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UP TO 20% EFFICIENT SOLAR CELLS ON MONOCRYSTALLINE SILICON WAFERS BY USING A KOH – HIGH BOILING ALCOHOL (HBA) TEXTURING SOLUTION

N. Ximello[1], J. Junge[1], S. Seren[1], G. Hahn[1], E. Epple[2]
[1]University of Konstanz, Department of Physics, Jacob-Burckhardt-Str. 29, 78464 Konstanz, Germany
Phone: (+49) 7531 883731, Fax: (+49) 7531 883895, e-mail: jose.ximello-quiebras@uni-konstanz.de
[2]Lotus Systems GmbH, Sautierstraße 23, 78187 Geisingen, Germany
Phone: (+49) 7704 9233-155, Fax: (+49) 7704 9233-60, e-mail: Ernst.Epple@Lotussystems.de

ABSTRACT: We have textured (100) p-type Czochralski (Cz) monocrystalline Silicon (Si) wafers by using an aqueous solution of potassium hydroxide (KOH) and a High Boiling Alcohol (HBA). Cz-Si wafers textured with the KOH-HBA solution were processed into solar cells via the standard industrial screen printing method and an advanced industrial process (selective emitter process). Also, high quality float zone (FZ) Si material was textured and processed into solar cells by using a lab-type cell process. Industrially processed cells achieve efficiencies of 17.6% and 18.2%, respectively. Lab-type processed cells (2x2 cm^2) achieve an efficiency of up to 20%. In addition, for the standard KOH-Isopropyl alcohol (IPA) etching solution a new etching bath setup has been developed. The new bath setup allows the recuperation of IPA during the texturisation process, as well as vacuum processing steps during the texturisation, which considerably reduces etching time.
Keywords: silicon, solar cell efficiencies, texturisation.

1 INTRODUCTION

Looking for a substitute of isopropyl alcohol (IPA) in the aqueous solution of potassium hydroxide (KOH)-IPA is a matter of current investigation in the photovoltaic community. This is due to the disadvantage of IPA. For example, the KOH-IPA solution is very sensitive to the surface condition of as-cut monocrystalline silicon (Si) wafers, i.e. different sawing methods lead to different surface characteristics of the as-cut silicon wafers. Therefore, the same standard KOH-IPA solution cannot be used for all assortments of as-cut silicon wafers. During the etching process constant evaporation of IPA takes places and hence the price of IPA is another important reason why different substitutes are being investigated. Some efforts have been carried out in the last years and some of them have been successfully transferred into the mass production of solar cells [1,2].

In this paper we propose two different solutions to the IPA problem. The first one consists in usage of another alcohol, we call it high boiling alcohol (HBA) because it has a boiling point above 200°C, and we call the new solution KOH-HBA solution. Thus, etching temperatures of around 100°C are used without evaporation losses of the alcohol and with reduced etching times [3]. Further reduction of etching time (15 min) is achieved if first the saw damage of as-cut silicon wafers is removed [4]. The second solution consists in recovering of the evaporated IPA. Here, a new etching bath setup has been developed from the wet etching company Lotus Systems. In a cooling chamber located on top of the new etching bath IPA will be cooled down and then conducted to a reservoir. Apart from the cooling system of the new etching bath setup, a vacuum system has been adapted which allows the acceleration of the etching process and therefore a considerable reduction of etching time is achieved.

In this work, the pyramidal texture obtained by using the KOH-HBA solution is successfully used to produce solar cells via the standard industrial screen printing method, a selective emitter process [5], and by an advanced photolithography based process [6]. Czochoralski (Cz) and float zone (FZ) silicon wafers are textured and processed into solar cells.

2 EXPERIMENTAL

2.1 Texturisation

To texture (100) p-type Si wafers, two etching solutions are used. The first one consists of 6 liters of deionized (DI) water, KOH and HBA. A temperature of 100°C and an etching time of 30 min are used. With this etching solution Cz-Si (200 µm thick) and FZ-Si (230 µm thick) wafers with a resistivity of 1-3 Ωcm and 1 Ωcm, respectively, have been textured. The etching process takes place in a glass beaker heated by a hot plate.

The second etching solution consists of DI water, KOH and IPA. A temperature of 80°C, and etching times of 30 min and 16 min are used, respectively. Here, the new etching equipment is used (no glass beaker). The new etching equipment allows us to apply vacuum in the etching chamber. Vacuum pulses during the texturisation process were applied to accelerate the etching process, and therefore it was possible to reduce etching time to 16 min. Without vacuum pulses during the etching process an etching time of 30 min is required. Furthermore, with the new etching equipment it was possible to recover IPA from the etching chamber. Here, only 12,5x12,5 cm^2 Cz-Si wafers were used. In order to characterize the pyramidal texture, reflection measurements and scanning electron microscope (SEM) pictures are carried out.

2.2 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 via the standard industrial screen printing method and an industrial advanced method (selective emitter). Textured FZ-Si wafers were processed into solar cells via an advanced photolithography based process.

The screen printing base process starts with a $POCl_3$ diffusion to form a p-n junction on textured silicon wafers. The emitter has a sheet resistivity of 50 Ω/□. After that, the phosphorous glass is removed. Then a plasma enhanced chemical vapor deposition (PECVD) silicon nitride (SiN_x:H) layer of approximately 75 nm is deposited as an antireflective coating. Then, front and rear aluminum contacts are applied by the screen printing method. After that, a firing process is carried out. Finally, solar cells edges are removed by sawing.

The processing scheme of the selective emitter process is very similar to the screen printing processing scheme. There are only two differences between these two cell processes. The first one is that the selective emitter process starts with a stronger emitter diffusion which leads to an emitter with a sheet resistivity of 30 Ω/□. The second difference consists on the formation of a selective emitter. This is carried as follows: after $POCl_3$ diffusion an acid resistive mask is selectively screen printed on the emitter which protects it from further acid etching. Then by using an acid solution (HF, HNO_3) the emitter is lightly etched until it reaches a sheet resistivity of 50 Ω/□. After that, the printed mask is removed. Front contact fingers are printed on regions with high phosphorous doping, i.e. regions which were not etched back.

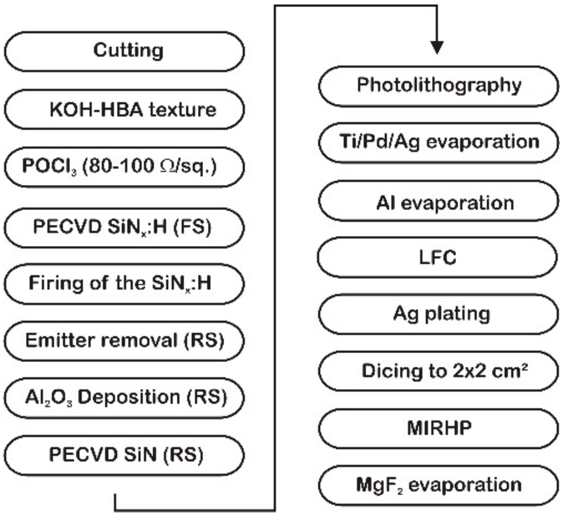

Figure 1: Process flow chart depicting the photolithography-based process featuring the Al_2O_3 rear side (with an optional SiN_x:H rear side capping layer).

The photolithography based process (see Fig. 1) starts with the cutting of the FZ-Si wafers to a size of 5x5 cm^2 to fit the requirements of the photolithography equipment at the University of Konstanz. After that, the wafers are textured as explained before. The $POCl_3$ diffusion process is carried out to form an emitter with a sheet resistivity of 80-100 Ω/□. Subsequently, the wafers receive a PECVD SiN_x:H layer as anti-reflection coating. After that, a firing step is carried out in a conventional belt furnace. Then the front side is 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. After this a dielectric rear side passivation layer of aluminum oxide (Al_2O_3) is applied by atomic layer deposition and an optional SiN_x:H layer is deposited to protect the very thin passivation layer. Afterwards, the front contacts are defined by photolithography and evaporation of Ti, Pd and Ag. Aluminum is evaporated on the rear side. Then the rear contact is established using a laser fired contact (LFC) process. The front contacts are thickened by silver plating. Finally, four solar cells (2x2 cm^2) 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. After IV characterization of all solar cells, the best cells additionally receive a second antireflection coating (DARC) by means of thermally evaporated magnesium fluoride (MgF_2).

3 RESULTS AND DISCUSSION

3.1 Texturisation results: vacuum

Scanning electron microscope pictures of a KOH-IPA textured surface are shown in Fig. 2.

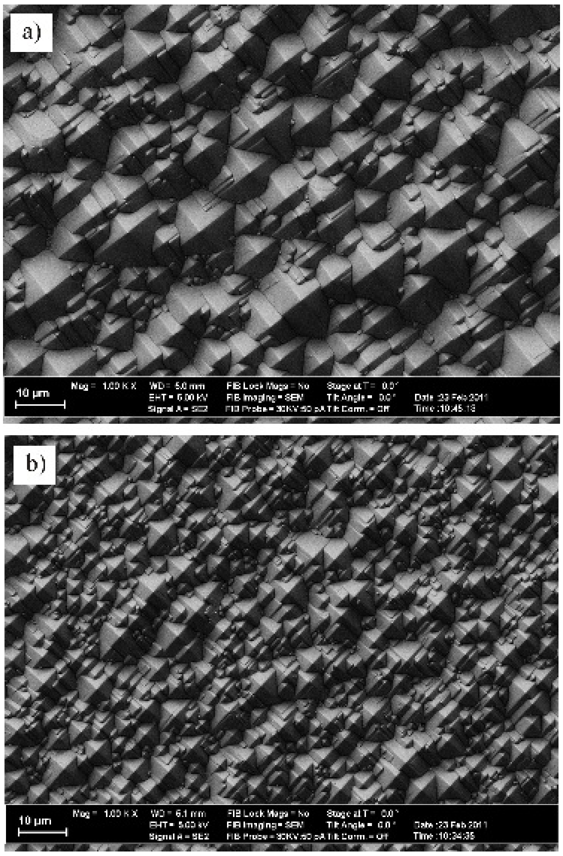

Figure 2: SEM pictures of textured Si wafers. Wafers were textured in a KOH-IPA solution. a) shows the texture of a silicon wafer textured at atmospheric pressure, whereas b) shows the textured silicon wafer by using an extra vacuum steping process.

Comparing Fig. 2 a) and b) we observe a decrease of pyramid size in b). The decrease in pyramid size is due to the vacuum process used during the texturisation. Vacuum steps in the etching chamber allow a very fast detachment of hydrogen bubbles from the silicon surface. Hydrogen bubbles do not have enough time to increase and so the chemical etching process can further take place. The vacuum process applies an extra force to hydrogen bubbles (in the upward direction) and therefore the chemical etching process is accelerated. The small pyramid size is comparable with that observed in KOH-HBA textured Si wafers (see Fig. 4).

Fig. 3 shows reflection measurements of textured silicon wafers shown in Fig. 2.

From Fig. 3 it is observed that Cz-Si wafers textured with the KOH-IPA solution and with the vacuum process

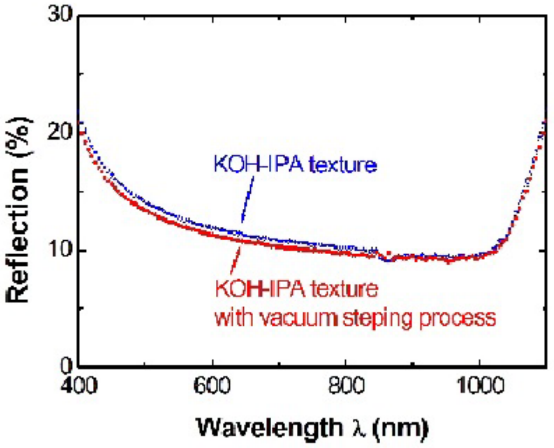

Figure 3: Reflection measurements of Cz-Si wafers textured with a KOH-IPA solution. Vacuum pulses during the texturisation process were used to accelerate the etching process.

show slightly lower reflection values for wavelengths lower than 850 nm. For the vacuum assisted etching process an etching time of 16 min was used. Comparing with the etching time used in the standard KOH-IPA etching process, which lasts between 30 and 40 min, a decrease on etching time of around 50% was achieved.

3.2 Texturisation results: HBA

Scanning electron microscope pictures of a KOH-HBA textured surface are shown in Fig. 4.

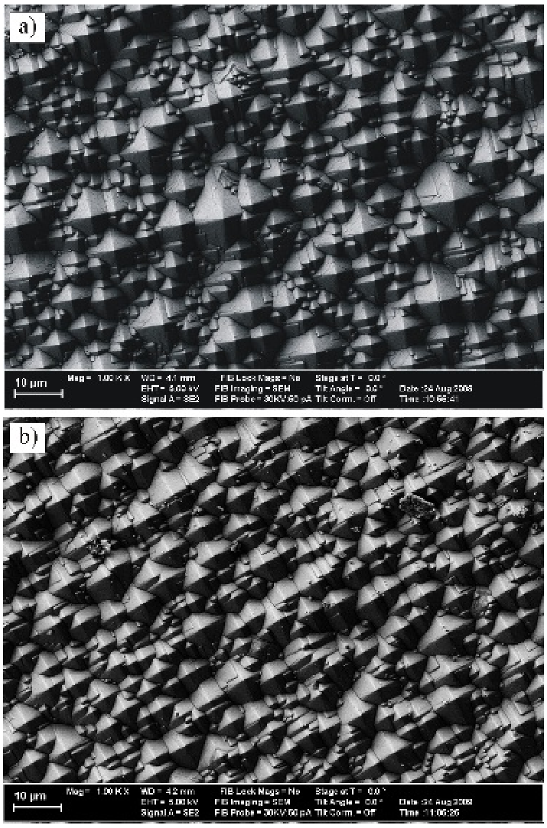

Figure 4: a) shows a Cz-Si wafer textured with a KOH-HBA etching solution. The picture below corresponds to a FZ-Si wafer textured with the same etching solution.

For the textures shown in Fig. 4, an etching time of 30 min was used for both materials. The highest homogeneity is observed on the textured FZ-Si wafer. This high homogeneity can be assigned to the correspondingly higher quality of the FZ-Si wafer material.

Fig. 5 shows reflection measurements of the textured Si wafers shown in Fig. 4.

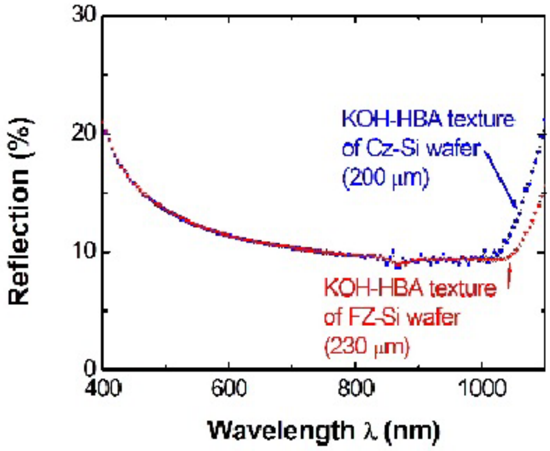

Figure 5: Reflection measurements of Cz and FZ-Si wafers textured in a KOH-HBA etching solution.

From Fig 5, it can be observed that both kinds of textured Si wafers (Cz and FZ-Si) show almost the same reflection values. A small difference on reflection values is observed at wavelengths larger than 1050 nm, which is due to the varying thicknesses of the wafers.

3.3 Solar cell results

In Table I the IV data of the processed solar cells are shown.

Table I: IV results of the processed solar cells. Textured Cz-Si wafers with an area of 12.5x12.5 cm^2 are processed into solar cells via the standard screen printing method (average over 8 cells) and by the selective emitter method (average over 10 cells). Textured FZ-Si wafers with a size of 5x5cm^2 are processed into 2x2 cm^2 solar cells via the advanced cell process (best cell).

Material/Texture/ Cell process	j_{sc} (mA/cm^2)	V_{oc} (mV)	*FF* (%)	η (%)
Cz / KOH-HBA / Screen printing	35.5	628	79.0	17.6
Cz / KOH-HBA / Selective emitter	36.5	637	78.3	18.2
FZ / KOH-HBA / Photolithography	39.3	660	77.6	20.0

Comparing the results between both industrial processed solar cells, we observe a gain in solar cell efficiency of 0.6% absolute for solar cells processed via the selective emitter process. This increase is mainly caused 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 assigned to the better blue response on etched back regions (thinner dead layer and less Auger recombination) and the resulting better surface passivation.

Although reflection values are almost the same for the silicon wafers textured with the KOH-HBA solution, the solar cell processed on the FZ-Si wafer via the advanced process reaches the highest j_{sc} (39.3 mA/cm^2), which is near the theoretical value of j_{sc} (42.5 mA/cm^2) estimated for the technologically achievable AM1.5G efficiency limit of Si solar cells [7]. This result demonstrates that the texture on FZ-Si wafer shows appropriate characteristics to developed solar cells with efficiencies closer to the technological limit.

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

4 CONCLUSIONS

The KOH-HBA solution is used successfully to texture both Cz and FZ monocrystalline silicon wafers. A very homogeneous texture with small pyramid size is observed. The KOH-HBA textured Si wafers are processed into solar cells via the standard industrial screen printing method, the selective emitter method and by an advanced process. Cz-Si wafers etched with the KOH-HBA solution and processed via the standard industrial screen printing method and the selective emitter method reach a solar cell conversion efficiency 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 achieve an efficiency of up to 20.0%.

Besides the advantages of the KOH-HBA solution at texture and solar cell level, the use of HBA in the KOH solution has other advantages, for example, the HBA shows less evaporation losses than IPA, elegant waste recycling is possible, the chemical process is less selective on wafer material, and it is cheaper than IPA (considering the quantity of alcohol used in the etching bath and the almost complete avoidance of constant re-dosing of the HBA in the KOH-HBA solution).

Due to the advantages of the HBA process the wet process company Lotus Systems GmbH is ready to introduce this process to the market. It has designed systems which are tailored to the specific characteristics of the HBA process. The new etching bath shows very interesting advantages in the texturisation process. By using the new etching bath and the standard KOH-IPA solution to texture silicon wafers, it has been possible to recover IPA and to accelerate the etching process. IPA will be cooled down in a cooling system and then it is conducted to a reservoir. The etching process will be accelerated by an innovative vacuum process during the texturisation. Vacuum steps are applied and thus an extra force is applied to the hydrogen bubbles situated at silicon surface. In this way hydrogen bubbles will be removed very fast from the wafer surface and the growth of large hydrogen bubbles will be avoided, which results in an accelerated etching process and a pyramidal texture with small pyramid sizes.

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6 REFERENCES

[1] K. Birkmann, M. Zimmer, J. Rentsch, *Fast alkaline etching of monocrystalline wafer in KOH/COH*, Proc. 23rd EUPVSEC, Valencia 2008, 1608.

[2] K. Wijekoon, T. Weidemann, S. Paak, K. MacWillians, *Production ready novel texture etching process for fabrication of single crystalline silicon solar cells*, Proc. 35th IEEE PVSC, Honolulu 2010, 3635.

[3] N. Ximello, H. Haverkamp, G. Hahn, *A new KOH-etch solution to produce a random pyramid texture on monocrystalline silicon at elevated process temperatures and shortened process time*, Proc. 24th EUPVSEC, Hamburg 2009, 1958.

[4] N. Ximello, A. Dastgheib-Shirazi, S. Scholz, G. Hahn, *Influence of pyramid size of chemically textured monocrystalline silicon wafers on the characteristics of industrial solar cells*, Proc. 25th EUPVSEC, Valencia 2010, 1761.

[5] A. Dastgheib-Shirazi, H. Haverkamp, B. Raabe, F. Book, G. Hahn, *Selective emitter for industrial solar cell production: A wet chemical approach using a single side diffusion process,* Proc. 23th EUPVSEC, Valencia 2008, 1197.

[6] J. Junge, J. Ebser, S. Graf, B. Terheiden, S. Seren, G, Hahn, M. Käs, *Evaluating the efficiency limits of low cost mc Si materials using advanced solar cell processes,* Proc. 25th EUPVSEC, Valencia 2010, 1722.

[7] A.G. Aberle, P.P. Altermatt, G. Heiser, S.J. Robinson, A. Wang, J. Zhao, U. Krumbein, M.A. Green, *Limiting loss mechanism in 23% efficient silicon solar cells*, J. Appl. Phys. 77 (1995) 3491.