Investigation on surface morphological and optical properties of black silicon fabricated by metal-assisted chemical etching with different etchant concentrations

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Abstract. In this study, the surface morphological and optical properties of black silicon (b-Si) fabricated by two-step metal-assisted chemical etching (MACE) process are investigated. The two-step MACE combines low-temperature annealing of silver (Ag) thin film to produce Ag nanoparticles (NPs) and short etching duration of crystalline silicon (c-Si) wafer. The etching is carried out in HF:H₂O₂:DI H₂O solution for 70 s with different etchant concentrations (represented in the form of volume ratio). The MACE process produces b-Si nanopores on the wafer. Compared with planar c-Si reference, broadband reflection (in 300-1100 nm wavelength region) of the b-Si is significantly lower. B-Si wafer with volume ratio of 1:5:10 exhibits the lowest broadband reflection of 3% at wavelength of 600 nm, which is believed to be due to refractive index grading which leads to enhanced light coupling into the b-Si wafer. The best b-Si wafer (with lowest reflection) shows 50 nm average pillar width and 300 nm height. The increased broadband light absorption results in the highest maximum potential short-circuit current density (J_{sc(max)}) of 40.9 mA/cm². This represents 55.4% enhancement, if compared with the planar c-Si reference wafer, assuming unity carrier collection.

1. Introduction

Crystalline silicon (c-Si) solar cells dominate more than 90% of the photovoltaic (PV) industry due to maturity of the technology and economies of scale [1]. The dominance of c-Si-based solar cells in the PV market is expected to increase in the future. As an absorber material, c-Si exhibits naturally high reflectivity (around 35%) in 300-1100 nm spectral region, which is important for PV performance [2]. Besides, c-Si is a semiconductor material with indirect band gap and with low absorption coefficient. These factors result in poor light absorption in the c-Si absorber which leads to low photocurrent in solar cells. To further enhance photocurrent in the c-Si solar cells, light absorption needs to be maximized and one way to achieve this is by reducing reflection losses from the cells. Black silicon (b-Si) is a semiconductor material produced by surface modification of c-Si. After the modification, the surface of
c-Si is covered by a layer of nanostructures or microstructures [3]. Due to this, broadband reflection losses are minimized through improved light coupling and light trapping by the b-Si nanostructures and microstructures respectively. This results in enhanced light absorption in 300-1100 nm wavelength region, hence photocurrent from the solar cells [4].

To fabricate b-Si, many methods have been investigated, including reactive ion etching (RIE) [5], plasma immersion ion implantation (PIII) [4] and femtosecond laser [6]. Metal-assisted chemical etching (MACE) is another approach being intensively studied due to its simplicity and low-cost nature. MACE includes one-step method; electroless metallization and etching of the c-Si surface in a single step and two-step method; deposition of noble metal such as Au or Ag on c-Si followed by chemical etching [7]. For two-step method, the metal deposition can be done via sputtering, evaporation, or in solution (i.e. via electrochemical or electroless deposition [8]). After that, the c-Si wafer is etched in aqueous solution of HF with an oxidizing agent. In the literature, various chemicals can be used as an oxidizing agent such as hydrogen peroxide (H2O2), potassium permanganate (KMnO4) and sodium persulfate (Na2S2O8) [9,10]. Nevertheless, H2O2 is the most commonly used oxidizing agent for the two-step MACE method. For the two-step approach, formation of porous Si has been reported by Chartier et al. by depositing Ag film through electroless metallization (using AgNO3 precursor) before etching in HF:H2O2:H2O [10]. In another work, Si nanowire arrays have been fabricated by two-step MACE. A thin Ag film was evaporated on c-Si wafer and annealed at low temperature for 10 min. This is followed by etching for 5-20 min, and 0.5-2 μm-long nanowires were produced. However, no optical results were shown in this work [11]. Recently, two-step MACE approach has been used to texture 500 μm-thick c-Si wafers by depositing 80 nm-thick Ag film by sputtering process. The c-Si wafers were then annealed at high temperature (300°C - 800°C) for 60 min and etched in HF:H2O2 solution for 30 min at 50°C [12]. To make the b-Si fabrication process more appealing, annealing of Ag film at low temperature can be combined with etching at short duration in the two-step MACE process. To date, this combination has not been systematically and thoroughly investigated [13].

This paper investigates the fabrication of b-Si absorber material by two-step MACE method, which combines low temperature annealing of Ag film with short etching duration of the c-Si wafer. The process involves Ag NPs produced from deposition of Ag thin film followed by a low-temperature annealing. Etching is carried out in HF:H2O2:DI H2O solution for 70 s with different etchant concentrations, represented in the form of volume ratio. The effects of etchant concentration towards surface morphologies and optical properties of b-Si are then analyzed. Maximum potential short-circuit current density (Jsc(max)) is calculated to relatively estimate the light coupling performance of b-Si, in the 300-1100 nm spectral region. The calculated potential Jsc(max) can be used to predict the maximum achievable photocurrent once the solar cell is fabricated on the optimized b-Si absorber material.

2. Experimental method

In this experiment, p-type mono c-Si wafers (250 μm thickness) with 1-10 Ω.cm resistivity are used as the substrate. The wafers are pre-cleaned using RCA technique to remove contaminations. To fabricate b-Si, the c-Si wafers are deposited with 15 nm of Ag film using RF sputtering. To produce Ag NPs, the wafers are annealed for 40 min at 230°C in N2 atmosphere (with flow rate of 2 L/min) [14,15]. The wafers are then etched in aqueous solution which contains HF (50%): H2O2 (30%): DI H2O [4, 14]. The volume ratio of the solution is given as X:Y:Z, corresponding to the volume of HF, H2O2 and DI H2O respectively. The volume ratios used in this experiment are 1:5:5, 1:5:10 and 1:5:20. The etching is conducted at room temperature with 70 s of etching duration. After the etching, the b-Si wafers are
rinsed in DI H$_2$O and then cleaned by sonication in concentrated HNO$_3$ at room temperature to remove residues of Ag NPs from the b-Si wafers. The wafers are rinsed again with DI H$_2$O.

Surface morphology of the b-Si wafers is characterized by Field Emission Scanning Electron Microscopy (FESEM). FESEM is used to study and characterize the top view and cross section of the b-Si nanopores. From the FESEM images, ImageJ software is used to analyze average diameter, surface coverage and interparticle distance of b-Si nanopores on the wafer. To investigate the optical properties of the b-Si, hemispherical reflection (R) is measured using Cary 5000 UV-Vis-NIR spectrophotometer which is equipped with an integrating sphere. From the reflection measurement, absorption (A) is calculated using equation $A=100\%−R−T$. Since the wafer is opaque, transmission (T) is assumed to be zero. From the absorption result, light coupling performance of b-Si is assessed, using a concept of potential $J_{sc(max)}$ (see Eq. 1 below) for 300-1100 nm spectral region [16].

$$J_{sc(max)} = q \int E Q E(\lambda).S(\lambda) d\lambda$$

(1)

In Eq. 1, q is the electron charge and $S(\lambda)$ is the standard spectral photon density of sunlight for AM1.5 solar spectrum. The calculation assumes unity charge collection in the b-Si absorber.

3. Results and discussions

Figure 1 shows images of c-Si reference (untextured) and b-Si wafers fabricated by two-step MACE process with varying etchant concentration. With volume ratio of 1:5:5, the c-Si wafer turns to silver-grey in colour. After the MACE process, with 1:5:10 and 1:5:20 volume ratios, the c-Si wafers turn to be dark black. To better understand how the varying etchant concentration affects surface morphological properties of the wafers, FESEM images are shown below.

![Figure 1](image_url)

Figure 1. The images of c-Si reference and b-Si produced with varying etchant concentration; (a) reference c-Si (b) 1:5:5 (c) 1:5:10 (d) 1:5:20.

![Figure 2](image_url)

Figure 2. Top view SEM images of b-Si wafers fabricated using different etchant concentrations (HF:H$_2$O$_2$:DI H$_2$O) (a) 1:5:5 (b) 1:5:10 (c) 1:5:20.

To obtain more information on the effect of the varying volume ratio on the surface morphological properties of the b-Si wafers, FESEM imaging is carried out and the images are illustrated in Figure 2. After the etching, dense nanopores can be seen on the wafer surface after Ag NPs are removed by HNO$_3$. 
C-Si wafer with volume ratio of 1:5:5 results in nanopores with an average diameter of 101.2 nm. Surface coverage of the nanopores is about 40%. The nanopores are big in diameter and are scarce on the wafer surface. Some areas on the wafer are still flat and untextured. This morphology is responsible for the silver-grey colour of the wafer after the MACE process, as previously shown in Figure 1. With etchant concentration of 1:5:10, the nanopores exhibit lower average diameter (84.1 nm) with increased surface coverage (51%). The wafer surface is densely packed with the random b-Si nanopores. B-Si wafer with etchant concentration of 1:5:20 produces nanopores with an average diameter of 74.9 nm. Surface coverage of the nanopores reduces to 45%.

Figure 3. (a) Reflection and (b) absorption curves of b-Si wafers after being etched in different etchant concentrations. C-Si reference is used for comparison. Values of reflection and absorption at wavelength of 600 nm are included in the legends.

Figure 3 (a) and (b) demonstrate hemispherical total reflection and absorption of b-Si wafers after being etched in different etchant concentrations. C-Si reference wafer is included for comparison. The wavelength of 600 nm of main interest since it is the peak of the AM1.5 solar spectrum [17]. At wavelength of 600 nm, the c-Si reference has 35% reflection. After the MACE process, the b-Si wafer etched with volume ratio of 1:5:10 demonstrates lower broadband (300-1100 wavelength region) reflection when compared to the c-Si reference. The reflection is around 3% at wavelength of 600 nm. This can be attributed to the effect of refractive index grading by the dense b-Si nanopores on the wafer, which leads to increased light coupling into the c-Si absorber [14,18,19]. This results in enhanced light absorption throughout the spectral region [4]. On the other hand, the wafers etched with volume ratios of 1:5:5 and 1:5:20 show lower reflection only from wavelength of 300 nm up to 930 nm, when compared to the reference. This is expected for the wafer with 1:5:5 volume ratio since some of the areas on the wafer are still flat and untextured, as previously shown by the top view SEM images. The reflection only reduces to 12% (at 600 nm). The reflection profile for the wafer with 1:5:20 volume ratio resembles the profile for the wafer with 1:5:5 ratio even though the surface exhibits formation of denser nanopores. The slightly bigger nanopores on the wafer (if compared with 1:5:10 ratio) is believed to cause escape reflection from the wafer and this is observed as a high reflection in the long wavelength region (above 800 nm). In the visible region, the light absorption for the b-Si with 1:5:20 volume ratio almost matches with the b-Si produced by 1:5:10 ratio, but it is lower beyond 800 nm wavelength. From the optical results, it is evident that the volume ratio of 1:5:10 gives the highest broadband light absorption. The enhanced broadband absorption is required to enable higher photocurrent from the solar cell fabricated on the b-Si absorber.
Figure 4. Average interparticle distance and reflection (at 600 nm) of b-Si wafers after etching in different etchant concentrations. Figure 5. Cross-sectional SEM image of b-Si wafer after being etched with 1:5:10 etchant concentration. The reflection of this sample is 3% at 600 nm.

Figure 4 shows the relationship between average interparticle distance of b-Si nanopores and reflection (at wavelength 600 nm) after being etched in HF:H₂O₂:DI H₂O solution with different concentrations (i.e. volume ratios). The interparticle distance of the b-Si nanopores is extracted from the top view SEM images using ImageJ software. The figure shows that higher interparticle distance (i.e. bigger nanopore size) leads to higher reflection at wavelength of 600 nm. The b-Si wafer etched in 1:5:10 has the smallest interparticle distance of 30.4 nm, which leads to the lowest reflection (3%) at wavelength of 600 nm. The interparticle distance increases to 47.2 nm for volume ratio of 1:5:20 which results in higher corresponding reflection (6%) at the same wavelength. The volume ratio of 1:5:5 gives the longest interparticle distance (153.7 nm). As a result, this leads to the highest reflection (12%). From the results, it is crucial to optimize the etchant concentration (i.e. volume ratio) to produce densely packed nanopores that can couple maximum incident light into the b-Si absorber for maximum photogeneration of electron-hole pairs.

Figure 5 exhibits image of cross-sectional SEM for the b-Si nanopores prepared using volume ratio of 1:5:10, which gives the highest broadband light absorption in the 300-1100 nm spectral region. The image shows that the nanotextures are uniformly formed on the surface. The nanotextures have average pillar width of about 50 nm and height of 300 nm. The dimension of the textures leads to increased light coupling into the b-Si since the surface is seen as a homogenous medium with a gradually increasing refractive index (n) (from air with n=1 to bulk Si with n=3.6) by the incident light [20]. This results in low reflection from the surface and causes the surface to appear black.

| Etchant concentration (Volume ratio) | Potential J_{sc(max)} (mA/cm²) | Potential J_{sc(max)} enhancement (%) |
|-------------------------------------|---------------------------------|--------------------------------------|
| c-Si reference                      | 26.3                            | -                                    |
| 1:5:5                               | 34.6                            | 30.4                                 |
| 1:5:10                              | 40.9                            | 55.4                                 |
| 1:5:20                              | 36.9                            | 40.3                                 |
Table 1 summarizes potential $J_{sc(max)}$ of the b-Si wafers after being etched in different etchant concentrations. Potential $J_{sc(max)}$ enhancement is also calculated, which uses $J_{sc(max)}$ of the c-Si wafer as the reference. The c-Si reference has potential $J_{sc(max)}$ of 26.3 mA/cm$^2$. When etched with volume ratio of 1:5:5, the b-Si wafer results in potential $J_{sc(max)}$ of 34.6 mA/cm$^2$, which represents 30.4% enhancement when compared to c-Si reference. The enhancement is due to the lower reflection by the b-Si nanopores which enhances the coupling of the incident light in 300-930 nm wavelength region. With volume ratio of 1:5:10, the potential $J_{sc(max)}$ improves up to 40.9 mA/cm$^2$, or 55.4% enhancement. This owes to the low broadband reflection by the dense nanopores on the surface, which leads to efficient light coupling and enhanced light absorption in the b-Si absorber. This volume ratio represents the highest potential $J_{sc(max)}$ obtained in this work. Volume ratio of 1:5:20 gives potential $J_{sc(max)}$ of 36.9 mA/cm$^2$ (40.3% enhancement). When compared with 1:5:10 volume ratio, this is expected since the b-Si nanopores for the 1:5:20 ratio have lower surface coverage. From this analysis, it can make concluded that the volume ratio of 1:5:10 gives in the highest potential $J_{sc(max)}$ in the b-Si absorber, in the 300-1100 nm spectral region. The calculation provides a theoretical benchmark of the maximum achievable photocurrent that can be obtained once solar cell based on the optimized b-Si absorber is fabricated in the future.

4. Conclusion

In this paper, surface morphologies and optical properties of b-Si fabricated with different etchant concentrations have been investigated. The work combines low temperature annealing of Ag thin film and short etching duration of the c-Si during the two-step MACE process to produce b-Si nanopores on the wafer. From surface morphological results, c-Si wafer etched with volume ratio of 1:5:5 exhibits nanopores with an average diameter of 101.2 nm with surface coverage about 40%. Some areas on the wafer are still untextured. With ratio of 1:5:10, the wafer surface is covered dense and random b-Si nanopores. The nanopores exhibit lower average diameter (84.1 nm) but surface coverage increases to 51%. B-Si wafer with etchant concentration of 1:5:20 produces nanopores with diameter of 74.9 nm with surface coverage of 45%.

The b-Si wafer etched with volume ratio of 1:5:10 demonstrates lower broadband (300-1100 wavelength region) reflection when compared to the c-Si reference. The reflection is 3% at wavelength of 600 nm, which can be attributed to refractive index grading effect by the dense b-Si nanopores on the wafer surface. This enhances light absorption throughout the entire 300-1100 nm wavelength region. The wafers etched with volume ratios of 1:5:5 and 1:5:20 show lower reflection only from wavelength of 300 nm up to 930 nm, when compared to the c-Si reference. The findings show that higher interparticle distance leads to higher reflection. The b-Si wafer etched in 1:5:10 has the smallest interparticle distance of 30.4 nm, which is responsible for the lowest reflection (3%) at wavelength of 600 nm. The interparticle distance increases to 47.2 nm for volume ratio of 1:5:20 which results in higher corresponding reflection (6%). The volume ratio of 1:5:5 gives the longest interparticle distance (153.7 nm), which produces the highest reflection (12%) when compared to other b-Si wafers. The sample with volume ratio of 1:5:10 which exhibits the lowest broadband reflection has b-Si nanotextures with 50 nm width and 300 nm height. When etched with volume ratio of 1:5:5, the b-Si wafer has potential $J_{sc(max)}$ of 34.6 mA/cm$^2$ (30.4% enhancement in comparison to c-Si reference). The enhancement is due to the lower reflection by the b-Si nanopores which increases light coupling in 300-930 nm wavelength region. With volume ratio of 1:5:10, the potential $J_{sc(max)}$ increases up to 40.9 mA/cm$^2$ (or 55.4% enhancement). This volume ratio represents the highest potential $J_{sc(max)}$ obtained in this work, owing to efficient light coupling into the b-Si absorber. Volume ratio of 1:5:20 gives the potential $J_{sc(max)}$ of 36.9 mA/cm$^2$ (40.3% enhancement).
5. References

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Acknowledgment

Authors would like to thank Universiti Sains Malaysia (USM), Penang, for funding this research through Short-Term Grant 304/PFIZIK/6315063.