

Investigation of frontal functional nanolayers of solar silicon using electrochemical technologies of porous silicon

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Introduction

The aim of this work was to develop and study frontal functional nanolayers of solar silicon (SC) using electrochemical and chemical technologies of porous silicon (PSi) to obtain efficient and cost-effective technological processes for the production of photoelectric converters of sunlight. These technological processes should be adapted to the processes of production of silicon solar cells. In this study, an in-depth analysis of existing PSi models was performed to obtain frontal functional nanolayers of solar cells. As solar energy comes from an unlimited source, the energy capturing process is pollution-free and the technology is established, it stands out amongst the other alternatives as the brightest long-term promise towards meeting the growing demand for energy. One of the more promising methods among the many alternatives is employing solar energy to provide clean auxiliary energy. It is now widely accepted that the rapid reduction of fossil fuel resources together with global warming treaties has necessitated an urgent search for alternative energy sources to partially or completely meet our demands for fossil fuels in the future. When using porous silicon as a texture and anti-reflective coating, the porous layer is formed directly on the silicon surface and along with the enlightenment, it must also provide passivation of the surface of the FEP. However, research in this area has shown that the passivating properties of porous silicon are insufficient to minimize surface recombination. The study of all stages of formation of the porous structure on the basis of the chosen technology and identification of patterns that affect the characteristics of the obtained nano-, meso-, macropores, are very important because most parameters of porous layers are laid at the initial stage. Partial improvement of the passivating properties of porous silicon was achieved by thermal and anodic oxidation of the porous layer, as well as by plasma spraying on its surface of silicon nitride. However, none of these methods allowed to achieve the required level of surface passivation and its stabilization over time. Electrochemical hydrogenation (ECG) in hydrogen-enriched electrolytes can be a more effective method of improving the passivating properties of porous silicon. With this treatment, efficient hydrogenation of broken bonds at the interface between porous silicon / monocrystalline or polycrystalline silicon can be achieved, which will help to reduce the rate of surface recombination. Compared with other methods of hydrogen saturation, electrochemical hydrogenation has a number of advantages. First, it can be combined with the anodizing process and will not complicate the technology of manufacturing FEP. Second, electrochemical hydrogenation is a controlled process that allows the penetration of hydrogen atoms into the volume of the semiconductor to a given depth and the passivation of broken bonds without damaging its crystal lattice. The aim of this work is investigation of frontal functional nanolayers of solar silicon using electrochemical technologies of porous silicon on the surface of a silicon multicrystalline substrate of the Baysix type, which can be used to create highly efficient solar cells.

To achieve this goal the following tasks were set:

Analysis of existing technologies for creating porous silicon;

Development of an efficient and cost-effective coating that should be maximally adapted to the processes of creating silicon solar cells;

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The study of all stages of formation of the porous structure based on the chosen technology and identification of patterns that affect the characteristics of the obtained nano-, meso- and macropores are very important, as most parameters of porous layers are laid at the initial stage. When using porous silicon as a textural and anti-reflective coating, the porous layer





Hiol HF solution

is formed directly on the surface of silicon and together with the antireflective coating it must also provide passivation of the surface of the solar cell (SC). The introduction of porous silicon into the structure of solar cells (SC) will allow to control their conversion efficiency while reducing the cost of energy produced and achieve a goal that would consistently increase their conversion efficiency while reducing the cost of SC. Functional porous materials can be obtained in the form of layers with a sufficiently large range of porosity, with a pore diameter of nanometers to tens of micrometers. Their creation is based on electrochemical and chemical production technologies. The use of nano-PS layers will simplify the technological cycle, reduce the cost of the product and improve performance, and will increase the efficiency of SC manufacturing technology. We can compare the surfaces of multicrystalline silicon samples before and after hydrogenation in hydrogen in an electrolyte based on hydrofluoric acid, both in the spectra of secondary ions and in the images of the distribution of elements on the surface, ionic microprobe mode and mass spectral ionic microscope. Silicon surface texturing, both chemical and electrochemical etching, is an integral part of modern high-performance silicon SC technology. The texture on the front surface of the SC not only reduces reflection losses, but also helps to capture long-wavelength light in the structure of the SC, thereby expanding its operating spectral range and increasing the short-circuit current. Of particular interest is the study of the PSi layer in nanotextures by mass spectroscopy on the functional properties of the pre-textured frontal silicon surface. Electrochemical hydrogenation in hydrogen-enriched electrolytes may be a more effective method of improving the passivating properties of PSi. With this treatment, efficient hydrogenation of broken bonds at the interface between PSi/monocrystalline, polycrystalline or multicrystalline silicon can be achieved, which will help reduce the rate of surface recombination. Compared with other methods of hydrogen saturation, electrochemical hydrogenation has a number of advantages. First, it can be combined with the anodizing process and does not complicate the technology of SC manufacturing. Second, electrochemical hydrogenation is a controlled process that allows hydrogen atoms to penetrate the semiconductor volume to a given depth and passivated broken bonds without damaging its crystal lattice. In order to improve the passivating properties of PSi layers used in SC, a study of the process of electrochemical hydrogenation of PSi was performed both on p-type silicon substrates with a resistivity of 0,1...10 Ohms and on substrates with formed emitter transition n + -p conductivity.

Fig.1. The surfaces of multicrystalline silicon samples for solar cells.





Fig. 2. The process of obtaining a texture based on porous silicon with columnar pores.

Fig. 3. Photo of the frontal surface of a silicon sample obtained using an electron (SEM) microscope with a texture based on porous silicon with columnar pores.

Study of Frontal Functional Nanolayers of Solar Cell by Mass Spectroscopy

A number of samples (9 samples) were measured depending on the treatment time in an electrolyte based on hydrofluoric acid and ethanol. Hydrogen passivation of the surface of Baysix multicrystalline samples took place in an electrolyte based on hydrofluoric acid (HF:C₂H₅OH=10:1) at a stable current of 1 mA/cm². Processing modes: sample №1 – 10 min.; sample №2 – 25 min.; sample № 3 – 45 min.; sample № 4 – 55 min.; sample № 5 – 80 min.; sample №. 6 – 95 min.; sample № 7 – 110 min.; sample N $_{2.8}$ – 140 min.; sample N $_{2.9}$ – 160 min. The amount of hydrogen on the surface of the samples was measured by the relative intensity of the current of secondary of hydrogen H2+ ions and the current of secondary ions of molecular SiH₂⁺ for the surface passivated with hydrogen by the hydrogenation method. Analysis of hydrogenation modes based on the relative current intensity of secondary H_2^+ hydrogen ions on the surface of multicrystalline Baysix silicon samples shows that hydrogenation reaches saturation after 2 hours. processing The relative amount of molecular SiH₂⁺, recorded by the intensity of the secondary ion current, does not change with the processing time. An experiment was conducted on etching the surface of a hydrogenated multicrystalline silicon substrate of the Baysix type in dynamic mode on a TOF5 SIMS mass spectrometer with the determination of the amount of hydrogen from the surface to the depth of the studied sample. Sample No. 8 was selected for etching, as one of four samples, № 6, № 7, № 8, and № 9, which showed saturation according to the relative intensity of the secondary H_2^+ hydrogen ion current in the previous experiment. The passivation of multicrystalline sample № 8 with hydrogen lasted for 140 minutes. in an electrolyte based on hydrofluoric acid (HF:C2H5OH=10:1) at a stable current of 1 mA/cm². During the surface etching experiment in dynamic mode, secondary ions Si, H_2^+ and CH_3^+ were recorded. As it should be, the intensity of secondary Si ions does not change. The fact that this is not a surface contamination means that the intensity of secondary ions on silicon is constant (in the case of surface contamination, we would see a minimum of silicon). The concentration of hydrogen, determined by the intensity of secondary H₂⁺ ions, is higher on the surface and monotonically decreases deeper into the sample, but where this hydrogen is concentrated (for example, at the boundary of grains or blocks of a multicrystalline substrate) cannot be determined, the scanning area is too large - 1000 x 1000 μ m² and the final the result is centered on it.



Fig. 4 Relative intensity of the current of secondary ions of H2+ hydrogen and the current of secondary ions of molecular SiH2+ for a surface passivated with hydrogen by the hydrogenation method.

Fig. 5. Picture of the TOF5 SIMS mass spectrometer dial window of the surface (206 x 206 μm2) of a Baysix-type multicrystalline silicon substrate in dynamic surface etching mode. Intensity (counts) – intensity (number of pulses read). Time(s) – surface etching time in seconds.

Conclusions

The best thing in this work is to use a mass analyzer, which is tuned to a certain mass, the signal from which is used to modulate the monitor, the scan of which is synchronized with the scan of the ion beam. Analysis of hydrogenation modes based on the relative current intensity of secondary H_2^+ hydrogen ions on the surface of multicrystalline Baysix silicon samples shows that hydrogenation reaches saturation after 2 hours. processing The relative amount of molecular SiH₂⁺ recorded by the intensity of the current of secondary ions does not change with the processing time. The study of all stages of formation of hydrogenated porous structure and identification of technological patterns that affect the characteristics of the obtained nano-, meso-, macropores are very important, because most of the porous parameters are laid at the stage of formation of nucleation (seed) centers. Etching of the surface of a hydrogenated Baysix type multicrystalline silicon substrate in dynamic mode on a TOF5 SIMS mass spectrometer with determination of the amount of hydrogen from the surface to the depth of the sample under study, which is greater on the surface and monotonically decreases in the depth of the sample, where this hydrogen is concentrated (for example, at the boundaries of grains or blocks of the multicrystalline substrate).Thus, we obtain a 2D image (size 200x200 µm) of the surface of the current of secondary ions of molecular SiH₂⁺ surface passivated by hydrogen by hydrogenation of the multicrystalline substrate Baysix.

