The wettability between etching solutions and the surface of multicrystalline silicon wafer during metal-assisted chemical etching process

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Abstract. In order to investigate the wettability of multicrystalline silicon (mc-Si) with the etching solutions during metal-assisted chemical etching process, different surface structures were fabricated on the p-type multi-wire slurry sawn mc-Si wafers, such as as-cut wafers, polished wafers, and wafers etched in different solutions. The contact angles of different etching solutions on the surfaces of the wafers were measured. It was noted that all contact angles of etching solutions were smaller than the corresponding ones of deionized water, but the contact angles of different etching solutions were quite different. Among the contact angles of the etching solutions of AgNO3-HF, H2O2-HF, TMAH and HNO3-HF, the contact angle of TMAH solution was much larger than the others and that of HNO3-HF solution was much smaller. It is suggested that the larger contact angle may lead to an unevenly etching of silicon wafer due to the long retention of big bubbles on the wafers in the etching reaction, which should be paid attention to and overcome.

1. Introduction

Since silicon surface with a nano texture (also called a black Si) have a very strong light-trapping and can improve the power conversion efficiency of solar cells by reducing light reflection [1,2], the surface nano texture fabrications are becoming a focus of attention. To save the manufacturing costs, nano texture can be fabricated using wet etching texturing method, which is also compatibility with mass production and absence of a residual mechanically damaged layer after etching [3]. Wet etching texturing includes alkaline etching, acid etching and metal-assisted chemical etching (MACE) [1,4,5]. Wet etching usually contains several different chemical solution treatments and between each treatment the deionized water (DI water) cleaning must be used. In addition, almost all of the wet etching will be accompanied by the generation of gases on the Si surface. Then, the gases will grow up to bubbles and adsorb on the Si surface as the reaction carrying on [6, 7]. Whether the bubble releasing fast or not from the Si surface depends on the wettability between etching solution or cleaning solution and Si surface [8, 9], so that the wettability is a very important issue and the studying it is indispensable on whether for the etching or cleaning. In reports [10-15], the contact angles of pure water on the different surfaces of Si were studied. These surfaces included the polished surface, the
micro-structure surfaces with different roughness and the nano-structure surfaces. In our previous research work [16], the wettability between deionized water and different surface of Si wafer has been investigated systematically. Also, the contact angles of chemical solutions on the different surfaces of Si were studied in some researches [17,18]. These solutions involved pure and surfactant-added KOH etchants, NH₄OH, TMAH, tetrabutylammonium hydroxide (TBAH), and a mixture of isopropyl alcohol (IPA) and TMAH. Unfortunately, up to now, there has been rare report about a systemic research on the wettability between etching solutions and Si wafers during black silicon fabrication using MACE, during which the solutions of AgNO₃-HF, H₂O₂-HF, TMAH and HNO₃-HF solutions were often used [19,20]. In this paper, the contact angles of these etching solutions on different surfaces of multicrystalline silicon wafers were systemically measured and the wetting characteristics of these solutions on the silicon surface were investigated in detail.

2. Experimental

The traditional p-type multi-wire slurry sawn mc-Si wafers (180-μm-thick, 156×156 mm²) were supplied by Linuo Solar Power Holdings Co., Ltd. The wafers were divided into four groups (a, b, c and d). The four groups of samples were treated separately to form different surface structures, which are shown as follows. In order to emphasize application significance, the etching solutions were made according to chemical compositions used in the production process of the black silicon.

a: As-cut wafer sample with mechanical damages layer resulted from the wafer cutting.

b: Polished in a mixed acid solution (V/V: 70%HNO₃: 49%HF= 6:1) for 3 min at room temperature.

c: Etched (textured) in a mixed solution (V/V: 70%HNO₃: 49%HF: DI-water= 4:1:2) for 3 min at 8°C to obtain the micro-structured surface. The etched samples are called RENA textured wafer hereafter.

d: Micro-nano etched (textured) using MACE. Sample of Group c was chosen as a substrate and textured using MACE. Silver nanoparticles were electrolessly deposited on the silicon wafers in a solution of 8mM/L AgNO₃ and 4 vol.% HF for 15s at room temperature. Nanoporous silicon was formed in a solution (V/V: 30%H₂O₂: 49%HF: DI-water= 2:2:7) for 60 s at room temperature. In this work, the surface of Sample d is called a micro-nano textured surface hereafter.

During surface treatment of the samples, the samples were rinsed two times in deionized water (DIW) at room temperature after the polishing or etching.

Before the contact angle measurements, all samples were immersed in 5 vol.% HF for 60s at room temperature to remove the SiO₂ layer formed in air and rinsed two times in deionized water (DIW) at room temperature. The SL1000 automatic contact angle meter was used to test the contact angle of all samples; the surface morphologies of samples were analyzed by means of OLS4000 confocal lasers scanning microscope (CLSM) and S4800 scanning electron microscope (SEM).

3. Results and discussion

![Figure 1](image1.png)

Figure 1. Micrographs of wafer surfaces

a as cut wafer  b polished wafer  c RENA textured wafer
As the studied in our previous research work [16], the surface structure of the silicon wafer has a strong influence on the contact angle. Therefore, the surface morphology of the as cut, RENA textured and the polished samples of the slurry sawn mc-Si wafers are shown in Figure 1. The polished one has a very smooth surface, the as cut and RENA ones present the micron size structure and the fluctuation of the latter is more intense.

Figure 2 shows the shape change of the AgNO₃-HF solution droplet on the surface of RENA textured wafer with time. With the increase of time, the shape of the droplet does not change obviously and no evident bubble appears in the droplet. This is mainly because the concentrations of AgNO₃ and HF are very low, the precipitation reaction of Ag is weak and the gas generated in the reaction is less. The optical photographs of the shape change of the droplet on the as cut and the polished samples is similar to that on the RENA textured wafer, but the contact angles of the AgNO₃-HF solution droplet on the surfaces of these three samples are obvious different as shown in Figure 3. It can be seen that three contact angles of AgNO₃-HF solution on three wafers are lower respectively than corresponding contact angles of water. The ordering of the solution contact angles is in agreement with that of the water contact angle [16], i.e., the contact angle on textured wafer > the contact angle on as cut wafer > the contact angle on polished wafer. With the increase of time, three solution contact angles decrease slightly.

The appearance of wafers after deposition of Ag is shown in Figure 4. Because the surface of the as cut sample or the RENA sample with a micron size structure is in a big fluctuation, the light trapping effect is relative stronger, so that it has a darker color (shown in Figure 4b) compared with the polished sample (shown in Figure 4a). Due to the deposition amount of Ag is very little, Ag particles can not change the surface fluctuation of the three samples except for the appearance color. Figure 5 shows the water contact angle and the change of the solution contact angles with time variation. The solution contact angle of solution is much smaller than that of water on the corresponding wafer, and the contact angle decreases with the increase of time. Figure 6 shows the pictures of H₂O₂-HF solution
droplet on the surface of a polished silicon wafer, on which the Ag particles had been deposited. As shown in the pictures, there exist many bubbles in the droplet, which are generated during etching reaction between H$_2$O$_2$-HF solution and Si wafer under the catalysis of Ag. The bubbles grow to about 0.2mm, rise and break away from the droplet at last.

Figure 4. Appearance of mc-Si wafers after the deposition of Ag
a polished wafer  b as cut wafer or RENA textured wafer

Figure 5. The water contact angles and changes of H$_2$O$_2$-HF (volume ratio: 30%H$_2$O$_2$: 49%HF: DI-water= 2:2:7) solution contact angle with time variation
a as cut wafer; b polished wafer; c RENA textured wafer

Figure 6. The shape change of H$_2$O$_2$-HF solution droplet with the time variation

Textured structure of the sample of Group d that described in experimental section is shown in Figure 7. The diameter of nano pores on the surface are about 10nm [16], so that their light trapping is very strong and the color of the wafer is black. As can be seen from the Figure 8, the initial contact angle of TMAH solution on the silicon wafer is very large, about 140 degree and as the reaction time increases to 60s the contact angle decreases to 113 degree. In contrast, the initial contact angle of the HNO$_3$-HF mixed acid solution on the silicon wafer is small, about 49 degree, and it decreases slightly with the time increases.
Figure 7. The surface morphology of nano-textured wafer (Group d)

Figure 8. The changes of contact angle of 1%TMAH solution and 4.8M/L HNO$_3$-1.3M/L HF mixed acid solution on the nano textured surfaces (Sample d) with time variation

Figure 9 shows the pictures of TMAH solution droplet on the surface of sample of Group d. There exist some big bubbles in the droplet. Different from the bubbles in H$_2$O$_2$-HF liquid droplet, the size of bubbles in TMAH solution droplet is in a larger range from about 0.2mm to about 3mm. The formation of the big bubbles is attributed to the big contact angle (about 120-140 degree) between the TMAH solution and the wafer. Because of the agitation of the reaction gas, some of the little bubbles are separated from the wafer surface before they grow up, so that the size of bubbles is scattered. Contrarily, as shown in Figure 10, the contact angle of the HNO$_3$-HF mixed acid solution on the wafer is only about 50 degree (shown in Figure 9) and the bubbles are separated easily from the wafer surface, so that the bubbles in the mixed acid solution droplet are small and in uniform size.

Figure 9. The shape change of 1%TMAH solution drop on Sample d with the time variation
Figure 10. The shape change of 4.8M/L HNO₃-1.3M/L HF mixed acid solution drop on Sample d with the time variation.

The measurement condition of the contact angle for each solution mentioned above were tried to keep similar to those in the actual production process, including wafer surface state and the composition of the solution, in order to correspond to the actual situation in production. The initial contact angles of the different solutions are shown in Figure 11.

Figure 11. The average contact angles for six cases:
a RENA textured sample contacting with water; b RENA textured sample contacting with AgNO₃-HF solution; c Ag deposited sample contacting with H₂O₂-HF solution; d Nano size textured sample contacting with water; e Nano size textured sample contacting with TMAH solution; f Nano size textured sample contacting with HNO₃-HF solution.

Due to the surface structure of the sample has a great influence on the contact angle, the contact angle of pure water on the nano size textured surface is obviously much larger than that on the micron size textured surface [16]. Compared with the contact angle of pure water, different etching solutions appear different contact angles. In case of the micro size textured surface (Case a-c), the contact angle of H₂O₂-HF solution is much smaller than that of water, but the contact angle of AgNO₃-HF solution is close to it since the concentration of AgNO₃-HF in solution is very low. In case of the nano size textured surface (Cases d-f), the contact angle of HNO₃-HF solution is the smallest among the three cases. Similar to the situation of AgNO₃-HF solution, 1%TMAH solution is also a low concentration solution and its contact angle is close to the contact angle of water.

Generally, after inorganic substances are added into water, surface tension (γᵢ) will increase to some extent. The more substances added, the greater the surface tension. A large surface tension often leads to a larger contact angle [21]. However, the experiments in this paper shows opposite results, as shown in Figure 11. Combined with Figure 12 and formula 1 [22], it can be analyzed as follows. After acid or alkali or salt is added into water, assuming that γᵢ does not change, then the increase of γᵢ
will result in the decrease of $\cos \theta_C$ or the increase of $\theta_C$ due to $\gamma_{SG}$ is not affected by the addition of solutes. However, the experimental results in this paper show that instead of increasing, $\theta_C$ decreases, which indicates $\gamma_{SL}$ reduced. In the actual case of Si etching in the solution, the reaction takes place between the etching solutions and Si wafers, which suggests that there are affinity between Si atoms and the related atoms in the solutions, and hence $\gamma_{SL}$ decreases. Thus, the balance of the three forces shown in Figure 12 is broken and $\theta_C$ must decrease to build up a new balance. Therefore, no matter whether the solution concentration is high or low, the contact angles of AgNO$_3$-HF, H$_2$O$_2$-HF, TMAH and HNO$_3$-HF solutions are less than that of water due to affinity between Si atoms and the atoms in solutions. Since both H$_2$O$_2$-HF and HNO$_3$-HF solutions are higher concentration solution and there exists strong affinity, their contact angles on the Si wafers are much smaller.

According to the degree of the initial contact angle size, the order of the solutions, from big to small, is TMAH$>$AgNO$_3$-HF$>$H$_2$O$_2$-HF$>$HNO$_3$-HF as shown in Figure 11. As a result, according to the size of bubble generated in droplet, the order of the solutions, from big to small, also is TMAH$>$AgNO$_3$-HF$>$H$_2$O$_2$-HF$>$HNO$_3$-HF (shown in the related figures above), The bigger contact angle or the bigger bubble means that the bubbles are more difficult to leave from the surface of wafer and detain longer on the surface. Meanwhile, the bigger bubbles cover larger area of the surface of wafer, so that the big detained bubbles hinder the etching of wafer under the bubbles. From this point of view, the etching of Si wafer by TMAH solution may be more likely to cause uneven etching [23].

It should be pointed that, from Figure 3, 5 and 8, with increasing time the contact angles of etching solutions decrease at different speeds. The reason for the decrease of contact angle may come from two aspects. Firstly, because Si is very easy to be oxidized the surface might be contaminated in the atmosphere before dropping. When the surface is dropped on a droplet, the contamination is gradually etched and the solid-liquid contact becomes better, so that the affinity is gradually strengthened. This takes place at the initial stage. Secondly, since every solution mentioned above can etch Si wafer, with increasing residence time of the etching solution droplet on the Si wafer the surface structure of the wafer changes gradually. For the AgNO$_3$-HF solution droplet, the surface structure of the wafer under the droplet changed very little, but Ag deposited on the surface improved the wettability of the surface. With increasing deposition time the amount of deposited Ag increased and the contact angle of the droplet decreased. For H$_2$O$_2$-HF solution droplet, the surface structure of the wafer tends to form nano size texture because nano pores were dug under Ag particles [24] and the specific surface area of the wafer increased. Since Si wafer was in a hydrophilic state in case of contacting with H$_2$O$_2$-HF solution, the increase of specific surface area of the wafer might improve its hydrophilic property, and the larger the surface area, the smaller the contact angle [16]. Therefore, with the increasing the residence time of the droplet, the specific surface area increases, and the contact angle decreases continuously. It should be pointed out that, during the production process, the surface texture after the etching of H$_2$O$_2$-HF solution must be adjusted from nano size texture to a submicron one using the etching of TMAH or HNO$_3$-HF in order to reduce surface defects and heavy doping [1, 24]. Therefore,

\[ \gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cdot \cos \theta_C \]
the contact angle measurements of TMAH or HNO$_3$-HF solution need a nano size textured surface. Thus, the surface used in the measurement was an already prepared nano size texture surface and there existed gas in the pores [25]. With increasing the residence time of TMAH or HNO$_3$-HF solution droplet, the gas trapped in nano pores would run out gradually together with the reaction gas. As a result, the wafer surface area contacting with the solution are increased and the contact angles of the etching solutions reduced.

4. Conclusions
During metal-assisted chemical etching process of multicrystalline silicon wafer, several different etching solutions and cleaning deionized water (DI water) must be used. In this paper, the contact angles of different etching solutions on the surfaces of the wafers were systemically measured. It was noted that all contact angles of etching solutions were smaller than the corresponding ones of deionized water, but the contact angles of different etching solutions were quite different. Among the contact angles of the etching solutions of AgNO$_3$-HF, H$_2$O$_2$-HF, TMAH and HNO$_3$-HF, the contact angle of TMAH solution was much larger than the others and that of HNO$_3$-HF solution was much smaller. It suggests that the larger contact angle may make the silicon wafer etched unevenly due to the long retention of big bubbles on the surface in the etching reaction and it should be paid attention to and overcome.

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