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Abstract

The results of the experiments on the "black" *mc*-Si surface fabrication by the nanosecond pulses of the YAG laser second harmonic and on application of the introduced laser texturing method for the *mc*-Si solar cells efficiency improvement are represented. The developed version of laser texturing permits producing a low-reflection *mc*-Si surface with the reflectance of ~3% in the spectral range of 0.3-1.1 μm. The application of the introduced laser texturing method in *mc*-Si solar cells fabrication makes it possible to increase the short circuit current density and quantum efficiency.

Introduction

Nowadays laser systems are widely used in various industrial processes owing to the unique features of laser radiation: selectivity, monochromaticity, high energy density in a pulse, etc. The precise control of the spatial, temporal and energy parameters of the laser beam allows operating different processes which occurre in semiconductors under laser action [1,2]. In addition, the application of lasers in technological processes instead of industrial ones makes it possible to reduce the total cost of production lines [3].

The main task of photovoltaics is to reduce the cost of electricity produced by solar panels. The most obvious trend in the manufacture of solar cells is replacing most expensive technologies with new ones. That is why the investigations are currently being carried out to use the laser technologies in different stages of solar cells fabrication: creation of contact structures (laser scribing for buried contacts, laser-fired contacts, depth-selective laser ablation, thin-film selective removal), surface texturing to reduce reflection, deposition of transparent conductive oxides, laser doping, etc [4-12]. The application of laser radiation for crystalline silicon solar cells manufacture is especially prospective for the following reasons. The technologies of silicon solar cells production are almost perfected, and the struggle for fractions of a percent in their efficiency improvement is carried out. The silicon solar cells are the basis of photovoltaic power engineering and this state of affairs will remain in the near future [13].

The present work reports the experimental results of the laser texturing process application for multicrystalline silicon (*mc*-Si) solar cells fabrication. This direction of research has been chosen because in the case of *mc*-Si solar cells the problem of reflective losses is very acute as the conventional methods of chemical surface texturing do not yield the desired result due to the randomized crystallographic orientation of multicrystalline silicon grains. The developing methods are rather complicated and cannot be introduced into industry. That is why the laser texturing process is a very attractive method of *mc*-Si reflectance reduction. In the literature the results of *mc*-Si laser texturing experiments are presented: laser-induced periodic surface structure (LIPSS) generation using optical interference, spike formation using femtosecond laser irradiation, laser groove fabrication, etc [14-20]. Here we represent the generalized experimental data on the "black" *mc*-Si surface fabrication via 3-D structures created by nanosecond laser pulses and on application of the developed version of laser texturing method for the improvement of the *mc*-Si solar cells efficiency.

Experimental details

The investigations of laser-induced 3D structures formation on the Czochralski silicon (*c*-Si) surface and the *mc*-Si surface texturing process were performed in the vacuum chamber evacuated to the pressure of 10^{-6} Torr. The second harmonic Q-switched Nd:YAG laser (10 ns, 10 Hz, 250 mJ) was employed. The polished 4.5 Ω·cm *n*-type (100) (*c*-Si) wafers, 1 Ω·cm *p*-type *mc*-Si wafers and the industrially textured *p*-type (100) *c*-Si wafers were used in the experiments. The wafers were provided by the Solar Wind Company. The silicon surface morphology studies were performed with the scanning electron microscope Carl Zeiss LEO 1430VP. The reflectance measurements were conducted using the LOMOspektr SF-56 spectrometer equipped with an integrating sphere. For more detail see the paper [21]. Then the *mc*-Si solar cells were fabricated by the Laminated Grid technology developed in the SINP MSU [22,23] and studied. The (n^+pp^+)*mc*-Si structures were obtained by simultaneous diffusion of boron and phosphorus from spin-on deposited glasses using industrial equipment. The fluorine doped and tin doped indium oxides (IFO and ITO) were grown using the pyrosol method. For more detail see the paper [24].

Results and discussion

1. Laser-induced high aspect ratio microstructures on the c-Si surface

The *mc*-Si surface consists of grains with different crystallographic orientations (domains); therefore it was not clear how the conditions of 3D structures formation would be distinguished on different domains. So the first experiments were conducted using polished *c*-Si wafers with crystallographic orientation (100) in case of multipulse irradiation of the sample surface. The goal of this step was the determination of the optimum conditions (laser energy fluence, number of laser pulses) for the uniform laser-induced structures formation having high aspect ratio (depth to width) in the region of laser spot. We have demonstrated that multipulse laser irradiation of the *c*-Si surface leads to the 3-D conical microstructures formation [21].

The formation of these microstructures is caused by the interference of the diffracted laser radiation on the original surface roughness. This effect creates the space-time periodic intensity distribution of light energy in the surface layer leading to non-uniform heating and melting of the surface [1,2]. The waves of the spatially inhomogeneous surface melt present the initial heterogeneity for the conical structures formation process. When the energy fluence exceeds the silicon melting threshold (0.37 J/cm^2) and remains below the silicon ablation threshold (less than 2 J/cm^2) the stable structures form on the irradiated silicon surface and gradually fill the laser spot area. According to [1], the formation of these structures is mainly determined by the effect of the spatially periodic thermocapillary force, and the regenerative feedback is realized due to the dependence of the surface tension σ on the temperature. The interference instability of the spatially nonuniform evaporation dominates when energy fluence exceeds the threshold of ablation. In this case the regenerative feedback is realized due to the recoil pressure and the process of material removal. The conical structures having high light absorption capacity and the aspect ratio ~ 1 form on the silicon surface at energy fluences of 2-3 J/cm^2 (Fig. 1*a*).

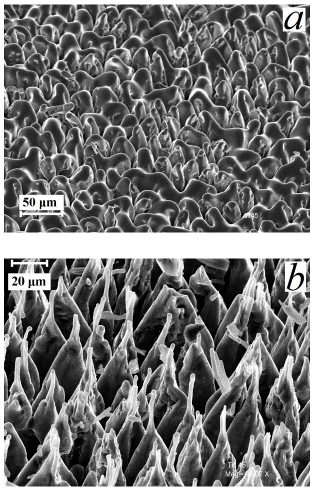

Fig. 1. The laser-induced high aspect ratio microstructures fabricated on the *c*-Si surface (2 J/cm^2, 5000 pulses; 3 J/cm^2, 1000 pulses).

At energy fluences of 3-4 J/cm^2 the conical structures begin to form inhomogeneously over the laser spot area. As the laser pulses grow in number, the ablation texture becomes more pronounced (aspect ratio > 3) and the cavities between the individual spikes penetrate deep into the silicon wafer (Fig. 1*b*). The surface patches emerge on the surface of molten columnar structures with further increase of the energy fluence. Thus it was found that the laser energy fluence is required in the range of 3-4 J/cm^2 to form the conical structures in the region of laser spot with high aspect ratio.

2. Fabrication of the "black" mc-Si surface

The second step of the research was the fabrication of the "black" *mc*-Si surface by the nanosecond laser pulses. The studies of the laser-induced microstructures formation processes on the *c*-Si surface made it possible to determine the preferred scheme of texturing the *mc*-Si surface with the laser beam. The *mc*-Si samples were placed on the computer controlled X-Y stage to enable scanning of its whole surface area. The experiments in this direction have permitted us to produce uniformly textured *mc*-Si samples. The relief (or texture) formed by laser radiation consists of the conical structures with aspect ratio ≥ 3. The height of the conical microstructures is more than 45 µm and the distance between them is about 15 µm (Fig. 2).

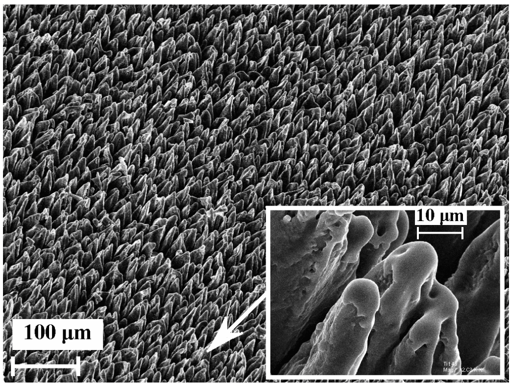

Fig. 2. A microphotograph of the laser textured "black" *mc*-Si surface.

The studies of the laser-textured *mc*-Si samples morphology has shown that the texture is rather homogeneous and the presence of areas with different crystallographic orientations has no effect on the geometry of the texture formed by laser radiation [21]. The analysis of reflectance spectra of the laser-textured *mc*-Si samples shows that the laser texturing process reduces the reflectance of *mc*-Si surface by an order (Fig.3).

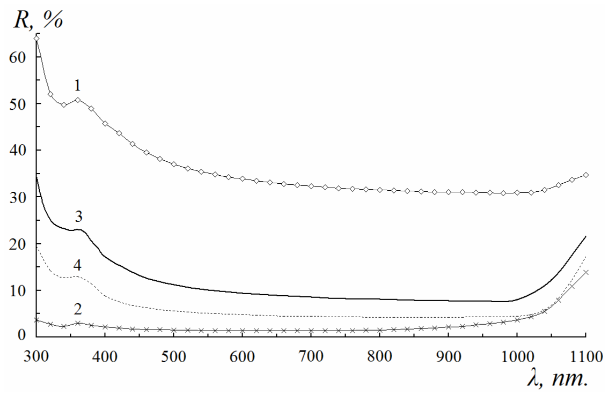

Fig.3 The reflectance spectra of the samples: 1 – untextured *mc*-Si; 2 – laser textured *mc*-Si; 3 – *c*-Si after industrial chemical texturing; 4 – laser textured *mc*-Si after acid etching (55 min).

Numerous phase transitions during the formation of laser-induced structures result in generation of defects in the near-surface region, dramatically reducing the diffusion length of the charge carriers [25]. One of the ways to remove the surface layer is chemical etching. The experiments on acidic etching of the laser textured samples have been conducted. It has been demonstrated that even after long acidic etching the spike structures survive and their geometry does not depend on the *mc*-Si grain orientation [21].

So, as the result of the second-step experiments we have developed the version of *mc*-Si surface laser texturing that allows us to form the texture on the *mc*-Si surface, consisting of the conical microstructures with the aspect ratio ≥ 3. The geometrical parameters of the conical structures do not depend on the *mc*-Si grains orientation. The reflection spectra of the samples with laser textured surface demonstrate a cardinal decrease in reflectance (~3%) in the wide spectral region of (300-1100) nm not only in comparison with the reflectance of the untextured *mc*-Si samples but also with that of the industrially textured *c*-Si samples.We have demonstrated the ability of reflectance retention at the value (~5%) in the spectral region of (300-1100) nm even after long acidic etching.

3. Application of laser texturing method for mc-Si solar cells fabrication

The final step of the research was the fabrication of *mc*-Si solar cells using the developed version of the *mc*-Si surface laser texturing method and the study of the solar cells characteristics [24].The general parameters of the fabricated *mc*-Si solar cells (laser textured and untextured) are presented in Table 1, where V_{OC} – open-circuit voltage, J_{SC} – short-circuit current density, FF – fill factor, η – solar cells efficiency. Since the thickness of the laser textured wafers was reduced down to 140 µm after etching, the untextured reference wafers were also appropriately thinned.

Type of solar cell	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
untextured	606	28.5	77.4	13.4
laser textured	576	33.7	70.4	13.7

The application of the laser texturing method for the *mc*-Si solar cells fabrication has led to the significant increase of J_{SC} (~18%) compared to the untextured solar cells. Despite the lower values of V_{OC} and FF, the efficiency of the laser textured solar cells is higher. We suppose that the lower values of V_{OC} and FF for laser textured solar cells are caused by the unoptimised diffusion process because the sheet resistance of a n^+ diffused layer for the laser textured solar cells (~200 Ω/sq) is higher than that for the untextured solar cells (~40 Ω/sq). The analysis of the external (Q_E) and internal (Q_I) quantum efficiency spectra both for the textured and untextured solar cells (Fig. 4) shows the increase in quantum efficiency for the laser textured solar cells.

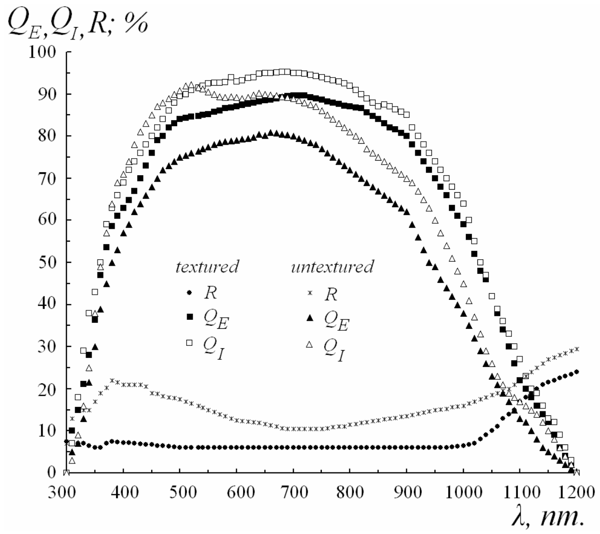

Fig. 4. The external (Q_E) and internal (Q_I) quantum efficiency and reflection spectra of the laser textured and acid etched IFO/(n^+pp^+)*mc*-Si/ITO solar cells measured with an integrating sphere. The data for the untextured solar cells are also presented.

The external quantum efficiency is measured using the solar cell calibrated in Fraunhofer ISE $Q_E^{test}(\lambda) = \dfrac{J_{SC}^{test}}{J_{SC}^{calibrated}} Q_E^{calibrated}(\lambda)$, where J_{SC}^{test} – current density of the tested specimen, $Q_E^{calibrated}(\lambda)$ and $J_{SC}^{calibrated}$ – external quantum efficiency and current density of the calibrated specimen. The internal quantum efficiency is calculated using the following equation: $Q_I(\lambda) = \dfrac{Q_E(\lambda)}{1-R(\lambda)}$. It is clearly seen from Fig. 4, that the external quantum efficiency of the laser textured solar cells is higher than that of the untextured solar cells. The Q_I values show a marked improvement for the wavelengths higher than 600 nm.

So we have demonstrated that the laser texturing method causes an increase in the quantum efficiency and short circuit current density of the *mc*-Si solar cells.

Conclusions

As the result of conducted experiments we have fabricated a "black" *mc*-Si surface using the YAG laser second harmonic nanosecond pulses with the energy fluence exceeding the threshold of silicon ablation. The formed laser relief (texture) consists of the spike array structures with aspect ratio of ≥3 (depth to width), and the geometrics of the laser-induced structures does not depend on the crystallographic orientation of the *mc*-Si surface grains. The introduced method of *mc*-Si laser texturing permits producing a low-reflection surface with the reflectance of ~3% in the spectral range of 0.3-1.1 μm. The application of the laser texturing method in mc-Si solar cells fabrication makes it possible to increase the short circuit current density and external quantum efficiency by ~18%. To improve in the sequel the solar cells efficiency, we have to optimize the process of defect layer chemical etching or to use another method of defect layer removal (e.g. laser etching) because the acidic etching causes a reduction of the thickness of wafers from 200 μm down to 140 μm. The diffusion process should also be optimized to reduce the sheet resistance of a n^+ layer for laser textured solar cells. So we have demonstrated the potential of the laser texturing technique application in the conventional fabrication of *mc*-Si solar cells.

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