International Journal of Computational and Experimental Science and Engineering (IJCESEN)
Vol. 1-No.2 (2015) pp. 7-11
http://dergipark.ulakbim.gov.tr/ijcesen

***ISSN:* 2149-9144**

Research Article

Comparative study of etching silicon wafers with NaOH and KOH solutions[#]

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[#] Presented in "2[nd] International Conference on Computational and Experimental Science and Engineering (ICCESEN-2015)"

Keywords
Surface morphology
Surface passivation
Carrier lifetime
Optical reflection

Abstract: In this study, we investigated the effects of alkaline post-etching surface morphology on minority carrier lifetime of the p-type monocrystalline silicon wafers. A Sodium hydroxide and potassium hydroxide solutions at 30% and 23%, respectively, have been used at constant temperature. The surface states were characterized by calculation of the arithmetical average roughness (Ra) and the UV–visible-NIR optical reflectivity, whereas, the electrical characterization was done by means of quasi-steady state photoconductance measurements, which revealed a correlation between the resulted surface state and the minority carrier lifetime. The Measured surface roughness shown that potassium hydroxide solutions at 23% by weight gave a high minority carriers lifetime.

1. Introduction

M With the extraordinary increasing performance of electronic devices, the influence of the surface states of silicon wafers is becoming paramount for a highly competitive industry in the field of semiconductors in general and Photovoltaic (PV) in particular. Currently, the chemical treatments of silicon substrate surface represent a capital step in PV technology. They are used to improve electrical and optical properties of devices [1].

Indeed, the surface of silicon wafers is an important source of charge carriers recombination due to the presence of several crystalline defects among which the discontinuity of the crystal lattice is the most important. The density of these defects are expressed as a density of interface states, which in statistical Shokley-Read-Hall (SRH), are characterized by their energy levels in the band gap and their capture cross section (σ_n, σ_p) [2-3-4] .

However, this surface carriers recombination centers will mainly affect the device electrical performance. So, to reduce the surface recombination, we must have firstly a good surface in terms of dangling bonds and roughness. In their works Shui-Yang Lien et al. [5], have shown that there is a dependency between the surface condition and the lifetime of the minority carriers.

In this work, we investigate the effects of surface morphology on silicon wafer minority carrier lifetime by utilization of two alkaline solutions, KOH and NaOH. To identify the KOH solution providing the smoothest Si surface, in the first step, we optimize the KOH solution by investigating four different concentrations at a constant temperature of 90 °C. In the second step, we compared the results of the optimized KOH solution in terms of surface states which obtained with the usual solution of NaOH 30% by weight. Finally, a correlation between the surface states and the lifetime of the minority carriers was investigated.

2 Experimental

The etching experiments were carried out on p-type boron doped <100> oriented Cz-monocrystalline silicon (c-Si), with a thickness of about 420 µm and resistivity of 1–3 Ω cm. After a conventional cleaning process, the double sided thinning and polishing of silicon substrates was done in several KOH bath at a constant temperature, to reach a final thickness of 320 µm. The concentrations investigated are 15%, 23%, 30% and 40%. The aim of this study is firstly, to determine the KOH concentrations which shows the smoothest etched silicon surface and then the optimum of KOH concentration obtained in term of low surface roughness, is compared with surfaces obtained by NaOH bath prepared at 30% by weight, which is widely refer in several works. So, it is important to note that each silicon substrate is etched in a freshly prepared alkaline hydroxides solution. The polishing bath was maintained at a constant temperature of 90 °C for KOH bath and 100 °C for NaOH.

A continuous nitrogen gas bubbling was introduced in the solution from the bottom of the polishing bath to keep the solution composition and temperature uniform. After polishing, the wafers were rinsed in DI water for 5min and then dried by nitrogen flow [6].

The quality of the etched surfaces was inspected using a calculation of the arithmetical average roughness (Ra), using TESA-RUGO Surf roughness depth measuring equipment, with a course of 5 µm and the UV–visible-NIR optical reflectivity using Carry 500 spectrophotometer.

The Carry 500 spectrophotometer is a dual beam system with a spectral range extending from 175 to 3300 nm [7].

The correlation between the surfaces treated with the two different alkaline hydroxides solution and the carriers lifetime was highlighted by Quasi-Steady State Photo-Conductance (QSSPC) measurement, which was performed by SINTON WCT-120 tester, these measurements allow the determination of the injection level dependent minority carrier lifetime [5].

3 Results and Discussion

3.1 Surface analysis

3.1.1 Evaluation of roughness for optimum KOH concentration

The surface Roughness of the KOH solution for varying concentrations was experimentally determined and plotted as shown in Figure 1. The roughness of the different surfaces can be calculated as an arithmetical average roughness Ra [8]:

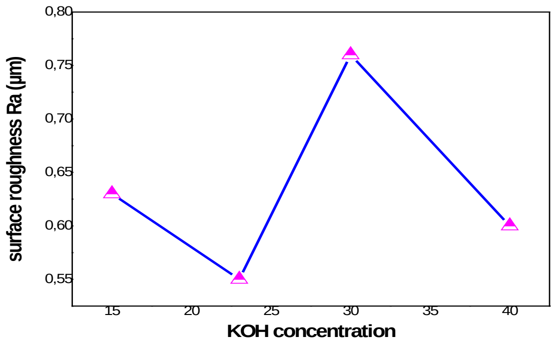

Fig.1 Influence of KOH concentration on roughness of <100> silicon (Etchant: 90°C-KOH)

Figure 1 shows the influence of KOH concentration on the surface roughness of the wafers etched for 20 minutes at a constant temperature of 90 °C, we compared the roughness of <100> silicon wafers etched by KOH-water solutions of four different KOH concentrations, 15% wt., 23% wt., 30% wt. and 40% wt.

K. Sato et al. shows in their work, that the roughness decreases with an increase in KOH concentration on <110> silicon [9]. But in our study, after several tests on several samples, we found that there is no linearity between KOH concentration and the roughness on <100> silicon.

From Figure 1, we observed that the roughness of less than 0.55 µm in Ra was achieved under the condition of 23% wt. KOH concentration, when the etching depth was about 100 µm.

For the other measurements of Ra at different KOH concentration, we found:

Ra (15%) = 0.63 µm, Ra (30%) = 0.76 µm and Ra (40%) = 0.60 µm. In conclusion we can say that the concentration of 23% represents the concentration which gave the best surface roughness.

Marvell Nanofabrication Laboratory of the University of California, Berkley, found the same results, and report in their lab manual that 24% by volume KOH etch rate is the fastest and shows the smoothest etched Si surface on <100> p-type Si wafers at a temperature of 80 °C [10].

3.1.2 Surface reflectivity

To confirm the tests undertaken previously, we studied the surface reflectivity by a spectrophotometer, and the weighted reflectance was evaluated.

It's widely known that, reflection off of smooth surfaces such as mirrors leads to a type of reflection known as specular reflection.

Reflection off of rough surfaces leads to a type of reflection known as diffuse reflection. Whether, the surface is microscopically rough or smooth has a tremendous impact upon the subsequent reflection of a beam of light. The diagram below depicts two beams of light incident upon a rough and a smooth surface [11].

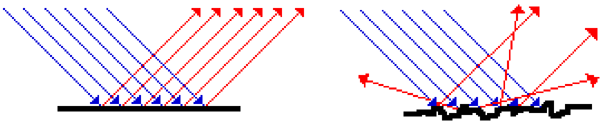

Fig.2 Different type of reflection on solid surface

From these above definitions, we can write the empirical equation for the total reflection:

$$R_{tot} = R_{diffuse} + R_{specular} \quad (1)$$

This equation has the consequence that, for low surface roughness, the diffuse reflection tends to zero; this result was used for the surfaces characterization, of our samples.
As depicted in Figure 3 the reference sample (pink curve) which represents poly-optical silicon wafer, the reflection is a specular type (mirror surface), and thus, the diffuse reflection is practically equal to zero. By comparison of the absorption spectrum of the reference sample and the other absorption spectra of different samples, as shown in Figure 3, we can notice that the reflectivity can be affected by the solution concentration for a fixed etching duration and temperature; because the reflectivity is related to the surface quality which is related to the concentration of hydroxide etchant solution.

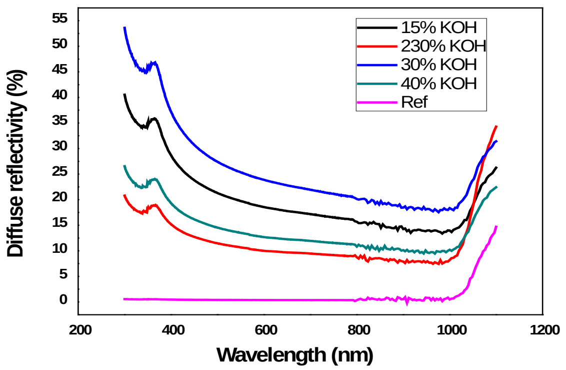

Fig.3 Reflectivity of c-Si surface polished with different KOH concentration

Moreover, Figure 3 shows a perfect correlation between the arithmetical average roughness calculation and reflectance results. We can see on the diagram of reflectivity, that the reflection of the surface which was treated by 23% KOH concentration displayed the lowest reflection than the better surface in term of roughness; this result is well confirmed by its Ra which is equal to 0.55 µm, such results remains valid for the other concentration of KOH, the correlation between the arithmetical average roughness and the surface reflectance represented by the weighted reflection is shown in the following Table.

Table 1. Correlation between arithmetical average roughness and weighted reflection at different concentration of KOH solution.

KOH concentration	Ra (µm)	Weighted reflectance
15% wt.	0.63	19.25%
23% wt.	0.55	10.84%
30 % wt.	0.76	23.95%
40 % wt.	0.60	13.03%

It is quite clear from the table above that, for the lower value of Ra (µm) we have the lowest value of the weighted reflectance and then, for the highest value of Ra (µm), we have also the highest value of the weighted reflection. This is also valid for intermediate values.

3.1.2 Comparison of Surface treatments by KOH 23% wt. and NaOH 30% wt.

In this section, we conducted the same study that previously, the figure 4 represents the reflectivity of c-Si surface polished with KOH 23% wt solution and NaOH 30% wt.

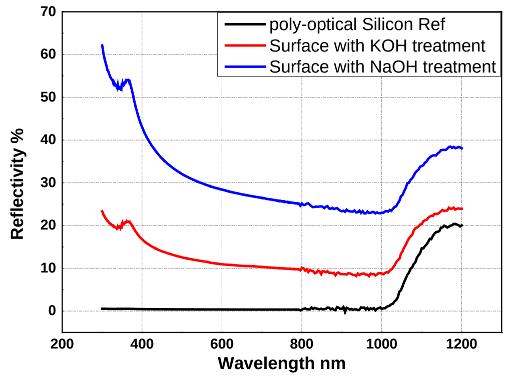

Fig.4 Reflectivity of c-Si surface polished with KOH 23% wt solution and NaOH 30% wt solution

The results obtained from the figure 4 in terms of weighted reflectance and roughness calculation of the two different polishing processes are listed in Table 2.

Table 2. Overview over results obtained for NaOH and KOH surface treatment.

Chemical solution	Ra (µm)	Weighted reflectance
KOH 23% wt. - 90°C	0.55	10.84%
NaOH 30% wt.-100°C	0.73	28.5%

According to these results, it is clear that the KOH polishing gives the best results in terms of surface quality comparing to the results obtained by NaOH treatment.

The optical weighted reflection (Rw) of KOH treatment is the lowest value of 10.84%, and the Rw value of NaOH treatment is about 28.5%. This value is higher comparing to the KOH results. These results are confirmed by the Arithmetical average roughness calculation Ra represented on table 2.

4. Impact of the surface quality treated with optimized NaOH and KOH solution on electrical properties of silicon wafers

4.1 Minority carrier lifetime evaluation

The minority carrier lifetime (τ_{app}) is measured using the Sinton WCT-120 lifetime tester in generalized Quasi-Steady-State Photoconductance (QSSPC) mode. The measurements are carried out on silicon substrates treated with KOH at 23% by weight concentration and NaOH at 30% weight concentration.

The impact of polishing by KOH and NaOH solution and resultant surface quality on carrier lifetime is investigated. The results obtained by QSSPC measurements are presented in Figures 4, which shows the dependence of the apparent lifetime on the injection level of the two surfaces treated respectively by 23% wt. KOH and 30% wt. NaOH before and after Iodine-Ethanol passivation.

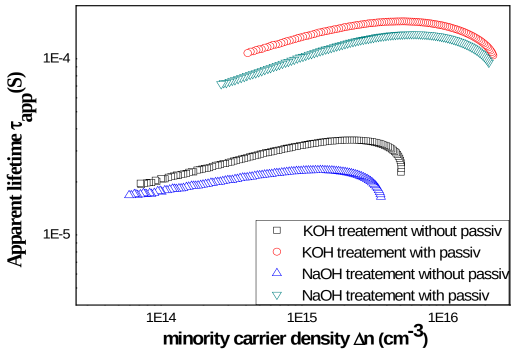

Fig.4 Apparent lifetime vs. minority excess carrier

It can be seen as depicted in Figure 4, and by the comparison of the two surfaces states, that, the roughest surface presents the weakest carrier lifetime, while the smoothest surface gives the highest lifetime. The experimental values of carrier lifetime of the two surfaces which treated by KOH and NaOH are respectively, τ_{app}(NaOH) = 101.6 µs and τ_{app}(KOH) = 132 µs with Iodine-Ethanol surface passivation, and τ_{app}(NaOH) = 23 µs, However, τ_{app}(KOH) = 32 µs without Iodine-Ethanol surface passivation at the injection level $\Delta n = 1.10^{15}$ cm^{-3}. In any case, we note that the surfaces treated with 23% KOH represents the best results in terms of carrier lifetime, it seems to be clear that the enhancement between these results is closely related to the surface treatment.

This result could be related to increased surface defect states due to expanded surface area, this would involve additional dangling bonds and therefore increases the surface recombination velocity, leading to a decrease of the measured τ_{app} [12, 13]. Always from Figure 5, we can deduce that the effect of traps is negligible in Cz-silicon samples, because the trapping leads to an increasing apparent in lifetime with decreasing injection density [7].

Conclusion

An investigation of the surface state of silicon after alkali solution polishing has been presented. Several alkaline based wet chemical etching sequences are tested in terms of resulting surface roughness, electrical and optical performance. All the flatness parameters obtained from our analysis clearly indicate the superiority of the KOH polishing process as compared to NaOH polishing.

Our study also reveals that the KOH thinning-polishing at 23% by weight concentration process gives the smoothest surface comparing with the NaOH treatment and KOH treatment gives also the lowest reflection is a controlled, this different parameters was correlated to electrical properties in terms of carrier lifetime. In conclusion, the aim of our study is to enhance the minority lifetime of the wafer by modifying its surface roughness.

Acknowledgement

This work is realized at the DDCS-Division/CRTSE and financed by the National Fund for Research of Algeria – DGRSDT/MESRS.

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