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Texturing of large area multi-crystalline silicon wafers through different chemical approaches for solar cell fabrication

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ABSTRACT

Surface texturing of silicon can reduce the reflectance of incident light and hence increase the conversion efficiency of solar cells. Comparatively lesser concentrated (10%) standard alkaline (NaOH/KOH) solution does not give good textured multi-crystalline silicon (mc-Si) surface, which could give satisfactory open-circuit voltage. This is due to grain-boundary delineation with steps formed between successive grains of different orientations. In this work an attempt has been made to obtain a well-textured mc-Si surface through three different approaches. The first two are with two different types of acid solutions and the third with concentrated alkaline NaOH. Solutions of $HF–HNO_3–CH_3COOH/H_2O$ system with different concentrations of HF and HNO_3 were used for texturing. The results on the effect of texturing of these three solutions on the surface morphology of very large area (125 mm × 125 mm) mc-Si wafer as well as on the performance parameters of solar cell are presented in this paper. Attempts have been made to study extensively the surface morphologies of mc-Si wafers in two effective regions of the isoetch curves of the $HF:HNO_3$:diluent's system. Also we studied the reflectance, uniformity, spectral response, short-circuit current, open-circuit voltage, fill factor and dark current–voltage of the cells fabricated using wafers textured with the three different methods. Short-circuit current of the solar cells fabricated using acid-textured wafers were measured to be in the range of 4.93 A. This value is 0.37 and 0.14 A higher than the short-circuit current values measured in the cells fabricated with isotextured and alkaline-textured wafers, respectively.

1. Introduction

Multi-crystalline silicon (mc-Si) surface texturing is a key issue in fabricating low cost and high-efficiency solar cells in mass production level. The well-established texturing method for mono-crystalline silicon is the anisotropic etching with aqueous solutions of potassium or sodium hydroxide (KOH/NaOH), which results in the surface covered with pyramids. This is due to the difference in etch rates of the ⟨100⟩ and ⟨111⟩ orientated planes of silicon [1]. The conventional alkali texturing is not so effective for mc-Si where the grains are randomly oriented. Moreover, mc-Si texturing with standard NaOH/KOH solution at comparatively lower concentration (10%) does not give textured surface, which could give satisfactory open-circuit voltage. This is mainly due to the grain-boundary delineation with steps formed between successive grains of different orientations. Several texturing techniques are under investigation, but none have reached the status of mass production for standard screen-printed solar cells [2–6]. Texturing with concentrated NaOH solution (40%) at high temperature introduces less effect on mc-Si grain boundaries. Although reactive ion etching (RIE) is one of the well established, one out of many techniques under investigation for texturing mc-Si surface for solar cell fabrication [7,8], it is a complicated processes and requires expensive instrumentation. Another disadvantage of RIE technique is the essential requirement of an additional etching step in order to achieve better cell performance, which ultimately hamper industrial production throughput. On this background, we made an attempt to texture the mc-Si wafers without exposing the etched steps at the grain boundaries and to obtain a near uniform surface. We also examined the viability of this approach for industrial application.

The wet texturing of silicon surface with solutions containing HF/HNO_3 leads to isotropical etching resulting in features with rounded structures on surfaces. We have investigated the effect of texturing the mc-Si wafer for solar cell application using solutions chosen from two different regions of the isoetch [9] curves of $HF–HNO_3–CH_3COOH/H_2O$ system. In some regions of isoetch curves of $HF–HNO_3–CH_3COOH/H_2O$ system, huge amount of heat is evolved during rapid etching, which results in polished surface. Solutions belonging to some other regions of the curve generate porous structures on the silicon surface, which ultimately convert

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into a uniform surface with significant etch pits to capture appreciable percentage of incident light.

An comparative study of the surface morphology of mc-Si wafers treated with solutions from the two different regions of the isoetch curves for silicon (HF:HNO_3:diluent's system) as well as with NaOH has been carried out in this work, along with the study of the performance parameters of the fabricated solar cells.

2. Experiment

2.1. Texturization

p-Type, mc-Si wafers with resistivity of about 0.5–2 Ω cm were used in this experiment. HF–HNO_3–CH_3COOH solution with varying volume ratios of HF, HNO_3, and CH_3COOH was employed in acid texturing process of the silicon surface. The etching time in each process was also varied. Seven sets of etching solutions with different ratios of HF, HNO_3, and CH_3COOH, which fall in the isoetch region, were used to carry out the etching process (Table 1). Another experiment was carried out with HNO_3–HF–H_2O solution where H_2O was used as the dilutent instead of CH_3COOH. In a third set of experiment, mc-Si wafers were etched with 30% and 40% NaOH solutions at different period of etching. During the texturing process with NaOH solution, a temperature-controlled hot plate and a flat polypropylene squire's tub filled with water were used to cover the etching vessel in order to prevent loss of chemical. Seven liters of solution of each type was taken to carry out the texturing. The surfaces of the mc-Si wafers were observed with an optical microscopic (Olympus 671998) after each etching process. A spectrophotometer (Scinco S-3100) was used to measure their surface reflectance. The surface morphology of selected multi-crystalline wafers was also studied by a scanning electron microscopy (SEM).

2.2. Solar cell fabrication

Conventional process steps such as $POCl_3$ diffusion; plasma-enhanced chemical vapor deposition (PECVD) for silicon nitride (SiN_x) deposition as anti-reflection coating (ARC), and screen-printed metallization were followed for the fabrication of mc-Si solar cells. All textured p-type silicon wafers (125 mm × 125 mm) were diffused by pentavalent impurity (phosphorus) in a open-tube furnace using a conventional $POCl_3$ diffusion source at 850 °C for 7 min as pre-deposition, followed by a 16 min of drive-in. After PSG removal by short time dipping in diluted HF solution, DI-water rinsing and drying were carried out. The sheet resistance of n^+ emitter layer was 50–55 Ω/cm. All the textured multi-crystalline wafers were then oxidized at 850 °C for 13 min. After edge isolation and oxide layer removal, about 70-nm-thick layer of SiN_x was deposited on the front side by means of PECVD at 450 °C as ARC. The refractive index of SiN_x film was maintained at 2.0. The front and back metallization was carried out by screen-printing technique using standard Ag (product no. 3349, Ferro Electronic Materials) and Al pastes (product no. Fx53-038, Ferro Electronic Materials). This was followed by baking and co-firing at a temperature of 750 °C in a conveyer belt furnace (Seirratherm).

The illuminated current–voltage (LIV) and dark current–voltage (DIV) characteristics and the spectral response (SR) of the mc-Si solar cells fabricated using the three different surface etching methods were measured.

Table 1
Different experimental conditions for acid etching in different regions of isoetch curves as given in Fig. 1

Etching point	Chemical composition	Volume ratio	Time of etching (min)
A	HF–HNO_3–CH_3COOH	2:15:5	1, 2, 3, 4, 5, 6
B	HF–HNO_3–CH_3COOH	1:8:1	1, 2, 3, 4, 5
C	HF–HNO_3–CH_3COOH	1:7:2	1, 2, 3, 4
D	HF–HNO_3–CH_3COOH	1:6:3	1, 2, 3, 4
E	HF–HNO_3–CH_3COOH	1:5:4	1, 2, 3, 4, 5, 6
F	HF–HNO_3–CH_3COOH	1:4:5	1, 2, 3, 4, 5, 6
G	HF–HNO_3–CH_3COOH	1:3:6	1, 2, 3, 4, 5, 6
H	HF–HNO_3–CH_3COOH	1:2:7	1, 2, 3, 4, 5, 6

3. Results and discussion

Most of the experiments related to acid texturing were carried out with a HF–HNO_3–CH_3COOH mixture in volume ratios and etching time as mentioned in Table 1. The composition of the acids in the mixture was such that the etching rate fell in the lower region of the isoetch curves as shown in the Fig. 1. In this region, the etching contour runs parallel to the lines of constant HF. There is an excess of HNO_3 and the etch rate is governed by the ability of the HF to dissolve the SiO_2 as it is formed and by the removal of soluble complexes by diffusion into the volume of the etchant. The overall etching process is preceded by an induction period during which autocatalysis of HNO_3 is initiated. This is followed by cathodic reduction of HNO_3, resulting in a supply of holes,which enter into the oxidation reaction to produce SiO_2 and reacts with HF to form soluble complex H_2SiF_6. The overall reaction equation is given as

$$Si + HNO_3 + 6HF = H_2SiF_6 + HNO_3 + H_2O + H_2$$

These etches are "self-passivating" in the sense that a freshly etched surface is already covered with a relatively thicker layer of SiO_2 (30–50 Å). Etching the silicon surface with this chemical in the lower region of the isoetch curves can yield orientation-independent texturing. It may be helpful for mc-Si polishing as well as texturing because mc-Si consists of different grains having different orientations. It is observed from the optical microscopic studies that there was no removal of saw damage marks from the surface of the mc-Si wafers after 1 min etching with different

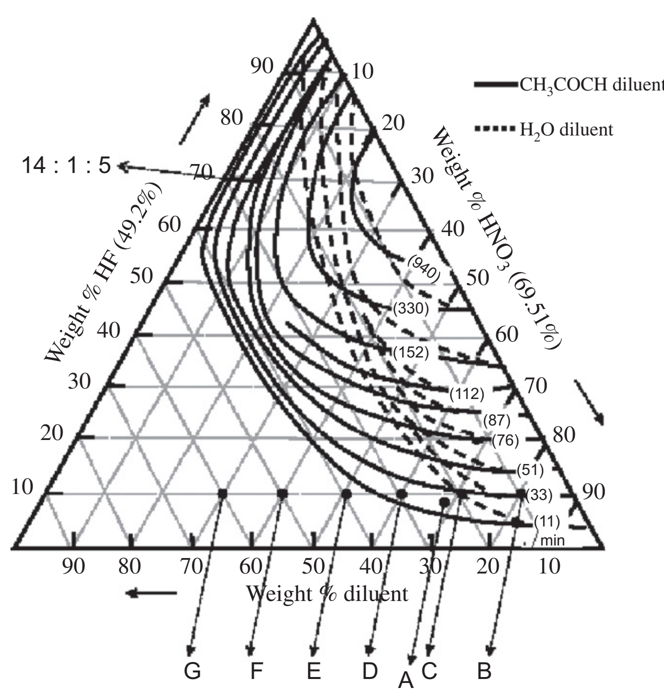

Fig. 1. Isoetch curves of HF–HNO_3–CH_3COOH/H_2O system.