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Compositions based on porous silicon and nickel oxide obtained by cooperative synthesis

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Abstract. In this work, nanocompositions based on porous silicon and nickel oxide were obtained by cooperative synthesis with and without the addition of alcohol. The XPS method was used to study the surface of the samples, and nickel oxide particles were also studied by the SEM method. The results showed the effect of the difference in synthesis on the ratio of elements in the composition of the resulting NiO-porSi samples.

Keywords: nickel oxide, porous silicon, X-ray photoelectron spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy

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Материалы конференции
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Композиции на основе пористого кремния и оксида никеля, полученные совместным синтезом

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Аннотация. В этой работе нанокомпозиции на основе пористого кремния и оксида никеля были получены совместным синтезом с добавлением спирта и без него. Для исследования поверхности образцов использовался метод XPS, а частицы оксида никеля

также изучались методом SEM. Результаты исследования показали влияние разницы в синтезе на соотношение элементов в составе полученных образцов NiO-porSi.

Ключевые слова: оксид никеля, пористый кремний, рентгеновская фотоэлектронная спектроскопия, сканирующая электронная микроскопия, энергодисперсионная рентгеновская спектроскопия

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Introduction

Due to the large surface area and the presence of nanopores, porous silicon (porSi) is a promising material for applications in micro- and optoelectronics, photovoltaics, sensors, as well as for medical problems [1, 2].

Composite materials based on porous matrices with incorporated particles are of great interest for the creation of new devices with improved characteristics for sensors, catalysis, and alternative energy. Varying the technological parameters of the syntheses used to obtain such substances makes it possible to obtain a wide range of certain characteristics of the final materials.

One suitable material for the porous matrix is porous silicon. Porous silicon has a large surface area, and the method of electrochemical etching used to obtain it makes it possible to obtain porous developed structures with a pore diameter from nm to μm. Thus, it is possible to create a suitable structure for incorporating particles of different sizes to obtain new compositions.

According to studies [3, 4], nickel oxide removes changes in the properties of porous silicon, including optical ones. These NiO-porSi structures show the best sensitivity for gases in gas sensors based on such structures. Thus, the aim of the work was to study the possibility of using the method of X-ray photoelectron spectroscopy to study NiO-porSi systems obtained by joint synthesis.

One of the most common methods for obtaining porous silicon is electrochemical synthesis, varying the parameters of which makes it possible to obtain samples with the possibility of controlling the formation of various porous structures and pore sizes (from nm to microns). The possibility of creating matrices with a multiporous structure makes it possible to use porous silicon in gas sensors. Interest in the use of this material is also due to the high surface to volume ratio, ease of formation, compatibility with modern technologies for the manufacture of silicon microelectronics [5].

The main field of application of composites based on porSi matrices with metals and metal oxides is gas sensing. The use of such composites makes it possible to increase the selectivity of gas sensors and reduce the reaction and relaxation times [6–8]. They are also used, for example, to create self-cleaning coatings [9].

In this work, we study porSi-NiO samples obtained by the method of chemical co-deposition of nickel oxide [10] directly in the porous silicon substrate itself. The codeposition method is a simple and inexpensive way to obtain nanoparticles. In the course of the work, the possibility of synthesizing NiO particles inside a porous silicon matrix is studied in order to simplify their incorporation.

Materials and Methods

Porous silicon

Porous silicon was obtained by electrochemical etching of single-crystal silicon with (111) orientation and n-type electrical conductivity [11–13]. Hydrofluoric acid diluted with water was used

as the electrolyte. The resulting porous matrices were washed in alcohol to purify electrolyte residues.

NiO-porSi composition

To obtain NiO-porSi compositions, the synthesis method of NiO by chemical deposition in the presence of a porous substrate was used. For the synthesis, solutions of nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) were used [10].

The porous silicon substrate was preliminarily soaked in a NiCl solution for two days. Sodium hydroxide solution was added dropwise to the solution with the substrate and mixed with a magnetic stirrer. Next, the substrate was air-dried for two days at room temperature and then annealed in a muffle furnace for 3 hours at 500 °C.

Thus, several NiO-porSi samples were obtained: with the addition of a small amount of alcohol in the synthesis (sample 1) and with the use of water (sample 2).

The morphology of porous silicon used in this work was investigated in previous work [12].

The NiO-porSi samples obtained in this work were studied by X-ray photoelectron spectroscopy (XPS). The XPS method is widely used for chemical analysis of the surface of samples. It is used to detect contamination and analyze the presence of certain substances on the surface, as well as to control processes occurring from the volume to the surface and vice versa. The essence of the method is to measure the energy of photoelectrons knocked out from different energy levels of atoms when a substance is irradiated with X-rays [14]. In the work, the XPS study was carried out using the K-Alpha equipment.

Nickel oxide powders, also obtained during the synthesis of NiO-porSi compositions, were also additionally studied by electron microscopy (SEM) and energy dispersive X-ray spectroscopy (X-ray diffraction microanalysis) (EDX) using a Zeiss Supra25 scanning electron microscope (Carl Zeiss, Germany).

Results and Discussion

Fig. 1 and 2 show the overview XPS spectra for two samples.

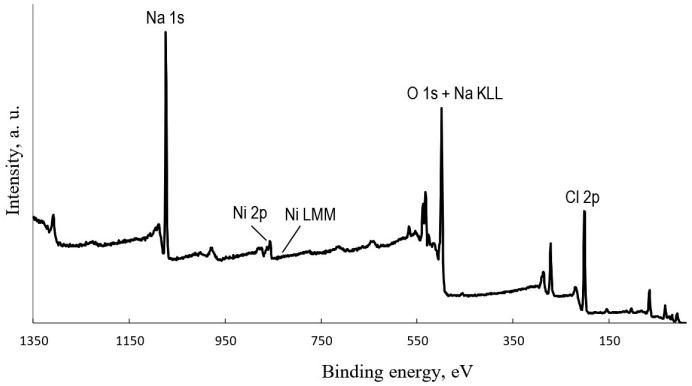

Fig. 1. Overview XPS spectrum for the sample 1 (NiO-porSi composition with the addition of alcohol during synthesis)

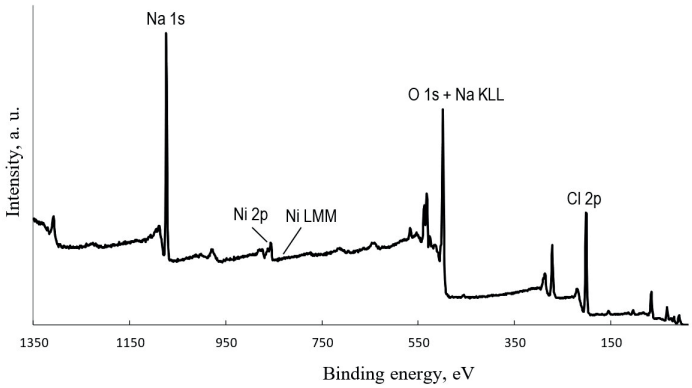

Fig. 2. Overview XPS spectrum for the sample 2 (NiO-porSi composition with the addition of water during synthesis)

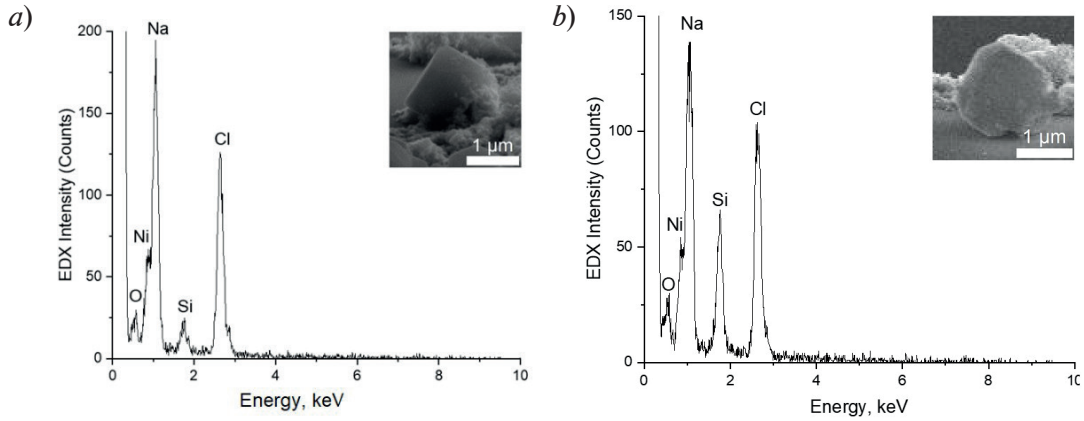

Fig 3. EDX and SEM spectra of obtained nickel oxide powders: sample 1 (*a*); sample 2 (*b*)

The results of the study of nickel oxide powders are shown in Fig. 3.

It can be seen from the survey spectra that the surface contains the formed nickel Ni 2p (856 eV) and Ni LMM (843 eV, Fig. 1). From the spectrum in Fig. 1 it can be seen that there are residues of reaction components Cl 2p (202 eV), Na 1s (1074 eV), O 1s (533 eV) on the surface of the sample with an overlapping Na KLL region. The O 1s peak with an energy of 533 eV in both spectra indicates the presence of metal hydroxide on the surface [15], which indicates that the reaction of nickel oxide formation by heating at high temperatures of nickel hydroxide obtained during synthesis was partially incompletely completed. The presence of sodium and chlorine also indicate the presence of NaCl reaction products, which can be removed by thoroughly washing the samples before annealing. Since carbon-containing substances did not participate in the synthesis reaction, it can be assumed that the C 1s peak (284 eV) in Fig. 2 is associated with carbon contamination, as most samples exposed to the atmosphere will have a detectable amount of incidental carbon contamination.

Analysis of SEM images made it possible to estimate the size of the synthesized powder particles: from 200 nm to 2 μm, typical SEM images of powder particles with a size of about 2 μm are shown in Fig. 3. An analysis of the EDX spectra showed the presence of Ni and O peaks associated with the synthesized nickel oxide; in addition, there are also Na and Cl peaks, the procurators of synthesis, as well as a Si peak (the powder was transferred to an auxiliary silicon substrate). The EDX data fully correlate with the results of the study of porSi-NiO samples by the XPS method (XPS), however, allow us to estimate the mass concentrations of nickel and oxygen for the synthesized samples as 17.4 and 22.8% (mass) for (*a*), as well as 19.1 and 15.8% for (*b*), respectively.

Conclusion

According to the obtained research results, it can be concluded that the addition of a small amount of alcohol affects the ratio of elements in the composition of the obtained NiO-porSi samples. The presence of Na and Cl elements can be explained by the residual precursors and reaction products, which can be reduced by washing the samples.

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