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Hierarchical etching for improved optical front-side properties of monocrystalline Si solar cells

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Abstract

We investigate a hierarchical surface structuring process to reduce the optical reflectance of monocrystalline Si solar cells to below the reflectance of state-of-the-art alkaline texturing. First, alkaline texturing is performed, yielding random pyramids with a few micrometers in size. Second, plasma etching forms step-shaped structures smaller than the wavelength of visible light. Eventually, the surface morphology is formed by <111> planes with many steps, edges and inverted pyramids in a few hundreds of nanometers scale. We investigate the reflectance on double-side textured samples with SiN_x/Al_2O_3 front-side and SiN_x rear-side passivation. These dielectric stacks exhibit a low reflectance for conventional alkaline textured surfaces. The short circuit current density potential of the best hierarchical structured samples is 0.4 mA/cm^2 higher when integrating the AM1.5G spectrum from 300 nm to 1000 nm. Furthermore, our results suggest that structures with dimensions smaller than the thickness of an antireflection- and passivation (AR) layer cannot be covered conformal by the AR layer when using plasma-enhanced chemical vapor deposition. Thus, there seems to be a lower limit for the structure size, and wet chemical cleaning sequences – performed after plasma etching - have to be adjusted accordingly.

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1. Introduction

Solar cells based on monocrystalline Si usually feature an alkaline front side texture with random upright pyramids that are a few micrometers in size. For multi-crystalline solar cells, texturing with structures on micrometer

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scale is performed either by an acid wet chemical etching step or by reactive ion etching [1]. Structures with a few tens of nanometers in dimension can be formed by reactive ion etching. A two-scale approach, i.e., the combination of surface structures on micrometer scale with structures in the nanometer regime was suggested to exhibit optical properties that are superior to the standard random pyramidal texture [2 - 6]. It is the purpose of this work to quantify the advantage of a hierarchical texture in combination with a state-of-the art dielectric anti-reflection coating. Since this work is part of the development of *n*-type PERT (passivated emitter, rear totally diffused) cells with front-side boron emitter [7], we investigate an Al_2O_3/SiN_x layer stack as anti-reflection coating. However, our results could be directly transferred to SiN_x anti-reflection coating, as commonly used for *p*-type cells with phosphorus front-side emitter.

Furthermore, some of the previously reported surface morphologies are very rugged [2, 3] which raises the question whether conventional doping, passivation and screen-printing techniques can be applied. Here we aim at non-rugged hierarchical structured surface. For this purpose, we applied plasma etching on a previously alkaline textured (100) oriented mono-crystalline Si wafers. Varying the plasma etching parameters yields various shapes of the nano-scale structures that we characterize by scanning electron microscopy (SEM) and reflectance measurements.

2. Experimental

Figure 1 illustrates the sample structure. Monocrystalline silicon wafers (*n*-type, Cz, 2 Ωcm, <100>) are textured on both sides in an alkaline solution, yielding random pyramids with a size up to 4 µm. Both sides are nano-structured in a Roth & Rau AK800 reactive ion etching (RIE) system using Ar, O_2 and SF_6. We investigate four recipes by varying process pressure, etching time and gas flows. In case of recipe 1 we apply an additional Ar preconditioning step prior to the etching process. Table 1 shows the differences of the four recipes qualitatively.

Table 1. Recipe variations

Parameter	Recipe 1	Recipe 2	Recipe 3	Recipe 4
Process Pressure	low	medium	medium	high
Etching time	100 %	50 %	100 %	100 %
Ar gas flow	low	high	medium	high
O_2 gas flow	medium	high	low	high
SF_6 gas flow	medium	high	low	high

Wet chemical cleaning with different amounts of silicon removal follows. We then apply a front-side passivation that simultaneously acts as anti-reflection coating (ARC). The stack consists of 10 nm Al_2O_3 deposited by atomic layer deposition (ALD) and 60 nm SiN_x with a refractive index of 1.9 deposited by plasma-enhanced chemical vapor deposition (PECVD). For the rear-side passivation a layer of 100 nm SiN_x with a refractive index of 2.05 is used. The passivation scheme is similar to that of our *n*-type PERT front junction cells. The samples are finally fired in a belt furnace.

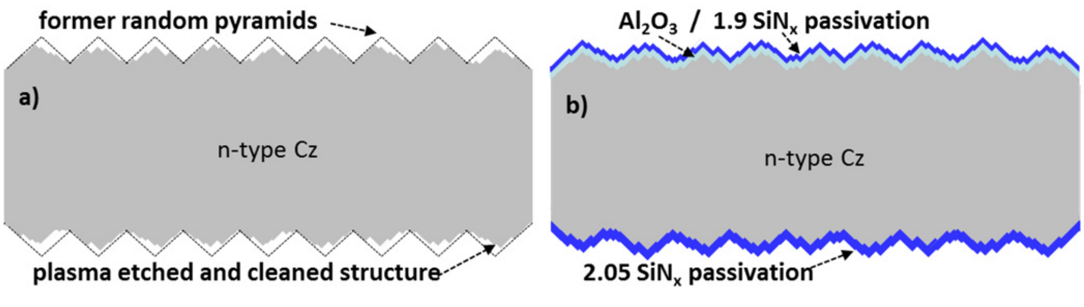

Fig. 1. Illustration of the hierarchical etched structures (a) after plasma etching and cleaning, b) after subsequent passivation. In (a), the former shape of the micrometer-sized pyramids after the alkaline texturing is also indicated

Structural investigations are performed using a Hitachi S-4800 scanning electron microscope (SEM). Optical measurements are performed using a Varian Cary 5000 UV-VIS-NIR-spectrometer.

Lifetime measurements are carried out with a Sinton instruments WCT-120 photoconductance lifetime tester on symmetrical test structures with hierarchically etched surfaces, which have been cleaned in the sequence with marginal Si removal. These samples have been implanted either with boron and phosphorus ions on both sides, and subsequently annealed afterwards at 1050°C [7]. The boron doped references have been passivated with an Al_2O_3/1.9 SiN_x-stack on both sides, the phosphorous samples with 2.05 SiN_x on both sides. The saturation current densities J_0 are determined by using the method of Kane and Swanson [8].

3. Results and Discussion

Figure 2 shows the SEM images of the alkaline textured reference (a + b) and all four recipes investigated after plasma etching and after cleaning. There are significant differences in the surface morphologies after hierarchical etching (Fig. 2 c - f) due to the different process parameters / plasma etch recipes. For all samples shown in Fig. 2 (g - n), a cleaning sequence with significant Si removal is applied. Thus, the smallest structures vanish upon cleaning, in particular for recipe 3 und 4. Eventually, the surface consists of <111> planes for all recipes, with a varying number of steps, edges and inverted pyramids. The scale of these structures is a few tens to a few hundreds of nanometers on all samples.

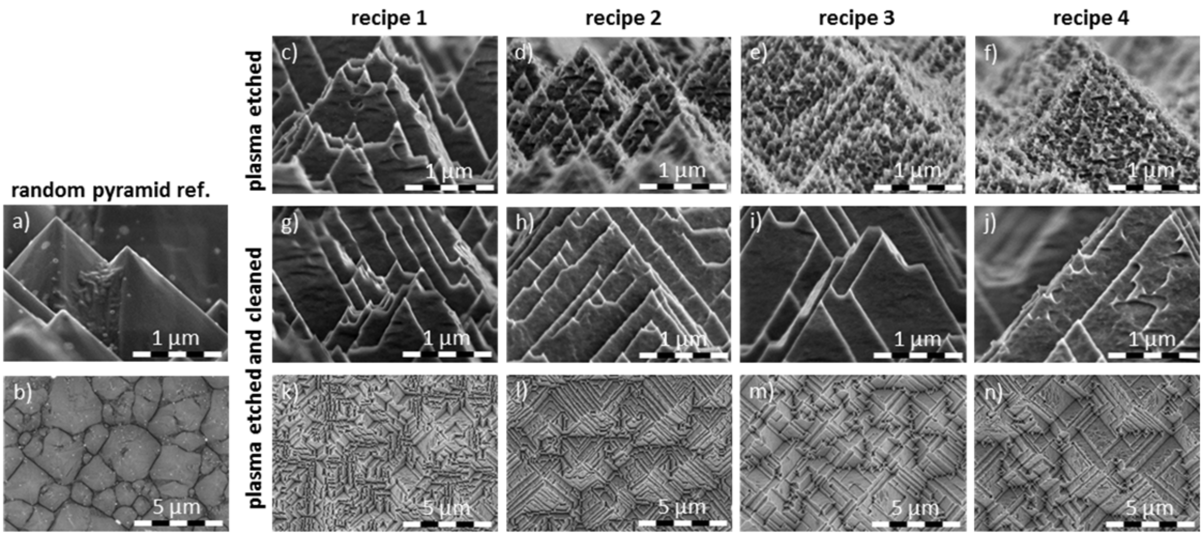

Fig. 2. SEM images of hierarchical structured samples, image a) and b) random pyramid reference. Top line (c – f): recipes 1 to 4 directly after plasma etching, line 2 and 3(g – n) after subsequent cleaning sequence with significant Si removal. Upper two lines: tilted 85°, bottom line: top view

If the cleaned surface consists of small <111> planes it is most likely compatible with conventional doping, passivation and screen-print metallization schemes. Indeed, an Al_2O_3/SiN_x anti-reflection layer stack can be deposited conformal on hierarchical structured and wet chemically cleaned small <111> surfaces as to see in Fig. 3(a).

By contrast, in the case that a cleaning sequence with only marginal Si removal is applied after plasma etching using recipe 3, many needle tips and structures a few nanometers to a few tens of nanometers in scale remain on the surface. On those samples, the PECVD deposited SiN_x does not grow conformal (Figs. 3(b)-top view, 3(c)-cross sectional view). The PECVD-based SiN_x layer growth obviously starts at many starting points with different orientations, and shading effects occur. Eventually, cavities in the SiN_x layer and voids between the SiN_x and the Si form, which compromises both – passivation quality and the antireflection properties of the surface (see Fig. 4 (b)).

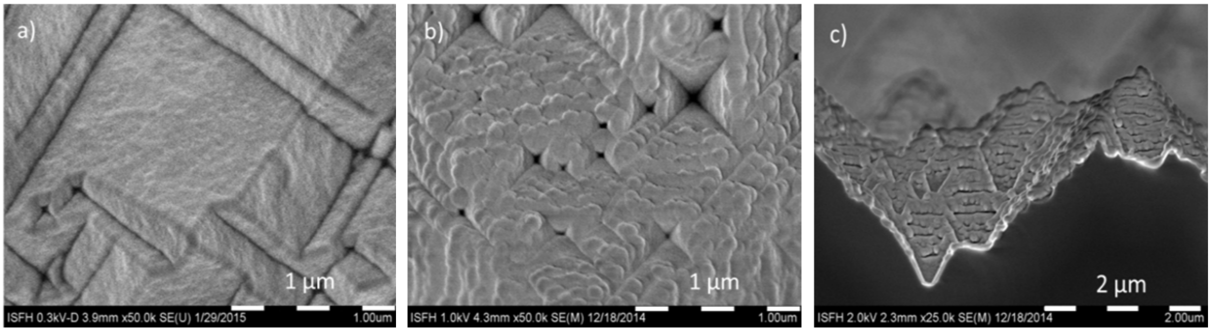

Fig. 3. SEM images of hierarchically etched surfaces after Al_2O_3/SiN_x layer stack deposition: (a) conformal coverage on a surface morphology partially formed by a wet chemical cleaning step with significant Si removal, (b and c) SiN_x layer with cavities and voids on a surface with plasma-shaped structures of a few nanometers in size, which remained after wet chemical cleaning with marginal Si removal.

Figure 4(a) shows the reflection of the hierarchically-structured samples and the solely alkaline-textured reference after cleaning with significant Si removal. For wavelengths smaller than 1050 nm, the reflection of the hierarchically-structured samples is lower than that of the random pyramid reference. There are differences between the recipes. In particular, recipe 2 shows a higher reflection.

After anti-reflection coating, the difference in reflection between the hierarchically-structured samples and the alkaline-textured reference becomes smaller (Fig. 4(b)). In the inset a magnification of the reflection values in the section between 700 nm and 1050 nm wavelength is displayed. On a needle tip surface, processed in a cleaning with marginal Si removal, the reflection is significantly higher (yellow curve). By contrast, all four etching recipes show a lower reflection than the alkaline-textured reference if the cleaning sequence results in small <111> surfaces.

For a wavelength range from 300 nm to 1000 nm, a weighting of the reflectance curves of the hierarchical structured samples with the AM1.5G spectrum yields an increase in the short circuit current density potential of up to 0.4 mA/cm2 compared to the exclusively alkaline textured reference.

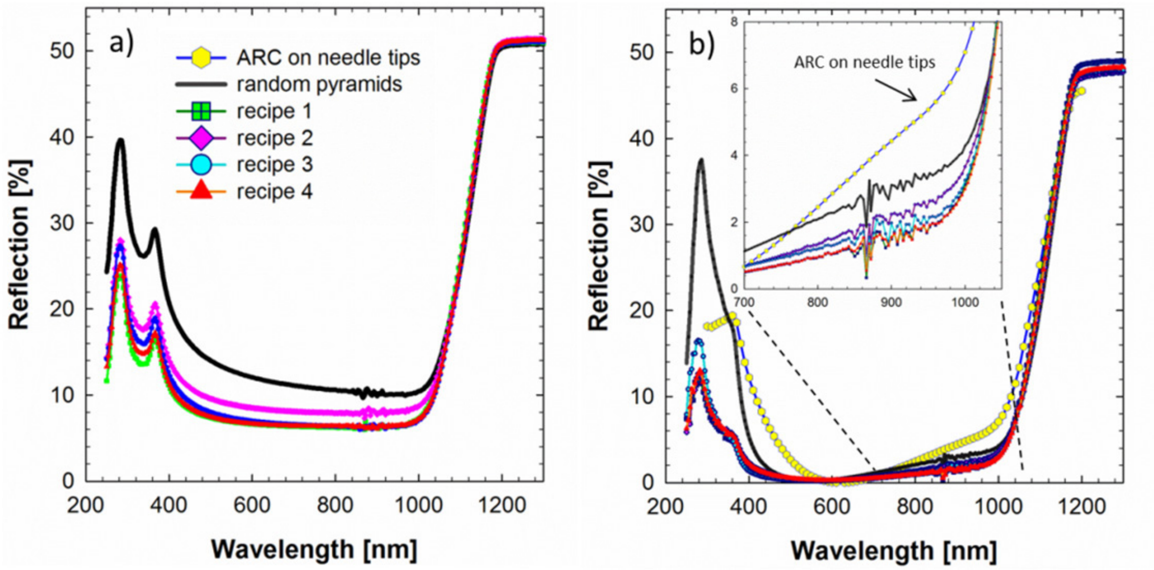

Fig.4. Comparison of the reflection of the hierarchical structured samples for all recipes and the exclusively alkaline textured reference after plasma etching and cleaning (a) and after anti reflection coating (b). The increased reflection on surfaces with needle tips is also shown in (b). Please note that for wavelengths > 1050nm, the measurement data are not reliable

The plasma etching process obviously induces a certain amount of plasma damage at the sample surface. On *n*-type Cz samples passivated directly after the hierarchical etching and subsequent cleaning with significant Si removal, effective lifetimes up to 237 µs at $\Delta n = 10^{15}$cm^{-3} have been obtained by QSSPC (compared to 2 ms on passivated, exclusively alkaline textured references). However, this is not a fundamental issue. Rather, in a cell process sequence, the hierarchical etching is supposed to be performed prior to the emitter formation, which (i) implies a high temperature steps which possibly cures the plasma damage, and (ii) yields a certain field effect passivation of the front surface. First evaluations of this aspect have been performed and saturation current densities J_0, as determined by using the method of Kane and Swanson [8] are summarized in Tab. 2. Although the not optimized subsequent cleaning process yields the formation of needle tip-shaped structures on the surface strongly compromising the conformity of the passivation (Fig. 3 (b, c)), we obtained promising results. In particular, etching recipe 3 implies only slightly increased J_0 values compared to the exclusively alkaline textured reference. We expect that the remaining difference between the saturation current densities of the exclusively alkaline textured references and the hierarchically etched samples is mainly implied by the imperfect surface passivation of the latter (Fig. 3 (b, c)). When applying the cleaning sequence with significant Si removal and a resulting conformal surface passivation (Fig. 3 (a)), the saturation current densities of the hierarchically etched samples are expected to be as low as the respective values of the alkaline textured references. Work in this direction is under way.

Table 2. Saturation current densities measured on ion implanted, annealed and passivated samples, either with exclusively alkaline textured surfaces or with hierarchically structured surfaces of different recipes

Implant species	Alkaline textured reference	Hierarchically structured (Recipe 1)	Hierarchically structured (Recipe 3)
boron	26 fA/cm²	69 fA/cm²	36 fA/cm²
phosphorus	79 fA/cm²	132 fA/cm²	93 fA/cm²

4. Conclusion

Monocrystalline silicon surfaces featuring structures with a few tens of nanometers in size on top of micrometer-sized random pyramids are fabricated by using a hierarchical etching procedure, consisting of an alkaline texturing and a subsequent plasma etching step. By varying the plasma etching parameters, we obtain differently shaped sub-wavelength structures. Test samples with this hierarchical surface morphology on both sides, an Al_2O_3/SiN_x front- and a SiN_x rear-side passivation show significantly lower reflection than exclusively alkaline textured references. The advantage corresponds to a current density gain of 0.4 mA/cm^2 under AM1.5G illumination and prior to cell encapsulation.

A prerequisite for a reduced reflection is a conformal deposition of the SiN_x anti-reflection coating. Obviously, there is a lower limit for the size of surface structures which can be covered conformal by PECVD-deposited SiN_x. An appropriate wet chemical cleaning sequence can remove structures of dimensions comparable to the anti-reflection layer thickness, enabling a conformal SiN_x deposition. Since the resulting surface morphology of the hierarchical structured samples consists exclusively of <111> planes, these surfaces are compatible with conventional doping, passivation and screen-print metallization schemes.

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