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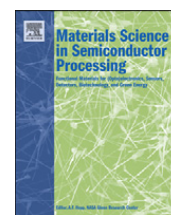
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## Review

Texturization of silicon wafers with  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  solutions for heterojunction solar-cell applications

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## ABSTRACT

The formation of pyramidal structures by anisotropic etching of  $\langle 100 \rangle$ -oriented mono-crystalline silicon wafer surfaces is an effective method to reduce reflection losses originating on the front side of conventional silicon solar cells and silicon-heterojunction (SHJ) solar cells. One of the most common methods of texturization used in the solar-cell industry is based on aqueous solutions of NaOH or KOH and isopropyl alcohol (IPA). However, IPA is toxic and relatively expensive, so efforts are being made to replace it. Among the potential alternatives, solutions based on  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  mixtures have been proposed. In the present study, solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  mixtures were prepared in order to form pyramidal structures on silicon wafer surfaces. It was not possible to obtain uniform and completely textured surfaces by using aqueous solutions consisting only of  $\text{Na}_2\text{CO}_3$ .  $\text{NaHCO}_3$  must be added in order to achieve uniform textured surfaces with low hemispherical reflectance suitable for SHJ solar-cell applications. Textured surfaces with good uniformity and low average hemispherical reflectance (15.4%) were prepared from  $\langle 100 \rangle$  silicon substrates with relatively low etching times (25 min). Good surface passivation (lifetime  $> 600 \mu\text{s}$  and implicit open-circuit voltage of  $690 \pm 10 \text{ mV}$ ) on these p-type textured wafers were achieved.

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## 1. Introduction

In the past few years, silicon-heterojunction (SHJ) solar cells have attracted interest from the photovoltaic industry owing to the good properties of crystalline silicon (c-Si) and the versatility of thin-film technology [1,2]. These SHJ solar cells are formed by deposition of thin-film amorphous or microcrystalline silicon onto c-Si wafers. They are mainly characterized by their high conversion efficiencies, high open-circuit voltages, and low temperature coefficients [3]. The nature of these solar cells makes them interface dominated [4–7].

The properties of SHJ solar cells can be improved by using textured silicon substrates and an appropriate antireflection coating (ARC) on the front surface, by which reflection losses are reduced considerably [8–12]. One of the most common methods applied to texture  $\langle 100 \rangle$ -oriented monocrystalline-silicon wafers is based on anisotropic etching by solutions consisting of NaOH or KOH, isopropyl alcohol (IPA) and deionized water (DIW) [13–17]. In this type of solution IPA performs an indispensable role as a moisturizing and surfactant agent [18]. However, the use of IPA entails serious disadvantages derived from its toxicity and relatively high cost [19,20]. Moreover, the low boiling point of IPA limits the process temperature, and product losses caused by evaporation during reaction should be prevented. Etching rates also diminish as process temperature is lowered, so longer times are required to complete the surface texturization. As a result of these disadvantages, different compounds have been studied for their application to anisotropic etching of monocrystalline-silicon substrates [19–22]. Although the pyramid formation mechanism is still under discussion, it is known that, in general, alkaline solutions are able to texture  $\langle 100 \rangle$ -oriented monocrystalline-silicon surfaces as long as enough hydroxyl ions are provided for the texturing reaction. Thus, aqueous solutions based on  $\text{Na}_2\text{CO}_3$  have been shown to be a suitable alternative to replace solutions including IPA [13,22,23].

$\text{Na}_2\text{CO}_3$  is an economical compound, commercially available, and used widely in the glass industry. By contrast, when  $\text{Na}_2\text{CO}_3$  solutions are used to texture silicon substrates, the process temperatures can be raised as high as  $90^\circ\text{C}$ , at which the etching reactions proceed at significantly higher rates. The objective of this study was to prepare textured surfaces, from different types of monocrystalline-silicon substrates, with suitable properties for their application in SHJ (a-Si:H/c-Si) solar cells by using  $\text{Na}_2\text{CO}_3$  solutions and  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  aqueous mixtures. The present paper describes a systematic and comprehensive study of the main parameters of anisotropic etching and their influence on morphology and reflectance of textured surfaces in order to find optimum texturization to make good SHJ solar cells based on  $\langle 100 \rangle$ -oriented monocrystalline-silicon wafers. This method could also be used in conventional crystalline-silicon solar cells.

## 2. Material and methods

### 2.1. Preparation

The texturization process was first assayed on  $1\text{--}5\text{-}\Omega\cdot\text{cm}$ -resistive p-type  $\langle 100 \rangle$ -oriented polished float

zone (FZ) silicon wafers. Once the optimum conditions of texturization were determined, the process was applied to other types of substrates, such as  $1\text{--}2\text{-}\Omega\cdot\text{cm}$ -resistive p-type  $\langle 100 \rangle$ -oriented polished- and as-cut Czochralski (CZ) monocrystalline substrates in order to validate the texturization process for commercial silicon wafers. The thickness was  $255\text{--}305\text{ }\mu\text{m}$  for FZ wafers and  $280\text{--}320\text{ }\mu\text{m}$  for CZ wafers. The diameter of the wafers was  $100\text{ mm}$  but the size of the samples assayed was  $40\text{ mm} \times 40\text{ mm}$ . Immediately before the texturization process, samples were cleaned with ethanol in an ultrasonic bath. Then, the samples were etched in a  $1\text{ wt}\%$  HF:DIW (HF diluted in  $18.2\text{ M}\Omega\cdot\text{cm}$ -resistivity DIW) solution at ambient temperature to remove the native oxide [24,25], and finally rinsed with DIW. For the texturization process, the wafers were immersed in a capped vessel containing the texturizing solution. This solution had been previously heated at the assay temperature using a digitally controlled hot plate provided with a stainless-steel temperature sensor. When the etching time had elapsed, samples were removed from the solution and rinsed with DIW in order to stop the chemical reaction.

In addition, aluminum-doped ZnO films (ZnO:Al) were deposited on the wafers for which the best texturization had been obtained in order to analyze the effect of the antireflection coating from the hemispherical-reflectance spectra. These antireflection coatings (ARCs) were deposited by RF magnetron sputtering. The thickness of the films was  $\sim 80\text{ nm}$ . This is the optimum thickness of ZnO:Al layers for their application as ARCs in SHJ solar cells [4].

Finally, in order to analyze the surface quality of the wafers, silicon carbide films (a-SiC<sub>x</sub>:H) were deposited by plasma-enhanced chemical vapor deposition on both sides of the best-textured silicon wafers [26]. These resulting samples were used for quasi-steady-state photoconductance (QSSPC) measurements [5,27].

### 2.2. Characterization

The hemispherical reflectance [ $R_{\text{hem}}(\lambda)$ ] of the textured silicon surfaces was measured from  $300$  to  $1250\text{ nm}$  by means of a Lambda 1050 UV/Vis/NIR spectrophotometer (Perkin-Elmer) equipped with a  $6\text{-mm}$  integrating sphere. The surface morphology of the wafers was observed with a JEOL JSM-6400 scanning electron microscope (SEM).

The sheet resistance of the ZnO:Al films deposited onto  $10^4\text{-}\Omega\cdot\text{cm}$ -resistive monocrystalline-silicon wafers was measured using a commercial Veeco-Instruments model FPP5000 4-point probe. Layer thicknesses ( $d$ ) were estimated using the hemispherical-reflectance spectra measured by the UV/Vis/NIR spectrophotometer, illuminated from the ARC side according to the following equation [4,28]:

$$nd = \lambda_{\min}/4$$

where  $n$  is the refraction index of the ZnO:Al films and  $\lambda_{\min}$  the wavelength for which the hemispherical reflectance is minimum between  $300$  and  $1250\text{ nm}$ .

The minority-carrier lifetime and the implicit open-circuit voltage of the passivated samples were measured using a Sinton Consulting Instrument [5].



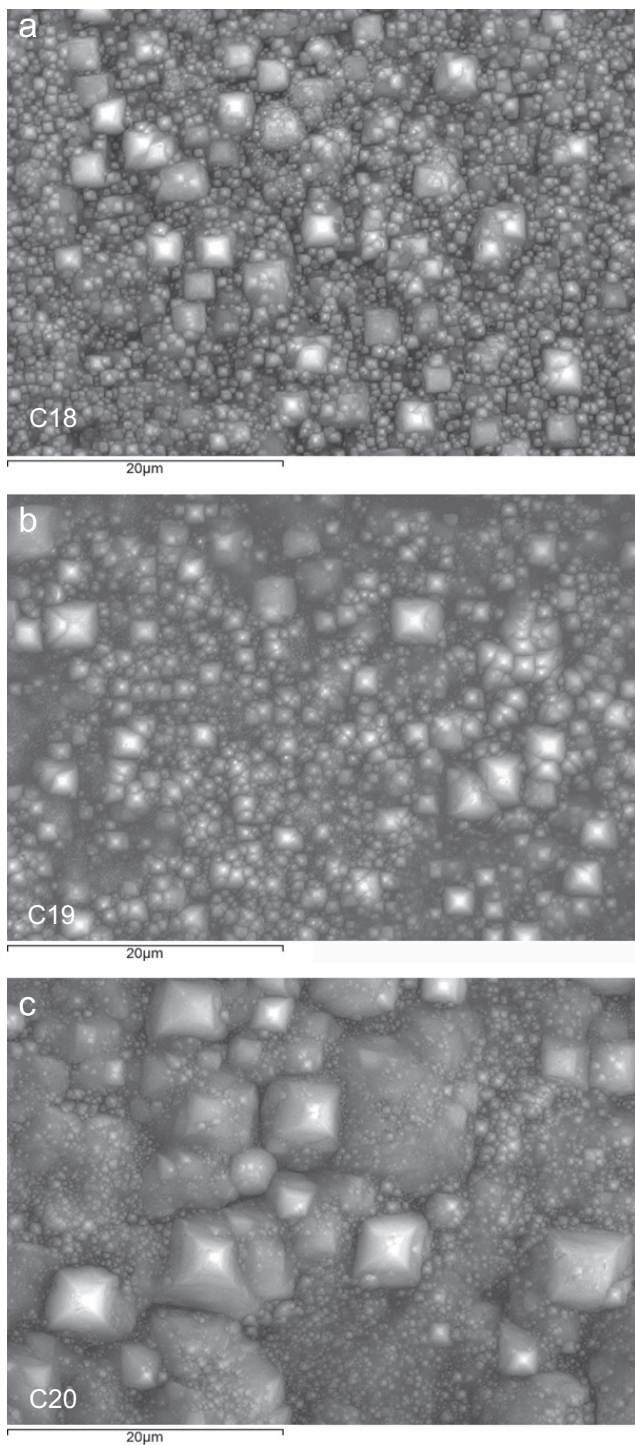
### 3. Results and discussion

#### 3.1. Fit of process temperature

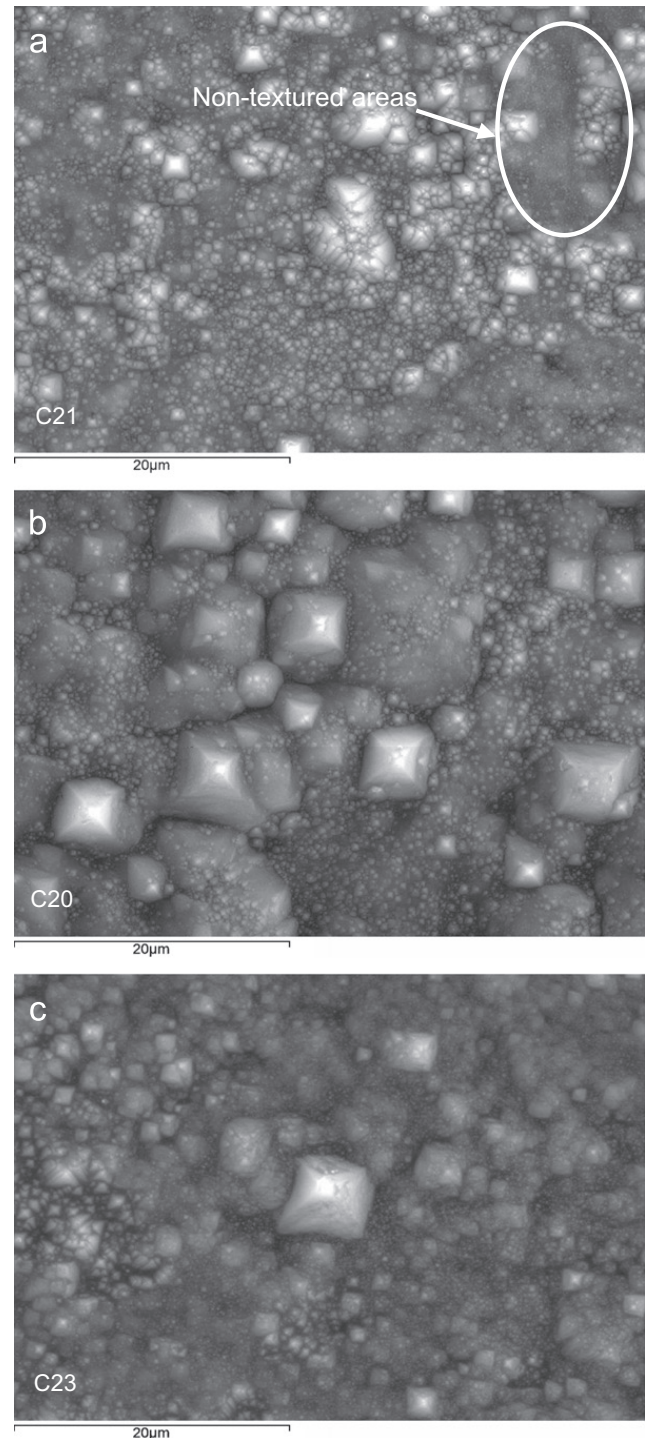
A set of p-type  $\langle 100 \rangle$ -oriented polished FZ monocrystalline wafer samples was treated using  $\text{Na}_2\text{CO}_3$  solutions at moderate concentrations (10 wt%). The temperature was varied from 60 to 90 °C and the treatment time was kept at 30 min for all assays. It was found that 70 °C was a

sufficiently high temperature to texture the surfaces fully. Yet, as the temperature was raised to 90 °C the size of the pyramids ( $\sim 5 \mu\text{m}$ ) forming the textured surface increased (Fig. 1). For this reason, 90 °C was considered the optimum temperature, although the surfaces treated were not yet homogeneously textured.

In order to achieve good uniformity at 90 °C, the etching time was varied from 20 to 60 min. Thirty minutes was



**Fig. 1.** SEM images of FZ  $\langle 100 \rangle$  textured wafers at 90° incidence angle used to analyze the effect of temperature. Samples were textured in 10 wt%  $\text{Na}_2\text{CO}_3$  solutions for 30 min at 70 °C (a), 80 °C (b) and 90 °C (c).



**Fig. 2.** SEM images of wafers at 90° incidence angle. Samples were textured using 10 wt %  $\text{Na}_2\text{CO}_3$  at 90 °C: for 20 min (a), 30 min (b) and 50 min (c). Nontextured areas appeared when etching times fell below 30 min.

estimated as the optimum value, because for shorter times (e.g., 20 min) the surfaces showed bright regions without etching. By contrast, when the time was prolonged above 30 min no improvement of the textured surfaces was noticed (Fig. 2).

### 3.2. Influence of $\text{Na}_2\text{CO}_3$ concentration

The influence of  $\text{Na}_2\text{CO}_3$  concentration was evaluated by varying the concentration between 5 and 30 wt%. As the concentration was increased, a significant deterioration of surfaces was observed at first sight. The reaction became more vigorous and created many large bubbles that adhered to the surface of the sample. These hydrogen bubbles acted as a mask on the surface, inhibiting the texturization reaction. As a result, the surfaces were not uniform and exhibited wide bright zones in which the texturization process was not successful.

The hemispherical-reflectance measurements performed on the best surfaces obtained in these first tests with  $\text{Na}_2\text{CO}_3$  solutions yielded average values of  $\sim 21.5\%$  between 400 and 1100 nm. These values were significantly higher than those obtained by using alkaline solutions with IPA (11–12%) [12,17,18].

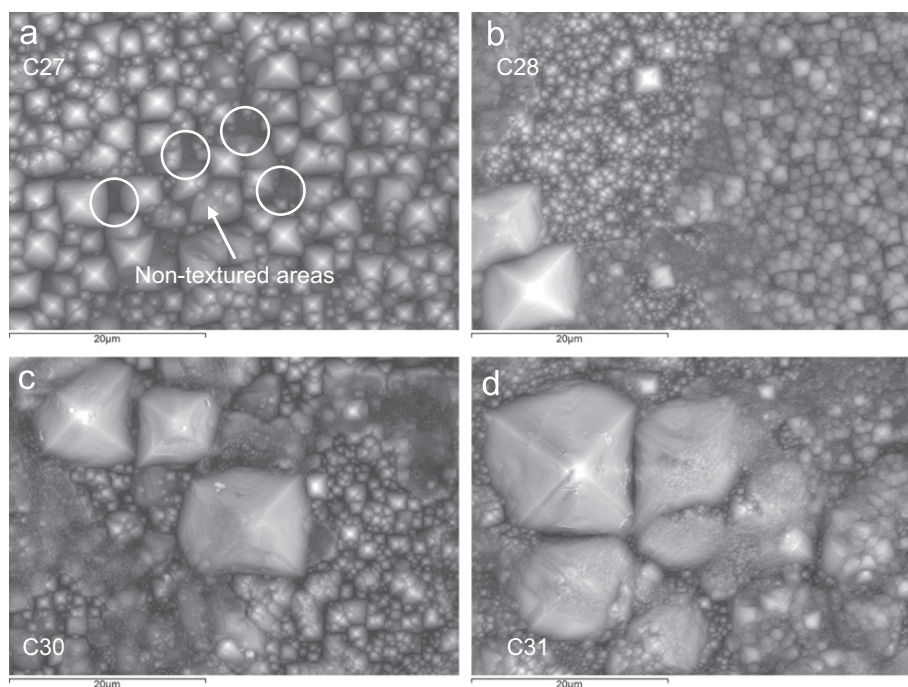
The role of  $\text{CO}_3^{2-}$  ions present in the texturing solutions could be the same as that played by IPA, that is, to act by retarding the explosive reaction and detaching effectively hydrogen bubbles formed at the surface of the samples [29]. Moreover, the surfactant nature of these compounds improves surface wettability of silicon wafers and promotes nucleation and size increase of pyramids [21,23]. Therefore, the quantity of  $\text{CO}_3^{2-}$  ions in solution yielded by the high concentrations of  $\text{Na}_2\text{CO}_3$  used (2.36 mol/l for  $[\text{Na}_2\text{CO}_3]=25\text{ wt}\%$ ) should be enough to avoid a vigorous etching reaction. However, such solutions resulted in

surfaces that were not completely textured, as previously described. Thus, the influence of  $\text{HCO}_3^-$  ions on etching reactions was studied by the addition of moderate amounts of  $\text{NaHCO}_3$  to the solutions.

### 3.3. Influence of $\text{NaHCO}_3$ in $\text{Na}_2\text{CO}_3$ solutions

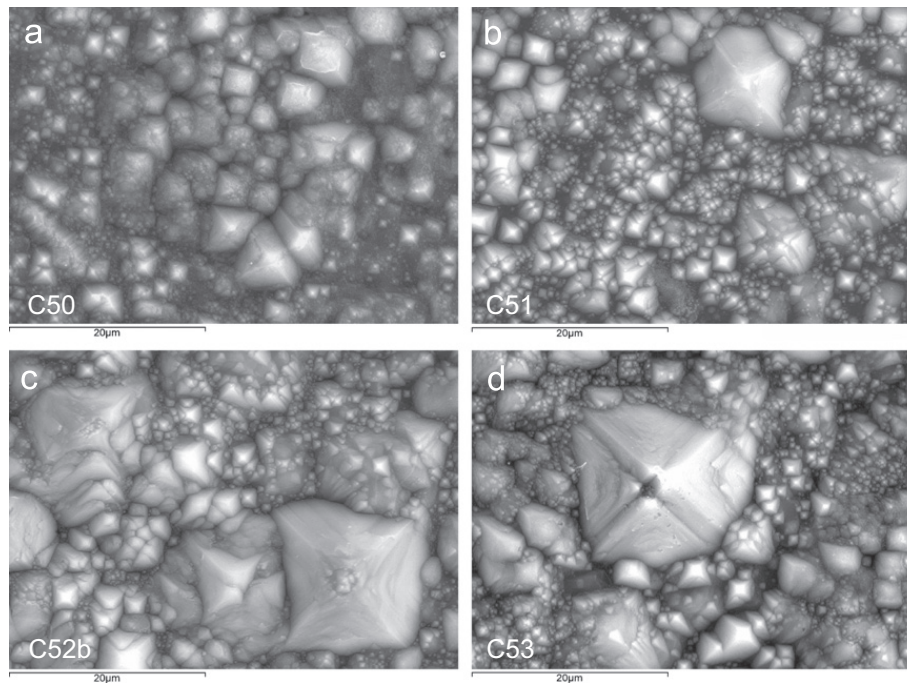
A set of different  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  aqueous solutions was prepared, in which  $\text{NaHCO}_3$  concentration was kept at 4 wt%, while sodium concentration was varied between 5 and 25 wt%. According to the preceding assays, the etching time and temperature were maintained at 30 min and  $90^\circ\text{C}$ , respectively. Addition of  $\text{NaHCO}_3$  indeed led to a reduction in the size of the bubbles adhered to the wafer surfaces, producing thoroughly textured surfaces with uniform appearance even at a  $\text{CO}_3^{2-}$  concentration as high as 25 wt%. Scanning electron microscopy (SEM) (Fig. 3) showed that, at 5 wt% concentration, the sample surface was not fully etched. As  $\text{Na}_2\text{CO}_3$  concentration was increased, so too did the number and size of larger pyramidal structures. The hemispherical reflectance of these samples textured with  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  solutions decreased ( $R_{\text{hem}} = 16.0\text{--}19.0\%$  on average, depending on  $\text{Na}_2\text{CO}_3$  concentration) with regard to samples textured with  $\text{Na}_2\text{CO}_3$  solutions ( $R_{\text{hem}} = 21.5\%$  on average). Therefore, it can be considered that the  $\text{HCO}_3^-$  ions perform an important role in moderating etching reactions.

Next, an analysis of etching time of the solutions consisting of 25 wt%  $\text{Na}_2\text{CO}_3$  and 4 wt%  $\text{NaHCO}_3$  at  $90^\circ\text{C}$  was carried out by varying the time from 10 to 35 min. An optimum treatment time of 25 min was determined for these conditions. A shorter time was insufficient to texture completely the surfaces, or the surfaces mainly consisted of pyramidal structures that were too small. By contrast, when treatment time was prolonged over 25 min, larger pyramids could not develop correctly and some pyramids showed



**Fig. 3.** SEM images of FZ  $\langle 1\ 0\ 0 \rangle$  wafers at  $90^\circ$  incidence angle textured with  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  mixture solutions.  $\text{NaHCO}_3$  concentration was 4 wt% and  $\text{Na}_2\text{CO}_3$  concentrations were 5 wt% (a), 10 wt% (b), 20 wt% (c) and 25 wt% (d). Nontextured areas appeared when  $\text{Na}_2\text{CO}_3$  concentration was  $< 10\text{ wt}\%$ .



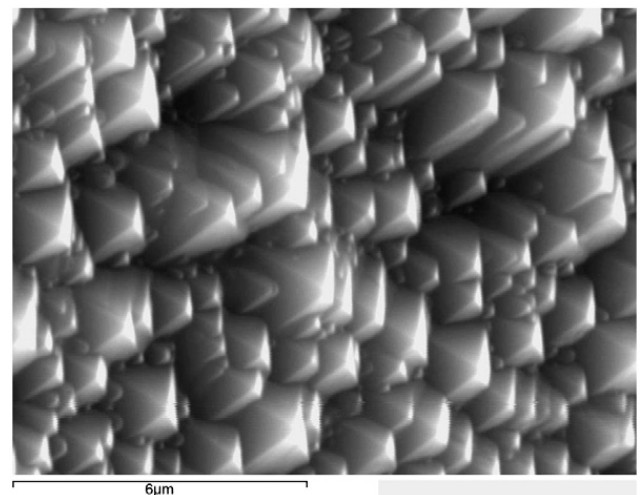


**Fig. 4.** SEM images of FZ  $\langle 100 \rangle$  samples at  $90^\circ$  incidence angle textured using 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  solutions at  $90^\circ\text{C}$  for 15 min (a), 20 min (b), 25 min (c) and 35 min (d).

significant deterioration (Fig. 4). The lowest value of the hemispherical reflectances (15.4 on average between 400 and 1100 nm) was achieved for a time of 25 min. The surfaces of silicon samples textured using these optimum conditions (25 wt%  $\text{Na}_2\text{CO}_3$ ; 4 wt%  $\text{NaHCO}_3$ ;  $90^\circ\text{C}$ ; 25 min), were composed of pyramidal structures with sizes similar to those obtained with mixtures of alkaline solutions and IPA (5–10  $\mu\text{m}$ ) in a previous work [16].

#### 3.4. Influence of the ratio of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ concentrations

The influence of the ratio of  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  concentrations on pyramidal density and morphology was studied. Samples were etched with texturing solutions in which the ratio of concentrations was varied from 0.16 to 0.53. The samples etched with solutions of low ratios between 0.16 and 0.27 showed an appreciable improvement in the pyramidal morphology (i.e., flatter facets and less rounded tops). The best morphology was obtained when the ratio was 0.27 (4 wt%  $\text{NaHCO}_3/15$  wt%  $\text{Na}_2\text{CO}_3$ ) (Fig. 5). However, when were treated with etching solutions with higher ratios ( $r=0.40$ – $0.55$ ) a clear worsening of morphology of their textured surfaces was observed. As it has been noted previously, the addition of  $\text{NaHCO}_3$  into the  $\text{Na}_2\text{CO}_3$  texturing solution produces an increase of  $\text{HCO}_3\text{H}^-$  species that improved the pyramidal morphology. On the contrary, this addition also led to a reduction in  $\text{OH}^-$  concentration, as determined from pH measurements ( $6 \times 10^{-3}$  mol/l for 25 wt%  $\text{Na}_2\text{CO}_3$  solutions and  $1 \times 10^{-4}$  mol/l for 25 wt%  $\text{Na}_2\text{CO}_3/4$  wt%  $\text{NaHCO}_3$  solutions). The chemical reaction mechanism of silicon is most commonly described as a two-step mechanism [30]. The  $\text{OH}^-$  ion acts as catalyst for the initial oxidation of hydrogen-terminated surface silicon atoms. The subsequent etching step results



**Fig. 5.** SEM image of textured FZ  $\langle 100 \rangle$  wafers at  $45^\circ$  incidence angle. Samples were textured using 4 wt%  $\text{NaHCO}_3$  and 15 wt%  $\text{Na}_2\text{CO}_3$  ( $r=0.27$ ) solutions for 30 min at  $90^\circ\text{C}$ .

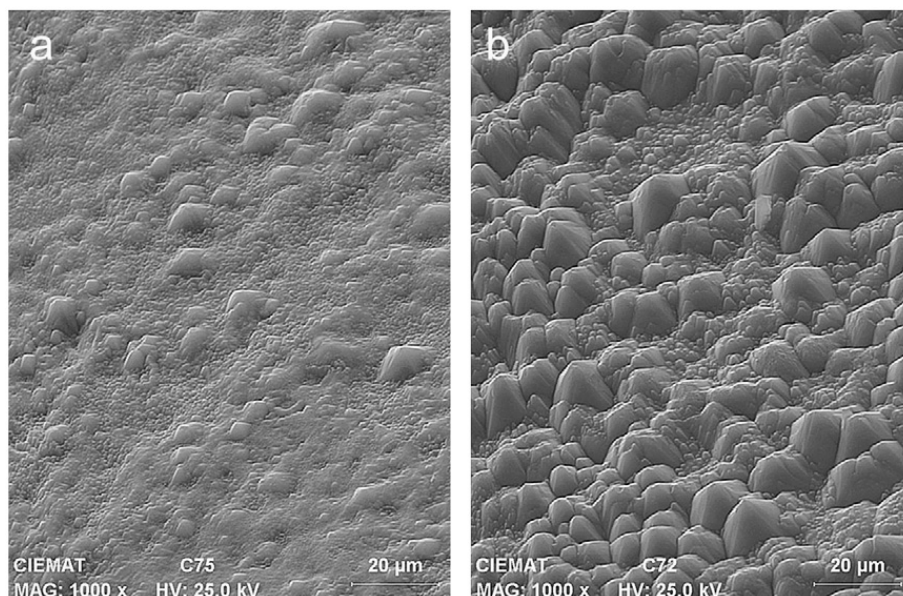
in a dissolved  $\text{Si}(\text{OH})_x$  and a newly exposed hydrogen-terminate Si atom. This soluble species is formed at  $\text{pH} > 13$ , so the  $\text{OH}^-$  ions are considered as reactants in the overall etching reaction [31]. If the reduction in  $\text{OH}^-$  concentration becomes excessive, the resultant surfaces would be heterogeneous and exhibit a lower density of pyramids. This could explain the deterioration of the surface morphology of the samples etched with solutions with  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  ratios  $> 0.40$ , in which the pH values decreased below 9.73 (i.e.,  $\text{OH}^-$  concentration  $\leq 6 \times 10^{-5}$  mol/l). Moreover, as  $r$  increased, a more prolonged etching time was necessary to texture entirely the silicon surfaces (for example, 25 min for 0.16, 40 min for 0.4, and 1 h for 0.53 ratios).

With regard to the hemispherical reflectance, although for  $r=0.27$  better-defined pyramids were obtained than for  $r=0.16$ , the reflectance values were significantly worse:  $r=0.27$ ,  $R_{hem}=19.0\%$  and for  $r=0.16$ ,  $R_{hem}=15.4\%$  on average. Therefore,  $r=0.16$  was considered to be the optimum  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  ratio.

Not only a suitable  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  ratio is required in order to provide textured surfaces with good quality. The presence of sufficient amounts of  $\text{CO}_3^{2-}$  ions in the solutions should be ensured. This can be deduced from the comparison of wafers etched with a solution of 2.4 wt%  $\text{NaHCO}_3$  and 15 wt%  $\text{Na}_2\text{CO}_3$  to those etched with a solution of 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  solutions (Fig. 6). In both cases, the solutions corresponded to  $r=0.16$ . Their pH values were 10.22 and 10.12, respectively. When pH is  $< 13$ , it is possible that the formation of  $\text{SiO}_2$  occurs. The formed oxide can passivate the surface of the sample, preventing any further chemical etching of

silicon [32]. It is known that  $\text{CO}_3^{2-}$  reacts with  $\text{SiO}_2$ , resulting in soluble silicates, thus the presence of such species could reduce and even avoid surface passivation. The solution consisting of 2.4 wt%  $\text{NaHCO}_3$  and 15 wt%  $\text{Na}_2\text{CO}_3$  did not supply enough  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  ions to the texturing solution, so etched surfaces were not of good quality (compare Fig. 6a and b) and their hemispherical-reflectance average values were too high ( $R_{hem}=21.7\%$  on average).

Table 1 summarizes the results concerning morphology, average hemispherical reflectance, and  $\text{OH}^-$  concentration of samples that were textured with different  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  concentration ratios and with different treatment times. A compromise has to be reached in order to provide textured surfaces with a high pyramid density without excessive detriment of pyramidal morphology, by which a low reflectance can be achieved. With texturing carried out using 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  solutions at  $90^\circ\text{C}$



**Fig. 6.** SEM images of FZ  $\langle 100 \rangle$  textured wafers at  $45^\circ$  incidence angle. Samples were textured using a mixture of 2.4 wt%  $\text{NaHCO}_3$  and 15 wt%  $\text{Na}_2\text{CO}_3$  for 30 min (a), or using 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  solution for 25 min (b), both at a temperature of  $90^\circ\text{C}$  and equal ratio of concentrations (i.e.  $r=\text{NaHCO}_3/\text{Na}_2\text{CO}_3=0.16$ ).

**Table 1**

Comparison of the results obtained for FZ  $\langle 100 \rangle$  polished wafers that were textured with solutions with different  $[\text{NaHCO}_3]/[\text{Na}_2\text{CO}_3]$  ratios. This table also shows samples that were textured with a similar  $[\text{NaHCO}_3]/[\text{Na}_2\text{CO}_3]$  ratio but different treatment times. The uniformity could be appreciated at a naked eye and the pyramidal morphology through SEM images. The  $[\text{OH}^-]$  were calculated from pH measurements of the solutions.

ID	$t$ (min)	$[\text{NaHCO}_3]$ (wt%)	$[\text{Na}_2\text{CO}_3]$ (wt%)	$[\text{NaHCO}_3]/[\text{Na}_2\text{CO}_3]$ ratio	Fully etched	Uniformity	Flatter facets and well defined tops	$R_{hem}(\lambda)$ (%)	$[\text{OH}^-]$ (mol/l)
C20	30	0	10	0	No	Low	Regular	21.5	$4.0 \cdot 10^{-3}$
C15	30	0	25	0	No	Low	Regular	–	$5.6 \cdot 10^{-3}$
C69	60	8	15	0.53	Yes	Regular	Regular	20.0	$< 5.4 \cdot 10^{-5}$
C67	40	6	15	0.40	Yes	Regular	Regular	17.5	$5.6 \cdot 10^{-5}$
C28	30	4	10	0.40	Yes	Low	Regular	19.0	$6.0 \cdot 10^{-5}$
C61	40	4	15	0.27	Yes	High	Very Well	19.0	$1.1 \cdot 10^{-4}$
C30	30	4	20	0.20	Yes	Regular	Regular	19.0	$1.0 \cdot 10^{-4}$
<b>C72 &amp; C52</b>	<b>25</b>	<b>4</b>	<b>25</b>	<b>0.16</b>	<b>Yes</b>	<b>High</b>	<b>Well</b>	<b>15.4</b>	<b><math>1.3 \cdot 10^{-4}</math></b>
C50	15	4	25	0.16	No	Regular	Regular	23.0	$1.3 \cdot 10^{-4}$
C75	30	2.4	15	0.16	Yes	Regular	Regular	21.7	$1.7 \cdot 10^{-4}$



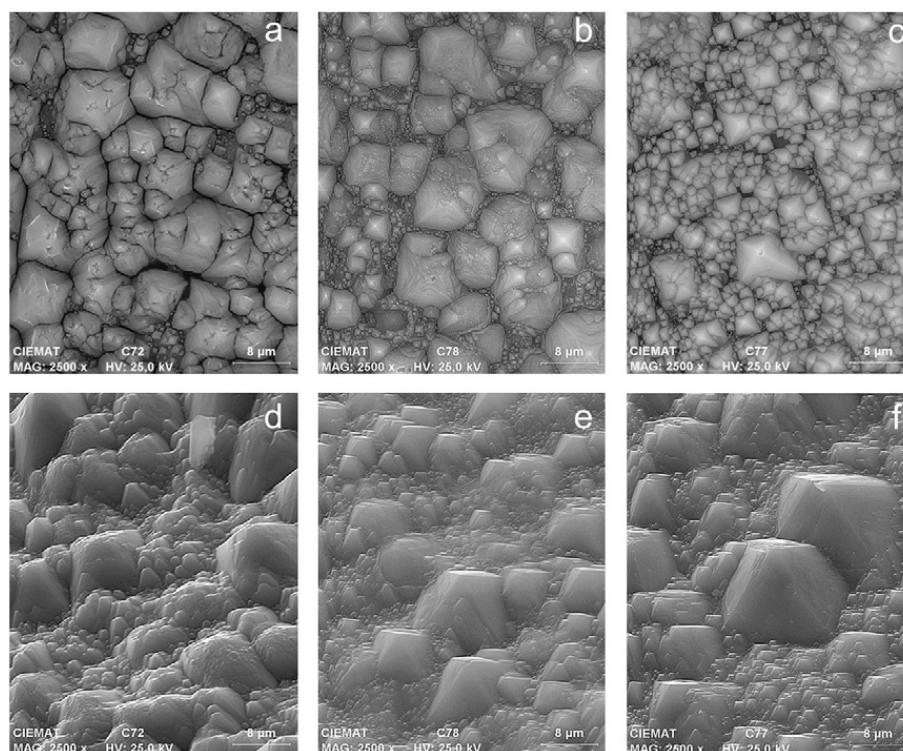
this compromise can be attained for relatively low etching times (25 min).

The validity of the optimized texturization process for FZ wafers was demonstrated for polished and as-cut CZ monocrystalline substrates. SEM showed that as-cut samples had textured surfaces with less-uniform pyramid sizes, while the textured surfaces of both polished substrates (FZ and CZ) were similar (Fig. 7). The homogeneity of the wafer surfaces greatly improved when wafers were immersed in the solution vertically instead of horizontally (Fig. 8). The average hemispherical reflectance values were 13.8–16.0% in the three types of silicon substrates treated, as can be seen in the spectra in Fig. 9. The reflectance decreased when wafers were textured vertically. The etching rate of this optimum texturization process (i.e. 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$ , 25 min) was also evaluated. It was found that the etching

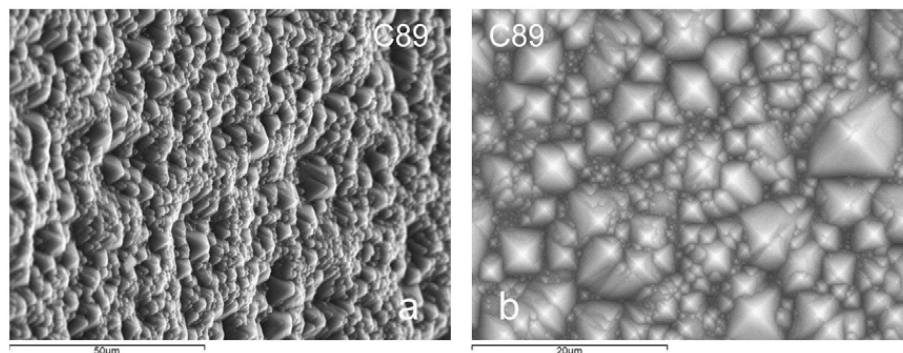
rate depended on the initial surface morphology of the wafers:  $0.37 \mu\text{m}/\text{min}$  for as-cut and  $0.11 \mu\text{m}/\text{min}$  for polished CZ silicon wafers.

In addition, ZnO:Al films of  $\sim 80 \text{ nm}$  thickness were deposited on the best-textured wafers to analyze the effect of the ARC through the hemispherical reflectance spectra. A decrease in hemispherical reflectance down to 5% was observed after the coating was deposited on textured FZ silicon samples (Fig. 10). This value is comparable to that obtained from FZ silicon substrates textured by using NaOH and IPA solutions ( $R_{\text{hem}} = 3\%$  on average) [16,17].

Finally, minority carrier lifetime  $> 600 \mu\text{s}$  and implicit  $V_{\text{oc}} 690 \pm 10 \text{ mV}$  measured by QSSPC (1 sun) were obtained when the best-textured wafers were cleaned with standard Radio Corporation of America (RCA) treatments [33] and

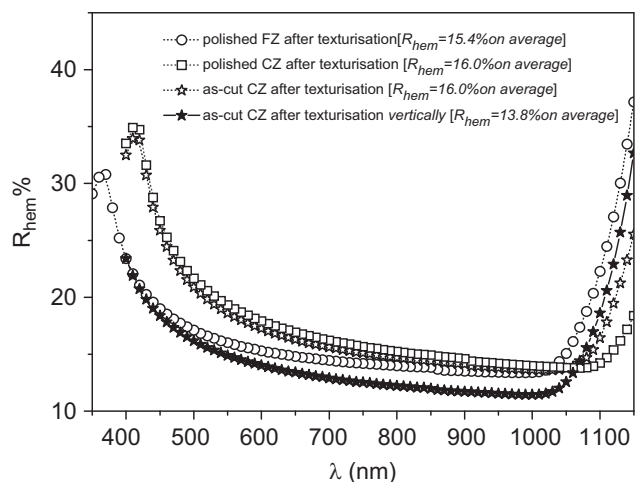


**Fig. 7.** SEM images at  $90^\circ$  (a–c) and  $45^\circ$  (d–f) incidence angle. Samples were textured according to the optimum conditions: 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  solutions for 25 min at  $90^\circ\text{C}$ . (a) and (d) correspond to polished FZ  $\langle 100 \rangle$  wafers, (b) and (e) to polished CZ  $\langle 100 \rangle$  wafers, and (c) and (f) to rough-(as-cut) CZ  $\langle 100 \rangle$  wafers.

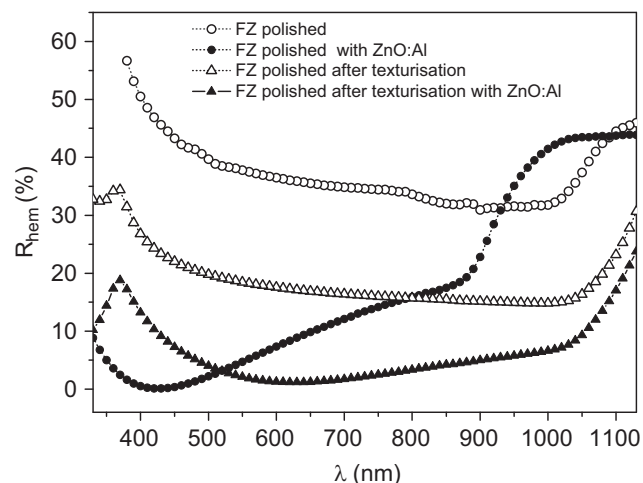


**Fig. 8.** SEM images at  $45^\circ$  (a) and  $90^\circ$  (b) incidence angle of as-cut CZ wafer textured according to the optimum conditions: 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  solutions for 25 min at  $90^\circ\text{C}$ . Wafer was immersed vertically in a capped vessel containing the solution.





**Fig. 9.** Hemispherical reflectance spectra of polished FZ and polished and as-cut CZ wafers after the optimum texturization process.



**Fig. 10.** Hemispherical reflectance spectra of FZ wafers after the texturization process by using  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  solutions. The effect of a ZnO:Al ARC is also shown.

passivated with a-SiCx:H films [34] The lifetimes obtained could be considered suitable for their possible application both in silicon solar cells and in SHJ solar cells.

#### 4. Conclusion

This study investigated the texturization of  $\langle 100 \rangle$  polished FZ and rough (as-cut) and polished CZ silicon wafers with  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  aqueous solutions. The results show that it is not possible to obtain uniform and completely textured surfaces by using aqueous solutions containing only  $\text{Na}_2\text{CO}_3$ . Moderate amounts of  $\text{NaHCO}_3$  must be added in order to achieve entirely textured surfaces of higher quality. Thus, it can be considered that  $\text{HCO}_3^-$  ions perform an important role in moderating etching reactions. The presence of sufficient  $\text{CO}_3^{2-}$  ions in solution should be ensured in order to avoid the formation of  $\text{SiO}_2$  that could passivate the surfaces and prevent the etching process.

Aqueous solutions based on 4 wt%  $\text{NaHCO}_3$  and 25 wt%  $\text{Na}_2\text{CO}_3$  were able to etch anisotropically both polished

FZ and as-cut and polished CZ silicon wafers. Average hemispherical-reflectance values between 13 and 16% between 400 and 1100 nm were obtained for the three types of silicon wafers assayed. These values decreased to 5% on average when appropriate ARCs were deposited onto the textured wafers. These results could be considered sufficiently low for SHJ solar-cell applications. Results greatly improved when wafers were immersed vertically into the texturing solution. Furthermore, QSSPC measurements demonstrated the good quality of the surfaces of these silicon wafers textured with  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  mixtures for their applicability in SHJ solar cells.

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