum $10^{-8}$ Pa to 100–120 °C. The cleaning quality was estimated by Auger electron spectroscopy (AES).
Internal levels and valence band were studied by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα source with a spot size 1×8 mm. The energy resolution (Au 4f line) was 0.6 eV, energy scanning step was 0.05 eV. The samples charge was suppressed by low energy electrons beam. Binding energies of electronic levels \( E_b \) were calculated using basic XPS equation:

\[
E_b = h\nu - E_{\text{kin}} - e\phi,
\]

where \( h\nu = 1486.6 \) eV is an excitation quantum; \( E_{\text{kin}} \) is a measured energy of electrons and \( e\phi \) is a work function assumed as a constant equal 3.81 eV for the spectrometer.

The intraband and interband transitions were studied by high resolution electrons energy losses spectroscopy (HREELS) using EMU-50 monochromatic electrons source (FWHM = 17 meV, \( E_0 = 9.5-13.5 \) eV). The analyzer was operating in high resolution mode with energy scanning step 0.025 eV. Fine structure of spectra was analyzed using UNIFIT 2007 [3] software.

3. Results and discussion

We have investigate in this work the regularities in changes of internal electronic levels positions, or electrons binding energies, densities of states (DOS) in valence bands, band gaps widths, work functions of materials as functions of characteristic size: diameters of crystals and rods, thickness of films. Earlier we reported in [4] and [5] about studies of PbS nanocrystals of various size. The size dependent transformations in electronic structure of ZnO thin films and whiskers were presented in [6]. The paper [8] was dedicated to tracing fine electronic structure changes in thin metal Ag layers in multilayer nanolaminate TiAlN/Ag coatings.

XPS lines Zn 2p\(_{3/2, 1/2}\) and O 1s recorded from ZnO nanofilms with different thicknesses are presented in figures 1(a), (b). One can see that donor and acceptor lines are moving to higher binding energies due to size shift. These movements have the same values in accuracy limits of the experiment that is about ± 0.05 eV.

![Figure 1. ZnO nanofilms. XPS lines Zn 2p\(_{3/2, 1/2}\) (a), O 1s (b), size shift vs. film thickness (e).](image)

The dependence of size shift vs. a nanostructure size is described well by empiric proportion:

\[
\Delta E(D) \sim \ln((D/D_0)^{-n/3}),
\]

where \( \Delta E(D) \) is size shift of the electronic level binding energy, eV; \( D \) is a characteristic size of the nanosystem, nm; \( n \) is number of nanodimensions: 3 for equiaxial particles, 2 for nanorods, 1 for thin films; approximation parameter \( D_0 \) corresponds to minimal size of nanocomponents when binding energies of XPS lines are located at their standard values. In relatively big nanosystems the size shifts are driven by classic mechanism due to growth of surface atoms in the system. The linear “classic” branch on figure 1(c) corresponds to this phenomenon. While characteristic size is small, we observe accelerated growth of such shifts due to quantum size effects. The second tangent line (a quantum branch) corresponds to this part of the plot. The crossing point of these right lines corresponds to the characteristic size \( D_q \) manifesting transition to nanoregion. \( D_0 \) and \( D_q \) have the following values for substances under investigation: PbS nanocrystals on neutral Si – 430 and 155 nm; PbS nanocrystals on \( n \)-doped Si – 270 and 155 nm; ZnO whiskers – 106 and 22 nm; ZnO nanofilms – 106 and 21 nm; Ag
nanolayers in TiAlN/Ag – 200 and 24 nm. It is interesting that quantum threshold in PbS is significantly bigger than IUPAC limit.

Regularities described by proportion (2) are fulfilled also for outer fully occupied levels but sifts of these levels are significantly bigger than for inner ones. Figure 2 demonstrates size shifts dependencies for the set of donor and acceptor levels in PbS nanocrystals. The analogous results on electrons levels shifts in Pd nanoparticles with various size were published in [7].

Generalizing obtained experimental data on measured energies of various levels in the nanomaterial with characteristic size \( D < D_0 \), we can plot the differences between energies of various levels in this object comparing to the bulk material reference. Such sketch is presented in figure 3.

Figure 2. Size shifts of various levels in PbS nanocrystals.

Figure 3. Increasing of binding energies of various levels in a nanomaterial comparing to a “bulk” reference.

Increasing of energies on this scheme means the shift of corresponding levels down from vacuum level. One can see that outer fully occupied levels located below valence band have maximal increase of binding energies. Shifts of deeper levels are lower due to screening effects. We observe also widening of band gap with its alignment in various directions of reciprocal space in semiconductors. Metal (Ag) demonstrates increasing intensity of Ag 5s XPS peak in consequence of localization electrons from conduction band at metal layers thinning [8]. Some input into observed growth of binding energies is provided by work function increasing. This part is enough small as can reach approximately 0.3 eV comparing to 3.0 eV shift of S 3s level.

4. Conclusions
1. There were determined common regularities of electronic structure transformations in metallic and semiconductor nanomaterials with different composition and morphology in wide ranges of characteristic dimensions from several hundred to units of nanometers.

2. As binding energies of different electronic levels are changing non-uniformly with a nanosystem size decreasing, we can conclude that such transformations are stipulated by rearrangement of the substance’s electronic system rather than by “final state” phenomena in atoms after photoelectrons emission.

3. The two-stage mechanism of electronic structure transformations with decreasing of characteristic size of nanosystem was demonstrated. The threshold values \( D_0 \) corresponding to electronic structure transformations start and \( D_1 \) manifesting beginning of strong changes driven by quantum size effects were determined for materials under investigation.
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