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Solutions used in the texturization of monocrystalline silicon

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ABSTRACT

Texturization of (100) monocrystalline silicon (mono-Si) for solar cells is still an issue in the industrial production of standard screen-printed mono-Si solar cells. This fact is due to the properties of isopropyl alcohol (IPA), which is used together with potassium hydroxide (KOH) in the standard etching solution KOH-IPA (or used with sodium hydroxide NaOH in NaOH-IPA). The low boiling point of IPA (82.4°C) limits the etching temperature and thus the processing speed. Furthermore, KOH-IPA etching solution is very sensitive to the wafer pre-treatment characteristics of as-cut mono-Si wafers. Two ways to overcome these disadvantages are presented in this paper. The first approach involves the use of a high boiling alcohol (HBA) instead of IPA in the standard KOH-IPA etching solution. This allows higher etching temperatures to be used, without evaporation losses of the alcohol, but with reduced etching times. The second approach consists of using a closed etching bath in which vacuum (low-pressure) steps (i.e. pressure oscillations between atmospheric and below-atmospheric pressure) are achievable; in addition, a cooling system located on top of the etching bath allows the liquefaction of the evaporated IPA. The second texturing approach considerably decreases the etching time of mono-Si wafers. Examples of mono-Si wafers were textured using the new KOH-HBA etching solution and then processed into solar cells; the current-voltage results of the processed solar cells are presented.

Introduction

The industrial production of standard screen-printed (p-type) monocrystalline silicon (mono-Si) solar cells consists of a relatively small number of process steps. It begins with the texturization of the as-cut mono-Si wafers. In this first step, by using an aqueous solution of potassium hydroxide (KOH) and isopropyl alcohol (IPA), the saw damage is removed and a random pyramidal texture is produced on both wafer surfaces – the pyramidal texture decreases the total light reflection of mono-Si wafers. After that, a phosphorus ($POCl_3$) diffusion on textured mono-Si wafers is carried out in order to form the emitter (n-type region). Then, by using (for example) the plasma etching method, the edges of the silicon wafers are removed in order to electrically isolate the front side (n-type) from the bulk of the wafer (p-type). Subsequently, a thin film of hydrogenated silicon nitride (SiN_x:H) is deposited on the front side of the wafer using the plasma-enhanced chemical vapour deposition (PECVD) process in order to further decrease the total light reflection and to passivate the front surface. Front silver and back aluminium contacts are printed by using screen printing. Finally, a firing step is used to sinter the metal contacts and establish good front and back contacts. After completion, the solar cells are characterized by current-voltage measurements under AM1.5 illumination conditions [1].

Besides the chemical etching method used [2,3] to texture mono-Si wafers, texturing can be carried out through mechanical grooving [4], laser grooving [5] or plasma etching [6]. Out of these methods, chemical etching is the only one that allows a random pyramid structure because of the anisotropy of the chemical etching process. Here anisotropy means that the etch rate depends on crystal orientation of the mono-Si wafer [7]. The wet chemical texturization process of mono-Si wafers is mainly carried out using an aqueous solution of deionized water, IPA and potassium hydroxide (KOH). The etching solution is heated to a temperature of 80°C and the silicon wafers are placed in it. After approximately 30 min of etching time, the silicon surface (on both sides) is covered with small pyramids (size ≈ 10μm), referred to as a pyramidal texture, and about 10μm of silicon is removed from each side of the silicon wafers. This etching process is well known in the photovoltaic industry as the standard KOH-IPA texturization process for mono-Si wafers. Although this chemical etching method is well established in industrial production of screen-printed mono-Si solar cells, new developments in the wafering processes hinder the effectiveness of the standard KOH-IPA etching solution, as will be explained below.

Because the photovoltaic community is always trying to decrease the cost of solar cells, and therefore the price of solar electricity, new approaches have been tried in order to achieve this goal. For example, the thickness of Si wafers has been reduced (from 240μm to currently around 180μm), and new improved wire-sawing technologies for cutting silicon ingots have been introduced. Thus, less silicon is wasted during the cutting of silicon ingots. But, unfortunately, both the sawing method used for the cutting process and the washing/cleaning procedure employed vary between the different silicon wafer producers, which means that as-cut silicon wafers show different surface characteristics [8]. As a consequence, the same standard KOH-IPA solution cannot be used for all types of as-cut silicon wafers, because the KOH-IPA solution is very sensitive to the surface characteristics of the wafers [9]. Because of the constant evaporation of IPA during the etching process, another disadvantage of the KOH-IPA solution is the cost of replenishing the IPA.

In order to overcome these disadvantages, the search for a substitute for IPA in the aqueous solution of KOH-IPA is a topic of current investigation in the photovoltaic community. To this end, some efforts have been made in the last few years and some of them have been successfully carried over to the mass production of solar cells. For example, Birmann et al. [10] used 1,4-cyclohexanediol instead of IPA. Because of the high boiling point of the alcohol, an etching temperature of 90°C was used, and therefore the etching time was reduced to 10 min; additionally, the pyramid size was decreased. Wijekoom et al. [11] used a polymer (with a boiling point above 100°C) as a substitute for IPA. By using the new additive in the etching solution, a pyramidal texture with pyramid heights of approximately 1μm was obtained. The same authors also produced standard screen-printed mono-Si solar cells that achieved a solar cell efficiency of up to 17.8%. It follows from the work of these authors that good results can be achieved by using IPA substitutes with a higher boiling point in the KOH etching solution; on the one hand, this allows texturing processes to be carried out at higher temperatures and therefore for shorter etching times, and, on the other, evaporation losses of the alcohol are reduced and thus texturing costs are lower.

> “With KOH-HBA, higher etching temperatures of around 100°C can be used, without evaporation losses of the alcohol, but with reduced etching times.”

In this paper, two approaches for solving the IPA problems are proposed. The first approach involves the use of another alcohol, referred to as high boiling alcohol (HBA) because it has a boiling point above 200°C; the new etching solution will therefore be referred to as KOH-HBA solution. Thus, with KOH-HBA, higher etching temperatures of around 100°C can be used, without evaporation losses of the alcohol, but with reduced etching times [12]. A further reduction of the etching time (15 min) is possible if, in an initial etching step, the saw damage of the as-cut silicon wafers is removed [13].

The second approach proposed involves recovering the evaporated IPA. For this a new etching bath setup has been developed by the wet-etching company Lotus Systems. IPA is cooled down (liquefied) in a cooling chamber located on top of the new etching bath, and is then conducted to a reservoir. Apart from the cooling system of the new etching bath setup, a vacuum system has been adapted, allowing the application of vacuum to the etching chamber; the etching process is therefore accelerated and a considerable reduction in etching time is achieved. This texturization process with vacuum pulses was introduced for the first time in Ximello et al. [14]; no previous studies have been found that mention the use of this technique for texturing mono-Si wafers.

This paper shows that the pyramidal texture obtained using the KOH-HBA solution can be successfully achieved in the production of solar cells via the standard industrial screen-printing method, a selective emitter process [15] and an advanced photolithography-based process [16]. Czochralski (Cz) and float zone (FZ) silicon wafers were textured and processed into solar cells.

Experimental

Texturization

Two etching solutions were used to texture (100) p-type Si wafers. The first consisted of deionized (DI) water, KOH and HBA. A temperature of 100°C and an etching time of 30 min were used with this etching solution to texture Cz-Si (200µm thick) and FZ-Si (230µm thick) wafers with resistivities of 1–3Ωcm and 1Ωcm, respectively. The etching process took place in a glass beaker heated by a hotplate.

The second etching solution consisted of DI water, KOH and IPA. A temperature of 80°C, and etching times of 30 min and 16 min were used to texture 12.5cm × 12.5cm Cz-Si wafers. To do this, the new etching equipment was used, which allowed the application of vacuum in the etching chamber. Compared to the standard KOH-IPA texturization process, which takes place at atmospheric pressure, vacuum (or more precisely lower pressure than the atmospheric pressure) is applied in the closed etching chamber (around 65% of atmospheric pressure is applied for one second). The frequency of the vacuum pulses can be varied from a few seconds to several minutes during the etching process, and it was possible to reduce the etching time to 16 min. Without vacuum pulses during the etching process, an etching time of 30 min was required. In addition, with the new etching equipment, it was possible to recover IPA from the etching chamber. To characterize the pyramidal texture, reflection measurements and scanning electron microscope (SEM) pictures were taken.

Solar cell processes

Only wafers textured with the KOH-HBA solution were processed into solar cells. Textured Cz-Si wafers were processed into solar cells using the standard industrial screen-printing method and the advanced industrial selective-emitter method. Textured FZ-Si wafers were processed into solar cells via an advanced photolithography-based process.

The screen-printing-based process starts with a $POCl_3$ diffusion to form a p-n junction on textured silicon wafers; the emitter has a sheet resistivity of 50Ω/sq. After that, the phosphorus glass is removed. A silicon nitride (SiN_x:H) layer with a thickness of approximately 75nm is then deposited as an anti-reflective coating, and front silver and rear aluminium contacts are applied by the screen-printing method. After co-firing, the edges of the cells are removed by sawing to achieve electrical isolation.

The processing scheme of the selective-

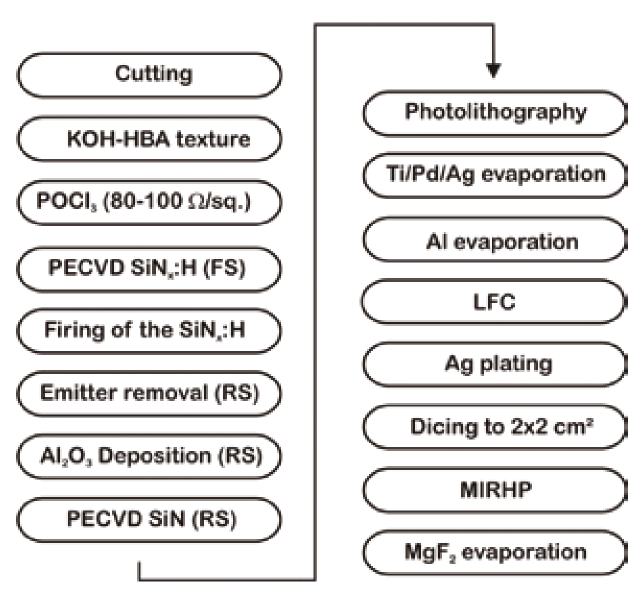

Figure 1. Process flow chart showing the photolithography-based process, featuring a Al_2O_3 rear side (with an optional SiN_x:H rear-side capping layer).

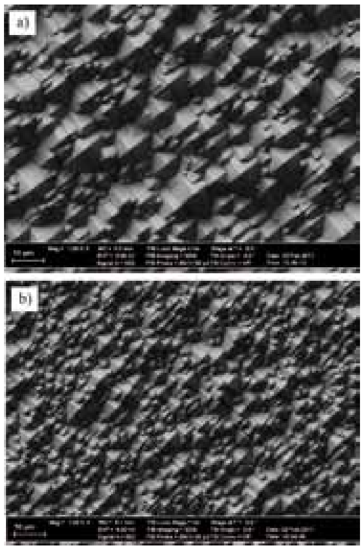

Figure 2. SEM images of Si wafers textured in a KOH-IPA solution: (a) textured at atmospheric pressure; (b) textured using the vacuum process.

Figure 3. Texturing of a mono-Si wafer in a KOH-IPA etching solution by using a closed etching bath in which vacuum steps are applied: (a) a mono-Si wafer covered by hydrogen bubbles (vacuum off), thus slowing down the etching process on this wafer; (b) the same wafer, with hydrogen bubbles detaching from the surface when a short vacuum-process step (vacuum on) is applied; (c) a picture taken immediately after the vacuum step in (b), showing the wafer to be almost free of hydrogen bubbles (vacuum off), and therefore allowing the etching process to accelerate again. The vacuum steps are applied periodically during the etching process – by doing this, the etching time is considerably reduced.

emitter process is very similar to the one just described for screen printing, with only two differences. The first is that the selective-emitter process starts with a stronger emitter diffusion, which leads to an emitter with a sheet resistivity of 30Ω/sq. The second difference is in the formation of a selective emitter, which is carried out as follows: after $POCl_3$ diffusion, an acid-resistive mask is selectively screen printed on the emitter to protect it from further acid etching. By using an acid solution (DI water, HF, HNO_3) the emitter is then lightly etched through the formation of porous Si until it reaches a sheet resistivity of 50Ω/sq. After this, the printed mask, the porous Si and the P-glass are removed. Front contact fingers are printed on regions with high phosphorus doping, i.e. the regions that were not etched away.

The photolithography-based process (see Fig. 1) starts with the cutting of the FZ-Si wafers to a size of 5cm × 5cm, to satisfy the requirements of the photolithography equipment at the University of Konstanz. After this has been done, the wafers are textured as explained earlier. The $POCl_3$ diffusion process is carried out to form an emitter with a sheet resistivity of 80–100Ω/sq. Subsequently, the wafers receive a PECVD SiN_x:H layer as an anti-reflective coating. This is followed by a firing step carried out in a conventional belt furnace to ensure good hydrogenation from the SiN_x:H layer. The front side is then masked with a hot melt ink, and the emitter at the rear side is removed in a polishing etch consisting of HF, HNO_3 and CH_3COOH. The next step is the application, by atomic layer deposition, of a dielectric rear-side passivation layer of aluminium oxide (Al_2O_3); an optional SiN_x:H layer is deposited to protect the very thin

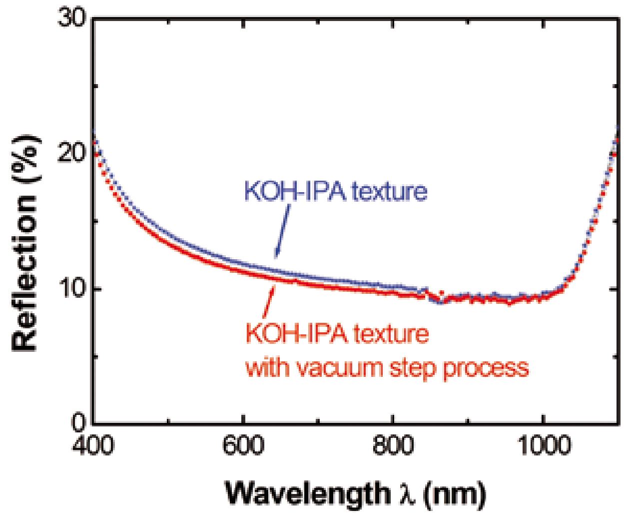

Figure 4. Reflection measurements of Cz-Si wafers textured with a KOH-IPA solution. Vacuum pulses during the texturization process were used to accelerate the etching process.

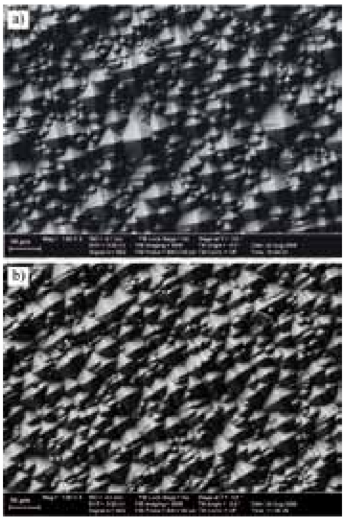

Figure 5. SEM images of surfaces textured with a KOH-HBA etching solution: (a) Cz-Si wafer; (b) FZ-Si wafer.

passivation layer. Afterwards, the front contacts are defined by photolithography and evaporation of Ti, Pd and Ag; aluminium is evaporated on the rear side. The rear contact is then established using a laser-fired contact (LFC) process, and the front contacts are thickened by silver plating. Finally, four solar cells (2cm × 2cm) are cut with a dicing saw. After preliminary characterization, a microwave-induced remote hydrogen plasma (MIRHP) step is implemented to enhance hydrogen passivation, improve the rear surface passivation and sinter the front contacts. When *I-V* characterization of all solar cells is complete, the best cells additionally receive a second, dielectric, anti-reflective coating (DARC) by means of thermally evaporated magnesium fluoride (MgF_2).

Results and discussion

Texturization results: vacuum

SEM images of a KOH-IPA textured surface are shown in Fig. 2. Comparing Figs. 2(a) and (b), a decrease in pyramid size can be observed in (b) and is due to the vacuum process used during the texturization. The application of vacuum steps in the etching chamber allows a quick detachment of hydrogen bubbles (which form during the chemical etching process) from the silicon surface. An extra force is applied to the hydrogen bubbles by the change in pressure during the vacuum cycling (see Fig. 3); a better recirculation of the etching solution is also provided. These two facts mean that the etching process is speeded up. The resulting small pyramid size is comparable to that observed with KOH-HBA textured Si wafers (see next section).

Fig. 4 shows reflection measurements of the textured silicon wafers in Fig. 2. It is observed that Cz-Si wafers textured with KOH-IPA solution and with the vacuum process show slightly lower reflection values for wavelengths below 850nm. An etching time of 16 min was used for the vacuum-assisted etching process; compared to the etching time used in the standard KOH-IPA etching process, which lasts between 30 and 40 min, a decrease in etching time of around 50% was achieved.

Texturization results: HBA

SEM images of KOH-HBA textured surfaces for the two types of wafer are shown in Fig. 5; an etching time of 30 min was used for both materials. The best homogeneity is observed on the textured FZ-Si wafer: this high homogeneity may be attributed to the correspondingly higher quality of the FZ-Si wafer material.

Fig. 6 shows reflection measurements

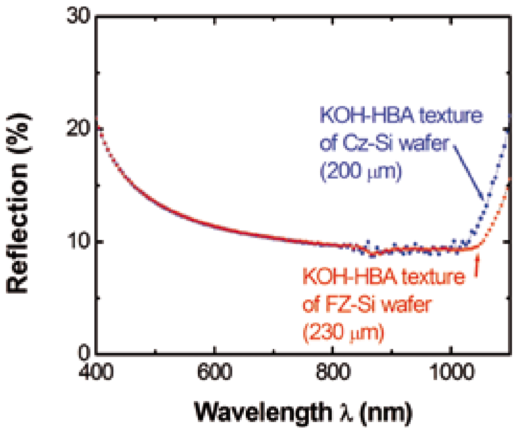

Figure 6. Reflection measurements of Cz-Si and FZ-Si wafers textured in a KOH-HBA etching solution.

Material/Cell process	J_{sc} [mA/cm^2]	V_{oc} [mV]	*FF* [%]	η [%]
Cz / Screen printing	35.5	628	79.0	17.6
Cz / Selective emitter	36.5	637	78.3	18.2
FZ / Photolithography	39.3	660	77.6	20.0

Table 1. *I-V* results of the processed solar cells. Cz-Si wafers (12.5cm × 12.5cm), textured using the KOH-HBA solution, were processed into solar cells by the standard screen-printing method (average over eight cells) and by the selective-emitter method (average over ten cells). Textured FZ-Si wafers (5cm × 5cm) were processed into 2cm × 2cm solar cells by an advanced photolithography-based cell process (best cell).

of the textured Si wafers in Fig. 5: it can be seen that the two kinds of textured Si wafer (Cz-Si and FZ-Si) have almost the same reflection values. A small variation is observed at wavelengths above 1050nm, which is due to the difference in thicknesses of the wafers.

Solar cell results

The current-voltage (I-V) data of the processed solar cells are shown in Table 1. It is important to note here that only wafers textured using the KOH-HBA etching solution were processed into solar cells.

A comparison of the results of both industrial processes reveals a gain in solar cell efficiency of 0.6% absolute for solar cells processed via the selective-emitter process. This increase is mainly due to the higher short-circuit current J_{sc} and open-circuit voltage V_{oc} of these cells. The increase in J_{sc} and V_{oc} is attributed to the better blue response on the etched back regions (thinner dead layer and thus less Auger recombination) and the resulting better surface passivation.

Although reflection values are almost the same for both types of silicon wafer textured with the KOH-HBA solution, the solar cell created from the FZ-Si wafer via the advanced process achieves the highest J_{sc} (39.3mA/cm^2), which is near the theoretical value of J_{sc} (42.5mA/cm^2), estimated for the technologically achievable AM1.5G efficiency limit of Si solar cells [17]. This result demonstrates that the texture exhibits appropriate characteristics for developing solar cells with efficiencies close to the technological limit, at least with FZ-Si wafers.

> “The etching process with the vacuum steps reduces the etching time of mono-Si wafers by about 50% – to 16 min compared to the etching time of 30–40 min used in the standard KOH-IPA etching process.”

The photolithography cell process allows the definition of very narrow front metal contact fingers, which, in combination with a lightly doped emitter, explains the high short-circuit current J_{sc} achieved for this solar cell. It also shows the importance of the high-quality passivation layer of Al_2O_3 on the rear side, which results in a high open-circuit voltage V_{oc}. Moreover, this cell process shows very encouraging results due to its low thermal budget.

Conclusions

A new alcohol – HBA – has been used as a substitute for IPA in the standard KOH-IPA texturing solution. Because of the high boiling point of HBA, lower evaporation losses are realized than with IPA. The new KOH-HBA solution has been used successfully to texture both Cz and FZ mono-Si wafers. A very homogeneous texture with small pyramid size was observed, as was the fact that the KOH-HBA etching solution was less sensitive to the pre-treatment of as-cut mono-Si wafers.

The KOH-HBA textured Si wafers were processed into solar cells by the standard industrial screen-printing method, a selective-emitter method and an advanced cell process. Cz-Si wafers etched with the KOH-HBA solution and processed via the standard industrial screen-printing method and the selective-emitter method demonstrated solar cell conversion efficiencies of 17.6% and 18.2%, respectively. FZ-Si wafers textured with the KOH-HBA solution and processed into solar cells via an advanced photolithography-based cell process achieved an efficiency of up to 20.0%.

A new etching bath setup, developed by the wet-etching company Lotus Systems, was used with the standard KOH-IPA solution to texture silicon wafers, making it possible to recover IPA and accelerate the etching process. Evaporated IPA is cooled down in a cooling system and is then conducted to a reservoir, and the etching process is accelerated by an innovative vacuum procedure during texturization. Vacuum steps are employed and thus

an extra force is applied to the hydrogen bubbles situated on the silicon surface. These hydrogen bubbles are removed very effectively from the wafer surface, and the growth of large hydrogen bubbles is avoided, resulting in an accelerated etching process and a homogeneous pyramidal texture with small-sized pyramids. The etching process with the vacuum steps reduces the etching time of mono-Si wafers by about 50% – to 16 min compared to the etching time of 30–40 min used in the standard KOH-IPA etching process.

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Jose Ximello-Quiebras studied physics at the National Polytechnic Institute (IPN), Mexico, and received an M.Sc. in 2005 for research on the properties of cadmium sulphide (CdS) thin films deposited by chemical bath and sputtering methods for CdS/cadmium telluride (CdTe) solar cells. From 2006 to mid-2008 he worked as a researcher on the photoluminescence of porous silicon at the University of Stuttgart, Germany. Since mid-2008, Jose has been working towards his Ph.D. at the University of Konstanz and is investigating texturing solutions for monocrystalline and multicrystalline silicon wafers for solar cells.

Johannes Junge studied physics at the University of Karlsruhe, Germany, and received his Ph.D. in physics from the University of Konstanz in 2012. Johannes is currently working in the New Materials group within the photovoltaics division of the University of Konstanz, where his research interests include defect engineering and the determination of solar cell efficiency potential for all kinds of Si wafer material.

Sven Seren studied at the University of Konstanz, where he earned his Ph.D. in 2007 for research on low-cost solar cells fabricated from fast-grown silicon ribbon materials. Since then Sven has headed the New Materials group at the University of Konstanz, with a research emphasis on the characterization and processing of multicrystalline silicon ribbon materials.

Giso Hahn studied physics at the University of Stuttgart, Germany, and received a Ph.D. degree in the same subject from the University of Konstanz in 1999. Since 2009 he has been a professor in the physics department at the University of Konstanz, and is currently the head of the photovoltaics division, which focuses on crystalline silicon materials and solar cell process development. Giso's research interests include the characterization of promising low-cost materials for photovoltaic applications and the development of adapted solar cell processes for these and other materials.

Ernst Epple studied at the University of Hohenheim in Stuttgart and graduated in engineering. After having worked for around 20 years for several wet-process technology companies, Ernst took on the position of chief technology officer at Lotus Systems GmbH. His work there focuses on process and system engineering with the aim of lowering production costs in the manufacture of solar cells.

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