Plasma chemical silicon etching process

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Abstract. The cryogenic plasma chemical silicon etching process is developed, able to form the structured silicon layer with system of deep holes with high aspect ratio.

Keywords: betavoltaic element, p-i-n diode, cryo process, scalloping.

Introduction

The articles [2-5] studies silicon diode structure characteristics and their production methods, applicable for neutron detector creation. Shown, that planar epitaxial diode structures with narrow junction field region has leakage at the level ~ 1 uA/cm². In the same p-i-n diode structures with wide junction field region, leakage can be obtained at the level of 20 nA/cm².

It would be logical to assume, that if the structured silicon layer with formed on surface contiguous p+ layer gets to depletion area, it can not increase the leakages. It is clear that an area of junction will be greatly grow. Such variant of the structure was simulated in [1], that it confirms of idea about possibilities of the location of all structured silicon layer in the field of p-n junction, and maintaining leakage current at low level, that is typical for the planar p-i-n structure.

In this research, authors decide one of the basic task: research about possibilities of the high-aspect etching for forming of the structures with the developed geometry.

Methods of creation silicon structures with high aspect ratio

Usually for silicon structures with deep holes used Bosch-process of plasma-chemical etching, widespread for production of microelectromechanical and nanoelectromechanical systems (MEMS and NEMS).

It is based on two-step cyclic process of plasma etching with a step of forming structure walls passivation and a step of its anisotropic etching. As a result, holes could be formed with a depth up to hundreds of microns in silicon. However, this method has some features, that can not always be combined with the requirements of micro- and nanoelectronics.

In particular, it is inevitable effect of scalloping walls, i.e. a type of roughness, which has a form of regular circular grooves (Figure 1).

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Figure 1. Typically cross-section view of etched, Bosch-process.

This disadvantage could be flattened by reducing the duration of steps; however, it is impossible to completely get rid of it. If one form p-n junction on such surface side, it would be inevitably lead to increase the leakages in sharp places because of the field-effects.

The second feature is stubborn remnants of a thin polymer film in the holes (~1-3 nm). It polluting surface and has the potential opportunity to affect on the electrical characteristics of this structure. Therefore, in this research, we investigated the possibilities of another process, in particular the cryogenic process of deep plasma-chemical etching of silicon. Using of the cryogenic etching permits to get the structures with high aspect ratio and smooth walls. This method permit to use a plasma SF$_6$O$_2$ without gases that produce a polymers (such as different freons) and without modulation plasma composition during the etching process.

In particular, low temperatures (from -100°C to –130°C) permit to eliminate the isotropic spontaneous etching of the structure sidewalls by atomic fluorine, which carry out with purely chemical isotropic mechanism. As the result, it has the Arrhenius temperature dependence. Besides, for the same reason that one can achieve high silicon etching selectivity relative to the rigid mask of photoresist or silicon dioxide. During etching, oxygen formes protective coating composition SF$_x$O$_y$ on the sidewalls, which prevents spontaneous etching by fluorine. The continuous process of cryogenic silicon etching is completely devoid of effect “scalloping”, that permits to get etching structure with a minimum roughness of the walls. In this paper, wall roughness after etching of silicon in cryoprocess was investigated by authors.

An additional advantage of this process is the potential opportunity to permit managing etching profile (angle of inclination a wall). For etching on the specified depth is necessary apply highly selective lithographic mask. Use of an aluminium oxide mask was proposed. In the fluorine-containing plasma, the aluminium oxide forms non-volatile aluminum fluoride, which ensures high selectivity etching process.

Mask of aluminium oxide was deposited by atomic layer deposition method. As the organometallic precursor was used trimethylaluminium; as the oxidative precursor was used oxygen plasma.

To produce the structures was used templates for contact optical lithography with «honey comb» structure with 5 um holes in diameter. Deep etching performed with the chamber with cryogenic table through the mask of aluminium oxide with autopsied windows. The plate temperature was maintained at -110°C.
Firstly, the technological process was fine-tuned on etching holes, as it is easier to get a cross-section image. The etching result shows in a figure 2. The image shows that the obtained vertical walls have depth of 40 μm, with a small positive angle of 89 deg., the size's offset does not exceed of 20 nm. The selectivity with a respect to the mask is better than 1:30000. The wall roughness study shows that this quantity is at most of the surface of the walls, with the exception of adjacent to a mask fields, and doesn’t exceed the resolving power of scanning electron microscope (SEM), i.e. it is in the range 1-3 nm.

![Figure 2. Cross-section view of etched by cryogenic process holes.](image)

Designed cryo process was used for etching the structure with holes (Figure 3). The image shows that the desired structure holes without distortion geometric dimensions was achieved. Unfortunately, for this pattern is difficult to get a split, which perpendicular to the surface, and observe the etching profile without geometric distortion. However, carried out investigations permit to estimate the depth of the etching, offset of the sizes and the verticality of hole's walls.

![Figure 3. The structures of cylindrical holes, received with cryogenic etching (View up- left, split – on the right).](image)
Further progress in the betavoltaic power source creation consist in practical realization of the formation of the radioactive $^{63}$Ni continuous layer on the inner surface of the holes. The process technology of not radioactive nickel deposition into the pores is known and described in detail [6].

**Conclusion**

It was developed a cryogenic process of plasma-chemical etching silicon, which permits to develop the structured silicon layer, with a system of deep holes (5 um in diameter) with a depth of 45 um. The silicon layer has the necessary parameters for creating a microstructured 3D p-i-n junction with low reverse current. It permits to suggest, that made by PIII method p-n junction with a wide depletion area would be had leakages, acceptable for betavoltaic power source.

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