Synthesis of silicon nanowires using plasma chemical etching process for solar cell applications

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Abstract. Recently, research on silicon nanowire solar cells has been developed rapidly and it is one of the very young research fields. The production of highly oriented long silicon nanowires is a challenging task. Here, in this article we report the optimization of successful synthesis of highly oriented long silicon nanowires on silicon substrates by plasma chemical etching process. The produced silicon structures were firstly examined using scanning electron microscopy (SEM). The SEM results clearly show the highly oriented nanowires on the silicon substrate. The flowing carrier gas, temperature, pressure and voltage are main parameters responsible for the formation of the silicon nanowires. The successful synthesis of silicon nanowires shows bright perspectives for further research on silicon nanostructure properties.

1. Introduction

Nowadays, silicon nanowires (SiNWs) are of the great interest due to their special properties and wide range of potential applications in different fields of science. For example, they can be used in biosensing structures as well as in chemical-sensing, in photovoltaic, microelectronic and etc. Properties and parameters of silicon nanowires must be taken into account for use in the manufacture of optical devices [1]. The article [1] provides reader with some information on solar cell application. Some researchers use the thin-film technology to present the use of grating structure for the enhancement of optical absorption [2-3].

In nanowire structure the charge carriers (photo-excited electrons and holes) travel very short distance before being collected by the electrodes. As a result, higher conversion efficiency were obtained in the nanowire structure. It allows to use lower quality silicon because of the higher tolerance of the material defects. The core-shell structure of the silicon nanowires solves the problem of charge carrier collection, this is one of the key factor that affects on the efficiency of the solar cell. There is another key factor – efficiency of the photon capture in the nanowire structure, but this parameter is not determined yet.

There are several methods to obtain cone or peak like structure on the surface of the sample. Some research groups have developed and used different methods to get pillars with nanometer range [4-6]. A standard method is to use lithography techniques, but it is limited by resolution of this method. It can be overcome by using the methods using shorter wavelengths. Using electron beam lithography with special resists it possible to produce 10 nm silicon pillars on the surface [4]. Another possible
technique for producing nanowire structure on the surface is the plasma chemical etching, also known as Bosch-process. It has its own advantages. Unlike liquid etching, etching is performed anisotropically, regardless of the crystallographic planes of the object being processed. However, obtained walls have a rough surface [7].

Bosch process is a cyclical process consisting of two stages. The first stage is the etching stage in which fluoride ions formed from SF₆ gas react with silicon to form the SiF₄ gaseous compound, which is pumped out of the system by vacuum pumps. Etching process is isotropic. The etching stage is followed by a passivation stage. At this stage, the plasma is created from C₄F₈ gas. C₄F₈ ions form a polymer similar to Teflon, which is deposited on the sample surface. This polymer does not react with the etching plasma and provides protection against further etching for the silicon that is under it. Before the next stage of etching, this polymer must be removed from the bottom of the etched groove. For this purpose, ions are used that move under the action of an electric field practically along the normal to the bottom of the groove and knock the polymer from the surface. Thus, the polymer is removed only from the bottom, and the groove walls remain protected from etching. Further alternation of the processes of etching and passivation allows anisotropic silicon etch to the desired depth [8].

The purpose of the work is to obtain the necessary properties and parameters to get the silicon nanowires on the silicon surface using the plasma chemical etching (Bosch-process).

2. Experiment

In this work, we used silicon substrates previously purified with HF acid. The next step was to fix the substrate on the stand. This should be done as carefully as possible in order to have a tight fit. Otherwise, the formation of the desired structures may not begin. After that, air was pumped out of the chamber. The state of vacuum was obtained by two pumps: air and liquid. After selecting the parameters, the process was started. The ratio of gases maintained at 1:1, the time of etching selected for 3.5 seconds and passivation for 2.1 seconds. During the experiment, four cycles of 20 Bosch-process cycles were performed. Between each of the four cycles there was a pause of 1 minute. It should be noted that this process of obtaining structures is extremely unstable and depends on a large number of parameters. Having the same voltage, different results can be obtained in different experiments. It depends on the fact that in some cases there is an uncontrolled re-passivation process, which results in the presence of SiNWs. The schematic representation of plasma chemical etching system is shown on Figure 1.

![Figure 1. Schematic representation of the plasma chemical etching chamber for SiNWs growth: 1 – C₄F₈; 2 – SF₆; 3 – pumping system; 4 – chamber; 5 – sample; 6 – gas flows; 7 – ICP plasma source; 8 – cooling system; 9 – RF electrode; 10 – pumping chamber system.](image-url)

After finishing of cycles the process stops. The gaseous supply is stopped resulting the formation of plasma is also stopped. Air is pumped into the chamber to restore atmospheric pressure. As soon as pressure is restored, it becomes possible to remove the sample from the chamber. The presence of the desired SiNWs can be identified by the colour of the mordant. The chance of positive result is higher with the black colour of the sample. After that, it is possible to analyse the obtained sample using a scanning electron microscope and other characterization techniques. Considering all the previous
results and after optimization of process parameters, it was possible to achieve a needed result. The optimal value of the ICP inductor source power was 205 W, the source frequency was 13.56 MHz. It was also possible to vary the pressure value in the etching chamber during the experiment. The varied pressure range varied from 0.216 mbar and higher.

After experimentation, the number of passivation and etching cycles were varied for the needed optimize results. From previous results, it was observed that there was need to increase the number of etching cycles till 100 with the oxygen (O₂) supply to the chamber, and then another hundred cycles without the oxygen supply to the chamber. About a minute passed between these series of cycles, while the substrate was not removed from the plasma-chemical etching chamber.

This time the etching took place without the use of a mask dividing the substrate into zones, as well as without a ceramic clamp. The etching took place on the entire surface of the sample. Cooling was maintained stable. The time of the passivation and etching steps are changed to achieve the best result. The passivation time was kept 4 seconds and 2.3 seconds for etching, respectively. The complete process of growing SiNWs on the sample surface took 28 minutes. After the process was completed, air was again inserted into the plasma-chemical etching chamber to equalize the internal and external pressure. After which the substrate was removed. A primary visual inspection showed that SiNWs may appear on the sample surface.

The sample was conditionally divided into several zones, which later underwent a more thorough study.

3. Results and discussion
The used technology allowed us to create the needed structures on the substrate surface. Fig.2 and Fig. 3 clearly showed the obtained structures on the sample surface. These obtained structures can be detected by use of scanning electron microscopy. The resulting peaks are the result of a cyclic process. The average thickness of obtained SiNWs on surface of sample is around 714 nm and it is shown in Fig.4. Fig.5 shows different NWs structure at two different locations named as Area 1 and Area 2 respectively.

**Figure 2.** SiNWs on the sample surface (Fragment 1, SEM).

**Figure 3.** SiNWs on the sample surface (Fragment 2, SEM).

**Figure 4.** SiNWs on the sample surface (Fragment 3, SEM). The typical size of the peak is marked. Average thickness is around 714 nm.
Figure 5. The general view of the sample with SiNWs: 1 – First area of SiNWs location, 2 – Second area of SiNWs location.

Figure 6. Area with SiNWs on the surface of the sample with a magnification of 40,900 times.

Figure 7. Area with SiNWs on the surface of the sample with a magnification of 29,900 times.

Fig.6 and Fig.7 shows SEM images of obtained SiNWs structures at different magnification to provide clarity to viewers. The obtained samples were investigated with the use of spectrophotometry. The Shimadzu UV-2450 spectrophotometer (Kyoto, Japan) has been used in the range of 350 nm to 950 nm which is useful for photovoltaic applications.

Figure 8. The reflection spectrum of Area 1.

Figure 9. The reflection spectrum of Area 2.
The reflection spectrum is taken on two areas and are shown in Fig. 8 and Fig. 9 respectively. Part of reflected energy varies from 0.8 % to 2.5 % for Area 2, while it varies from 0 to 0.17% for Area 1. Area 1 has reflection spectrum nearly like absolutely black body for visible range. It is clear from results that Area 2 has higher reflection percentage in visible part of spectrum and it is already known that higher reflection percentage results lesser absorption in nanowire structures.

4. Conclusion
Used technology allowed us to obtain peak-like surface, but the technological Bosch-process to be optimized. Further experiments will be directed to find the optimal values of etching time, temperature and gas flow ratio to obtain better structure. Besides, UV-spectrometry will be used for additional characterization of samples.

5. References
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