Effects of plasma treatment parameters on the adsorption properties of tin dioxide-based nanomaterials

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Abstract. We have studied the effect of nitrogen plasma exposure on the adsorption properties of SnO$_2$-based nanomaterials synthesized by the sol-gel method. We have established the correlation between the adsorption properties and plasma treatment parameters. The scanning electron microscopy has confirmed integrity violation of the original structure of nanomaterials and an increase in their specific surface area with high-power plasma source.

1. Introduction

The use of nanomaterials having a developed hierarchical structure with a fractal type of spatial organization is promising in the development of adsorption-type gas sensors. Due to high specific surface area and a pore network system, such materials provide high sensitivity to the analyzed gases. Despite numerous fundamental and applied studies [1, 2], the problem of designing a simple and cheap technique to manufacture nanomaterials with high selectivity, due to similar changes in the material conductivity caused by the adsorption of particles of the analyzed different type gases, is still urgent [3].

One of the possible ways to modify the adsorption properties of sensitive nanomaterials is plasma treatment [4-6]. In this work, we investigate the effect of various nitrogen plasma powers on the adsorption properties of SnO$_2$-based nanomaterials synthesized by the sol-gel method.

2. Experimental Technique

SnO$_2$-based hierarchical nanomaterials with a fractal type of spatial organization, being a dielectric matrix with tin dioxide clusters embedded therein were synthesized by the sol-gel method using tetraethoxysilane [7]. A film-forming sol, having been aged for a day before ripening, was deposited onto glass substrates by centrifugation at 2750 rpm. The final stage of the formation of nanomaterials was their thermal annealing at a temperature of 575°C for 50 minutes in air. The samples of nanomaterials to be investigated with a scanning electron microscope (SEM) were formed on an aluminum foil under the same modes.

Inductively coupled plasma processing of nanomaterials was performed with an etching machine under various modes of nitrogen plasma treatment. The modes were selected so that the ions of the process gas break the chemical bonds between atoms only located in the surface layer of the SnO$_2$-based nanomaterial for redistribution of adsorption centers, rather than etching the film material. The power of inductively coupled plasma source $P_1$, which determines the energy and density of plasma, and the power of supplementary high-frequency source $P_2$, which characterizes the ion flux intensity and direction, were chosen as variable parameters.
An analysis of adsorption site distribution on the surface of synthesized samples was carried out by the adsorption method of acid-base indicators in combination with spectrophotometry prior to and following additional processing. The main investigated parameter in the analysis of adsorption sites on the surface of solid-phase systems is acid strength pKa. If adsorption is observed, then the centers are assigned the acid strength corresponding to the indicator-adsorbate molecule, that is, the acid strength of the center corresponds to the acid strength of the indicator. Ten indicators having acid strength values pKa in the range from 0.8 to 11.1 were selected for the experiment.

3. Results and Discussion
To analyze the adsorption site concentration of certain acid strength, three solutions were prepared for each sample and the selected indicator. The spectrophotometer was used to measure the transmittances of the solutions, which were then recalculated into the absorption factors according to the formula:

$$A = \log\left(\frac{100}{T}\right),$$

where T is the prepared solution transmittance, %. Based on the obtained results, the concentration of adsorption sites was estimated for each pKa value according to the following equation:

$$Q(pKa) = \frac{C_{\text{ind}} \cdot V_{\text{ind}}}{A_0} \left| \frac{A_1 - A_0}{m_1} \pm \frac{A_2 - A_0}{m_2} \right|,$$

where $C_{\text{ind}}$ is the concentration of the indicator in the solution, $V_{\text{ind}}$ is the volume of the indicator solution, $m_1$ and $m_2$ are the masses of the studied nanomaterials, $A_0$, $A_1$, $A_2$ are the corresponding absorption factors based on the calculated transmittances with a spectrophotometer.

The surface of a solid is bifunctional, since it is a combination of Lewis and Brønsted acid and base sites. Brønsted acid and base adsorption sites are formed due to the adsorption of water molecules or its fragments at the corresponding Lewis sites.

The histogram shown in Figure 1 confirms that Brønsted acid sites prevail on the surface of the studied plasma-untreated SnO$_2$-based nanomaterials. These sites are protons bound to surface oxygen atoms in various configurations. The main Brønsted centers, represented by hydroxyl groups, have the Sn–OH structure in various configurations, and are identified on the surface of the investigated materials.

![Figure 1. Distribution of adsorption sites on the surface of SnO$_2$-based nanomaterials.](image-url)
The total number of adsorption sites on the surface of nanomaterials has decreased after plasma treatment due to the formation of defects, being a result of ionic bombardment, and due to thermal action (Figure 2). Besides, this phenomenon is explained by the transformation of some Brønsted sites into Lewis ones due to plasma action.

An adsorption site with an acid strength of $pK_a = 6.4$ was selected within the research into the dependence of distribution of the adsorption sites of SnO$_2$-based nanomaterials on the parameters of plasma treatment by the indicator method. The choice is explained by the fact that such adsorption site is characterized by a high concentration on the surface of the films, as follows from Figure 2.

![Figure 2. Distribution of adsorption sites on the surface of SnO$_2$-based nanomaterials prior to and following nitrogen plasma treatment.](image)

Degradation in the structure of nanomaterials at high plasma power $P_1$ values is confirmed by the data of scanning electron microscopy (SEM) (Figure 4).

![Figure 3. Dependence of the concentration of adsorption site, having acid strength of $pK_a = 6.4$, on the power of an inductively coupled plasma source (a), and on the power of a high-frequency source (b).](image)
4. Conclusions
Nitrogen plasma treatment of SnO$_2$-based nanomaterials leads to modification of their surface properties due to partial destruction of quasi-spherical aggregates (Figure 4, a), typical for nucleophilic increase in sol-gel systems. This ensures the formation of supplementary macro-, meso-, and micropores in nanomaterials (Figure 4, b), thus increasing their specific surface area. With high-power plasma sources, the overall integrity of the structure of nanomaterials is violated due to the effect of high-energy ions.

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