MODIFICATION OF MONOSILICON SOLAR CELLS PARAMETERS BY HYDROGEN PLASMA TREATMENT

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An overview of the influence of hydrogen plasma treatment on monocrystalline silicon solar cells (SCs) parameters (efficiency, diffusion length of minority carriers L_D, spectral response $I(\lambda)$) was investigated. Moreover the influence of pre-hydrogenation on radiation hardness of such SCs was studied. It is shown that hydrogenation of SCs at the appropriate processing regimes leads to the increase both efficiency and radiation hardness.

Introduction

Development of low-cost highly-effective SCs is one of the important tasks of modern semiconductor material science. In the present work the influence of hydrogenation on the properties of standard SCs is investigated. There are a lot of the basic mechanisms for the mentioned influence. As is shown, for example, in [1], atomic hydrogen can easily penetrate into the bulk of silicon and passivate electrically active imperfections. Besides atomic hydrogen promotes the enhanced thermal donor gradient formation that creates the buried "pulling" electric field causing an additional collection of generated minority carriers (MiC) [1-4]. At last, the etching of SC surface by atomized hydrogen can result in the development of its roughness and therefore reduction of light reflectance. All these effects should result in the increase of SCs efficiency. There is one further useful effect of hydrogen plasma treatment connected with the accumulation of molecular hydrogen in the bulk of SC. If such saturated by molecular hydrogen SCs operate under irradiation conditions, high densities of radiation defects (vacancies and interstitials) are introduced. In accordance with [5], the generation of mobile vacancies and interstitials in the vicinity of hydrogen molecules has to result in their dissociation on atomized constituents. After the dissociation the two hydrogen atoms can diffuse very quickly by the crystal and passivate the radiation defect dangling bonds. This effect of radiation defect self-passivation by hydrogen introduced in silicon from a plasma is equivalent to an increase of the radiation hardness of the SC.

In our experiments we used SCs manufactured on the basis of boron doped monocrystalline Cz-Si wafers of different quality with resistivities 1-3 Ω·cm and diffusion lengths of MiC 25-150 μm. The surface of wafers was textured in the alkaline environment with addition of organic and then p-n-junction formed at the depth of 0.5 μm due to phosphorous diffusion at the temperature 900 °C. And at last contact metallization was rendered on the samples. Note that due to a specificity of experiments the antireflective coatings were not superimposed on the surface of SCs. Besides, the initial samples of SCs were cut on several parts so efficiency of the studied SCs before hydrogenation was less then for standard SCs (13-14 %) and was, as a rule, about 10-11 %.

Measurements of efficiency were carried out under the conditions appropriate to standard AM1. The parameters of SCs were extracted from their light current-voltage characteristics by means of standard procedure [6]. Also the L_D of MiC in substrates was measured SC spectral response [7].

I. Development of SC efficiency

As was mentioned above (see Introduction), there are some mechanisms of interaction of hydrogen plasma with SC which are capable to result its efficiency in change. The separating of these mechanisms and establishment of their relative role in the efficiency changes was one of the main tasks of this work.

The first part of our experiments on SC hydrogenation was carried out at temperatures less than 450 °C. This allowed us to exclude the thermal donor formation so that the changes of SCs parameters, in our opinion, were connected only with (i) the passivation of defect centers at the surface and in the bulk of SC; (ii) the creation of new hydrogen-induced defects near the surface; (iii) transformation of surface relief under influence of hydrogen etching. The given below results of the experiments allow to judge the processes occurring during hydrogenation of SCs.

The SC efficiencies before and after hydrogenation (25-35 °C, energy 200 eV, current density 0.1 mA/cm^2) are presented in the Tab. 1.

Tab. 1.
The efficiency of SC before and after hydrogenation

Time of hydro-genation, min	Efficiency, %	
	Initial	Hydrogenated
5	10,1	10,9
10	10,0	10,6
20	9,9	10,4
40	9,8	9,8

As is shown from Tab. 1, the hydrogenation in such regime leads to increase of SC efficiency. However the increment of efficiency decreases with the time of treatment and depends on the quality of substrates (their diffusion lengths). The L_D of MiC in the SCs manufactured on the low-quality substrates and estimated from spectral dependencies of photocurrent are shown in Tab. 2.

Tab. 2.
The L_D of MiC before and after hydrogenation

Time of hydrogenation, min	Diffusion length, um	
	Initial	Hydrogenated
5	16	29
10	15	38
20	13	24
40	16	25

The comparison of Tabs. 1 and 2 shows that the changes in the SC efficiency correlates with the changes of their diffusion lengths. This points that, in this case, hydrogenatlon causes passivation of active defects in the material that just leads to the SC efficiency increase.

Similar experiments were conducted for the SCs manufactured on the base of more high-quality substrates (with the essentially greater values of diffusion lengths). The results of these measurements are presented in Tabs. 3 and 4.

Tab. 3.
The SCs efficiency before and after hydrogenation

Time of hydrogenation, min	Efficiency, %	
	Initial	Hydrogenated
10	10.6	10.8
20	10.1	10.6
40	7.8	8.3

Tab. 4.
The L_D of MiC before and after hydrogenation

Time of hydrogenation, min	Diffusion length, um	
	Initial	Hydrogenated
10	133	41
20	126	42
40	143	44

The analysis of Tabs. 3 and 4 forces to assume, that at the SC hydrogenation alongside with passivation of defects there is an additional channel for the growth of the efficiency. On one side, the profilometric measurements has exhibited the transformation (increase of microroughness) of the SC surface under hydrogen etching effect that should lead to decrease of light reflection and improvement of the SC efficiency. So the above mentioned reduction of diffusion length in the high-quality substrates may be explained by generation of hydrogen-related defects (like nanoblisters, platelets, etc.) in the near-surface region during hydrogenation. Their formation is especially probable taking into account of low temperature of hydrogenatlon (and therefore weak diffusivity of hydrogen) that can result in its accumulation mainly at the surface of SC.

To have more information about the contribution of various processes in the changes of SC parameters, experiments with implantation of hydrogen and helium atoms at the identical conditions was carried out. If the passivation of defects could be neglected, changes in SC properties would be identical because hydrogen and helium ions have very close masses and should cause similar changes in the surface relief and, hence, efficiency. The Tabs. 5 and 6 show the results of such experiments. The implantation was done at the room temperature and ion energy 4 keV.

Tab. 5.
The SC efficiency before and after hydrogen implantation

Time of implantation, min	Efficiency, %	
	Initial	Implanted
5	11.2	11.3
20	11.1	10.4

Tab. 6.
The SC efficiency before and after helium implantation

Time of implantation, min	Efficiency, %	
	Initial	Implanted
5	8.5	7.2
20	10.3	8.2

The Tabs. 5 and 6 show that in the first case (hydrogenation) the SC efficiency practically is not changed, while in the second one significantly decrease of efficiency takes place. It can be explained, in our opinion, that both types of ions with the energy 4 keV cause radiation defects in SCs. The latter increase the carriers recombination and lead to reduction of SC efficiency. But, at the same time, in the case of incorporated hydrogen ions they passivate introduced defects, while helium ions can not passivate ones that explains the observed difference.

II. Radiation hardness improvement

As mentioned in Introduction, the atomic hydrogen incorporated into silicon at enough low temperatures is partly transformed into a molecular state occupying interstitial positions. I this case it does not introduce any significant changes in the properties of the material. The production of mobile vacancies (due to hard irradiation of SC) near such molecule results may lead to decay of such molecule (due to the field of elastic stresses near the defect) on atomic constituents [5]. The latter having higher diffusivity can passivate nucleated radiation defects. This self-passivation effect will make the degradation of the SC parameters to low. Note that in our earlier work [8] this effect was exhibited in monocrystalline silicon at γ-irradiation.

To check experimentally this idea of the radiation hardness improvement the initial (unhydrogenated) and hydrogenated SCs were irradiated by 1 MeV electrons. During these experiments the changes of SC efficiency and spectral response were measured. The results are presented below.

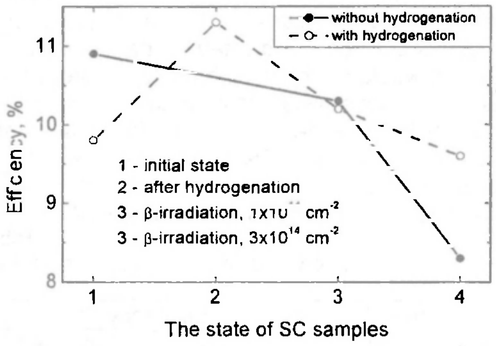

Fig. 1. Changes in SC efficiency due to β-irradiation

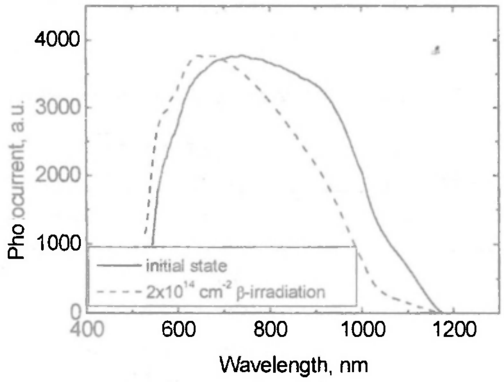

Fig. 2. Spectral response for unhydrogenated SC before and after β-irradiation

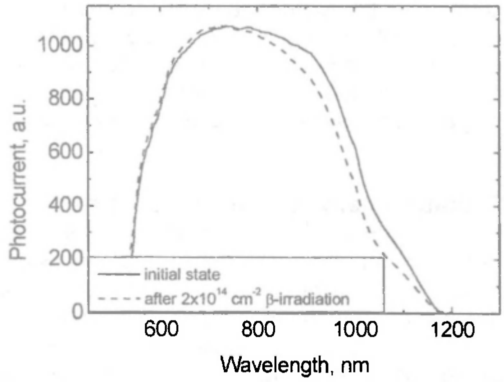

Fig. 3. Spectral response for hydrogenated SC before and after β-irradiation

Fig. 1 shows that for unhydrogenated SCs the efficiency degradation under subjection to electron irradiation is much higher than for hydrogenated ones.

As is evident from Figs. 2 and 3, in a case of unhydrogenated samples β-irradiation causes decrease of diffusion length (decrease of photocurrent in the long-wave part of spectrum and its increase for the short-wave part). At the same time, for hydrogenated sample the both curves are very similar. The estimations of diffusion lengths from the spectral response show that for unhydrogenated samples subjected to electron irradiation with the fluence 3x10^{14} cm^{-2} L_D reduces by a factor of six while for hydrogenated ones it decreases only by a factor two.

The presented data are direct evidence that treatment of SC by hydrogen plasma significantly improves their radiation hardness.

Conclusion

The carried out study allows to assert that hydrogenation of monosilicon-based SCs can result in passivation of defect centers, generation of new near-surface defects and transformation of the surface relief. The relation between these processes depends on hydrogenation conditions (temperature, time of exposure and energy of ions). The choice of optimal hydrogenation parameters results in the relative raise of SC efficiency up to 20 % in comparison with the initial state. Besides we exhibited the improvement of SCs radiation hardness subjected to hydrogenation.

References

1. *Ulyashin A.G., Fedotov A.K., Job R., Fahmer V.R., Mazanik A.V.* // Physics and Chemistry of the Materials Treatment.-2000.- N5.-p. 22.
2. *Ulyashin A.G., Petlitskii A.N., Job R., Fahmer W.R., Fedotov A.K., Stognii A.I.* // Solid State Phenomena. – 1999. – v.69-70. – p.409.
3. *Ulyashin A.G., Bumay Yu.A., Fedotov A.K., Voropaev A.G., Katz E.A., Bondarenko V.P., Dorofeev A.M.* // Advanced Technologies for Material Processing and Repairing of Worn-out Parts: Proceedings of the First Belarussian - German Seminar. - Minsk, 1996. - p.165-172.
4. *Ulyashin A.G, Bumay Yu.A., Shlopak S.A.* // Advanced Technologies for Material Processing and Repairing of Worn-out Parts: Proceedings of the First Belarussian - German Seminar. Minsk, 1996. - p.157-164.
5. *Estreiher S.K., Hastings J.L., Fedders P.A.* // Phys. Rev. - v.57. – №20. R12663-R12665.
6. *Koltun M.M.* Optics and metrology of solar cells. – M.: Nauka, 1984. – 280 p.
7. *Zuev V.A., Satchenко A.V., Tolpygo K.P.* Unequilibrium near-surface processes in semicondurtors and semiconductor devices. – M.: Sovetskoe radio, 1987. – 256p.
8. *Fedotov A.K., Mazanik A.V., Ulyashin A.G.* // proc. Of the 10th Sede Boqer Symp. on Solar Electricity Production. – Sede Boqer, 2001. (in print).

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