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Development of betavoltaic cell technology production based on microchannel silicon and its electrical parameters evaluation

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ABSTRACT

In the paper a manufacturing process of three-dimensional (3D) microchannel structure by silicon (Si) anodic etching was discussed. The possibility of microchannels formation allows to increase the active area more than 100 times. In this structure the p-n junction on the whole Si surface was formed. The obtained data allowed to evaluate the characteristics of the betavoltaic converter with a 3D structure by using isotope 63Ni with a specific activity of 10 Ci/g.

1. Introduction

The energy of beta particles can be converted into electrical energy by using betavoltaic converters. On the basis of their principle of operation as well as the structural and technological performance, betavoltaic cells (BVC) are similar to solar cells. BVC sources use β-radiation instead of a light source for generating a current. The stimulus for research on the development of such devices was the need for durable and reliable sources of energy to power electrical devices in remote locations, and for backup power modules in space vehicles and systems with low power consumption.

When designing betavoltaic element, ^{63}Ni was selected as a β-source radionuclide because it has a long half-life (100 years), and the maximum beta particles energy is well below the threshold of defect in silicon (Si) (spectrum beta particle energy is limited to 67 keV, with the maximum at 17.4 keV). Furthermore, ^{63}Ni is a good conductive material and it can easily be integrated in semiconductor technology. ^{63}Ni was also selected because of security concerns; during disintegration, it becomes stable ^{63}Cu, and because of low-energy beta particles, it does not require the development of special shielding enclosures. A disadvantage that needs to by considered in the development of BVC, is the low specific activity (59 Ci/g) of ^{63}Ni radioisotope.

Effective energy conversion of β-radiation into electrical energy and the development of the current sources with a long service life can be solved by using semiconductor structures with p-n junction. With regard to the choice of the converter material, Si is attractive because of its well-developed technological treatment as compared to other semiconductors such as GaAs, GaN and SiC; wide availability; and relatively low cost. The efficiency of such converters is greatly improved when the planar p-n junctions [Krasnov et al., 2016; Krasnov et al., 2015; Ulman and Desai, 2009] are replaced with the structures formed based on Si surface [Starkov et al., 2015; Sun et al., 2005].

The aim of this work is to technologically develop three-dimensional (3D) Si structures for a betavoltaic converter and to evaluate the characteristics for the p-n junction with Ni contact layer formed by the reducing reaction across the strongly developed Si microchannel surface in the electron irradiation modes.

2. Materials and methods

The calculated data suggest that the power density of a planar Si BVC with ^{63}Ni isotope does not exceed 3×10^{-7} W/cm^2 [Olsen, 2014]. Therefore, to increase the source power it is advisable to use a 3 BVC structure with the maximum surface area. This construction can be realized by forming microchannel (macroporous) layers in monocrystalline Si. The process of creating a microchannel structure should not significantly complicate the subsequent formation of the shallow p-n junction on the microchannels surface and the desired thickness of the Ni layer. Ni will act as the metal contact to the n$^+$ layer of the p-n

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junction and the use of ^{63}Ni isotope will make it a β-radiation source.

Depending on the location topology and microchannels morphology it is possible to control the increase in the effective surface area by one to two orders. It should be expected that the power value of the 3D BVC structure will be proportionally exceed the power value of the BVC 2D structures that are manufactured by planar technology [Krasnov et al., 2016].

The most accessible method for the controlled formation of a microchannel Si structure with the desired morphology is deep anodic etching [Vyatkin et al., 2002]. In the experiments monocrystalline Si with p-type conductivity and orientation surface (100) was used. After deep anodic etching to the polished surface of the silicon wafer the spontaneous distribution of pores on the surface was identified and the subsequent formation of the so-called disordered structure of microchannels (randomly pores formation - RPF) occurred. The location of the nucleation centers on the surface in such a structure tends to be the most dense, quasi-hexagonal arrangement of pores [Emel'yanov and Starkov, 2006]. The diameter of the cross section of microchannels is defined by the specific Si resistance, the distance between the pores (wall thickness) depends on the current density of the anodic etching and the depth of the microchannels is defined by etching time [Starkov et al., 2001]. Fig. 1 shows a general view of microchannel structure for a control sample formed in the Si with p-type conductivity and resistivity $\rho_v = 25\ \Omega$ cm. Etching was performed in the RPF mode at a current density of 5.5 mA/cm^2 in a solution of HF: DMF = 1: 10 for 60 min. The porous layer thus formed had a thickness of 45 µm, a pore diameter of 1.7 µm, and a pore density of 12.25×10^6 cm^{-2}. The presented structure increases the observed surface area by 30 times. By increasing the etching time up to 200–210 min the etching depth or the thickness of the porous layer increased up to 155–160 µm. This increases the effective area of the p-n junction, formed on the surface of the chip with a size of 1 cm^2 to more than 100 cm^2.

For the manufacture test samples of microchannel BVC structures Si was used with higher resistivity 1000 Ω cm, and the plate thickness was 200 µm. Anodic etching plates were placed in the RPF mode at a constant current density of 6 mA cm^{-2} in solution HF: DMF = 1:10, with the etching time of 240–250 min. The depth of etching samples was 160–163 µm, and the average microchannels sectional diameter was 5–6 µm. The average distance between pore centers was 10 µm (Fig. 1).

These geometric characteristics of microchannels with quasi-hexagonal arrangement on the surface of the examined structures provide a surface area of not less than 50 cm^2. To form the relatively shallow structure of the p-n junction on the developed microchannels surface it phosphorus diffusion was carried out at 900 °C for 10 min in an argon stream. The depth of the junction was 0.4–0.5 µm, with a surface resistance of 26–32 Ω/□. The usage of the gas diffusion process allows to dope Si sufficiently homogeneous across the depth of the microchannel structure; thus the structure was characterized by the required homogeneity along the walls of microchannels, which was confirmed by the electron microscopy analysis of the p-n junction cross-section of the induced current.

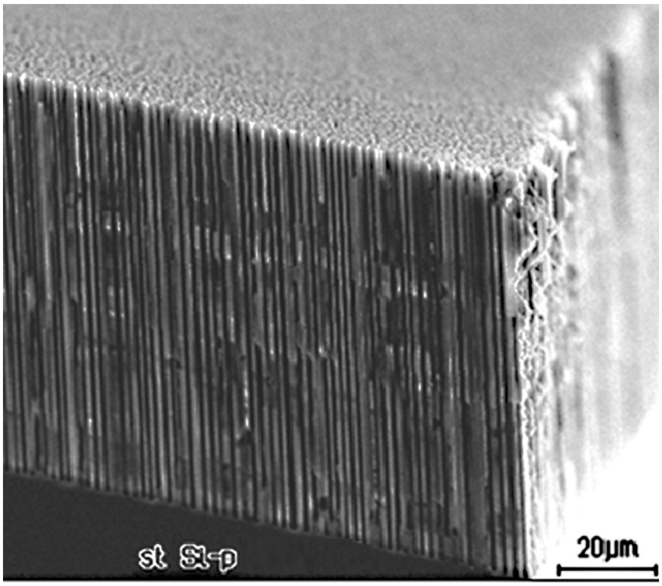

Fig. 1. The cleavage image of the microchannel structure formed in the RPF mode after phosphorus diffusion. Etching depth is 45 µm, and pore diameter is 1.7 µm.

3. Results and discussion

The p-n junction at the microchannels bottom was investigated by a scanning electron microscope (SEM) in the induced current mode. The evaluations show that the space charge region (SCR) width is about 7.7 µm and that the SCR overlap occurs in neighboring microchannels. This fact helps to reduce the recombination losses in the lateral regions of the structure.

Nickel has an acceptable electrical conductivity, and by forming a continuous metal film on the surface of the developed microchannel, it serves as an acceptable electron collector. The maximum thickness of the deposited layer of the ^{63}Ni radioisotope is determined by its self-absorption, and should not exceed 2.2 µm [10].

Thee preparation of macroporous Si included: degreasing by dimethylformamide (DMF) and treatment (2 min) in a concentrated solution of H_2O / NH_4OH / H_2O_2 (5: 1: 1) at 75 °C to remove organic contaminants. Silicon oxides are removed from the surface by treatment with an HF (5%) aqueous solution.

Stable Ni was used for the Ni deposition process onto the inner surface of micropores. The incorporation process of Ni into porous Si structure is described in the literature in considerable detail [Granitzer and Rumpf, 2010; Xu et al., 2007; Zhang et al., 2006; Gorostiza et al., 2000; Dolgiy and Kholostov, 2009]. Typically, the cathodic process is used for this purpose. Depending on the pores morphology (diameter, aspect ratio, pore density, Si type) the optimum current density stationary or galvanostatic pulse power mode frequency and pulse duration are chosen.

For Ni deposition into macropores [Dolgiy and Kholostov, 2009] used the galvanostatic cathodic deposition mode of the electrolyte composition 0.6 M $NiSO_4{\cdot}7H_2O$ + 0.3 M H_3BO_3 at a current density of 10 mA/cm^2. A Ni layer was successfully formed on an inner surface diameter of 1.5 µm and the microchannels nickel tubes with a wall thickness of 0.5 µm to the entire depth of up to 25 µm were achieved.

A similar result was obtained in the present work in the Ni layer deposition on the inner surface of the substantially deeper microchannel diode structures formed by the RPF process. The process involves the formation of a Ni layer by substitution for Ni-Si from an aqueous electrolyte composition of 154.76 g/l $NiSO_4$ + 92.55 g/l NH_4F + 0.88 g/l with the addition of coumarin sodium lauryl sulfate as the wetting agent at the thermo-galvanostatic mode at a current density of 10 mA/cm^2 and the deposition temperature of 60 °C.

By using arbitrary cleavages, the depth of microchannels in the samples was defined and it was found to be 154 − 163 µm. The SEM analysis results of the Ni layer deposition in 3D microchannel diode structure are shown in Fig. 2.

Fig. 2 shows a rather homogeneously thick Ni film with a closed form at the bottom of the tube. The wall thickness of Ni coating is 1 µm, and the internal diameter of Ni tube is 4 µm. Fig. 2b shows the Ni layer structure.

The general assessment of the homogeneity process of filling the RPF microchannels with Ni was carried out by microprobe analysis using a SEM (TESCAN VEGA LMH). Fig. 3 shows the microanalysis images of RPF sample surface of microchannel Si metalized with Ni, in modes of the various characteristic emissions (Fig. 3a–c). Fig. 3d shows