NA_2CO_3 AS AN ALTERNATIVE TO NAOH/IPA FOR TEXTURISATION OF MONOCRYSTALLINE SILICON

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ABSTRACT: Na_2CO_3-texturing has been shown to be an effective alternative to conventional NaOH/IPA-texturing of monocrystalline silicon material, and has been demonstrated, on an industrial level, to be a cost-effective and environmentally-friendly technique for multicrystalline material. It has, however, not yet been established for industrial use on monocrystalline silicon wafers. In work progressing in this direction, we have optimised the conditions for laboratory-scale texturing of as-cut monocrystalline silicon. The optimal size, uniformity and distribution of the pyramids on the as-cut silicon surface was achieved with 19 - 23 wt% Na_2CO_3, 90°C - 95°C etching temperature and 20 - 25 minutes etching time. The achievable reflection is similar to that obtained with NaOH/IPA-texturisation. In order to assess the feasibility of the technique for solar cell production, we processed buried contact solar cells on 12.5×12.5 cm^2 as-cut Cz Si wafers produced by two companies (A and B). We observed an increase in J_{sc} of about 3 mA/cm^2 compared to cells made using non-textured Cz Si wafers. Average efficiencies of 17.9 % (material A) and 18.3 % (material B) with a maximum efficiency of 18.5 % were achieved, representing an increase of 1.2 % and 1.7 % absolute with respect to non-textured cells respectively. Future work will concentrate on up-scaling this process to demonstrate suitability on an industrial scale.
Keywords: Texturisation - 1, c-Si – 2, Etching - 3

1 INTRODUCTION

Anisotropic texturing of monocrystalline silicon is a well known technique. Most commonly, a wet etchant, typically NaOH and IPA (isopropyl alcohol) or KOH and IPA is used. These solutions rely on the difference in etch rate between (100) and (111) oriented planes and result in random, upright pyramids on a (100) oriented surface. The average reflection from the silicon surface in the wavelength range 400 to 1100 nm is reduced from about 36 % to about 12 %.

One disadvantage of random pyramid texturing in an industrial environment is that the results are not always reproducible. This is mainly because reasonable etching rates are only achievable at temperatures close to the boiling point of IPA (~82ºC). Consequently, during the texturing process, IPA evaporates and the composition of the solution is constantly changing. Evaporation of IPA is difficult to control and refilling of the bath is rarely optimal. In addition, IPA has high initial and disposal costs, is a health hazard and an explosive substance.

Chaoui et al. [1] demonstrated that KOH/IPA may be replaced by K_2CO_3. They achieved an average reflection (R_{av}) of ~ 12% by etching for 30 minutes in 30 wt% K_2CO_3 at 100°C. However, the high concentration of K_2CO_3 and the high temperature involved preclude the transfer of the process to mass production of solar cells. Nishimoto and Namba [2] found that Na_2CO_3 can also be used to texture silicon wafers. Wafer reflections lower than 12% were achieved at 20 wt% Na_2CO_3 and 95°C in only 15 minutes. Addition of 1 wt% $NaHCO_3$ resulted in a similarly low reflectance, but was achieved in only half the time. The etching experiments were, however, done using 2.5×2.5 cm² samples in glass beakers. Up-scaling seems to be difficult: The lowest reflectance Sparber et al. achieved for 10×10 cm² wafers was about 16% [3]. On the other hand, the Mitsubishi Electric Corporation has applied the technique to large area mc-Si wafers [4].

In this work, we present firstly the results of an optimisation of the Na_2CO_3-texture parameters and secondly cell results for large area wafers that were textured using the new parameters.

2 EXPERIMENTAL

2.1 Optimisation of the technique

Optimisation experiments were carried out using 5×5 cm² samples in a glass beaker. In contrast to [1, 2 and 3], we chose to work with as-cut silicon in order to reduce the number of process steps that would need to be applied in an industrial process. No pre-cleaning or saw damage removal was required. After texturisation the samples were cleaned in DI-water and diluted HF and subsequently dried. Conditions for optimisation of texturisation varied between 15 and 25 wt% Na_2CO_3, which is near maximum solubility, 5 and 30 minutes etching time, and 70°C and 95°C. Temperature was controlled to ± 1°C.

The main aspect for optimisation was the average reflection in the wavelength range 400 to 1100 nm. Reflectance was measured using a VARIAN Cary 5 Spectrophotometer equipped with an integrating sphere. The etching depth, which was determined by weighing the samples, was kept constant at 11-12 μm/side, in order to completely remove the saw damage. Moreover, as a more qualitative parameter, size, homogeneity, and density of the pyramids was studied with a JEOL JM-840A Scanning Electron Microscope (SEM).

2.2 Up-scaling

The homogeneity and quality of the Na_2CO_3-texturing at the optimum etching conditions was then proven for 10×10 cm^2 and 12.5×12.5 cm^2 CZ Si-wafers, which were also etched in a 10-l glass beaker.

2.3 Revising the feasibility of Na_2CO_3-texturing

In order to revise the feasibility of Na_2CO_3-texturing for industry, buried-contact solar cells were processed on 12.5×12.5 cm^2 as-cut Cz Si wafers produced by two companies (A and B). Processing steps are shown in Figure 1. A detailed description of this process is given in [5].

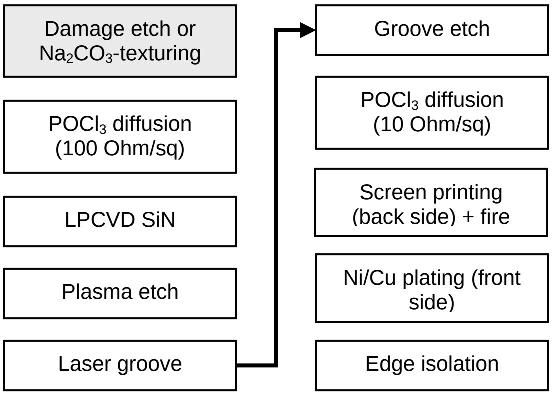

Figure 1: Scheme of cell processing used for the cells presented in this work.

3 RESULTS

3.1 Optimal etching parameters

The results of the optimisation showed that the etch rate and texture morphology with Na_2CO_3 are very dependent on the etch temperature. Up to temperatures of 75°C, the etching rate is less than 0.2 µm/min. Increasing the temperature by 20°C resulted in an increase of the etch rate to 0.55-0.6 µm/min. The temperature could not be increased above 98°C, as this resulted in unacceptably high levels of water evaporation.

With etch temperatures in the optimal range (from 75°C to 98°C) the morphology is strongly dependent on the Na_2CO_3 concentration (see Figure 2). Increasing the Na_2CO_3-concentration from 15 wt% to 25 wt% resulted in a substantial improvement in the regularity of size and density of the pyramids.

The optimal size and density of the pyramids was reached with etching times of between 20 and 25 minutes. These results are supported by the reflection measurements. The average reflection in the wavelength range 400-1100 nm decreases with increasing etch time and reaches a minimum after approximately 20 minutes.

The dependence of the average reflection on the concentration and temperature of the etching solution is shown in Figure 3. From Figure 3 it is also clear that the lowest average reflection is achieved using a concentration of approximately 20 wt% and a temperature of more than 90°C. The results of the exact optimisation of the etching conditions in this region are shown in Figure 4. From Figure 4 it is also clear that the average reflection with Na_2CO_3-texturing is comparable to or better than that achieved using NaOH/IPA.

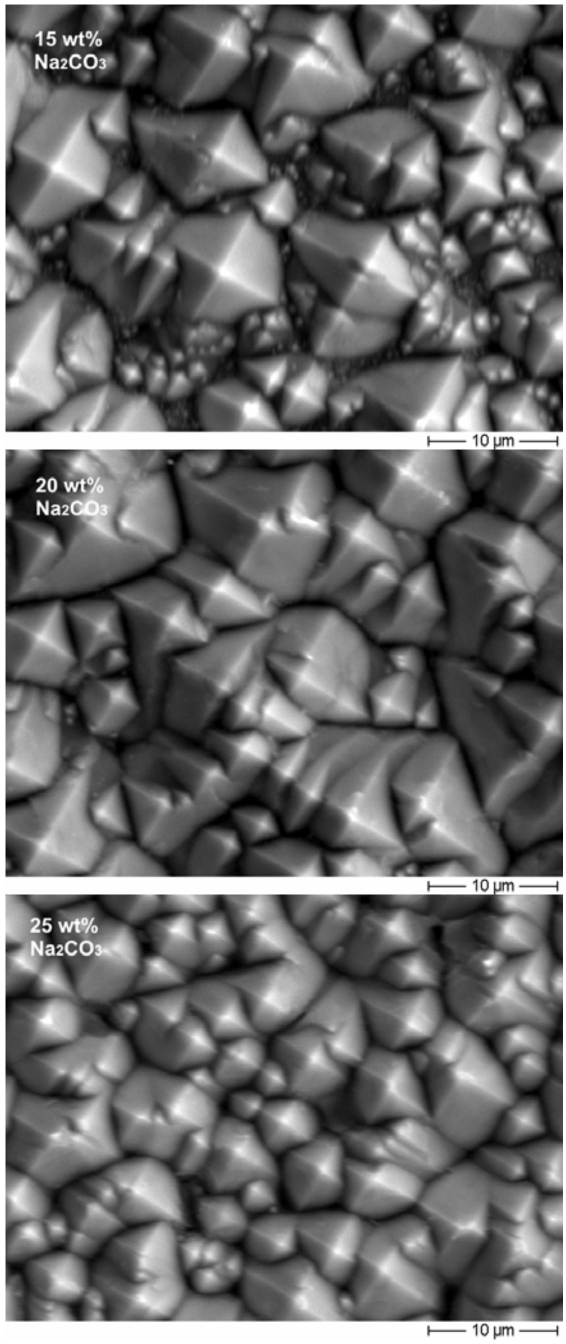

Figure 2: Surface morphology of wafers etched at 90 °C for 25 minutes and different concentrations of Na_2CO_3.

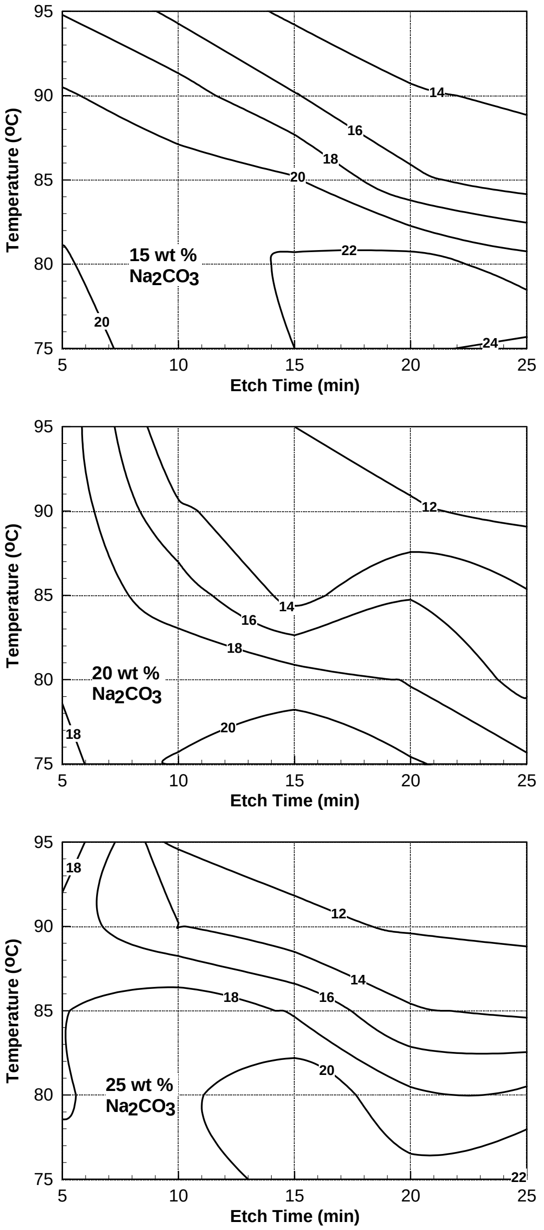

Figure 3: Reflection vs. temperature and etch time for different concentrations of Na_2CO_3.

The optimal size, uniformity and distribution of the pyramids on the silicon surface were achieved using etching temperatures above 90°C. At 95°C average reflections (R_{av}) lower than 12% may be achieved for a quite broad range of Na_2CO_3-concentrations (19 wt% to 23 wt%) and etching times (15 to 30 minutes) (see Figure 4) which is less than that typically required for IPA-containing etch solutions.

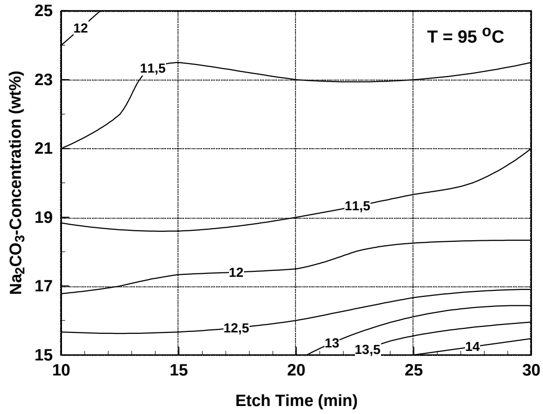

Figure 4: Reflection vs. Na_2CO_3-concentration and etch time at 95°C.

3.2 Solar cells

We observed an increase in J_{sc} of about 3 mA/cm^2 compared to non-textured Cz Si buried contact solar cells (see Table I). Average efficiencies of 17.9 % (company A) and 18.3 % (company B) were achieved, representing an increase of 1.2 % and 1.7 % absolute with respect to non-textured cells respectively. For the best textured cell an efficiency of 18.5 % has been reached which is very promising for a buried contact cell process on this wafer size. With this it is clearly shown that not only the optical parameters are comparable to NaOH/IPA texturing, but also cell efficiencies are at least on the same level. This indicates there is neither a negative effect on the surface nor a contamination problem.

Table I: IV-data for non-textured and Na_2CO_3-textured Cz buried contact solar cells on 12.5×12.5 cm^2 as-cut Cz Si wafers produced by two companies (A and B).

Material		FF [%]	V_{OC} [mV]	J_{SC} [mA/cm²]	Eff. [%]
A	non-textured	80.8	622	33.2	16.7
	Textured	80.4	620	35.9	17.9
B	non-textured	80.4	621	33.3	16.6
	Textured	80.7	620	36.4	18.3

4 CONCLUSIONS AND OUTLOOK

In contrast to former experiments, our results clearly demonstrate the effectiveness of the Na_2CO_3-texturisation. The optical parameters of the wafers are comparable to those achieved using standard NaOH/IPA texturisation. In addition, the results of buried contact solar cells made with this texture are promising. On CZ-Si wafers (12.5x12.5 %) an average efficiency of 18.3 % and a maximum value of 18.5 % have been reached.

The question of whether Na_2CO_3-texturisation can be adapted as an industrially feasible, cost-effective and environmentally-friendly alternative to conventional NaOH/IPA-texturisation for monocrystalline silicon material must be investigated in further experiments. In particular the lifetime of the etching solution should be checked.

5 REFERENCES

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