Effects of silver nanoparticles layer thickness towards properties of black silicon fabricated by metal-assisted chemical etching for photovoltaics

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Abstract

This paper investigates effects of silver nanoparticles (Ag NPs) layer thickness towards properties of black silicon (b-Si) fabricated by two-step metal-assisted chemical etching for potential application in photovoltaic (PV) devices. Ag NPs with different layer thicknesses (1.3–5.1 μm) are deposited on monocrystalline silicon (mono c-Si) wafers by electroless chemical deposition in AgNO_3/HF aqueous solution for 10–40 s. This is followed by etching in $\text{HF}:\text{H}_2\text{O}_2:\text{DI H}_2\text{O}$ aqueous solution for 20 s. Surface morphological investigation confirms presence of b-Si nanowires with height of 250–577 nm and diameter of 100–200 nm. The b-Si nanowires suppress broadband reflectance from the wafers over 300–1100 nm wavelength region, due to refractive index grading effect. Sample with Ag NPs layer thickness of 5.1 μm exhibits b-Si nanowires with average height of 577 nm and average diameter of 200 nm after etching. This sample demonstrates the lowest weighted average reflectance of 5.5% compared to other samples. This sample exhibits absorption of 96.5% at wavelength of 600 nm. The enhanced broadband light absorption leads to maximum potential short-circuit current density ($J_{\text{sc(max)}}$) of 39.7 mA/cm^2 , or 51% relative enhancement compared to planar reference sample.

Keywords Silver nanoparticles · Black silicon · Absorption · Short-circuit current density

1 Introduction

Crystalline silicon (c-Si) solar cells dominate about 95% of photovoltaic (PV) market due to technology maturity and economies of scale [1]. This is despite the c-Si's low absorption coefficient and high broadband reflection (around 40%) in 300–1100 nm wavelength region. To decrease the broadband reflection, alkaline texturing using potassium hydroxide (KOH) or sodium hydroxide (NaOH) has been employed by PV researchers and manufacturers. This is carried out to produce micron-sized random pyramidal textures on c-Si wafer surface. The pyramids improve light coupling, light scattering and absorption which result in higher short-circuit current density (J_{sc}) in solar cells. However, alkaline texturing can only suppress the broadband

reflection to around 10% [2]. To further reduce the reflection, a thin layer of silicon nitride (SiN_x), silicon oxide (SiO_x), titanium oxide (TiO_x) or indium tin-oxide (ITO), with intermediate refractive index between those of air and c-Si is usually used as an anti-reflective coating (ARC) on the pyramids [2]. This additional process step adds manufacturing cost hence technology cost (US $\$/\text{W}_p$) for the c-Si solar cells.

Black silicon (b-Si) is a promising alternative that offers low broadband reflection for c-Si within 300–1100 nm wavelength region. B-Si comprises nanowires on the surface of c-Si wafer, which increase broadband light coupling into the solar cells through refractive index grading effect [3]. B-Si can be fabricated via various approaches, ranging from chemical to a combination of physical and

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chemical methods such as metal-assisted chemical etching (MACE), reactive ion etching (RIE) and plasma immersion ion implantation (PIII) [4]. Among these methods, MACE is the most promising, facile and low-cost in nature. MACE can reduce broadband reflection of the c-Si to lower than 10%, without the need of additional ARC [5]. MACE can be carried out by two approaches; one-step and two-step processes [6]. In two-step MACE, nanoparticles (NPs) of noble metals (e.g. silver (Ag), gold (Au), copper (Cu)) are deposited either in a chemical solution, spin coating, sputtering or thermal evaporation followed by subsequent etching in hydrofluoric acid/hydrogen peroxide (HF/H₂O₂) solution [7, 8]. This method produces b-Si nanowires of 250–1000 nm in lengths with similar suppression of broadband reflection compared to one-step MACE [9]. Smith et al. studies the effects of silver nanoparticles (Ag NPs) diameter and percentage coverage on b-Si formation in two-step MACE process [10]. This is done by alternating the Ag NPs deposition time prior to etching. In their studies, three regions of Ag NPs growth were presented; region where Ag NPs grows linearly with deposition time, region where Ag NPs diameter and Ag NPs percentage coverage on c-Si surface does not change with deposition time and region where Ag NPs diameter size increases with deposition time without increase in Ag NPs surface coverage. Li et al. reported an investigation on the effects of Ag NPs deposition time on morphology and structures of b-Si nanowires fabricated by two-step MACE [11]. In their work, it was observed that density of b-Si nanowire arrays decreases with increasing Ag NPs deposition. Besides, Ag NPs diameter was smaller and was more uniform with increasing deposition time. It was concluded that Ag NPs deposition time has small influence on b-Si nanowires growth rate. Recently, Nichkalo et al. investigated the role of Ag NPs morphology and AgNO₃ molarity on the size of b-Si nanowires produced by two-step MACE [12]. From their findings, it was demonstrated that the Ag NPs diameter and surface density increased with deposition time and larger Ag NPs were formed with longer deposition time, which adversely affected the morphology of the b-Si nanowires to the best of our knowledge, there has been no reported work addressing the effects of Ag NPs layer thickness towards properties of b-Si nanowires produced by two-step MACE process.

This paper reports the effects of Ag NPs layer thickness on formation of b-Si nanowires based on two-step MACE process. Surface morphological properties of Ag NPs and b-Si nanowires are investigated. Besides, optical properties of the b-Si nanowires are characterized. From absorption results, maximum potential photocurrent (or $J_{sc(max)}$) is calculated to relatively estimate maximum photocurrent that can be realized when solar cells are fabricated on the b-Si absorber. Relationship between Ag NPs layer thicknesses,

length of b-Si nanowires, broadband reflection and $J_{sc(max)}$ for each sample are also analyzed and discussed.

2 Materials and methods

P-type 250 µm-thick mono c-Si wafer with resistivity of 1–10 Ω cm is used as substrate in this work. Prior to experiments, Radio Corporation of America (RCA) cleaning process is performed to clean and remove organic residues, oxide layer and metallic contaminants on wafer surfaces [13]. Silver nitrate (AgNO₃) with 169.87 g/mol (from Sigma Aldrich) and HF with 20 g/mol (49%) are used to deposit Ag NPs on the wafer. For this purpose, AgNO₃:HF solution with volume ratio of 5:6 (total volume of 110 ml) is prepared in a polypropylene beaker. Then, the c-Si wafers are dipped in this solution at room temperature for different times (10 s, 20 s, 30 s and 40 s) to deposit Ag NPs with different layer thicknesses. This is followed by etching in a solution of HF:H₂O₂:DI H₂O with 2:1:5 volume ratio (total volume of 80 ml) for 20 s. After the etching, the Ag NPs are removed using concentrated Nitric acid (HNO₃) (60%) in sonication bath for 5 min. Then, native oxide on the b-Si is removed by a 15 s dip in 5% HF.

Field Emission Scanning Electron Microscopy (FESEM) (model: FEI Nova NanoSEM 450) is used to characterize top 30° oblique surface morphological and cross-sectional properties of Ag NPs layers and b-Si nanowires. ImageJ software is used to analyze the FESEM images and calculate average diameters of Ag NPs. Atomic Force Microscopy (AFM) (model: Dimension EDGE, BRUKER) is used to study height and root mean square (RMS) roughness of b-Si nanowires. For the AFM, scan range of 10 × 10 µm² and resolution of 512 pixels are used. Hemispherical reflection is measured by Cary 5000 UVVISNIR spectrophotometer (equipped with an integrating sphere) over 300–1100 nm wavelength region. To assess light coupling performance of the b-Si nanowires, weighted average reflectance (WAR%) is calculated by integrating the reflection of the b-Si nanowires with AM1.5G solar spectrum over 300–1100 nm wavelength region. This is expressed in Eq. (1) [14, 15], where $R(\lambda)$ is the reflection and $S(\lambda)$ represents the AM1.5G solar spectrum.

$$WAR = \frac{\int_{300nm}^{1100nm} R(\lambda)S(\lambda)d\lambda}{\int_{300nm}^{1100nm} S(\lambda)d\lambda} \quad (1)$$

From the hemispherical reflection results, absorption (A) is calculated using $A = (100 - R - T)\%$. Transmission (T) is assumed to be zero as c-Si wafer is an opaque material, so that A is approximately (100 - R)%. From the absorption curve, potential $J_{sc(max)}$ is calculated using Eq. (2) [16, 17]. In

this equation, q is electron charge and $S(\lambda)$ is the standard spectral photon density for AM1.5G solar spectrum [17]. In the calculation, unity charge collection is assumed (i.e. internal quantum efficiency, $\text{IQE} = 1$, using the relationship $\text{EQE} = \text{IQE} \times A$). From the result, potential $J_{\text{sc(max)}}$ enhancement of the b-Si samples produced by Ag NPs layers with different thicknesses is calculated by normalizing their potential $J_{\text{sc(max)}}$ to that of the reference c-Si wafer.

$$J_{\text{sc(max)}} = q \int_{300 \text{ nm}}^{1100 \text{ nm}} \text{EQE}(\lambda) \cdot S(\lambda) d\lambda \quad (2)$$

3 Results and discussion

Figure 1 presents c-Si wafers deposited with Ag NPs layers of different thicknesses. The deposition of Ag NPs starts when silver ions (Ag^+ ions) inject holes into valence band (VB) of c-Si as a result of interfacial electron exchange. Then, the Ag^+ ions are reduced to Ag NPs on c-Si surface [18, 19]. Immersing the c-Si in $\text{AgNO}_3:\text{HF}$ solution for duration of 10 s and 20 s produces Ag NPs on the wafer with average diameter of around 84.2 nm and 100.7 nm respectively, and surface coverage of about 70% in both cases, as revealed by ImageJ analysis. Cross-sectional FESEM images show that the thickness of the Ag NPs for both cases are 1.3 μm and 2.6 μm respectively. The Ag NPs start to grow cylindrically from the c-Si surface and later proceeds as vertical growth in the form of layers. This is as the result of

continuous Ag^+ ions coalescing on the previously formed Ag NPs as mentioned earlier. The phenomenon is more pronounced when the deposition time is increased to 30 s where Ag NPs thickness increases to 5.1 μm . For this layer, Ag^+ ions migrate to energetically favored sites (sites with already grown nuclei of Ag NPs instead on bare c-Si) and Ag NPs appear as slightly bigger dendrites with average diameter of 200.3 nm.

This is the reason for the slight decrease in Ag NPs density, surface coverage (to about 65%) and increased average inter-particle distance between Ag NPs. Similar findings are also reported by another work while fabricating b-Si nanowires on inverted pyramids [20]. Distribution of some etch pits are carefully observed between Ag NPs on c-Si for this Ag NPs layer thickness. This is because Ag NPs have since grown bigger (dendrites) and started to diffuse down into c-Si bulk (initial pits formation) as reported by other methods [10, 21]. When the deposition time is increased to 40 s, the deposited Ag NPs grow like bigger precipitates on c-Si surface and drop back into the $\text{AgNO}_3:\text{HF}$ solution. Due to this problem, the deposition is terminated. Ag NPs appears like tree branches conjoined on c-Si with slight decrease in average diameter (to 120.4 nm) when compared to 30 s deposited sample. This results in lower thickness of the Ag NPs (about 1.5 μm), as evident in the cross-sectional FESEM image (Fig. 1h).

To further elucidate the effect of Ag NPs layer thickness on formation of b-Si nanowires, subsequent immersion in $\text{HF}:\text{H}_2\text{O}_2:\text{DI H}_2\text{O}$ (2:1:5) aqueous etching solution is employed for 20 s. This results in H_2O_2 -aided HF etching

Fig. 1 Top oblique (30°) and cross-sectional FESEM images of Ag NPs layers with different thicknesses on c-Si produced using different deposition durations; **a, e** 10 s (thickness ~1.3 μm), **b, f** 20 s (thickness ~2.6 μm), **c, g** 30 s (thickness ~5.1 μm), **d and h**

40 s (thickness ~1.5 μm). The scale bar is with 1 μm length for top oblique (30°) images and 3 μm length for cross-sectional FESEM images

due to continuous galvanic displacement of c-Si via formation of many local nano-electrochemical cells (having reactions at cathode and anode) with Ag NPs acting as the catalyst. For the HF:H₂O₂:DI H₂O etching solution, it has been reported that potential energy of the redox pair H₂O₂/H₂O is 1.78 V while VB energy of c-Si is 0.62 V [10, 22]. It is therefore evident that potential energy of redox pair H₂O₂/H₂O is much more positive than the VB of c-Si. Due to this reason, H₂O₂/H₂O can then extract an electron from c-Si's VB or equally inject hole into the VB of c-Si (cathodic process) which is required for etching of c-Si. The current density (i.e. electrons extracted) of the cathodic process can be enhanced by reducing the activation energy of the process which will increase the rate of the reaction. Therefore, the catalytic activity of the Ag NPs is to enhance reduction in activation energy of the cathodic reaction, such that the reaction involving the reduction of H₂O₂ is greatly accelerated at the Ag NPs deposited regions of c-Si surface [19]. With Ag NPs on c-Si, electrons then move from c-Si to Ag⁺ ions faster. At contact vicinity between Ag NPs and c-Si, the c-Si underneath the Ag NPs becomes more positive than the areas without the Ag NPs. Therefore, as preferential reduction of H₂O₂ at the vicinity of the Ag NPs continues in the etching solution, concurrent oxidation of c-Si underneath the Ag NPs and its subsequent dissolution by HF takes place [23, 24]. With longer time, the oxidation and dissolution of c-Si beneath these conjoined (Fig. 1.) Ag NPs continues. This will result in downward movement of the conjoined Ag NPs along vertical path deeper into the c-Si bulk substrate. Due to this, the regions between the Ag NPs on c-Si are free from the etching process. This leads

to the formation of vertically aligned b-Si nanowires as presented in Fig. 2. Details on the mathematical equations of current density of the cathodic process and chemical equations of the two half reactions of the redox couple (reactions at cathode and anode) can be found in related literatures [25–27].

From Fig. 2, the top (30°) oblique and cross-sectional FESEM images of b-Si nanowires fabricated using different thicknesses of Ag NPs layer are presented. For Ag NPs layer thickness of 1.3 μm, b-Si nanowires (Fig. 2a, e) with nanowire length of about 250 nm are obtained. When Ag NPs layer thickness increases to 2.6 μm due to an extended Ag NPs deposition time (20 s), the b-Si nanowires appear denser (Fig. 2b, f) with an increase in length to around 322 nm after the etching. The diameter of the nanowires exhibits a slight increase when increasing the deposition time from 10 to 20 s. For 30 s deposition time (Ag NPs layer thickness of 5.1 μm), denser b-Si nanowires are formed on the surface. The nanowires have average length of 577 nm and average diameter of 206 nm (Fig. 2c, g). This can be attributed to the full dendrites formation during Ag NPs deposition as highlighted before. Behera et al. recently reported similar research findings while fabricating b-Si nanowalls via two-step MACE using Ag NPs as catalyst [27]. For the 40 s deposition (1.5 μm Ag NPs layer thickness), the length of the b-Si nanowires reduces to around 437 nm with a slight decrease in average diameter (about 130.4 nm) after etching (Fig. 2d, h). This is due to the damage of some initial pits formed during Ag NPs deposition before the deposition was terminated, as previously mentioned.

Fig. 2 Top oblique (30°) FESEM and cross-sectional FESEM images of 20 s etched b-Si nanowires produced using Ag NPs layers with different thicknesses; **a, e** 1.3 μm, **b, f** 2.6 μm, **c, g** 5.1 μm, **d, h** 1.5 μm. The scale bar is with 1 μm length

Figure 3 shows AFM images of b-Si nanowires produced using different Ag NPs layer thicknesses, followed by 20 s etching process. All samples are characterized by random and dense nanowires, which show a good corroboration with the FESEM images presented in Fig. 2. The height and lateral width of the nanowires increase with Ag NPs layer thicknesses between 1.3 and 5.1 μm and decrease to slightly lower value for sample with Ag NPs layer thickness of 1.5 μm after the etching. Besides, RMS roughness of the formed b-Si nanowires after etching exhibits an increasing trend with Ag NPs layer thicknesses between 1.3 and 5.1 μm and slightly decreases for sample with Ag NPs layer thickness of 1.5 μm prior to etching, which is in good agreement with the cross-sectional FESEM images. The RMS roughness values are 77.3 nm, 82.1 nm, 159.4 nm and 138.2 nm respectively.

The surface reflectance and absorption of b-Si nanowires fabricated with different Ag NPs layer thicknesses are presented in Fig. 4 for 300–1100 nm wavelength region.

For both curves, planar c-Si is used as a reference. The c-Si reference has WAR of 40%. This corresponds to about 60% of light absorption over the spectral region (300–1100 nm). After the b-Si nanowires formation, all samples demonstrate lower broadband reflectance, which leads to enhanced light absorption throughout the wavelength region. This is due to refractive index grading effect at the interface of air and b-Si caused by nanowires with dimensions lesser than the wavelength of the incident light [28]. This leads to increased broadband light coupling into the b-Si absorber. With Ag NPs layer thicknesses of 1.3 and 2.6 μm , the WAR reduces to 22.4 and 16.2% respectively after etching. When the Ag NPs layer thickness increases to 5.1 μm , WAR decreases further to 5.5% after etching process. This is attributed to the increased density of the b-Si nanowires on the c-Si surface as reported by other research findings [29, 30]. For 40 s deposition time (with Ag NPs layer thickness of 1.5 μm), the WAR increases to 13.3% after etching. This is expected since the length of

Fig. 3 AFM images of b-Si nanowires produced using different Ag NPs layer thicknesses (followed with 20 s etching time); **a** 1.3 μm , **b** 2.6 μm , **c** 5.1 μm , **d** 1.5 μm

Fig. 4 **a** Reflectance curves for b-Si nanowires etched at 20 s etching time with different Ag NPs layer thicknesses. **b** Absorption curves for b-Si nanowires etched at 20 s etching time with different

Ag NPs layer thicknesses. For both curves, reference c-Si (planar) is used for comparison

nanowires formed after etching is lower compared to the sample with 30 s deposition. From this work, after etching, sample with 5.1 μm Ag NPs layer thickness (before etching, which corresponds to 30 s Ag NPs deposition time) presents the lowest WAR (i.e. 5.5%) for the wavelength region of interest (300–1100 nm).

Table 1 summarizes length of nanowires, WAR and calculated $J_{sc(max)}/J_{sc(max)}$ enhancements of fabricated b-Si nanowires samples from different Ag NPs layer thicknesses on c-Si. From the table, potential $J_{sc(max)}$ of reference c-Si wafer is 26.3 mA/cm^2 . After 20 s of etching, samples with Ag NPs layer thicknesses of 1.3 μm and 2.6 μm present $J_{sc(max)}$ of 33.6 mA/cm^2 and 34.2 mA/cm^2 respectively. This represents 7.3 mA/cm^2 (27.8% enhancement) and 7.9 mA/cm^2 (30% enhancement) when compared to the reference c-Si. This enhancement contributed by enhanced light coupling by the b-Si nanowires which improves broadband absorption of the c-Si. For sample with Ag NPs layer thickness of 5.1 μm , the calculated potential $J_{sc(max)}$ increases significantly to

39.7 mA/cm^2 (51% enhancement compared to c-Si). This records the highest achievable value of the calculated potential $J_{sc(max)}$. This can be attributed to the formation of the denser dendritic Ag NPs on the wafer prior to the etching process. This is expected since the sample shows superior light absorption as presented in Fig. 4. For sample with Ag NPs layer thickness of 1.5 μm , the potential $J_{sc(max)}$ is 34.0 mA/cm^2 (29.3% enhancement compared to c-Si). This is 5.7 mA/cm^2 decrease in potential $J_{sc(max)}$ when compared to sample with Ag NPs layer thickness of 5.1 μm . The decrease is due to the increased WAR% of the sample. From these findings, it can be concluded that the WAR (hence light absorption) of all the samples is determined by the length of nanowires, which in turn depends on the Ag NPs layer thickness on c-Si prior to etching. These findings also establish a relationship between the Ag NPs layer thickness and its effect on potential $J_{sc(max)}$, which is dependent on the WAR within the 300–1100 nm region of the b-Si nanowires.

Table 1 Length of nanowires, WAR and calculated $J_{sc(max)}/J_{sc(max)}$ enhancements of fabricated b-Si samples with different Ag NPs layer thicknesses. C-Si is used as reference

Wafer sample	Ag NPs layer thickness (μm)	Length of nanowires (nm)	WAR (%)	Potential $J_{sc(max)}$ (mA/cm^2)	Potential $J_{sc(max)}$ enhancement (%)
Ref. c-Si	—	—	40.0	26.3	—
1	1.3	250	22.4	33.6	27.8
2	2.6	322	16.2	34.2	30.0
3	5.1	577	5.5	39.7	51.0
4	1.5	437	13.3	34.0	29.3

4 Conclusion

In this work, the effects of Ag NPs layer thickness on the properties of b-Si nanowires based on two-step MACE process have been investigated. Mechanism of b-Si nanowire formation in relation to size, dimension and Ag NPs layer thickness has been studied. From FESEM results, samples with Ag NPs layer thicknesses of 1.3 μm and 2.6 μm demonstrate b-Si nanowires with lengths of 250 nm and 322 nm respectively, with average diameters of ~ 100 nm after etching. When Ag NPs layer thickness increases to 5.1 μm , b-Si nanowires with 577 nm length and 200 nm diameter are formed. For Ag NPs layer thickness of 1.5 μm , a decrease in diameter and length of b-Si nanowires is observed.

For absorption results, samples with b-Si nanowires show decreased WAR over 300–1100 nm wavelength region compared to the planar reference c-Si. This owes to refractive index grading effect at air-c-Si interface due to the presence of b-Si nanowires. Samples with Ag NPs layer thicknesses of 1.3 μm and 2.6 μm exhibit WAR of 22.4% and 16.2% respectively. With Ag NPs thickness of 5.1 μm , WAR decreases to 5.5% due to the formation of densely packed b-Si nanowires. For the sample with 1.5 μm Ag NPs layer thickness, WAR slightly increases to 13.3% due to washing away of Ag NPs and damage of initially formed pits on c-Si sample.

Samples with Ag NPs layer thicknesses of 1.3 μm and 2.6 μm demonstrate $J_{\text{sc(max)}}$ of 33.6 mA/cm^2 and 34.2 mA/cm^2 respectively. This corresponds to 27.8% and 30.0% enhancement in $J_{\text{sc(max)}}$ compared to the c-Si reference sample. The sample with Ag NPs layer thickness of 5.1 μm shows the highest $J_{\text{sc(max)}}$ compared to all other samples, with 39.7 mA/cm^2 (51% enhancement). This is due to the formation of dense nanowires on the surface which leads to superior broadband absorption in the 300–1100 nm wavelength region. The $J_{\text{sc(max)}}$ for the sample with Ag NPs layer thickness of 1.5 μm reduces to 34.0 mA/cm^2 (or 29.3% enhancement) due to the terminated deposition.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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