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Abstract. In this work, nickel thin films were deposited on silicon and silicon dioxide by chemical deposition for creation a nickel-63 isotope beta radiation source on the active window of a silicon betavoltaic converter. The effects the samples pre-treatment and the process parameters on the nickel deposits quality were investigated. The practical recommendations for implementation of nickel plating and reuse of processed electrolytes are given.

1. Introduction

Currently, the technology of creating betavoltaic power sources is being actively developed. In the past few years, several workable laboratory samples of betavoltaic sources have been obtained, the technology is being developed to an industrial level. Although the power output of such sources is quite small, they have compactness, sufficiently high reliability and a long service life. Modern technologies of the electronic industry make it possible to create a whole class of micropower (from 1μW to 10 mW) devices, for which power supplies of this type can be effectively applied.

The radiation sources for such devices can have a different design, depending on the design of the semiconductor betavoltaic converter. The following source variations are described in the literature:

- applied to a flat transducer in the form of a metal plat [1-6] or foil [7-10];
- electrochemically deposited isotope layer on a flat surface [11-13] or in the cavity of the surface microrelief [14, 15] of semiconductor betavoltaic converter;
- magnetron sputtered [16];
- formed by cluster deposition in the gas phase [17];
- by molecular beam epitaxy on silicon using the self-assisted vapor-liquid-solid method [18];
- even applied in liquid form [19].

In most of the constructions described, the source is applied to the active window of the transducer, however, such a method inevitably entails losses in the air gap "source-transducer", as well as constructional difficulties to ensure reliable fixation of superimposed thin films of the radioactive source.

The electrochemical isotope deposition on the semiconductor surface significantly reduces the quality of the obtained p-i-n junction, since there is a high probability of a silicon-nickel substitution reaction, and the surface of the p-i-n junction is "corroded" and a huge current leakage occurs. Even the thickness increase of the silicon dioxide passivating layer on the surface of the active window cannot solve this problem.

The beta radiation source is a critical element of the device [20, 21], since it is necessary not only to create it (film), but also to ensure the transfer of radiation to the chip. In the isotope, the emission spectrum has the form of a decaying exponent, i.e., the main amount of beta particles is in the low-energy part, so ideally the nickel layer (optimum thickness is 6 μm) should be located directly on the silicon surface.

It is possible to solve this problem of creating a nickel isotope layer with using the chemical reaction of deposition nickel films from a nickel salt electrolyte. This is the simplest option for the implementation on the radiochemical production.

Since low-energy nickel radiation is actively absorbed in nickel itself, it is therefore necessary to obtain a large surface area with a small layer thickness. Therefore, by creating not a continuous flat nickel layer, but in the form of a wavy "corrugated" surface, or even better separate microparticles (globules), it is possible to obtain a high level of irradiation of the planar surface of the chip.

Reagents containing stable (non-radioactive) isotopes of nickel are used in this research, since radioactive and non-radioactive isotopes have identical chemical properties due to the same structure of the electron shells of the atom.

2. Features of the method of chemical nickel plating

The chemical method of nickel plating is widely used in electroplating, because it allows to obtain uniform thickness coatings on samples with complex relief. Chemically deposited metal has a denser and stronger structure due to lower porosity than electrochemically reduced.

For chemical deposition of nickel, sodium hypophosphite can be used, which reduces nickel ions. The total reduction reaction is represented as

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni + 2H_2PO_3^- + 2H^+ + H_2$$
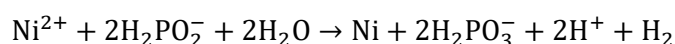
Simultaneously with the nickel reduction, disproportionation of hypophosphite to elemental phosphorus occurs (as a result, the level of phosphorus in the nickel coating is about 5\%). Hydrogen is the coproduct of the process:

$$2H_2PO_2^- \rightarrow H_2PO_3^- + P + OH^- + H_2$$
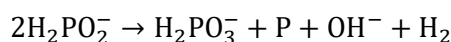
Due to the incorporating of phosphorus in the precipitate, the coatings have enhanced chemical resistance and hardness compared to pure metals.

The nickel reduction begins spontaneously only on the surface of some metals - nickel, cobalt, iron, palladium and aluminum. In the case of coating non-metallic surfaces, a preliminary deposition of a metal layer on them is necessary.

One of the main factors, determining the process rate, is the temperature of the solution. It is established that the process practically does not proceed at low temperature. The optimal temperature is 96-98°C. A significant effect on the rate of chemical nickel deposition has the acidity of the solution. The best results of the process rate and the quality of nickel coatings are obtained at pH = 4,7-5,5. The nickel reduction rate varies little with the concentration of sodium hypophosphite while maintaining a constant concentration of all other components. Only by changing the ratio between the concentrations of nickel and hypophosphite can change the process rate:| the higher this ratio, the higher the metal reduction rate. However, at a high concentration of nickel salt, spontaneous decomposition of the

electrolyte begins, due to the reduction of the metal in the bulk solution. To increase the stability of solutions, a certain ratio of concentrations of nickel ions and sodium hypophosphite is maintained and, in addition, complexing agents, stabilizing additives (crystalline poisons), surfactants and buffer compounds are used.

The reaction between the nickel ions and sodium hypophosphite is autocatalytic. Thus a rapid decomposition of the solution begins when a small amount of nickel metal is formed in the bulk solution. The nickel reduction can occur not only on the metal surface, but also in the bulk solution, therefore, choosing optimal conditions and to manage the technological parameters in a very precise way are necessary.

3. Materials and methods

3.1. Method of chemical activation of the samples surface

Before the nickel plating, the samples were cleaned of contaminants (fingerprints, etc.) in soap solution, washed with distilled water and ethanol. Three different treatment reagents were used for chemical activation:

No.1 - A mixture of concentrated acids HNO_3 (68%) and HF (50%), in volume ratio 1:1 (The White Reagent);

No.2 - A mixture of concentrated acids: HNO_3 (68%), HF (50%) and Glacial acetic acid (99%), in volume ratio 1:1:3, respectively;

No.3 - 1M H_2SO_4.

Activation was carried out in a 20 ml plastic vessel, the samples were held at room temperature for a specified time (30s - 15min), then they were washed with distilled water. Some samples were used without etching.

3.2. A procedure of nickel deposition

Prepared and activated samples were helded in the electrolyte (table 1) and the process was conducted in a water bath for a determined time at 98°C. A heat-resistant 100 ml beaker with a lid was used, the sample was fixed with a PVC holder. In some experiments, metal nickel was deposited not only on the sample surface, but also on the holder and the vessel walls.

Table 1. The composition of the studied electrolytes.

No.	Components of the solution	Concentration	pH	T, °C
1	$(CH_3COO)_2Ni \cdot 4H_2O$	15 g/l		
	$NaH_2PO_2 \cdot H_2O$	30 g/l	4,5-5,5	98
	Glycine	15 g/l		
2	$NiSO_4 \cdot 7H_2O$	36 g/l		
	$NaH_2PO_2 \cdot H_2O$	25 g/l		
	Thiourea	2 mg/l	4.5	98
	Sodium acetate	10 g/l		
	Acetic acid (99%)	6,2 ml/l		
3	$NiCl_2 \cdot 6H_2O$	32 g/l		
	$NaH_2PO_2 \cdot H_2O$	30 g/l	4,2-4,3	98
	Succinic acid	15 g/l		
4	$NiSO_4 \cdot 7H_2O$ (or $NiCl_2 \cdot 6H_2O$)	36 g/l (or 32 g/l)		
	$NaH_2PO_2 \cdot H_2O$	30 g/l		
	Ammonia, aqueous	10 ml/l (12M)	8,5-9,0	98
	Ammonium chloride	30 g/l		

3.3. Microscopy of the coatings

The surface of the initial samples and the obtained coatings was analyzed using SEM Hitachi S5500 microscope (secondary electron mode), and Hitachi TM3000 (back-reflected electron mode), which allows to judge the homogeneity of the elemental composition of the sample by phase contrast. The composition of the samples was analyzed by Bruker x-Flash 430 probe.
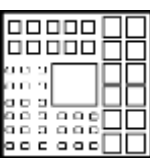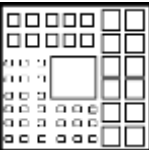
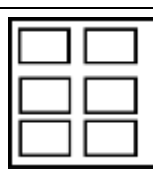## 4. Results of chemical nickel plating of Si/SiO$_2$ samples

Samples for nickel plating (with the exception of sample 1) are silicon wafers 5x5 mm in size, coated with a layer of silicon dioxide with a thickness of 80-100 μm (see figure 1). In some places, the so-called "islands of growth", which are clearly visible in figure 1, the thickness of the SiO$_2$ layer exceeds 200 μm.

a)   b)
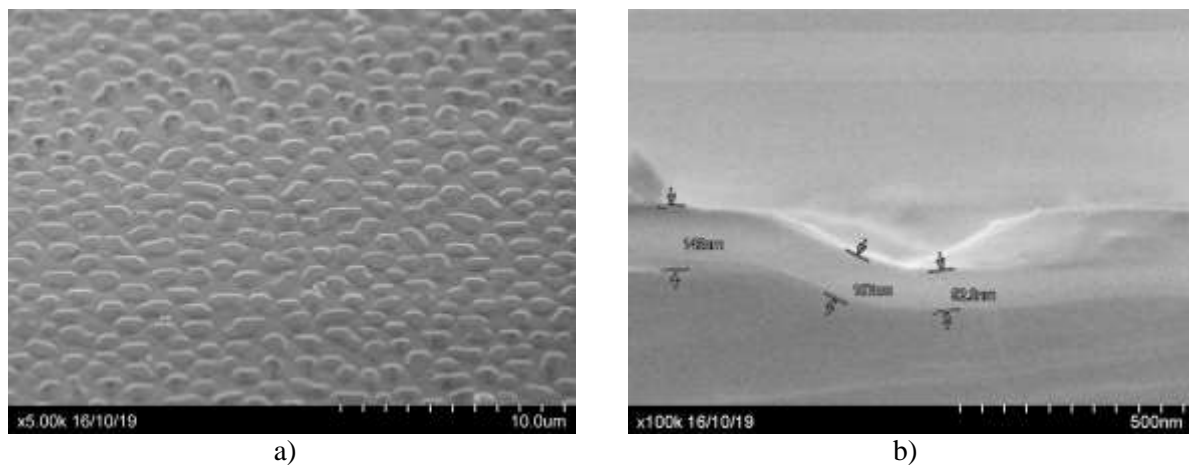
Figure 1. Micrographs of the surface (a) and cut (b) of sample 2 before processing.

Table 2. Investigated samples.

No.	Description	Topology	Comment
1	Pure Si plate		Size 10x10 mm
2	Si with ~100 nm SiO$_2$ surface layer		Size 5x5 mm
3	SiO$_2$ coated Si plate, with Ni dots of different sizes		Nickel adhesion to the surface of SiO$_2$ is low, Ni-film exfoliates during chemical treatment
4	SiO$_2$ coated Si plate, with Al dots of different sizes		Al films crack after deposition of nickel on them and peel off

5	Si plate with a SiO2 film, covered with nickel ~1μm dots. The plate is divided into 6 sections, with different dot density. The degree of nickel coating areas is 1-10% of the sections area. Nickel layer thickness ~50 nm.		Size 5x5 mm. The most of the nickel points peel off during processing

a)   b)
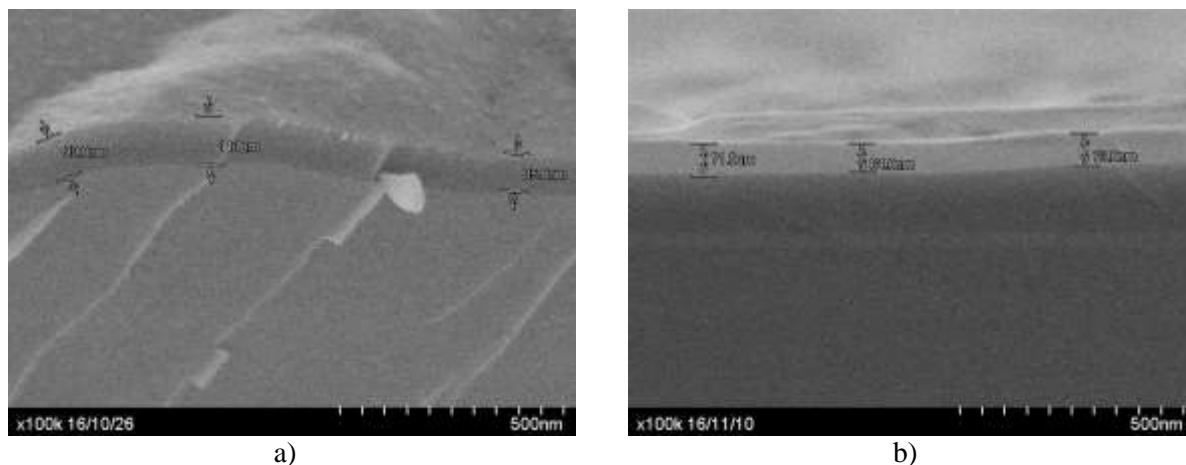
Figure 2. Micrographs of the sample 2 cut, after processing in etchant A for 10 s (a) and 60 s (b).

Before applying the nickel coating, to activate the samples they were treated in etchant solutions: $HF+HNO_3+CH_3COOH$ (etchant A) and H_2SO_4 (etchant B), according to the procedure described above. Established (figure 2), that etching for 60 s or more leads to a decrease in the SiO_2 layer to 60-70 nm and a noticeable loosening of the surface of SiO_2, so further processing for 30 s was used.

*4.1. The optimization of the chemical nickel deposition operated conditions*
Chemical nickel deposition on the sample 2 with using an electrolyte No.1 (table 1) was ineffective, probably due to the presence of SiO2 insulator layer. Experiments on chemical nickel deposition of sample 1 without a surface layer of silicon dioxide showed the formation of a dense layer of nickel on the silicon surface with a thickness of about 0.6 microns.
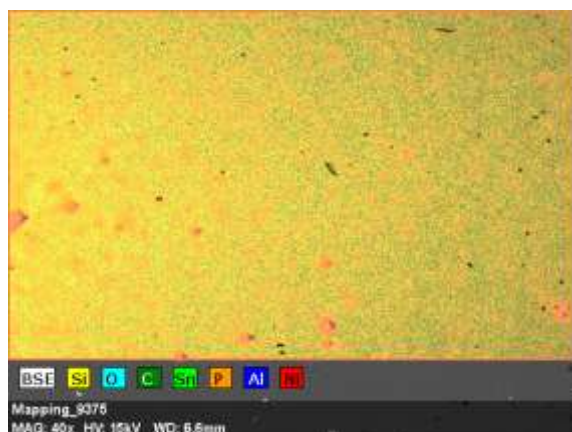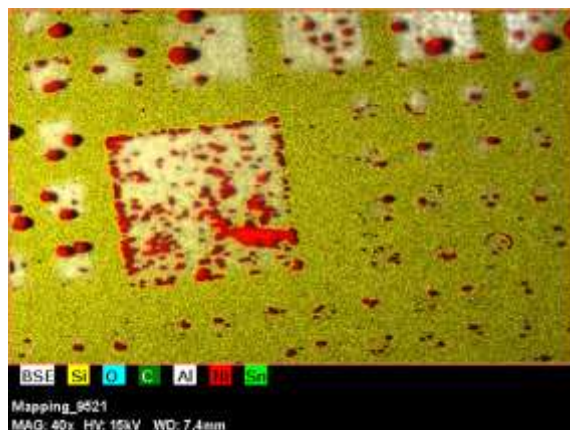

Figure 3. X-ray distribution map of Ni on the sample 2 surface, after chemical nickel plating (electrolyte No.1, time 60 min).
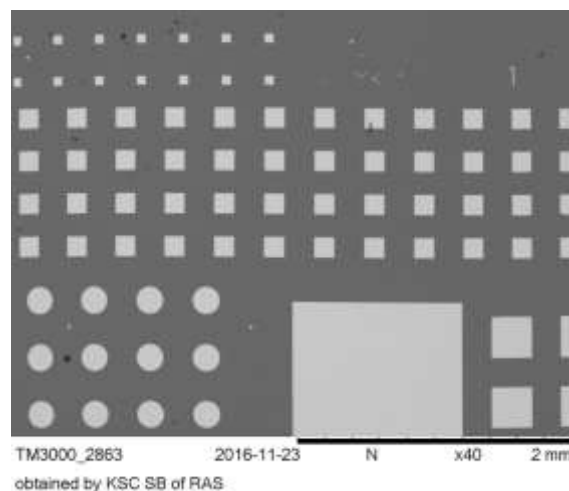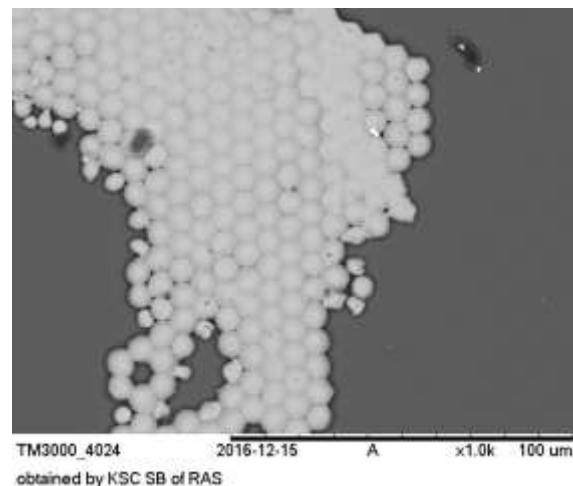
Figure 4. Micrograph of the initial sample surface with deposited Ni dots.

a)   b)
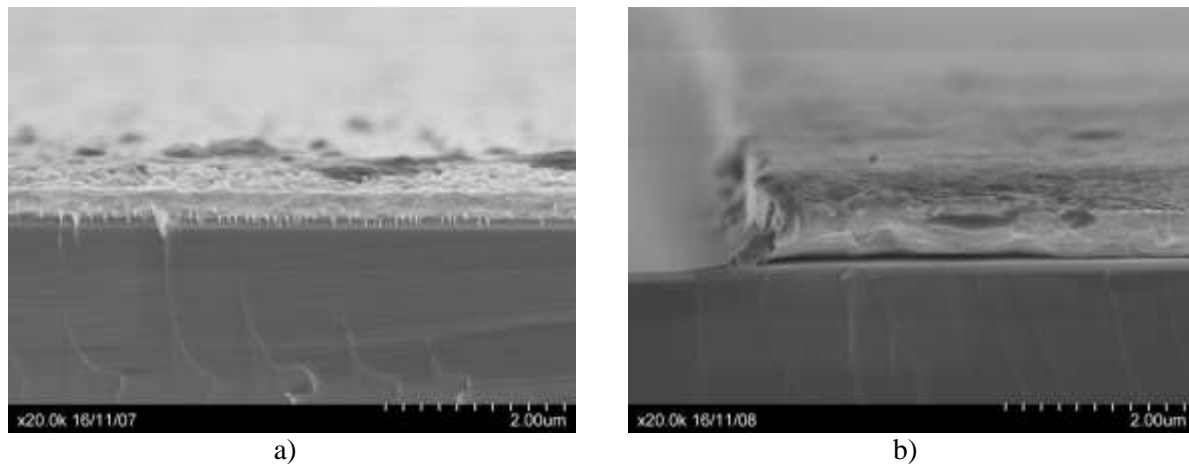
Figure 5. Micrographs of the initial samples surface, deposited with Al (a) and Ni (b).

Figure 6. X-ray map of the sample 4 surface (with Al-coated dots) after chemical nickel plating (electrolyte 2, 1 hour). Elements: Si-yellow, Al-white, Ni-red.

Figure 7. Micrographs of part of sample 5 surface after chemical nickel plating (electrolyte 1), visible areas covered with nickel.

In order to fix nickel on the surface of silicon oxide, dots of aluminum and nickel of various shapes and sizes were previously deposited on the plates by vacuum spraying; their sizes varied from 0.1 mm to 1.2 mm (figure 4, sample 3 in table 2).

The vacuum-applied aluminum coating has a thickness of about 600 nm (figure 5) and is characterized by increased friability and porosity. In the case of nickel, a less porous coating with a thickness of 600 to 900 nm was obtained at different areas, but it has cracks and has low adhesion properties and is poorly fixed to the surface (this is clearly seen in figure 5 b). During the chemical nickel plating of sample 3 (with nickel dots), they peeled off from the plate. Additional experiments have shown that exfoliation occurs already during the sample pretreatment for the activation or washing by distilled water at 96-98°C. Thus, sample 3 cannot be used for further research. It is necessary to select the vacuum deposition of the preliminary layer of nickel and aluminum operated conditions.

Table 3. Elemental composition of the samples surface, depending on the nickel plating conditions.

Process conditions	Elemental composition					Comment
	Al	Ni	P	S	F	
Sample 3						
Before processing	-	8.45	-	-	-	Source sample with Ni sublayer
Sample 4						
Before processing	13.73					Source sample with Al sublayer
Etchant 3, electrolyte 1, 1 h.	9.10	0.67	1.48	0.01	-	
Etchant 2, electrolyte 1, 1 h.	6.48	0.94	1.47	-	0.13	
Etchant 2, electrolyte 2, 1 h.	0.68	1.60	0	0.09	-	Sublayer crumbled
Etchant 2, electrolyte 2, 1 h.	3.18	3.26	-	0.03	-	
No etchant, electrolyte 2, 1 h.	2.98	2.66	-	-	-	Figure 6
Etchant 2, electrolyte 1, 1 h.	0.27	7.91	1.27	-	-	Al sublayer partially crumbled with nickel coating
Etchant 2, electrolyte 1, 40 min	0.45	5.93	1.17	-	-	Al sublayer partially crumbled with nickel coating
Without etchant, electrolyte 1, 1 h., 90°C (water bath)	5.46	0.57	0.65	-	-	Coverage is inefficient
Sample 5						
Before processing	0.27	6.00	-	-	-	Source sample with Ni dots
Without etchant, electrolyte 1, 1 h.	0.29	0.40	-	-	-	
Without etchant, electrolyte 2, 1 h.	0.28	0.15	-	-	-	

5. Conclusion and recommendations

Based on the obtained results, the following conclusions can be drawn:

- the chemical nickel deposition process was ineffective on a non-conducting SiO_2 layer;
- on the aluminum surface nickel forms a continuous layer, which, however, exfoliates, especially from large Al dots, or forms globules with size hundreds of microns depending on the process conditions. Globules can be formed on the surface of a solid layer of nickel;
- the etching by reagent 2 is preferable, since more nickel is fixed to the surface, but on some plates it led to delamination of metal dots;
- the amount of remaining etching reagent on the surface is negligible;
- chemical nickel plating in electrolyte No.2 (sulfate) is less effective than in electrolyte No.1 (acetate), and does not give a continuous layer of nickel;
- usage of electrolyte 4 is impossible due to the dissolution of Al-dots in alkaline solution;
- nickel plating time can be reduced to 40 minutes, but reducing the temperature even to 90°C dramatically reduces the process rate.

For effective chemical nickel plating on the non-conductive Si/SiO_2 surface, it is necessary to apply a metal sublayer a continuous layer or dots of nickel or aluminum, well fixed to the initial surface and not flaking off during chemical treatment at a temperature of 98°C.

The process of chemical nickel plating is better with the acetate electrolyte (No. 1) for 40 min. Sulfate electrolyte (No. 2) is less effective and does not give a solid metal layer, but also can be used if necessary, since it is obtained from the initial metal nickel through fewer stages, and therefore with less loss of the source material.

Surface activation with fluorine etching reagent (No.2) is more effective, but can lead to cracking and shedding of deposits if samples have poorly fixed metal sublayer. It is possible to carry out the process without etching, but with a slightly lower efficiency.

When a 2 μm solid metal nickel layer is formed on the 5x5 mm sample surface, about 0.5 mg of nickel can be deposited on the sample. On a salt weight, it is about 2.5 mg. The volume of the electrolyte ($NiSO_4 \cdot 7H_2O$) for nickel plating is 60 ml, and it will contain 2.16 g of nickel salt or 0.45 g of nickel (converted to pure metal). For one cycle of nickel deposition 6 samples can be used simultaneously and electrolyte can be depleted not more than 1%. It can be produced about 50 process cycles and 300 samples covered by nickel before the electrolyte depletion (50%).

However, one must consider:

- losses of electrolyte during the handling of records (preliminary estimation: 1% per cycle);
- growth of nickel globules on surface defects, ranging in size from a few to tens of microns (can not be estimated, depends on many parameters);
- reduction of metal in solution in powder form, deposited on the walls of the reaction vessel (estimation: 10-15% per cycle).

It is necessary to monitor the deposition of metal in a bulk solution, as it leads to a rapid electrolyte decomposition (the process is autocatalytic).
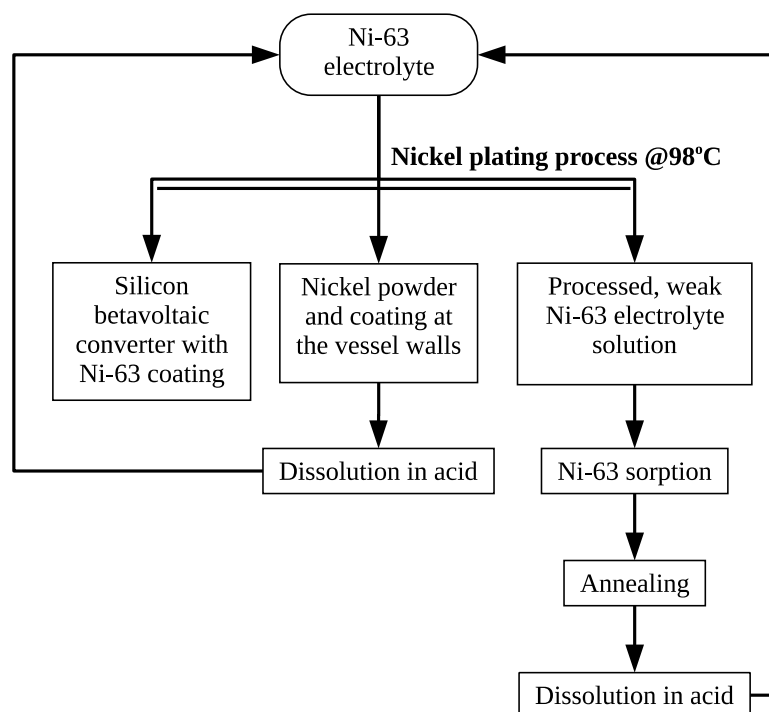
Figure 8. Ni-63 plating workflow of betavoltaic silicon chip.

Thus, the number of the process cycles is not expected to be more than 10-15 (60-90 samples). The processed electrolyte solution can be reused after adjustment of the composition.

The precipitated nickel powder and coating from the vessel walls can be dissolved in sulfuric acid and used to prepare the solution. Nickel from processed electrolyte solution can be extracted using ion exchange resins. After resin burning nickel oxide forms which can be dissolved in sulfuric acid to transfer to the electrolyte solution and used again. After the separation of nickel the solution can be also reused (figure 8).

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