JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 11 No 5, 05003(5pp) (2019) ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 11 № 5, 05003(5cc) (2019)

Basic Study of Mono-like Silicon Material Properties under Chemical Treatments: Comparison with Single and mc-Silicon

G. Benseba[1,*], A. Moussi[2,†], S. Meziani[2], D. Hocine[1], M.S. Belkaid[1]

[1] *Advanced Technologies Laboratory of Electrical Engineering (LATAGE), University Mouloud Mammeri of Tizi-Ouzou (UMMTO), BPN 17 R.P, Tizi Ouzou, Algeria*
[2] *DDCS Division, Research Center for Semiconductor Technology for Energy (CRTSE), Algeria, 02 Bd. Frantz Fanon, B.P 140 Alger –7 Merveilles –Algiers Algeria*

(Received 07 May 2019; revised manuscript received 23 October 2019; published online 25 October 2019)

In this paper, we present the study of the silicon mono-like (ML-Si) material. Its physical and chemical properties are analyzed and compared to those of Czochralski-monocrystalline silicon (Cz-Si) and multicrystalline silicon (mc-Si). After chemical treatment of each material, the surface is analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). We observe that Cz-Si and ML-Si present the same morphology and crystallographic orientation. FTIR analysis shows an (interstitial) oxygen content of the same order for three materials but with values of ML-Si closer to that of mc-Si. Substitutional carbon concentration is intermediate for ML-Si between those of Cz-Si and mc-Si. Reflectivity of ML-Si is 5 % higher than that of Cz-Si and much lower than mc-Si surface after NaOH texture. Photoluminescence analysis indicates that ML-Si and Cz-Si materials present better homogeneity than mc-Si material. At the final, we present the advantages and drawbacks of ML-Si material with regard to Cz-Si and mc-Si. ML-Si has better material properties, having fewer grain boundaries and dislocations compared to mc-Si. In addition, containing a single grain allows a lower surface reflectance to be obtained by using alkaline texturing. We also find that ML-Si is almost identical to Cz-Si.

Keywords: Mono-like (quasi-single crystalline) silicon, Physico-chemical properties, Chemical treatment, Analysis, Texturing.

DOI: 10.21272/jnep.11(5).05003 PACS numbers: 65.40.gk, 77.55.df, 81.40. – z

1. INTRODUCTION

The cost of silicon wafers is expected to be reduced for the next few decades, in order to make photovoltaic (PV) production more attractive and cost-effective solution to energy and environmental problems. The solar energy is more environmentally friendly than fossil fuels [1].

The most dominant substrates for the fabrication of solar cells in recent industry (PV) are the two types of silicon: monocrystalline silicon (Cz-Si) and multicrystalline silicon (mc-Si) [2-3].

Directional solidification (DS) has become an important growth process for mc-Si used as substrates for solar cells. It has been largely preferred technique due to its relatively low production costs compared to Czochralski (Cz) method, which is used to produce higher quality but expensive Cz-Si [4].

However, the growth of mc-Si ingots by directional solidification can generate many defects, such as grain boundaries (GBs), dislocations [5, 6], which have a detrimental effect on solar cells performances since they cause high recombination activities.

A new type of growth method has emerged in recent years consisting on DS using Cz-Si seeds to produce high-quality ingots [7-8] called mono-like or quasi-monocrystalline silicon (ML-Si), which is introduced in PV technology [9-11].

The use of ML-Si wafers for the elaboration of solar cells is a novel approach that combines the quality of Cz-Si and the low manufacturing costs of mc-Si. These "mono-like" cells represent an ideal compromise between efficiency and manufacturing costs [12]. The ML-Si is a marked improvement in the crystal quality of mc-Si. Additionally, the ML-Si placed at the bottom of the crystallization furnace (in DS technique) makes it possible to orient the growth of the silicon in order to obtain a good crystallographic quality similar to that of Cz-Si material [7]. This ML-Si can be considered as a perfect material for silicon solar cells [13] due to its several advantages, such as a square shape limiting the loss of material, single crystalline, low structural defect density and low fabrication cost.

In fact, the increase in efficiency of mono-like cells is explained by the lower concentration of impurities in the ingot, the almost non-existent GBs and the significant reduction in reflectivity.

It is well known that surface texturing of crystalline silicon wafers improves the conversion efficiency of solar cells by the rise of light trapping and the reduction of optical losses [14]. For this raison, wet chemical etching is regularly used in the solar cell industry for the texturization of silicon [15].

The chemicals such as alkaline solution (NaOH or KOH) used for surface texturing can be effective in reducing the surface reflectance with low silicon losses. Defects with very high dislocation densities and high surface reflectance after texturing can limit the application of mc-Si [14-16]. The objective of this work is to chemically treat surfaces of ML-Si, Cz-Si and mc-Si using an anisotropic (alkaline) chemical solution in order to improve the quality of their surfaces.

* ghaliabenseba@yahoo.fr
† a-moussi@crtse.dz

2. EXPERIMENTAL

We used in our experiments three types of wafers: <100> Cz-Si, ML-Si and heat exchanger method (HEM) mc-Si.

2.1 The Chemical Texturing

Surface texturing of crystalline silicon wafer improves the surface property and light trapping. Surface texture has been successfully produced by anisotropic chemical solutions of KOH or NaOH [7]. It is known that texturing involves exposition of (111) crystallographic planes, which yield pyramids on (100) oriented wafers.

2.2 The First Step is to Texture the Silicon Samples

All the ML-Si, Cz-Si and mc-Si samples were first etched in NaOH to remove saw damage material of 10 μm thick from each side of wafers and after that rinsed in HF (10 %). All the chemical processes were completed by rinsing in deionized water and drying in N_2.

By plunging them into a bath of KOH (or NaOH), anisotropic etching occurs on the surfaces of crystallographic orientation (100); pyramids then appear. The interest of texturing is thus also to improve silicon absorption of incident photons. Indeed, the created relief increases the number of reflections for the same photons, which multiplies its chances of being absorbed. Moreover, it deviates the trajectory of the photons and leads to an absorption closer to the surface.

The next step is the characterization of these samples.

2.3 Characterization of Crystalline Silicon

Three types of characterization were used to evaluate the quality of crystalline silicon:

- A compositional characterization

The Fourier transform infrared spectroscopy (FTIR) technique was used to determine the oxygen concentration of interstitial oxygen (Oi) and substitutional carbon (Cs).

- A structural characterization

Surface morphology was studied by scanning electron microscopy (SEM), photoluminescence (PL) and X-ray diffraction (XRD).

- Electrical characterization of materials was also achieved through resistivity measurement.

3. RESULTS AND DISCUSSION

3.1 Reflection Reduction by Alkaline Texture Etching

In order to improve the performance and, in particular, the output current of crystalline silicon-based PV devices, it is known to modify the texturing of the crystalline silicon surface by forming numerous irregular pyramid-shaped sections by a process of anisotropic engraving.

The process of anisotropic wet chemical etching in an alkaline medium used to form pyramids has the consequence of producing valleys, whose bottom has sharp edges. The valley is the area connecting the base of the pyramids.

This experiment is carried out on Cz-Si, ML-Si and mc-Si substrate pieces of size (2.5 cm×2.5 cm).

In our work, we used basic texturization (NaOH).

Fig. 1 shows the characteristic reflection of ML-Si, Cz-Si and mc-Si surfaces textured by chemical treatment in aqueous alkaline solution (NaOH).

The result of the chemical treatment allowed reducing the reflection by ~ 6 % after the texturization. Spectra measured in the wavelength range of 300-1200 nm show that reflectivity of ML-Si is 5 % higher than that of Cz-Si. This indicates that surfaces of ML-Si and Cz-Si are quite similar. Reflection of mc-Si surface is much higher due to the random crystallographic orientation of silicon grains.

This difference between the three types of materials (mono/mono-like/multi) can be explained by the crystallographic orientation, which will be confirmed by the characterization of XRD (Fig. 3) and (SEM) Fig. 2.

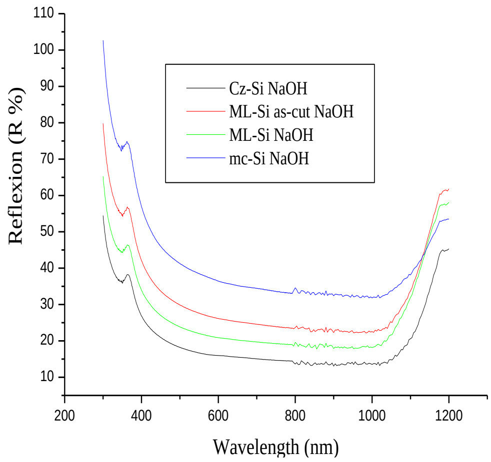


Fig. 1 – Reflectivity curve of Cz-Si, mc-Si and ML-Si crystalline substrates after texturing in the NaOH solution as a function of wavelengths

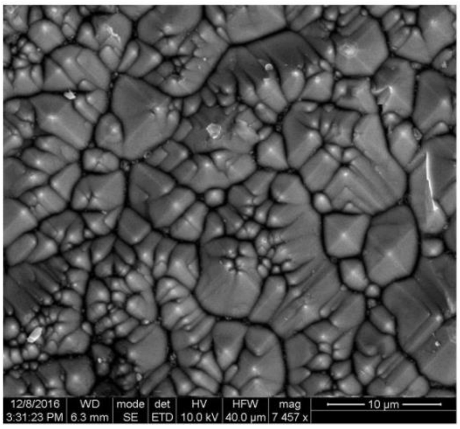
3.2 Surface Morphology by Scanning Electron Microscopy (SEM)

The density of pyramids tends to vary widely over the wafer surface. Dark patches are visible where pyramid density is high, covering approximately 80-90 % of the silicon (ML-Si, Cz-Si) surface and light patches with polished surface where pyramid density is low.

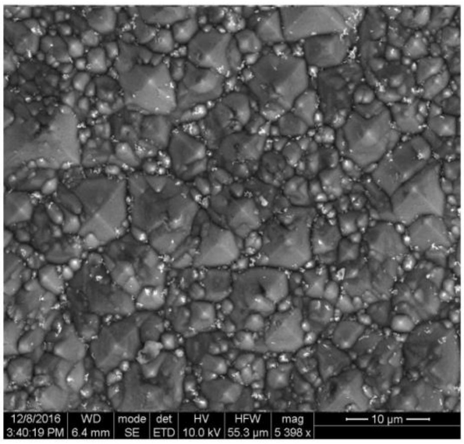
In general, it can be said that the surface roughness is observed for all the samples, and also a certain similarity of the morphology of the surface is observed between Cz-Si and ML-Si. Morphology of Fig. 2 suggests uniform etching, dense distribution of pyramids and reasonable pyramid size for sample (a) Cz-Si and (b) ML-Si. We note also that pyramids are straight indicating that Cz-Si and ML-Si materials have <100> orientation. Fig. 2c shows non-uniform textures because of different orientation in case of mc-Si sample.

The dominant structure for Cz-Si and ML-Si is a form of pyramids. These pyramids are with variable sizes; small pyramids of 1 to 2 μm height and other pyramids at the beginning of formation between some large pyramids that are already formed.

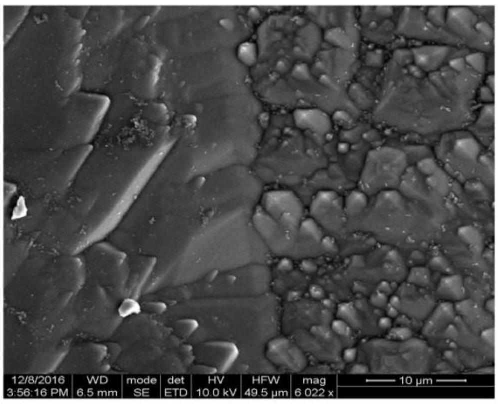
The size of the engraving (texturing) depends on the duration of the etching.



a



b



c

Fig. 2 – The morphology of the three types of silicon textured by the NaOH solution: Cz-Si (a), ML-Si (b) and mc-Si (c)

3.3 The X-ray Diffraction (XRD)

We present in Fig. 3 the XRD spectra obtained for the three types of silicon. The ML-Si and Cz-Si present the same crystallographic orientation at 69.17° which corresponds to (100) orientation, but mc-Si has different peaks with predominant orientations (111) and (220) related to 28.42° and 47.30° angles.

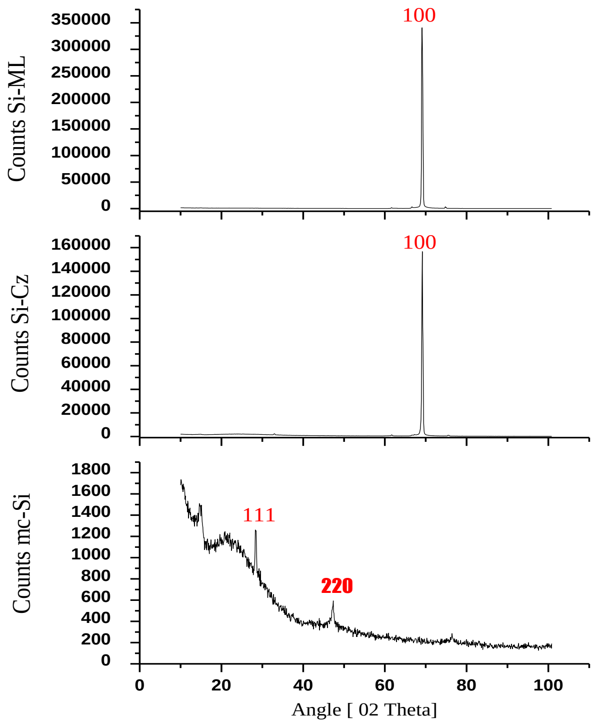


Fig. 3 – XRD spectra for mono, multi and mono-like silicon

3.4 The Photoluminescence (PL)

PL is a tool for rapid mapping of defective areas in silicon. However, the size of the pixels of the CCD camera limits the resolution of the obtained image and does not make it possible to observe point defects of a few microns.

From the PL mapping, we note the homogeneity of the Cz-Si (Fig. 4a) and Si-ML (Fig. 4b) surfaces. No crack pattern is observed. In the contrary, we observe a high contrast between the grains in the mc-Si (Fig. 4c). The lines reveal the GBs, which cause the lower carrier lifetimes.

3.5 The Fourier Transform Infrared Spectroscopy (FTIR)

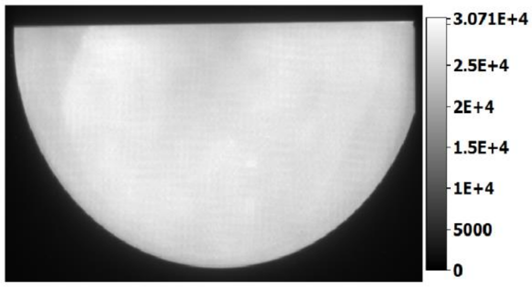
We measured the substitutional carbon and interstitial oxygen concentrations with the FTIR method using the relationship (1). For quantification of [O_i] and [C_s], we used the carbon and oxygen absorption peaks at 609 cm^{-1} and 1107 cm^{-1}, respectively [17]:

$$N = K \cdot \gamma, \; K = \left(\frac{1}{d}\right) \boldsymbol{ln}\left(\frac{T_{max}}{T_{min}}\right),$$

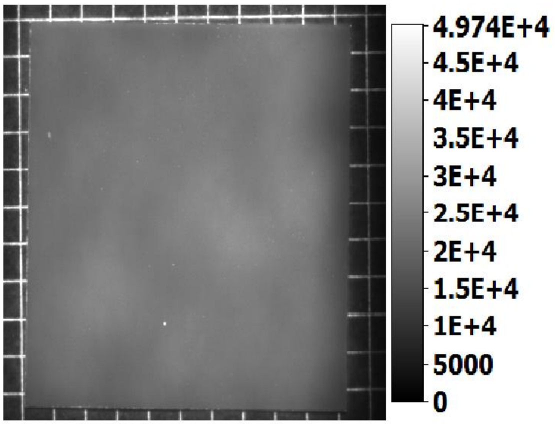
where d is the thickness of the sample in cm, T_{max} is the absorption mode peak, T_{min} is the value of the base line of the peak in absorption mode, γ is the conversion factor, for O_i $\gamma_O = 2.45{\cdot}10^{17}$ cm^{-2}, for C_s $\gamma_C = 1.1{\cdot}10^{17}$ cm^{-2}.

As shown in Table 1, the ML-Si shows a low oxygen content comparatively to Cz-Si, whereas we obtained a value in the same range for mc-Si. It can also be seen that the carbon concentration in ML-Si approximately approaches that of Cz-Si, but inferior to that of mc-Si.

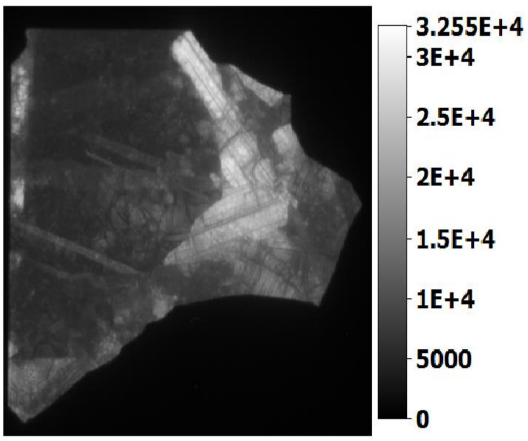
These results show the good characteristics of ML-Si compared to mc-Si. Thus, the ML-Si offers a great potential as a promising material for PV application.



a



b



c

Fig. 4 – PL mapping of silicon samples: Cz-Si (a), ML-Si (b) and mc-Si (c)

Table 1 – Measurement of oxygen and carbon concentrations

Wafers	**Multi (mc-Si)**	**Mono (Cz-Si)**	**Mono-like (ML-Si)**
[O_i] (cm^{-3})	$3.76 \cdot 10^{17}$	$6.31 \cdot 10^{17}$	$3.36 \cdot 10^{17}$
[C_s] (cm^{-3})	High $9.53 \cdot 10^{17}$	Low $3.78 \cdot 10^{17}$	Medium $1.2 \cdot 10^{17}$

Table 2 – Measurement of average electrical resistivity

	thickness (μm)	**Average *R* Ω/□**	**Average resistivity, *ρ* (Ω·cm)**
Cz-Si	357	20.5	0.73
ML-Si	170	50.3	0.85
mc-Si	350	25.6	0.89

3.6 Electrical Characterization

We measured the electrical resistivity of three types of silicon with a four-point technique.

Resistivity of silicon wafers is an important parameter that can affect the device characteristics such as depletion width and breakdown voltage of a *p-n* junction.

The following Table 2 shows the resistivity and values of the three types of silicon. These values show that the three types of samples have a low resistivity, which explains why they have good electrical conductivity.

From these results, we can confirm that the values of material resistivity are of the same order and adequate for solar cell processing. The ML-Si with this interesting property is a good material for PV applications.

4. CONCLUSIONS

Wet chemical texturing techniques meet the demand for high throughput, superior stable and certified processing qualities. These inexpensive and low-risk products have contributed greatly to the simplification of the steps and to the reduction of the cost of the device while simultaneously allowing the thinning of the wafers and the growth of pyramids on the surface or texture.

This work studied the effect of the chemical treatment on the morphological, optical and electrical properties of the three types of silicon: Cz-Si, mc-Si and ML-Si dedicated for PV applications.

The SEM characterizations reveal the dense and compact appearance of ML-Si films after chemical etching.

From optical characterization, we deduced that the chemical treatment lowered the surface reflectance of ML-Si comparatively with that of Cz-Si or mc-Si. As known, the reduction of reflectivity improves the photogenerated current density of solar cells.

Chemical contents with lower O_i concentration indicated that ML-Si has better performance than mc-Si.

The electrical characterization reveals the low resistivity about 1 Ω·cm of the three types of silicon wafers which confirm their good electrical properties.

These results confirm the great potential of ML-Si material as a promising and interesting candidate for PV application.

ACKNOWLEDGEMENTS

The authors are grateful for financial support by the University Mouloud Mammeri of Tizi-Ouzou (UMMTO) and Research Center for Semiconductor Technology for Energy (CRTSE), Algeria.

REFERENCES

1. E.A. Alsema, M.J. de Wild-Scholten, V.M. Fthenakis. *21th European Photovoltaic Solar Energy Conference* (Dresden: 2006).
2. D. Cunningham, A. Parr, J. Posbic, B. Poulin, *Proceedings of 23rd European Photovoltaic Solar Energy Conference and Exhibition (EUPVEC'08)*, 2829 (Valencia: Spain: 2008).
3. H. Faltakh, R. Bourguig, M.B. Rabha, B. Bessais. *Superlattice Microstr.* **72**, 283 (2014).
4. V. Prakash, A. Agarwal, E.K. Mussada, *Silicon* **11**, 1617 (2018).
5. H. Zhang, L. Zheng, Ma X, B. Zhao, C. Wang, F. Xu, *J. Cryst. Growth* **318**, 283 (2011).
6. S. Würzner, R.C. Helbig Funke, H.J. Möller, *J. Appl. Phys.* **108**, 083516 (2010).
7. X. Gu, X. Yun, K. Guo, L. Chen, D. Wang, D. Yang, *Sol. Energy Mater. Sol. Cells* **101**, 95 (2012).
8. V.A. Oliveira, M. Rocha, A. Lantreibecq, M.G. Tsoutsouva, T.N. Tran-Thi, J. Baruchel, D. Camel, *J. Cryst. Growth* **489**, 42 (2018).
9. Y. Yang, Z. Li, Z. Bian., G. Xu, P. Verlinden, Z. Feng, Q. Huang, *Energy Procedia* **27**, 214 (2012).
10. M. Banerjee, S.K. Dutta, U. Gangopadhyay, D. Majumdar, H. Saha, *Solid State Electron.* **49** No 8, 1282 (2005).
11. V.A. Oliveira, H.C. Sio, A. Faujour, L. Piot, A. Chabli, D. Camel, *Energy Procedia* **92**, 755 (2016).
12. F. Jay, D. Muñoz, T. Desrues, E. Pihan, V.A. De Oliveira, N. Enjalbert, A. Jouini, *Sol. Energy Mater. Sol. Cells* **130**, 690 (2014).
13. A. Lantreibecq, M. Legros, N. Plassat, J.P. Monchoux, E. Pihan, *J. Crystal Growth* **483**, 183 (2018).
14. S. Zhou, C. Zhou, W. Wang, Y. Tang, J. Chen, B. Yan, Y. Zhao, *Int. J. Photoenergy* **713791**, 8 (2013).
15. A. Hamdi, C. Amri, R. Ouertani, H. Ezzaouia, *J. Mater. Sci. Mater. Electron.* **28** No 6, 4807 (2017).
16. C. Sethi, V. Kumar An, K. Walia, S.C. Sood, *Tech. Int. J. Comp. Sci. Commun. Technol.* **5** No. 1, 0974 (2012).
17. F. Boufelgha, Y. Chettate, S. Belhousse, *Universal J. Phys. Appl.* **10** No 2, 40 (2016).

Фундаментальне дослідження властивостей квазімонокристалічного кремнію після хімічної обробки: порівняння з монокристалічним та багатокристалічним кремнієм

G. Benseba[1], A. Moussi[2], S. Meziani[2], D. Hocine[1], M.S. Belkaid[1]

[1] *Advanced Technologies Laboratory of Electrical Engineering (LATAGE), University Mouloud Mammeri of Tizi-Ouzou (UMMTO), BPN 17 R.P, Tizi Ouzou, Algeria*
[2] *DDCS Division, Research Center for Semiconductor Technology for Energy (CRTSE), Algeria, 02 Bd. Frantz Fanon, B.P 140 Alger –7 Merveilles –Algiers Algeria*

У роботі представлено дослідження квазімонокристалічного кремнієвого матеріалу (ML-Si). Його фізичні та хімічні властивості аналізуються та порівнюються із властивостями монокристалічного кремнію Чохральського (Cz-Si) та багатокристалічного кремнію (mc-Si). Після хімічної обробки кожного матеріалу поверхню аналізують за допомогою скануючої електронної мікроскопії (SEM) та рентгенівської дифракції (XRD). Ми спостерігаємо, що Cz-Si та ML-Si мають однакову морфологію та кристалографічну орієнтацію. Аналіз FTIR показує вміст кисню того ж порядку для трьох матеріалів, але зі значеннями ML-Si, ближчими до значень mc-Si. Заміщуюча концентрація вуглецю є проміжною для ML-Si між концентраціями Cz-Si та mc-Si. Коефіцієнт відбиття ML-Si на 5 % вищий, ніж для Cz-Si, і набагато нижчий, ніж для mc-Si, після текстури NaOH. Аналіз фотолюмінесценції показує, що матеріали ML-Si та Cz-Si мають кращу однорідність, ніж матеріал mc-Si. На завершення, ми представляємо переваги та недоліки ML-Si у порівнянні з Cz-Si та mc-Si. ML-Si має кращі властивості матеріалу, має небагато меж зерен та дислокацій порівняно з mc-Si. Крім того, оскільки ML-Si містить одне зерно, це дозволяє отримати менший коефіцієнт відбиття поверхні за допомогою лужного текстурування. Також ми виявили, що ML-Si майже ідентичний Cz-Si.

Ключові слова: Квазімонокристалічний кремній, Фізико-хімічні властивості, Хімічна обробка, Аналіз, Текстурування.