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NFM

Oxide semi-conductors usagein beta-voltaic elements

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Making beta-voltaic cells (nuclear batteries) is nowadays a promising line for developing a new generation of semiconductors. Improving characteristics of these cells requires development and use of new semiconducting materials and technologies of their manufacturing which should provide an effective ionizing radiation energy transformation, continuous operation life and manufacturability. It is proposed a polycrystalline semiconducting materials usage in order to provide stable characteristics of nuclear batteries during their service life. The distinctive feature of these materials in comparison with the high-ordered monocrystals is their less sensitivity to radiation-induced defects in the lattice, arising under the influence of ionizing radiation. Discussed are the prospects of polycrystalline semiconducting oxides usage for increasing efficiency of energy transformation in beta-voltaic cells under the prolonged exploitation conditions. It is shown that ^{63}Ni may be simultaneously used as a radiation source and as a part of semiconductor converter based on the Schottky barrier junction or a rectifying heterostructure. It is suggested that the heterostructure with the required properties can be obtained when forming the TiO_2 – NiO successive layers on titanic substrate. An experimental sample of such structure has been obtained and an electronic microscopical analysis of the interface element composition has been implemented. Applicability of the proposed approaches to making the ^{63}Ni-based beta-voltaic cells is shown.

Key words: beta-voltaic element, oxide semi-conductors, ^{63}Ni, rectifying contacts, energy converter, nuclear battery.

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Introduction

Interest to elaboration of miniature sources of electric power based on nuclear batteries using beta-emitting radionuclids has recently grown [1–5]. Batteries of the given type consist of elements, which include an isotopic source of beta rays and a semiconductor converter of radiation to electric energy. The ^{63}Ni radioisotope-based radiation sources exhibit the most promise for elaborated beta-voltaic elements. The ^{63}Ni usage prospect is stipulated by a long half-value period (100.1 years), high specific power intensity ($5.7 \cdot 10^{-3}$ W/g, with the maximal

and medium energy of beta-particles equal to 65.9 and 18.0 keV, respectively) and absence of gamma radiation. Characteristics of a beta-voltaic element are also determined by perfection of a semiconductor converter of ionizing radiation energy. Selection of semi-conductors for the converter represents the topical problem and certainly should be an issue of comprehensive investigations.

Semiconductor converters of beta-voltaic elements and their service conditions

The semiconductor converters designed for beta-voltaic elements are in many ways similar to the semiconductor photoelectric cells (SPC), which use a light emission. Their principle of operation is based on generating the nonequilibrium carriers of unlike electric charge (electron-hole pairs) in a semiconducting material under the influence of beta rays and separating them by electric field of the rectifying contact, which carries an electric current only in one direction.

A semiconductor *p*–*n* junction is used in SPC as a rectifying contact. However, in view of the smaller depth of beta-particles penetration into the semiconducting material as compared with the light quantums, it is appropriate to use in converters of beta-voltaic elements the following items:

– contacts based on the Schottky barrier junction, which arises on the boundary metal – semiconductor;

– the rectifying semiconductor heterostructures.

Degradation of the nuclear batteries characteristics is determined by lessening the radioactive emanation intensity as an isotope decays in the source, as well as by decreasing an efficiency of the energy transformation as a result of due to the radiation-induced defects accumulation in the crystal structure of semiconducting materials. The radiation-induced defects serve as additional recombination centers for the generated nonequilibrium carriers of electric charge. To estimate a life time of the electric charge carriers in the irradiated semiconductors, the following relation is used [6]:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + C\Phi, \qquad (1)$$

where τ_0 — the charge carriers life time in the non-irradiated material (from 10^{-6} s for monocrystal silicon to 10^{-8} s and under in the gallium arsenide epitaxial films); Φ — an integral irradiation flow; C — a constant for the given material. In accordance to the data on the monocrystal silicon radiation treatment by high-energy electrons [7], $C \approx 6 \cdot 10^{-6}$ cm^2/s, hence, at the surface activity of ~ $(1 \div 2) \cdot 10^3$ MBq/cm^2, typical for the beta rays sources based on high-enriched ^{63}Ni, the τ value will halve as compared with τ_0 in about three minutes of irradiation.

The relationship (*1*) allows to infer that the use of polycrystalline or amorphous semiconducting materials, possessing higher initial concentration of defects and relatively small values of the charge carriers life time in comparison with the highly-ordered monocrystals used in SPC, will increase the behaviour stability of beta-voltaic cells.

Application of the oxide-based rectifying contacts

The oxide semiconductors were among the first polycrystalline materials used in rectifying contacts of crystal diodes until the 1970s. Later on, practically all these units have been replaced by the diodes based on monocrystal elementary semiconductors (germanium, silicon) and the binary compounds (gallium arsenide). The distinctive features of semiconducting oxides along with properties of modern semiconductors [8–12] are represented in the Table.

Properties of semiconducting materials

Semiconductor	Si	GaAs	Cu_2O	TiO_2	SnO_2	NiO
Conductivity type	*n*, *p*	*n*, *p*	*p*	*n*	*n*	*p*
Band-gap energy, eV	1.12	1.42	1.9–2.0	3.06	2.4–3.5	1.7–1.9
Permittivity	12	11.1	8.75	~100	2–24	5–10

Many years of experience in the application of oxide semiconductors in rectifying equipment in combination with the sophisticated understanding of their properties and characteristics allow these materials to show a considerable promise with reference to the objective of the beta-voltaic cells making.

Application of ^{63}Ni isotope in beta-voltaic cells also provides the possibility of its usage as a metal, which form the Schottky barrier junction with oxide semiconductors or as a component part of rectifying semiconducting heterostructures based on compound oxides.

Nickel possesses a comparatively high photoelectric work function of electrons (4.91 eV) as well as the noble metals, but in contrast to the latter, it is prone to oxidation in contact with the oxygen-containing substances. Therefore, not the nickel metal but a thin oxide film on its surface should be considered in this case.

Nickel protoxide possesses the semiconducting properties with the hole conduction in impurity and intrinsic bands. The acceptor level stipulated by a non-stehiometry of the NiO_{1+x} ($x<0.5$) lattice, is situated above the limit of valence band by 0.75 eV [13]. Titanium oxide, which has the acid properties, and this compound form a complex oxide with ilmenite structure ($FeTiO_3$). Thus, rectifying properties of the contacts based on nickel and titanium oxide will be dictated by properties of the NiO- and TiO_2-based heterostructures [14].

Making and investigating the NiO- and TiO_2-based heterostructures

A TiO_2 – NiO heterojunction has been formed on titanium substrate by low-temperature magnetron sputtering on a Luch-13 (“Луч–13”) plant manufactured by

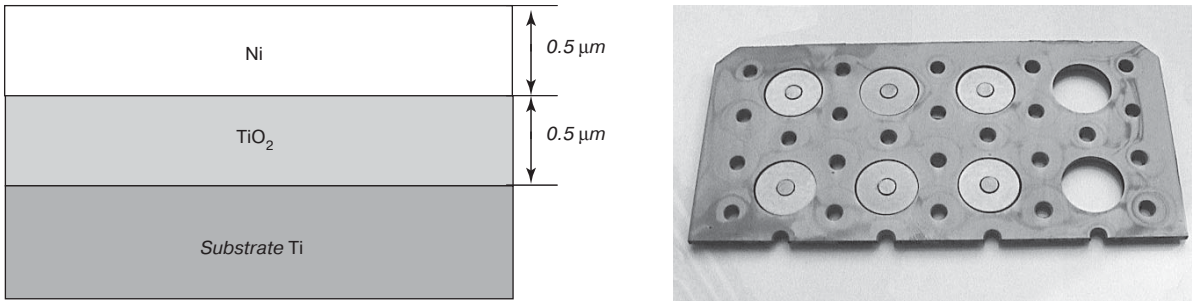

Fig. 1. Structure of the samples before an oxidation process (*a*) and their outward appearance after it (*b*)

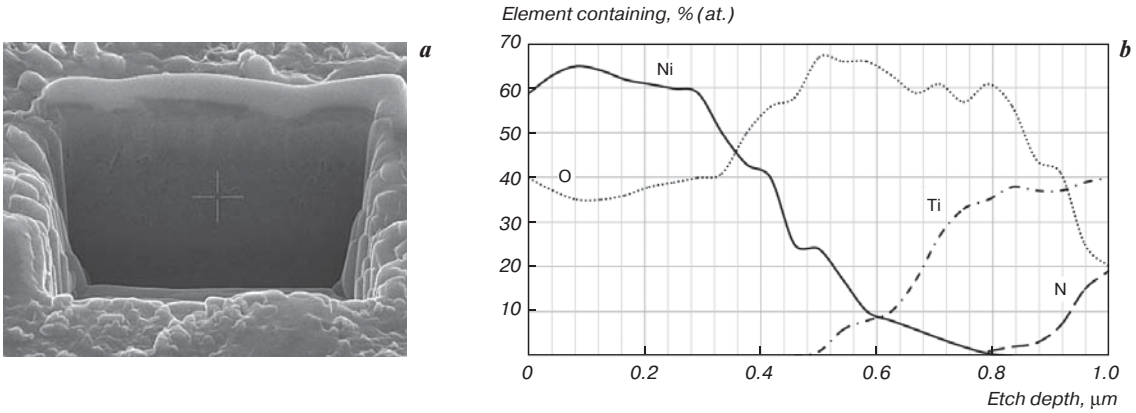

Fig. 2. Electron-microscope image of the area under consideration (*a*) and concentration of the main constituent elements depending on etch depth (*b*)

the "Luch" Science and Production Association. Purity of the used nickel and titanium amounts 99.99%. View of a thin-film structure is represented schematically in Fig. 1, *a*.

Preliminary, an ionic cleaning of titanium substrate has been carried out before the functional layers depositing. Then, a magnetron reactive sputtering of titanium has been fulfilled at room temperature (fore vacuum is $2 \cdot 10^{-5}$ mm Hg, current is 2.4 A, voltage is 450 V, distance to the substrate is 0.1 m) in the mixture of argon (50%) and oxygen (50%) and a 0.5 μm thick layer of *n*-type (TiO_2) semiconductor has been formed. The next operation was a 0.5 μm thick nickel layer depositing in argon medium at pressure of $2 \cdot 10^{-3}$ mm Hg At the final stage, the generated structure oxidation has been realized in the air at the temperature of 600 °C (Fig. 2, *b*).

Quantitative investigations of the elements distribution across the thickness of the sample has been conducted on a TESCANVEGA 3 XMU electronic microscope in the hard vacuum mode. During the investigations, a layer-by-layer ionic etching of the surface has been conducting (Fig. 2, *a*) along with the element composition detecting by *X*-ray photoelectron spectrometry. The obtained dependency of concentrations of the main constituent components on etching depth is depicted in Fig. 2, *b*.

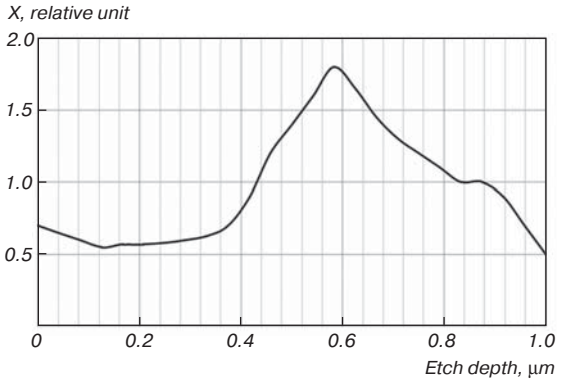

Fig. 3. The deviation from the stochiometric composition (*X*) dependence on etch depth

The value *X*, which characterizes deviation from the stochiometric composition of the generated oxides, has been estimated by the following formulца:

$$X = \frac{[O]}{\sum_i (n_i \cdot [C_i])}, \quad (2)$$

where [O] — oxygen concentration; $[C_i]$ — concentrations of the other remaining elements; n_i — number of oxygen atoms per atom of the ith element in its most likely compound with oxygen (oxides and/or salts of stochiometric composition).

In Fig. 3, *a* dependence of deviation from the stochiometric composition (*X*) on the etch depth is shown.

Depicted in Fig. 2 and 3 relationships are evidences of keeping the required thickness of a nickel-containing coating after the sample surface high-temperature oxidation. It should be also pointed out impurity (nitrogen) segregation to the substrate. The oxygen content lessening near the sample surface can be caused by insufficient nickel oxidation during annealing in the air or by partial reduction of its oxide during ionic etching.

Noted is a significant growth of the *X* parameter values at depths of (0.4–0.7) μm. This fact and the figures of the oxygen content allow to assume that the given area of the sample is characterized by presence of a $NiTiO_{3+x}$-type compound.

Hence, the fulfilled investigations and obtained NiO – TiO_2 heterostructure demonstrate applicability of the proposed approach to making beta-voltaic cells, in which ^{63}Ni and its oxide are used in a beta source while NiO and TiO_2 are used in a semiconductor ionizing radiation energy converter.

Conclusions

1. It has been shown that polycrystalline materials are worthwhile to be used for increasing the behaviour stability of beta-voltaic cells in their semiconductor converters.

2. It has been made an inference about the prospects of the oxide-based polycrystalline materials application in the p–n-junction rectifiers and rectifying contacts based on ^{63}Ni *and titanium dioxide.*

3. Experimental specimens of the NiO – TiO_2C *heterostructure have been made by magnetron reactive sputtering.*

4. Results of the electronic microscopical investigations of the specimens corroborate applicability of the proposed approach to making beta-voltaic cells.

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