

A NEW KOH-ETCH SOLUTION TO PRODUCE A RANDOM PYRAMID TEXTURE ON MONOCRYSTALLINE SILICON AT ELEVATED PROCESS TEMPERATURES AND SHORTENED PROCESS TIMES

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ABSTRACT: Texturization of monocrystalline silicon for solar cells is still an issue due to the properties of the isopropyl alcohol (IPA) in the standard Potassium Hydroxide KOH (or Sodium Hydroxide NaOH)-IPA etching solution. The low boiling point of IPA (82.4°C) is limiting etch temperature and by this processing speed. Furthermore, IPA has other disadvantages like waste recycling problems. A better alternative for IPA, not only regarding processing time, is a High Boiling Alcohol (HBA). In this paper we show, that our newly found KOH-HBA texture also gives lower reflection results than our KOH-IPA texture. Finally, we produced solar cells with both textures and current-voltage measurements are compared.

Keywords: Texturization, Etching, Solar cells

1 INTRODUCTION

Structures to reduce total reflection on monocrystalline silicon (Si) are usually carried out through chemical etching [1, 2], mechanical grooving [3], laser grooving [4] or the plasma etching method [5]. From these methods, the chemical etching method is the only one which allows a random pyramid structure because of the anisotropy of the chemical etching process. Here, anisotropy means that the etch rate depends on the crystal orientation of the monocrystalline Si [6].

Chemical etching is mainly carried out in an etch solution which consists of Potassium Hydroxide (KOH), Isopropyl Alcohol (IPA) and water (Standard KOH-IPA etch solution). The etch solution is usually heated at a temperature of 80°C and silicon wafers are put into the etch solution. The etch process lasts approximately 40 minutes. After etching, approximately 25 µm of Si (in sum for both sides of the Si wafer) is removed, and the monocrystalline silicon wafer is covered by small pyramids. However, this standard etching solution suffers of some drawbacks. At the etching temperature, a constant evaporation of IPA occurs because the boiling point of IPA is 82.4°C [7], thus a re-dosing of IPA into the etch solution is necessary. For this reason, the main problem of the standard chemical etch solution is the higher consumption of IPA and, on the other hand, the price of IPA. Therefore, it is important to find a suitable alcohol which could substitute IPA in the standard KOH (or NaOH)-IPA etch solution.

Different approaches have been carried out in order to reach this purpose. For example, 1,4 cyclohexanediol (CHX) has been used instead of IPA in the KOH-etch solution [8]. Although other substitutes of IPA have been found and good textures have been achieved, the production of solar cells with Si wafers etched with the new etching solutions show only moderate solar cell efficiency [8].

In this work, we present a new chemical etch solution which makes use of potassium hydroxide (KOH), a high boiling alcohol (HBA) and water (new KOH-HBA etch solution). The HBA allows us to texture at a temperature of 100°C, which reduces etching time to 30 minutes,

avoids the constant re-dosing of HBA and requires only a small quantity of this HBA in the etch solution to texture monocrystalline Si wafers. After texturization of Si wafers, a homogeneous pyramid coverage was obtained. Pyramids have an average height of 1-5 µm and an average width of 2-6 µm. By using the screen printing method and monocrystalline silicon wafers textured with the standard KOH-IPA and new KOH-HBA etch solution we produced standard industrial monocrystalline large area silicon solar cells [9]. We obtained solar cells with an average efficiency of 17.7% and 17.8% (average over 5 cells) for the KOH-IPA and KOH-HBA texture, respectively .

2 EXPERIMENTAL

In the experiments, p-type Czochralski silicon wafers (Cz-Si) with (100) orientation were used. The resistivity was 1-3 Ωcm. Two etch solutions were used to texture silicon wafers. In the first etch solution, consisting of 120 g of potassium hydroxide (KOH), 300 ml of isopropyl alcohol (IPA) and 6 liters of deionized water (standard KOH-IPA etch solution), a temperature of 80°C and an etching time of 40 min was used. In the second etch solution, consisting of KOH, high boiling alcohol (HBA) and 6 liters of deionized water (new KOH-HBA etch solution), a temperature of 100°C and an etching time of 30 min was used. In order to optically characterize the texture on Si wafers, reflection measurements were carried out and Scanning Electron Microscope (SEM) pictures were taken. Silicon removal was calculated by weighing silicon wafers before and after the etching process.

Silicon wafers textured by using the standard KOH-IPA and the new KOH-HBA etch solution were used to produce standard industrial monocrystalline silicon solar cells. Initially, a n-type region with a sheet resistance of 50 Ω/sq on the p-type silicon wafer was formed through Phosphorus diffusion (POCl₃), then an antireflection coating of silicon nitride (SiN_x:H, 75 nm, n=2.0) was deposited, after that, silver front and aluminum back contacts were deposited by screen printing. Then a co-firing step was carried out. Finally, edges of solar cells were isolated by sawing. After production of the solar

cells, current-voltage measurements under AM 1.5 illumination conditions were performed.

3 RESULTS AND DISCUSSION

Figure 1 shows reflection measurements of silicon wafers etched with the standard KOH-IPA and the new KOH-HBA etch solution. An AM 1.5-weighted reflection in the wavelength range between 400–1100 nm of 12.6% and 11.5% was obtained for the KOH-IPA and KOH-HBA texture, respectively. Thus, reflection values for KOH-HBA texture are approximately 1 % absolute lower than the values obtained with the standard KOH-IPA texture. This fact could be due to the small pyramid size obtained from the new KOH-HBA etch solution (see Figure 2). Silicon removal of silicon wafers textured with the standard KOH-IPA etch solution was 26.6 μm . In case of the new KOH-HBA etch solution, it was 26.1 μm .

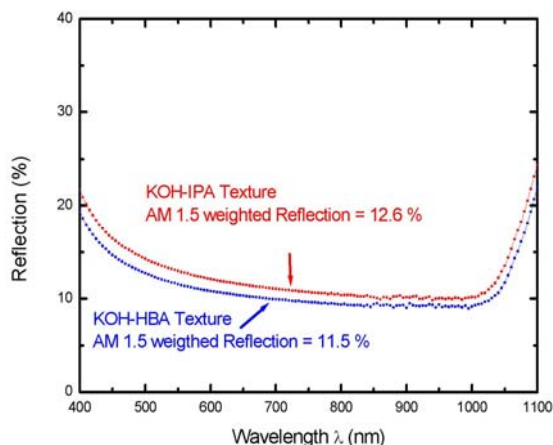


Figure 1: Reflection measurements of a p-type monocrystalline silicon wafer with (100) orientation and resistivity of 1-3 Ωcm etched with the standard KOH-IPA and new KOH-HBA etch solution.

We used the same KOH-HBA etching solution four times to texture monocrystalline silicon wafers (batch size: 5 wafers) without re-dosing of the HBA or water. In spite of consumption of KOH and water evaporation during the etching process we obtained silicon wafers with almost the same texture characteristics, i.e. reflection and silicon removal values were almost the same. This fact could be due to the high KOH concentration used in the etch solution. In the same way, evaporation losses in the KOH-HBA etch solution did not have detrimental influence on the texturing process.

Figure 2 shows SEM pictures of a silicon wafer textured with the new KOH-HBA and standard KOH-IPA etch solution. We observe a strong influence of the etching temperature on pyramid size. On the surface of the silicon wafer textured with the new KOH-HBA (etching temperature 100°C), an average pyramid size of 3-5 μm is observed. A homogeneous coverage of pyramids on this silicon wafer is observed, too. In case of the KOH-IPA texture (etching temperature 80°C), larger pyramids can be observed. An average pyramid size of 8-10 μm is detected.

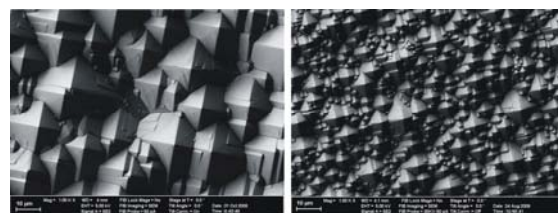


Figure 2: SEM pictures of random pyramid textures with KOH-IPA (80°C, 40 min, left) and KOH-HBA (100°C, 30 min, right).

In table I, current-voltage measurements of silicon solar cells processed with silicon wafers textured with the standard KOH-IPA and new KOH-HBA etch solution are presented. Average solar cell efficiencies were obtained over 5 cells. The slightly higher short circuit current density (j_{sc}) value obtained for the KOH-HBA is due to the lower reflection value (weighted reflection 11.5%) of the wafer surface compared with the reflection value of the KOH-IPA texture (weighted reflection 12.6%).

Table I: Current-voltage results of screen-printed Cz silicon solar cells (125x125 mm^2) produced from silicon wafers textured with the standard KOH-IPA and new KOH-HBA etch solution (Averaged over 5 cells).

	IPA	HBA
V_{oc} [mV]	625.4	625.7
j_{sc} [mA/cm^2]	36.6	37.0
FF [%]	77.1	76.8
η [%]	17.7	17.8

4 SUMMARY

We found a higher boiling alcohol (HBA) which could substitute isopropyl alcohol in the standard potassium hydroxide-isopropyl alcohol (KOH-IPA) etch solution. We have textured monocrystalline silicon wafers (batch size: 5 wafers) four times in the new KOH-HBA etch solution without HBA or water re-dosing. After four times of etching in the same solution, reflection and silicon removal stay almost the same. By increasing etching temperature up to 100°C we were able to reduce etching time to 30 min (silicon removal = 26.1 μm) and a very good homogeneous texture was obtained. The average pyramid size was 3-5 μm . An AM 1.5-weighted reflection in the wavelength range between 400 – 1100 nm of 12.6% and 11.5% was obtained for the KOH-IPA and KOH-HBA texture, respectively. In addition, the properties of the used HBA allows very elegant way for disposal.

By using the screen printing method we processed standard industrial silicon solar cells on 125x125 mm^2 Cz material which achieved an average solar cell efficiency of 17.7 % for the standard KOH-IPA texture and 17.8 % for the new KOH-HBA texture. Therefore, the new KOH-HBA etch solution has the potential to be implemented in the industrial production of solar cells.

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