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Aromatic compounds as substitutes for 2-propanol as texturing additive in aqueous alkaline solutions

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ABSTRACT: Two aromatic organic substances, a micelles-forming agent, an aromatic acid, and a complex-forming agent, an aromatic alcohol, were tested on 50 mm x 50 mm Cz-Si-wafers as texturing agents for mono-crystalline silicon solar cells according to the weighted reflectance of the processed surfaces and the etch-rates of the texturing-solutions in dependence of their composition. The results were compared with those of the standard organic texturing agent 2-propanol (*iso*-propanol, IPA). It could be shown, that the aromatic acid can compete with IPA as texturing additive while etching solutions based on the aromatic alcohol were less successful. After that the system containing the aromatic acid was tested on large number of 125 mm x 125 mm Cz-Si-wafers in an industrial pilot production line of Innovalight Inc., where even better results were reached in shorter time-scales in comparison with the standard texturing process.

Keywords: texturing Cz-Si-wafers, new texturing agents, organic aromatic acid, organic aromatic alcohol, complex forming additive, micelle forming additive

1. INTRODUCTION

In solar cell industry *iso*-propanol is often used as standard texturing additive for mono-crystalline silicon solar cells in aqueous alkaline solutions [1-6]. However this organic additive has some important disadvantages. That's why the search for adapted substitutes is pushed forward since a few years by many working groups in photovoltaic research [7-13].

Some aromatic acids and alcohols (see **Fig. 1**) for example could be promising alternatives for the standard texturing agent 2-propanol because they possess some important advantages for silicon solar cell processing which makes them easier to handle compared to *iso*-propanol (IPA). Both groups of compounds are – like IPA – important substances in chemical industry and can be produced in large quantities at low costs. The solubility in water of some of these substances is high, like that of IPA (see **Tab. 1**), so that they can be used even in high concentrated baths if necessary.

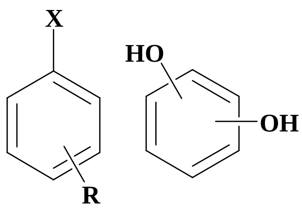

Fig. 1: *Molecular structure of an aromatic acid (left) and an aromatic (poly-)alcohol (right. **-R: -(CH$_2$)$_{0\text{-}12}$-CH$_3$; -X: -COOH , -SO$_3$H , -PO$_3$H***

Because of their high boiling points (well above 100°C) it is possible to raise the bath temperature over the level of 80°C, the standard process temperature at the IPA texturing process. This way higher etching rates and lower processing times can be obtained.

The low vapour pressure of these substances prevents high losses of the texturing agent from the etch-bath during the texturing process, which often is an important reason for low texture-qualities and poor stability of the texturization process using IPA.

The high flash points reduce danger of fire or explosions initiated by hot components of the technical systems, e.g. hot plates of the texturing bench.

On the other hand it must be remarked here that strong organic acids, like some aromatic acids, can neutralize an equivalent amount of hydroxide ions in the alkaline etching bath what could lead to a remarkable reduction of the etch-rate of the bath. This may be disadvantageous for the texturing process itself, because under certain conditions enlarges the time needed to eliminate the surface damage on as-cut wafers in the etch-solution.

A comparative overview of selected relevant physical properties of the standard texturing agent IPA and the two new additive classes is given in **Tab. 1**:

Physical Properties	**IPA**	**Aromatic organic acids**	**Aromatic organic alcohols**
Solubility in H_2O [g / 1000 g H_2O]	no limitation	> 500	> 500
Boiling Point [°C]	82°C	> 100°C	> 100°C
Flash point [°C]	12	> 100°C	> 100°C
Acidity [pK_A]	15	< 1	8 – 12
Vapor pressure [hPa]	43	≤ 1	≤ 1
Hazard Code	F, Xi	Xi, Xn or N	Xi, Xn or N **but not F**

Tab. 1: Selected *relevant physical properties of three texturing additives tested in this work. Disadvantageous properties of the additives for the texturing process are marked in color red.*

2. EXPERIMENTAL PROCEDURE

The influence of 5 different KOH concentrations and 6 different concentrations of the additive on the texturing behaviour on mono-crystalline silicon surfaces was examined. The weighted reflectance of the surfaces and the etch-rate of each etch-bath were determined.

For this, 5 silicon wafers for every possible concentration-combination were etched for 20 minutes at a bath-temperature of 80 ± 1°C respectively. The results were averaged.

The silicon substrates for the experiments were as-cut and cleaned 50 x 50 mm^2 Cz-Si-wafers with 1×10^{16} boron atoms/cm³ doping concentration. The wafers possessed an approximately 18 µm thick area with crystalline defects caused by the multi-wire-slurry-saw during the wafering process on both sides of the wafer. The damage depth in the wafers was determined by LAWave at the Fraunhofer IWS in Dresden [14-15].

The weighted reflectance of the surfaces was calculated by Eq. 1 supported by [16]:

Eq. 1:

$$R_w = \frac{\int_{\lambda_1}^{\lambda_2} \phi(\lambda)\cdot IQE(\lambda)\cdot R(\lambda)\cdot \frac{q^{\lambda}}{hc}\, d\lambda}{\int_{\lambda_1}^{\lambda_2} \phi(\lambda)\cdot IQE(\lambda)\cdot \frac{q^{\lambda}}{hc}\, d\lambda}$$

Where:
R_w = weighted reflection [%];
$\phi(\lambda)$ = spectrum AM 1.5 global [kW/m²]
$IQE\ (\lambda)$ = typical internal quantum efficiency [%]
q = elementary charge $= 1.602177\times10^{-19}C$
λ = wavelength [nm]
h = Planck´s Constant $= 6.62608\times10^{-34}\ J\cdot s$
c = velocity of light in vacuum $\approx 2.9979\times10^{8} ms^{-1}$;

In general substrate-textures which are characterized by a complete coverage of the surface with random pyramids with edge-lengths of approximately 10 µm lead to values for the weighted reflectance of about 12-13%.

Surface textures with pyramid-edges lower than 10 µm mostly possess values for R_w < 12. These are very good texture qualities.

For determination of the etch-rate the weight of the wafers was measured before and after etching with a high precision balance. In best case the value for the average etch-rate exceeds 1 µm/min. Under these conditions it is guaranteed, that during an etch-time between 15 and 20 minutes the saw-damaged areas of the as-cut silicon wafer surfaces are completely removed.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Laboratory test on low area silicon wafers

The experimental results for the weighted reflectance and the average etch-rates for each texturing additive and each concentration-combination tested in this work are shown in the graphics in **Fig. 2a-f**.

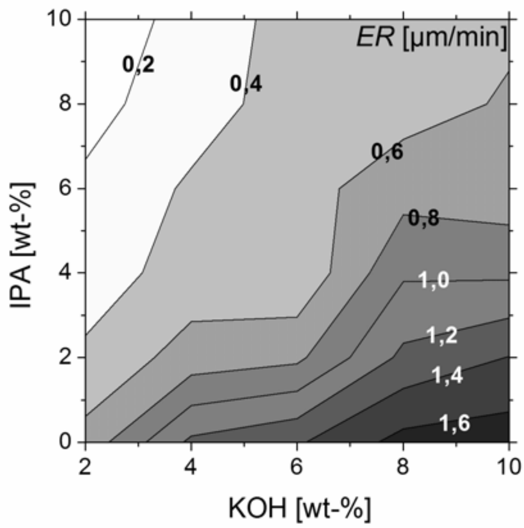

Fig. 2a: *Dependence of the etch-rate ER of bath composition at the KOH/ IPA-system.*

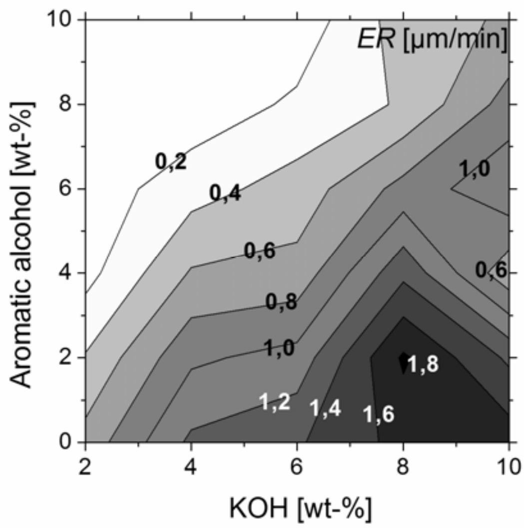

Fig. 2b: *Dependence of the etch-rate ER of bath composition at the KOH/ aromatic-alcohol-system.*

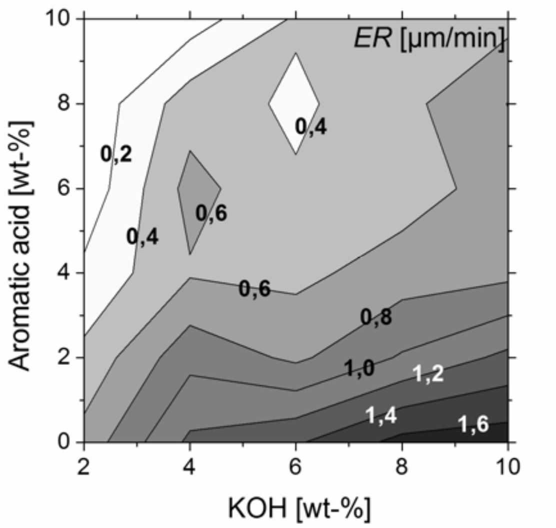

Fig. 2c: *Dependence of the etch-rate ER of bath composition at the KOH/ aromatic-acid-system.*

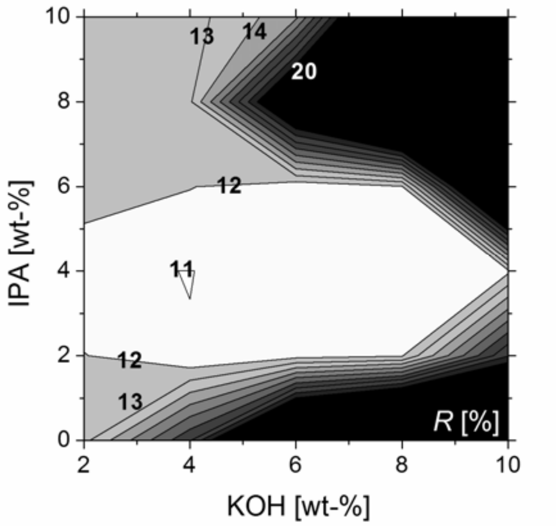

Fig. 2d: *Dependence of the weighted reflectance R of bath composition at the KOH/ IPA-system.*

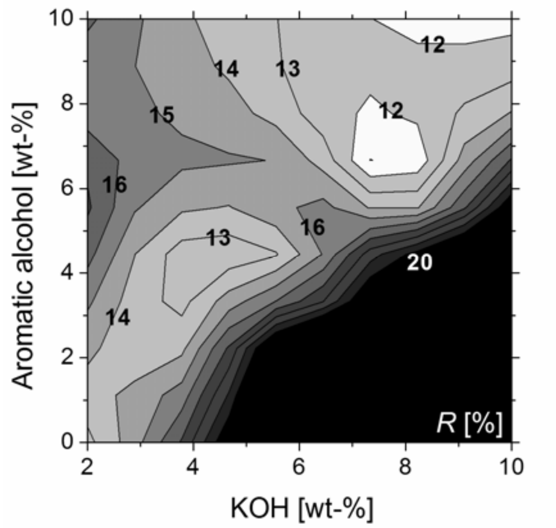

Fig. 2e: *Dependence of the weighted reflectance R of bath composition at the KOH/ aromatic-alcohol-system.*

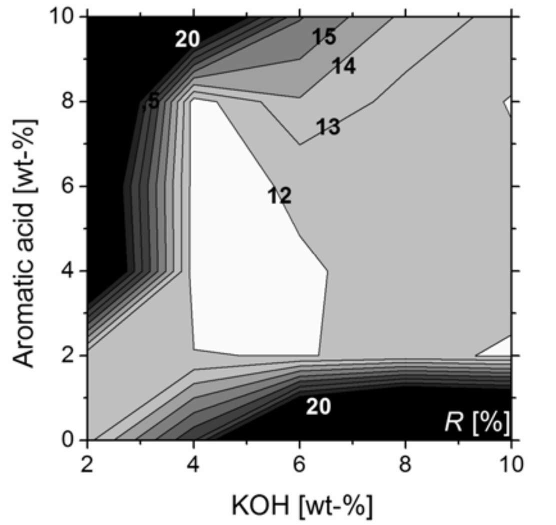

Fig. 2f: *Dependence of the weighted reflectance R of bath composition at the KOH/ aromatic-acid-system.*

Tab. 2 shows the best values for the weighted reflectance and the highest etch-rates for all the three texturing systems respectively. In **Tab. 3** the best two additive/KOH-concentration-combinations for all the three texturing systems are summarized respectively.

Parameter \ Etch-additive	**IPA (reference)**	**Aromatic alcohol**	**Aromatic Acid**
Lowest value for Weighted Reflectance *R* [%]	11,0	11,8	11,5
Percentage of concentration-combinations with *R* < 12 % (very good texture quality)	40	12	28
Percentage of concentration-combinations with *R* < 13 % (good texture quality)	68	28	68
Highest value for average **E**tch-**R**ate *ER* [µm/min] ever reached for one conc.-combination	1,406	1,832	1,251
Average Etch-Rate for all concentration -variations ER_{all} [µm/min]	0,571	0,598	0,536

Tab. 2: *Characteristic values describing the etch- and texturing-behaviour of the three texturing systems tested in this work.*

Parameter \ Etch-additive	IPA (reference)		Aromatic alcohol		Aromatic Acid	
Example	1	2	1	2	1	2
Concentration KOH [wt-%]	10	8	8	10	10	8
Concentration additive [wt-%]	4	4	6	10	2	2
Weighted Reflectance *R* [%]	11.8	11.8	11.9	11.7	11.9	12.2
Average Etch-Rate *ER* [µm/min]	0.963	0.972	0.869	0.629	1.251	1.023

Tab. 3: *Comparison of the two best concentration combinations of each of the three texturing systems tested in this work.*

Between the etch-rate of the texturing solution and the received texture-quality on the processed surfaces there exists a relation characterised by the fact that etch-baths with very high etch-rates on silicon lead to textures with lower quality (dark regions in the graphics of the etch-rate (*ER*) in **Fig. 3**). This tendency can be observed at all the three systems tested in this work. At the system with the aromatic acid and the system with the aromatic alcohol also very low material removals are disadvantageous for the texture quality received (see **Fig. 4**).

The reason for this is the fact, that at low KOH-concentrations a significant amount of damaged material remains at the substrate surface after etching and no random pyramids are formed, while baths with high KOH concentrations and very low amounts of additive possess a polishing effect rather than a texturing effect (see **Fig. 4c**).

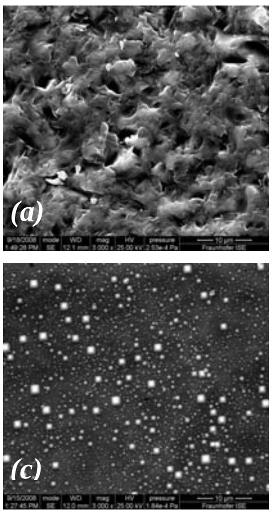

Fig. 4*: Surfaces etched with different bath compositions: (a): 10 wt-% aromatic acid + 2 wt-% KOH; (b): 4 wt-% aromatic acid + 4 wt-% KOH; (c): no organic additive but 10 wt-% KOH.*

The best texture quality is still received on 50 mm x 50 mm substrates with an etch solution containing IPA as texturing additive. However the average etch-rate of this solution is with approximately 0.4 µm/min too low for fast texturing processes.

Supposing the texture-quality as being well enough when a value for $R_W < 13$ % is received IPA and some aromatic acids are similar effective as texturing additives while aromatic alcohols are worse.

As supposed, the highest average etch rate of the system based on the aromatic acid is lower than at the other two systems. A reason for this may be the lower hydroxide-ion-concentrations in the texturing baths in case of an aromatic acid as bath additive. However, the system offers the best concentration-combination of all the three systems, where an etch-rate higher than 1.2 µm/min is received while the weighted reflectance of the processed surface is lower than 12 %.

In seems obvious but it should be mentioned here again, that in most cases high KOH-concentrations (8 or 10 wt.-%) are needed, when high etch-rates and parallel good texture qualities should be received.

3.2. Texturing experiments in the pilot production line on large area silicon wafers

In a second experimental step a new texturing system based on an aromatic acid as texturing additive was used to process two thousands of 125 mm x 125 mm Cz-Si wafers in the pilot production line of Innovalight Inc. The results were compared with those reached with the standard texturization process. The bath temperature at the standard IPA texturing process was 80°C. The etching time was 30 min. At the new process a bath-temperature of 85°C was used while the process-time was 15 min.

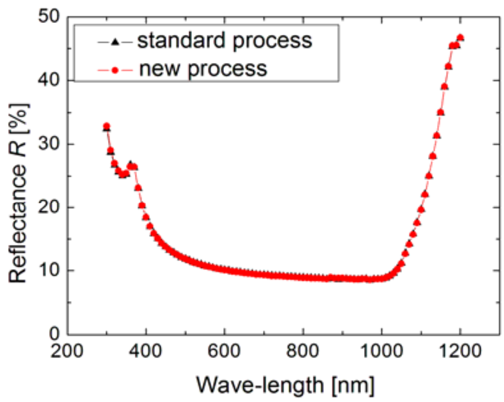

Fig. 5*: Reflectance of 125 mm x 125 mm Cz-Si substrates textured with the standard texturing system and a new texturing system based on an aromatic acid as bath additive.*

The reflectance results are shown in **Fig. 5** It can be easily recognized that with the new system texture-qualities can be received over a wide range of wavelengths comparable to those when the standard system is used, while the etching time is half as long as at the standard texturing process. In both cases, the standard process and the new process, a value for the weighted reflectance of 12.3 % was reached.

Finally the new texturing system based on an aromatic acid as bath additive was used for processing two different substrates on an industrial scale (2000 wafers for each type of substrate). One type of substrate possessed a damaged zone at the wafer surface of approximately 11 µm thickness while the other type of substrate was damage-free.

While in first case pyramids with an average diameter of approximately 15 µm were reached, this value was much lower on damage-free substrates (approx. 6 µm). In both cases the processed surfaces were covered entirely with random pyramids.

4. CONCLUSIONS

Selected aromatic acids are very promising substances as bath additives in texturing processes for mono-crystalline silicon wafers, where they can substitute the standard texturing agent 2-propanol without sharing the disadvantages of this substance.

The physical properties of new additives, especially their high boiling points and their lower flammability compared to the standard texturing additive enable working at higher process-temperatures.

The etch-rates of some solutions with these substance are with values above 1.2 µm/min high enough for being used in inline processes. This is not possible with IPA.

In the pilot-production a new texturing process based on an aromatic acid as texturing additive reached the same texture qualities like the standard process in half the time.

It was also demonstrated in the pilot production that the new texturing process can be used for different substrate qualities. However on damage-free surfaces the texture quality is a little bit higher, the middle edge-length of the random pyramids is lower than in cases, where as-cut wafers with strong crystalline defects are used.

5. ACKNOWLEDGEMENTS

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