Improving light capture on crystalline silicon wafers

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Abstract:
In this article the optimization of a method to increase the photon capture efficiency of crystalline silicon (c-Si) wafers is presented. The method is based on metal assisted chemical etching (MACE) using hydrogen peroxide (H_2O_2) and hydrofluoric (HF) as etchants and silver atoms to catalyze the reaction. P-type monocrystalline silicon wafers (100) with 1Ω.cm were used. The etching time was varied between 10 and 30 minutes and different reagent concentrations were tested. The results obtained proved the capability of MACE to produce silicon wafers with an effective reflectance of 4.3%. Furthermore, a strong correlation between the etchants' molar ratio $\rho = [HF]/([HF] + [H_2O_2])$ and the effective reflectance was observed.

Keywords: Semiconductors; Optical materials and properties; Solar energy materials; Surfaces; Texture

1. Introduction

One of the most efficient ways to improve the efficiency of a solar cell is increasing the number of photons absorbed in the active material. The use of very performant light capture strategies has the potential to significantly increase the path covered by the photons in the solar cell material, which can be several times higher than its thickness, thus decoupling the solar cell's optical path length from its physical length [1]. Achieving such decoupling not only allows a reduction of the material consumption, as enables the use of inferior quality materials with low diffusion lengths [2].

In the last years considerable efforts have been put in the development of advanced light capture techniques to improve light absorption on solar cells. A lot of different paths have been followed such as the introduction of plasmonic structures, that can increase light absorption either by promoting light scattering (or light trapping), near-field enhancement or resonant energy transfer [3]. Another approach that has been followed is the nanopatterning of the solar cell surface. Reactive ion etching (RIE) texturing, can provide a single-side controllable nanostructure patterning [4]. When compared to RIE, chemical texturing has the advantage of being easier to implement and allowing a faster processing of large areas. The usual industrial process to perform surface texturing on c-Si solar cells is chemical texturing either alkaline or acidic [5].

In the last years the use of metal assisted chemical etching (MACE) to obtain highly antireflective structures has been growing. The principle of MACE is the use of a noble metal to locally catalyze the chemical etching. Since the noble metal accelerates the oxidation of the substrate, etching will be deeper wherever there are noble metal particles present. The texturing structure produced is thus highly dependent on the profile of the noble metal distribution [6]. A major advantage of MACE is its simplicity that allows fast processing and the fact that it can be accomplished with inexpensive equipment. Also, MACE allows the control of the nanostructures' features by a careful choice of parameters [7]. A drawback of the MACE process is the fact that it significantly increases the number of surface states, making the surface passivation particularly demanding [8]. Nevertheless Huang et al achieved an excellent passivation of MACE textured of high doped p-type c-Si [9].

In this work c-Si samples were etched with a MACE method based on the use of H_2O_2, HF as etchant reactants and silver as catalyzer, the experimental details are presented on section 2.

2. Materials and methods

2.1 Samples

During this work 5 ′′ Czochralski p-type monocrystalline silicon polished wafers (100) with 1 Ω.cm were used as substrates. Before etching, the wafers were cut in samples 25 × 25 mm^2 and cleaned with an RCA solution (HCl: $H_2 0_2$:5$H_2 0$).

2.2 MACE process

The samples were etched with a solution of H_2O_2, hydrofluoric acid (HF), and $AgNO_3$ (as source of silver). H_2O_2 oxidizes the substrate while HF removes the silicon oxide (SiO_2) formed. Silver atoms donate holes, locally catalyzing the oxidation of silicon, as the reaction continues the metal sinks in the silicon, creating by this means a high aspect ratio structure [10].

Our study was divided in two phases. In phase I, the concentration of $H_2 0_2$ was varied between 0.6 and 1 M, and HF concentration between 2 and 4 M. An etching time of 30 minutes was used and during etching the reacting beakers were mechanically agitated. Although in this phase after MACE several wafers achieved a very low reflectance, the etchings were not homogeneous, consequently in phase II during etching a magnetic stirrer was placed inside each beaker, also an etching time of 10 minutes was used. In this phase the variation range of $H_2 0_2$ concentration was kept between 0.6 and 1 M, HF concentration was varied between 6 and 4 M.

2.3 Characterization

The reflectance of the etched samples was measured in the range 350 -1100 nm with an UV-vis spectrophotometer, and the effective reflectance of the samples was determined by weighting the measured values with the reference AM1.5 spectrum [11] according to the equation (1), where R_λ is the reflectance at the wavelength λ, and $n_\lambda$is the number of photons in the reference spectrum for the same wavelength.

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

Furthermore, the nanostructures obtained were visually characterized using a scan electron microscope.

3. Results and discussion

3.1 Reflectance measurements

In phase I of our study, a few samples reached an effective reflectance values lower than 7%, being the 4.3% the lowest. Fig.1 presents the spectral reflectance of the five samples with $R_{\text{eff}} < 7\%$ in this phase of the study.

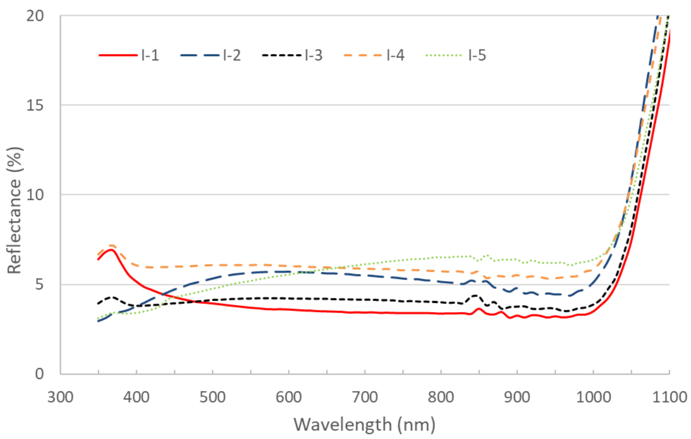

Fig. 1: Spectral reflectance of samples etched in phase I with $R_{\text{eff}} < 7\%$.

The use of a magnetic stirrer and the reduction of the etching time in phase II allowed an improvement of the homogeneity of the etched surfaces while maintaining low reflectance values. In phase II the lowest R_{eff} obtained was 5.0% and several samples reached an $R_{\text{eff}} < 6\%$ after MACE, Fig.2 shows the spectral reflectance for these samples.

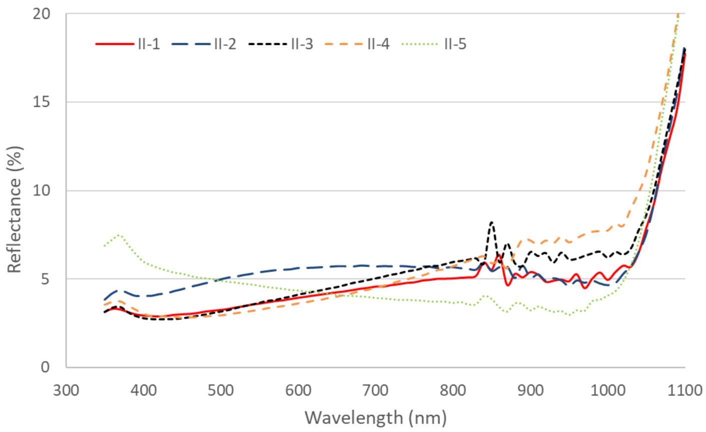

Fig. 2 Reflectance of samples etched in phase II, with $t_{\text{etch}} = 10$ min and magnetic stirrer.

For the samples with $R_{\text{eff}} < 6\%$ the reflectance is lower than 10% in all the range 350-1000 nm.

From Fig. 1 and Fig. 2, it can be observed that for all these samples the reflectance is lower than 10% along the range 350-1000 nm. Also, the low R_{eff} values of these samples confirm the significant reduction of the surface reflectance during MACE.

3.2 Molar ratio ρ

The influence on the etching dynamics and on the characteristics of the etched samples of the reactants molar ratio ρ, defined by equation (2), has been an issue of several studies [12],[13].

$$\rho = \frac{[HF]}{[HF] + [H_2O_2]} \tag{2}$$

The morphology and reflectance of the samples etched during our work were analyzed in the light of the parameter ρ. It was observed that samples processed in etching solutions with similar values of ρ, not only show similar light trapping structures but also display similar reflectance values.

In Fig. 4 the R_{eff} values of the samples etched during this work are plotted against ρ. The samples analysed in the previous section are highlighted.

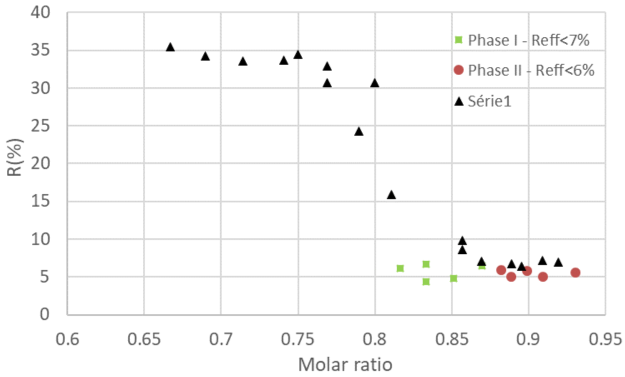

Fig. 3 R_{eff} values as function of the molar ratio ρ.

As it can be observed in Fig. 3 there is a clear correlation between R_{eff} and ρ. Also, there seems to be a threshold value of ρ around 0.75-0.8 over which the reflectance is strongly reduced during etching.

3.3 Morphology characterization

SEM images of the etched samples display continuous spreads of nanowires each a few tens of micrometers high. The height and density of the wires seems to change with etching conditions, namely with ρ, further observations must be made to clarify this aspect.

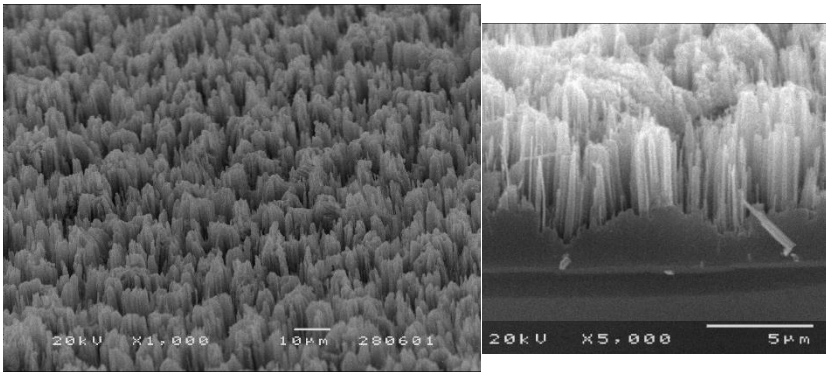

Fig. 4 SEM image of sample after MACE: (a) Upper view; (b) cross-section.

4. Conclusions

During the study here presented the reflectance of monocrystalline silicon samples was significantly reduced through the MACE technique. In phase I of our study an etching time of 30 minutes and a mechanical stirrer was used during etching experiences, and R_{eff} values as low as 4.3% could be obtained, but a lack of homogeneity of the etched surfaces was observed. On phase II, where a magnetic stirrer was introduced and the etching time was 10 minutes, a R_{eff} of 5% could be obtained and the etched surfaces were more homogeneous. The use of a lower etching time as well the higher level of homogeneity of the etched surfaces make these conditions a better option to be applied in the industrial production of c-Si solar cells.

The importance of the molar ratio ρ for the etching process was demonstrated. Results suggest that there is threshold value for ρ over which silicon reflectance is strongly reduced during MACE.

Additional studies must be completed having as main goals the reduction of the R_{eff} while maintaining a high homogeneity of the etched surfaces and further decreasing etching times.

Acknowledgements

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