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Investigation of the transformation of the surface architecture of zinc oxide powders synthesized by grinding during etching with argon ions

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Abstract

Purpose: The aim of the work is to study by X-ray photoelectron spectroscopy the transformation of the surface architecture of zinc oxide powders, previously obtained by mechanical milling, during their etching with argon ions.

Experimental: The etching was carried out in two steps of 30 s duration each at a current of 1 μA. It was found that on the surface of initial powders 45 % of zinc is a part of the crystal lattice of ZnO, and the remaining 55 % exist in the form of hydroxide.

Conclusions: The first etching step reduced the fraction of hydroxyl groups on the surface to 1 per 5 zinc cations in the ZnO lattice, and further etching showed the impossibility of deeper purification of the sample from OH-groups. In contrast, the carbon atoms almost completely left the powder surface after the end of the second etching step.

Keywords: Zinc oxide, Etching, X-ray photoelectron spectroscopy, Surface

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1. Introduction

Semiconducting metal oxides are materials with applications in gas sensing, catalysis and photocatalysis, transparent conductive coatings, etc. Often the useful properties of this group of materials are determined by their surface condition [1–3]. For example, the sensitivity of tin dioxide to ethanol can be regulated by the ratio of surface Lewisian and Brönsted centers [4]. The efficiency of photocatalysts depends both on the rate of surface recombination of photogenerated charge carriers and on the ability of the semiconductor surface to adsorb water, carbon dioxide, and oxygen particles. In this regard, the study of surface architecture is of great interest. However, the peculiarity of this group of materials is the intensive interaction of the environment with their surface, which complicates the research process without additional sample preparation. In X-ray photoelectron spectroscopy (XPS), Ion etching is usually used as a pre-treatment. The aim of the present work is to investigate the transformation of the surface architecture of zinc oxide by XPS method during argon ion etching. The object of the study was zinc oxide powder, obtained on the basis of commercial (LLC “Vekton”, St. Petersburg, Russia) by grinding in an attritor for 5 h in isopropyl alcohol (grinding process parameters: grinding media material – zirconium dioxide; grinding media diameter – 3 mm; grinding media mass ratio to ZnO mass – 18:1; grinding speed - 400 rpm) [5].

2. Experimental

The surface structure of the samples was investigated using a Scanning electron microscope VEGA 3 SBH (TESCAN, Czech Republic) with a reflected electron detector. Crystal structure was determined by Powder diffraction on an automatic X-ray diffractometer DRON-3M (CJSC “Burevestnik”, Russia) with Co*K*α-radiation in the range of 35°< 2θ < 85° X-ray photoelectron spectra were measured under ultrahigh vacuum conditions (10-7 Pa) using an Escalab 250Xi spectrometer (Thermo Fisher Scientific Inc., USA) with photon energy Al-*K*α = 1,486 eV. The energy scale of the spectrometer was calibrated using the sputter-cleaned Au surface as a reference, so that the binding energy of the Au 4*f*7/2 peak was set at 84.0 eV. The etching of the sample surface with argon Ar+ ions took place at a current of 1 μA for 30 s (mode 1) and 60 s (mode 2), respectively.

3. Results and discussion

Fig. 1 shows the diffractogram of the initial sample and a micrograph of its surface.

It can be seen that the ZnO powder is represented by crystallites with a large size variation in the range of 50 nm – 1 μm. Analysis of the diffractogram shows the presence of reflexes (100), (002), (101), (102), (110), (103), (200), (112) and (201) corresponding to the crystal structure of wurtzite [6], other phases were found in the sample. A joint calculation of the sizes of the coherent scattering regions [7] and microstrains of the sample showed that the average crystallite size is ~ 21 nm at strains of ~ 0.575 %, indicating that the material is in a sufficiently stressed state, and the crystallites visualized by scanning electron microscopy are organized from a large number of single crystals.

Fig. 2 presents an overview X-ray photoelectron spectrum of the original zinc oxide sample, indicating the presence of elements corresponding both to the chemical composition of the material (Zn and O) and resulting from contamination of its surface with organic components (C).Low-energy components of the spectrum corresponding to the Valence band (Zn3*d*, Zn3*p*, Zn3*s*), high-energy components of core levels (Zn2*p*3/2 and Zn2*p*1/2), and Auger peaks such as the Zn LMM are reliably identified.

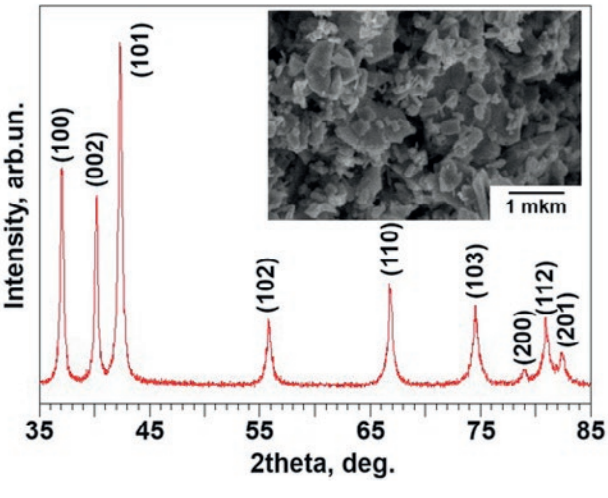


Fig. 1. X-ray diffraction pattern of a sample of zinc oxide powder and micrograph of its surface

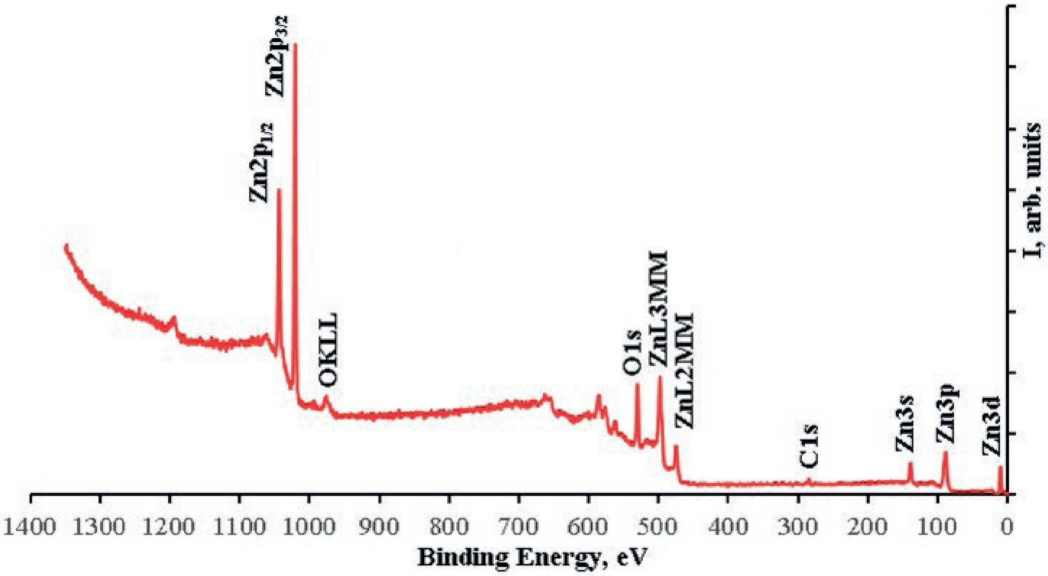


Fig. 2. Survey X-ray photoelectron spectrum of zinc oxide before argon ion etching

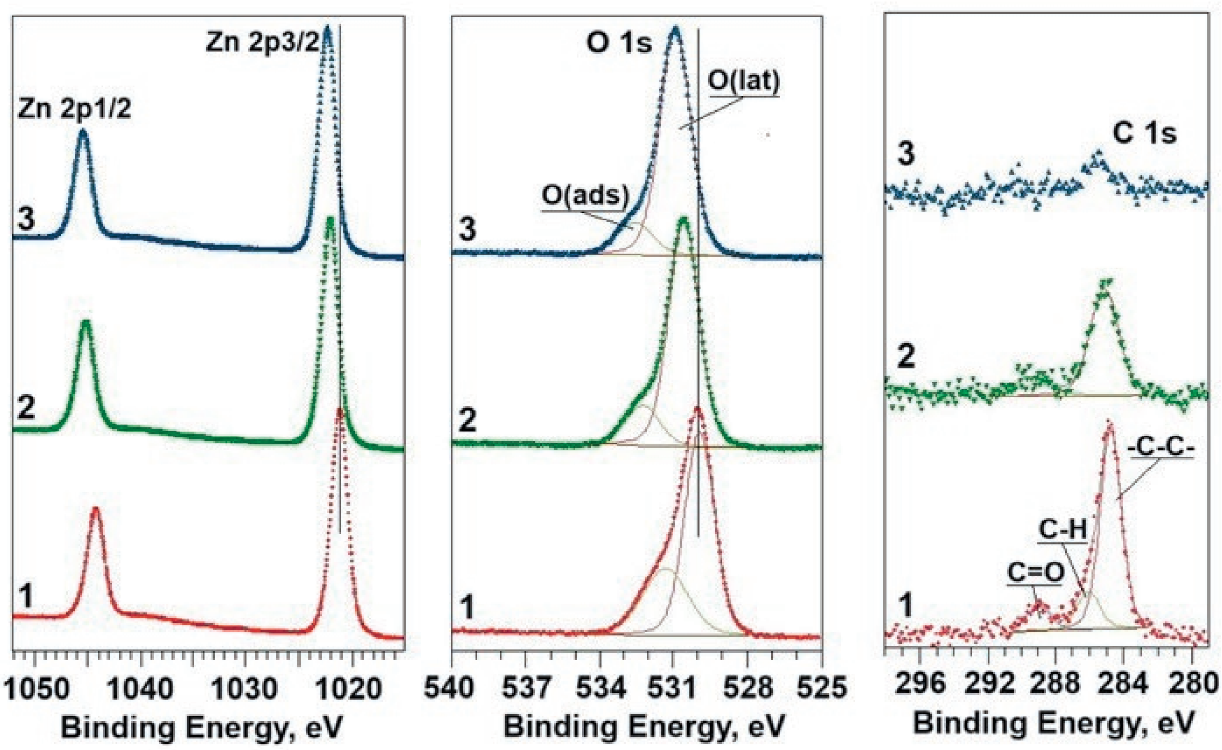
The individual components of the X-ray photoelectron spectra of the original and the sample treated in both modes are shown in Fig. 3, and the Table 1 gives the chemical composition. Consider the characteristics of the initial powder (*curve 1* of Fig. 3). The Zn2*p* spectrum is represented by a duplet with *BE* binding energies of 1021.08 eV (Zn2*p*3/2) and 1044.50 eV (Zn2*p*1/2). We will use Zn2*p*3/2 for further analysis. This curve has a symmetrical appearance and, as a rule, the value of binding energy allows us to attribute it to the zinc cation Zn^{2+} in the crystal lattice ZnO. Nevertheless, practice shows that at the same *BE* values it is possible to identify the zinc cation in the $Zn(OH)_2$ hydroxide molecule, so it is not possible to reliably distinguish between zinc oxide and hydroxide by the XPS method [8]. The spectrum of O1*s*, on the contrary, is asymmetric and two shapes can be distinguished in it:O(*lat*) with a binding energy of 529.9 eV (corresponding to the oxygen anion O^{2-} in the ZnO crystal lattice) and O(*ads*) with a binding energy of 531.30 eV (corresponding to oxygen in molecules adsorbed on the surface: OH-groups, CO_2, etc.) [9].The C1*s* spectrum is also asymmetric and can be decomposed into three components with Binding energies of 285.00, 286.20, and 289.00 eV: the first corresponds to -C-C- bonds in the graphite structure (which is the Control point of the spectrum); the second corresponds to surface C-H groups; and the third corresponds to C=O groups formed on the powder surface due to chemical adsorption of atmospheric carbon dioxide [10].

Since the atomic fractions of [Zn] and [O(*lat*)] in the original sample are not equal to each other, then, based on the ratio in [Zn(*lat*)] = [O(*lat*)] in zinc oxide, it can be assumed that part of the zinc atoms in the sample does not occupy a position in the crystal lattice, but is probably in the hydroxylated state in the form of $Zn(OH)_2$. The calculation shows that only 45% of zinc cations on the unetchable surface can be attributed to ZnO – Table 2.

Let us consider the processes occurring on the sample surface during its etching by argon ions. The Zn(*lat*)/Zn ratio increases in the first etching step from 0.45 to 0.55, with the second step no longer having any effect on the fraction of zinc atoms included in the oxide. Apparently,

Table 1. Chemical composition of the surface according to XPS data

Sample	Zn, at.%	O, at.%	C, at.%	O(*lat*), at.%	O(*ads*), at.%
0	54.00	36.08	9.92	24.08	12.00
1	57.68	38.09	4.23	31.66	6.43
2	60.08	37.44	2.49	32.26	5.18



a b c

Fig. 3. XPS spectra of Zn2*p* (a), O1*s* (b) and C1*s* (c) (*curve 1* – initial sample; *curve 2* – etching in mode 1; *curve 3* – etching in mode 2)

Table 2. Ratios of surface forms according to XPS data

Sample	Zn(*lat*)/Zn	Zn(*lat*)/O(*ads*)	Zn(*lat*)/C	Zn(*lat*)/(O(*ads*)+C)	*BE* Zn2*p*3/2, eV
0	0.45	2.03	2.45	1.11	1021.08
1	0.55	4.93	7.50	2.98	1022.08
2	0.54	6.26	13.03	4.23	1022.33

this is primarily due to the desorption of surface hydroxyl groups, which is completed already at the first etching stage, and the second stage practically does not affect this process. The Zn(*lat*)/O(*ads*) ratio shows that, if on the initial sample on average 1 oxygen atom in the composition of adsorbed particles corresponded to 2 Zn^{2+} cations in the ZnO lattice, then after the first etching step it was already five, and after the second – a little more than six. Together with the fact that the values of Zn(*lat*)/Zn after the first and second etching steps are almost the same, this indicates that not all O(*ads*) particles are bound directly to zinc cations in the form of hydroxyl groups. There are other surface forms which, judging from the chemical composition of the sample, contain carbon.

Consider the transformation of the Zn(*lat*)/C ratio during the etching process. In the original sample, on average, one carbon atom accounts for 2.45 zinc cations; the first etching step increases this number to 7.5 and the second to ~13.This shows that during two etching steps it is possible to remove almost completely carbon from the sample surface both in the form of residues of organic molecules and carbonate-like forms and in the form of graphite. Also the Table 2 shows the ratio Zn(*lat*)/(O(*ads*)+C), which characterizes the number of adsorbed particles per Zn^{2+} cation in the ZnO lattice. Before etching, Zn(*lat*) ≈ (O(*ads*)+C), indicating that the powder surface is heavily contaminated. The first treatment step with argon ions reduced the amount of impurities on the surface to one particle per three

Zn^{2+} cations, while the second step reduced the amount of impurities to 4.23.

The increase in the binding energy of Zn2*p*3/2 during etching should also be noted (Table. 2). This process is accompanied by an increase in the binding energy of O1*s* by about the same values, while the binding energy of C1*s* does not change. This indicates a change in the effective oxidation degree of the zinc cation and a change in the ratio of Zn and O ions occupying regular positions in the nodes of the oxide crystal lattice. This indicates the removal process from the Zn(*lat*) surface and the formation of vacancies in the zinc V_{Zn} sublattice [11]. In connection with this process, the argon ion beam energy corresponding to a current of 1 µA was chosen: at a higher value, not only the adsorbed particles are discharged, but also the surface structure of crystallites is destroyed; a lower value does not allow effective removal of surface hydroxyl groups. Processing times of 30 and 60 s were chosen as typical times, clearly demonstrating the physicochemical processes occurring on the surface.

4. Conclusions

The transformation of surface groups of zinc oxide powders, previously obtained by mechanical milling, during etching with argon ions has been studied by the XPS method. The powders had a wurtzite crystal structure with an average size of coherent scattering regions ~ 20 nm. It was found that on the surface of the original sample only 45 % of zinc atoms were included in the crystal lattice of ZnO, the rest existed in the form of hydroxide. The first etching step increased the proportion of zinc atoms in the oxide lattice to 55 %, but the second step did not change this ratio. Detailed analysis showed that for powder there is a limiting ratio of one hydroxyl group per 5–6 zinc cations in the crystal lattice, and deeper purification from OH-groups by increasing the etching time is difficult. On the contrary, carbon atoms (existing both in the form of graphite and in the composition of organic molecules) and oxygen particles included in the residues of organic groups in combination with carbon are almost completely removed from the surface: after two etching steps, there was only 1 C atom per 13 zinc cations.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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