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Novel and efficient texturing approach for large-scale industrial production line of large-area monocrystalline silicon solar cell

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Abstract Texturing monocrystalline silicon (c-Si) for solar cell fabrication is still a key issue due to consumption of a large amount of costly isopropyl alcohol (IPA) in conventional NaOH/KOH solution. Controlling IPA amount in NaOH/KOH-texturing bath for longer life of the solution in industrial batch production is a difficult task. This article reports the use of a chemical bath with a composition of NaOH–NaOCl (sodium hydroxide–sodium hypochlorite) for texturing monocrystalline silicon surface for solar cell fabrication. We report such a novel concept of texturing of the c-Si surface without using IPA and discarding the saw damage removal step. The optimized etching condition with NaOH–NaOCl-containing solution does not have any negative effect on monocrystalline silicon solar cell efficiency. Easy control of the process due to the self-controlled reaction is one of the major advantages and there is no need of sophisticated temperature-controlling system during texturing in the industrial batch process. Moreover, FTIR analysis shows the formation of Si–Cl bond during texturing, which improves the quality of diffused junction due to the gettering effect of Cl. Solar cell of conversion efficiency 14.5–15.8 % on CZ–Si substrate of area 125 mm × 125 mm was successfully fabricated using a novel texturing approach in industrial production line with yield >85 %.

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Introduction

Texturing of monocrystalline silicon is necessary for fabrication of better-quality solar cells. Therefore, industrial production of large-area monocrystalline silicon for solar cell fabrication needs effective and economically viable technique for texturing of monocrystalline silicon (c-Si). Conventionally, anisotropic chemical etching of silicon is performed with a mixture of alkaline solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH), and isopropyl alcohol (IPA) is widely used for texturing of monocrystalline silicon wafers [1–3]. In a typical texturing condition, the IPA concentration is higher than the NaOH (or KOH) concentration. IPA increases the wettability of silicon surface, but increasing IPA concentration beyond a limit decreases the rate of silicon removal very strongly [1]. Therefore, excessive IPA addition to the texturing solution leads to the detrimental effect of no texturization even after long-time treatment. Moreover, IPA is a volatile compound and so it has to be added frequently to the texturization bath during the batch process to compensate for the evaporated amount, leading to a higher consumption of IPA. Controlling IPA amount in NaOH/KOH-texturing bath for longer life of the solution in the industrial batch production is a difficult task [4]. IPA is also expensive. All these together are the constraints of NaOH/KOH-texturing processes during monocrystalline silicon solar cell fabrication in large-scale industrial production line. However, due to the high cost of IPA and constraint on controlling its excess amount, there is always a search for an alternate chemical composition for texturing without using IPA. So, elimination of IPA during texturing of the commercial solar cell fabrication is the key issue of the overall texturing cost reduction approach, as well as maintenance of the continuous flow of texturing batch process in industrial

process line. To overcome these constraints, use of sodium carbonate (Na$_2$CO$_3$) or potassium carbonate (K$_2$CO$_3$) has been reported by some researchers [5, 6]. This article reports the use of a chemical bath with a composition of NaOH–NaOCl (sodium hydroxide–sodium hypochlorite) for texturing monocrystalline silicon surface without using IPA for solar cell fabrication. Moreover, this proposed novel concept for texturing of silicon surface also discards the saw damage removal step in the industrial production line. The optimized etching condition with NaOH–NaOCl-containing solution does not have any negative effect on monocrystalline silicon solar cell efficiency. Self-controlling reaction is one of the major advantages of the NaOH–NaOCl texturization process, which leads to much less complicacies of using a temperature control system in the industrial batch process. The role of NaOH–NaOCl solution for cleaning organic contaminations while texturing c-Si and comparison of this process with conventional NaOH-IPA approach have been reported in this paper.

Experiment

Texturing

In our experiment, we have used *CZ* p-type, monocrystalline silicon (c-Si) with resistivity of about 0.5–2.0 Ωcm for texturing. In our texturization experiment, we varied the three different concentrations of NaOH solution (i.e., 10, 20 and 40 %) for a fixed 12 % NaOCl solution each time. The ratio of the amounts of NaOH to NaOCl also varied along with the time of etching. All the etched wafers were studied under optical microscope and etching thickness was studied with a standard gravimetric method. Scanning electron microscopy (SEM) and FTIR were studied for selected monocrystalline wafers. Evaluation of surface reflectance after texturing was also completed. We used all these measurement tools in the case of conventional NaOH-IPA texturing and compared the results of the two different approaches.

Solar cell fabrication

During the solar cell fabrication experiment, textured *CZ* p-type monocrystalline silicon (c-Si) wafers were diffused by pentavalent impurity (phosphorus) in an open-tube furnace using conventional POCl$_3$ diffusion source at 850 °C for 7 min pre-deposition followed by 16 min drive-in. PSG removal was done by short time dipping in BHF solution followed by DI-water rinsing and drying. The sheet resistance of n$^+$ emitter layer was 55–60 Ω/sq. All textured c-Si wafers were oxidized at 850 °C for 20 min. After edge isolation and oxide layer removal, about 70 nm

layer of SiNx (refractive index $\sim$2.0) was deposited on the front side by means of PECVD at 450 °C for ARC. The front and back metallization of the diffused silicon wafers was carried out using standard Ag paste (product no. 3349, Ferro Electronic Materials) and Al paste (product no. Fx53-038, Ferro Electronic Materials) for screen-printed metallization technique followed by baking and co-firing at the temperature of 750 °C in a conveyor belt furnace (Seirra-Therm, USA).

The illuminated current–voltage (LIV) characteristics, dark current–voltage (DIV) characteristics of NaOCl–NaOH-textured and conventional NaOH-IPA-textured c-Si solar cells were determined.

Results and discussion

For etching performance comparison with two different approaches, (a) proposed NaOH–NaOCl solution and (b) conventional NaOH-IPA solution, we used contaminated c-Si wafers. Prior to the texturization experiment, FTIR analysis of the c-Si samples was done. From the FTIR analysis of the samples, it was observed that at the start all silicon wafers had significant contamination [7, 8] all over the surface as shown in Fig. 1. Three different values of concentration of NaOH such as 10, 20 and 40 % were taken and the ratio of NaOH:NaOCl was considered as 1:2 for the first four experiments. The etching time durations for those experiments were set between 15 and 20 min. In the next set of experiment, mainly the ratio of NaOH:NaOCl was varied in the textured solution and only three different time settings were considered. The details of the experimental conditions along with average reflectivity of the different etched monocrystalline silicon(c-Si)
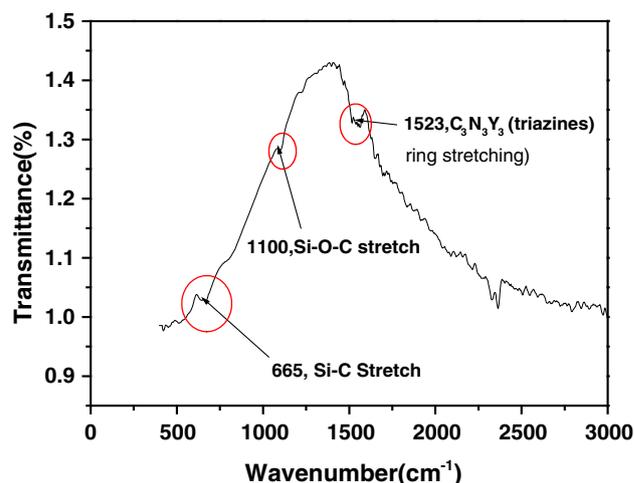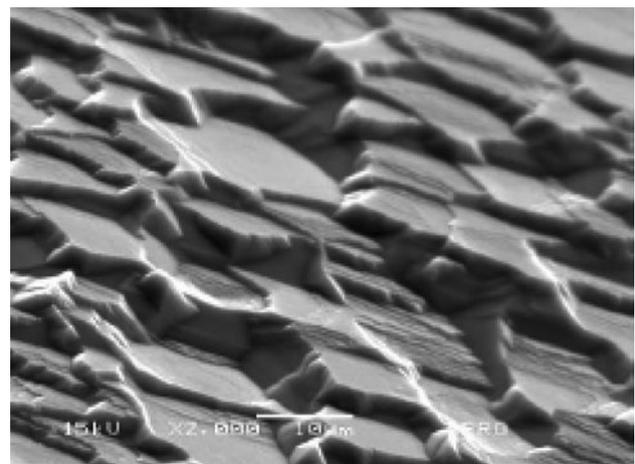

Fig. 1 FTIR analysis of the starting c-Si wafer before the texturization experiment

Table 1 Different conditions of NaOH–NaOCl texturing

Sample ID	Conc. of NaOH (%)	Conc. of NaOCl (%)	NaOH:NaOCl	Time of etching (min)	Average reflectivity (%)
S1	10	12	1:2	20	19.19
S2	20	12	1:2	20	18.31
S3	40	12	1:2	15	18.37
S4	40	12	1:2	20	19.56
S5	40	12	1:3	30	19.28
S6	40	12	1:4	10	17.49
S7	40	12	1:4	24	21.03
S8	40	12	1:5	10	17.12
S9	40	12	1:5	24	20.85
S10	40	12	1:6	10	15.47
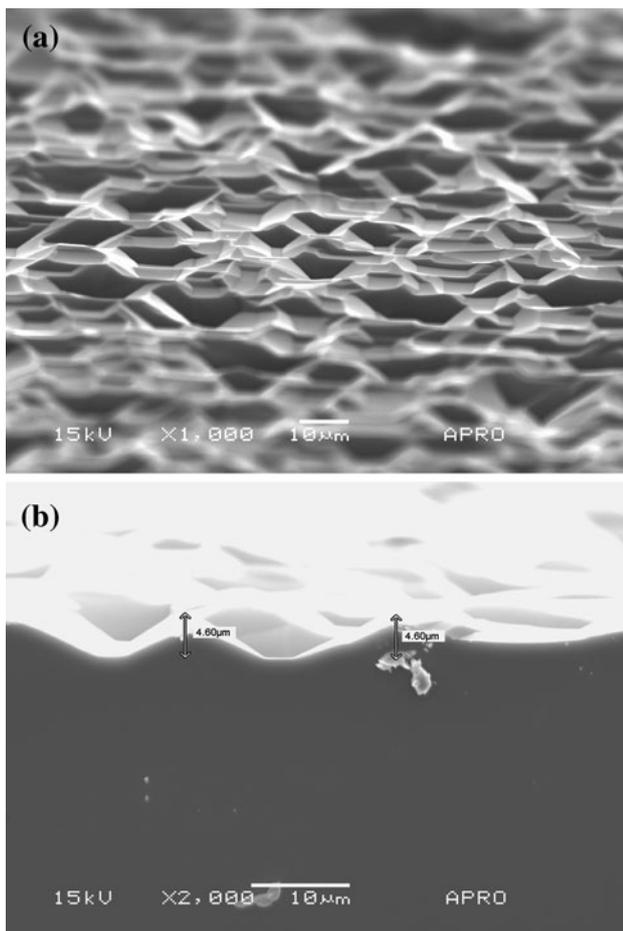
Fig. 2 SEM picture of NaOH–NaOCl-textured c-Si wafer: **a** surface, **b** cross-sectional edge view where NaOH (40 %): NaOCl = 1:2, textured time 20 min

Fig. 3 Surface morphology of a typical NaOH–NaOCl-textured c-Si with higher NaOH and NaOCl ratio (for typical 1:4)

surfaces are listed in Table 1. It was observed that the average reflectivity of the textured sample S2 was lowest compared to samples S1 and S3. This might be due to the different etching mechanism of NaOH–NaOCl solution for different combination ratios. As NaOCl is a strong oxidizing agent [9], it oxidizes the silicon layer first on dipping in NaOH–NaOCl solution. This was followed by etching due to the presence of NaOH in the solution. Moreover, as the silicon layer was chemically oxidized, the probability of growth of non-uniform oxide on the silicon layer was significantly large. Anisotropy of NaOH solution is highest at its 20 % concentration [10]. The chance of inverted pyramidal structure formation through the automatically unintentionally formed oxide mask on the c-Si surface is more than that in the other two cases, i.e., 10 and 40 % in NaOH:NaOCl = 1:2 ratio (sample S1 and S2). So, sample S2 was more textured than S1 and S3. This was probably due to the lowest average reflectance of sample S2 out of the three samples (S1, S2 and S3). The calculated standard deviation for reflectivity of the c-Si samples under the experiment is 1.7 using standard deviation formulas. Figure 2 shows the SEM micrograph of a typical NaOH–NaOCl-textured surface with etching condition as mentioned in Table 1 for sample 2. Inverted pyramidal structures were formed at some places on the surface of c-Si as shown in Fig. 2a. The etch depth was around 4 µm as
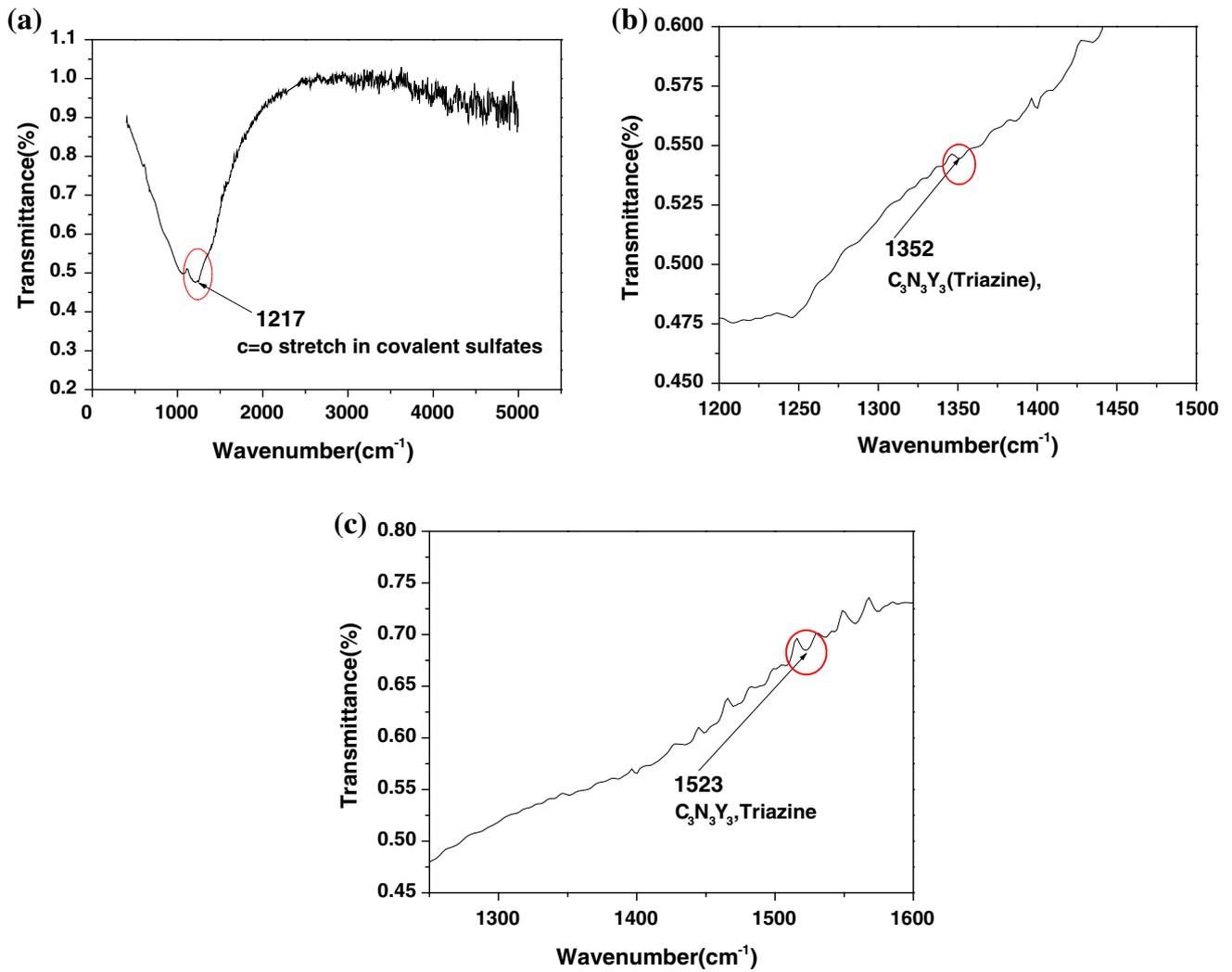
(a)

(b)

(c)

Fig. 4 FTIR analysis of NaOH–NaOCl c-Si surface after short time texturing (10 min) of s samples S6, S8 and S10, respectively
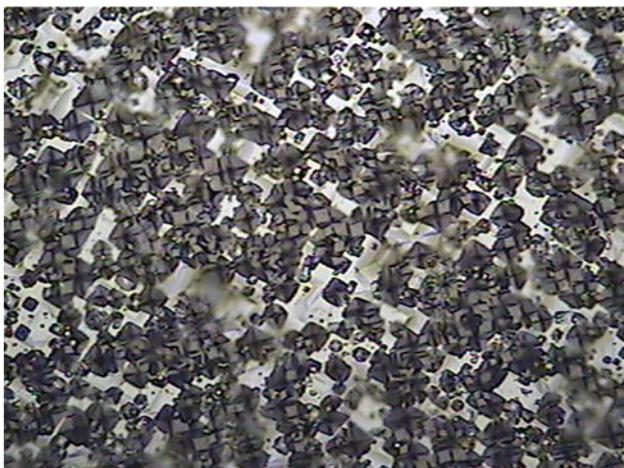

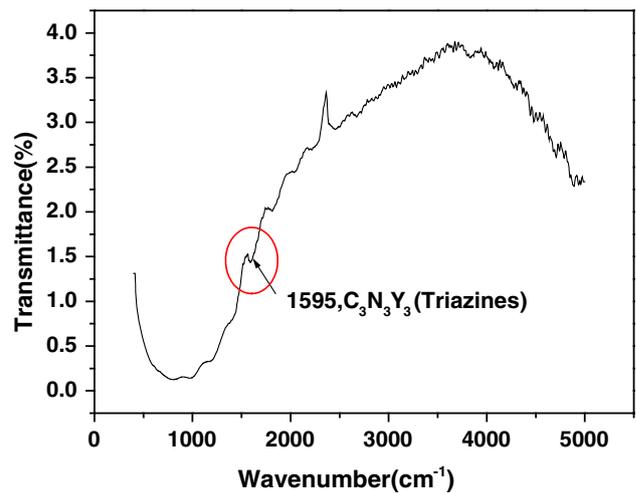**Fig. 5** Optical micrograph of a conventional NaOH-IPA-textured c-Si surface

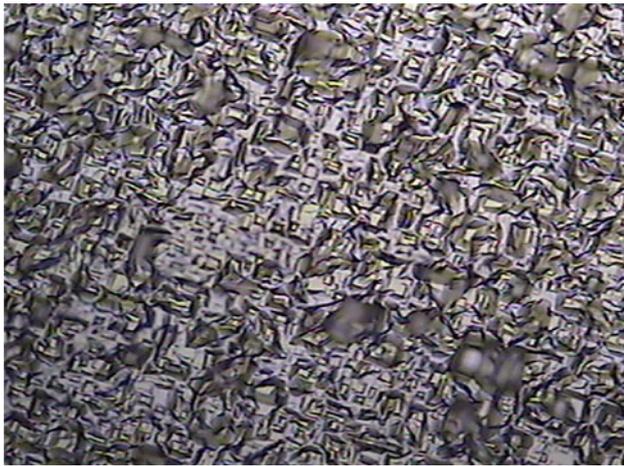**Fig. 6** FTIR analysis of NaOH-IPA-textured c-Si surface

Fig. 7 Optical micrograph of a typical NaOH–NaOCl-textured c-Si surface (condition of texturization: concentration of NaOH: 20 %, concentration of NaOCl: 12 %, NaOH:NaOCl = 1:2 and time = 20 min.)
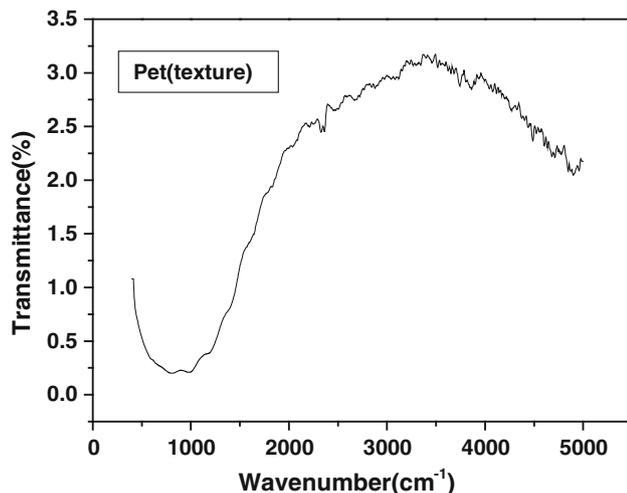

Fig. 8 FTIR analysis of a typical NaOH–NaOCl-textured c-Si surface with texturing time >10 min

indicated in Fig. 2b. Moreover, it was also observed that the average reflectance (wavelength range 300–1,100 nm) of textured c-Si wafers depended on the three major

experimental parameters, such as concentration of NaOH, ratios of NaOH:NaOCl and times of etching for a fixed NaOCl concentration as mentioned in Table 1. In this case, NaOCl plays a dominating role due to its higher amount compared to NaOH, as a result of which the etch rate is strongly reduced in the $\langle 100 \rangle$ direction and increased in the $\langle 111 \rangle$ direction, resulting in a much flatter surface. Higher reflectance compared to 20 % NaOH in a 1:2 ratio was due to the flatter surface nature of the samples S5, S7, S9 and S10, as shown in Table 1. Figure 3 shows the nature of surface structure formed with a higher amount of NaOCl in the NaOH–NaOCl solution. However, for lower time ($\sim$10 min), the samples S6, S8 and S10 showed low average reflectance. This was due to the very less etching rate of the silicon surface after the addition of NaOCl to the etching solution, resulting in lesser amount of contaminant removal from the surfaces of S6, S8 and S10 samples, as indicated in FTIR analysis curves (Fig. 4a–c). Therefore, we did not use the samples S6, S8 and S10 despite their lower reflectance values, because the surface contaminants were still present even after texturization. As done earlier, we thoroughly analyzed the NaOH-IPA-textured c-Si samples via optical microscopic study and FTIR analysis, respectively. It was observed from optical microscopic study throughout the entire c-Si surface that the textured c-Si surface was not at all satisfactory even after 2 min saw damage removal followed by 45 min of NaOH-IPA texturization as shown in Fig. 5. FTIR analysis of the NaOH-IPA-textured c-Si sample showed some impurity still present on the silicon surface as indicated in Fig. 6, hindering the initiation of the texturing process. In the case of surface texturization with our proposed NaOH–NaOCl approach, we discarded the saw damage removal step. From the optical microscopic study of the surface throughout the NaOH–NaOCl-textured surface, it was observed that the surface of c-Si was uniformly textured with the NaOH–NaOCl-texturing approach as shown in Fig. 7. The FTIR observation of NaOH–NaOCl-textured surface indicated the complete removal of organic contaminants from the surface of c-Si during texturing in

Fig. 9 SEM micrographs of textured c-Si surface using **a** conventional NaOH-IPA solution and the **b** proposed NaOH–NaOCl solution, respectively, for texturing
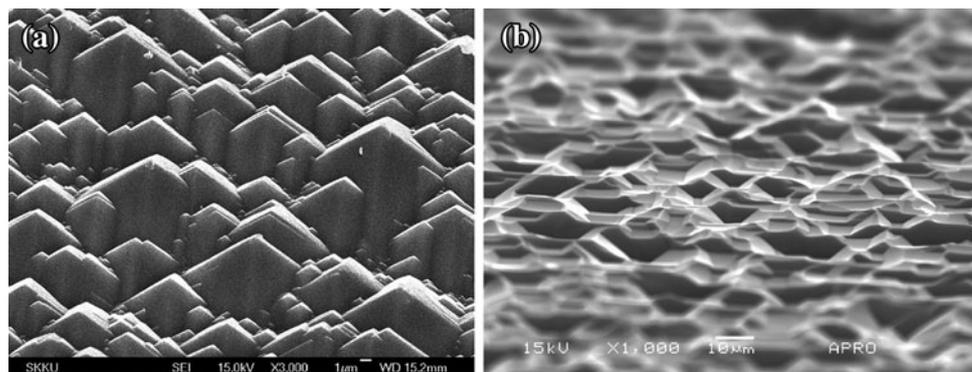
NaOH–NaOCl bath as shown in Fig. 8. This was due to the NaOCl present in the texturization solution, which oxidized all organic contaminants from the c-Si surface. The oxidized contaminants thus formed were finally etched out by NaOH present in the textured solution. This chemical process might help in the initiation of the texturization process. From the SEM analysis as showed in Fig. 9, we observed that the nature of the NaOH–NaOCl-textured surface was entirely differently structured than that observed in the case of conventional NaOH-IPA-textured surface. Inverted pyramidal structures might have originated on the c-Si surface during the NaOH–NaOCl texturization sequence. Formation of inverted pyramidal structures on the c-Si surface in this case was likely observed in the case of selective texturization through an oxide mask [11]. The formation of inverted pyramid structures in the case of the proposed NaOH–NaOCl etching might be due to the combined effect of in situ non-uniform oxidation via etching due to the presence of constituent chemicals NaOCl and NaOH in the texturing solution. The oxidizing chemical NaOCl present in the textured solution may help in the formation of thin, non-uniform oxide growth on the c-Si surface, and OH^- in the NaOH solution might help in c-Si surface etching. Moreover, the chance for formation of more inverted pyramids through an unintentional opening window of oxide is more due to the highest anisotropy of the 20 % concentrated NaOH solution.

Figure 10 shows the reflectivity of c-Si wafers textured using conventional NaOH-IPA and new NaOH–NaOCl-texturing approaches. It was observed that the overall reflectance (wavelength range 300–1,100 nm) of c-Si wafer textured using conventional NaOH-IPA approach was lower than that using the proposed NaOH–NaOCl
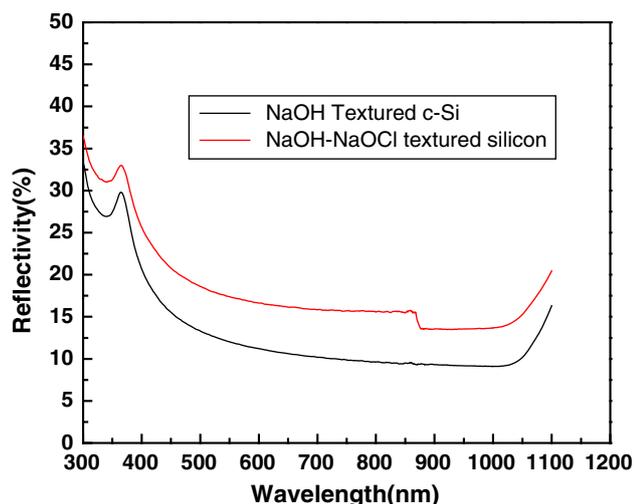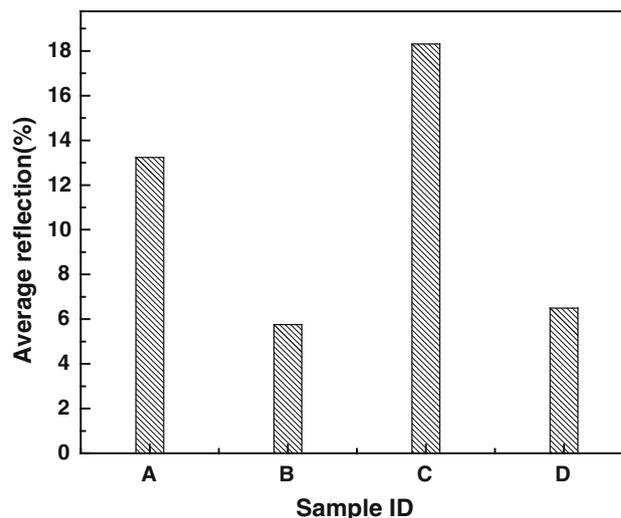

Fig. 11 Average reflectance of textured c-Si surface without silicon nitride (SiNx) ARC: NaOH-IPA textured [sample ID-A], NaOH–NaOCl textured [sample ID-C] and with SINx ARC: NaOH-IPA textured [sample ID-B] and NaOH–NaOCl textured [sample ID-D]

approach. One important point is that the reflectivity of the c-Si surface does not have such a serious effect on the conversion efficiency of the fabricated solar cell, because $SiNx/TiO_2$ film as AR (antireflective) coating is usually used for all commercial silicon solar cells after texturization. Moreover, after SiNx coating on NaOH–NaOCl-textured c-Si wafer, the average reflectivity drastically reduces from 18.31 % to around 6.49 % whereas for NaOH-textured *c-Si* wafer it is reduced from 13.23 to ∼5.75 % after SiNx AR coating. as shown in Fig. 11.

Illuminated current–voltage characteristics of the fabricated c-Si cells with the NaOH–NaOCl as well as conventional NaOH-IPA approaches were observed under global spectrum of AM 1.5, which are shown in Fig. 12. It
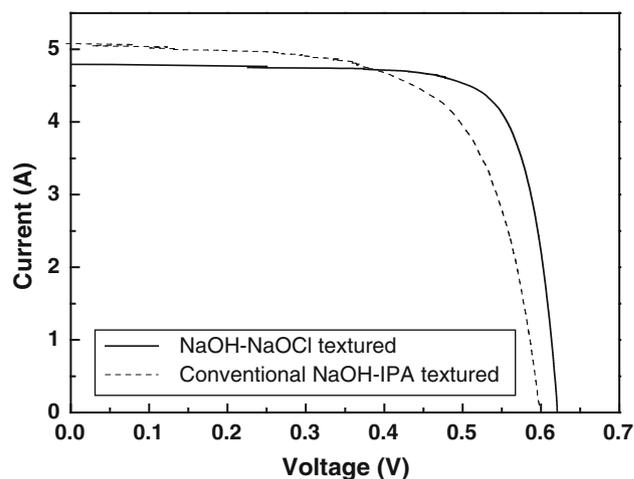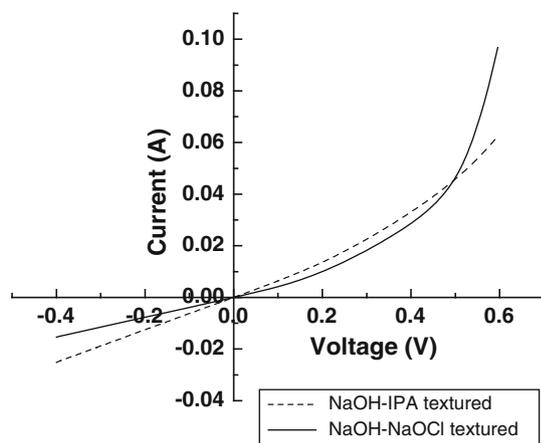

Fig. 10 Reflectance of NaOH-IPA-textured and NaOH–NaOCl-textured c-Si surfaces

Fig. 12 LIV characteristics of NaOH-IPA-textured and NaOH–NaOCl-textured c-Si solar cells

Table 2 Performance parameters of NaOH–NaOCl-textured and NaOH-IPA-textured large-area (125 mm × 125 mm) c-Si solar cells

Texturization solution	V_{oc} (V)	I_{sc} (A)	V_m (V)	I_m (A)	P_m (W)	FF	R_{sh} (Ω)	R_s (mΩ)	Eff. (%)
NaOH–NaOCl	621.4	4.80	527.10	4.40	2.32	0.78	14.50	3.00	15.78
NaOH	598.7	5.08	472.54	4.29	2.03	0.67	6.43	5.03	13.78

V_{oc} open circuit voltage, I_{sc} short circuit current, V_m voltage at max. power point, I_m current at max. power point, P_m max. power output, FF fill factor, Eff efficiency, R_{sh} shunt resistance, R_s series resistance

was observed from these graphs that the overall efficiency achieved in the current approach of surface texturing by using NaOH–NaOCl was much higher than that of the conventional approach with NaOH-IPA. This was reflected in the electrical parameters of the solar cell for two different texturing approaches as shown in Table 2. The low open circuit voltage (V_{oc}) and fill factor (FF) of the c-Si solar cell fabricated using NaOH-IPA texturing might be due to its higher value of leakage current compared to the NaOH–NaOCl-textured solar cell. Reverse characteristics of dark voltage–current characteristic (DIV) as shown in Fig. 13 give a clear indication of significantly large leakage of current for NaOH-textured compared to NaOH–NaOCl-textured c-Si solar cells. For comparatively higher leakage current, the observed shunt resistance was lower (6.43 Ω) in the case of NaOH-textured than that of NaOH–NaOCl-textured c-Si solar cell (14.5 Ω) as shown in Table 2. Lower value of leakage current in the case of NaOH–NaOCl-textured cell might be due to uniform surface structure throughout the area (125 mm × 125 mm) of c-Si with relatively smaller steps of <5 μm. As a result, no surface contaminants were present after texturing of the contaminated c-Si wafer as shown in Fig. 8. This effectively improved the dark current and also other electrical parameters of solar cells as mentioned in Table 2. The decrease in series resistance (Rs = 3 mΩ) of NaOH–NaOCl-textured silicon solar cell also indicated the
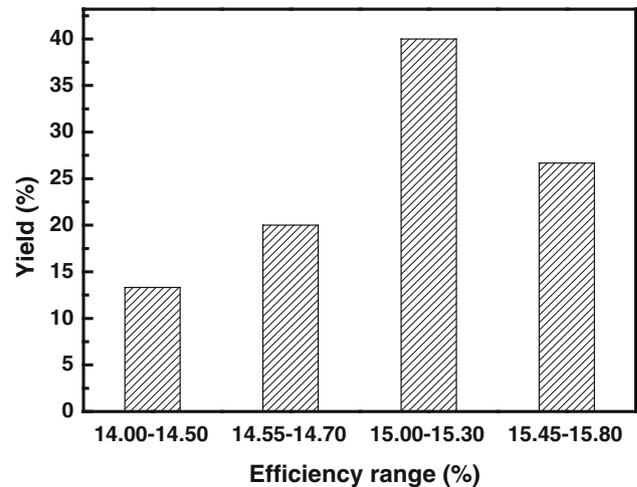
Fig. 14 Percentage of industrial yield of NaOH–NaOCl-textured large-area (125 mm × 125 mm) c-Si solar cell

reduction of surface contaminant present on the solar cell surface. Actually, series resistance and other electrical parameters of the solar cells were strongly dependent on front and back contacts. The presence of surface contaminants degrades the conventional NaOH-IPA-textured c-Si solar cell performance parameters, except for short circuit current as mentioned in Table 2 in spite of using a huge amount of costly IPA in the industrial process sequence. A slightly higher value of short circuit current in conventionally textured c-Si cells compared to that in NaOH–NaOCl-textured cells is due to its lower value of reflectance after texturing.

We successfully achieved around 85 % yield in the efficiency range 14.5–15.8 % using NaOH–NaOCl-texturing approach as shown in Fig. 14, whereas in conventional NaOH-IPA-textured solar cell the yield percentage in the efficiency range 13.5–14.0 % was around 80 % only, as shown in Fig. 15. Higher open circuit voltage (V_{oc}) of NaOH=NaOCl-textured c-Si solar cell compared to NaOH-IPA-textured solar cell had two reasons. The first one was due to less etch depth (<5 μm) generated on very large-area c-Si substrate with no significant surface contaminations after NaOH–NaOCl texturing and the second reason was the effect of chlorine attachment with silicon (Si–Cl bond) during treatment of c-Si with NaOH–NaOCl solution at 80 °C, as shown in the FTIR characteristics of Fig. 16.

Fig. 13 DIV characteristics of NaOH-IPA-textured and NaOH–NaOCl-textured c-Si solar cells
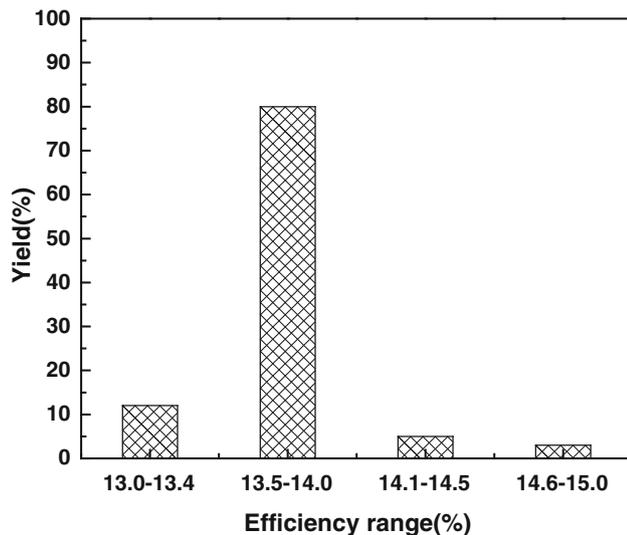
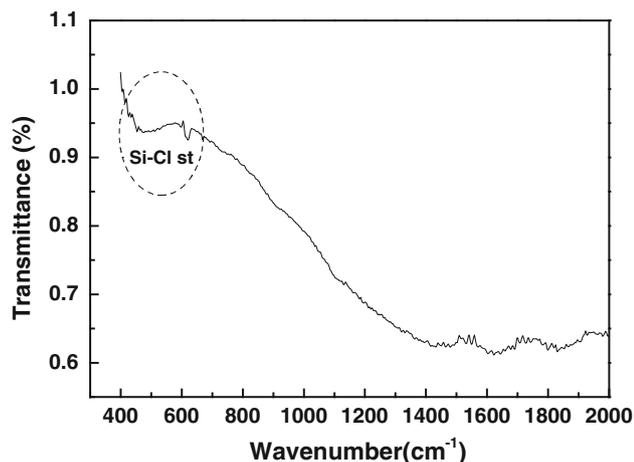Fig. 15 Percentage of industrial yield of NaOH-IPA-textured large-area (125 mm × 125 mm) c-Si solar cell

Fig. 16 FTIR analysis of NaOH–NaOCl-textured c-Si solar cell

This Si–Cl bond might have helped the gettering during diffusion of NaOH–NaOCl-treated wafers [10, 12]. It clearly indicates that this newly developed NaOH–NaOCl approach of c-Si texturing discussed in this article can easily be applied to c-Si wafer surface with additional effect of surface contamination removal for commercial production of very large-area c-Si solar cell of reasonably acceptable efficiency and contamination of c-Si wafers even without costly IPA addition.

Conclusion

The proposed texturization technique generated inverted pyramidal structure of etch depth 4 μm without any additional oxide masking step, which was normally needed for forming inverted pyramid structure during etching with any anisotropic etching solution. NaOCl in our proposed technique is a key material for growing in situ oxide masking layer on monocrystalline silicon (c-Si) surface during etching in NaOH–NaOCl bath. Our findings reported in this paper are based on comparative studies of optical/SEM imaging as well as FTIR spectroscopy of the c-Si sample before and after conventional NaOH and proposed NaOH–NaOCl texturization process along with the observed electrical parameters of solar cells. The comparative study of electrical parameters of the cells fabricated with conventional NaOH-IPA and the proposed cells brings out a significant improvement of parameters for solar cells. Open circuit voltage of 621.4 mV and a fill factor as high as 0.78 were the parameters achieved as a key for the high efficiency of ($\sim$16 %) crystalline silicon solar cell of area (125 mm × 125 mm) compared to conventional NaOH-IPA approach due to its additional surface contaminant removal behavior. Moreover, FTIR analysis indicated that the Si–Cl bond created during texturing with NaOH–NaOCl solution finally helped in gettering during phosphorus diffusion with $POCl_3$ dopant. This Cl gettering helps in the improvement of open circuit voltage of a c-Si solar cell. We are probably the first group to report on such a novel idea of using NaOH–NaOCl solution for monocrystalline silicon surface texturing with formation of maskless inverted structured for solar cell fabrication of area 125 mm × 125 mm and yield around 85 % in the conversion efficiency range 14.5–15.8 %, compared to 80 % yield in the efficiency range of 13.5–14.0 % of the conventional NaOH-IPA approach. This process can be applied as a key step to the industrial production of very large-area monocrystalline silicon solar cells.

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