Wet chemical etching for crystalline silicon solar cells

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1. INTRODUCTION

Alkaline etching is frequently used in the processing of silicon into solar cells. High temperatures (above 100°C) and concentrations (> 10 M) of typically NaOH or KOH solutions are used for the fast removal of saw-damage for the wafers as-cut from the ingot. At low concentrations (less than 10 M) and temperatures (< 100°C) these solutions are used particularly on monocrystalline (100) oriented silicon wafers for the formation pyramidal etch structures having excellent anti-reflective properties.

In this latter case, the etch anisotropy leads to the exposure of slow etching planes, apparently of {111} orientation, which intersect at tilt angles of 54.7° to the wafer surface normal to form upright four-sided pyramids with square bases up to 10 x 10 μm². The texture geometry serves to reduce the wafer front surface reflectance compared to polished silicon, since light reflected away from a texture facet on initially will fall re-incident upon the silicon. These textures thereby allow as much light as possible to be absorbed and converted to electrical current in the solar cell. In general for normally incident light falling upon periodic textures for example, facets with tilt angles above 30° will start to exhibit this effect, initially at the base of the textures, so that by tilt angles of 45° and 60° respectively double and triple bounce incidence of light will be ensured. Under glass encapsulation as in the finished module, reflection can potentially be reduced further through the confinement of escaping light at the glass-air interface by total internal reflection (TIR), this light being re-directed towards the silicon surface. Facet tilt angles as low as 20.9° satisfy the conditions for TIR at the glass-air interface according to Snell's laws of refraction (e.g. [1]), assuming refractive indices of $n_{air} = 1$ and $n_{glass} = 1.5$.

In addition to anti-reflective properties, since light is coupled obliquely into the geometrically textured silicon, the pathlength of light for absorption is increased within the silicon and light which may otherwise be transmitted out of the silicon prior to absorption may be confined within the cell by TIR if an optically less dense medium encapsulates the silicon. This "light trapping" is particularly important in view of the low absorption coefficient of silicon at near-infrared wavelengths, and the trend towards the use of thinner wafers in silicon cell production. Finally, the oblique passage of the light within the silicon ensures it will be absorbed closer to the surface and thereby the junction of the cell (formed between n-type emitter and p-type bulk regions of the cell), thereby increasing the probability of its collection.

Currently, multicrystalline silicon (with crystal grain sizes of ~1mm-10 cm [2] and wafer thicknesses of ~300 μm) as sawn from ingots formed from melting and recrystallising the silicon feedstock, is most frequently used commercially. Multicrystalline silicon accounts for approximately two-thirds of the silicon solar cells produced compared to one-third for monocrystalline (100) silicon. These wafers have been shown to have random grain orientations [e.g. 3], whereby only a proportion of crystals will be of near (100) orientation to benefit from the anti-reflective pyramidal structures formed by alkaline etching. This has lead to an increase in the application of acidic etchants based on $HF:HNO_3$ solutions for the formation of textures on multicrystalline wafers. The isotropic action of these etchants upon the various crystal orientations silicon, both in terms of the etch rate and the surface morphologies obtained, make acidic etching an attractive alternative to alkaline etchants.

2. AIM AND EXPERIMENTATION

The aim of this work is to determine etch conditions optimal to reflectance reduction for multi- and mono-crystalline silicon when alkaline and acidic etching are employed. Work focuses upon relating the etch composition to the resulting etch surface morphologies and reflectances, on a per orientation basis as well as for complete multicrystalline wafers.

Multicrystalline Solsix wafers and monocrystalline wafers of 7 orientations spread over the principal (111):(110):(100) triangle are used to investigate the etch surface geometries on a per orientation basis. The mono-wafers were initially polished/lapped; the surfaces were therefore sandblasted with Al_2O_3 powder followed by thorough rinsing and cleaning step to give a starting surface equivalent to the as-cut multicrystalline wafers.

Wafers were cut to 30 x 30 mm^2 and etched in either a typical NaOH based low concentration alkaline texture etch solution, a high concentration alkaline saw-damage etch solution, or in acidic based solutions with varying $HF:HNO_3$ ratios (using stock 49% HF and 70% HNO_3) using either glacial acetic acid or water as a diluent. Various etch durations were employed in order to observe the development of the surface textures as a function of etch depth. Reflectance properties were observed for the wafers in air and under glass-EVA (= ethyl vinyl acetate) encapsulation.

In all cases the resulting etch surface morphologies were observed by optical or scanning electron (SEM) microscopy, and total hemispherical reflectance measurements were performed using an integrating sphere and spectroradiometer set-up. In addition, for the quantification of the etch surface geometries, specially developed experimental methods using Atomic Force Microscopy (AFM facet transforms), localised laser reflectance patterns and Laue photography as described in [4] were employed.

3. RESULTS

For the high concentration saw-damage etch, several crystallographic planes are stable to the etch, namely the {100}, {110}, {111}, {311} & {211}. This leads to etch structures with low facet angles (<30°) often bounded by several different crystallographic planes and yielding high reflectances in air. Under encapsulation however, central orientations in the vicinity of (321) and (110) benefit from reflection reduction due to the presence of a number of facets with angles >20.9° satisfying the conditions for TIR at the glass-air interface (extensive quantification of the alkaline etch surface morphologies in terms of facet tilt/azimuth angles, etc. are given in [4,5]). Despite this, multicrystalline reflectances for alkaline saw-damage etching remain higher than for either alkaline texture etching or the lowest reflecting isotropic etch textures, even under encapsulation (with encapsulated reflectances of ~ 12, 11 & 8 % at an arbitrary visible wavelength of 0.9 μm for alkaline saw-damage, alkaline texture and acidic "tub" etches respectively, these latter textures being described below). As such, saw-damage etching is best employed for reflection reduction on encapsulated {110} oriented silicon or silicon with a preferred {110} orientation, where it should be seen as a lesser alternative to isotropic etching (in terms of the resulting reflectances) in this case.

For the low concentration texture etch, (tilted) pyramidal structures bounded by facets tending to {111} planes form on near (100) orientations and yield the lowest reflectances. The pyramidal textures become better defined crystallographically with etch duration, and their density increases over the wafer surface (e.g. from sporadically distributed nucleation pyramids initially on the (100) orientation with bases < 1μm, to densely populated pyramids of 10 x10 μm^2 almost devoid of non-etched regions between features on prolonged etching). Under encapsulation, pyramidal structures formed on orientations further removed from the (100), with dominant facets having lower tilt angles with respect to the wafer surface normal, experience multiple bounce incidence of light due to TIR at the glass-air interface. Not only {111} but also {XXY} crystallographic planes between (111) and (110) are stable to the etch (X and Y are integers). Orientations in the region of (111) and (110) initially yield triangular etch pits and grooved structures respectively which etch flat with increasing etch duration so that reflectances are equivalent to polished silicon. In summary, alkaline texture etching provides the lowest reflections for (100) oriented monocrystalline wafers. For multicrystalline wafers this etch may be used preferably at low etch durations. In this case textures on {XXY} orientations (which are found beneficial to light trapping [5]) are still well defined crystallographically whilst the developing (tilted) pyramid structures on near (100) orientations with also yield low reflectances. This etch type is not recommendable for wafers with a predominantly (110) or other {XXY} orientation.

In the case of isotropic acidic etchants, for the undiluted $HF:HNO_3$, etch rates were found to peak at $HF:HNO_3$ ratios of approximately 65:35. On increasing dilution, the peak broadens and etch rates generally decrease. In the region of the etch rate peak at low dilutions, concave "tub"-shaped etch pits (Fig. 2) are formed whose curvatures lead to reduced reflection in air and particularly under encapsulation, in the latter case down to as low as ~10% (Fig. 3). However, defects and grain boundaries are preferentially attacked by the etch at these ratios, which is a problem when texturing multicrystalline wafers. Defect etching can be minimised whilst retaining the favourable etch pit geometries by keeping etch depths to a minimum, since etch pits become flatter and reflectance higher as the etch depth is increased. The acidic etchants appear appropriate for texturisation of multicrystalline silicon in particular, and for texturisation of silicon with a (preferential) (110) orientation. The commercially available "T1" acidic solution which is supplied and was developed by ECN [6] yielding pitted structures, gives multicrystalline reflectances in air of 20% at a wavelength of 1 μm, and reflectances in air as low as 10-15% at 1 μm have been achieved with the most recently developed "T2" solution [6], which is equivalent to pyramid textures on (100).

4. ETCHING OF ALTERNATIVE CRYSTALLINE SILICON MATERIALS

Having determined the etch surface morphologies and optical properties on a per orientation basis for multi- and monocrystalline silicon, it is interesting to see if optimal etch conditions are equally appropriate for other crystalline silicon wafer materials used in the solar cell industry. We take the example of silicon grown by the EFG (edge defined crystal growth) process. In this case, silicon is extracted directly from the melt in sheets or "ribbons" of the required thickness, being pulled vertically from the top of a graphite die into which the melt is fed by capillary action (e.g. [7]). This reduces the amount of feedstock required for wafer formation, eliminating the approximately 50 % kerf (sawing) losses inherent in the ingot process, but introduces other problems such as a high intergrain defect density (dislocations, twin boundaries) and a non-uniform wafer thickness [8].

EFG material has grains with a preferential {110} orientation [9,10]. From the results above, one may intially infer that isotropic texturisation should be employed for optimal reflectance reduction in this case. However, the high defect density present in the EFG wafer means that acidic etching in the reflection reducing "tub" region leads to a strong attack on grain boundaries and macroporous structures (see Fig. 3) up to 30 μm deep. Such features would be detrimental to further wafer processing, for example in the formation of the emitter, and to the eventual electrical characteristics of the cell, for example causing high levels of (surface) recombination. In this case, a high concentration alkaline saw-damage etch would appear most favourable for reflectance reduction.

5. CONCLUSIONS

Acidic etching of silicon in $HF:HNO_3$ solutions to form concave pit or "tub" texture geometries would appear the most appropriate etching method for ingot grown multicrystalline silicon, yielding low reflectances on all orientations. Low concentration alkaline texture etching gives the lowest reflectance values for (100) oriented monocrystalline wafers by virtue of the upright pyramid textures formed. High concentration saw-damage etching is an appropriate alternative to acidic etching for predominantly (110) oriented wafers, particularly where high defect densities make application of acidic etchants inappropriate due to preferential defect etching in the "tub"- regime .

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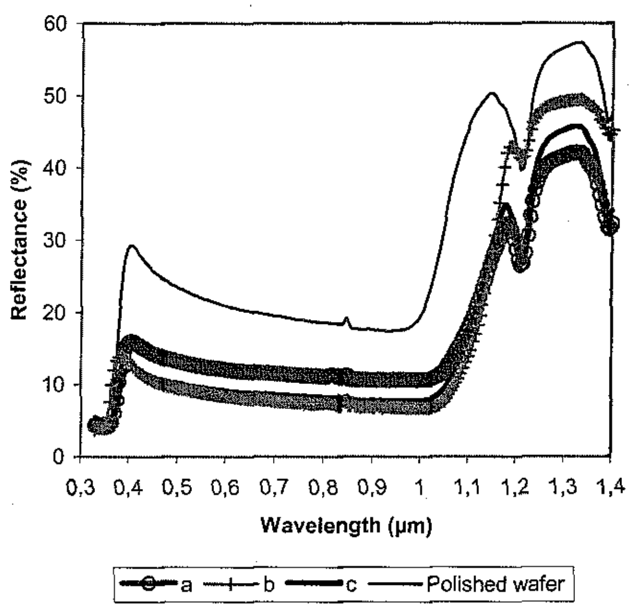

Fig 1: Lowest achieved encapsulated reflectances per etch type. a: Alkaline saw-damage etch on (110) orientation.
b: Alkaline texture etch on (100) orientation. c: Acidic etch in pitted "tub" region (miscellaneous orientation).

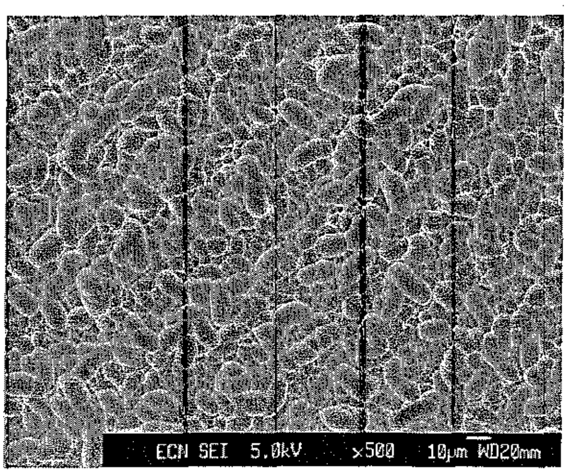

Fig. 2: SEM picture of isotropic pitted texture on multicrystalline silicon

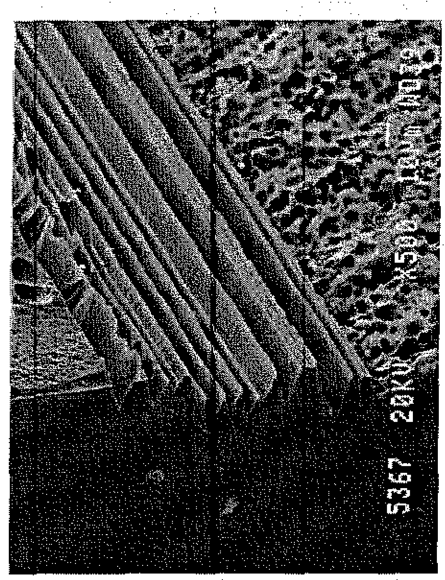

Fig. 3: Defect etching by acidic etching in pitted texture regime on EFG silicon