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Review

Surface modification via wet chemical etching of single-crystalline silicon for photovoltaic application

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The potential of solar cells have not been fully tapped due to the lack of energy conversion efficiency. There are three important mechanisms in producing high efficiency cells to harvest solar energy; reduction of light reflectance, enhancement of light trapping in the cell and increment of light absorption. The current work represent studies conducted in surface modification of single-crystalline silicon solar cells using wet chemical etching techniques. Two etching types are applied; alkaline etching (KOH:IPA:DI) and acidic etching (HF:HNO_3:DI). The alkaline solution resulted in anisotropic profile that leads to the formation of inverted pyramids. While acidic solution formed circular craters along the front surface of silicon wafer. This surface modification will leads to the reduction of light reflectance via texturizing the surface and thereby increases the short circuit current and conversion rate of the solar cells.

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1. Introduction

The effective modification of silicon solar cells front surfaces is one of the most important process steps in increasing conversion efficiency of solar cells. It is known that in order to improve the short circuit current, there are three mechanisms that should be catered for; reduction of reflectance, light trapping in the cell and higher absorption of light that closer to the p–n junction (Peng et al., 2013; Panek et al., 2005; Cheng et al., 2011; Basu et al., 2010; Vallejo et al., 2007; Barrio et al., 2012). In silicon solar cells with a simple geometry, light rays entered the cell through the front surface that had been texturized and deposited by the anti-reflective coating thin layer (Lipinski et al., 2003; Rabha and Bessaïs, 2010; Johan et al., 2010). Both texturized surfaces and thin layer of anti-reflection coating (ARC) are the important parameters in photoelectrical conversion by minimizing the reflectivity losses and thereby increasing the cells efficiencies (Markvart and Castaner, 2005). Surface modification can be applied not only on silicon based photovoltaics, but also thin films (Fauzi et al.,

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2010), organic (Vairavan et al., 2011) and hybrids solar cells (Reshak et al., 2013). Texturized surface or saw-damage surface can be formed by various techniques such as wet chemical etching, reactive ion etching (RIE), microporous silicon etching and pyramidal structurization using lithography (Lipinski et al., 2003; Rabha and Bessaïs, 2010; Markvart and Castaner, 2005; Huang et al., 2008; Yae et al., 2006; Surek, 2005). In order to facilitate a higher trapping capability of solar cell with a low reflection coefficient, the ARC layer is needed. ARC layer acts as a multifunction layer, such as dielectric layer, passivation layer, which protect the silicon surface and also as a catalyst for increasing the light absorption into the cells.

Processing techniques and materials need to be carefully selected for the maximum cost reduction while maintaining relatively high efficiencies (Markvart and Castaner, 2005). In realizing this aim, this paper focuses on the improvement of surface texturization of single-crystalline silicon solar cells by using wet chemical etching technique. The technique is first carried out using alkaline etching with a cocktail composed of potassium hydroxide, isopropyl alcohol and deionized water (KOH:IPA:DI) (Park et al., 2009; Macdonald et al., 2004). This alkaline solution resulted in anisotropic profile of etching that lead to the formation of inverted pyramids along the front surface of silicon wafer. The second technique is using an acidic solution of hydrofluoric acid, nitric acid and deionized water (HF:HNO_3:DI). In this case, regular circular craters were formed on the surface of cells (Peng et al., 2013; Panek et al., 2005; Cheng et al., 2011; Basu et al., 2010; Vallejo et al., 2007; Barrio et al., 2012). Partially crystallized silicon plays a principle role in the trapping levels, interacting with the phonons which in return determine the transport for the photocarriers (Ebothé et al., 2003, 2006). These surface modifications lead to the reduction of light reflectance from the surface and thereby increase the short circuit current and conversion efficiency of the solar cells (Park et al., 2009; Macdonald et al., 2004). This paper discusses on fabrication procedures for both acidic and alkaline etching for single-crystalline silicon to be used in photovoltaic applications. All samples are the characterized based on their surface morphology and electrical characteristics on different lighting conditions. These results will pave way for simple and characterized surface modification procedures on photovoltaics.

2. Experimental procedures

Texturization of <100> oriented single crystal silicon wafers with appropriate anti-reflection coating (ARC) has become a well-established method in photovoltaic industry for minimizing reflection loss. This is an important step to improve cell parameters by increasing the light trapping into the cell. The first technique is carried out using the alkaline etching cocktail composed of KOH:IPA:DI (Park et al., 2009; Macdonald et al., 2004). This etching method is varied into three possible time variable, which is 30, 40 and 50 min. The alkaline solution forms anisotropic etching profile that leads to the formation of inverted pyramids along the front surface of the silicon wafer. It is known that the second technique of the wet chemical etching, which is using the acidic solution of HF:HNO_3:DI can also improve the effects of the surface texturization by forming circular craters. This kind of improvement will leads to the reduction of light reflectance from the surface and thereby increase the short circuit current and conversion of the solar cells (Park et al., 2009; Macdonald et al., 2004). The acidic etching experiments are varied into three etching time; 10, 20 and 30 s. The summary of experiments carried out is shown in Table 1.

The ARC layer is aimed to increase the absorption of light by trapping the light into the cell. A layer of silicon nitride is chosen as the ARC layer as the refractive coefficient is quite high (2.05) (Mauk, 2003; Wright et al., 2005; Yang et al., 2011; Zhou et al., 2011; Li et al., 2013, 2010). This layer can be deposit using Plasma Enhanced Chemical Vapor Deposition (PECVD). A ∼50 nm thick layer of silicon nitride is deposited on the textured surface of all samples. Each solar cell is characterized using atomic force microscopy (AFM) for surface profile measurements. The diode properties of each solar cell are also monitored for the determination of their threshold voltage. A simple light to volt conversion experiment is also done using fluorescent lamp and sun light. The voltage generated is measured and compared.

Table 1
Chemical composition and process condition.

Etching	Solution	Temperature	Sample	Etching time
Alkaline etching	KOH:IPA:DI (4 g:10 ml:400 ml)	75 °C–80 °C	A	30 min
			B	40 min
			C	50 min
Acidic etching	HF:HNO_3:DI (10:1:1)	26 °C–30 °C	D	10 s
			E	20 s
			F	30 s

3. Results and discussion

3.1. Surface modification via wet etching

Texturization using alkaline solution of KOH and IPA is purposely done to form random inverted pyramids as this kind of saw-damage surface brings a reduction in surface reflectance. The surface modification is expected to increase the conversion efficiency. IPA or isopropyl alcohol is added into the alkaline etchant to control the etching rate and thereby prevent an explosive reaction between the silicon surface and the hydroxide ions.

From the observation in Fig. 1, at the etching time of 30 min, the inverted pyramid structures formed irregularly of width approximately 200 nm. It is assumed that as more numbers of random inverted pyramids are formed, the better the device to trap light. From the 2D AFM images in Fig. 1c and d, the sample is anisotropically etched and formed inverted pyramidal structures of depth up to 140 nm. By comparing and contrasting all AFM images of the three samples, it is observed that as the etching time is increased, more random inverted pyramids are formed and the distance between each inverted pyramids are reduced as shown in the schematic diagram in Fig. 2. Summary of all results are shown in Table 2.

In contrast with the profile of alkaline etched surface, acidic etch surface shows isotropic etch in <100> direction of the single-crystalline silicon wafer used. The etching process formed a rough surface covered with circular craters and nano-pits as shown in Fig. 3a and b. Table 3 shows the summary of results for the sizes between two nano-pits, the diameters of craters and the saw-damages surface thickness of all samples.

For acidic etching of 10:1:1 (HF:HNO_3:DI) solution, the formation of saw-damage layer and the textured surface is obtained in one process. The acidic solution produced simultaneously circular craters and nano-pits. The layer obtained after the etching process are also typically found micro cracks in damaged layer after slicing and exposed by acidic etching (Peng et al., 2013; Panek et al., 2005; Cheng et al., 2011; Basu et al., 2010; Vallejo et al., 2007; Barrio et al., 2012). The kinetics of pits formation is determined by the high speed of etching along the crack surface due to a very fast diffusion of solution into the cracks. If the time of etching is too long, the texturization disappears and the dislocations and grains boundary appear. Therefore, this can possibly caused mechanical weakening