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One-step-MACE nano/microstructures for high-efficient large-size multicrystalline Si solar cells

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ABSTRACT

We have employed a one-step (direct etching) metal-assisted chemical etching (MACE) technique to grow large-area Si nanostructures with smoother surface morphology and much less porous Si (PS) defects than those under the two-step (depositing and etching) MACE. A 17.63%-efficiency of the nano/microstructures (N/M-Strus) based multicrystalline Si (mc-Si) solar cells has firstly surpassed that (17.45%) of traditional-micro-textured one with a standard solar wafer size of 156 × 156 mm^2. The key to success lies in the reduction of electrical loss by removing PS defects and employing shorter one-step-MACE-smoothened N/M-Strus, together with the optical gain from the combined antireflection of mc-Si N/M-Strus and SiN$_x$:H thin films. The present work opens a way to the mass production of high efficient Si nanostructures based solar cells with a less-process-step and lower-cost approach.

1. Introduction

Vertically aligned silicon (Si) nanostructure arrays have been arising great interests in photovoltaic applications, due to the excellent light-trapping features over a broad range of incident angles [1–3], which may maximize the light absorption and achieve improved efficiency (η) of solar cells. Considering the remaining high reflectance of traditional-micro-textured multicrystalline Si (mc-Si) solar cells, the optical superiority of the Si nanostructures provides an effective approach to obtaining high η of mc-Si solar cells. However, the optical advantage of Si nanostructures has not been facile to be fully converted into the η-gain of solar cells [4–15], which is mainly ascribed to the poor electrical properties, *i.e.*, high recombination on the surface and in the bulk of Si nanostructures. Over the past several years, substantial progresses in improvement of the electric performance have been made by carrying out various process methods such as the surface passivation [16–20], properly increasing sheet resistance [21,22] and optimization of morphology of mc-Si nanostructures [11,13,14,19]. Using the optimized textured structure, Zhong et al., [23] and Xiao et al., [24] have reported ηs of 15.99% and 17.46% for mc-Si nanostructures based solar cells with the standard solar wafer size of 156 × 156 mm^2 through reactive ion etching (RIE), respectively. Liu et al., [22] have further improved the performance of the mc-Si nanostructures based solar cells by employing acidic-RIE textured technique and high sheet resistance.

As an morphology-easily-controlled method to prepare Si nanostructures, the widely studied metal-assisted chemical etching (MACE) has demonstrated promising advantages for mass productions due to its simplicity, room-temperature process, low cost, and compatibility with current production lines [5,17,19,20]. Generally, MACE is divided into one-step (direct etching) and two-step (depositing and etching) MACE, and the difference between these two methods lies mainly in the less process step and the absence of H_2O_2 (oxidant) for the one-step MACE. Up till now, most of works have focused on two-step MACE, for example, Huang et al., [25] and Lin et al., [26] have reported ηs of 11.86% and 15.58% for the mc-Si nanostructures based solar cells through the two-step-MACE technique. Due to the existence of the oxidant H_2O_2, the Si nanostructures synthetized by the two-step MACE have a mass of porous Si (PS) defects, which is detrimental to the electrical performance of the solar cells. Xie et al., [27] have shown that the Si nanostructures grown by the two-step MACE with lower H_2O_2 concentration have smoother morphology and less PS defects. In short, compared with the two-step MACE, the one-step technique without H_2O_2 is a simpler, less-process-step and lower-

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cost approach to grow large-area Si nanostructures with smoother surface morphology, and thus possesses more promising applications to the mass production of Si nanostructures based solar cells. Using the one-step MACE, Liu et al., [28] have achieved an η of 15.8% on mc-Si nanostructures based $156\times156\ \text{mm}^2$ solar cells with a stack passivation of SiO_2/SiN_x. Hsu et al., [29] have further improved the η to 16.38% for the 6" one-step MACE mc-Si nanostructures based solar cells. Nevertheless, the conversion efficiencies of either the two-step or one-step MACE nanostructured silicon solar cells are still far from satisfactory, especially when compared to the efficiencies of the conventional counterparts.

In this paper, we have successfully fabricated the mc-Si nano/microstructures (N/M-Strus) based solar cells with the standard solar wafer size of $156\times156\ \text{mm}^2$, by employing one-step MACE technique. The η of 17.63% is firstly reported to be higher than the traditional-micro-textured one of 17.45%. The shorter one-step-MACE-smoothened N/M-Strus have been proved to play a key role in reducing the electrical loss of N/M-Strus based solar cells, by suppressing the surface recombination, Auger recombination and Shockley–Read–Hall (SRH) recombination. Together with the optical gain from the combined antireflection of the one-step-MACE N/M-Strus and SiN_x:H thin films, the reduced electrical loss enables higher-than-traditional-micro-textured ηs to be realized. The present achievement of the improved η displays promising future for the mass production of the mc-Si nanostructures based solar cells.

2. Experimental

2.1. Preparation of Si N/M-Strus

p-Type, 200 ± 10-μm-thick, ~2-Ω cm-resistivity, mc-Si wafers with the standard solar wafer size of $156\times156\ \text{mm}^2$ were used for this work. The mc-Si N/M-Strus consisting of the traditional-micro-textures and the nanowires were sequentially prepared in mixed acid solution and MACE solution. The traditional-micro-textures were firstly prepared in the mixed acid solution $HF{:}HNO_3{:}DIW = 1{:}3{:}2.5$ (volume ratio) for ~2.5 min at ~8 °C. Subsequently, the mc-Si N/M-Strus were synthetized through the MACE including the one-step and two-step process as shown in Fig. 1(a) and (b). For the one-step MACE, the cleaned as-traditional-micro-textured mc-Si wafers were directly etched to form the nanostructures on the surface of the traditional-micro-textures in the etching solution of 4.0 M HF/0.01 M $AgNO_3$ for a certain time at room temperature. For the two-step MACE, the cleaned as-traditional-micro-textured mc-Si wafers were firstly dripped in the aqueous solution of 5.0 M HF/0.02 M $AgNO_3$ for 60–100 s to obtain the Ag^+-deposited layer, and then the Ag^+-deposited wafers were immediately immersed in the mixed solution of 5.0 M HF and 0.1–1.0 M H_2O_2 for 60 s at room temperature, to form the nanostructures. Finally, to wipe off the residual impurities, all the mc-Si wafers with as-etched N/M-Strus were immersed in the $HNO_3{:}DIW = 1{:}1$ (volume ratio) solution for 20 min, followed by rinsing with excess copious deionized water and drying with N_2.

2.2. Fabrication of one-step-MACE N/M-Strus based mc-Si solar cells

After the standard RCA cleaning, the mc-Si wafers with one-step-MACE N/M-Strus were placed in a tube furnace to carry out the one-side (double-sides for some wafers) phosphorous diffusion (Meridian, BTU) with $POCl_3$ liquid source for about 40 min at ~800 °C. The phosphorous silicate glass (PSG) was removed by a dilute HF solution (9% by volume). After that, the antireflection and passivation layer of SiN_x:H was deposited on the front surface by plasma enhanced chemical vapor deposition (PECVD) (E2000 HT410-4, Centrotherm) for ~40 min at 400 °C, meanwhile the same SiN_x:H layers were deposited on both sides of the double-side diffused and no-diffused samples for the purpose of testing the saturation current of the emitter and minority carriers lifetime, respectively. Finally, a conventional front grid pattern and back contacts as well as back surface aluminum were performed by the screen-printing (LTCC, BACCINI), followed by a co-firing step at 750 °C for a short duration.

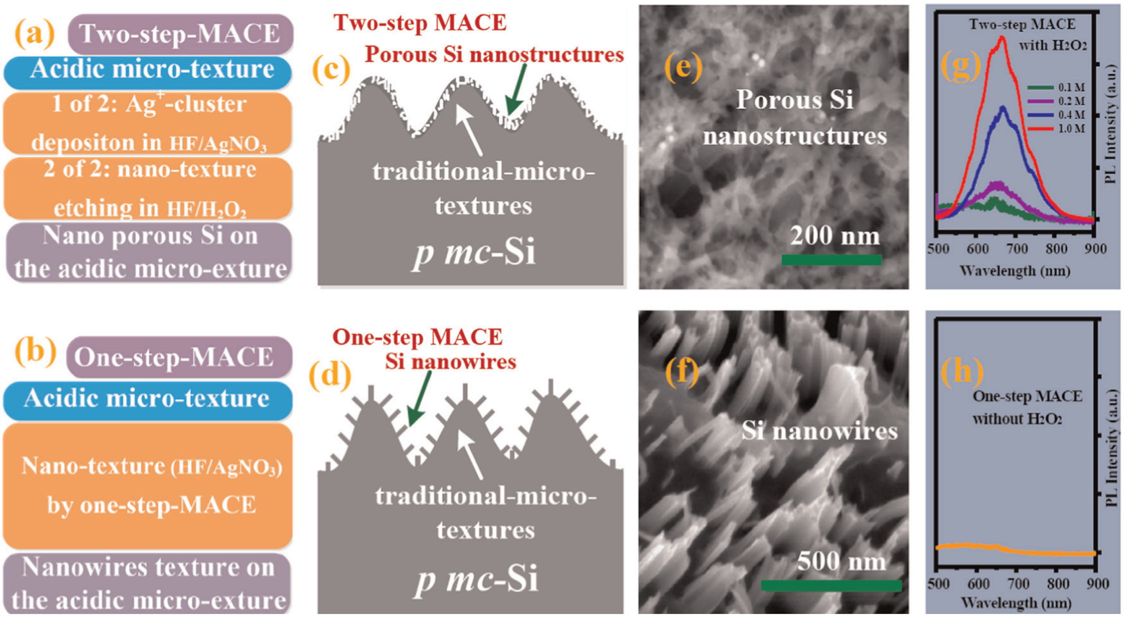

Fig. 1. Comparison between the one-step and two-step MACE. (a) Process flow of two-step MACE. (b) Process flow of one-step MACE. (c) Schematic morphology of the PS nanostructures by the two-step MACE. (d) Schematic morphology of the Si nanowires by the one-step MACE. (e) Oblique-view high-resolution SEM image of PS nanostructures by the two-step MACE. (f) Oblique-view high-resolution SEM image of Si nanowires by the one-step MACE. (g) Room-temperature PL spectra of PS nanostructures by the two-step MACE with different H_2O_2 concentrations of 0.1 M, 0.2 M, 0.4 M and 1.0 M. The excitation wavelength is 325.0 nm. (h) Near zero room-temperature luminescence of Si nanowires by the one-step MACE without H_2O_2.