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 reflections 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 (~82°C). 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 reflexion 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.
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 1: Overview over best results obtained for different types of surfactants (all results at 98°C).

<table>
<thead>
<tr>
<th>surfactant</th>
<th>weight-% surfactant</th>
<th>time refl.*</th>
<th>refl.* [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>“M14”</td>
<td>0.00080</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>“Reiny”</td>
<td>0.00100</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Ammonyx LO</td>
<td>0.00500</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>Tegotens EC11</td>
<td>0.00016</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Rewoteric AM2</td>
<td>0.00150</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Tegotens DO</td>
<td>0.00500</td>
<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>

* unweighted mean reflection between 400 and 1100 nm.

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

Figure 1: Reflection-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 reflection is mainly depending on the etch rate (figures 2a and 2b). Reflections 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 reflection 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 reflections of 11.3% (11.8%) are for example obtained at 90°C (85°C) in 15 (20) minutes. The corresponding etch depth is 9.8 (7.8) microns per wafer side.
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.

REFERENCES


ACKNOWLEDGEMENT

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REFERENCE NOTE

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