Electrochemical deposition of a radionuclide nickel-63 on betavoltaic cells for a nuclear battery based on silicon p-i-n junctions

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Abstract. This paper highlights the manufacturing process of two types of betavoltaic cells with a source coated with $^{63}$Ni: the flat one and one with a three-dimensional (3D) microchannel structure, obtained by anodizing silicon (Si). Thin-layer deposition of a nickel-63 radionuclide was carried out from the ammonium-citrate based electrolyte solution, designed for production until exhaustion.

Keywords: betavoltaic effect, anode etching, microchannel silicon, plating on silicon, radionuclide nickel-63, until-exhaustion electrolyte.

The first proposal betavoltaic power element dates back to 1951 [1], however, studies and research are still relevant nowadays [2-4]. A betavoltaic element consist of a $\beta$-radioactive source, a non-conductive layer, which electrons pass through, and collecting layer, gathering electrons. Such source is a basic unit for building no-break power cells. The efficiency of the betavoltaic element and estimated power of cell grows continuously, as well as a range of application [5-7].

The simplest way to produce a betavoltaic element seems to be a unit of a silicon wafer layer with a planar diode structure and an apressed layer of planar nickel sealed radioactive source (SRS). This approach is attractive as linking two or more standard items is assumed, but wasn't supported insofar as using SRS means a loss in beta-stream and additional Bremsstrahlung due to substrate absorption as a side-effect.

The second attractive approach, from the production simplicity point of view, is an element of a silicon planar or micro-channel diode structure plated by nickel-63. The downsides of the former are proved to be mitigated with the latter [8]. However, there is a production obstacle, of choosing the optimal plating process here to be solved.

Nickel-63 is used to be plated electrochemically due to avoiding significant waste of high-costed source material. Taking to account the relation between the ion flow density and massic activity of depositing radionuclide (Figure 1), using of nickel volume-maintainable electrolyte seems to be economically unviable, as far as source material cost grows exponentially as massic activity increases, and sensitivity to impurities disallows longstanding and/or multiple electroplating. The purpose of this research is the development and comparison analysis of optimal technologies for plating on silicon diode structure, planar one and microchannel one. In addition, to test the hypnotical applicability of...
ammonium-citrate based electrolyte solution, designed for production until exhaustion by RITVERC JSC.

Electroplating of nickel was performed from ammonium-citrate based electrolyte solution, designed for production until exhaustion by RITVERC JSC with following speciation: \((\text{NH}_4)_2\text{C}_6\text{H}_6\text{O}_7 + (\text{NH}_4)_2\text{SO}_4 + \text{NH}_3\cdot\text{H}_2\text{O} (\text{exc.}) + \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} + ^{63}\text{NiCl}_2\). Electrolysis was carried out in the galvanodynamic mode with a linear increase in current density from 1.5 to 30 mA / cm\(^2\) at a temperature of 20 ± 5 °C. An excess concentration of ammonia in the solution provided buffering capacity of the electrolyte and maintained pH value in the range of 8.5–9.0.

Silicon p-i-n structures with overall dimensions of 11x11 mm and a thickness of 470 μm were used as substrates. The square electrode was adapted to electroplating the 63Ni layer. A metal layer of Ti/Ni (20/20 nm) was evaporated to form the p+ ohmic contact. Titanium was used as an adhesive layer. The samples were annealed at 300 ° C for 60 s in N\(_2\) ambient.

The plating area was 1 cm\(^2\). The preparation of the substrate included degreasing with dimethylformamide and activation with a 10% sulfuric acid solution. The optimal thickness of the \(^{63}\text{Ni}\) radionuclide layer is determined by its self-shielding [9] and is approximately 1.5 μm for galvanic nickel (density 8.9 g / cm\(^3\)), which is equivalent to applying 10 mCi for an agent with a massic activity of 10 Ci / g.

The activity of the layer was determined as the exhaustion ratio of electrolyte from the nickel-63 radionuclide and was monitored using the SKS-07P-B11 liquid scintillation spectrometric complex. Under these conditions, the exhaustion of the electrolyte in nickel to a concentration of 4.2–4.6 Bq / μl over a period of 490–510 minutes was archived, which corresponds to plating of 99.999% initial activity. Moreover, according to the empirical deposition curve, the deposition of 90% of the material is achieved in 210-220 minutes, and 99% of the material in 350 minutes.

Ten samples with close short-circuit currents (≈ 65 nA) were selected from the obtained betavoltaic elements (Figure 2), which were assembled into a betavoltaic cell with the following characteristics: the value of the short-circuit current was 64 nA, the value the open circuit voltage was 1 V, the maximum output power was 32 nW, the overall dimensions of the assembly without a casing were 11x11x6 mm (more in [10]).
Further improvement of the characteristics of the betavoltaic power cell implies the use of a radionuclide preparation with a higher specific activity of the material (according to Figure 1) and the use of three-dimensional microchannel silicon structures as substrates [11-14]. This is due to the fact that the average geometric characteristics of the pores obtained by the deep anode fluoride etching method and the quasi-hexagonal arrangement of microchannels provide an increase in surface area by 1-2 orders of magnitude [15]. At the same time, the fact that the depth of the microchannels is, on average, 160-163 microns with a diameter of 5-6 microns and a distance between one center to another of 10 microns, significantly limits the set of available plating process applicable for such structures.

The most popular and cited method was the chemical displacement deposition proposed in 2007 [16]. It implies immersion of the substrate for 4 hours in a solution containing 1 M NiSO4, 2.5 M NH4F, 0.6 mm coumarin, 0.7 M sodium dodecyl sulfate with continuous stirring and a temperature of 60 °C at pH 7-8 to deposition of the natural nickel sublayer of 1-micron thickness. The deposition of radionuclide nickel-63 is proposed to be carried out under the same conditions on a nickel sublayer, replacing stable nickel sulfate in the electrolyte with radionuclide sulfate nickel-63 with a massic activity of 7.5 Ci / g.

To reduce the loss of electron flow in the stable nickel sublayer and to minimize the consumption of the radionuclide agent, it was decided to modify the method. The first change was a multifold reduction in the time of applying the sublayer to reduce its thickness. The second change involved the replacement of a highly concentrated nickel fluoride electrolyte with a low-nickel variable-concentration electrolyte for the deposition of nickel-63 radionuclide. The testing of the modes of deposition of nickel in micropores was carried out on stable nickel. The efficiency of the process for filling microchannels with nickel was studied on side sections using scanning electron microscopy and X-ray microanalysis using a TESCAN VEGA LMH electron scanning microscope.

The preparation of microporous silicon included: degreasing with dimethylformamide (allowing to reduce the next stage of preparation by a factor of 3 in time), removing other organic pollutants by washing in an aqueous solution of ammonia and hydrogen peroxide (H2O / NH4OH / H2O2 = 5/1/1) at 75 °C and activation with a 5% solution of hydrofluoric acid. The next change in the nickel plating mode was an increase in the operating temperature, forced due to the low intensity of the process led to the buildup of the metal layer from the surface deep into the material and often led to clogging of pores in the near-surface region (presumably as a result of the slow growth of SiF2 and SiF4 gas bubbles) (Figure 3).

Carrying out the process at a temperature of 70-75 °C allowed to exclude gas clogging of the pores, however, did not provide satisfactory plating. As one can see (Figure 4), the displacement process is not uniform, which in some areas ensures the growth of the nickel layer at a speed of the order of 1.5 μm / day and leads to the complete displacement of silicon atoms by nickel atoms in the space between the pores.

![Figure 2. The schematic structure of Si betavoltaic cell](image_url)
Figure 3. Surface plating on unstructured porous silicon

Figure 4. Plot of a microchannel structure where nickel atoms completely displace silicon.
Since the decrease in current density did not give positive results, further work was carried out with a change in the qualitative and quantitative composition of the electrolyte. The optimum plating was achieved by nickel deposition from an aqueous solution containing 154.76 g/l of nickel sulfate, 92.55 g/l of ammonium fluoride, 0.88 g/l of coumarin with the addition of 0.03 g/l of sodium lauryl sulfate as a wetting agent at 60 °C (Figure 5). The pH of the solution was 5.6, deposition time 120 minutes.

![Figure 5. A slice of plated microchannel silicon](image)

The second stage of nickel plating (deposition of a radionuclide) was carried out by the reduction reaction of citrate-ammonium nickel electrolyte. However, without any leveler in the hydrogen fluoride electrolyte, the surface of the natural nickel sublayer got a loose structure, which led to the impossibility of using a low concentrated electrolyte until exhaustion. Satisfactory results of planting without gas plugs were achieved from an aqueous solution containing 26.31 g/l sodium citrate, 14.35 g/l nickel sulfate heptahydrate, 2.14 g/l ammonium chloride, and 2.36 g/l hydrazine hydrate. The pH of the solution was maintained by ammonia at a concentration of 9.1 g/L. The process was accompanied by a slight occlusion of the solution into the coating, as evidenced by a decrease in the content of oxygen and sulfur impurities during the galvanodynamic electrolysis mode with a linear increase in current density from 2 to 30 mA per 1 cm² of silicon wafer area for 120 minutes (Figure 6).
Figure 6. Analysis of the elemental composition of the structure with plated pores (the top is the elemental composition of the coating obtained in the galvanostatic electrolysis mode with a current density of 20 mA / cm², below is the elemental composition of the plating obtained in the galvanodynamic mode)

Thus, the archived result confirms the applicability of ammonium-citrate based electrolyte solution, designed for production until exhaustion by RITVERC JSC in order to plate nickel-63 radionuclide on planar diode silicon structures. For microporous silicon, the hypothesis was not confirmed; However, the authors proposed a plating technology for such structures using a citrate-ammonia electrolyte with a relatively low concentration of nickel-63 radionuclide.

In a further, the possibility and viability of using a radionuclide agent (raw material) with a higher and/or maximum possible massic activity of a nickel-63 radionuclide should be carefully considered. The authors also find it promising to look for a way to reduce the thickness of the natural nickel sublayer, plated to the microporous structure, without loss in the uniformity of deposition.

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