Effects of texturization due to chemical etching and laser on the optical properties of multicrystalline silicon for applications in solar cells

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Abstract. In this work we carried out the texturization of surfaces of multicrystalline silicon type-p in order to decrease the reflection of light on the surface, using the chemical etching method and then a treatment with laser. In the first method, it was immersed in solutions of $HF:HNO_3:H_2O$, $HF:HNO_3:CH_3COOH$, $HF:HNO_3:H_3PO_4$, in the proportion 14:01:05, during 30 seconds, 1, 2 and 3 minutes. Subsequently with a laser (ND:YAG) grids were generated beginning with parallel lines separated $50\mu m$. The samples were analyzed by means of diffuse spectroscopy (UV-VIS) and scanning electron micrograph (SEM) before and after the laser treatment. The lowest result of reflectance obtained by $HF:HNO_3:H_2O$ during 30 seconds, was of 15.5%. However, after applying the treatment with laser the reflectance increased to 17.27%. On the other hand, the samples treated (30 seconds) with acetic acid and phosphoric acid as diluents gives as a result a decrease in the reflectance values after applying the laser treatment from 21.97% to 17.79% and from 27.73% to 20.03% respectively. The above indicates that in some cases it is possible to decrease the reflectance using jointly the method of chemical etching and then a laser treatment.

1. Introduction

Silicon is the main element in the construction of solar cells, besides its extensive applications in the electronics industry for the construction of semiconductor devices. The multicrystalline silicon is the one that is used the most in the manufacture of terrestrial solar cells [1] due to its low cost compared to monocrystalline silicon. Since that the first solar cells were manufactured with multicrystalline silicon, was tried to implement methods to improvement of the efficiency. One methods is texturization through a chemical etching on surface of the cell. [2-4]. The acid solutions are based on a combination of flourhydric acid with nitric acid, this composition has been studied very much, as well as its effects on the optical and electrical properties [5], and the alkaline solutions are based on a solution of potassium hydroxide or sodium hydroxide, and it is the method that is currently used for the texturization of monocrystalline silicon that is implemented in the manufacture of the solar cells. Another method in order to texturize is by means of laser beam generating grooves on the surfaces in the shape of parallel lines and in the shape of grids [6,7]. The objective of this work is to see the effects caused on the optical properties of multicrystalline silicon in the process of texturization by means of chemical etching and laser applying the two methods simultaneously.

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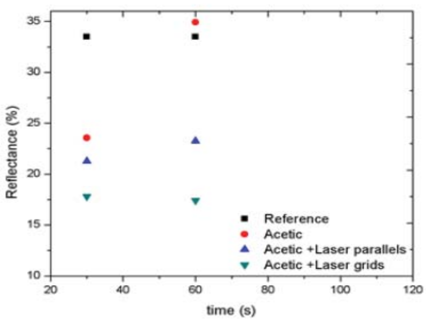
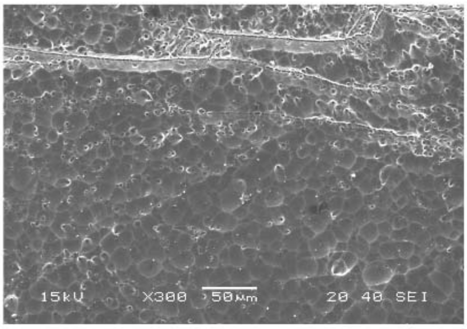
2. Experimental methods

The samples used in this work were of multicrystalline silicon type p, cut in 2*cm*x2*cm* pieces, with a thickness of 200μm and a resistivity of 0.5$\Omega.m$. First we carried out texturizations of multicrystalline silicon samples by means of chemical etching of HF: HNO_3, with three different diluents: HF:HNO_3:H_2O, HF:HNO_3: CH_3COOH, HF:HNO_3:H_3PO_4, in the proportion 14:01:05, during 30 seconds, 1, 2 and 3 minutes. Subsequently on the surface of these texturized samples, grooves of 20μm of width were generated in the form of parallel lines separated 50μm from center to center, using a laser pulsed of Nd:YAG with a wave longitude of 1064*nm*, a pulse power of 265*mW* and a pulse energy of 94.3*mJ*. For the generation of the groove (line) in a straight line on the sample, it was passed through a cylindric lens that was 2.2*cm* of diameter, separated from the sample 12.8*cm*, 3 pulses of laser beam. Then, beginning with these parallel grooves grids with grooves perpendicular to the first ones were generated and also at 50μm of separation. The results obtained were compared with a sample of raw multicrystalline silicon. Each one of the samples was treated before and after the laser application, they were analyzed by means of diffuse spectroscopy using a Shimadzu 2600 UV–VIS spectrophotometer and scanning electron microscopy (SEM) using a Joel JSM 5600 microscope.

3. Results and discussion



(a)

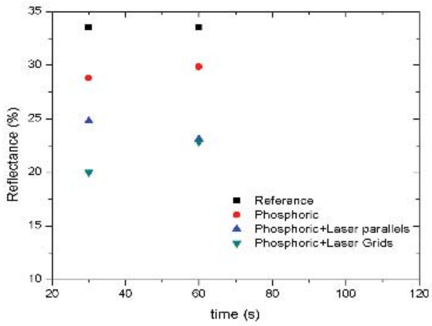


(b)

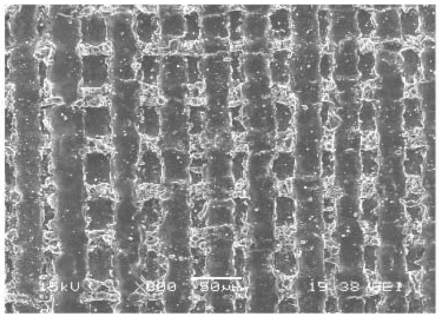
Figure 1. (a) Average Reflectance for samples that were etched chemically with acetic acid during 30 seconds and 1 minute and then with laser in the form of parallel lines and grids. (b) Images obtained by SEM micrograph (300X)for a sample chemically etched using acetic acid as diluent during 1 minute.

3.1. Chemical texturization with acetic acid as diluent and laser over-texturization

In Figure 1(a), shown average reflectance of the raw samples, those texturized with acetic acid as diluent, and those that have the laser over-texturized in parallel grooves and in grids for 30 and 60 seconds of chemical texturizing. These values show a single trend for the two times indicated, in the decrease of the average reflectance, and we could observe that beginning with the raw sample with an average reflectance of 33%, and up to the grooves in grid with laser on the chemically texturized samples, we obtained a decrease of this coefficient up to 17.41% of average reflectance. However, an anomalous behavior occurs for the chemical texturization with the acetic acid as diluent for a period of 60 seconds, overcome the average reflectance of the raw sample. It is possible that when we increase the time with the acetic acid as diluent this produces on the surface something like bowls whose diameter - depth ratio increases, which could produce an increase in the average reflectance. In Figure 1(b), we show the SEM micrograph of this chemical texturization at 60 seconds, and we could observe a morphology that is mostly uniform with the semblance of depressions of an almost circular section with the diameter – depth (d/h) ratio greater than the unit and some sectors that suggest formations of defects. However, in the SEM micrograph of the sample over – texturized with laser, we observed a greater homogenization of the surface, but now the width - depth (W/H) ratio, still continues being greater than the unit. In the SEM micrograph show the laser grid, and we could observe a much rougher surface that includes some defects of the sample. These grids have the shape of trunks and they generate a greater trapping of the light in accordance with the smaller average reflectance that was obtained.



(a)



(b)

Figure 2. (a) Average reflectance for samples that were etched chemically with phosphoric acid during 30 seconds and 1 minute and then with laser in the form of parallel lines and grids. (b) SEM micrograph (300X) Sample initially etched with acetic acid as diluent during 1 minute and then with laser in grids.

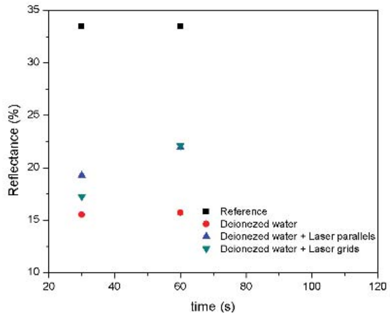
3.2. Chemical texturization with phosphoric acid as diluent and laser over-texturization

In Figure 2(a), we could observe that the samples that were chemically texturized with phosphoric acid as diluent and then over-texturized with laser during 30 and 60 seconds decrease their average reflectance with a very similar trend, and we were able to reduce this coefficient by tracing the grooves in grids with the laser up to a minimum of 20.03% of average reflectance. In this figure we can also observe that the minimum average reflectance, is very close for the parallel grooves and of the grooves gridded, which suggests that the effective area of reflection of the light is not modified significantly for the two samples over-texturized with the laser. Also, we could observe in SEM micrographs that texturization with phosphoric acid generates deeper depressions towards the inside of the sample but with a distribution that is more spaced out. This produce an average reflectance a smaller than the one obtained with the acetic acid as diluent. In the Figures 2(b) we can see the surfaces in grids. In these micrographs we can see that the draw of the laser in order to form grids produced the shaping of trunks in an alternated way, which makes it possible that the average reflectance does not differentiate itself significantly with respect to the average reflectance obtained with the parallel grooves.

3.3. Texturization with deionized water as diluent and laser over-texturization

The samples that were chemically texturized with deionized water as diluent decreased their average reflectance by 15.55% and increased after applying the over texturization with laser in the form of parallel lines and in grids, as we can see in Figure 3(a). In the micrograph of the Figure 3(b), we can observe a very uniform morphology for the chemically texturized sample, we do not see defects such as boundaries that the etching is mostly isotropic, with a roughness the like undulations of which contribute to a better trapping of the incident light. With the application of the laser we obtain a flat effective surface with a width depth ratio that is much greater than the unit, as we can observe in the Figures 3(c) and 3(d).

The draw of grids does not have a great influence on the decrease of the average reflectance. This result suggests that the over-texturization with laser for samples that were chemically texturized with deionized water as diluent, do not introduces any improved.



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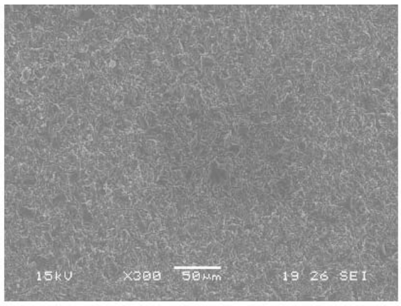

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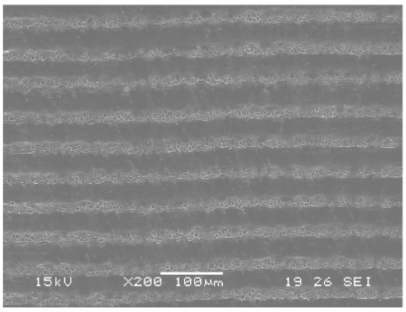
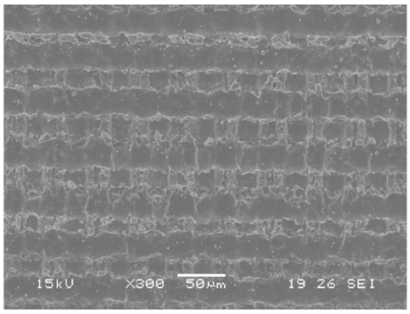


(c)



(d)

Figure 3. (a) Average reflectance for samples than were chemically etched with deionized water as diluent, and then with laser in the form of parallel lines and grids. (b) Images SEM (300X) for a sample that was chemically etched using deionized water as diluent during 1 minute, (c) Images SEM (200X) of sample that was etched initially with deionized water as diluent during 1 minute and then textured with laser in the form of parallel lines, (d) Images SEM (300X) of sample that was etched initially with deionized water as diluent during 1 minute and then with laser in grids.

4. Conclusions

We applied chemical texturization and laser methods simultaneously in order to reduce the reflectance on the surface of the multicrystalline silicon. The lowest reflectance results were obtained with the solution HF:NHO_3:H_2O in the proportion 14:01:05 during 30 seconds with a value of 15.55%. Besides, this solution shown that the etching is totally isotropic and a very uniform morphology is obtained. For the samples that were treated with this solution it is not convenient to treat them with laser, because increases the reflectance applying the laser in the form of parallel lines or in grids. On the other hand, the samples that were etched initially with acetic acid and phosphoric acid decrease the average reflectance with respect to the reference sample, and they decrease even more when we apply over those surface etched the laser texturization in the form of parallel lines as also in the form of grid.

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