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Efficiency improved by acid texturization for multi-crystalline silicon solar cells

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Abstract

In this paper, we will show that efficiency of multi-crystalline silicon (mc-Si) solar cells may be improved by acid texturization. In order to enhance overall efficiency of mc-Si for solar-cell applications, the surface treatment of texturization with wet etching using appropriate solutions can improve incident light into the cell. Alkali etchant cannot produce uniformly textured surface to generate enough open circuit voltage (V_{OC}) and high efficiency of the mc-Si due to the unavoidable grain randomly oriented with higher steps formed during etching process. Optimized acid etching conditions can be obtained by decreasing the reflectance (R) for mc-Si substrate below levels generated by alkali etching. Short-circuit current (I_{SC}) measurements on acid textured cells reveal that current gain can be significantly enhanced by reducing reflection. The optimal acid etching ratio $HF:HNO_3:H_2O = 15:1:2.5$ with etching time of 60 s and lowering 42.7% of the R value can improve 112.4% of the conversion efficiency (η) of the developed solar cell. In order to obtain more detailed information of different defect region, high-resolution light beam induced current (LBIC) is applied to measure the internal quantum efficiency (IQE) and the lifetime of minority carriers. Thus, the acid texturing approach is instrumental to achieve high efficiency in mass production using relatively low-cost mc-Si as starting material with proper optimization of the fabrication steps.

Keywords: Texturization; Alkali etching; Acid etching; Solar cell performance; Conversion efficiency; Internal quantum efficiency

1. Introduction

Crystalline silicon (c-Si) is a material commonly used by terrestrial photovoltaics (PV) industry because of non-toxicity and abundance (25% of the Earth's crust). In recent years, the multi-crystalline silicon (mc-Si) has become the most important substrate material for solar-cell applications. For the worldwide PV market, mc-Si solar cells account for around 50%, which is expected to steadily increase in the near future (Panek et al., 2005; Gangopadhyay et al., 2007). This is mainly because mc-Si solar cells have the lowest manufacturing cost at the mass production level (Goetzberger et al., 2003; Poullikkas, 2010).

The mc-Si wafers contain high concentrations of impurities and defects, which are detrimental to the minority-carrier lifetime (Nelson, 2005) and lead to loss of conversion efficiency of the solar cells, thus degrading the electrical properties of the bulk material. Meanwhile, commercial mc-Si solar cells have lower efficiencies than those of single-crystalline silicon (sc-Si) cells. It is known that texturization

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technology can reduce the reflection losses (Gangopadhyay et al., 2007), thus overall efficiencies on mc-Si solar-cell applications can be improved. It has been a growing interest in the development of surface treatment to enhance light-trapping cells by several methods, such as the use of physical anti-reflection sputter (Ho et al., 2005; Cheng et al., 2010; Hsu and Lee, 1998), reactive ion etcher (RIE) (Macdonald et al., 2004), laser process (Dobrzański and Drygala, 2007), or chemical wet etching (Steinert et al., 2005; Nishimoto et al., 1999; Yair and David, 2003; Singh et al., 2001). Among these methods, the wet etching for texturing the surface is the major industrial process because of its low-cost, high etching rate, and large-area uniformity.

It is well accepted that changes of etching condition will have a great influence on the surface morphology of mc-Si substrates. There are two well-known conditions for the wet-etching texturization on the mc-Si surface morphology, i.e., acid and alkali etching solution. Alkaline random texturing is not suitable to apply on mc-Si substrate due to its anisotropic nature. Because of various grain orientations, alkali texturization for the mc-Si has little usefulness and cannot generate sufficient open circuit voltage (V_{OC}) (Hauser et al., 2003).

Acid texturing, performed with solutions containing hydrofluoric acid (HF) and nitric acid (HNO_3) that tend to isotropically etch, can result in features with rounded (pit) surfaces, as opposed to flat-sided features which arise from alkaline etches. Thus, acid texturization is an economical way to improve the V_{OC} value. Because the acid texturization is very simple, cheap, fast and suitable for mass production, present technology is very promising for mc-Si solar cells manufacturing. For the HF:HNO_3:H_2O mixture used in our research, the reactions between the mixture and mc-Si are given as follows (Shimura, 1989):

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O \tag{1}$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{2}$$

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O \tag{3}$$

According to Robbins and Schwartz (1959, 1960, 1961), HNO_3 creates an oxide layer at the silicon wafer surface (Eq. (1)) that can subsequently be etched away with HF (Eq. (2)). The overall etching reaction is written in Eq. (3). The actual reaction mechanism is quite complicated and involves many elementary reactions.

In order to increase the light-trapping as mentioned above, surface structure analogous to an oval pit is formed for mc-Si after acid etching. To simplify the model, we hypothesized that a partial hemisphere makes up a surface, as shown in Fig. 1, in which the second reflections (SR1 and SR2) cannot occur for some light that meets the bottom of such a partial hemisphere, while several reflections could happen for some other incident light. On the basis of partial hemisphere structure, the surface reflectance (R) can be calculated as follows (Nishimoto et al., 1999):

$$R = \frac{\sum_{i=1}^{n} \left\{ [f(\theta)]^i \times \pi r^2 \int d(\sin^2\theta) \right\}}{\pi(2rH - H^2)} \tag{4}$$

$$f(\theta) = \frac{1}{2}\left[\frac{\sin^2(\theta-\phi)}{\sin^2(\theta+\phi)} + \frac{\tan^2(\theta-\phi)}{\tan^2(\theta+\phi)}\right] \tag{5}$$

where r and H separately refer to radius and height of the partial hemisphere; θ and ϕ are angles of reflectance and transmittance, respectively. The ratio of H to r (H/r) of acidic etching hemisphere determines the value of surface reflectance, for which the minimal R value is required for higher H/r value (Cheng et al., 2010). Higher ratios increases the probability of second bounce in hemisphere structure for incoming photons.

Increasing overall efficiency of solar cells is technically feasible in laboratory as described previously. However, the PV industry needs non-destructive technologies permitting the mapping and detection of impurity and defect content in the solar cells. In fact, lower efficiencies in large-area applications are mainly due to localized regions of high minority carriers recombination. These defects may be sites of excess recombination, like grain boundaries being characterized by decreasing the I_{SC} values as mentioned above. Thus, mc-Si wafer mapping is performed using the LBIC technique to measure the diffusion length and the lifetime of the minority carriers.

The measured short-circuit current I_{SC}, the power P_L of the incident light and the reflection coefficient R can be

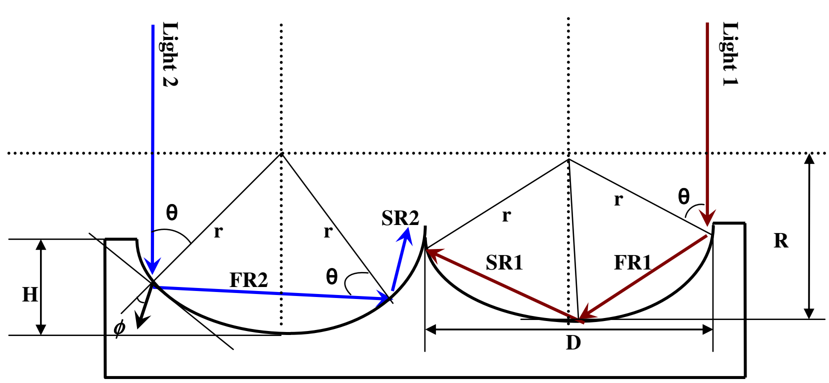

Fig. 1. The partial hemispherical structure of surface reflection after acid etching mc-Si with HF:HNO_3:H_2O solution. There are two simplified incident light with the first reflections (FR1 and FR2) and the second reflection (SR1 and SR2), respectively.