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Photovoltaic Cells based on Textured Silicon

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The paper describes a chemical etching technique as one of the promising methods to create Si nanostructures. The aim of this work is the development of Si photovoltaic converters using modern resourse-saving manufacturing methods for silicon micro- and nanostructures based on isotropic and anisotropic chemical etching techniques. It is shown that proposed surface texturing technique gives 23.15% increase in conversion efficiency of the solar cells.

Keywords: Silicon nanostructures, Photovoltaic cell, Isotropic and anisotropic etching.

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1. INTRODUCTION

Nowadays there are a lot of growth technics for nanostructures including molecular beam epitaxy, a laser based catalytic growth, growth from supercritical phase of liquid solution, laser ablation or simple evaporation [1-3]. However, these methods are energy-consuming and expensive. Therefore one of the major problems in the development of nanotechnologies for subsequent use in nanoelectromechanical devices is using cheap technologies to create Si nanostructures. One of these technologies is a chemical etching, which has been compatible with the technology of manufacturing the micro-and nanoelectronic devices for a long time[4, 5].

The aim of this work is the development of Si photovoltaic converters using modern resourse-saving manufacturing methods for silicon micro- and nanostructures based on isotropic and anisotropic chemical etching techniques.

2. FORMATION OF SI TEXTURED SURFACES BY CHEMICAL ETCHING

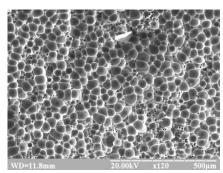
We have developed a technique for creation of textured surface for solar cells based on isotropic chemical etching [6]. In order to obtain surface textures by chemical method for solar cells, using annealing we create thermal oxide on the surface of silicon wafer. Using the photolithographic method, we obtained a grid of small windows on the surface with a clearly defined period, that is followed by isotropic chemical etching at room temperature, horizontally immersing the sample in a Teflon tub of acid solution, which is placed in an ultrasonic mixer.

Reducing the cost of surface textures of solar cells leads to exclusion of photolithography from the manufacturing process, which is the most expensive part of a solar cell manufacturing. Reducing the number of technological steps and the exclusion of complex equipment leads to simplification of the overall process.

However, this complicates the technological component of the etching process and results in apply-

ing of additional components of etchants as surface activator and inhibitor of the surface reactions of etchant. In that case, the entire process comes down to one multistage etching, while the number of additional components in the solution could increase up to ten.

Since the development is based on the crateriform's surface, it is necessary to make clear the basis of the process of crater's formation. A gradual etching of the material, step by step, leads to the formation of an ideal hole with ellipse shape. If necessary, this type of geometric model can be defined by mathematical methods. We have two sizes that are easy to change technologically – it's depth and diameter of the semi ellipse. Such technological approach essentially simplifies the entire development process and leads to the creation of chemical surface texture (see Fig. 1).



 ${f Fig.}~1-{
m SEM}$ image of textured silicon surface

Creating the texture on the front surface of the silicon wafer by chemical etching in combination with further diffusion of dopant through its volume allows to get profile of the p-n junction with a complex shape and achieve a significant increase in the effective surface area for the volumetric space charge (VSC). The photocurrent of solar cells increases proportionally to the increase of volumetric space charge. This is the cause of increasing output power of solar cells and leads to an increase in the value of the photoelectric conversion efficiency, and provides the following benefits:

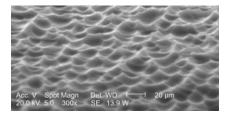
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1) using the porous silicon that is used in the solar cells structure increases its photoactive area and volumetric space charge, also it is technologically simpler than similar methods which require long anisotropic etching, laser or mechanical processing of the surface of solar cells, and the application of special textured layers;

2) using of the proposed organic supplements accelerates chemical interaction and eliminates the need for large amounts of expensive additional component of the solutions (e.g. H_3PO_4) and intensifies the etching in the depth of the material.

The creation of the texture on the front surface of the silicon substrate is based on the chemical interaction of silicon monocrystal with the components of the solution (concentrated acids). Adding small amounts of organic compound with functional amide group improves humification of the surface of material by working solution, and, therefore, facilitates the etching and stabilizes these processes. As a result of complex chemical interaction it becomes possible to obtain the desired shape of the texture more quicker (Fig.2).



 $\mathbf{Fig.}\ \mathbf{2} - \mathbf{SEM}\ \mathrm{image}\ \mathrm{of}\ \mathrm{pyramid\text{-}textured}\ \mathrm{silicon}\ \mathrm{surface}$

The resulting texture has low integral reflection coefficient of the light flux from the surface, is well passivated, and is well handled for further technological processing to obtain the resulting device.

Eelectrolyte creation features: this process is modulated by the ratio of acids HF/HNO₃. According to the dependence of reaction rate on the percentage of acid in the solution you choose needed composition of base solution for etching on the left or right branch of dependence of reaction rate on the molecular ratio of these acids (see Fig.3).

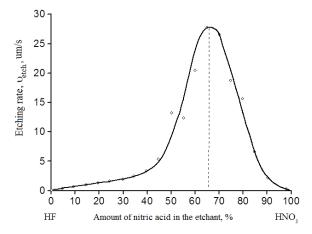


Fig. 3 – Dependence of etching rate on the ratio of acids in the etchant HF/HNO $_3$: 0–100% HF, 100–100% HNO $_3$

chosen basis for preparation of the technological etching solution of the substrate in most cases was located to the right from the curve's extremum so amount of HF prevailed in the electrolyte. It is explained by the fact that HNO₃ acts as oxidant for the silicon surface and forms dense thin layer of SiO₂ on it, which later was being etched with hydrofluoric acid and formed H₂SiF₆. Despite the classical isotropic etchant, which often has large quantities of acetic acid as a supplement that acts like a solvent and inhibitor of the reaction, in the model of the technological process the amide compound dimethylformamide (DMF) was proposed for use as a surface activator, which also partially serves as the inhibitor of the reaction. This substance has the ability to moisten the surface of the silicon non-interacting with it and thus contribute to the adsorption on her of the solvated ionic complexes that oxidizes and then etches this surface, creating a desired texture.

During the chemical interaction the nitrogen oxides is being formed and rapidly diffuses to the surface of the solution and mixes it. Adding the activating annex initially stimulates the process of forming the texture, but its content more than 3-5% in the solution has a negative impact on these processes. This can be explained by the interaction of the organic supplement with the concentrated $\rm HNO_3$ and its oxidation that leads to depletion of the solution on $\rm NO_3^-$, and consequently to slow down the etching processes of the surface. Textured surface in PV devices is necessary to minimize these reflection loss and maximal increase of the spectral range of solar cells.

We have used the technological stages of anisotropic etching and texturing of the surface for (100) silicon solar cells. Microrelief of the surface in this case, consists of randomly located tetrahedral pyramids with different sizes.

3. MODELS OF PHOTOVOLTAIC CELLS BASED ON TEXTURED SILICON

To create a textured solar cells the anisotropic chemical etching of silicon wafer was performed. For texturing of (100)-oriented surface of solar cells in the form of randomly spaced tetrahedral pyramids were used anisotropic etching technology. Light which flows on the textured surface, usually falls on the side of one of the pyramids, partially passes through it under the certain angle, reflects in the other side of the pyramid and completely absorbed by it. This pattern of optical absorption in comparison with the absorption of solar cells with planar surface allows to achieve two important advantages:

1) optical reflectance value of solar cells surface decreases from ~35% (for a flat surface) to ~20% (for textured surface) that leads to the growth of short-circuit current:

2) not perpendicular light beam entering towards the solar cell enables to absorb closer to the VSC, making optimal use of textured surfaces for "violet" solar cells.

Fig. 4. shows the structure of the solar cells, which uses the above mentioned features: a textured front surface; optimized design of contact combs; increased photosensitivity in violet part of the solar spectrum;

electric field "built at" the back surface. The result of this modernization of the structure of solar cells increased its efficiency up to 17%.

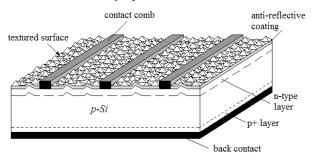
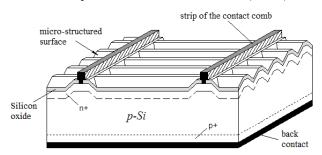


Fig. 4 - The structure of textured silicon solar cell

Minimization of the contact surface area is the most efficient method for reducing the recombination loss at the metal-semiconductor. Thus, solar cells with the high-quality emitter passivation and reduced contact area near the workspace of semiconductor (Fig. 5) were identified as passivated-emitter solar sells (PESC).



 ${\bf Fig.~5}$ – The design of the passivated emitter solar cell (PESC) with mechanically micro-structured front surface.

Reducing the influence of surface recombination on the absorption efficiency of photogenerated charge carriers in PESC allowed to use more widely the advantages of high-quality silicon substrates for well-known structures of solar cells. As a result, the efficiency of PESC based on high-quality silicon substrates obtained by floating zone process exceeded 20%.

4. CONCLUSIONS

We established that an effective tool for influencing the functionality and texturing of photovoltaic cells is the use of chemical etching of the surface of silicon substrate. It was shown that modified isotropic and anisotropic etching methods are applicable to create a microrelief on the surface of silicon substrate. In particular, the randomly located tetrahedral pyramids ("Honeycomb"-structures) with various size and porous textures could be obtained.

The solar cells models based on mono- and multicrystalline silicon substrates using functional porous silicon were developed and manufactured. The conversion efficiency of these models are $\sim 18.6\%$ at AM 1.5 in spectral range of 400–1000 nm. The conversion efficiency of solar cells of "Honeycomb"-structures with antireflective coating increased up to 23.15% (from 13.01% to 16.42%).

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