Study of surface chemical composition of oxide nanostructures by X-ray photoelectron spectroscopy

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Abstract. Zinc oxide and zinc stannate nanowires were synthesized by hydrothermal method. Zinc oxide nanowires were doped by iodine. The formation of multicomponent and doped oxides was studied by X-ray photoelectron spectroscopy. It was found that formation of zinc stannate from zinc oxide nanowires occurs in 1 hour. The percentage of OH-groups increases on the surface of zinc oxide nanowires as a result of doping by iodine.

1. Introduction

Currently, doping [1–4] and the fabrication of multicomponent and composite structures [5, 6] are widely used to control the properties of semiconductor metal oxide materials. ZnO (3.37 eV) and ZnSnO$_3$ (3.6 eV), well-known wide direct band-gap semiconductors, are considered as promising materials for gas sensors and catalysis [7–13]. The properties of ZnO nanostructures depend on their dimensions and morphologies [14]. Large surface-to-volume ratio and direct carrier conduction path are main advantages of 1D nanostructures over other types of nanomaterials [15]. To synthesize ZnO nanowires, various growth methods have been proposed, such as hydrothermal synthesis [16–19], physical vapour deposition [20], metal organic chemical vapour deposition [21], chemical vapour deposition [22] and thermal evaporation [23]. Among these methods, the hydrothermal synthesis is an easy and convenient method for the growth of ZnO nanowires.

While ZnO on its own captured a large interest, doping or mixing with other binary compounds brings a new level of possibilities, as the material properties can be improved for different applications by changing the cationic ratio [24].

An important task is to analyze changes in the material chemical composition during doping. X-ray photoelectron spectroscopy (XPS) allows us to study the surface chemical composition and evaluate the content of surface atoms in various bound states. XPS is widely used to determine the valence state of ions, the nature of the bond (ionic or covalent), and the acid-base properties of oxides.

In previous works [25–28], the redistribution of surface sites during the formation of the zinc ferrite and porous silicon was shown, as well as the dependence of the oxide gas-sensitive and structure properties on the surface functional composition. It was found that the oxide adsorption properties are determined by the concentration of water molecules on their surface, as well as negatively charged oxygen ions and their own defects, mainly oxygen vacancies. Determining the ratio of various oxygen forms on the surface of metal oxides is of considerable interest for gas sensors.
The aim of this work was to analyze the redistribution of electron density on the surface of zinc oxide nanowires during the formation of the zinc stannate, as well as during doping with iodine, by X-ray photoelectron spectroscopy.

2. Experiment
The initial materials were layers consisting of faceted ZnO nanowires synthesized by a low-temperature (85 °C) hydrothermal method using a seed layer formed by ultrasonic spray pyrolysis [29]. Synthesis was performed in an aqueous-alcohol solution of potassium stannate trihydrate and urea in an autoclave at 170 °C with a variation in the synthesis time (0.5 h – 3 h) and the concentration of precursors KSnO₃·3H₂O (20 mM and 10 mM) and (NH₂)₂CO (0.25 M and 0.125 M).

The synthesis of doped zinc oxide nanowires was carried out by a low-temperature hydrothermal method with the addition of sodium iodide (10 mM) to the growth solution. Prepared samples were annealed in a muffle furnace (350 °C) to remove organic pollutants from the layer surface.

Experimental spectra of synthesized samples were obtained using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al X-ray source of 1486.6 eV. Survey spectra that allow us to determine all the elements in the samples were obtained in the range of binding energies from 0 to 1350 eV. The spectra of individual elements were taken in order to more accurately determine the position of the peaks. Deconvolution (decomposition) of oxygen core levels spectra was performed.

3. Results and discussion

3.1. Study of zinc stannate samples
The spectra of the initial ZnO nanowires used for synthesis of zinc stannate samples were studied. As can be seen from the survey spectrum (figure 1), zinc, oxygen and carbon are observed on the surface of the nanowires. The positions of the peaks on the spectrum of Zn 2p level (1022.3 eV and 1045.3 eV) correspond to Zn²⁺ charged state [30]. It was found that on the surface of zinc oxide nanowires two bound states of oxygen are observed: O²⁻ (530.8 eV), which is part of the zinc oxide crystal lattice, and oxygen of surface hydroxyl groups (532.8 eV) [26].

Analysis of the spectra of zinc stannate samples synthesized for 30 min showed that the substitution process was not occurred. Peaks of zinc, tin, oxygen, and carbon are observed on the survey spectrum (figure 2). The positions of the peaks on the spectrum of Zn 2p level remain unchanged compared to the initial nanowires. There is a shift of the peaks of oxygen in the form of O²⁻ and OH-groups towards lower binding energies by 0.1 eV and 0.3 eV, respectively. The peaks on the spectrum of Sn 3d level (495.6 eV and 487.2 eV), shown in Figure 2, correspond to Sn⁴⁺. In [31], when considering the formation of zinc stannate, the presence of SnO derivatives in Sn 3d₅/₂ spectrum is associated with the formation of oxygen vacancies in the crystal lattice and, consequently, a decrease in the surface oxygen concentration. In our case, this may confirm incomplete embedding of tin in the crystal structure of zinc oxide nanowires.

The survey spectrum of zinc stannate samples synthesized for 1 hour also contains peaks of zinc, tin, oxygen, and carbon (figure 3). The successful substitution of zinc atoms in nanowires during hydrothermal synthesis for 1 hour can be confirmed by shifts in the binding energy of zinc and oxygen. The spectrum of zinc core level shows a shift of peaks by 0.3 eV (Zn 2p₁/₂) and 0.4 eV (Zn 2p₃/₂) towards lower binding energies compared to the initial zinc oxide nanowires. There is a shift of the oxygen peaks by 0.4 eV (O²⁻) and 0.8 eV (OH-groups) towards lower binding energies. The binding energy of the peaks on the spectrum of Sn 3d level (486.6 eV and 495 eV), shown in figure 3, corresponds to Sn⁴⁺ [31], the position of the peaks is shifted by 0.6 eV towards lower binding energies compared to the sample synthesized for 30 minutes.
Figure 1. Survey spectrum of zinc oxide nanowires.

Figure 2. Survey spectrum of Zn-Sn-O sample synthesized for 30 min (inset: spectrum of tin core level).

Analysis of the zinc stannate spectra synthesized for 3 hours indicates the dissolution of oxides and destruction of the structure of nanowires. The zinc content on the surface is 1.98 %, and there are no peaks corresponding to tin on the spectrum. Also, in contrast to the other samples, the peak from the silicon substrate (27.47 %) is clearly visible, as well as nitrogen (2.05 %), formed due to the decomposition of urea.

Thus, the substitution of zinc atoms and the formation of the zinc stannate occurs during 1 hour synthesis, with a shorter synthesis time, the substitution process practically did not occur, and during synthesis for 3 hours, the oxides are dissolved and the structure of the nanowires is destroyed [32].

Figure 3. Survey spectrum of Zn-Sn-O sample synthesized for 1 hour (inset: spectrum of tin core level).

Figure 4. Survey spectrum of Zn-Sn-O sample synthesized for 3 hours.

The mechanism of formation of zinc stannate nanowires is proposed in [33]. Firstly, K₂SnO₃ reacted with ZnO nanowires and formed ZnSnO₃/ZnO composite nanowires and then they underwent an Ostwald ripening process forming ZnSnO₃ nanowires. It was shown by energy dispersive spectroscopy that most ZnO nanowires are translated into ZnSnO₃ nanowires, and little is dissolved into the solution.
3.2. Study of iodine doped zinc oxide samples

On the survey spectra of doped and pure zinc oxide nanowires, shown in the insets in figures 5 and 6, peaks of zinc, oxygen and carbon are observed. It should be noted that there are no peaks of iodine, which is due to its removal during annealing.

![Figure 5](image-url). Survey spectrum of undoped zinc oxide nanowires (inset: spectrum of oxygen core level).

![Figure 6](image-url). Survey spectrum of zinc oxide nanowires doped with iodine (inset: spectrum of oxygen core level).

The inserts in figures 5 and 6 show the spectra of core oxygen levels for doped and pure zinc oxide nanowires. The O1s peak (534 eV) shown in figure 5 corresponds to the binding energy of oxygen of adsorbed C-O and H2O groups. The spectrum of the oxygen core level of the iodine-doped samples shown in figure 6 shows peaks corresponding to the oxygen of OH groups (531.8 eV) and oxygen of the adsorbed H2O/C-O groups (533.5 eV). There is also a shift of the peak corresponding to H2O/C-O groups by 0.5 eV towards lower binding energies compared to pure sample.

Thus, the effect of iodine doping on the binding energy of oxygen in samples of zinc oxide nanowires was established. It was found that oxygen appears on the surface of iodine-doped samples in the form of OH groups (37%) as a result of annealing [34]. This effect can be used to reduce the influence of humidity on the characteristics of gas sensors based on zinc oxide nanowires.

4. Conclusion

This work shows the possibility of using X-ray photoelectron spectroscopy to estimate the formation of zinc stannate nanowires when replacing zinc atoms with tin, as well as to analyze changes in surface composition when doping zinc oxide nanowires with iodine.

When studying the process of hydrothermal synthesis of zinc oxide nanowires, it was found that the optimal synthesis time is 1 hour, when tin atoms are embedded in the crystal structure of zinc oxide nanowires, but the structure is not yet destroyed. The obtained samples of zinc stannate nanowires may be of interest for the development of gas sensors and photocatalysts with enhanced characteristics.

It was found that when zinc oxide nanowires are doped with iodine, the atoms of the impurity are removed during annealing with an increase in the proportion of surface hydroxyl groups. The developed samples may be of interest for the development of gas sensors that are resistant to the influence of water vapors.

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