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Ultrasonication pretreatment of diamond wire sawn multi-crystalline silicon wafers for texturing

Jinbing Zhang[a,b], Yeqing Peng[b], Xingfang Ye[a], Xiaoying Zhou[c], Gang Hao[b], Lang Zhou[a,*]

[a] Institute of Photovoltaics, Nanchang University, Nanchang 330031, PR China
[b] National Engineering Technology Research Center for Photovoltaics, LDK Solar Co. Ltd., Xinyu 338032, PR China
[c] School of New Energy Science and Engineer, Engineering Xinyu University, Xinyu 338004, PR China

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ABSTRACT

Ultrasonication vibration as the pretreatment process, combined with wet acid etching, was utilized for the texture of diamond wire sawn (DWS) multi-crystalline silicon wafers. The SiC particles in the ultrasonic device were imposed for cavitation-generating blasting action on the DWS wafers surfaces. The blasting action exceeding 5 min can remove saw marks and smooth zones on the DWS wafer surfaces by producing new pits. After wet acid etching，the texture morphology of ultrasonically pretreated DWS mc-silicon wafers was quite uniform as compared to wet-textured as-cut DWS mc-silicon wafers, similar to wet-textured slurry wire saw(SWS) mc-silicon wafers. Light reflectivity tests confirmed the beneficial effect of the ultrasonic pretreatment of DWS mc-silicon wafers. This technique could be a potential solution to the texturization problem of DWS mc-silicon wafers.

1. Introduction

As a type of renewable energy, solar energy has attracted significant attention. The materials of solar cells are dominated by silicon due to the corresponding durability, abundance and nontoxicity. The diamond wire saw (DWS) wafering technology, which has been developed rapidly in recent years, can lower the wafering cost significantly, as compared to the conventional slurry wire saw (SWS) wafering technology. Since 2016, the DWS has been almost completely applied for the wafering of mono-crystalline silicon wafers in production [1]. In contrast, up to now the DWS wafering technology has not been significantly successful in multi-crystalline silicon(mc-silicon) wafer production due to no compatible surface texturization to this type of wafers [2].

The surface texturization of wafers is an important process for the production of mc-silicon solar cells. It can reduce the reflected light of the front surface and increase the light absorption, consequently improving the solar cell efficiency. The microstructure of as-cut wafers' surfaces has a significant impact on the texture genrated by conventional acid-texturization process (commercially HF-HNO_3-H_2O etching solution for multi-crystalline silicon wafer) [3]. The conventional slurry wire sawn (SWS) wafers can be well textured by the conventional acid-texturization process, while diamond wire sawn (DWS) wafers can not. A thin amorphous silicon layer along the saw marks on the DWS wafers restrains the etching by the acidic etching solution [4]. Usually, subsequent to the conventional acid-texturization, the light reflectivity of DWS mc-silicon wafers is 3–5% higher in average than that of SWS mc-silicon wafers, in the visible light range [5,6].

Current attempts for texture improvement of DWS mc-silicon wafers in PV industry, such as Reactive Ion Etching(RIE) technique and Metal Catalyzed Chemical Etching (MCCE) technique, are either too expensive or too complicated [7–10]. Alternative effective texturization technologies should be developed for mass production of DWS multi-crystalline silicon wafers.

In this work, a new method for the texturing of DWS multi-crystalline silicon wafers was proposed. The present study focused on a pretreatment process on DWS multi-crystalline silicon wafers prior to conventional acidic texturization. The pretreatment was conducted through ultrasonication in a bath containing SiC powders. The effects of the pretreatment processes on weight loss and surface morphology of the DWS wafers, and their further effects on the subsequent conventional acid-texturization, were investigated. For reference, weight loss behaviour of SWS wafers and polished wafers under the ultrasonic treatment were parallely investigated, too.

2. Experimental procedure

The DWS p-type mc-silicon wafers of ~190 µm in thickness and 156

* Corresponding author.
E-mail address: lzhou@ncu.edu.cn (L. Zhou).

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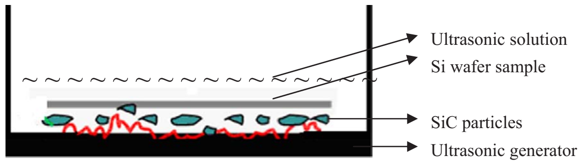


Fig. 1. Illustration of Si wafer ultrasonic vibration.

× 156 mm^2 in size were processed in this study. For comparison, samples of SWS mc-silicon wafers were also analyzed in parallel. All wafers were provided by LDK Solar Co. Ltd

The ultrasonic vibration(Ultrasonic generator, 40 kHz, Power max 900w, Durasonic Corporation), as a pretreatment for the uniform microstructure damages production on the surfaces, was tested on as-cut DWS mc-wafers. The suspension in ultrasonic pretreatment was prepared by the SiC particles(average grain size of 13 µm) and tap water mixing, whereas only tap water for ultrasonic solutions was also used as a reference. The height of suspension in the ultrasonic vibration tank was approximately 5 mm. This ultrasonic vibration process is presented in Fig. 1.

During the etching experiments, the wafer samples were textured with the Inline Texture Etching Machine(InTex, RENA Corporation) for 90 s at 8 °C. Also, the solution in the etching tank was the HF(49 wt%)-HNO_3(69 wt%)- H_2O of 1:4.4:2.7 in volume ratio. This etching process is also conventional for the SWS mc-silicon wafers in production.

The scanning electron microscope (SEM, S-3700N, Hitachi Corporation) was utilized to characterize the surface appearances of the wafers. A laser scanning confocal microscope (Olympus LEXT OLS4100 model) was utilized to examine the topography of the textured mc-silicon wafers. The light reflectivity of the acid-texturized samples was examined through an Ocean Optics USB4000 spectrometer. The average reflectivity in the wavelength range of 400–900 nm was utilized to represent the light reflectivity of the samples.

3. Results and discussion

3.1. Effects of process conditions on ultrasonic vibration

Ultrasonic vibration was utilized for the manufacturing of micro-defects on the surface of as-cut DWS mc-silicon wafers, whereas certain factors such as the SiC concentration in ultrasonic solutions as well as ultrasonic power, were of important consideration during the surface treatment. The manufacturing micro-defects on the surface will inevitably result in the weight loss of the DWS mc-silicon wafer. Consequently, the variation rule of ultrasonic vibration manufacturing of micro-defects was investigated through weight loss testing under different parameter conditions. The SiC concentration along with the ultrasonic power, were altered. Certain attempts with several parameters in the ultrasonic treatment for mc-silicon wafers were made, whereas each data element was derived from the average of three parallel samples. The results are presented in Figs. 2 and 3.

Fig. 2 presents the weight loss of the DWS mc-silicon wafer versus SiC concentration, whereas as it could be observed, the 10 wt% of the SiC concentration was regarded as a proper parameter in ultrasonic vibration according to the weight loss of the samples. A possible explanation for this was that fewer impacting particles existed at the relatively low concentration of SiC, which resulted in lower amount of micro-defect formations on the surfaces of the as-cut DWS mc-silicon wafers. In contrast, when the concentration of SiC exceeded 10%, the impact force of SiC particles to wafers was weakened due to higher amount of SiC particles being deposited at the bottom of the tank. The effects of ultrasonic power on the weight loss of DWS mc-silicon wafer presented in Fig. 3, and the weight loss increased as the power increased. The impact force of the SiC particles derived from the ultrasonic power. Also, the high ultrasonic power would supply the SiC

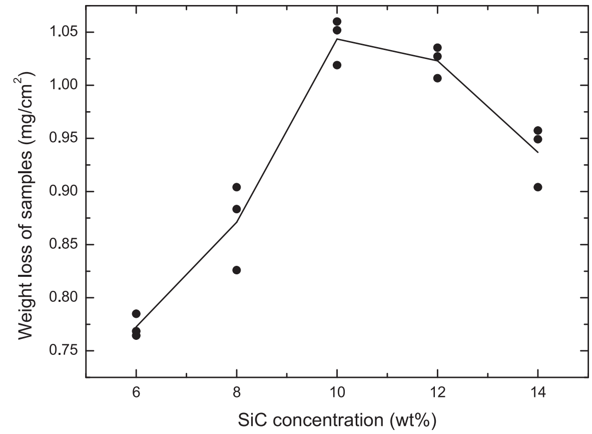


Fig. 2. Weight loss of as-cut DWS mc-silicon wafers under different SiC concentrations within 5 min and 900 W of maximum ultrasonic power.

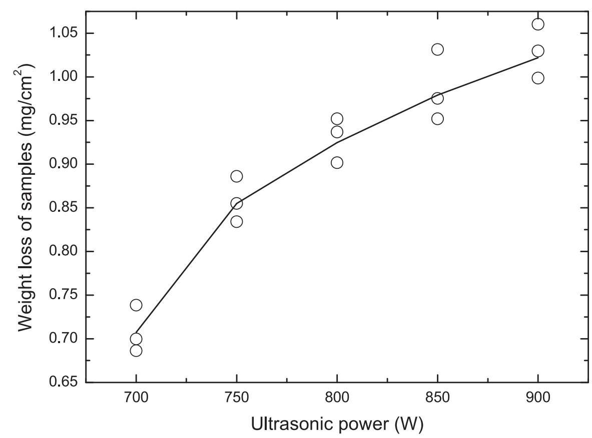


Fig. 3. Weight loss of as-cut DWS mc-silicon wafers under different ultrasonic power within 5 min and 10 wt% of SiC concentration.

particle energy for strong vibration, which would benefit the manufacturing of micro-defects on the surface of the DWS mc-silicon wafers.

In addition, the wafer surface condition effects on ultrasonic vibration was also studied for a better insight SiC blasting on the wafer surfaces. Three different surface states of silicon wafers such as the DWS wafers, the polished DWS wafers by an alkaline solution and the SWS wafers were researched in this work. The results are presented in Fig. 4.

As it could be observed from Fig. 4, the weight loss of the SWS wafers was the highest, whereas the polished wafers weight loss was the

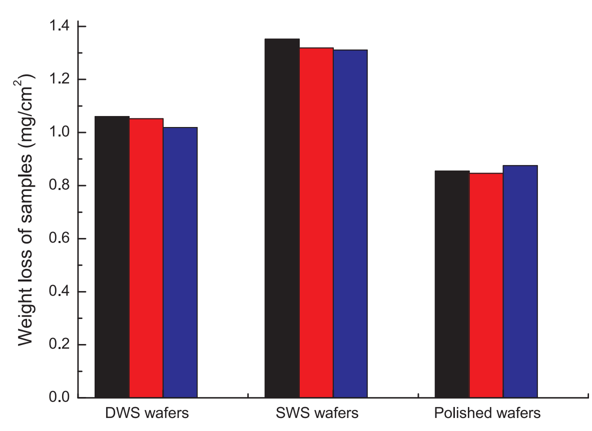


Fig. 4. Weight loss of different kinds of wafers under conditions of 5 min, ultrasonic power of 900 W and 10 wt% of SiC concentration. Each bar represents result of a sample.

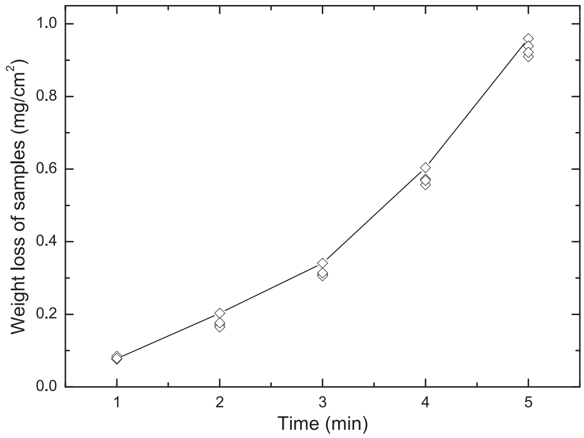


Fig. 5. Weight loss of DWS mc-silicon wafer versus ultrasonic pretreatment duration.

lowest among the three types of wafers with different surface states, under the same conditions of ultrasonic vibration. It is generally known that the subsurface crack depth induced by slurry wire sawing is higher compared to the fixed diamond wire sawing subsurface crack depth on the surfaces of the wafers [11]. Moreover, the subsurface crack depth of the polished wafers should be the least among all three wafer types. Therefore, the subsurface crack depth of the samples has an important effect on the manufacturing of micro-defects during ultrasonic pretreatment. The higher the original subsurface crack depth was on the wafer's surface, the easier the micro cracks were generated. In addition, in this paper, the ultrasonic pretreatment of DWS mc-silicon wafers was focused on, whereas the process conditions with the ultrasonic power of 900 W and 10 wt% of SiC concentration were fixed.

3.2. Evolution of ultrasonic vibration on as-cut DWS mc-silicon wafers

The weight loss of the DWS mc-silicon wafer versus ultrasonic pretreatment duration is plotted in Fig. 5 and three samples(A, B and C) were analyzed for comparison. As it could be observed, the ultrasonic vibration can induce the weight loss of the DWS mc-silicon wafer, whereas the weight loss curves of the three samples were similar, although they did not completely coincide. The slope of the weight loss curve became steeper as time passed, which meant that the weight loss per unit time of the DWS mc-silicon wafer increased as the ultrasonic pretreatment duration increased. According to the results of Figs. 2 and 4, this might be attributed to the difference in dispersion of the SiC particles in the solution as well as to different surface conditions with different impact resistance values on the wafers during ultrasonic pretreatment.

Fig. 6 presents a series of surface micrographs of the DWS mc-silicon wafer samples subsequently to different ultrasonic vibration conditions. As it could be observed from Fig. 6(a), the microstructure damages from slicing was uneven within the wafer surface. Also, a high amount of parallel saw marks, section smooth zones and certain pits existed on both sides of the as-cut DWS mc-silicon wafer, which were created through reciprocating diamond scribing as reported by Meinel et al. [6]. In the first two minutes of the ultrasonic vibration with SiC particles, a higher number of damaged pits occurred, somewhere certain areas remained with saw marks and smooth-section zones on the sample' side, front-facing the ultrasonic generator, as observed in Fig. 6(b). As the ultrasonic vibration continued, the morphology evolved differently. At 5 min of ultrasonic vibration with SiC particles, many new pits were formed and distributed on the front-facing side of the sample. Accordingly, the saw marks as well as the smooth-section zones completely disappeared, as presented by Fig. 6(c). Within 5 min, no apparent changes were observed on the sample's back side of the sample, such as to the side not facing the ultrasonic generator, as observed in Fig. 6(d). Following, one more minute of the ultrasonic vibration did not produce significant changes for the DWS mc-silicon wafer in the previous position, which was almost similar to Fig. 6(c) and (d). For comparison, the DWS mc-silicon wafer was treated by ultrasonic vibration without SiC particles for 5 min and both sides of the sample remained almost unchanged, as presented in Fig. 6(e).

A ultrasonic device can produce cavitation action, which will result in a certain amount of air bubbles (as cavitation nuclei) in the vibrating liquid and blew up rapidly [12,13]. A powerful bow wave was produced during cavitation action and it acted on the SiC particles with high-speed movement as well as blasting on the wafers by SiC particles. The constant blasting action would cause many newly damaged pits on the surface of the wafers, whereas the newly damaged pits would not appear when the ultrasonic solution was only water. Therefore, the ultrasonic pretreatment on the DWS mc-wafers was the combined effect of ultrasonic cavitation and particle mechanical impact. The blasting action of the particles was essential and could remove both the parallel saw marks and smooth-section zones from the surface of the DWS mc-wafers by producing damaged pits in the corresponding areas. In this ultrasonication pretreatment, the ultrasonic energy spread mainly by mean of longitudinal vibration, and the mechanical impacts of the particles acted on the surfaces of the DWS mc-wafers vertically, resulting in new damaged pits appearing on the sample side front-facing the ultrasonic generator,whereas not on the back-facing side.

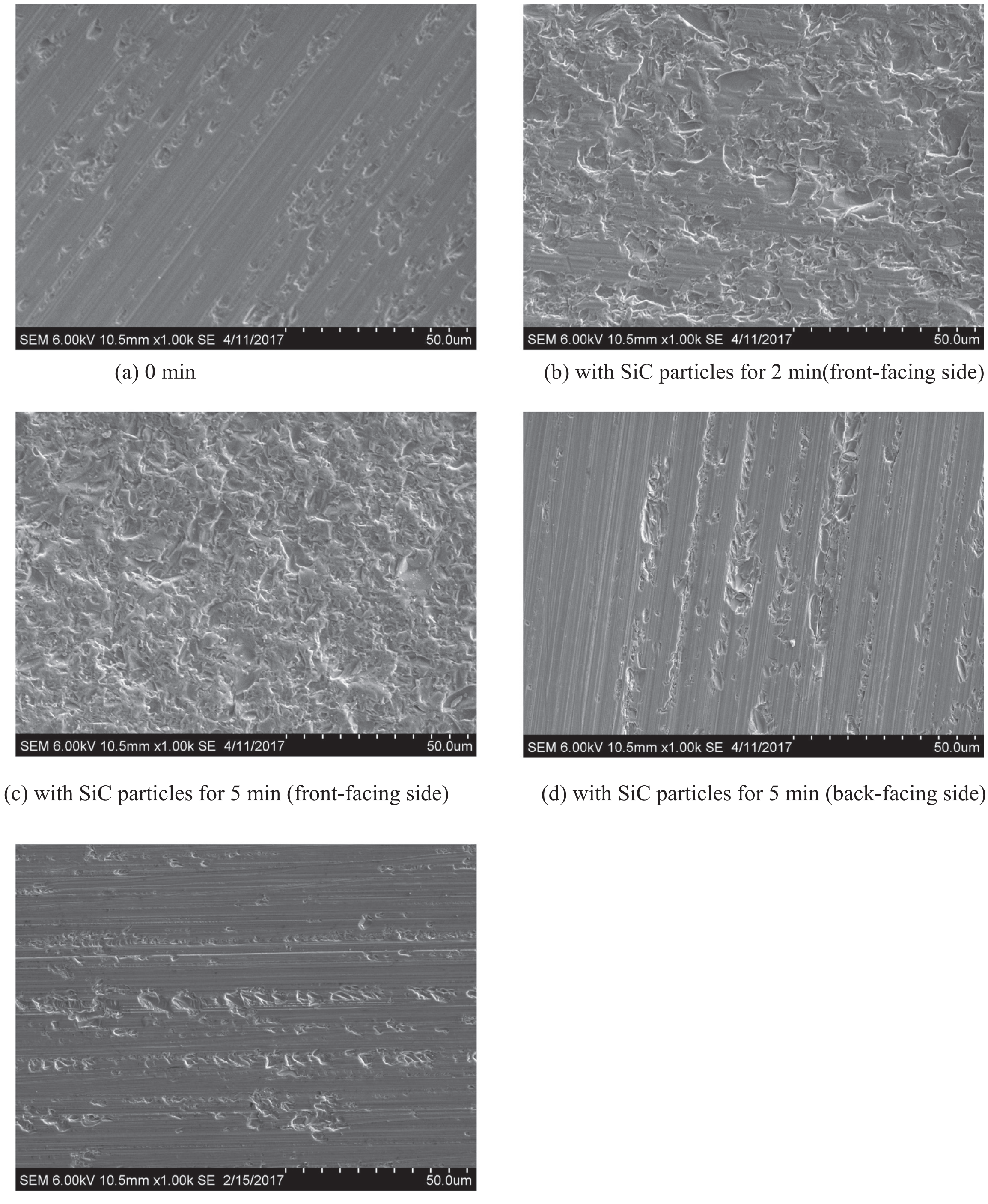
The DWS mc-wafer is a brittle material and the corresponding surface micro-defects are manufactured similarly to other brittle materials. This meant that the micro-defects process formation was the crack generation, the propagation and the spalling [14,15]. The additional mechanical damages was distributed on the surface of the DWS mc-wafers, where it was more favorable for the surface micro-defects formation during ultrasonic pretreatment. Therefore, the formation rate of the damage structure was increasingly higher and higher as pretreatment duration increased.

3.3. Surface morphology and reflectivity of textured mc-silicon wafers

Fig. 7 presents the surface morphology of the textured samples, which were from the as-cut DWS mc-silicon wafers, the DWS mc-silicon wafers pretreated by ultrasonication vibration as well as the SWS mc-silicon wafers. The three types of wafers were textured with the same etching conditions (conventional wet acid etching process). As it could be observed from Fig. 7(a), the textured as-cut DWS mc-silicon wafers displayed uneven textures with parallel saw marks and smooth-section zones, whereas similar results for DWS mc-silicon wafers were previously by Chen et al. [4]. As the ultrasonic vibration was applied in the DWS mc-silicon wafers pretreatment, the etched DWS mc-silicon wafers evolve with different textures, as presented in Fig. 7(b), which followed a uniform wormhole-like surface morphology, and similarly to SWS mc-silicon wafer of Fig. 7(c). In other words, the texture morphologies of Fig. 7(a) and (b) were respectively well associated with the corresponding previous surface micrographs of the DWS mc-silicon wafer samples, such as in Fig. 6(a) and (c).

In Fig. 8, it could be observed, in the visible light of 400–900 nm wavelength, the reflectivity curves of ultrasonication pretreating DWS wafer and as-cut SWS wafer subsequently to etching were similar, whereas distinctly different from the as-cut DWS wafer curves. Compared to the different types of textured mc-silicon wafers, and the reflectivity at the 600 nm wavelength was regarded as the representative. The reflectivity at 22.54% of ultrasonication pretreating DWS wafer following etching, which was near to 22.50% of the textured as-cut SWS wafer, was approximately 3% lower than the 25.57% of the textured as-cut DWS wafer. This occurred due to the uniform and deep wormhole-like texture formed on the surfaces of ultrasonication pretreating DWS wafer, which was also well consistent with the microtopography presented in Fig. 7.

The etching effect of the HF-HNO_3-H_2O mixed acid depends



(a) 0 min

(b) with SiC particles for 2 min(front-facing side)

(c) with SiC particles for 5 min (front-facing side)

(d) with SiC particles for 5 min (back-facing side)

(e) without SiC particles for 5 min (front-facing side)

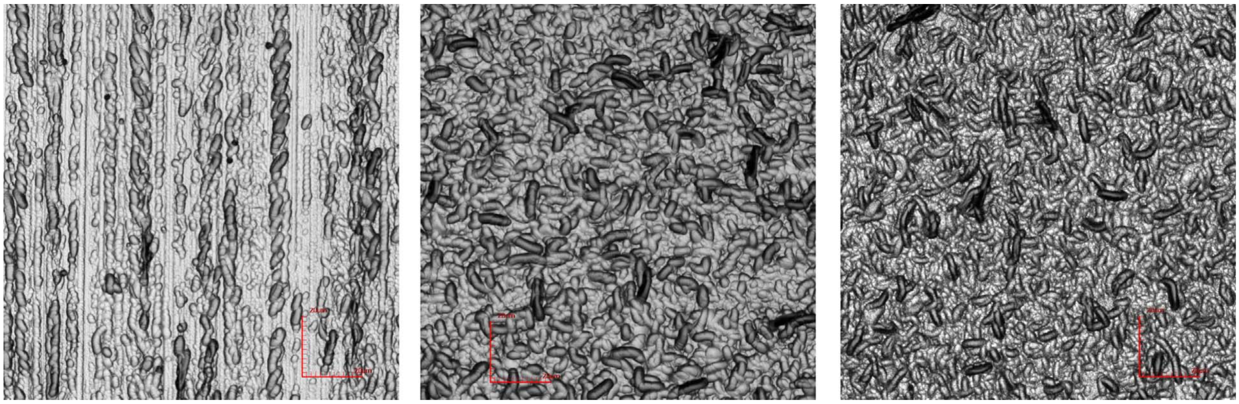
Fig. 6. Micrograph evolution of DWS mc-silicon wafers treated with ultrasonic vibration.

significantly on the surface defect of the mc-wafers, whereas the corrosion resistance of the smooth-section zones on the surfaces of the DWS mc-wafers was relatively strong, which would lead to a disadvantage of surface texture. More damaged pits were produced on the surface of the DWS mc-wafers, more uniform texture appeared in surface through wet acid etching. The texture morphologies of the mc-silicon wafers following etching were well associated with the previous surface micrographs. Also, the texture uniformity would be favorable to obtain low light reflectivity for the textured wafers.

It should be pointed out that, in the macro scale, the attacks generated by the ultrasonic vibration were not yet uniform on the wafer. Certain areas of the centimeter scale remained without being attacked even subsequently to 5 min of vibration with SiC particles being mixed, with the current experimental setup. The micrographs and the light reflectivity measurements forehand reported above were from the attacked areas. The problem of uniformity remains to be resolved in a further study.

4. Conclusions

Ultrasonic vibration in water-SiC powder mixture can produce newly damaged pits on DWS wafer sample surface facing the ultrasonic



（a）As-cut DWS wafer （b）Ultrasonication pretreating DWS wafer （c）As-cut SWS wafer

Fig. 7. Texture morphology of different mc-silicon wafers types.

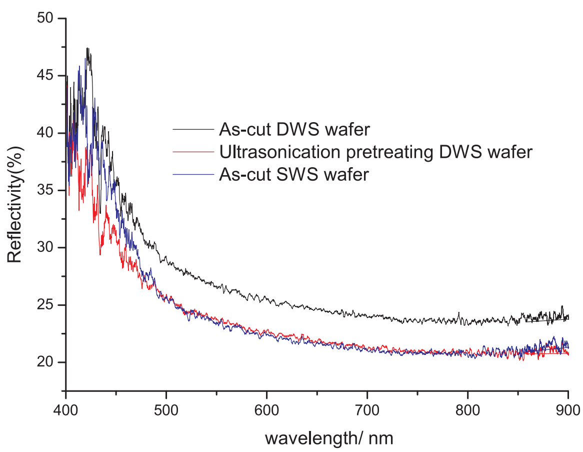


Fig. 8. Reflectivity of different types of mc-silicon wafers following wet acid etching.

generator, and completely remove the saw marks in five minutes. Following wet acid texturization, a surface texture very similar to that obtainable with SWS multi-crystalline silicon wafers was obtained on the ultrasonication pretreated DWS multi-crystalline wafers. Similar light refelecty further confirm the observation.

The results suggested that the ultrasonic vibration technique has the potential to be developed into a pretreatment for processing the DWS mc-silicon wafers for slolar call production in PV industry.

Acknowledgements

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