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Study of metal assisted anisotropic chemical etching of silicon for high aspect ratio in crystalline silicon solar cells

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ABSTRACT

Textured surface is commonly used to enhance the efficiency of silicon solar cells by reducing the overall reflectance and improving the light scattering. In this study, a comparison between isotropic and anisotropic etching methods was investigated. The deep funnel shaped structures with high aspect ratio are proposed for better light trapping with low reflectance in crystalline silicon solar cells. The anisotropic metal assisted chemical etching (MACE) was used to form the funnel shaped structures with various aspect ratios. The funnel shaped structures showed an average reflectance of 14.75% while it was 15.77% for the pillar shaped structures. The average reflectance was further reduced to 9.49% using deep funnel shaped structures with an aspect ratio of 1:1.18. The deep funnel shaped structures with high aspect ratios can be employed for high performance of crystalline silicon solar cells.

1. Introduction

The textured surface morphologies are used to enhance the light absorbing capability of silicon solar cells by improved light scattering and lower reflectance [1–5]. The textured surface structures increased the light absorption and the short circuit current density (J_{sc}) of solar cells [1,20,21]. Various texturing techniques like wet chemical etching, mechanical grooving, laser sculpturing and plasma etching have been used to texture the crystalline silicon (c-Si) and glass substrates. The wet chemical etching is preferred due to the low cost and less experimental process steps [2]. If the etching reaction is same in any direction then the etching is known as isotropic etching, whereas anisotropic etching is to remove the material in specific directions to get often flat and intricate shapes. The alkali solution is commonly used to form pillar shaped (standard pyramid) structures for crystalline silicon solar cells since 1974 [3,8]. The surface texturing for funnel shaped (inverted pyramid) structure was introduced in 1989 for high efficiency of passivated emitter and rear cell structured (PERC) solar cells [4,5].

Recently, metal-assisted chemical etching (MACE) has attracted an increasing interests due to its simplicity and low cost. The MACE can also control the Si orientation of nanostructures (e.g., nanowire, pore) relative to the substrate. Recently, Chern et al. used non-lithographic patterning with metal-assisted-chemical etching (MACE), to produce silicon nanowire arrays with defined geometry and optical properties in a manufacturable fashion [11]. The influence of etching solution composition has been found to be an important parameter in metal-assisted silicon chemical etching as reported by Chartier et al. [9]. Few detailed studies of metal-assisted silicon chemical etching have been reported by Huang et al. [6] and Li [8].

In this paper, we reported the funnel and deep funnel shaped structures with various aspect ratios (ARs) by metal assisted chemical etching (MACE). Metal materials such as Ag, Pt, Au, etc. with lower electro-negativity were deposited on the silicon surface and then etching was carried out by using HF solution. Since the oxidation occurred actively around the metal, the direction of etching was along the metal, vertical to the surface. The MACE method is quite simple to reduce the reflectance by light trapping [6,7]. The porous and oxide layers were formed at the reacted surfaces as the etching was carried out [9]. These layers need to be removed for the solar cells as they act as surface defects. The surface was partially etched by MACE and then the defects were removed by damage remove etching (DRE). Since the surface was etched by DRE, deep funnel shaped structures were realized by controlling

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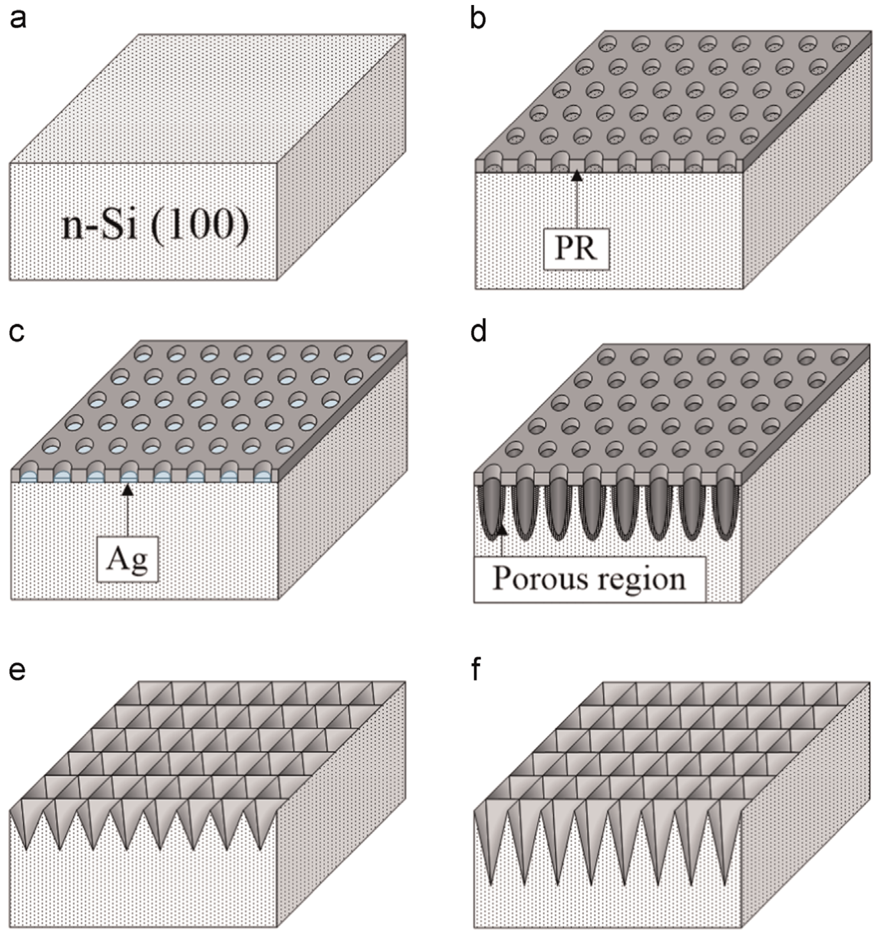

Fig. 1. Processing steps for the funnel shaped structures with metal assisted chemical etching: (a) silicon wafer; (b) photoresist (PR) pattern; (c) deposition of Ag by electrolysis metal deposition; (d) metal assisted chemical etching; (e) funnel shaped structures; and (f) deep funnel shaped structures.

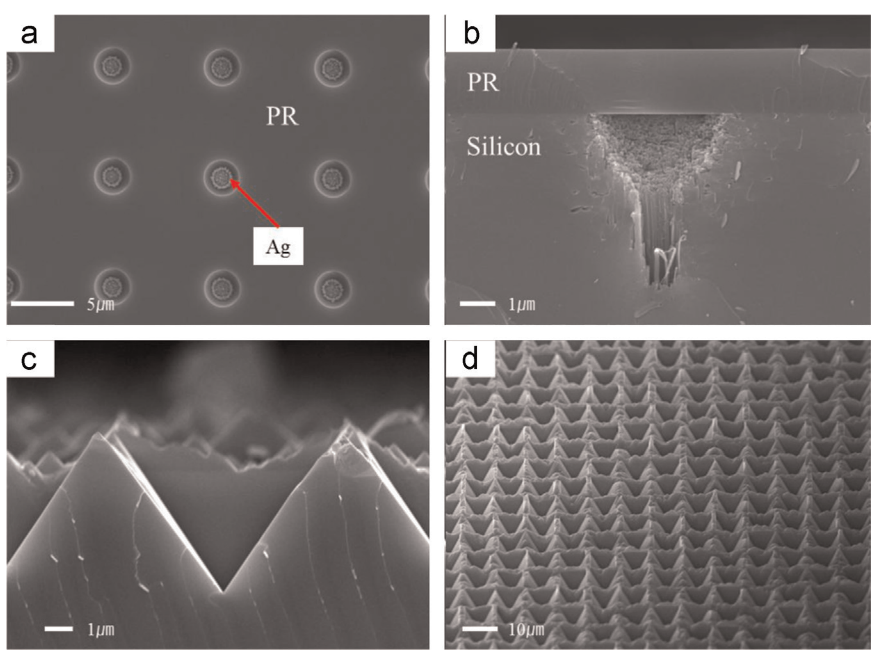

Fig. 2. SEM images for funnel shaped structure process: (a) photoresist pattern and Ag deposit; (b) metal assisted chemical etching; (c) cross section view; and (d) tilted view of funnel shaped structures.

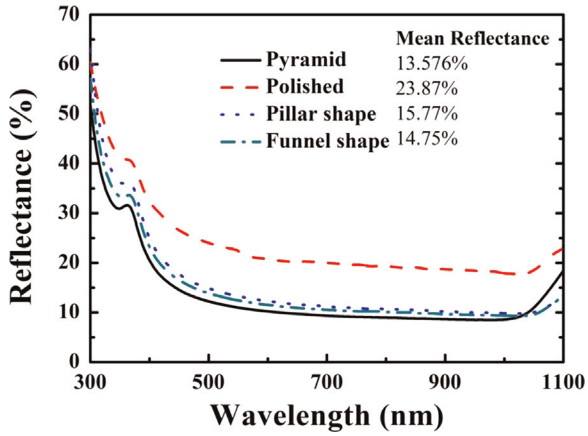

Fig. 3. Reflectance of polished and random pyramid silicon wafer along with pillar and funnel shaped structure.

the DRE solution. Both isotropic acid solution and anisotropic alkali solution were used for DRE.

2. Experimental details

We used mono-crystalline n-type silicon wafer with the thickness and resistivity of 550 μm and 1–10 Ω cm, respectively. The RCA (Radio Corporation of America) cleaning processes SC1 ($NH_4OH:H_2O_2:H_2O=1:1:6$, 75 °C, 10 min), SC2 ($HCl:H_2O_2:H_2O=1:1:6$, 85 °C, 10 min) and HF dip (3 min) were used to remove the native oxide and metallic impurities on the wafer surface. Positive photo-resist (PR) (AZ-7220) layer was deposited on the silicon surface by spin coater, followed by soft baking for 10 min at 110 °C. The round shape patterns with the dimension of $(3\times 6)\ \mu m^2$ were transferred onto the PR by ultra-violet (UV) photo-lithography process. Fig. 1(b) showed the schematic diagram of circular

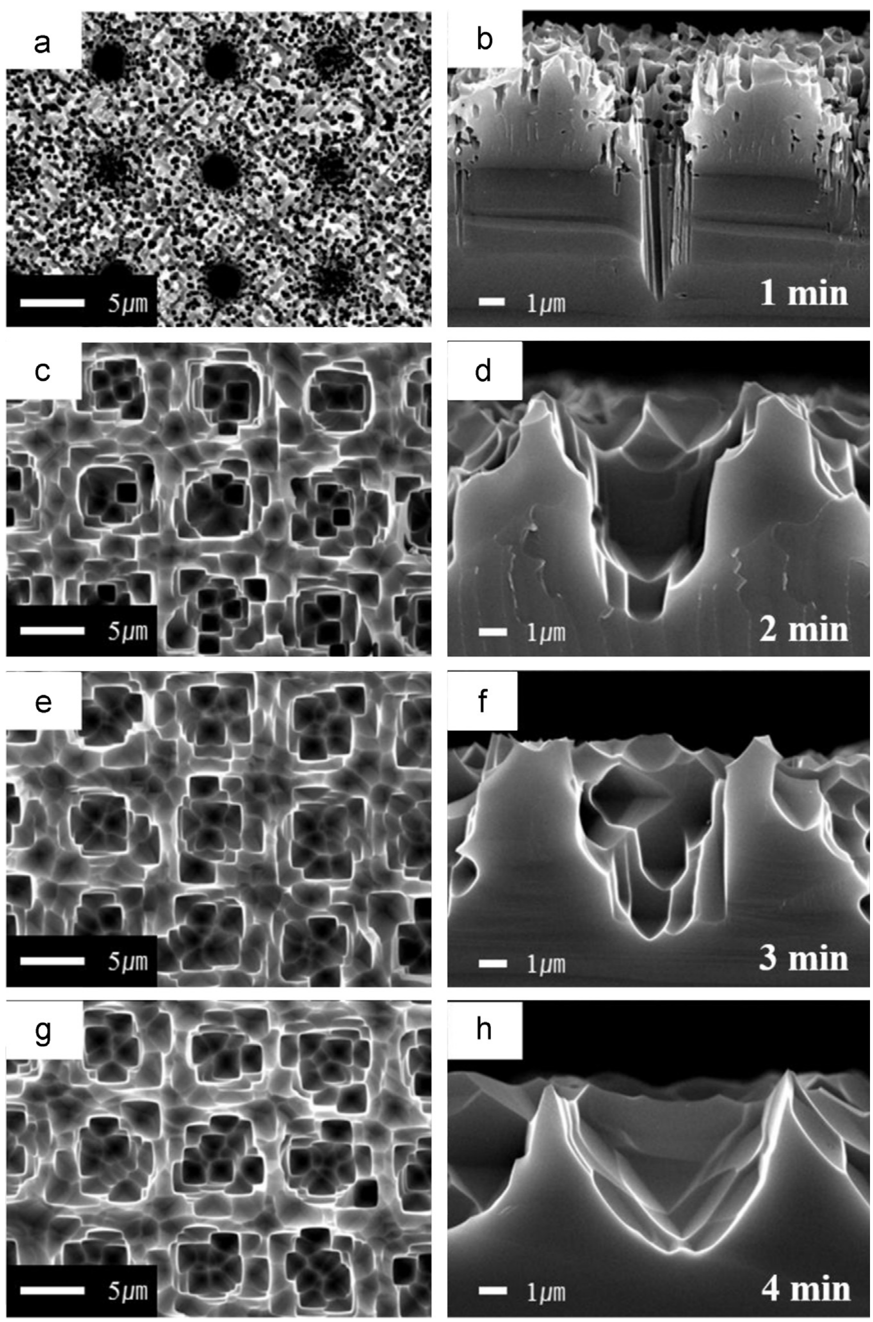

Fig. 4. SEM images of deep funnel shaped structure by isotropic etching for various etching times. Top and cross section view for: (a) and (b) 1 min; (c) and (d) 2 min; (e) and (f) 3 min; (g) and (h) 4 min.

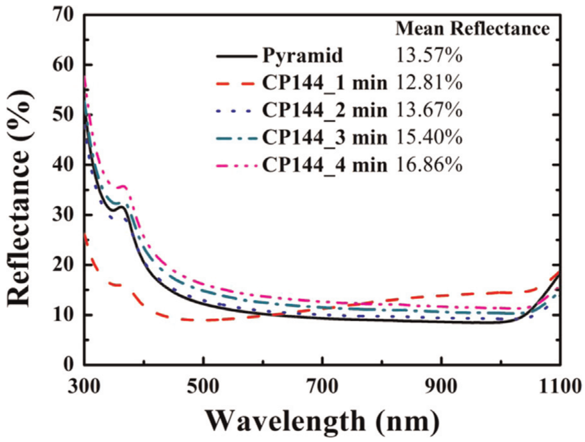

Fig. 5. Reflectance of deep funnel shaped structures by isotropic etching for various etching times.

patterns with the width and spacing of 3 μm and 6 μm, respectively.

The Ag metal was deposited on exposed silicon surface by $AgNO_3$ as shown in Fig. 1(c). The 0.6 μm thick Ag layer was obtained by reacting with HF (4.8 M) and $AgNO_3$ (0.01 M) for 5 s. The MACE process was carried out by reacting HF (4.8 M) and H_2O_2 (0.5 M) solutions at room temperature under dark condition [9]. The porous layer was formed after the MACE was removed by acid ($HF:HNO_3:CH_3COOH=1:4:4$, RT) or alkali solution ($NaOH:IPA:H_2O=2:10:88$, 90 °C).

The surface analysis (top and cross section view) of the etched surface was carried out by Field Emission-Scanning Electron Microscope (FE-SEM JSM-7600F). The reflectance was measured by QE/IPCE measurement system (quantum efficiency/incident photon to charge carrier efficiency).

3. Results and discussion

3.1. Funnel shaped structure

Fig. 2(a) shows the SEM image of Ag deposited circular patterns with width and spacing of 3 and 6 μm, respectively. The metal-assisted-chemical etching of Ag deposited circular patterns was performed by HF and H_2O_2 solutions with an etching rate of 0.5 μm/min. The etching direction of MACE was affected by the chemical solution ratio, temperature and surface conditions and not much by the substrate orientation [6,8]. The vertical etching was usually preferred for the metal-assisted-chemical etching [10,11]. The cross sectional view of the MACE with circular patterns was shown in Fig. 2(b). The top Ag deposited surface was mainly etched horizontally as well as vertically to form bowl like structure while the bottom surface was etched vertically to form a pit shape. Initially, the top surface of silicon in contact with Ag was etched horizontally and vertically. As the time passes by (10 min) the position of Ag got lowered and only vertical etching was proceeded. The upper surface without Ag was etched isotropically by HF and H_2O_2 to form a bowl like structure covering around 35% of total etching [9]. The maximum etching depth was recorded as 4.93 μm. The porous layer should be removed to reduce the surface recombination. The alkali solution was needed to obtain funnel shaped structures [4]. The angle of funnel as well as pillar shaped structure was around 54.74° with an aspect ratio of 1:0.7. The metal-assisted-chemical etching was carried out for 12 min. The remaining Ag was removed by HNO_3 and the photoresist (PR) was removed by acetone. The alkali solution ($NaOH:IPA:H_2O=2:10:88$, 90 °C) was used to obtain the funnel shaped structures. Fig. 2(c) and (d) shows the cross section and tilted view of the funnel shaped structures for the etching time of 5 min. Special attention should be given to the etching time as the etching process using alkali solution has to remove the porous layer that was created during MACE. Over etching for more than 5 min can damage the funnel shaped structures and result in pillar shaped structures formed by general texturing.

Fig. 3 shows the reflectance of different etching surfaces. The reflectance of polished c-Si wafer was 23.87%. The reflectance (13.57%) of random pyramid textured silicon wafer was included for the reference purpose. The reflectance of funnel shaped structures was recorded around 14.75% which was 1% less than that of random pillar shaped structures with the reflectance of 15.77%. The funnel shaped structures showed slight high reflectance in the wavelength range (300–400 nm). Recently, Finch et al. reported that even though the funnel shaped structures showed the less reflectance compared to the pillar shaped structures, it was difficult to enhance the current density of the solar cells [5]. To enhance the current density of solar cells the deep funnel shaped structure was required [12]. The higher aspect ratio can be achieved by increasing etching time of the metal-assisted-chemical etching.

3.2. Deep funnel shaped structure

Deep funnel shaped structures can be achieved by higher aspect ratio as shown in Fig. 1(f). To obtain the deep funnel shaped structures (~15 μm) with more than 1:1 aspect ratio, metal-assisted-chemical etching time was increased to 30 min. The MACE etching can be either isotropic or anisotropic. The chemical solution was used for removing surface defects, control of pyramid angles and to etch polycrystalline (CP144) silicon wafer [13,18]. The mixing ratio was chosen so that the aspect ratio and angle obtained from MACE could be maintained [14,17]. The etching rate was 2 μm/min and the maximum etching time was 3 min to have an aspect ratio of 1:1.

Fig. 4 shows the SEM images of silicon wafer for various etching times. There exists a porous layer after etching time of 1 min as shown in Fig. 4(a) and (b). Fig. 4(c) and (d) shows the top and cross sectional views for etching time of 2 min. The etching depth and aspect ratio was recorded as 8.58 μm and 1:0.95, respectively. Since the surface area of porous layer was large enough, the aspect ratio of 1:1 was achieved for 3 min due to active reaction. Further increase of etching time decreased the aspect ratio. Fig. 4(g) and (h) shows the top and cross sectional views for the etching time of 4 min. The surface structure for 4 min showed the etching depth of 6.4 μm with an aspect ratio of 1:0.71 that was the same as in the case of funnel shaped structure.

Fig. 5 shows the reflectance of deep funnel shaped structure for various etching times. The reflectance of deep funnel shaped structure increased from 12.81% to 16.86% with the increase of etching time from 1 min to 4 min. For the case of 1 min etching, the reflectance was lower in the range of (300–600 nm) but was higher in the range of (800–1100 nm). The surface roughness had more influence on the shorter wavelength region as shown in Fig. 5 [15]. The reflectance of the funnel shaped structure increased with the isotropic etching time as the angle decreased. The reflectance for 3 min of etching time was 15.41% almost similar to that of pillar shaped structure. Even though the etching time of 1 min showed the lowest reflectance of 12.91%, it was difficult to apply for the solar cells due to the presence of porous layer. The funnel shaped structure for 2 min of etching time showed the reflectance of 13.67% that was better than the pillar shaped structure due to surface morphology and reflectance. Therefore, the better results were obtained by etching with CP144 for 2 min with isotropic etching.

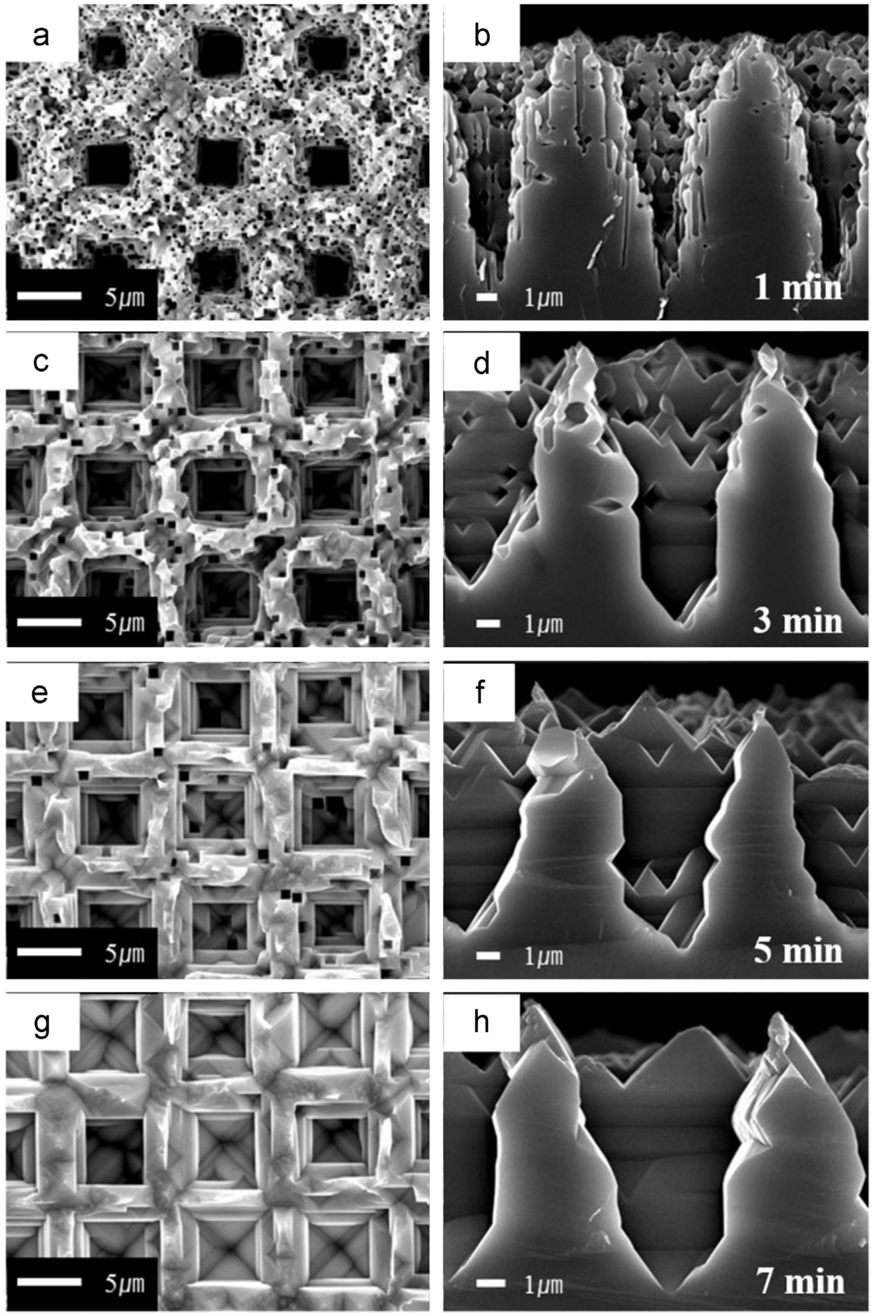

Fig. 6. SEM images of deep funnel shaped structure by anisotropic etching for various etching times. Top and cross section view for: (a) and (b) 1 min; (c) and (d) 3 min; (e) and (f) 5 min; (g) and (h) 7 min.

The alkali solution (NaOH:IPA:H_2O = 2:10:88, 90 °C) was used to obtain the deep funnel shaped structure. The etching rate of 0.5 μm/min with maximum etching time of 10 min was required to achieve the aspect ratio of 1:1. Fig. 6 shows the SEM images of deep funnel shaped structure by anisotropic etching for various etching times. It can be easily seen that the size of porous layer initially increased and then was removed with the increase of etching time. The aspect ratio of the deep funnel shaped structure decreased and then saturated with the etching time but angle of structure was decreased. After 7 min of etching time the porous layer was completely removed with an aspect ratio of 1:1.11.

Fig. 7 shows the reflectance of deep funnel shaped structure for various etching times by alkali solution. The reflectance of random pyramid textured silicon wafer is included for the reference purpose. For the etching time of 1 min, the reflectance was 12.81% that was lower than that of pillar shaped structure. The low reflectance was caused by higher light trapping and light path through porous layer. However, it had relatively higher reflectance in the longer wavelength range as it was less affected by surface structural characteristics [16–18]. As a result of highly porous layer on the surface, lower reflectance occurred at deep places. The damage remove etching removed the porous layer and the size of holes increased. The reflectance of deep funnel shaped structure decreased as a result of higher light trapping and light path length through the holes. The reflectance was decreased with the increase of etching time from 1 min to 5 min. The porous layer was completely removed and the lowest reflectance of 9.49% was achieved. After 5 min of etching time, the reflectance was further increased as the angle of the surface structure decreased [12]. A relatively higher reflectance of 11.55% occurred for the etching

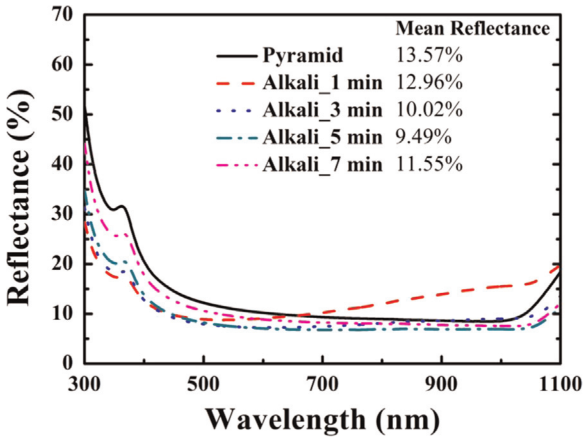

Fig. 7. Reflectance of deep funnel shaped structures by anisotropic etching for various etching times.

time of 7 min as shown in Fig. 6(h).

The deep funnel shaped structure showed the lowest reflectance of 9.49% using alkali solution while 12.81% was achieved using acid solution. The surface structure was examined for the lowest reflectance; there remained a porous layer when acid solution was used as shown in Fig. 4(a). Fig. 6(e) shows the surface structure with minimum porous layer using alkali solution. The highest aspect ratio was recorded as 1:1.26 with the acidic solution while 1:1.18 was recorded with the alkali solution. From these results, it can be said that the alkali solution is good for low reflectance and less porous surface structure while maintaining high aspect ratio [19].

4. Conclusion

We presented funnel and deep funnel shaped structures by the metal-assisted chemical etching of Si wafer. Funnel shaped structures showed an average reflectance of 14.75% that was bit higher than the reflectance (13.576%) of pyramid silicon wafer. To reduce the overall reflectance we tried the deep funnel shaped structures with high aspect ratio obtained by acidic and alkali solution for damage remove etching. The deep funnel shaped structures showed the lowest reflectance of 9.49% with high aspect ratio of 1:1.18 for the alkali solution. The maximum etching depth was recorded around ~9 μm with an aspect ratio of 1:1.26 by using acidic solution. Therefore, the deep funnel shaped structures with high aspect ratio using alkali solution are proposed for better light trapping with low reflectance in crystalline silicon solar cells.

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