Synthesis and Characterization of Tin(IV) Oxide Obtained by Chemical Vapor Deposition Method

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Abstract
The effect of precursors on the characteristics of tin oxide obtained by chemical vapor deposition (CVD) method was investigated. The synthesis of nanosized tin(IV) oxide was carried out with the use of two different precursors: tin(II) oxalate obtained using tin chloride(II) and oxalic acid; tin(II) oxalate obtained using tin chloride(II); and ammonium oxalate. The synthesized tin(IV) oxide samples were studied by electron microscopy, X-ray diffraction and optical spectra. The lattice parameters of tin(IV) oxide samples were defined, the bandgap of samples were calculated.

Keywords: Tin(IV) oxide, Tin(II) oxalate, CVD method, X-ray diffraction, Bandgap

Background
Metal oxides are the basis of modern diverse smart and functional materials and devices because physical and chemical properties of these oxides can be tuned.

Functional properties of metal oxides depends on many chemical and structural characteristics such as chemical composition, various kinds of deficiencies, morphology, particle size, surface-to-volume ratio, etc. By varying either of these characteristics, the electrical, optical, magnetic, and chemical properties can be regulated, giving the possibility of fabricating smart devices. Such unique characteristics make oxides the most diverse class of materials, with properties covering almost all aspects of materials science and physics in areas such as semiconductivity, superconductivity, ferroelectricity, and magnetism [1–4].

It is known that the reversible chemisorption of reactive gases on the surface of the oxide semiconductor is accompanied by reversible changes in conductivity. This makes semiconductors the most attractive materials for the manufacture of photodetectors electronic converters based on them. Conductivity of semiconducting oxides caused by deviations from stoichiometry and also defects such as interstitial cation or anion vacancies. Depending on type of determinate impurity (electron acceptor or electron donor) and conduction type (n- or p-type), the resistance of the sensitive layer of the sensor is increased or decreased. Oxidizing gases or electron acceptors such as NO₂ produce a decrease in the conductance of n-type semiconducting materials (i.e., electrons are the major carriers, such as ZnO, SnO₂, In₂O₃) and an increase in the conductance of p-type semiconducting materials (i.e., holes are the major carriers, such as CuO); reducing gases or electron donors such as H₂S, CO, H₂ and water vapor act in a reverse manner [5, 6].

Metal oxides SnO₂, ZnO, In₂O₃, and CdO are wide-bandgap n-type semiconductors and the most frequently used as a sensitive material for the gas sensors. They belong to a class of transparent conductive oxides due to a number of unique functional properties, of which the most important are the electrical conductivity, the visibility in a wide spectral range, and high reactivity of the surface [7, 8].

Metal oxide-based gas sensors are widely used due to its high sensitivity to harmful for human health or hazardous gases (such as CO, NO, NO₂, H₂ etc.) in conjunction with easy fabrication methods and low manufacturing costs. Tin(II) oxide is the promising sensor material among a wide set of semiconducting metal oxides [9–11]. It is known that nanocrystalline materials characterized the largest values of sensor response due to high surface-to-volume ratio and, therefore, higher absorption capacity [6].

To obtain nanocrystalline, SnO₂ uses different methods: sol-gel method [12], chemical vapor deposition [13],
hydrothermal [14], thermal evaporation [15]. Among a large number of approach methods of chemical vapor deposition (CVD), which is implemented of vapor-liquid-solid mechanism (VLS), deserves special attention. This method allows obtaining particles of very diverse morphology with a high degree of crystallinity [1, 16, 17]. In the articles [18–20], SnO$_2$ nanowires and nanoribbons (doped and pure) have been successfully synthesized using such precursors as Sn and SnO$_2$ powders. Also known to use other precursors for synthesis of SnO$_2$ nanowires are SnO powder, and a mixture of carbon powder and SnO$_2$ powder. However, from our point of view, it is interesting to research also other precursors, as has long been known that precursors have a significant impact on the final physicochemical properties of materials. In this paper, we investigate the effect of new precursor SnC$_2$O$_4$ (obtained from different reagents) on the characteristics of tin oxide obtained by CVD.

### Methods of synthesis

Tin(II) oxalate was obtained by sol-gel method from different precursors: in the first case tin chloride(II) and oxalic acid; in the second case – tin chloride(II) and ammonium oxalate. In both cases, hot oxalic acid (ammonium oxalate) solution was added to hot aqueous solutions of SnCl$_2$·2H$_2$O in a molar ratio of 1:1.5, respectively. The resulting solution was cooled. The precipitate formed was filtered, washed with distilled water while ions Cl$^-$ detected by reaction with AgNO$_3$ and dried in an oven at 378 K for 2 h. Thus, there were two obtained samples of tin oxalate: sample A – using oxalic acid and sample B – using ammonium oxalate (Table 1).

For tin(IV) oxide weighed tin(II) oxalate was loaded in an alumina boat, which was placed at the center of a quartz tube in a horizontal-type furnace. The furnace was heated to 1123, 1223, and 1323 K and kept in an inert atmosphere for 1 h. The inert atmosphere was implemented by nitrogen with 0.005 % oxygen impurity. The overall reaction of tin(II) oxalate decomposition:

$$\text{SnC}_2\text{O}_4 \rightarrow \text{SnO}_2 + 2\text{CO}$$

Obtained SnO$_2$ samples (Table 2) were analyzed by electron microscopy, X-ray diffraction and spectrophotometrically.

### Results and Discussion

#### Electron Microscopy

The particle sizes of the obtained samples were determined with a transmission electron microscope TEM 100-01.

Figure 1 displays TEM images of the obtained tin(II) oxalate samples. The figure shows that sample A has a wire-like form, while particles of sample B have an unspecified form and are more porous. These differences in morphology are caused by various pH of tin(II) oxalate precipitation. Presented appropriate selected area electron diffraction (SAED) patterns of the samples shows that the particles are polycrystalline.

Figures 2, 3, and 4 show high-resolution TEM images of the synthesized samples of SnO$_2$, in which the individual crystal sizes are in the range of 40–200 nm. The TEM images also show that the particles of the SnO$_2$ samples obtained from sample A are more agglomerated, characterized by smaller size (average size is 60–80 nm), and have are more uncertain form. While the particle size of the SnO$_2$ samples obtained from sample B reached 200 nm. Powders represented as individual particles that have a pronounced hexagonal shape, which is especially distinct for sample 6. Thus, to obtain better crystals of tin(IV), oxide preferably used ammonium oxalate as a precursor of tin(II) oxalate.

Presented SAED patterns of the samples demonstrate single-crystalline spots. And, it will allow obtaining sensitive materials with high values of sensor response. Since the crystal quality does not seem to be good, the development of synthesis technique for improving the quality of the single crystals is therefore necessary.

#### X-ray Diffraction

XRD (X-ray diffraction) measurements were conducted using X-ray diffractometer Ultima IV Rigaku with CuKα radiation.

Figure 5 shows XRD spectra of the obtained samples of tin(II) oxalate which fit to the pure tin(II) oxalate (according card no. 01-072-9689, PDF-2/Release 2011 RD, ICDD). Diffraction patterns have different intensities of the main peaks. These differences are due to different morphology of samples A and B.

| Table 1 Obtained SnC$_2$O$_4$ samples |
|----------------------------------------|
| Sample | Precursors | Treatment temperature, K |
|--------|------------|--------------------------|
| Sample A | Tin chloride(II); oxalic acid | 378 |
| Sample B | Tin chloride(II); ammonium oxalate | 378 |

| Table 2 Obtained SnO$_2$ samples |
|----------------------------------|
| Sample | Precursors | Treatment temperature, K |
|--------|------------|--------------------------|
| Sample 1 | Sample A | 1123 |
| Sample 2 | Sample A | 1223 |
| Sample 3 | Sample A | 1323 |
| Sample 4 | Sample B | 1123 |
| Sample 5 | Sample B | 1223 |
| Sample 6 | Sample B | 1323 |
Fig. 1 TEM images of sample A (1) and sample B (2) and corresponding SAED patterns.

Fig. 2 TEM images of sample 1 (1) and sample 4 (2) and corresponding SAED patterns.

Fig. 3 TEM images of sample 2 (1) and sample 5 (2) and corresponding SAED patterns.
Fig. 4 TEM images of sample 3 (1) and sample 6 (2) and corresponding SAED patterns

Fig. 5 The XRD patterns of SnC$_2$O$_4$

Table 3 The structural parameters of SnC$_2$O$_4$ samples

| Sample | hkl | $2\theta$, deg. | Glancing angle $d$, nm | Crystallite size, nm | Lattice constant, nm |
|--------|-----|-----------------|------------------------|----------------------|----------------------|
|        |     |                 |                        |                      | $a$                  |
| Sample A | 110 | 19.26           | 0.46058                | 45.7                 | 1.035                |
|         | −202| 22.30           | 0.39671                |                      | 0.549                |
|         | −112| 27.51           | 0.32391                |                      | 0.821                |
|         | −313| 37.71           | 0.23834                |                      |                      |
|         | −131| 51.11           | 0.17858                |                      |                      |
| Sample B | 110 | 19.29           | 0.45074                | 67.9                 | 1.033                |
|         | −202| 22.44           | 0.39596                |                      | 0.548                |
|         | −112| 27.57           | 0.32330                |                      | 0.820                |
|         | −313| 37.06           | 0.24239                |                      |                      |
|         | −131| 51.12           | 0.17855                |                      |                      |
Fig. 6 The XRD patterns of $\text{SnO}_2$: 1 – sample 1; 2 – sample 2; 3 – sample 3

Fig. 7 The XRD patterns of $\text{SnO}_2$: 1 – sample 4; 2 – sample 5; 3 – sample 6
The average crystallite sizes of the obtained samples of SnC₂O₄ are 45.7 and 67.9 nm, respectively. The structural parameters (crystal grain size, lattice constants) of SnC₂O₄ samples presented in Table 3.

X-ray diffraction of the samples, which were obtained by decomposition of tin(II) oxalate at different temperatures, shows that pure SnO₂ is formed in all cases besides powder obtained from sample A at temperature 850 K. Thus, 950 K is the minimum temperature for tin(IV) oxide synthesis from oxalate (Figs. 6, 7). Most distinct peaks on XRD patterns correspond to (110), (101) and (211) crystal faces (according card no. 1000062, USER (COD)). All diffraction lines can be indexed to the tetragonal rutile phase. For the samples, which were obtained from sample A the most distinct peak is (110), while for the samples, which were obtained from sample B, peak (101), that indicates the beginning growth of 1D nanostructures [21].

The comparison of the defined lattice constants for the samples with their standard values ($a = 0.476$, $p = 0.318$) shows that the crystalline lattice of SnO₂ in samples was not deformed.

Table 4 The structural parameters of SnO₂ samples

| Sample | hkl | $2\theta$, deg. | Glancing angle $d$, nm | Crystallite size, nm | Lattice constant, nm |
|--------|-----|-----------------|------------------------|---------------------|---------------------|
|        |     |                 | $\phi$                 |                     | $a$                 | $c$                 |
| Sample 1 | 110 | 26.59           | 0.33494                | 45.3                | 0.474               | 0.319               |
|         | 101 | 33.90           | 0.26419                |                     |                     |                     |
|         | 211 | 51.79           | 0.17637                |                     |                     |                     |
| Sample 2 | 110 | 26.59           | 0.33490                | 64.7                | 0.474               | 0.319               |
|         | 101 | 33.90           | 0.26419                |                     |                     |                     |
|         | 211 | 51.81           | 0.17632                |                     |                     |                     |
| Sample 3 | 110 | 26.59           | 0.33502                | 80.7                | 0.474               | 0.319               |
|         | 101 | 33.90           | 0.26425                |                     |                     |                     |
|         | 211 | 51.79           | 0.17637                |                     |                     |                     |
| Sample 4 | 110 | 26.64           | 0.33437                | 57.8                | 0.474               | 0.319               |
|         | 101 | 33.94           | 0.26391                |                     |                     |                     |
|         | 211 | 51.85           | 0.17620                |                     |                     |                     |
| Sample 5 | 110 | 26.67           | 0.33402                | 73.6                | 0.474               | 0.319               |
|         | 101 | 33.94           | 0.26393                |                     |                     |                     |
|         | 211 | 51.84           | 0.17621                |                     |                     |                     |
| Sample 6 | 110 | 26.60           | 0.33490                | 74.3                | 0.474               | 0.319               |
|         | 101 | 33.91           | 0.26415                |                     |                     |                     |
|         | 211 | 51.78           | 0.17641                |                     |                     |                     |

Fig. 8 Dependences of the absorption coefficient on wavelength
The structural parameters of SnO$_2$ samples are presented in Table 4. According to the data presented in the table, with increasing temperature of heat treatment, the average crystallite size (and therefore particle size) increases. This is caused by the process of sintering particles.

**Optical Spectra**

Bandgap of SnO$_2$ samples was determined by measuring the optical absorption of SnO$_2$ films. Measurements were performed on a spectrophotometer UV-5800 PC. 

Figure 8 shows dependences of the absorption coefficient on wavelength for samples 3 and 6. Limit wavelength values determined from the obtained diagrams are 328 and 336 nm for samples 3 and 6, respectively. The bandgap was calculated by the formula:

$$\Delta E = \frac{h \cdot c}{\lambda_{\text{opt}}},$$

where $h$ is the Planck constant and $c$ is the speed of light.

The absorption coefficient $a$ can also be expressed as:

$$(ahv)^2 \propto (hv-\Delta E),$$

where $hv$ is the photon energy. Plots of $(ahv)^2$ versus $hv$ can be derived from the absorption data in Fig. 8 as shown in the inset.

The values of the bandgap for samples 3 and 6 are different and equal to 3.78 and 3.69 eV, respectively. These data show that the precursor affects not only the morphology of particles SnO$_2$ samples, but also their electrical properties.

**Conclusions**

Characteristics of tin(IV) oxide highly depend on precursors used for the synthesis of tin(II) oxide, which is confirmed by studies of electron microscopy, X-ray analysis, and optical spectra. The individual crystal sizes of synthesized SnO$_2$ samples are in the range of 40–200 nm. The crystal lattice of SnO$_2$ samples had shown no significant singular deformations. It is typical for the beginning growth of 1D nanostructures for the samples, which were obtained using tin chloride(II) and ammonium oxalate.

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**Authors’ contributions**

SN carried out the experimental studies, analysis and interpretation of data, drafted the manuscript. VL carried out the experimental studies and analysis and interpretation of data. TD carried out the coordination of experimental research, analysis and interpretation of data, drafted the manuscript. IA had given final approval of the version of the manuscript to be published. All authors read and approved the final manuscript.

**Competing interests**

The authors declare that they have no competing interests.

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