KOH/SURFACTANT AS AN ALTERNATIVE TO KOH/IPA FOR TEXTURISATION OF MONOCRYSTALLINE SILICON

E. Wefringhaus, A. Helfricht
International Solar Energy Research Center Konstanz
Rudolf-Diesel-Strasse 15, D-78467 Konstanz, Germany
Author for correspondence: eckard.wefringhaus@isc-konstanz.de, phone: +49 (0)7531 36183-21

ABSTRACT: This work reports on the development of KOH/surfactant as an alternative to the conventional KOH/IPA solution for surface texture of monocrystalline silicon wafers. Replacement of IPA by surfactants of very low concentration below 0.01% allows much higher process temperatures close to the boiling point (~98°C) of the bath. Mean reflexions of less than 12% in the wavelength range of 400 to 1100 nm are achieved. High etch-rates reduce the process time to 10 minutes, allowing the texturing process economically attractive.
Keywords: Texturisation – 1, Manufacturing and processing - 2

1 INTRODUCTION

Anisotropic texturing of monocrystalline silicon is a well known technique. Most commonly, a wet etchant, typically KOH (or NaOH) and IPA (isopropyl alcohol) is used. These solutions rely on the difference in etch rate between (100) and (111) oriented planes and result in random, upright pyramids on a (100) oriented surface. The average reflection from the silicon surface in the wavelength range of 400 to 1100 nm is reduced from about 36 % to about 12 %.

One disadvantage of random pyramid texturing in an industrial environment is that the results are not always reproducible. This is mainly because reasonable etching rates are only achievable at temperatures close to the boiling point of IPA (~82ºC). Consequently, during the texturing process, IPA evaporates and the composition of the solution is constantly changing. Evaporation of IPA is difficult to control and refilling of the bath is rarely optimal. In addition, IPA has high initial and disposal costs, is a health hazard and an explosive substance.

In this approach, IPA was therefore substituted by surfactants, assuming that reduction of surface tension is the main role of IPA in the KOH/IPA texturing system. It has been demonstrated that surfactants influence anisotropic etching processes [1, 2, 3]. Moreover, surfactants have been successfully used as additives in KOH/IPA texturisation processes [4, 5]. Also simple KOH/surfactant systems have been used for texturisation [6, 7]. Di Franca et al. [7], however, did not achieve sufficient low reflexions: the best result was a minimum refexion of 12% at approximately 850 nm. The process in patent [6] is carried out at a quite high surfactant concentration (1%) and a temperature similar to the KOH/IPA-process (85°C). Also process time does not differ from KOH/IPA-processes (30 minutes plus 10 minutes for saw damage etch). A main advantage of IPA substitution by surfactants, however, is the chance of running the process at high temperatures near the boiling point of water (KOH), presumably resulting in high etch rates, i.e. short process times and high throughput. We therefore tried to reduce the process time by high process temperatures of up to 98°C. In addition, our aim was to investigate, which types of surfactants are suitable for anisotropic etching processes.

2 EXPERIMENTAL

Surfactants tested were

- the household cleaning agent "M14", containing 5-15% anionic surfactants, and 5-15% nonionic surfactants,
- the dishwashing agent "Reiny", containing < 5% nonionic surfactants, < 5% amphoteric surfactants, and > 30% anionic surfactants,

and, as pure single substances, delivered by Evonik Goldschmidt AG, Essen, Germany

- Ammonyx LO (lauryl-myristyl dimethylamine oxide, 30.1 % dodecyldimethylamine oxide), cationic,
- Tegotens EC 11 (end-group-closed fatty alcohol ethoxylate), nonionic,
- Rewoteric AM 2 C NM (40% aqueous solution of N-coconut fatty acid amidoethyl-N-(2-hydroxy-ethyl)glycinate, sodium salt), amphoteric, and
- Tegotens DO (aqueous solution of an alkyl dimethylamine oxide, 29.9% decyl dimethyamine oxide), cationic.

Texturisation was carried out in a cubic 40-l-vessel without stirring. All wafers used were monocrystalline <100> Cz-Si, as cut, p-type, 0.5-2.0 Ohm*cm with an area of 148.6 cm². Neither pre-cleaning nor saw damage removal was used before texturing. Surfactant concentrations, texturing time and texturing temperature were varied.

Reflexion was measured using a VARIAN Cary 5 Spectrophotometer equipped with an integrating sphere. Results are always given as unweighted mean reflexion in the wavelength range of 400 to 1100 nm. Etching depth and etch rates were determined by weighing the samples.

In order to find out, if reduction of surface tension is the dominant role of the surfactants in the texturing system, and, moreover, aiming at an avenue for process control, also surface tension of suitable process bathes was determined using a SITA science line t60/2 bubble pressure tensiometer.

3 RESULTS

For all types of surfactants suitable conditions for texturisation were found. The best results obtained (for 98°C) are summarised in Table I. Since the household cleaning and dishwashing agent resulted in unwanted foam at high temperatures, non-foaming and temperature stable surfactants, recommended and delivered by Evonik Goldschmidt AG were chosen as pure single substances.

Table I: Overview over best results obtained for different types of surfactants (all results at 98°C).

surfactant	weight-% surfactant	weight-% KOH	time [min]	refl.* [%]
"M14"	0.00080	5	10	11.1
"Reiny"	0.00100	3	10	11.4
Ammonyx LO	0.00500	4	30	11.6
Tegotens EC11	0.00016	3	10	11.9
Rewoteric AM2	0.00150	2	20	11.9
Tegotens DO	0.00500	3	10	12.4

* unweighted mean reflexion between 400 and 1100 nm.

Figure 1 shows the measured reflexion curves for the Tegotens DO and Tegotens EC11 example in Table 1.

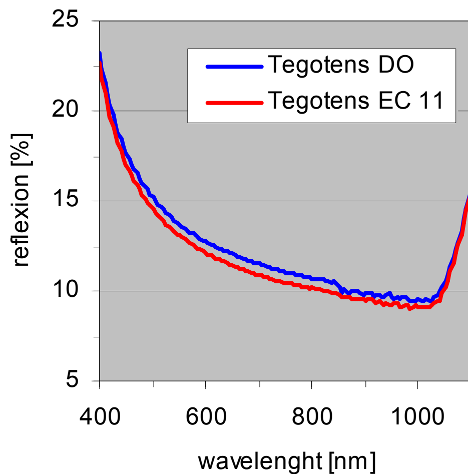

Figure 1: Reflexion-curves for surfactants Tegotens DO (50 mg/l) and Tegotens EC11 (1.6 mg/l), both in 3% KOH for 10 minutes at 98°C.

Figures 2a, 2b, 3a, 3b, and 4 depict detailed results for the cationic surfactant Tegotens DO. Obviously reflexion is mainly depending on the etch rate (figures 2a and 2b). Reflexions below 12% are only achieved at etch rates below 1.5 µm/side/min. Since a high etch temperature of 98°C results in etch rates above 1 µm/side/min, etch rates between 1 and 1.5 µm/side/min are suitable. Thus an acceptable reflexion may be obtained in 10 minutes. The corresponding etching conditions, however, result in quite high etching depths above 10 microns per wafer side (figure 3a and 3b). If low etch depths, i.e. small pyramids, are intended, a lower temperature and, corresponding, lower etch rates and longer etch times have to be chosen. Very low reflexions of 11.3% (11.8%) are for example obtained at 90°C (85°) in 15 (20) minutes. The corresponding etch depth is 9.8 (7.8) microns per wafer side.

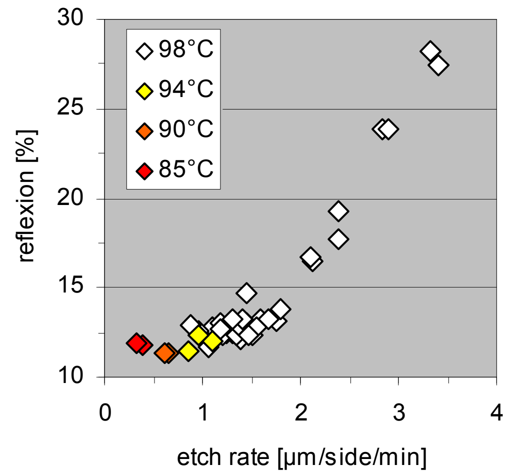

Figure 2a: Reflexion vs. etch rate for texturisation using Tegotens DO. Legend shows different texture temperatures.

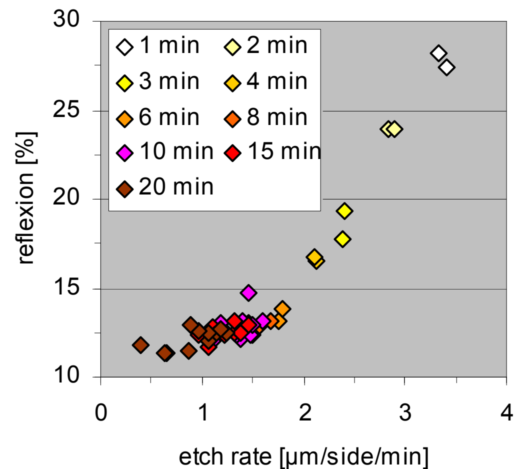

Figure 2b: Reflexion vs. etch rate for texturisation using Tegotens DO. Legend shows different texture times.

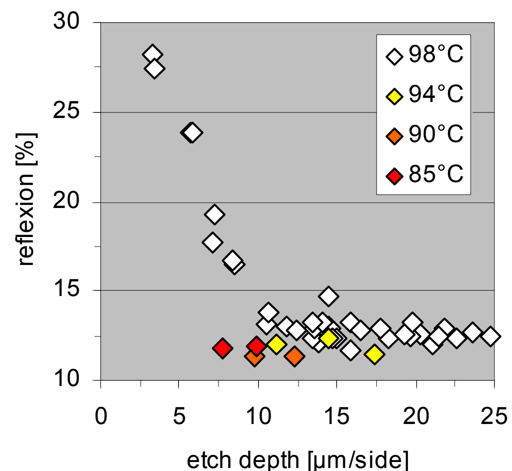

Figure 3a: Reflexion vs. etch depth for texturisation with Tegotens DO. Legend shows different texture temperatures.

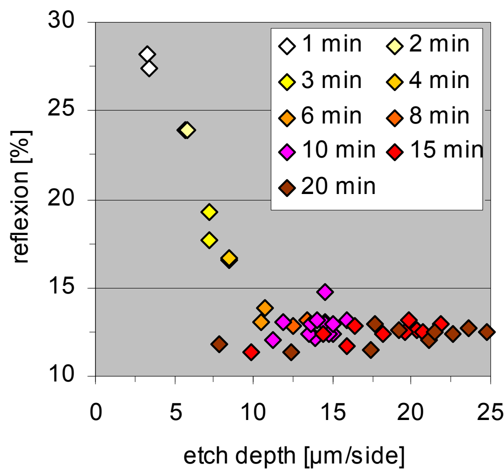

Figure 3b: Reflexion vs. etch depth for texturisation with Tegotens DO. Legend shows different texture times.

Figure 4 shows surface tension of KOH/Tegotens DO systems versus surfactant concentration and bubble life time (intrinsic parameter of the bubble pressure tensiometer). Since surfactant concentrations are very small, also reduction of surface tension compared to water (KOH) is very small. Surface tension in a (2% / 4%) KOH/IPA system at 20°C is approximately 50 mN/m. It therefore seems to be unlikely that reduction of surface tension is the dominant role of the additives, either surfactant or IPA, in a texturing system.

For process control high bubble lifetimes would be required to achieve reasonable sensitivity of a surfactant analysis. As an alternative a colorimetric method according to DIN 38409 H20 (H23-1, H23-2) could be used. This method, as demonstrated by Metrohm Prozessanalytik in Leinfelden-Echterdingen, Germany, is also automatable.

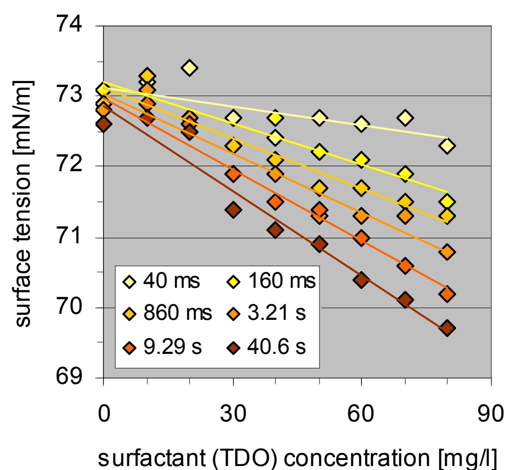

Figure 4: Surface tension vs. surfactant concentration for Tegotens DO (in 3% KOH at 20°C). Legend shows bubble lifetimes.

4 CONCLUSIONS AND OUTLOOK

KOH/surfactant is a suitable alternative to conventional KOH/IPA-texturing of monocrystalline silicon material. We have demonstrated that the process time of anisotropic texturisation can be reduced to 10 minutes (instead of 30-40 minutes) by substitution of IPA by surfactants in very low concentrations (< 0.01%). The short process time may allow to run anisotropic texturisation in an inline system.

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REFERENCE NOTE

The texturisation method is patent pending: WO 2008/022671.