Texturization of Multicrystalline DWS Wafers by $HF/HNO_3/H_2SO_4$ at Elevated Temperature

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Abstract. The acidic texturization of multicrystalline silicon diamond wire sawn wafers (mc-Si DWS) with smooth surfaces has been a challenge for years. One possibility to texture smooth surfaces is a solution consisting of hydrofluoric acid, nitric acid and sulfuric acid ($HF/HNO_3/H_2SO_4$). The favored texturing behavior of this solution instead of HF/HNO_3 might be due to the high viscosity and an enhanced NO_x^+ generation due to the sulfuric acid. As the $HF/HNO_3/H_2SO_4$ texturing process showed a decreasing reflection with increasing temperature, the temperature and time dependence of the etch depth and reflection has been evaluated. At temperatures above 45°C a texture with total reflection values of 22% at 600 nm was achieved at 15 µm total etch depth and a structure height of 2 µm in 60 s. The textured surface might be due to gas phase etching in the generated gas bubbles. This result poses a promising starting point for finding an adequate additive for the mc DWS texturing process.

INTRODUCTION

The sawing industry for photovoltaic silicon wafers replaced the multiwire slurry sawing process (MWSS) with a diamond wire process (DWS) for monocrystalline silicon. For multicrystalline silicon (mc-Si), however, the process has not been replaced because an adequate texturization process has not been developed yet. The saw damage of diamond wire sawn wafers consists of smooth grooves and amorphous silicon [1,2]. The acidic texturization with hydrofluoric acid (HF) and nitric acid (HNO_3) for multicrystalline silicon does not roughen a smooth DWS surface so that a reflection reducing surface structuring of the DWS wafers is not possible with this solution [3]. This problem has been known for edge-defined film-fed growth silicon (EFG) or for string ribbon silicon wafers [4]. Different options for texturing smooth silicon surfaces are mechanical roughening through sandblasting [5], using phosphoric acid with a surface active agent [6] or metal assisted chemical etching [7,8]. Other than that mentioned is sulfuric acid (H_2SO_4) a well-known additive [9–11]. Sulfuric acid added to HF/HNO_3 has been used by Watanabe at 16.2 mol/l [10], by Merck at 14.7 mol/l [12], by Lippold at 13.5 mol/l [13] or Sovello at 1.7 mol/l sulfuric acid and 0.4 Vol.% methyl cellulose [14]. 98% sulfuric acid has a molar concentration of 18 mol/l. A good texturization in a H_2SO_4 rich HF/HNO_3 mixture with total reflection values of about 20% at 600 nm has been reported in Lippold and Watanabe [9,10]. The favored texturing of the sulfuric acid rich mixture is based on a stabilization of NO_x^+, a reduced dissociation of nitric acid, the high viscosity of the sulfuric acid and a formation of fluorosulfuric acid (HSO_3F) that captures fluoride-containing species [15]. But the challenge of this texturing process is the handling of sulfuric acid in a large scale etching plant as the acid reacts strongly exothermally with water. Therefore the sulfuric acid should be replaced. The first approach for solving the texturing problem of mc-Si DWS is to find a process that textures mc-Si DWS wafers reliably. We increased the temperature of an HF rich HF/HNO_3 solution with 11 mol/l H_2SO_4 from 12°C to room temperature and found a lower reflection of the wafers at elevated temperature. In order to understand the $HF/HNO_3/H_2SO_4$ texturing process the temperature and the etching time at an elevated temperature level have been evaluated.

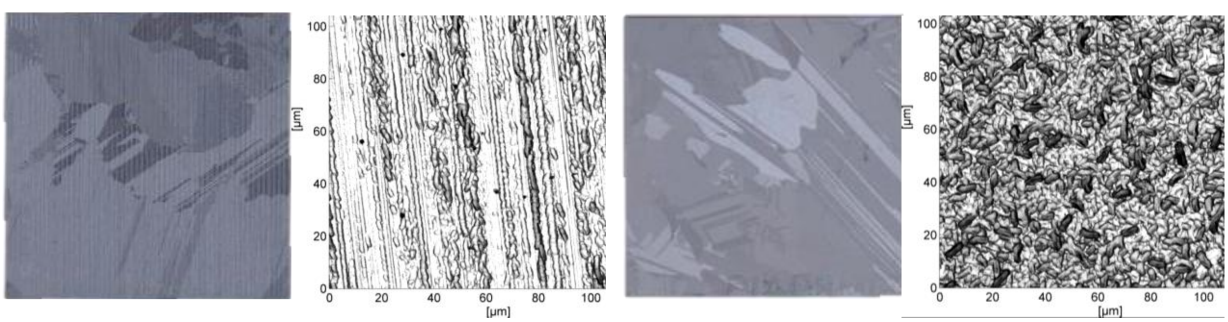
EXPERIMENTAL

A mixture of standard acids comprising of HF (50%), HNO_3 (69%) and H_2SO_4 (95-98%) was cooled inside of a thermostat or used right after mixing. The composition was usually HF:HNO_3:H_2SO_4 as 3:1:6, and is always given in the figure caption. 30x30 mm² mc-Si DWS and SDE (saw damaged etched in 30% KOH at 80°C) wafer pieces were etched vertically in a carrier in a 250 mL beaker in a new freshly prepared solution. The temperature of the HF/HNO_3/H_2SO_4 texturing process was varied from 3 to 60°C, etched for 60 s. The time variation was realized from 2 to 60 s at 45°C. 156x156 mm² wafers were etched vertically in a carrier in a 23 L basin of a wet bench. The total etch depth was determined by weight (analysis scale), the total reflection at 600 nm by the spectral photometer x-rite Ci64. The macroscopic wafer surface was recorded by the flatbed scanner Canon LiDE120, the microscopic wafer surface and roughness parameter mean height deviation S_q and the maximum height deviation S_z was determined by the confocal microscope Olympus Lext OLS4000.

RESULTS

Etching in a Solution of HF/HNO_3/H_2O

The traditional HF/HNO_3/H_2O texturing solution either in an HF or HNO_3 rich composition uses the saw damage from the slurry sawing to etch deeply into surface defects and then widen the hereby resulting holes. DWS wafers do not have such a deep damage and about 25% less micro-roughness compared to slurry sawn wafers [1]. A DWS wafer etched in HF/HNO_3/H_2O remained smooth and the sawing grooves were still visible as vertical lines (Fig. 1a). The etch depth for the DWS was 30% lower than the etch depth for MWSS wafers when using the same solution and time. This reduction of the etch depth might connected to a reduced surface area of the as cut DWS wafers. The textured MWSS wafer was macroscopically and microscopically homogeneous. The next step is to find, a texturing solution that can etch into the wafer.



(a) mc-Si DWS 3.5 µm etch depth, 32.1% reflection (b) mc-Si MWSS 5.0 µm etch depth, 25.7% reflection

FIGURE 1. Photograph (30x30 mm², left) and confocal laser intensity picture (right) of a mc-Si DWS (a) and mc-Si MWSS (b) wafer textured in 43 mL HF, 64 mL HNO_3, 29 mL H_2O, 67 s at room temperature.

Temperature Variation of HF/HNO_3/H_2SO_4

Instead of HF/HNO_3/H_2O, a mixture of HF, HNO_3 and H_2SO_4 was used for etching DWS wafers since sulfuric acid has been described as a promising additive for texturing smooth silicon surfaces [9]. The etch rate of DWS wafers in HF/HNO_3/H_2SO_4 was enhanced (15 to 20 µm/min, Fig. 3) compared to a HF/HNO_3 reaction (3 µm/min, Fig. 1). Usually, the HF/HNO_3 and HF/HNO_3/H_2SO_4 texturing process is carried out between 10°C and room temperature. At temperatures below 12°C the saw grooves were still visible and the macroscopic surface was inhomogeneous (Fig. 2). The low temperature of 3°C led to the lowest etch depth of the temperature variation experiment and to small height differences on the wafer surface, a S_q of 0.2 µm and a S_z of 2 µm despite to 8 µm total etch depth. Increasing the temperature of the mixture to 29°C increased the total etch depth up to 13 µm (Fig. 3a) and increased the S_q to 0.7 µm and 7 µm S_z (Fig. 2). The texturing height at 52°C was about 2 to 5 µm (Fig. 4) at 17 µm total etch depth.

Increasing the temperature of the mixture with sulfuric acid decreased the total reflection at 600 nm of the wafer surface from 37.1% at 3°C to 22.0% at 46°C. This is the opposite effect, known from the HF/HNO_3 solution, where the reflection decreases with decreasing temperature due to the lower etching rate. Therefore, a further increase of the temperature was conducted for DWS wafers (Fig. 3). At temperatures above 45°C the total reflection remained at 22%, and the macroscopic and microscopic texture was homogenous (Fig. 2). Deep holes that usually occur on wafers etched in HF rich HF/HNO_3 solutions without sulfuric acid could neither be seen on the scan image nor on the confocal image of a wafer textured in $HF/HNO_3/H_2SO_4$. Even for SDE surfaces that do not have a saw damage, the sulfuric acid texturing process led to 22% total reflection (Fig. 3).

These experiments have been carried out on small wafers. Larger wafers with an area of 156x156 mm², which are commonly used in PV industry, have been etched vertically in 18 L solution (Fig. 4). The averaged reflection was 20.8±0.1% (n=9) for DWS and 20.6± 0.1% for SDE (n=8) wafers for different runs. The scans show a homogenous surface without holes and saw marks (Fig. 4). The edge of the wafer was not textured because the wafers floated. In this edge part the saw marks were still visible, but in the textured part they vanished.

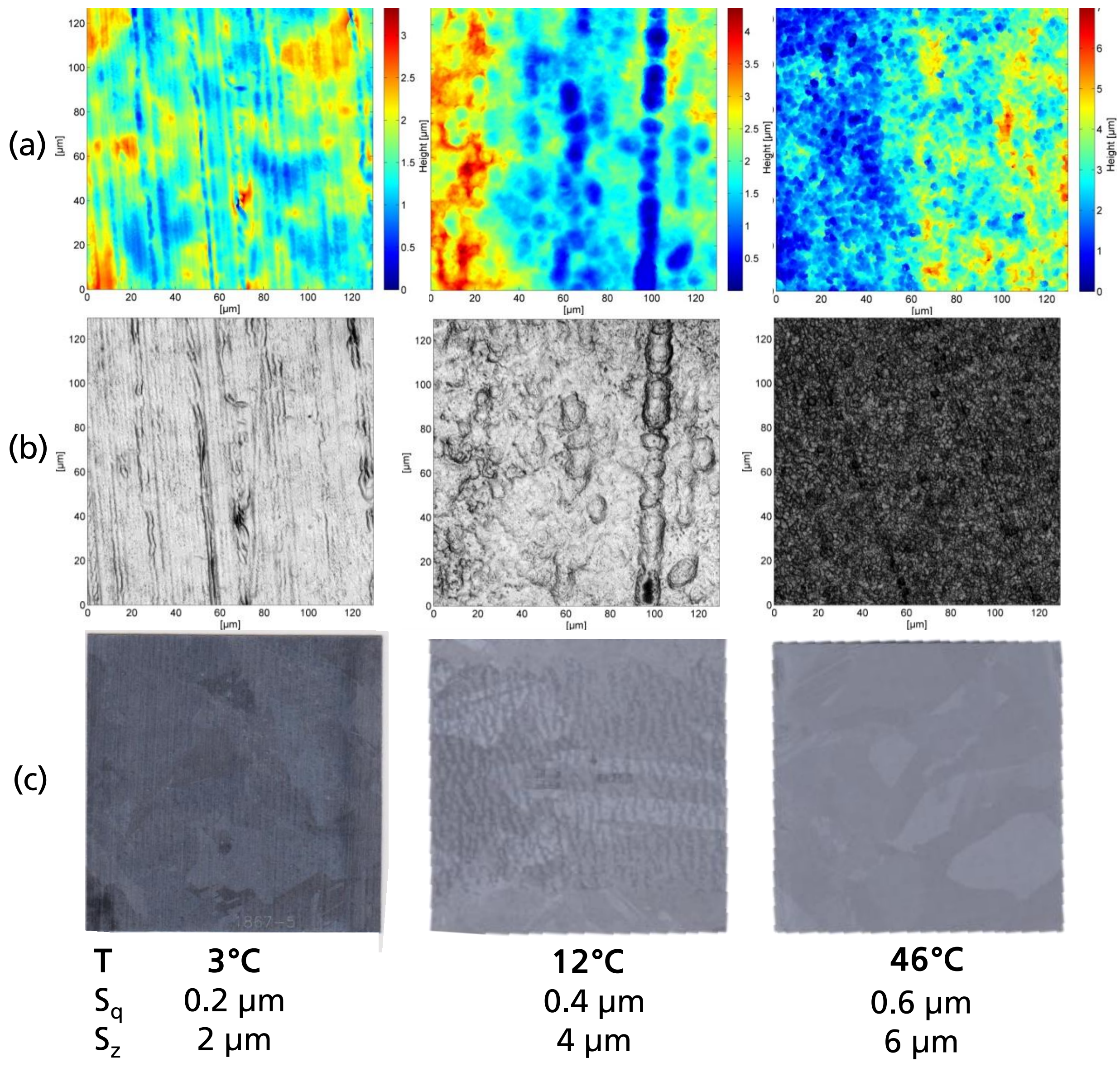
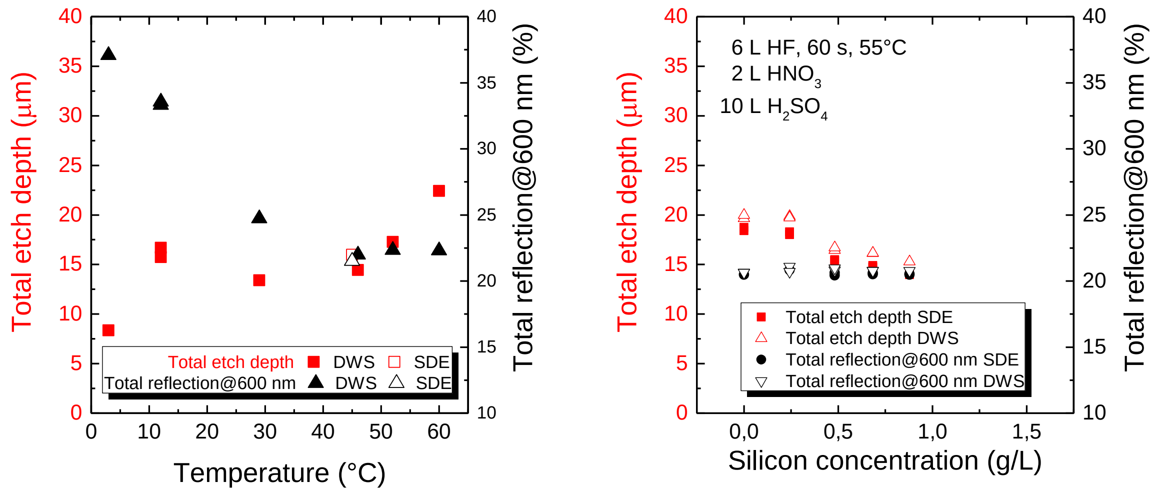
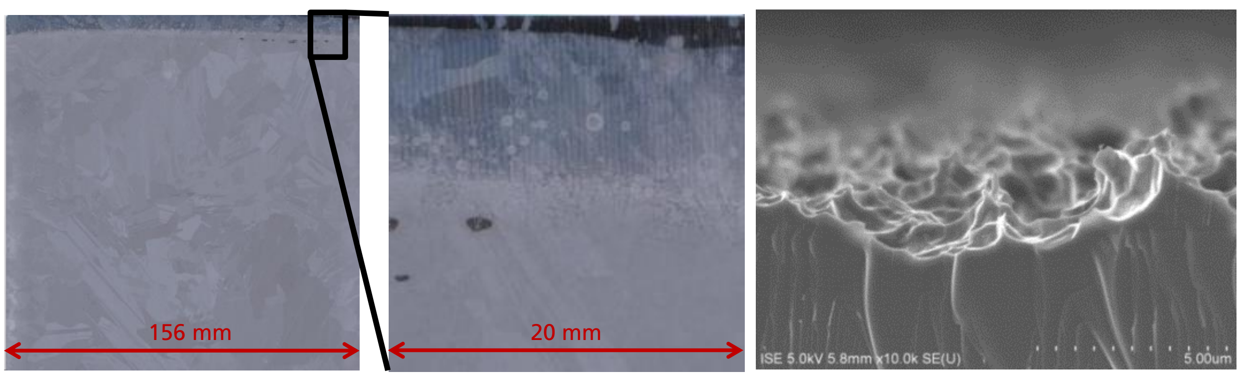


FIGURE 2. (a) Confocal height, (b) confocal laser intensity pictures and (c) photographs of 30x30 mm². mc-Si DWS wafers textured in 45 mL HF, 15 mL HNO_3, 90 mL H_2SO_4 at different bath temperatures for 60 s (new solution). At temperatures above 45°C the total reflection remained at 22%, and the macroscopic and the microscopic texture was homogenous.



(a) (b)

FIGURE 3. (a) Temperature variation for 30x30 mm² DWS wafers etched for 60 s in 45 mL HF, 15 mL HNO_3, 90 mL H_2SO_4. For each time temperature a new solution was used. (b) 156x156 mm² DWS and SDE wafer etched in 18 L solution.



(a) (b) (c)

FIGURE 4. (a) Top view photograph of a 156x156 mm² partly etched DWS wafer and (b) a detail etched in 6 L HF, 2 L HNO_3, 10 L H_2SO_4, 0 g/l Si at 55°C. (c) SEM cross section for DWS wafer textured in 45 mL HF, 15 mL HNO_3 90 mL H_2SO_4 at 52°C mc-Si DWS. 60 s etching time.

Time Variation in $HF/HNO_3/H_2SO_4$

In order to study the initiation of the etching attack and the etching progress, wafers were etched time-dependent with $HF/HNO_3/H_2SO_4$. The initial high etch rate of 49 µm/min for DWS wafers was reduced to 10 µm/min for etch depths bigger than 6 µm. So the DWS saw damage was completely removed after 6 µm total etch depth in this experiment (Table 1). The total reflection was reduced from above 35% after 2 s to 22% after 60 s for SDE and DWS wafers. The total etch depth was 18 µm for DWS and 16 µm for SDE wafers after 60 s.

The etched surface shows structure differences for DWS and SDE wafers (Fig. 5). For DWS wafers the saw damage grooves were etched as in HF/HNO_3. Around the grooves small etch pits appeared after 5 s. For DWS wafers the surface was nearly completely covered with etch pits of about 2 µm size after 10 s. The surface structure of SDE wafers without saw damage resulted in rough pits after 2 and 5 s (Fig. 5). These etch pits were about 5 to 10 µm in diameter. After 10 s small 2 µm etch pits appeared on the wafer surface, covering about 40% of the wafer. The pits multiplied until the whole surface was covered after 40 s. The resulting height and size structure was about 2 to 5 µm.

TABLE 1. Total etch depth, etch rate and total reflection at 600 nm for DWS and SDE wafers for etch time variation at 46°C in 45 mL HF, 15 mL HNO_3, 90 mL H_2SO_4. For each time a new solution was used. The etch rate was calculated by dividing total etch depth and etching time.

Time (s)	DWS Total etch depth (µm)	DWS Etch rate per side (µm/min)	DWS Total reflection	SDE Total etch depth (µm)	SDE Etch rate per side (µm/min)	SDE Total reflection (%)
0	0.0		42.0	0.0		
2	3.2	48.6	35.0	1.7	25.8	36.1
5	3.6	21.5	33.3	0.7	4.3	35.6
10	5.8	17.3	26.4	3.3	10.0	32.3
20	6.8	10.2	22.2	5.6	8.4	26.4
40	12.3	9.2	23.8	8.4	6.3	22.9
60	18.3	9.2	22.0	16.0	8.0	21.5

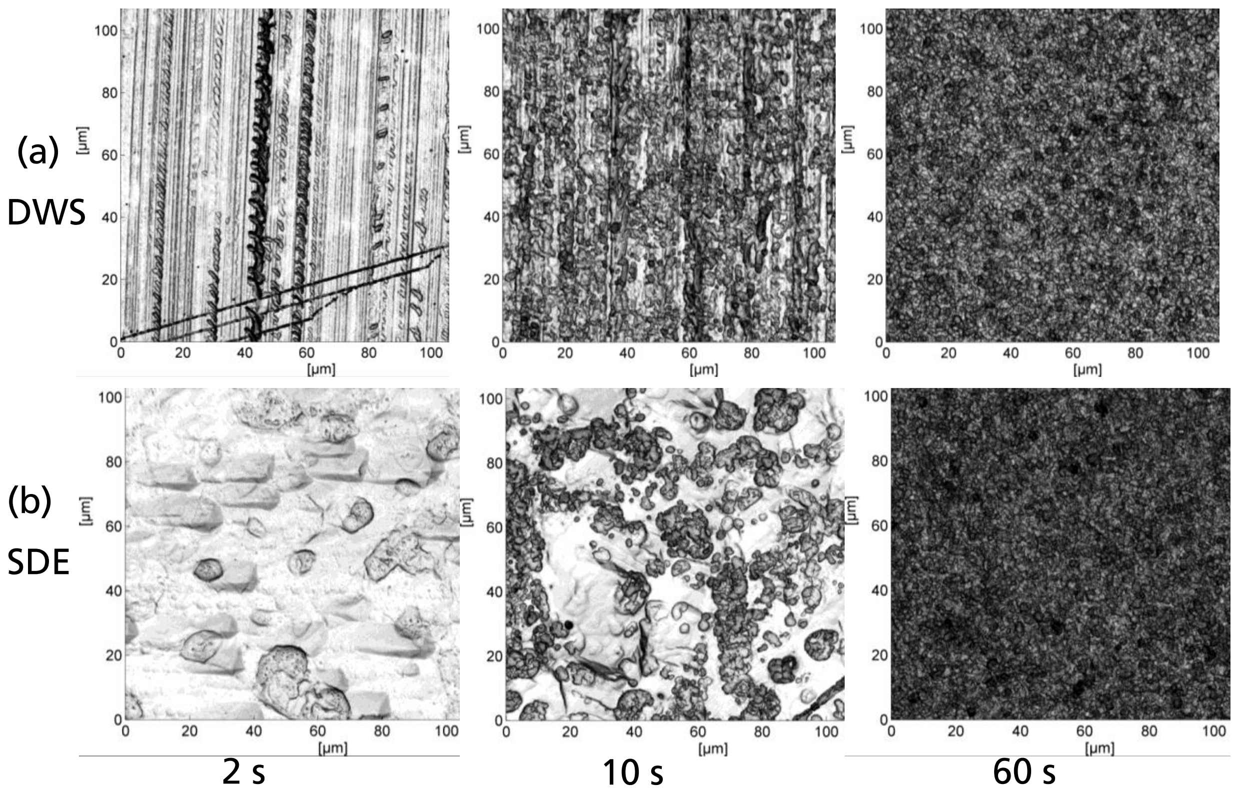


FIGURE 5. Confocal laser intensity images of etch time variation for (a) DWS and (b) SDE wafers etched in 45 mL HF, 15 mL HNO_3, 90 mL H_2SO_4 at 46°C. For each time a new solution was used. After 10 s small 2 µm etch pits appeared on the SDE and DWS wafers, covering about 40% of the wafer.

DISCUSSION AND CONCLUSION

A mixture of HF and HNO_3 does not roughen mc-Si DWS wafers compared to MWSS wafers. In order to texture DWS surfaces a mixture of HF/HNO_3 and sulfuric acid (H_2SO_4) at different temperatures has been tested. The temperature of the mixture strongly influenced the texturing process. A low process temperature of 3°C led to 2 µm texture height differences at 8 µm etch depth. A process temperature above 46°C yielded a reproducible texture with 15 µm total etch depth and a total reflection of 22% and a texture size of 2 µm. This decrease of reflection did not depend on the etch depth, since the etch depth was 14 to 16 µm at temperatures between 12 and 46°C (Fig. 3a). This reflection decrease was caused by the elevated temperature. This process can texture mc-Si DWS reliably to a reflection of 22%.

The sulfuric acid process successfully textured 156x156 mm² wafers homogenously up to total reflection of 22% at 52°C. Even SDE surfaces that do not have a saw damage could be texturized. Therefore, the texturing process does not depend on the initial wafer surface as it has been shown on shiny etched wafers [13].

A time variation revealed a time resolved texturing result for $HF/HNO_3/H_2SO_4$ at 46°C. For SDE and DWS wafers etch pits of about 2 µm size appeared after 10 s which was the resulting surface structure. The structures on the wafers of the time variation resemble structures on wafers of a time variation in a sulfuric rich $HF/HNO_3/H_2SO_4$ solution on shiny etched wafers of Lippold [13]. At 14 µm etch depth a etch pit structure of 2 µm size occurred. Liu (2015) demonstrated the formation of small and deep corrosive etch pits with the average size of 1 µm by using a simple vapor etching technique [16]. Liu (2015) heated HF/HNO_3 in a ratio of 1:3 to 90°C and etched the wafer in the vapor up to reflections of 12% at 600 nm after 15 min. The passivation quality of these vapor etched wafers was not mentioned. In our study the gas bubbles stuck on the wafers for a long time and expanded. The occurrence of bubbles in the $HF/HNO_3/H_2SO_4$ solution did not stop despite of the HF/HNO_3 reaction on DWS wafers. We suppose an etching mechanism of $HF/HNO_3/H_2SO_4$ producing gas bubbles containing NO_x. This mechanism might explain the temperature dependence, as the NO_x solubility is lower at high temperatures, the vapor pressure of HF is higher at higher temperatures so that the gas bubbles contain a better $HF_{(g)}/NO_x$ ratio.

The next research steps on this process should be further investigations to the etching mechanism including a detailed gas bubble study, showing a good surface passivation and a solar cell process. The mixture has to be further adjusted by reducing or replacing the sulfuric acid ratio of the solution in order to find a composition that is suitable for handling the mixture in a texturing plant.

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REFERENCES

1. W. Chen, X. Liu, M. Li, C. Yin, and L. Zhou, Materials Science in Semiconductor Processing **27**, 220 (2014).
2. A. Bidiville, K. Wasmer, R. Kraft., C. Ballif, “Diamond Wire-Sawn Silicon Wafers - from the Lab to the Cell Production,” in *24th EUPVSEC*. Proceedings (2009), 2CV.1.86, p. 1400.
3. B. Meinel, T. Koschwitz, C. Blocks, and J. Acker, Materials Science in Semiconductor Processing **26**, 93 (2014).
4. M. A. Green, Solar Energy **74**, 181 (2003).
5. H. Takato, I. Sakata, K. Mase, S. Ishibashi, T. Harada, Y. Kondo, and H. Asai, Method for fabricating substrate for solar cell and solar cell, US 2013/0306148 A1 .
6. Y. Nishimoto, J. Electrochem. Soc. **146**, 457 (1999).
7. Y. F. Zhuang, S. H. Zhong, Z. G. Huang, and W. Z. Shen, Solar Energy Materials and Solar Cells **153**, 18 (2016).
8. A. Kumagai, Solar Energy Materials and Solar Cells **133**, 216 (2015).
9. M. Lippold, F. Buchholz, C. Gondek, F. Honeit, E. Wefringhaus, and E. Kroke, Solar Energy Materials and Solar Cells **127**, 104 (2014).
10. R. Watanabe, S. Abe, S. Haruyama, T. Suzuki, M. Onuma, and Y. Saito, International Journal of Photoenergy **2013**, 1 (2013).
11. P.-C. Tsai, “HF–HNO3–H2SO4 system for texturing diamond wire sawn multi-crystalline silicon wafer,” in *International PVSEC-26 2016* (2016), 2_2-0021.
12. A. Kübelbeck, C. Zielinski, T. Gölzenleuchter, Verfahren zur Rauhätzung von Siliziumsolarzellen, DE19962136 A1 (22 December 1999).
13. M. Lippold, *Beiträge zum Verständnis des sauren nasschemischen Ätzens von Silicium - Das System HF-HNO3-H2SO4/H2O*, Dissertation, TU Bergakademie Freiberg, 2014.
14. H. Preising, V. Speer, G. Göthe, H.-J Axmann, M. Matthias, D. Seyboth, Ätzmischung zur Herstellung einer strukturierten Oberfläche auf Siliziumsubstraten, DE102009007136A1 (12 August 2010).
15. M. Lippold, S. Patzig-Klein, and E. Kroke, Z. Naturforsch. B **66**, 155 (2011).
16. 刘. LIU Xiao-mei, 李. LI Miao, 陈. CHEN Wen-hao, and 周. ZHOU Lang, ACTA PHOTONICA SINICA **44**, 1004 (2015).