

ACIDIC TEXTURING OF MULTICRYSTALLINE SILICON WAFERS

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ABSTRACT

In this paper, results from investigations of acidic texturing are presented. As-cut, multicrystalline and polished, single crystal Si wafers have been etched in a range of acidic mixtures. The mixtures contained hydrofluoric and nitric acid, with de-ionized water, phosphoric acid or sulphuric acid added as diluents. In the initial phases of the etching process, surface cracks originating from the wafer sawing were transformed into deep and elongated pits. The reflectance of such textures was low. However, as the etching proceeded beyond the damaged surface region, more reflective, bubble-like textures were obtained.

INTRODUCTION

The efficiency of a solar cell is determined by its ability to gather light. The reflectance of a polished silicon (Si) wafer is relatively high. Therefore, processes resulting in the formation of textured, less reflective surfaces are commonly applied to Si solar cells. Hitherto, the most common texturing technique has been wet etching in hot, alkaline solutions, which results in the formation of pyramids protruding from the surface of a Si wafer [1]. Although this technique is very efficient in reducing the reflectance of (100)-oriented single crystal Si (sc-Si) wafers, it is not suitable for texturing multi-crystalline Si (mc-Si) wafers, because the shapes of the pyramids depend on the local crystal orientation. Hence, the reduction in reflectance obtained for a mc-Si wafer will vary from grain to grain.

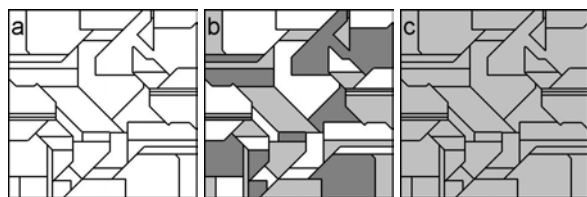


Fig. 1. A schematic depiction of a) an untextured, b) an anisotropically textured and c) an isotropically textured mc-Si wafer.

Much effort has recently been devoted to the development of techniques for creating more isotropic textures, further reducing the reflectance of mc-Si wafers (See Fig. 1). Several techniques have been investigated, including mechanical formation of V-

grooves [2], laser texturing [3], texturing using reactive ion etching [4] and acidic texturing [5-12]. Of these techniques, the latter has been devoted the most interest. Acidic texturing has been successfully applied to as-cut and polished sc-Si and mc-Si wafers, as well as to tri-crystalline Si wafers [7]. Successful integration with industrial solar cell processing has also been demonstrated [12].

Among the advantages of acidic texturing are the possibilities of a) avoiding step formation between grains, b) performing damage removal and texturing in one single processing step, c) the relatively small required etch depth and d) fabricating solar cells with an aesthetically pleasing uniform appearance [6].

When performing acidic texturing, Si wafers are immersed in mixtures typically containing hydrofluoric acid (HF) and nitric acid (HNO_3), as well as one or more additives. Although the overall chemical reactions occurring during dissolution of Si in such mixtures are well known [13], the mechanisms determining the various textures that can be obtained have yet to be described thoroughly.

In this paper, we present the results of investigations of acidic texturing of both as-cut mc-Si and polished sc-Si wafers. A range of different acidic mixtures containing HF and HNO_3 , as well as different diluents, namely de-ionized water (H_2O (DI)), phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4) have been used.

The textured surfaces have been investigated using scanning electron microscopy (SEM), optical microscopy, white light interferometry (WLI) and profilometry. The reflectance of the different textures has been measured.

Here, we discuss the correlation between the surface structure of a wafer and its reflectance, and report significantly lower reflectances than what is obtainable with conventional alkaline texturing of mc-Si wafers.

EXPERIMENTAL

Boron-doped 4" as-cut mc-Si wafers and polished Czochralski (Cz) sc-Si wafers with a (100) orientation, with resistivities of 0.5-2 and 10-15 $\Omega\cdot\text{cm}$, respectively, were used in this work. The mc-Si wafers were 330 μm thick, the sc-Si wafers 525 μm thick. The wafers were textured using acidic mixtures containing HF and HNO_3 , diluted with H_2O (DI), H_3PO_4 or H_2SO_4 . The texturing was performed at room temperature. However, during

texturing using the most aggressive mixtures, a significant heating was observed. After texturing, the Si wafers were thoroughly rinsed in H₂O (DI) and blown dry.

Most of the different mixtures resulted in the formation of a more-or-less isotropically textured surface covered by a thin porous Si film. Several research groups have successfully demonstrated the use of such films as anti-reflective coatings [14]. For the work described in this paper, these films were removed by immersing the wafers in a 1% aqueous solution of NaOH for a few seconds.

The various textures were characterized using a Hitachi S4800 SEM equipped with a field emission gun, optical microscopes, a WYKO NT-2000 white light interferometer, a Tencor Alpha-step 200 profilometer and a Mitutoyo digimatic indicator thickness measurement probe. The spectral reflectance of the various surfaces was measured using a custom-built setup for measuring spectral response. Reflectance values were determined by taking the average of measurements from several grains on each wafer.

RESULTS

Surface structure

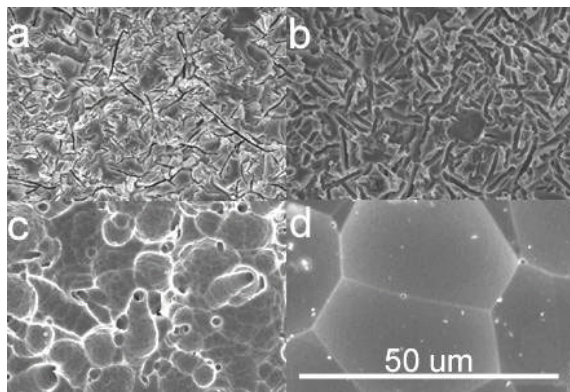


Fig. 2: Micrographs showing a series of as-cut mc-Si wafers etched in aqueous mixtures to different depths. a) A weakly etched wafer with a reflectance (R) of 20%. b) A more etched wafer with a crack-dominated texture and a R of 17%. c) A wafer etched beyond the damaged layer with randomly distributed etch pits and a R of 22%. d) A wafer etched well beyond the damaged layer with a bubble-like texture and a R of 33%.

A range of strikingly different textures was obtained on mc-Si wafers etched in the different acidic mixtures. However, a general trend was observed for all mixtures, namely a clear dependence of the texture on the etching depth.

SEM micrographs taken from a series of as-cut Si wafers etched to different depths in aqueous acidic mixtures (see Fig. 2. a-d) indicate the following trend. Initially, the wafer surface is very similar to the surface of an as-cut wafer. Narrow and long cracks are observed. While the lengths of these cracks can exceed

10 μ m, the widths are initially below 1 μ m. As the etching time and, thus, the etching depth, is increased, these cracks are gradually widened. Eventually, the cracks start to merge. Thereafter, the surface structure evolves into a bubble-like system of approximately hemispherical etch pits. The diameter of these pits can be up to 50 μ m. Polished sc-Si wafers that were textured in acidic textures also exhibited a very similar bubble-like texture.

The height variation of the different textures was measured using either WLI or profilometry and the depth-to-width ratios, also known as the aspect ratios, were calculated. The aspect ratio, obviously, was significantly larger for the narrow cracks than for the much shallower bubble-like etch pits (See Fig. 3.). The depth and width across a crack typically were on the order of 5 μ m and 1 μ m, respectively, giving an aspect ratio of approximately 5. Corresponding values for a typical bubble-like texture were 10 μ m and 20 μ m, giving a much lower aspect ratio of approximately 0.5.

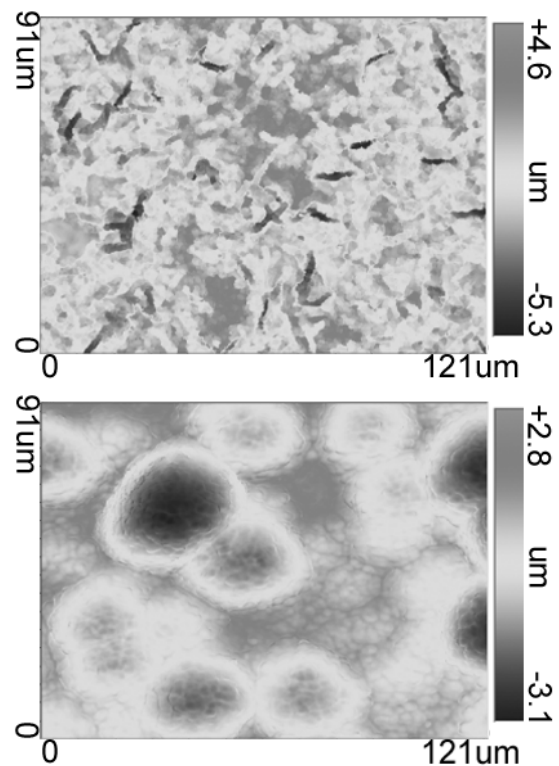


Fig. 3: WLI images illustrating the range of different aspect ratios exhibited by the different acidic textures. a) A crack-dominated texture obtained using an acidic mixture with H₂SO₄. b) A bubble-like obtained using an acidic mixture with H₃PO₄. Note the different depth scales.

Reflectance measurements

A clear correspondence between the observed texture and the reflectance was observed. The reflectance of an as-cut mc-Si wafer is typically between

25 and 30%. As the texturing proceeds, the reflectance initially is reduced. Reflectances as low as 15.0% were obtained for textures consisting of cracks expanded to cover most of the surface (See Fig. 4. and Fig. 5.). However, as the etching continues, the crack-like texture is gradually converted into a bubble-like texture. Eventually, wide and shallow etch pits are formed, and the reflectance increases towards 33.0%, a value comparable to what is expected for a polished Si wafer.

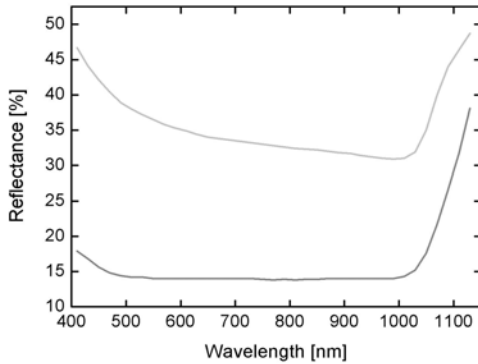


Fig. 4: Results of reflectance measurements of a polished wafer (lower graph) and a wafer textured using an aqueous acidic mixture (upper graph).

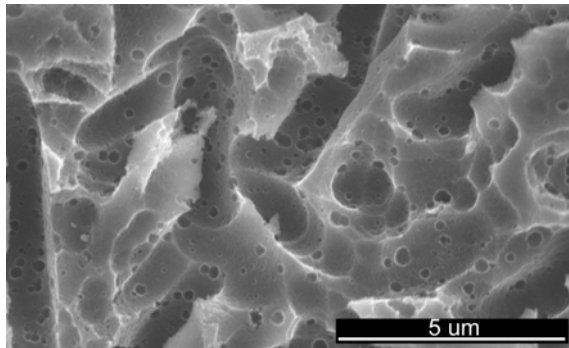


Fig. 5: Micrograph showing a crack-like texture with a reflectance of 15.0%, the lowest reflectance obtained in this work. The texture was obtained using an aqueous acidic mixture.

The effect of composition

The etch rates could be controlled both by varying the relative HF/HNO₃ ratio and varying the amount of the diluent used. This is in accordance with previous work on the dissolution of Si in similar mixtures [13]. Mixtures with etch rates ranging from above 100μm/min towards less than 1μm/min were tried out in this work.

The effect of the different diluents on the etch rate was determined comparing the etch rate observed when keeping both the HF/HNO₃ ratio and the amount of diluent constant. The mixtures containing phosphoric acid resulted in the highest etch rates, followed by the

mixtures diluted with sulfuric acid and, lastly, aqueous mixtures.

The etching of mc-Si wafers in acidic mixtures with phosphoric acid was aggressive. A significant heating occurred during the etching, and corrosive gases and foams were formed. The foams remained on the wafers until they were submerged in H₂O (DI).

DISCUSSION

The surface structure resulting when texturing as-cut mc-Si wafers in acidic mixtures is initially determined by the damaged surface. The micro-cracks formed during the wafer sawing are gradually widened. Eventually, as the texturing proceeds, these cracks merge and the surface structure becomes increasingly bubble-like. Similar bubble-like textures were also obtained by etching polished wafers in acidic mixtures, indicating that such textures are not independent of the initial surface structure, but rather determined by the etching process itself, possibly through the formation of gas bubbles during the etching.

A strong correlation between the texture and the reflectance was observed. Obviously, the ability of a given texture to reduce reflectance will be determined by the ability of a given texture to capture light, which is determined by the aspect ratio of the light trapping structures and by the fraction of the total surface area that is covered by such structures.

The surface of an as-cut wafer is covered with micro-cracks with a very high aspect ratio. However, the total area of these cracks is relatively small compared to the total surface area of the wafer, most of which is relatively smooth. Therefore, the reflectance of such a surface is relatively high. As the cracks are widened, the aspect ratio gradually decreases while the area fraction of the cracks increases. A surface completely covered with cracks of a sufficient aspect ratio will have the lowest possible reflectance. As the cracks start to merge into etch pits and a bubble-like texture is obtained, the aspect ratio eventually becomes too small for efficient light trapping. Although the entire surface area of the wafer is textured, the reflectance will increase towards values similar to what is expected for polished wafers.

If only the obtainable reduction in reflectance is taken into account when texturing mc-Si wafers, it is clear that crack-dominated textures are the best choice. Such textures might be used in purely back-contacted solar cell structures with a sufficient surface passivation. However, when using conventional screen-printing technology to process solar cells from mc-Si wafers, deep, narrow cracks and sharp, fragile edges create a range of problems. The shallower, bubble-like textures are also unsuitable because of the limited improvements they offer with respect to reflectance. An intermediate texture seems more suitable, as a significant reflectance reduction can still be obtained while avoiding problems during subsequent solar cell processing.

When texturing polished wafers or wafers where the damaged layer has been removed in a separate etching step, a bubble-like texture will be obtained. The bubble formation suggested to yield such textures can

be controlled by adding surface agents to the acidic mixture, as has been shown previously [10].

CONCLUSION

When texturing as-cut mc-Si wafers, the texture is initially determined by the damaged surface. However, as the etching proceeds, a bubble-like texture independent of the initial surface structure of the wafer is obtained. The reflectance depends strongly on the type of texture. The lowest reflectances are obtained with crack-dominated textures, while those with wide and shallow, bubble-like pits result in reflectances comparable with those of polished Si wafers. An intermediate texture seems most suitable for solar cell processing using screen-printing technology.

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