ADVANCED LIGHT-TRAPPING STRUCTURES FOR BACK-CONTACT SOLAR CELLS PRODUCED BY METAL-ASSISTED CHEMICAL ETCHING

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ABSTRACT: We present here an optimisation study of a method to reduce the reflectivity of monocrystaline silicon wafers. The method is based a metal-assisted chemical etching (MACE) technique that uses hydrogen peroxide (H_2O_2) and hydrofluoric (HF) as etchants, and silver as catalyst. During this study, several etching times and etchant concentrations were tested and the role of etchants molar ratio (ρ) was examined. The study shows that the method can severely reduce the effective reflectivity (R_{eff}) of the wafers, reaching values as low as 3.15%. Also, an interesting correlation between the processed wafers' R_{eff} and ρ was noticed. Scan electron microscope observations of the etched samples exhibited randomly created nanostructures with both high and low aspect-ratios.
Keywords: Crystalline, silicon, texturization, light-trapping

1 INTRODUCTION

One of the most promising paths to reduce the levelized cost of photovoltaic (PV) energy is the improvement of the PV systems conversion efficiency [1].

Increasing the light recovered by a solar cell is one of the most effective ways to increase the solar cell current and conversion efficiency. Furthermore, the use of advanced light-capture strategies allows the reduction of material use and opens the way to the employment of lower quality substrates [2].

In the last years, the development of advanced light-capture strategies has attracted a lot interest in the photovoltaic community. Different approaches have been adopted, such as the introduction of plasmonic structures [3], the nanopatterning of the solar cell surface using reactive ion etching (RIE) [4], or metal-assisted chemical etching (MACE). When compared to other methods MACE has as major advantages its simplicity, that facilitates integration in an industrial process, and the fact that it does not require the use of expensive equipment. On the other hand, the important increase of surface states during etching makes surface passivation more demanding [5].

In this article we present a characterization of a MACE based process to perform the texturization of monocrystalline silicon substrates and reduce the reflectivity of the wafers' front-surface. Such method is particularly suited to be used in the fabrication of back-contact back-junction solar cells.

The work here presented further develops the study started by Ivo et al [6]. The MACE method used is a mask-less method in which samples are dipped in a solution composed by hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2) as etchants and silver nitrate ($AgNO_3$) as silver source.

2 METHOD

2.1 MACE working principle

The MACE texturization process works as follows: after immerging the substrate on the etching solution, H_2O_2 oxidizes the substrate, HF removes the silicon oxide (SiO_2), while $AgNO_3$ provides silver ions (Ag^+) to the etching solution, that catalyse the oxidation reaction by donating holes (Figure 1). Wherever present the silver catalysation effect originates deeper texturizations, therefore making the textured structures shape largely determined by the silver particles distribution [5].

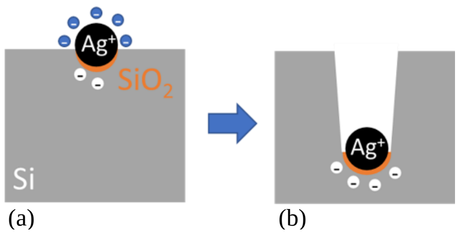

Figure 1: Diagram of MACE process: (a) the silver atoms (Ag+) catalyse surface oxidation; (b) the fast substrate etching near Ag+ creates the nanostructures.

The equations that describe the etching process are the following [5]:

Cathode (Ag^+):

$$H_2O_2 + 2H^+ \rightarrow H_2O + 2h^+$$

$$2H^+ + 2e^- \rightarrow H_2$$

Anode (Si):

$$Si + 4h^+ + 4HF \rightarrow SiF_4 + 2H^+$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

Overall:

$$\mathrm{Si} + H_2O_2 + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2$$

2.2 Experimental details

During this study 2×2 cm^2, 1 Ω.cm p-type Czochralski monocrystalline silicon polished wafers (100) were used.

The etching time was varied between 2 and 15 minutes, being the concentration of the etchant solutions adjusted accordingly.

$AgNO_3$ concentration was kept at 0.006 M, while H_2O_2 concentration was varied between 0.3 and 2 M and HF concentration between 2 and 12 M.

After texturization the wafers were cleaned with a nitric acid solution to remove silver deposits, and then characterized.

2.3 Characterization

To evaluate the efficacy of the texturization process, the spectral reflectance of the etched samples was measured in the range 350 to 1050 nm with a UV-vis Spectrophotometer Shimadzu UV – 2600 PC with integrating sphere (Figure 2).

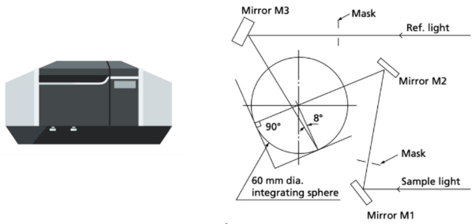

Figure 2: Spectrophotometer Shimadzu UV – 2600 PC with integrating sphere [7].

To better evaluate the interest of the etched structures produced, for photovoltaic applications, the effective reflectivity (R_{eff}) weighted with the AM1.5 reference spectrum [8] was obtained:

$$R_{\text{eff}} = \frac{\sum_\lambda R_\lambda n_\lambda}{\sum_\lambda n_\lambda} \quad (1)$$

where R_λ is the reflectance for the wavelength λ, and n_λ is the number of photons for the same wavelength in the spectrum AM1.5.

The morphology of the nanostructures created during the etching process was examined via scan electron microscope (SEM) observations.

2.4 Molar ratio

To examine the influence of the relative concentrations of HF and H_2O_2 on the etching dynamics, the molar ratio ρ, defined by equation (2) was introduced, and the etched samples' reflectivity and morphology were analysed as function of ρ [9].

$$\rho = \frac{[HF]}{[HF] + [H_2O_2]} \quad (2)$$

3 RESULTS

3.1 Reflectivity

It was observed that, for all the etching times tested, the reflectance of the samples textured with an etching solution with ρ > 0.82, was strongly reduced by the texturization process. Figure 3 depicts a photograph of a monocrystalline silicon sample etched with a solution with ρ = 0.92, where the strong reflectivity reduction is noticeable.

Figure 3: Photograph a of 2×2 cm^2 sample etched with a ρ=0.92 solution.

In Figure 4 the spectral reflectance of a sample, etched with ρ = 0.92 is presented. It can be observed that, when compared to a polished crystalline silicon sample, the reflectance is severely reduced over all the spectral range analysed. In fact, R_λ remained below 4% for λ < 1040 nm. The effective reflectance obtained for this sample was 3.15%, the lowest value obtained in this study.

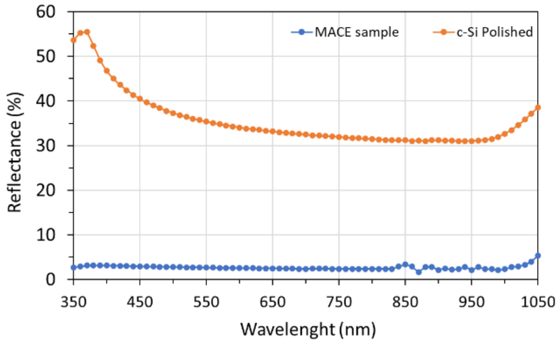

Figure 4: Spectral reflectance of sample etched with a ρ = 0.92 solution, compared to a crystalline silicon (c-Si) polished sample.

3.2 Morphology characterization

SEM observations of the textured samples display the random nature of the nanostructures created during etching, moreover both high aspect and low aspect-ratio structures can be detected (Figure 5). The presence of both high aspect and low aspect-ratio nanostructures in the etched samples is coherent with the observation of a strong reduction of the sample's reflectance over all the analysed spectra. Furthermore, SEM observations of the samples' sections showed that, for samples with R_{eff} < 10% the structures' heights range between 1 and 7 µm.

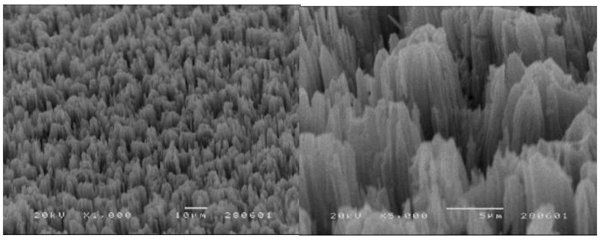

Figure 5: Scan electron microscope images of a sample etched with a ρ = 0.92 solution.

3.3. Molar ratio

To analyse the role of the reactants' molar ratio on the etching dynamics, the effective reflectivity of a large number of samples, etched with several different etching conditions, was plotted as function of ρ (Figure 6).

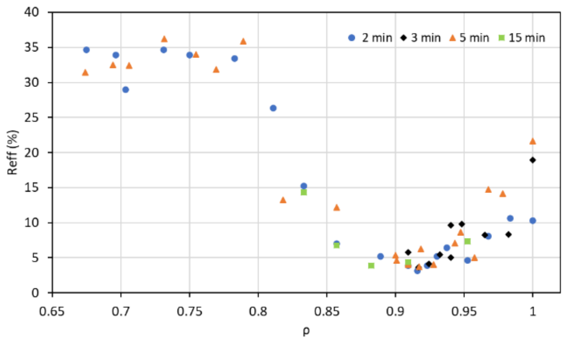

Figure 6: Effective reflectivity as a function of ρ, for an etching time of 2, 3, 5 and 15 min.

It can be observed that for all the etching times tested, a strong correlation between R_{eff} and the molar ratio ρ was detected. The R_{eff} results obtained suggest the existence of threshold value of ρ over which there is a significant reduction of the reflectivity.

For $\rho < 0.78$ the samples' reflectivity is not significantly reduced, occurring a transition from high to low reflectivity regime for ρ in the range [0.78,0.82].

Also, an apparent optimal range for ρ, between 0.88 and 0.93 for which the effective reflectivity is minimum was identified. In fact, for all the samples etched with a molar ratio in this range R_{eff} was below 5%.

In Figure 7, it is plotted the variation of R_{eff} with ρ in the range [0.8,1], for three different etching times. The variation of R_{eff} with ρ seems to follow the same trend independently of the etching time, which highlights the importance of the etchants' molar ratio on the reaction dynamics and the properties of the etched samples.

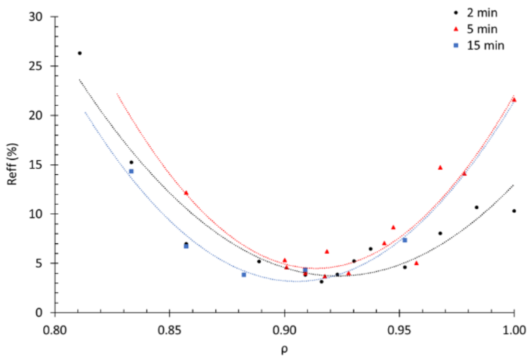

Figure 7: Effective reflectivity as a function of ρ in the range [0.8, 1], for an etching time of 3, 5 and 15 min.

The results obtained open good prospects for the application of this texturing method in the fabrication of monocrystalline silicon solar cells, as very low reflectivity values were repeatedly obtained, using relatively low etching times.

Also, the analysis of the structures' morphology showed that these low R_{eff} values can be obtained with nanostructures with average heights below 5 µm, which suggests that such structures can be effectively passivated with the industrial available methods. Therefore, the incorporation of this texturing method on the production of back-contact back junction solar cells seems feasible.

4 CONCLUSIONS

In this article an optimization study of a MACE based method to reduce the reflectivity of monocrystalline silicon samples is presented. The method is based on the use HF, H_2O_2 as etchants and $AgNO_3$ as source of silver, the catalyst agent.

It was observed that for all the etching times tested, the reflectance of the samples etched with $\rho > 0.82$, was significantly reduced over all the spectral range analysed (350-1050 nm). R_{eff} values lower than 5% were consistently obtained, and a minimum R_{eff} of 3.15% was obtained for =0.92.

Scan electron microscope images of the etched samples show that, during the etching process, the nanostructures are randomly created. Both high aspect and low aspect-ratios structures can be detected, such observation is consistent with the fact that reflectance is reduced over all the spectrum analysed.

The analyse of the role of the molar ratio in the etching reaction, evidenced the existence of a clear correlation between the molar ratio and effective reflectivity. Not only was identified a threshold value of ρ=0.82, over which R_{eff} is significantly reduced, as an apparent optimal range $0.88 \leq \rho \leq 0.93$ where R_{eff} has its lowest values, independently of the etching time used, was detected.

The fact that R_{eff} below 5% can be consistently obtained on uncoated monocrystalline silicon wafers, using etching times as low 2 or 3 minutes confirms the interest of the etching method for photovoltaic applications.

Moreover, the fact that such low reflectivity values can be obtained with nanostructures with an average height below 5 µm, suggests that these structures can be effectively passivated with the available industrial methods. Which opens very good prospects for the introduction of this texturization method in the industrial production of monocrystalline silicon solar cells, particularly in the production of back-contact back junction solar cells.

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6 AKNOWLEDGEMENTS

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