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Highly textured multi-crystalline silicon surface obtained by dry etching multi-step process

L. Cecchetto [a], L. Serenelli [a], G. Agarwal [b], M. Izzi [a], E. Salza [a], M. Tucci [a,*]

[a] ENEA—Research Centre Casaccia Roma, Italy
[b] Department of Physics, Bhavnagar University, Bhavnagar, Gujrat, India

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In this work we propose the use of a plasma dry etching technique to condition the morphology of a silicon surface. The low environmental impacted NF_3 halogen compound is adopted together with Ar to perform a multi-step process which helps to enhance the silicon surface texturing, thus reducing the time needed for the whole dry etching procedure, which also include saw damage removal on silicon wafers. A detailed study of surface reflectance and etching rate as a function of the dry plasma process parameters is discussed to achieve suitable multi-crystalline silicon surfaces for photovoltaic applications.

1. Introduction

Today the standard industrial process for silicon wafer saw damage removal, surface cleaning and texturing in solar cell fabrication involves wet treatments. These process steps are fundamental in the solar cell manufacturing to increase the photovoltaic conversion efficiency, minimizing the optical losses due to light reflection by silicon substrate surfaces. Effective and homogeneous texturing of multi-crystalline silicon (mc-Si) can be commonly obtained by wet acidic chemical etching. As illustrated by several studies [1–3] the acidic solution-based (CP4) treatment is effective in saw damage removal and it is able to perform an isotropic etching of the surface independently from the grain crystallographic orientation. In turn, a wet alkaline process is preferred on ⟨100⟩ orientation mono-crystalline silicon surface (c-Si) due to the spontaneous formation of pyramidal shape morphology [4], also leading to a more stable process with respect to the acidic one. The main drawbacks of these approaches are the de-ionized water cost and the waste chemicals management with the consequent environmental impact [5]. Moreover these processes do not permit to prepare the front and rear surfaces separately or independently, as required for thinner wafers in order to obtain improved yields [6]. Now it is possible to overcome the limits of wet acid treatment by using the dry plasma technology. The technique ensures the saw damage removal and the isotropic texturing of the as-cut Si wafers, with several further benefits: the front and rear surfaces can be separately treated, the degree of roughness can be controlled, and finally the process parameters and waste can be more easily managed [7–9]. The process involves the chemical reaction between the reactive gas dissociated into active species during the glow discharge and the substrate may turn into a complex. However, as already considered by Coburn and Winters [10] it must necessarily involve at least three main fundamental processes:

1. chemisorption of the reactive gas-phase species on the surface (dissociation of reactant can also partly occur during this step);
2. formation of volatile reaction products on the surface; and
a. desorption of volatile products.

The main halogen containing gases used for the dry etching of Si wafers are fluorinated gases, such as SF_6, CF_4 and NF_3, because of the high fluorine reactivity with Si. It has been observed [10] that for a silicon–fluorine (Si–F) system, the product formation step and the product desorption step proceed at very high rates, even at room temperature. Thus it is expected that, if no other relevant side reaction competes for fluorine consumption; the higher the quantity of reactive species in the gas phase, the higher the etch rate will be.

A comparative study in the literature reported more efficient generation of fluorine from NF_3 compared to CF_4 and SF_6 [11]; this is partly attributed to the lower reactivity of the nitrogen in the NF_3 molecules, which does not give side reaction products on the Si surface [10], as opposed to CF_4 or SF_6 which tends to give fluorocarbon or sulphur-based deposits on the substrate [10,12].

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* Corresponding author. Tel.: +39 347 320 7388.
E-mail address: mario.tucci@enea.it (M. Tucci).

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Also lower dissociation energy in NF_3 is justified [13–15] compared to CF_4. From the handling point of view, NF_3 is a thermodynamically stable gas [16,17], which presents a low reactivity at low temperature (under 250 °C) and pressure, which strongly limits the probability of side reactions with chamber walls and other components of the plasma reactor. For these reasons, it is considered as a viable gas for reactive ion etching and presents a growing interest for this application. It is worth noticing that fluorinated gases (NF_3 included) are green-house gases; hence the amounts of waste released by the plasma process are extremely small and their environmental impact can be considered low compared to wet chemistry. Moreover in wide application prospect, recycling solutions could be considered in order to further reduce waste release and improve the dry process advantages.

Several dry treatments have been reported in literature for Si wafers texturing based on gas mixtures such as CF_4/O_2 or SF_6/O_2. However carbonaceous or sulphurous chamber contamination occurs, even though an addition of oxygen percentage has been adopted to passivate residual sulphuric and carbonaceous compounds, which can always be residual on chamber surfaces, resulting in a contamination and formation of undesirable fluorine radicals on Si surface, not easy to passivate [18]. Moreover the unwanted fluorine based radicals on top Si still occur and are not easy to remove [19]. Very low reflectance profiles have been shown in the literature by using several dry treatments, but it is very rare to find articles showing a dry process for both saw damage removal and texturing in just one process.

Examples of dry texturing involving SF_6 [20–25], and H_2 [26–28] or F_2 [29] or even ClF_3 [30] (which avoids in principle compounds re-deposition) processes can be given in which the substrates have been previously treated by wet chemistry for saw damage etch by using alkaline or acidic solutions. ClF_3 is just outside the comparison, since it does not use a plasma, but just a gas dissociation at high pressure and room temperature, and it is effective only if performed after the emitter formation. Regarding H_2 and F_2 just monocrystalline Si has been explored, and in order to have effective surface passivation and solar cell production, a wet chemical treatment of smoothing is required. The process time needed to obtain only the surface texturing having $R_{\mathrm{eff}}=7$–8%, after smoothing can be up to 30 min, and the main concerns that should be considered are the diffusion process on such surfaces and possible shunting effects due to the high roughness, which also needs a care optimization for screen printed front contacts, to obtain high resolution patterns and good Fill Factors.

The roughness problem also affects the so-called black Si having R_{eff} of 3–4% [23,24] values always obtained starting from a clean, wet saw damage removed Si surface. The sharp peaks formed after plasma represent a problem when a low doped emitter region is formed [21]; so the common adopted solution is to smooth in some way the textured surface, or just to produce a lower texturing [21,26,27] with a multi-step process with optimized gas chemistry. Usually reflectances ranging from 7% [23] to 13% [25] on mc-Si are considered fine to have acceptable electrical properties. Generally the effectiveness of dry texturing is evaluated more at cell level than wafer one; however lifetime measurements have been carried out on mono-Floating Zone (FZ) wafers, as reported in [25] and [29], obtaining nearly 100 μs after the best passivation has been applied.

In our study we propose the use of NF_3 gas since it lowers the re-deposition of side-products with respect to SF_6 or CF_4; also the NF_3 compound allows higher ion and radical densities compared to other components, which is useful to enhance the etching rate.

Due to high throughput request by cell manufacturing industries, the time needed to perform both the saw damage removal and the texturing of Si surface is a constraint that should be considered. Therefore in present study we focus on the etching rate of dry process on mc-Si surfaces and propose a multi-step approach to reduce the time needed to perform suitable Si surface for photovoltaic applications. In particular this work is moving on from a recent study [31] in which results are reported concerning homogeneous textured surface obtained by dry etching on mc-Si, using a mixture of NF_3 and Ar within a given range of parameters.

The process we propose will lead to a 16.5% final R_{eff} with a 3 step process involving NF_3 and Ar. In total the process lasts less than 20 min, in which both saw damage etch and iso-texturing are performed. The so-formed surface does not need any post treatment for smoothing and it has a surface morphology which should not create problems when diffusion and screen printing steps are subsequently applied. The success of NF_3 in avoiding any sulphur or carbon compounds on the surface makes the silicon surface ready to be passivated by amorphous layers or silicon nitride as commonly used in solar cell applications.

2. Experimental approach and techniques

It is well known that different processes can take place in a reactive ion etching chamber, depending on the plasma operative parameters. The main dominant processes, according to the applied pressure, can be schematically described as the sputter etching, the energetic ion assisted etching and the chemical etching. Sputter etching is the dominant process at low pressures (< 1 mTorr), as the atoms mechanically removed from the energetic ion bombardment need a high free path to be ejected. At slightly higher pressure (few mTorr), the energetic ion assisted etching is the dominant process. In this case, energetic charged species hitting the surface promote reactions of reactants with the substrate. As the gas pressure is increased (next to 1 Torr), the density of chemical active species will tend to increase as well, but the energy of the incident particles on the surface will decrease, so that the etch rate will not involve anymore incident radiation and the dominant process will be the chemical etching. At higher pressures another kind of process can take place, involving a reaction between the substrate and the gas reactant mixture, and leading to the formation of an inactive thin layer on the surface.

Present experiments were performed in a Reactive Ion Etching (RIE) system, the AXIC BENCHMARK 800 II, equipped with a 13.56 MHz generator using different parametric conditions. We considered each treatment on the sample as a step and we referred to it according to the dominant plasma–surface interaction taking place. In particular we have used the two following conditions or steps:

(A) Plasma of a mixture of NF_3 and Ar gaseous etchants. The chamber pressure has been kept at 1 Torr, the Ar flow at 72 sccm, while the NF_3 flow has been varied between 8 and 48 sccm, corresponding to a NF_3/Ar flow ratio ranging from 0.11 to 0.66. The RF power was fixed at 200 W and the substrate temperature was kept at 25 °C by a cooling system.

(B) Plasma of Ar, non-reactive ion bombardment. For this purpose the Ar flow has been kept at 5 sccm, the pressure in the chamber has been settled at 40 mTorr, the applied RF power at 170 W and the substrate temperature has been kept at 25 °C by a cooling system. According to what was observed in a previous research [14], in such conditions the charged species in the Ar plasma are sufficiently energetic to activate the surface towards the next following treatments. It tends that the dominant process is an energetic ion-assisted damage of the surface, without etching.

Each treatment has been applied separately or in a combined multiple step sequence without interrupting the vacuum. The