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Surface Texturing of n- and p-Doped c-Si Using a Novel Plasma Chemical Texturing Process

Elena Dilonardo[a,b*], Giuseppe V.Bianco[b], Maria M. Giangregorio[b], Giovanni Bruno[b], Pio Capezzuto[a], Maria Losurdo[b]

[a]*Dipartimento di Chimica, Università degli studi di Bari, Via E. Orabona 4, 70126 Bari, Italy.*
[b]*Istituto di Metodologie Inorganiche e Plasmi, IMIP-CNR, Via E. Orabona 4, 70126 Bari, Italy.*

Abstract

n- and p-doped c-Si (100) are textured by a SF_6/O_2 plasma chemical etching, under conditions avoiding ion bombardment. The study of the effects of plasma parameters on morphology and on surface reflectance of textured c-Si reveals a strong impact of silicon doping on texturing characteristics. SF_6/O_2 plasma etches anisotropically n-type c-Si creating a square-based hillock-like morphology with a surface reflectivity of 6%. Conversely, for p-type Si, a H_2 plasma pretreatment is necessary to activate silicon etching and obtain a nano-textured surface with a reflectivity of 16%.

Keywords: Texturing; SF_6/O_2 plasma etching; Doped c-Si; Optical reflectance

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1. Introduction

Nowadays, the key issue in solar cell research is the development of low-cost fabrication methods able to produce cells with a high efficiency [1]. A way to reduce production costs is the use of ultrathin (<100 μm) c-Si wafers in solar cell fabrication, although the reduction of wafer thickness poses significant processing challenges. On the scientific side, thinner wafers have less light absorption; consequently, various approaches have been considered for photon harvesting, e.g., plasmonic solar cells [2], growth of antireflecting Si nanostructures [3] and surface texturing [4]. In particular, there is interest in developing dry texturing processes integrable with production schemes and with excellent light trapping capability and low silicon etching consumption. Although wet texturing is commonly used, it is difficult to apply it to thin silicon solar cell technology due to a large amount of silicon loss. Seeking for alternative

* Corresponding author. Tel.: +39 0805442007; fax: +39 0805443562.
E-mail address: elena.dilonardo@chimica.uniba.it.

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processes, various surface texturing methodologies have been developed recently, including laser-structuring [5], photo-lithographically defined etching [4], porous-Si etching [6], mask and mask-less RIE processing [7,8] where a low etch depth (~2 µm) has been achieved.

In this study, a radiofrequency (r.f.=13.56 MHz) SF_6/O_2 plasma chemical etching is proposed to texture c-Si , under conditions not assisted by ion bombardment. The silicon texture anisotropy is induced by the different reactivity of the silicon crystal planes towards the fluorine etching and the contemporary oxygen passivation resulting from the SF_6/O_2 plasma mixture [8-10]. A crucial effect of the doping of the silicon substrate is found on the effectiveness and morphology of the texturing because of the opposite polarity of space charge present in the depletion layer of n- and p-type c-Si [11, 12] driving the etching process by F-atoms, and because of the silicon oxidation rate, being the silicon-oxide thickness is higher for n-type silicon then for p-type [13]. The SF_6/O_2 plasma chemical etching of n-type c-Si forms anisotropic square-based hillock morphology with a surface light reflectance of 6%, comparable with that obtained using the commercial wet etched silicon. Conversely, a hydrogen plasma [14] surface pretreatment is necessary to activate an anisotropic texturing of p-doped c-Si to achieve a reflectance of 16%.

2. Experimental details

p-type and n-type c-Si (100) with a resistivity of 30 and 20 Ω·cm, respectively, covered by a native oxide layer of about 20 Å were used. An r.f. (13.56 MHz) capacitively coupled parallel plate plasma reactor was used. Degreased c-Si substrates were placed on the grounded electrode to prevent the ion bombardment. The texturing process was run by exposing silicon to SF_6/O_2 plasma for 5 min at 0.15 mbar and 100°C. For the p-doped c-Si a H_2 plasma pretreatment at 100°C for 5 min was also applied [15].

The spectral reflectance of the textured samples was obtained using a spectrophotometer (Ocean Optics) in the wavelength range of 400-800 nm.

Atomic force microscopy (AFM) was used to analyze the morphology of textured c-Si surfaces. AFM was performed in the intermittent-contact mode (IC-AFM) using an AutoProbe CP Thermomicroscope. A high aspect ratio probe-super sharp tip with a radius of curvature of 2 nm (ESP Series Probes-VEECO) was used.

3. Results and discussion

The texturing kinetic has been investigated by analyzing the surface reflectivity and morphology of n-type c-Si samples exposed to the SF_6/O_2 plasma for 2-7 min, as shown in Fig. 1. After 2 minutes of plasma exposure, the etching of the c-Si native oxide by fluorine atoms leads to a RMS roughness value of 44 nm and to a decrease of the surface reflectance. This early etching can be explained considering that native oxide is not uniform in thickness and composition, and the c-Si exposed to the plasma is etched faster than the oxide layer, therefore resulting in an hole-like structure with an increase of the RMS roughness value. For a longer plasma treatment time (5 min), reflectance strongly decreases due to the formation of square based hillocks whose size increases with time, resulting in a surface roughness of 252 nm. Nevertheless, by further prolonging plasma exposure (>7 min), an increase of surface reflectivity and a decrease of surface roughness back to 62 nm is found due to smoothing of the pyramidal features.

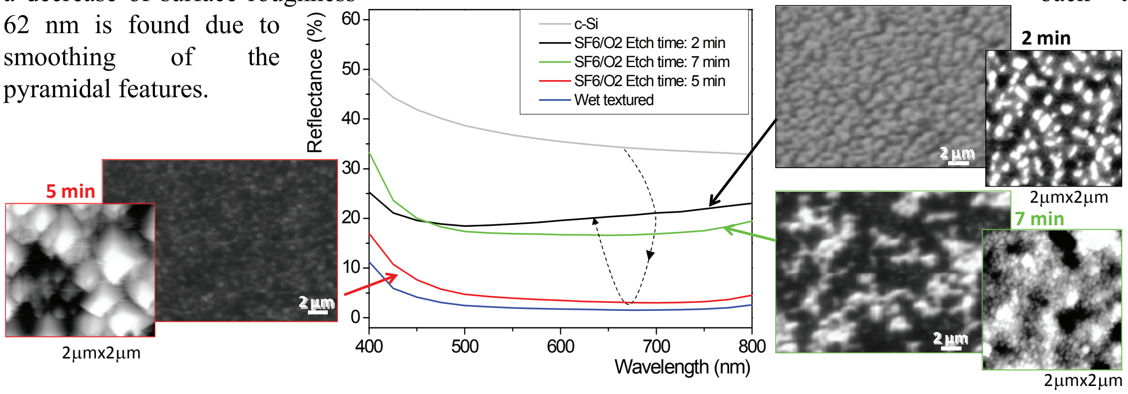

Fig. 1. Spectral reflectance of n-type c-Si etched by SF_6/O_2 for increasing time. The corresponding optical micrographs and AFM topographies are also shown.

Figures 2a and 2b show, respectively, the average reflectance in 400-800 nm spectral range and the corresponding morphology of n-doped silicon etched at different values of the SF_6/O_2 ratio. The highest RMS value and median height and, consequently, the lowest reflectance are obtained using a $SF_6/O_2=4$. The AFM image of the sample obtained under this condition reveals the formation of anisotropic square-based hillocks. A $SF_6/O_2>4$ results in the formation of a silicon texture with a lower RMS roughness and median height and, consequently, higher surface reflectance, due to a smoothing of the created features.

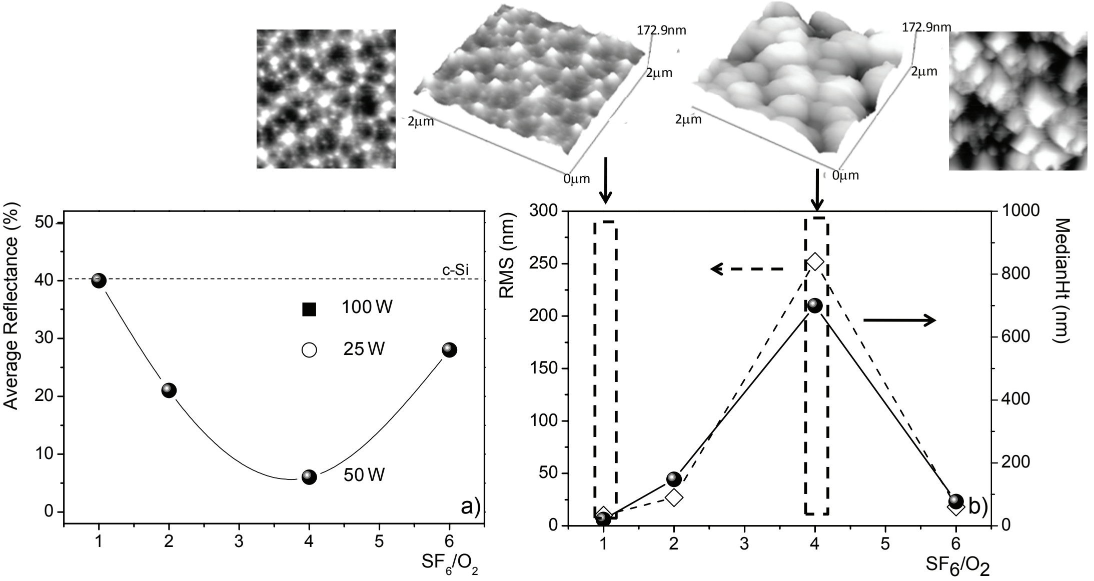

Fig. 2. a) Average reflectance values, in 400-800 nm spectral range, of n-type c-Si etched at different SF_6/O_2 ratio and input plasma power of 25W, 50W and 100W. b) RMS (Root Mean Square), median height ($\overline{Z}$ – Zmin where Z is the height) At the top 3D and corresponding 2D AFM images (2μm x 2μm) of samples etched with SF_6/O_2 =1 and 4 are also shown.

These results indicate that O_2 addition to the SF_6 etchant gas is important to achieve an anisotropic chemical plasma etching of silicon. Beside the preferential passivation of (100) Si crystal plane forming SiO_2, and $Si_XO_YF_Z$ as mask to reduce or prevent silicon etching [8,9], oxygen leads to the formation of SO_2F and SOF_4 species in the gas phase, which reduce the concentration of F-atoms that are promoters of surface etching [16]. However, an excessive amount of oxygen may further dilute the F-atoms concentration, reducing the etching rate. The average reflectance of c-Si etched at different input plasma powers is also reported in Fig. 2a, showing that lower reflectance is obtained at an input power of 50W. Figure 3 shows the correlation between the average reflectance in 400-800 nm spectral range and the morphology of n- and p-doped c-Si textured at 50W and $SF_6/O_2=4$; for comparison the reflectivity of a commercial anisotropic wet etched c-Si is reported as representing the limit case with the lowest (6%) reflectivity.

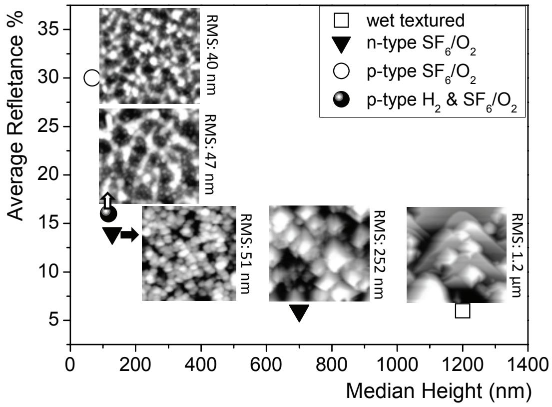

Fig. 3. Correlation between average reflectance in 400-800 nm spectral range and median height with corresponding AFM images (5µmx5µm) of wet textured Si, n-type and p-type c-Si textured by SF_6/O_2 and H_2 plasma pretreated p-type c-Si textured by SF_6/O_2 plasma.

As already demonstrated in Fig. 1, this plasma chemical process is able to texture n-type silicon in a broad range of experimental parameters (r.f. power and SF_6/O_2 ratio) yielding reflectance values in the range 30-6%, the latter being as low as that of commercially Si etched by alkaline solutions. Conversely, the same process run on p-type Si yields a 30% surface reflectance that does not decrease under different plasma process conditions. The morphology of textured n-type c-Si is analogous to the pyramidal structure formed by wet anisotropic etching. Conversely, the p-type c-Si shows a grainy-like structure with a median height of 67 nm. On the basis of these results, as show in Figure 3, the surface reflectivity decreases with the increase of the median height of features, as already reported in Fig. 1 and demonstrated in Ref. [17]. The different texturing behaviour observed for n- and p-type c-Si can be related to the doping effect on the etching reaction of silicon by F-atoms [11-13] as well as on the silicon oxidation [13]. While n-doping enhances both oxidation and etching, although with different rates, resulting in anisotropic texturing, the p-type doping inhibits the fluorine etching [13,14]. In order to promote chemical anisotropic etching of p-type Si, a hydrogen plasma pretreatment has been exploited to activate the surface, yielding a silicon reflectance decrease to 16%, as reported in Fig. 3. The decrease of the reflectance is accompanied by a change in the morphology induced by hydrogen pretreatment, as shown in Fig. 3. Specifically, AFM images of the hydrogen pretreated p-doped c-Si reveal a considerable increase of the median height to 117 nm, giving reason of the decrease of surface reflectivity to 16%. The positive role of the hydrogen pretreatment in texturing p-type Si can be rationalized considering the contribution of the following processes: (i) the electron donor character of hydrogen in silicon [18], (ii) the deactivation of the hole-bound states [19] and/or formation of B-hydrides complexes that compensate the B-acceptor, which is the Si etching inhibitor [13]; (iii) the surface roughening of silicon by hydrogen plasma [19].

4. Conclusion

In conclusion, the applicability and effectiveness of SF_6/O_2 plasma chemical etching to texture n- and p-type c-Si have been demonstrated. Anisotropic texturing of n-doped silicon creating a square-based hillock-like morphology with a surface reflectance as low as 6% is achieved. Conversely, p-type silicon requires hydrogen plasma pretreatment to achieve a grainy-like morphology with a reflectance of 16%. A mechanism based on the effectiveness of chemical etching of F-atoms on n- and p-type c-Si has been proposed to explain the observed different behavior. The proposed plasma chemical etching represents a potential process for texturing thin silicon wafers without using wet chemicals or photolithography additional steps.

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