

Pyramidal texturing of silicon solar cell with TMAH chemical anisotropic etching

P. Papet*, O. Nichiporuk, A. Kaminski, Y. Rozier, J. Kraiem,
J.-F. Lelievre, A. Chaumartin, A. Fave, M. Lemit

*Laboratoire de Physique de la Matière, UMR-CNRS 5511, Institut National des Sciences Appliquées de Lyon,
Bât Blaise Pascal, 7 avenue Jean Capelle, 69621 Villeurbanne Cedex, France*

Available online 19 April 2006

Abstract

High-efficiency silicon solar cells need a textured front surface to reduce reflectance and to improve light trapping. Texturing of monocrystalline silicon is usually done in alkaline solutions. These solutions are cheaper, but are pollutants of silicon technologies. In this paper, we investigate an alternative solution containing tetramethyl ammonium hydroxide ($((\text{CH}_3)_4\text{NOH})$, TMAH). This study shows the influence of different parameters (concentration, agitation, duration and temperature), to obtain uniform and reliable pyramidal texturization on different silicon surfaces (as cut, etched and polished). Under optimized conditions, TMAH-textured surface led to an average weighted reflectance of 13%, without any antireflection coating independent of the initial silicon surface. Unlike potassium hydroxide (KOH) texturing solution, characterization of silicon oxide layer contamination after TMAH texturing process revealed no pollution, and passivation is less affected by TMAH than by KOH texturization.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Solar cells; Texturing; Light trapping; Reflectance; TMAH

1. Introduction

With the purpose to increase the light collection and the efficiency of silicon solar cells, the reflection of the front surface needs to be minimized. This improvement is currently achieved by a textured surface covered by an antireflection coating. This surface pattern

*Corresponding author. Tel.: +33 4 72 43 85 40; fax: +33 4 72 43 85 31.

E-mail address: pierre.papet@insa-lyon.fr (P. Papet).

can be realized by different techniques: plasma etching, mechanical engraving, and chemical etching. The last one is actually a good compromise between cost and efficiency. Photovoltaic production widely uses potassium hydroxide (KOH) or sodium hydroxide (NaOH) as aqueous texturing solutions. These alkaline solutions etch the silicon anisotropically and form small pyramids on the silicon surface. Hence, light collection is increased by multiple reflections.

KOH and NaOH etching solutions are cost and time efficient but present some drawbacks: the potassium and sodium contaminations are detrimental for microelectronic devices, and are supposed to have the same effect on solar cell devices. A promising alternative solution is tetramethyl ammonium hydroxide ($((\text{CH}_3)_4\text{NOH})$, TMAH) [1]. This solution is widely used in microelectronic and MEMS, because it combines high etching rate and a good anisotropic etching with a full compatibility with microelectronic technologies. Moreover, this solution is clean room compatible, nontoxic and easy to handle [2,3]. TMAH solution also exhibits excellent selectivity towards silicon oxide and silicon nitride masks [4,5].

Many studies were reported about TMAH etching to obtain smooth surface for MEMS [5], but only few results were reported on the texturization of silicon surface to improve light trapping in solar cells. You [1] was the first to apply TMAH solution for random pyramidal silicon texturing. Their study was conducted for high concentrations of TMAH (5–25%) and characterized using normal incident reflectivity. Iencinella [6] reported another recipe for random pyramidal texturing using a 5% TMAH solution without surfactant. With their method, the texturization efficiency depends on the concentration of dissolved silicon in the solution, and uniform texture was only obtained when the initial etching solution contained dissolved silicon. In order to minimize the quantity of TMAH used and to simplify the TMAH texturing method, this study presents an alternative method to create uniform and reproducible pyramidal texture on silicon wafer with help of surfactant isopropyl alcohol (IPA) and agitation. In photovoltaic laboratories and firms, texturization can be realized on different initial surfaces: polished (high-quality FZ-Si wafers for laboratory cells or epitaxial layer), etched (not polished) or as-cut (after ingot sawing). Therefore, TMAH texturing method should work for all these initial surfaces. To optimize our solution, the texturing process was also conducted at different temperatures, solution composition and texturing times.

As the pollution of the passivation layer was an important point for the use of TMAH, we compared the influence of KOH and TMAH texturing solutions on the minority carrier's lifetime of textured wafer and on silicon oxide contaminations. Finally, reflectance measurements were performed using silicon wafer textured by the optimized TMAH solution and covered by hydrogenated silicon nitride $\text{SiN}_x\text{:H}$ antireflection coating (ARC).

2. Experimental

Experiments were carried out in a capped vessel in order to limit evaporation of the solution. The vessel was inserted in a heater to control the temperature. Texturing solutions were prepared using a 25% commercial TMAH solution, deionized water and standard IPA. All etching experiments were carried out using [100]-oriented, *p*-doped ($1\text{--}10\ \Omega\text{cm}$) silicon wafers. Before any etching process, samples were dipped in a 5% HF solution for 10 s in order to remove the native oxide, and subsequently rinsed in deionized

water. The weighted reflectance (WR) was calculated normalizing the hemispherical reflectance spectrum (350–1100 nm) by the AM1.5D spectrum [7].

For silicon oxide charge density measurements, 60 nm dry oxides were grown (20 min at 1050 °C in O₂ atmosphere) on Si wafers. Oxidized wafers were etched by HF on one side, cleaved and each part underwent either TMAH texturization (2% TMAH, 8% IPA, 80 °C, 30 min), or KOH texturization (1% KOH, 8% IPA, 80 °C, 30 min) [8], or nothing. Next, 1 μm thick aluminum contacts were evaporated on the etched side. On the oxidized side, 1.7×10^{-4} /cm² aluminum square patterns were deposited to create MOS structure. All samples were annealed for 10 min in forming gas (H₂/N₂) ambiance at 500 °C to allow charge diffusion in oxide and to improve Al contacts. Capacitance–voltage measurements were performed on a large frequency range (1 kHz–1 MHz using a HP4284A) to determine oxide thickness and charge density in silicon oxide layers.

Passivation comparison between KOH- and TMAH-textured surface was achieved by minority carrier lifetime measurements. From the same polished wafer, three parts underwent texturization with either KOH texturing solution (1% KOH, 8% IPA, 80 °C, 30 min), or TMAH texturing solution (2% TMAH, 8% IPA, 80 °C, 30 min), or nothing. Each part was then cleaned for 10 min in a mixture of H₂O₂:H₂SO₄ followed by 10 s in 5% HF. The SiN_x:H passivation layer was deposited on each surface and minority carrier lifetime measurements were performed.

The SiN_x:H film was deposited on silicon substrates by low-frequency (440 kHz) plasma-enhanced chemical vapor deposition (LF-PECVD). The reactor used was developed by SEMCO-Engineering. The near-stoichiometric SiN_x:H films were prepared using ammonia (NH₃) and silane (SiH₄) as reactant gas sources. The temperature was fixed at 400 °C, pressure at 1500 mTorr and the gas flow ratio NH₃/SiH₄ at 7.7. Spectroscopic ellipsometry measurements allowed to determinate the thickness $e = 75$ nm and refractive index $n(605 \text{ nm}) = 2$.

3. Results and discussion

3.1. Uniformity and reliability

The first trials were done using only diluted TMAH at different temperatures and etching times. Results indicated that during texturing, large hydrogen bubbles (3 mm size) stuck to the silicon surface, and created neither uniform textures (because of different sizes of pyramids) nor reproducible results. During etching, for aqueous chemical texturing with basic solution (e.g.: KOH, NaOH, TMAH), the population and size distributions of pyramids are governed by hydrogen bubbles [9–11]. These bubbles are generated during etching and easily stuck to the etched surface, and cause the “pseudo-mask” phenomenon. Stuck bubbles suppress the chemical reaction between the etching solution and the silicon atoms to create pyramids. In this case, the control of the distribution and the size of hydrogen bubbles will be the key point to obtain uniform and low-reflecting surfaces.

To avoid the formation of these large bubbles, we proposed and tested two solutions: (i) apply a forced convection by external agitation, or (ii) use a surfactant to increase the hydrophilic nature of silicon surface toward hydrogen bubbles. Consequently, bubbles are less able to adhere to the etched surface [12]. First, we tested admixture of surfactant; we chose IPA because it is often used in industry with KOH and NaOH. We obtained

encouraging results using 10% of IPA, large bubbles moved away from the silicon surface, however, only as-cut initial surfaces were uniformly textured (Table 1).

For etched and polished surfaces, we also decided to test two types of external agitations: driven stirring bar and ultrasonic (US) agitation. With the first one, we obtained a better reflectance (18%) than without agitation. Nevertheless, after etching, the uniformity was not reached, because the textured side presented different dark splashes (Table 1). The use of US led to a reproducible and uniform texture on the whole wafer surface. However, we measured a weighted reflectance of 28%. scanning electron microscopy (SEM) image showed that the surface was very rough. In so far, the surface

Table 1

Uniformity characterization by three different point measurements of weighted reflectance after texturization of each initial silicon surfaces

Type of agitation	As-cut wafer	Etched wafer	Polished wafer
No agitation	13.8	29	36.9
	13.6	22.9	30
	14	29	36.8
Stirring bar	12.4	20.6	17.6
	12.5	17.3	12.4
	12.1	23.4	18
Ultrasonic waves	12.4	12.4	12.7
	12.3	12.5	12.6
	12.2	12.4	12.4

TMAH texturing process: 2% TMAH, 8% IPA, 80 °C, 30 min.

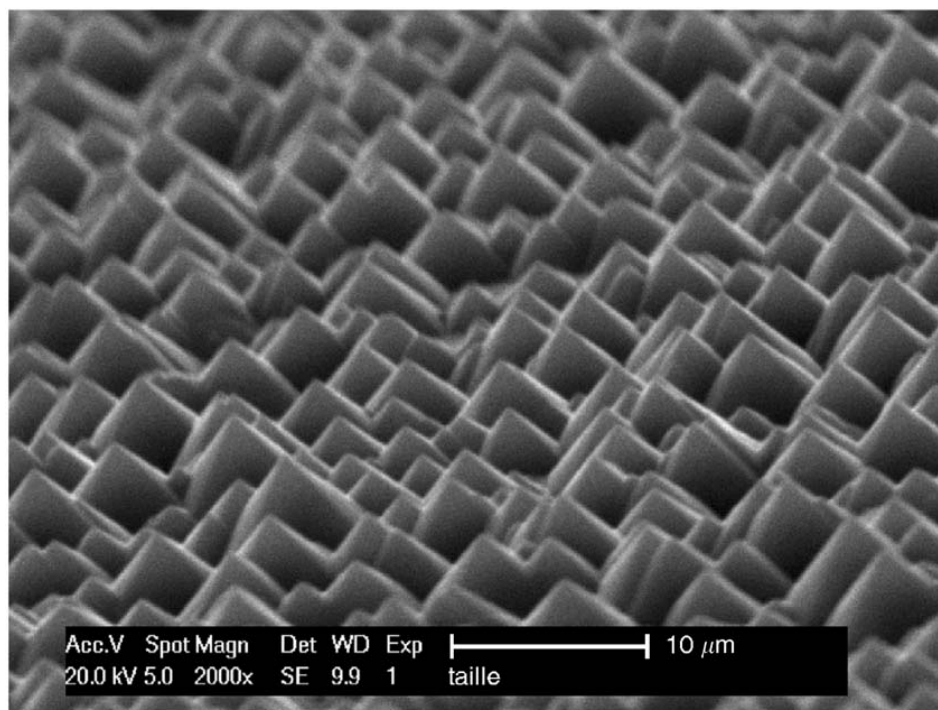


Fig. 1. SEM image of a TMAH-textured wafer after optimized etching: 20 min US + 10 min without agitation, 2% TMAH, 10% IPA, 80 °C.

was rough but not pyramidal-textured, we let the sample in the solution without agitation. After 10 min, we obtained uniform-textured surface covered by 5 μm high pyramids (Fig. 1).

Taking into consideration these results, the US use allowed formation of uniformly rough silicon surface. Thus, without agitation, this rough surface becomes a perfect area to obtain uniform pyramidal-textured surface. This assumption is confirmed (Table 2) for as-cut surfaces, which are very rough; uniformity is obtained whatever the type of agitation.

In this part, we defined the TMAH etching process for as-cut, etched and polished silicon surfaces. In the following part, the admixture containing the TMAH etching solution was optimized to increase light trapping. Various parameters were studied: TMAH concentration, IPA concentration, etching time and temperature.

Table 2

Silicon oxide thickness and positive charge density in oxide after different texturing methods extracted from CV measurements

	Initial	After TMAH texturing	After KOH texturing
Flatband voltage (V)	−1.5	−1.52	−4.3
Oxide capacitance at $V_g = -10$ V (F)	1.1×10^{11}	1.3×10^{11}	2.2×10^{11}
Oxide thickness (nm)	60	50	30
Positive charges in oxide ($/\text{cm}^3$)	7×10^{16}	9×10^{16}	1×10^{18}

TMAH texturing process: 2% TMAH, 8% IPA, 80 °C, 30 min. KOH texturing process: 1% KOH, 8% IPA, 80 °C, 30 min (V_g : gate voltage).

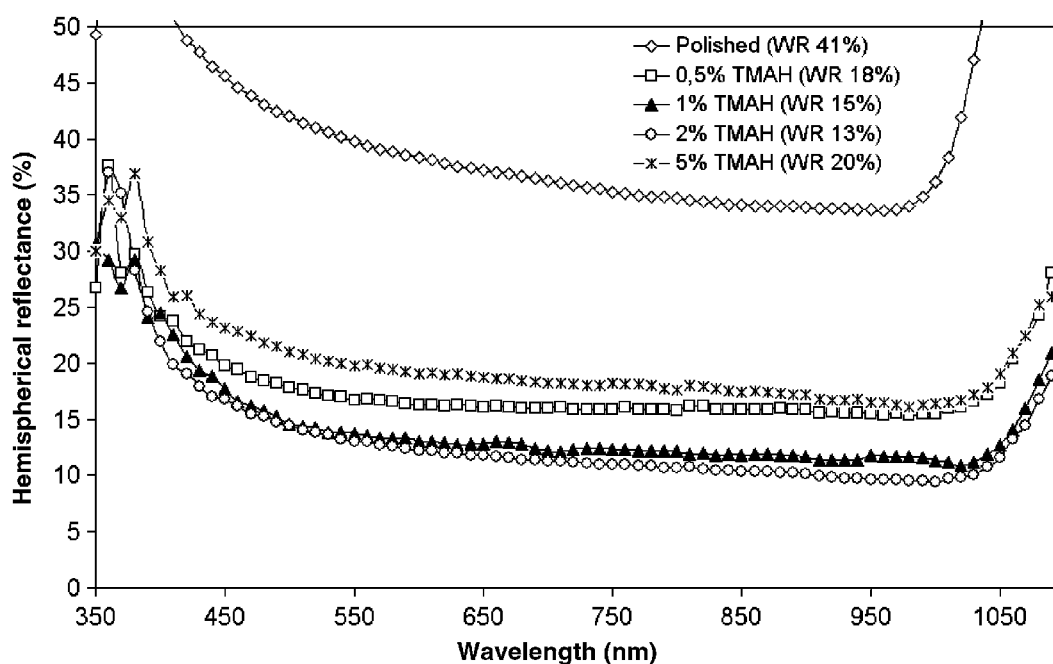


Fig. 2. Influence of TMAH concentration in the texturing solution. Texturing conditions: 20 min US + 10 min without agitation, 10% IPA, 80 °C.

3.2. Parameter optimization

First, we varied the TMAH concentration from 0% to 5%. As can be seen in Fig. 2, the reflectance was found to decrease with increasing TMAH concentration up to 2%. This result is explained by uniformity improvement. For a 5% concentration, the reflectivity was higher because pyramids were smaller, but the uniformity was still good. Even if TMAH solution is quite expensive, the only 2% concentration needed to texture surface makes this method very competitively priced.

As we said previously, IPA is a widely used surfactant to diminish the adherence of hydrogen bubbles to the etched surface. The dependence between IPA concentration and reflectivity is shown in Fig. 3. Reflectance decreases with IPA concentration up to 9% due to uniformity improvement. Beyond this concentration, good uniformity was always obtained, but the surface reflectance increased. Pyramids were smaller and therefore, we can make the assumption that the wettability was so important that bubbles stuck on silicon surface were too small to obtain high pyramids.

We had also optimized the duration of texturing on polished and etched samples. For the first step with US waves, we obtained uniform and reliable roughness for all the wafers after 20 min. The second step without agitation allowed the formation of pyramids with very good reflectance after 10 min. Beyond this time, wafer thickness decreased with an etch rate of approximately $10\text{ }\mu\text{m/h}$ without pyramid size modification.

To determine the temperature influence, experiments were carried out from 60 to $90\text{ }^{\circ}\text{C}$. Fig. 4 shows that the surface reflectance decreased with increasing temperature. Sundaram reported [12] that, with the increase of temperature, the etch rate of the (100) and (110) crystallographic planes increased faster than the etch rate of the (111) crystallographic

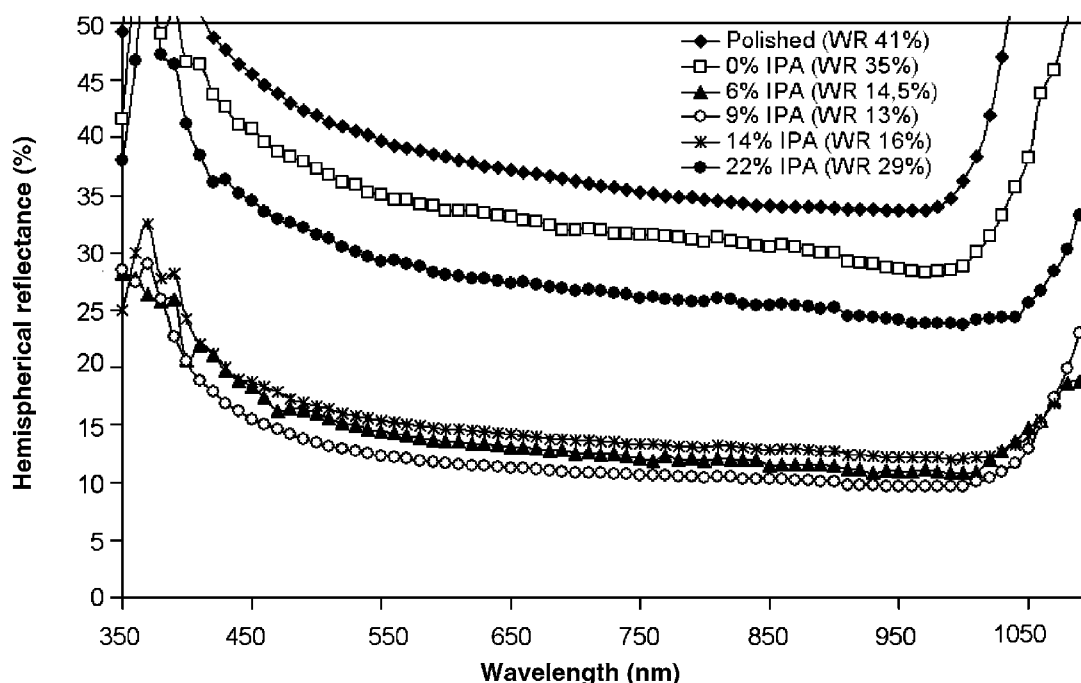


Fig. 3. Weighted reflectance of textured wafers versus isopropanol concentration. Texturing conditions: 20 min US + 10 min without agitation, 2% TMAH, $80\text{ }^{\circ}\text{C}$.

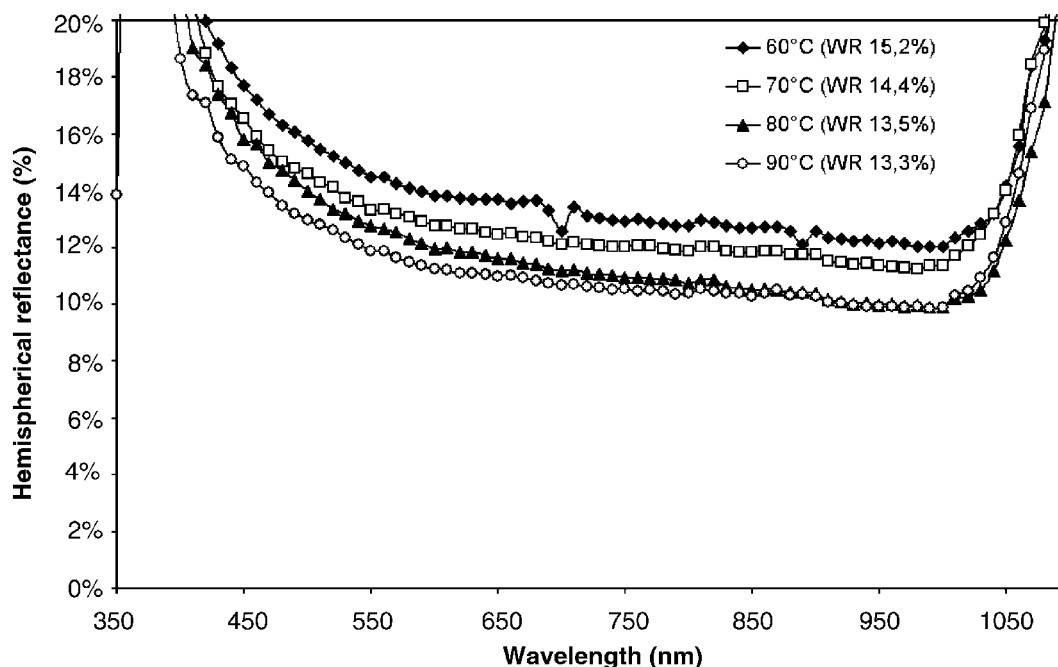


Fig. 4. Weighted reflectance of textured wafers versus temperature. Texturing conditions: 20 min US + 10 min without agitation, 2% TMAH, 10% IPA.

plane. When temperature increased, this difference of etch rate led to the formation of higher pyramids and to a decrease of the reflectance.

Sparber [8] reported a weighted reflectance of 12.5% obtained on silicon surface textured by an optimized solution of 1% KOH and 7% IPA at 80 °C. For our TMAH texturing method, results are similar, but in the following part, we present two major advantages of TMAH use.

3.3. Passivation and contamination

3.3.1. Oxide contamination

In our laboratory, we develop solar cells by the ELIT process [13] based on layer transfer: an epitaxial layer is grown by vapor phase epitaxy on porous silicon (previously realized on Cz–Si wafer). Oxidation, diffusion and deposition of interdigitated back contacts are realized on the surface of the epitaxial layer. Then the solar cell is detached via the sacrificial porous Si. Only after detachment, texturization and ARC are applied on the front surface of the cell. In this process, the silicon oxide layer situated between the back *n*- and *p*-type contacts passivates the back surface and the surface texturization is performed only at the end of the process. If this oxide presents a large density of positive charges, an inversion layer can be created, which shunts the *n/p* junction. This phenomenon reduces the efficiency of interdigitated back contact cells [14]. In order to compare KOH and TMAH surface contaminations, we calculated the charge concentration in silicon oxide after each texturing method by analyzing CV measurements. After 30 min in KOH texturing solution (1% KOH, 8% IPA, 80 °C) [8], flatband voltage moved from –1.5 to –4.3 V (Table 2). This difference is explained by an increase of positive charge in the oxide after KOH texturing, probably due to K^+ ionic impurities. On the other hand, 30 min in TMAH

texturing solution (2% TMAH, 8% IPA, 80 °C) modified slightly the flatband voltage, indicating that charge density modification was almost negligible.

Furthermore, these measurements allowed us to evaluate the difference in etch rate of the two solutions. After 30 min in KOH, the oxide capacitance increased from 1.1×10^{11} to 2.2×10^{11} F (Table 2). This corresponds to a decrease of the oxide thickness from 60 to 30 nm. With TMAH, the difference was only 10 nm.

Therefore, we can conclude that 30 min at 80 °C in an admixture of 2% TMAH, 8% IPA did not contaminate silicon oxide, and only 10 nm was etched. Hence, TMAH will be preferred to KOH for ELIT process.

3.3.2. Passivation quality

In photovoltaic industries, $\text{SiN}_x\text{:H}$ ARC is often deposited after texturing in order to increase light collection and to passivate silicon surface. In Fig. 5, we can see that minority carrier lifetime of a wafer textured by TMAH is slightly inferior to that of a polished surface. However, for KOH, the difference is more important. The TMAH-textured surface is better passivated by $\text{SiN}_x\text{:H}$ than the KOH-textured wafer. The difference is probably due to K^+ contamination.

3.4. Front surface cell reflectance

In order to estimate the hemispherical reflectance of a solar cell covered with an ARC, an optimized $\text{SiN}_x\text{:H}$ ARC was deposited on different surfaces (polished, pyramidal-textured). The reflectance graphs are shown in Fig. 6. The reflectance minimum at 600 nm is due to well-optimized ARC. Between the polished and the pyramidal texturing surfaces, Fig. 6 shows a large decrease of the reflectance over the entire spectrum. This difference

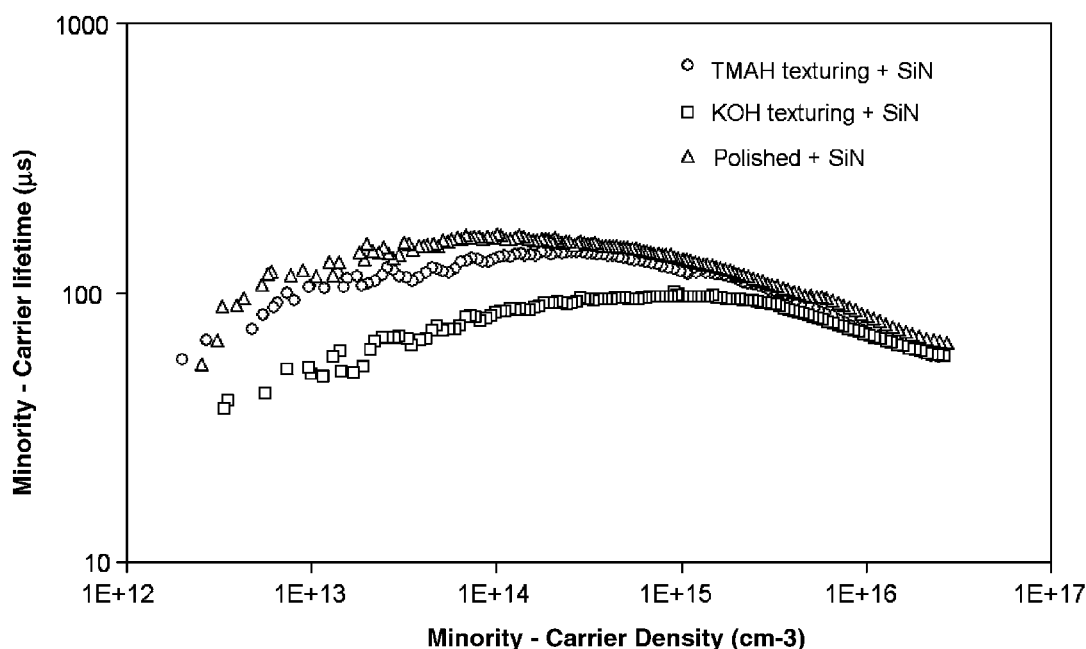


Fig. 5. Minority carrier lifetime measurements of silicon samples textured by KOH (1% KOH, 8% IPA, 80 °C, 30 min) or TMAH (2% TMAH, 8% IPA, 80 °C, 30 min), and covered by a double-side $\text{SiN}_x\text{:H}$ coating.

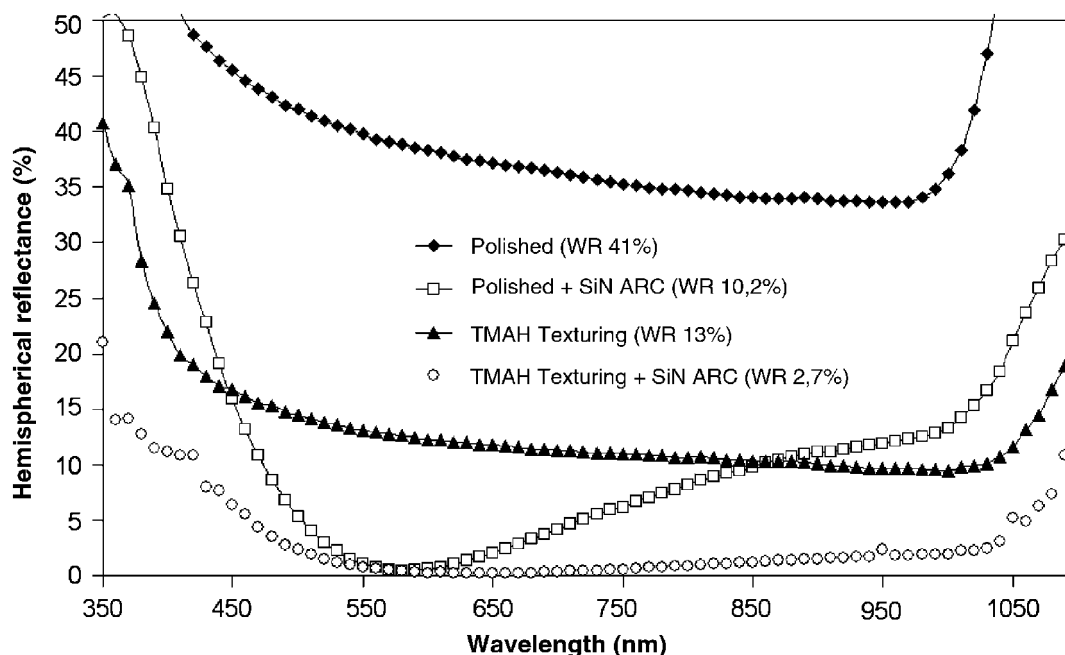


Fig. 6. Weighted reflectance of different silicon surface morphologies, and with or without ARC. TMAH texturing conditions: 20 min US + 10 min without agitation, 2% TMAH, 9% IPA, 90 °C.

can only be explained by light trapping improvement. A low weighted reflectance of 2.7% was obtained with a combination of TMAH pyramidal texture and $\text{SiN}_x\text{:H}$ ARC.

4. Conclusion

In this paper, we have shown that TMAH texturing solution can be a very worthwhile method to texture all types of silicon wafer surfaces. This texture was realized on polished and etched silicon surfaces with etching mixture of TMAH using two steps. The first one consisted of increasing the surface roughness by US waves (20 min). This surface preparation ensured uniformity. The second step without agitation (10 min) engraved pyramidal texture. For as-cut wafers, agitation was useless. Our optimized process lasted for 30 min at 80 °C using a solution containing 2% TMAH and 8% IPA. After texturing, for all the initial surfaces (as-cut, etched and polished), we obtained reliable and uniform pyramidal texturing surfaces with an average weighted reflectance of 13%. This study showed that TMAH texturing solution was not pollutant for silicon oxide unlike KOH, and surface textured by TMAH was easier to passivate than KOH. Moreover, TMAH was a little toxic and clean room compatible.

References

- [1] J.S. You, et al., *Sol. Energy Mater. Sol. Cells* 66 (1–4) (2001) 37.
- [2] J.T.L. Thong, W.K. Choi, C.W. Chong, *Sens. Actuat. A* 63 (1997) 243.
- [3] M. Shikada, K. Sato, K. Tokoro, D. Uchikawa, *Sens. Actuat. A* 80 (2000) 179.
- [4] M.J. Madou, *Fundamentals of Microfabrication*, CRC Press, London, 2002.
- [5] P.M. Sarro, D. Brida, W. Vlist, S. Brida, *Sens. Actuat. A* 85 (2000) 340.
- [6] D. Iencinella, et al., *Sol. Energy Mater. Sol. Cells* 87 (2005) 725–732.

- [7] C. Honsberg, S. Bowden, *Photovoltaics: Devices, Systems and Applications* (CD).
- [8] W. Sparber, et al., in: *Proceedings Third World Conference Photovoltaic Energy Conference*, Osaka, 2003, pp. 1372–1375.
- [9] C.-R. Yang, P.-Y. Chen, C.-H. Yang, Y.-C. Chiou, R.-T. Lee, *Sens. Actuat. A* 119 (2005) 271.
- [10] E.D. Palik, O.J. Glembocki, I. Heard, P.S. Burno, L. Tenerz, *J. Appl. Phys.* 70 (6) (1991) 3291.
- [11] S.A. Campell, K. Cooper, L. Dixon, R. Earwaker, S.N. Port, *J. Micromech. Microeng.* 5 (1995) 209.
- [12] K.B. Sundaram, A. Vijayakumar, G. Subramanian, *Micro. Eng.* 77 (2005) 230–241.
- [13] J. Kraiem, et al., in: *15th International Photovoltaic Science and Engineering Conference*, Shanghai, 2005, pp. 746–747.
- [14] J.W. Muller, A. Mekle, R. Hezel, in: *19th European Photovoltaic Solar Energy Conference*, Paris, 2004, pp. 990–993.