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Short Communication

Macroporous Silicon Formation on Low-resistivity p-type c-Si Substrate by Metal-catalyzed Electrochemical Etching

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Macroporous silicon with large aperture size was fabricated on p-type c-Si substrate with the resistivity of about 0.1-3 ohm·cm by metal–catalyzed electrochemical etching (MCECE). Firstly, Ag nanoparticle catalyst was fabricated on c-Si by immersing the substrate into an aqueous solution of HF and $AgNO_3$. Electrochemical etching was then performed in a HF-H_2O_2 solution. The synergetic effect of the Ag catalyst and the external applied electric field successfully facilitated the formation of macroporous silicon with large aperture size, which could not be obtained by single metal–catalyzed electroless etching (MCEE) or electrochemical etching (ECE). An etching model was proposed to illustrate the MCECE mechanism.

Keywords: Metal–catalyzed electrochemical etching (MCECE); Macroporous silicon; Etching model.

1. INTRODUCTION

Macroporous silicon on c-Si has shown a great application potential in fields ranging from photovoltaics[1,2], energy storage [3], chemical analysis [4], luminescence [5] and so on. Many top-down methods have been proposed to fabricate the macroporous silicon, such as reactive ion etching (RIE) [6], electrochemical etching (ECE) [7,8], and metal-catalyzed electroless etching (MCEE) [9-13]. RIE can be used for the fabrication of deep pores with the assistance of specific mask. But the high cost and the complex processes have limited its application to the small scale production. The ECE result depends on the doping level and the doping type of the c-Si, since the well-known 2Wsc (the width of the space charge layer) rule limits the feature size of the obtained macroporous silicon. It is almost impossible to obtain large-aperture macroporous silicon on p-type c-Si with low resistivity due to the difficulty to realize the selective etching [7,8]. And MCEE catches a lot of interests, due to its low cost and ability to fabricate various silicon nanostructures, such as nano-wires, nano-cones, nano-porous silicon, and so on [12]. MCEE is based on the metal-induced local oxidation and the anisotropic dissolution of Si in aqueous HF solution containing oxidizing agents, such as $Fe(NO_3)_3$ or H_2O_2. MCEE is independent on the doping level and the doping type of the c-Si. However, it is still difficult to obtain the macroporous silicon with large aperture size due to the small size of the metal particle catalyst [9-12].

Here, we proposed a method called metal–catalyzed electrochemical etching (MCECE) to fabricate macroporous silicon with large aperture size on p-type c-Si with low resistivity.

2. EXPERIMENTAL

P-type c-Si substrate with the resistivity of 0.1-3 ohm·cm was firstly chemically polished for 2-3 minutes in 20 wt.% NaOH aqueous solution at 85 ºC to remove the damaged surface induced by saw-cutting. Then, the MCECE method was performed as follows: The polished substrate was immersed into the aqueous solution of HF and $AgNO_3$ to deposit Ag particles on the surface. After that, the electrochemical etching was performed in a home-made two-electrode electrochemical bath using the galvanostatic condition (the current density was 5.7 mA/cm^2) for 60 min. $HF/H_2O_2/H_2O$ solution with the volume ratio of 3:10:24 was utilized as the electrolyte, and the c-Si was utilized as the anode. The former deposited Ag particles acted as the catalysts to promote the macroporous silicon formation. When the etching was finished, the remained Ag particles were removed by HNO_3. The obtained macroporous silicon was characterized via S-4800 scanning electron microscope (SEM). As comparisons, single MCEE and ECE were also performed to illustrate the advantages of the proposed MCECE method.

3. RESULTS AND DISCUSSION

The morphology of the deposited Ag particles depends on the concentrations of HF and $AgNO_3$, and the immersion time. The $Si/AgNO_3/HF$ system is composed of a redox couple: the cathodic reduction of Ag^+ ions and its counterpart, the anodic oxidation and dissolution of silicon [14]. The generated SiO_2 is then etched off by HF to expose the Si surface again. Thus, the reaction can continue and the formed Ag nuclei will grow up to particles. As shown in Fig. 1, high $AgNO_3$ concentration can increase the size of Ag particles, but the Ag particles will change to be irregular, even to merge together, if the size is overlarge. High HF concentration will result in Ag particles with high density and small size. As well known, if the reaction is so strong that Si is etched greatly, Si nano-wire array will be formed [15]. So the concentrations of HF and $AgNO_3$ should be controlled carefully to avoid the over etching of the c-Si substrate. Ag particles with relatively large size and large adjacent distance are expected for the formation of the expected large-aperture macroporous silicon. When the concentrations of 1×10^{-3} M for $AgNO_3$ and 0.035 M for HF are adapted, the suitable Ag particles are obtained after the c-Si substrate is immersed in the etching solution for 1 min. The obtained Ag particle size is about 150-200 nm and the adjacent distance is about 400-500 nm.

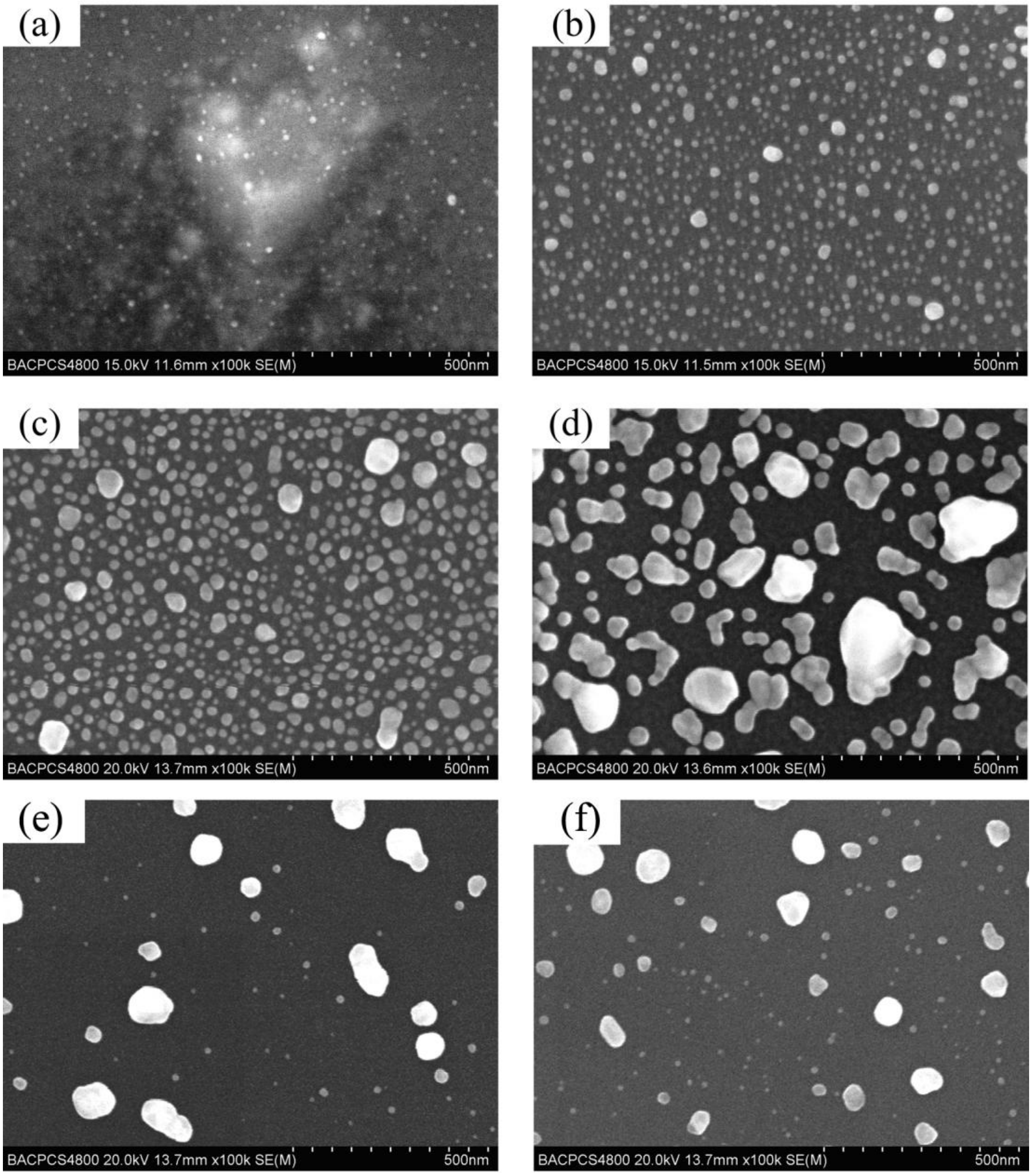

Figure 1. SEM images of the Ag particles obtained on c-Si substrates immersed in the aqueous solution of $AgNO_3$ and HF for 1 min. The components of the solution are (a) 5×10^{-5} M $AgNO_3$, 0.14 M HF; (b) 5×10^{-4} M $AgNO_3$, 0.14 M HF; (c) 1×10^{-3} M $AgNO_3$, 0.14 M HF; (d) 2×10^{-3} M $AgNO_3$, 0.14 M HF; (e) 1×10^{-3} M $AgNO_3$, 0.035 M HF; (f) 1×10^{-3} M $AgNO_3$, 0.07 M HF.

The results obtained by ECE, MCEE, and MCECE are shown in Fig. 2. Fig. 2(a) and (b) show the plan and cross-section views of the etched c-Si surface by ECE for 60 min without Ag particle catalysts. Notably, there is no macroporous silicon formed on the surface, and only some irregular cracks with a relatively large width (0.5-3 μm) can be found. The results obtained by single MCEE are presented in Fig. 2(c) and (d). The macroporous silicon is formed with the pore size of 150-200 nm. The cylinder-like pore has an almost constant diameter from the top to the bottom, which indicates that the etching reaction exactly occurs under the Ag particles. Fig. 2(e) and (f) show the plan and cross-section views of the resulted surface obtained by performing MCECE for 60 min. Clearly, the obtained morphologies are different from those obtained by MCEE, although the same Ag particle catalyst is utilized. The etched pores are cone-like with large aperture size of about 400-500 nm, which is much larger than that of the Ag catalyst particles. The synergetic effect of the Ag catalyst and the external applied electric field successfully makes it possible to realize the formation of the macroporous silicon with large aperture size.

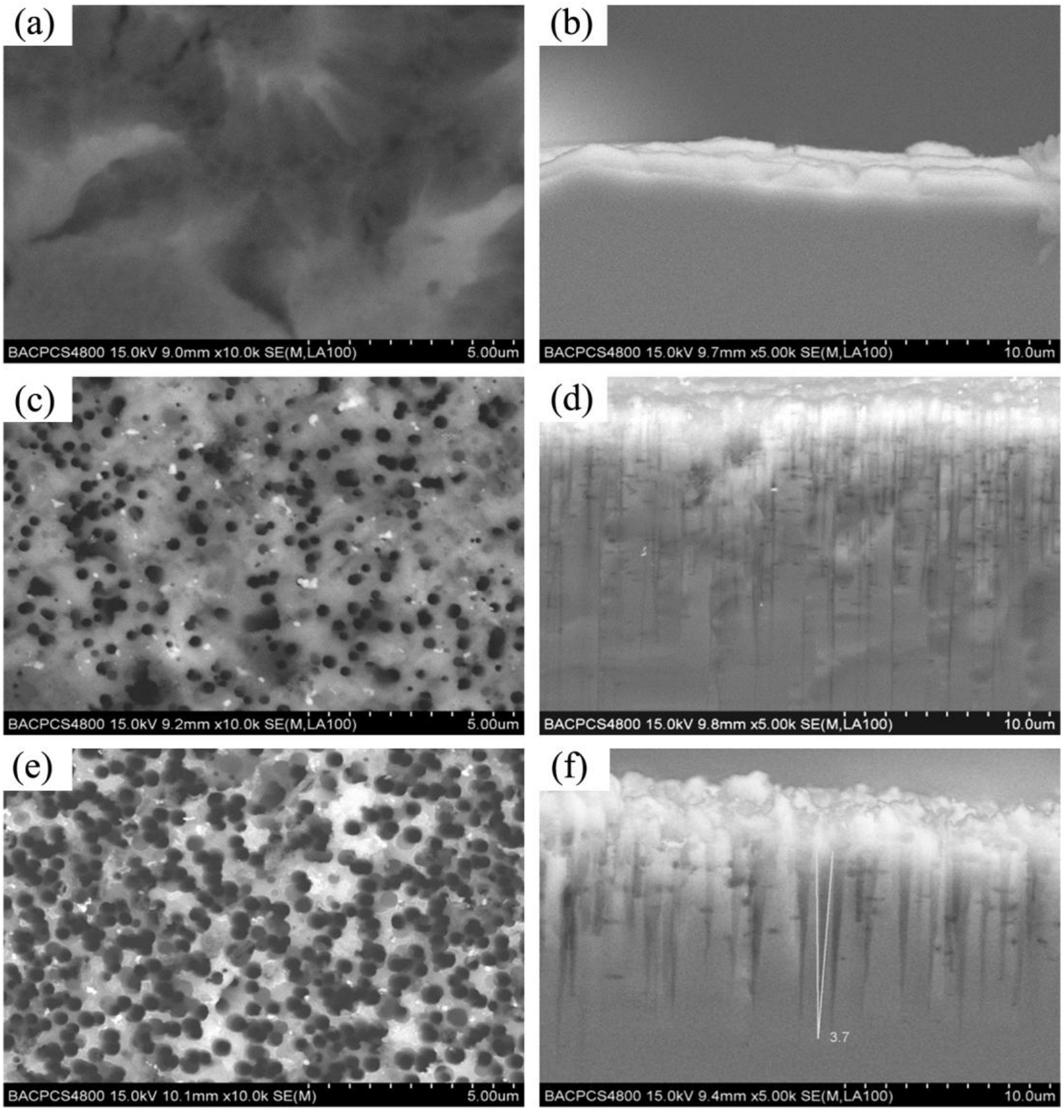

Figure 2. The plan and cross-section SEM images of the etched c-Si surface obtained by single electrochemical etching (ECE), single metal–catalyzed electroless etching (MCEE), and metal–catalyzed electrochemical etching (MCECE) in $HF/H_2O_2/H_2O$ solution with the volume ratio of 3:10:24 for 60 min. (a) and (b): ECE with the galvanostatic condition (the current density of 5.7 mA/cm^2). (c) and (d): MCEE with the Ag particle catalyst. (e) and (f): MCECE with the galvanostatic condition (the current density of 5.7 mA/cm^2) and the Ag particle catalyst.

In ECE, silicon is dissolved by [16]:

$$Si + 6HF + 2h^+ \rightarrow SiF_6^{2-} + 4H^+ + H_2 \uparrow \qquad (1)$$

Hole carrier (h^+) is necessary for the silicon dissolution. The hole concentration on the c-Si surface determines the etching rate. However, in order to obtain macroporous silicon, there must be a non-uniform distribution of the hole carrier on the c-Si surface to realize the selective etching. The contact between p-type c-Si and HF etching solution can be considered as a Schottky junction. The band diagram of such junction is shown in Fig. 3.

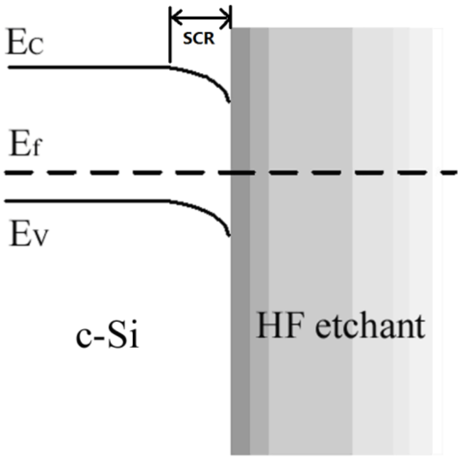

Figure 3. The band diagram of the Schottky junction between p-type c-Si and HF etching solution. E_C is the conduction band edge, E_V is the valence band edge, E_f is the Fermi level, and SCR is the space charge region.

There exists a space charge region (SCR) at the interface. The band bending direction determines that the built-in electric field in the SCR plays a potential barrier for the hole carrier to transport from the Si bulk to the contact surface. When the c-Si resistivity is low, due to the small width of the SCR, a lot of hole carriers can reach the Si surface easily and are available almost everywhere on the surface with the assistance of the external applied electric field. So almost the whole Si surface is etched and no vertical pores can be generated. It is the over high etching rate that induces the cracks on the surface.

In MCEE, it is well-accepted that the noble metal acts as a microscopic cathode on which the reduction of the oxidant occurs as the following [9-11,15]:

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+ \qquad (2)$$

The generated holes are then injected into the c-Si contacting with the noble metal. Accordingly, Si atoms under the noble metal are oxidized due to the hole injection and dissolved by HF. The hole concentration has its maximum at the Si/metal interface. Therefore, Si in contact with the noble metal is etched much faster by HF than bare Si without the metal coverage. That’s why the cylinder-like etched pores can be obtained in MCEE. The size of the etched pores is mainly determined by that of the noble metal. Although it is possible to widen the pore aperture by improving the diffusion of the holes from the bottom to the surroundings via reducing the concentration of the HF etchant, the etching rate will be limited greatly.

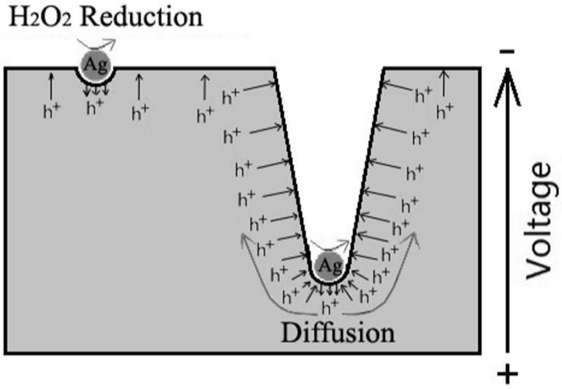

Figure 4. The model to illustrate the etching mechanism of the metal–catalyzed electrochemical etching (MCECE).

Based on the above etching mechanisms of ECE and MCEE, we can deduce that in MCECE, it is the synergetic effect of the metal catalyst and the external applied electric field that successfully facilitates the formation of the macroporous silicon with large aperture size. Such etching mechanism can be illustrated clearly by the following model. As shown in Fig. 4, at the beginning, ECE cannot induce the formation of the etched pores on the low-resistivity c-Si due to the uniform distribution of the hole carriers injected by the external applied electric field. However, MCEE can form the initial etched pits due to the catalysis effect of the Ag particles. Once the initial etched pits occur, the non-uniform surface morphology will change the local external applied electric field on the surface. At the pit bottom with large surface curvature, the local external applied electric field will be high, which leads to a decrease of the local SCR width and thus induces a high concentration of holes there. From the pit bottom to the pit aperture, the hole concentration will decrease gradually along the walls. The non-uniform distribution of the hole carriers makes the selective etching of ECE occur and the ECE etching rate decreases gradually form the pit bottom to the pit aperture. At the same time, MCEE also has the highest etching rate at the pit bottom, the cone-like macroporous silicon can be thus achieved with large aperture size finally.

4. CONCLUSION

We demonstrated the macroporous silicon formation on the low-resistivity p-type c-Si substrate by metal-catalyzed electrochemical etching (MCECE), and compared the new method with the traditional electrochemical etching (ECE) and metal-catalyzed electroless etching (MCEE). An etching model was proposed to illustrate the MCECE mechanism. The metal catalyst is the initiator for the pore formation. And the synergetic effect of the Ag catalyst and the external applied electric field successfully facilitates the formation of the macroporous silicon with large aperture size, which cannot be fabricated by single ECE or MCEE. The results indicate that MCECE can be an effective method for the fabrication of some nano- or micro- silicon structures for many potential applications.

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