Low-reflective Surface Texturing for Large Area Multicrystalline Silicon Using NaOH-NaClO Solution

Jing Dong and Shi-Hua Huang

Physics Department, Zhejiang Normal University, Zhejiang 321004, CHINA
e-mail: huangshihua@zjnu.cn

Multicrystalline silicon surface texturing using the mixed etching solution of the sodium hydroxide (NaOH) and of the sodium hypochlorite (NaClO) has been investigated. The reaction rate during the texturing process is easier to control due to the presence of NaOCl as an oxidizing agent in NaOH solution. The advantage of this etching is that the uniform mc-Si surface texturing with a low step height and less grain boundary delineation can be obtained. The Mc-Si surface after NaOH-NaOCl mixed etching with the 1:4 ratio in the case of 20% NaOH has the optimum light trapping effect. In the case of the optimum etching condition, the average reflectivity for the textured surface of a large area (156×156 mm^2) mc-Si can be reduced to less than 10%.

Keywords: *multicrystalline silicon, NaOH-NaOCl texturing, reflectivity.*

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INTRODUCTION

Surface texturing plays a critical role in the silicon solar cell performance, affecting both reflectance and light trapping. Numerous techniques for texturing monocrystalline or multicrystalline silicon have been examined in the past decades. For monocrystalline silicon, an isotropic etching by alkaline solution such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) results in the surface covered by pyramids, which can collect the reflected light and trap the light inside the cells by repeated reflections. As opposed to multicrystalline silicon (mc-Si), which is today the dominant technology for solar cells fabrication, this alkali texturing has little usefulness and cannot generate sufficient effect due to its inherently randomly oriented grains. Nowadays the industry-standard solution is an isotropic etching with hydrofluoric acid (HF) and nitric acid (HNO_3). This etching process simultaneously removes some saw damage and forms a scalloped surface texture, and is fast enough to be performed with an inline tool. However, its main drawback is that both cell voltage and current do not simultaneously maximize. The reason is that the typical isotropic etching process still leaves residual saw damage in the wafer, because a deeper etching would result in a non-textured surface.

A new method has been developed recently for mc-Si texturing [1], and isotropic etchants such as NaOH and sodium hypochlorite (NaClO) solution have been adopted. NaOH-NaClO texturing can generate low mc-Si grain boundaries and thus has an excellent isotropic etch characteristics to enhance related solar cell parameters [2]. For the industrial production of mc-Si solar cells, the NaOH-NaClO texturing can provide a convenient and low-cost alternative [3]. In addition, sodium chloride (NaCl) is the main reaction product formed during etching, so there is no special requirement for the disposal of the reaction product. However, NaOH-NaClO texturing is also having its inherent problems in the photovoltaic application due to its polishing effect [4].

The present paper reports the investigation of the surface morphology and the reflectance of mc-Si etched by NaOH-NaClO texturing method. Using the optimum etching conditions of the NaOH-NaOCl solution, the average reflectivity in the wavelength range of 350–800 nm for the textured surface of a large area (156×156 mm^2) mc-Si can be reduced to less than 10%.

EXPERIMENTAL DETAILS

Boron-doped *p*-type mc-Si wafers with the resistivity of 1.0~3.0 Ω/cm and the size of 156×156 mm^2 were used in the present study. The etchant solution was heated with a temperature-controlled hot plate. While texturing with the NaOH-NaOCl solution, the concentration of NaOH solution as well as the ratio of NaOH and NaOCl (AR, 10.5%) varied. The key parameters as studied here in the process steps of texturing with the solution of NaOH-NaCl can be described as follows: the ratio of NaOH and NaClO, the concentration of NaOH, the etching time, and the temperature. The temperature of mc-Si etching is an important technology parameter, and it is maintained on 80^0C during the entire etching process. When the etching temperature is lower than 80^0C, the etch rate reduces substantially. However, if the etching temperature is higher than 80^0C, the self-decomposition rate of NaOH-NaOCl to O_2 and NaCl increases greatly [5]. The concentration of NaOH in the solution varied from 5% to 40%, the ratio of NaOH:NaClO from 1:1 to 1:6, and the etching time from 5 to 20 min. After finishing the texturing process, all Si wafers were analyzed with an optical microscope, and also the etched-off thickness was calculated from the standard gravitometry. The surface morphology was observed by scanning electron microscope (SEM) and the surface reflectance was measured using a spectrophotometer.

RESULTS AND DISCUSSION

NaOH is a well-known anisotropic etchant widely used for crystalline Si solar cell texturing and in Micro-Electro-Mechanical Systems (MEMS) application, and NaOCl is a strong oxidizing agent [4, 6]. The strong oxidation is equally effective for all crystallographic directions. It has been assumed that the mechanism of silicon dissolution is shifted from the orientation-dependent process to the isotropic “layer-by-layer” removal. The appropriate ratio of NaOCl and NaOH in the etching solution, therefore, makes the change of the behavior of etching from anisotropic towards isotropic [7]. The conventional alkali (NaOH or KOH) etching of as-cut mc-Si wafers results in high steps between successive grains, which may result in tailing off or breaking of the metal lines in the metallization stage. Smaller steps along the grain boundaries were obtained using NaOCl–NaOH etching, because lower anisotropy leads to a lower etch rate difference between the differently oriented grains.

The etching process of NaOH-NaClO texturing mc-Si is composed of two parts: oxidation and dissolution. Firstly, NaClO is a strong oxidizing agent that controls the oxidation rate, and SiO_2 is produced on the surface.

$$NaClO = Na^+ + ClO^-,$$

$$ClO^- + H_2O = HClO + OH^-,$$

$$Si + ClO^- = SiO_2 + 2Cl^-.$$

Secondly, NaOH controls the etching of the oxide layer formed during the etching process. Namely, the SiO_2 layer can prevent NaOH rapid anisotropic corrosion.

$$NaOH = Na^+ + OH^-,$$

$$SiO_2 + 2OH^- = SiO_3{}^{2-} + H_2O.$$

The increase of the concentration of NaOH in NaOH-NaOCl solution can enhance the etching rate of the formed silicon oxide layer after the dissociation of NaOCl in the solution. However, too high concentration of NaOH solution will result in the polishing of mc-Si surface due to the rapid etching of the produced oxide layer. In order to minimize the impact of grain boundaries on the surface texturing, the mount of NaOH in NaOH-NaOCl mixed solution should be maintained at a reasonable value, which does not hinder the etching of the oxide layer produced by NaOH. A large proportion of NaClO in the mixed etchant will results in a large amount of the saw damage marks in the surface of the mc-Si wafers. It takes a long time to remove the damage marks, which ultimately affects the rate of industrial production. If the proportion of NaClO in NaOH-NaOCl mixed etchant is lower than a specific value, then NaOH plays the role of the rapid polishing rather than texturing. The etching time is one of the parameters that affects mc-Si surface morphology. When the etching time increases from 5 to 15 min in the case of texturing with NaOH (concentration varied from 5% to 40%) with different ratios of NaOH:NaOCl (from 1:1 to 1:6), the observation with an optical microscope indicates that the surface structures are not yet satisfactory. The etched-off thickness in almost all samples was not more than 10 μm after 15-min etching. A layer with the thickness of at least 10 μm should be removed before subjecting the silicon wafers to cell processing for proper cleaning and saw damage marks removal from the Si surface [8]. Therefore, in the present study, the etching time was fixed for 20 min for NaOH-NaOCl etching at different experimental conditions.

Figure 1 shows SEM micrographs of the textured mc-Si surfaces etched in NaOH:NaOCl = 1:1 solution with various NaOH concentrations (5%, 10%, 15%, 20%, 25% and 40%). When NaOH concentration is low, the etching of the mc-Si surface is not very sufficient, as shown in Figs. 1(a)–(c). With the increase of NaOH concentration, the etching rate of NaOH on the oxide layer formed after the dissociation of NaOCl enhances rapidly. However, too high concentration of NaOH in NaOH-NaOCl solution can cause the polishing effect on the Si wafer, as shown in Figs. 1(e) and 1(f), which results in the flattening of the mc-Si texturing surface. The surface morphology shown in Fig. 1(d) indicates that 20% concentration of NaOH in the etching solution of NaOH-NaOCl with the ratio of 1:1 is suitable. When the ratio of NaOH:NaOCl varies from 1:2 to 1:6, the changing trend of the texturing surface morphology is the same as that of 1:1 with the increase of concentration of NaOH. Figure 2 shows SEM micrographs of the textured mc-Si surfaces etched in NaOH:NaOCl solution, with the different ratio (1:1, 1:2, 1:3, 1:4, 1:5, and 1:6) and the 20% concentration of NaOH. When the NaClO ratio is small, the polishing effect of NaOH is stronger than its texturing effect, which leads to the flattening surface, as shown in Figs. 2(a)–(c). A too high ratio of NaClO can cause a large amount of the saw damage marks in the surface of the mc-Si wafers, which means that the texturing effect of NaOH:

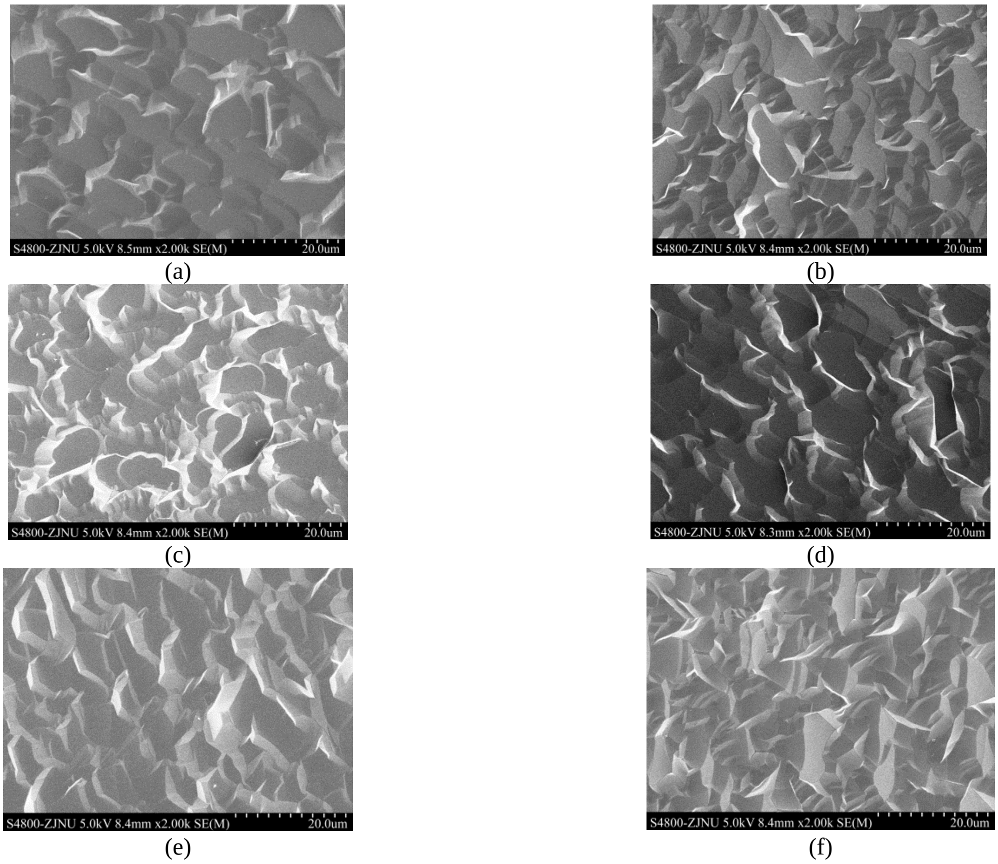

Fig. 1. SEM micrographs of textured mc-Si surfaces after etching in NaOH:NaOCl = 1:1 solution with NaOH concentrations of (a) 5%; (b) 10%; (c) 15%; (d) 20%; (e) 25%, and (f) 40%.

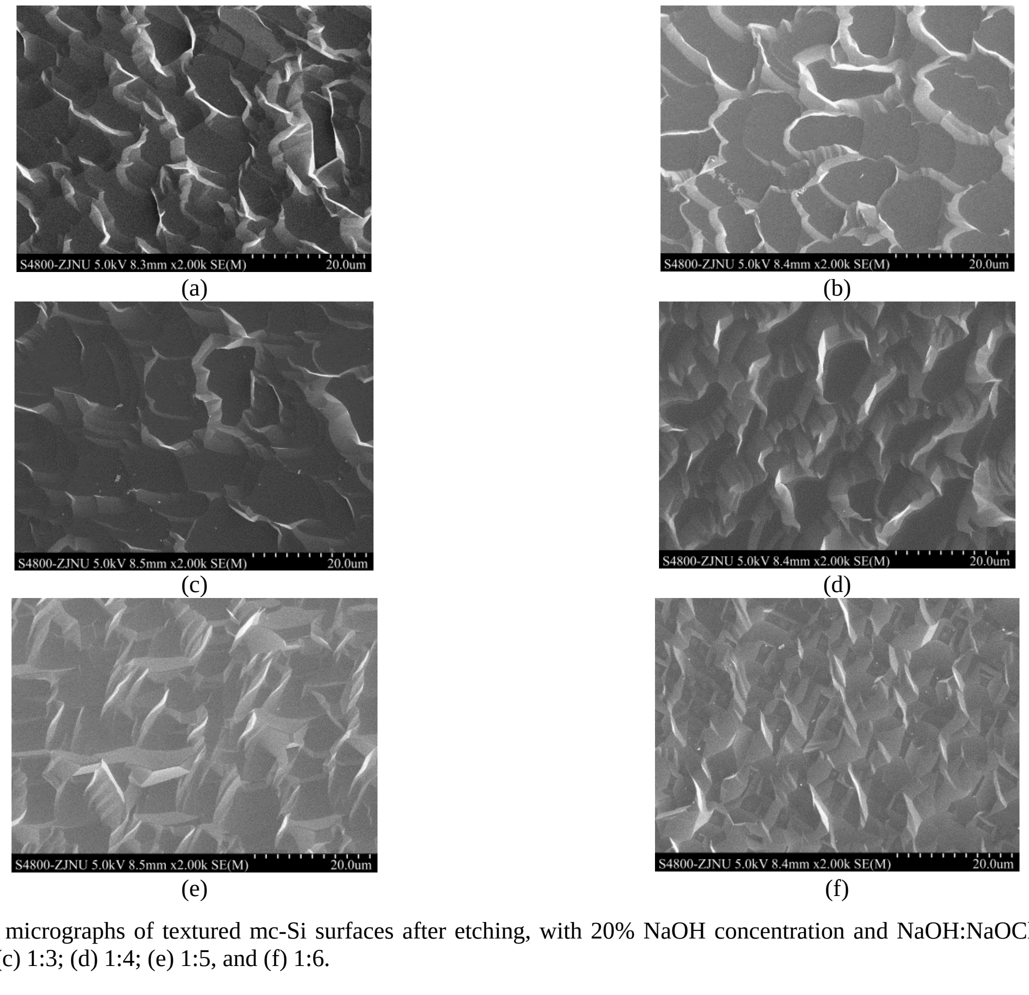

Fig. 2. SEM micrographs of textured mc-Si surfaces after etching, with 20% NaOH concentration and NaOH:NaOCl ratio of (a) 1:1; (b) 1:2; (c) 1:3; (d) 1:4; (e) 1:5, and (f) 1:6.

NaOCl etching solution becomes weak within the same etching time, as shown in Figs. 2(e) and 2(f). Therefore, in order to obtain a uniform mc-Si surface texturing with a low step height and less grain boundary delineation, the most appropriate is NaOH-NaOCl mixed etching solution with 1:4 ratio and the 20% NaOH.

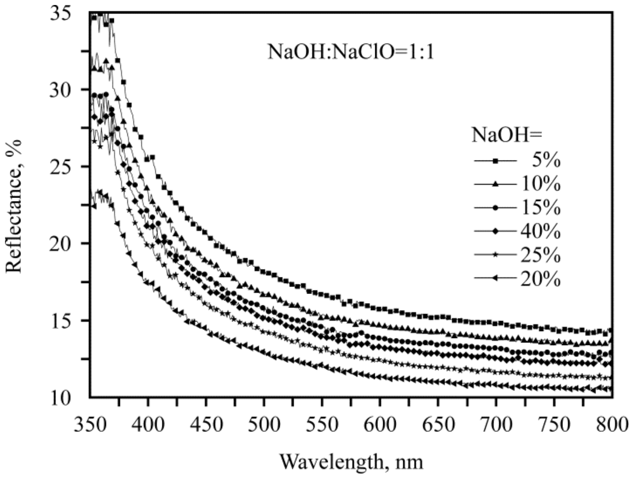

Fig. 3. Reflectance of textured mc-Si surfaces using NaOH:NaOCl = 1:1 etching solution with NaOH concentration of (a) 5%; (b) 10%; (c) 15%; (d) 20%; (e) 25%, and (f) 40%.

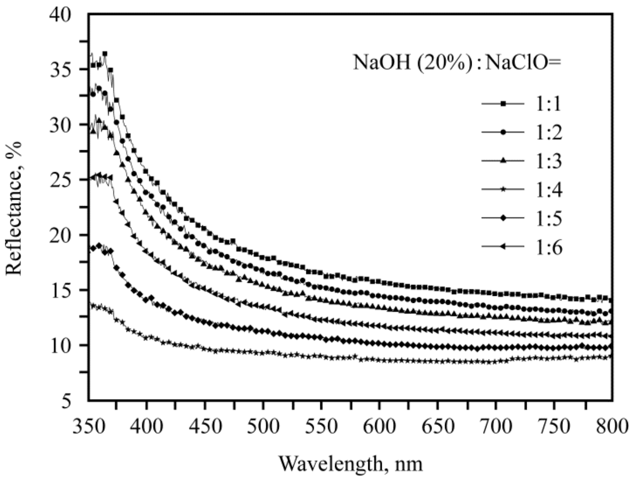

Fig. 4. Reflectance of textured mc-Si surfaces after etching with 20% NaOH concentration and NaOH:NaOCl ratio of (a) 1:1; (b) 1:2; (c) 1:3; (d) 1:4; (e) 1:5, and (f) 1:6.

To compare the light-trapping effect on the surfaces of mc-Si wafers etched with different approaches, the surface reflectance was measured after each etching. Figure 3 gives the reflectivity of the textured mc-Si surfaces etched in NaOH: NaOCl = 1:1 solution, with NaOH concentrations of 5%, 10%, 15%, 20%, 25% and 40%. With the increase of NaOH concentration, the reflectivity of the texturing surface first increases and then decreases. When NaOH concentration is 20% in the case of NaOH:NaOCl = 1:1, the reflectivity is minimal and its average value in the range of 350–800 nm is 13.1%. Figure 4 shows the reflectivity of the textured mc-Si surfaces etched in NaOH:NaOCl solution, with different ratio (1:1, 1:2, 1:3, 1:4, 1:5, and 1:6) and the 20% concentration of NaOH. With the increase of the ratio of NaOH: NaOCl, the reflectivity of the texturing surface first increases and then decreases. When the ratio of NaOH:NaOCl is 1:4, the reflectivity is minimal and its average value in the range of 350–800 nm is 9.5%. These results of reflectivity measurements are consistent with SEM results. The reduction observed in the reflectivity could be explained by a higher roughness of the surface. The higher the roughness, the higher the scattering and the lower the reflectance. The polished surface tends to a higher reflectance due to its lower light scattering. Mc-Si surface after NaOH-NaOCl mixed etching with the 1:4 ratio in the case of 20% NaOH has the optimum light trapping effect, and is suitable for achieving higher efficiency of solar cells compared to that with other etching condition.

CONCLUSIONS

In this work, multi-crystalline silicon surface texturing using NaOH-NaOCl mixed etching solution was investigated for solar cells fabrication of a very large area (156×156 mm^2). Compared with the traditional acid etching of HF-HNO_3, the reaction rate during NaOH-NaOCl texturing process is easier to control due to the presence of NaOCl as an oxidizing agent in NaOH solution. NaOH-NaOCl etching can generate the uniform mc-Si surface texturing with a low step height and less grain boundary delineation. Mc-Si surface after NaOH-NaOCl mixed etching with 1:4 ratio in the case of 20% NaOH has the optimum light trapping effect. In the case of the optimum etching condition, the average reflectivity in wavelength range of 350–800 nm for the textured surface of a large area (156×156 mm^2) mc-Si can be reduced to less than 10%. Using NaOH-NaOCl etching solution, the procedure of HCl disposal can be omitted, and the production environment is greatly improved.

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Реферат

Цель исследования – изучение текстурирования поверхности поликристаллического кремния, используя для травления смешанный раствор из гидроксида натрия (NaOH) и гипохлорита натрия (NaClO). Скорость реакции было проще контролировать благодаря присутствию гипохлорита натрия в качестве окислителя. Преимущество такого вида травления в том, что можно добиться однородного текстурирования поверхности поликристаллического кремния с меньшей высотой ступени и менее явным очерчиванием межзеренных границ. Оптимальный эффект светового клапана достигается на поверхности поликристаллического кремния в результате травления смешанным NaOH/NaOCl раствором в соотношении 1:4, при содержании NaOH в размере 20%. При оптимальных условиях травления средняя отражательная способность текстурированной поверхности поликристаллического кремния большой площади (156×156 мм^2) может быть 10% и меньше.

Ключевые слова: поликристаллический кремний, текстурирование с использованием раствора NaOH/NaOCl, отражательная способность.