Fabrication of the pyramidal microstructure on silicon substrate using KOH solution

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Abstract. The texturization of monocrystalline silicon wafers using a mixture of potassium hydroxide and isopropyl alcohol solutions has been investigated. The texture morphology and pyramid size are affected by the KOH concentration, the temperature and the time together. The surface reflectance and the surface morphology were measured with a UV-Visible Spectrophotometer and a scanning electronic microscope (SEM) respectively. We reported a relatively uniform size, dense arrangement pyramid microstructure on the basement of silicon texture. According to the reflectance and SEM patterns, we got the appropriate concentration of KOH, 20wt% and 25wt%, with the corresponding reflectance were 12.049% and 14.593%. It means that either too low temperature with a long time or too high temperature with a short can damage the formation. We got the surface morphology, which was consisted of 1-1.5 μm sized pyramids. From the pyramid dimension, the optimum process condition was found to be 20wt% KOH, 3wt% IPA, 60˚C and 5 min at which was reduced to 1.292μm. From the SEM images density and uniformity, the optimized condition is 20wt% KOH, 3wt% IPA, 70˚C and 15mins though its size has reached the 1.404μm.

Introduction

The microstructure of monocrystalline silicon influences their physical properties and determines the stability and effective of the optical absorption [1-3]. In traditional technological application, the silicic microstructure has been applied on the solar cell to reducing optical losses [4,5]. A lot of metallic substrates display unique surface plasmon properties that have attached enough scientific interest and great technological importance[2,4].Metallic microstructure has been widely used on the micromachining such as nanophotonic devices, data storage, and biosensor[3,4]. Recently, the silicon nanofabrication of crystalline silicon has been widely used with silicon nanoscale waveguide devices and quantum effect devices. If the silicon microstructure has reached nanometer , it also should can be used on technological field[3,4,6-8].To control the shape of pyramid microstructure in wet etching, it is necessary to meticulously design the etching conditions such as, the solution concentration, the temperature and the time[6-7,9].

In the process of monocrystalline microstructure fabrication, alkaline solution is customarily used to make pyramid structure with its anisotropic etching characteristic of <100> silicon. The theory is caused by the difference on the (100) and (111) directions since the etching rate on the (111) direction is much slower than (100) direction [5, 10-11]. Adding isopropyl alcohol (IPA) can improve the wettability of silicon surface and control the etching rate by preventing an explosive reaction between the silicon surface and the OH- ions [12-13]. Aqueous KOH solution etched Si is mainly via chemical equation below [10, 11].

$$Si + 4OH^- \rightarrow Si(OH)_4 + 4e^-$$

In this paper, texture of monocrystalline silicon wafers with a potassium hydroxide solution was studied. Meanwhile, the changes of size for pyramidal microstructure on silicon substrate with etching time, the concentration of KOH and temperature were also investigated.

Experimental

Microstructure preparation .

In this work, attempts have been made for comparative study of etching the monocrystalline silicon wafer surface by KOH. The monocrystalline silicon is 100 oriented, p-doped and the resistivity is about 0.5Ω~2Ω.The size is about 15mm×15mm that cut from the 125mm×125mm square.

Before etching, wafers were cleaned by the following procedures. The silicon etching process was mainly involved in the hydroxyl ion (OH-) which attacks the silicon surface by controlling affecting factors. Before etching, the samples were immersed in ethyl alcohol at ultrasonic clearing machine for 5 mins to remove impurity. Then, have treated wafer be rinsing with the flowing deionized water. After rinsing, the samples were dried on the drying cabinet in preparation for following steps. The cleaned wafer was took place in the alkaline mixture solution.

Microstructure fabrication .

The whole reaction process was conducted in heating magnetic stirring apparatus. First, the experiment was conducted that the KOH concentration was varied from 15wt% to 30wt%, for the 5wt% IPA addition interval. The purpose of this experiment is to get the minimum reflectivity and roughly find out the better morphology. Next, through the study of above, this work mainly concentrate on the 20wt% and 25wt% KOH with 3wt% IPA additive. The different reaction times and reaction temperatures could be adjusted. In this experiment, we considered the etching temperature (60˚C and 70˚C), the etching time (5min and 15min and investigated its effect on the texturization of the silicon wafer. We examined the effect by the change of temperature and time respectively. After the etching process, the samples were rinsed and dried again. Arrays of microstructure elements of size 1μm×1μm were patterned in a SiO2 layer by etching rate of the (100) silicon plane. The total hemispherical reflectance was measured by Shimadzu UV-2600 spectrophotometer (Shimadzu Inc., Japan) equipped with an integrating sphere. The surface morphology was studied with Zeiss EVO MA10 (Carl-Zeiss, Germany) scanning electron microscope (SEM).Table 1 shows the experiment groups and procedure.

Table 1 Experiment groups and procedures

Step	Procedure	Reagents and instruments
1	Rinse	XYE-10-H deionizer
2	Remove saw damage	hydrogen peroxide, ethyl alcohol
3	Texturing	KOH, IPA
4	Rinse against after reaction	ultrapure water, ethyl alcohol
5	Drying	drying machine
6	Measurement	UV-2006, The EVO MA15 type of scanning electron microscope

Results and discussion

At first, we investigated the dependence of the surface reflectance on KOH concentration. Etching was carried out at 80oC, 30min, and 5w% IPA. The reflectance with different concentrations of KOH(15wt%, 20wt%, 25wt% and 30w%) was investigated. The reflectance variation is shown in Fig. 1 line chart.

Table 2 shows the corresponding average reflectance of each concentration solution. The average reflectance was weighted in the spectrum range of 400-800nm. The weighted reflectance (WR) was calculated normalizing the pyramidal by UV-2600. Fig.2 (a-d) presents the SEM images of silicon substrate morphology that we can make a qualitative analysis [10-11].The low reflectance could be explained by the formation of uniformly and shaped pyramids on the surface of silicon etched using the appropriate concentration of KOH as observed in Fig. 2 (b) and (c). When the KOH concentration was increased to 30wt%, the pyramidal structure began to collapse.

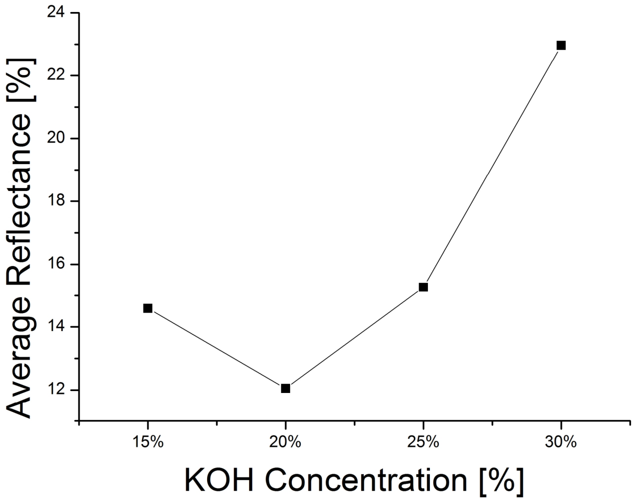

Fig.1. Pyramidal reflectance of KOH textured sample using 5wt% IPA surface active agent.

Table 2 Experimental condition of KOH texture in preliminary experiment

The concentration	15wt%	20wt%	25wt%	30wt%
The reflectance (%)	15.266	12.049	14.593	22.967

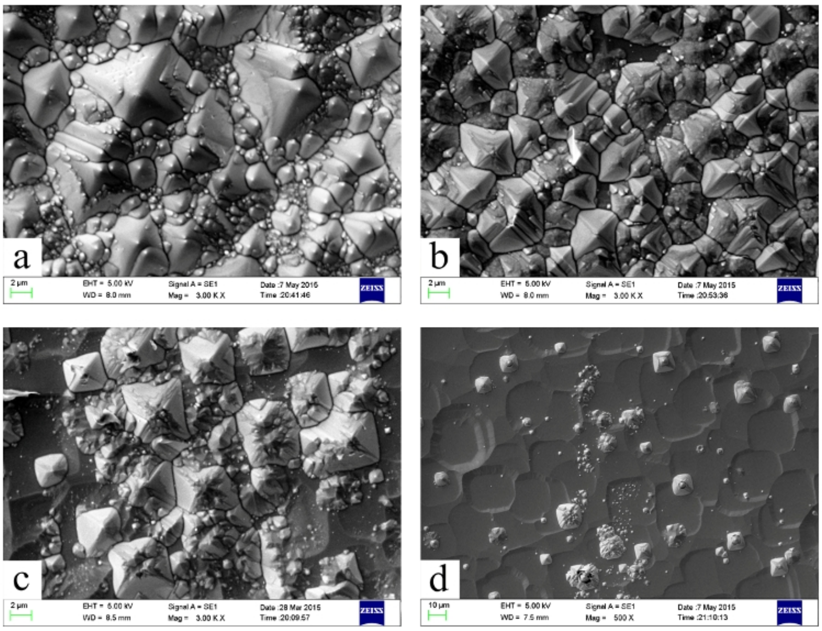

Fig.2. SEM images of silicon surface after etching with KOH + 5wt% IPA mixture solution: (a)15wt%KOH, (b) 20wt%KOH, (c) 25wt%KOH, and (d) 30wt%KOH heating in 80˚C water bath for 5mins.

And then, we investigated the surface reflectance about time and temperature separately. According to previous studies, the concentration of KOH was fixed at 20wt% and 25wt% respectively. Table 3 records the etching parameters respectively from Sample (a) - (d1).

By referring to the literature [13], we evaluated the homogeneity by calculating the pyramids average size. As the scale bar indicates 2μm, the length of line is 40μm. Then count the number of pyramids caught by the diagonal lines. Table 4 displayed the length of diagonal by number of pyramid gave the average value of pyramids size.

When subsequently texturing is processed, random pyramids are formed on the silicon substrate. The pyramids of Sample (b) (c) (b1) (d1) are 1.5-2μm. By comparison, the Sample (a) (d) (a1) (d1) are just 1-1.5μm which was excellent.

Figure.3 (a-b) shows the results of texturing using 20wt% KOH with time variation under 60˚C.As the etching time is increased, the number of pyramids per unit area decreases and the pyramids become larger. The same situation exists on the 25wt% KOH. However, when temperature is 70˚C, the change about the number of pyramids per unit area and the pyramids size is opposite. The rules about change the pyramid values has elaborated that the proportion of temperature and time used on the texturization must be suitable. Either too low temperature with a long time or too high temperature with a short can damage the formation of more uniformly sized and shaped pyramids. So, the evaluation fabrication of nanostructure pyramid is a manifestation of small dimension, dense, uniformly distributed structures formed on the surface of the silicon wafers upon texturization.

The minimum size of average of etched wafer was found to be 1.292μm. The SEM image of wafer textured at the optimum is shown in Fig.3 (a). The densest and the most uniform structure were shown in Fig. (d) though its size is 1.404μm.

Table 3 Etching solution proportioning and reaction conditions

Group	Etching solution	Surfactant	Temperature	Time
1#	20w%KOH	3w%IPA	60˚C	5mins
2#	20w% KOH	3w% IPA	60˚C	15min
3#	20w% KOH	3w% IPA	70˚C	5mins
4#	20w% KOH	3w% IPA	70˚C	15mins
5#	25w% KOH	3w% IPA	60˚C	5mins
6#	25w% KOH	3w% IPA	60˚C	15mins
7#	25w% KOH	3w% IPA	70˚C	5mins
8#	25w% KOH	3w% IPA	70˚C	15mins

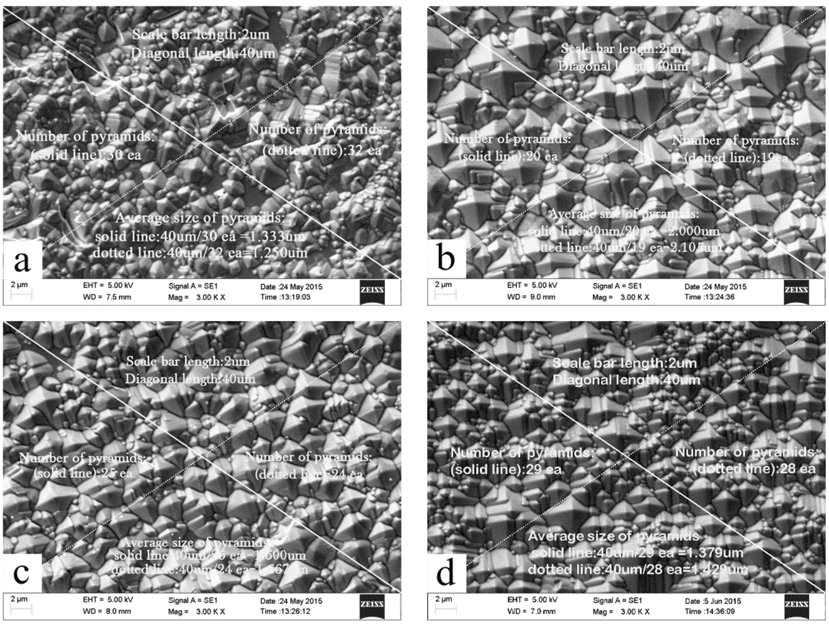

Fig.3. shows the pyramid microstructure on the Si surface on the 20wt% KOH. Sample (a) and Sample (b) are in different time under 60˚C. Sample (c) and Sample (d) are in different time under 70˚C. All the SEMS finally were displayed by this form which attached some explanatory word.

Table 4 The average size of pyramids on the two diagonals

Group(μm)	1#	2#	3#	4#	5#	6#	7#	8#
Solid line	1.333	2.000	1.600	1.379	1.429	1.905	1.739	1.379
Dotted line	1.250	2.105	1.667	1.429	1.333	2.000	1.818	1.333
Average size	1.292	2.053	1.634	1.404	1.381	1.953	1.779	1.356

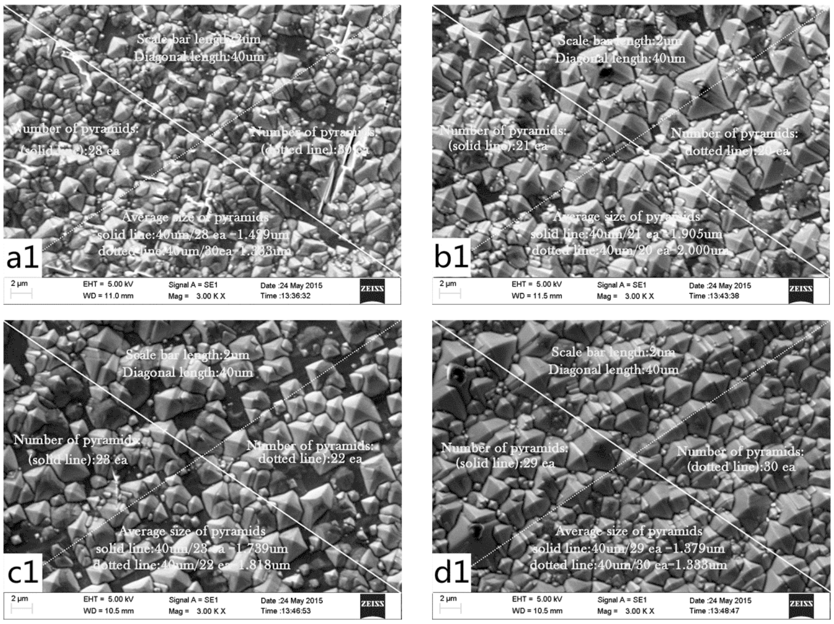

Fig.4. shows the pyramid microstructure on the Si surface on the 25wt% KOH. Sample (a1) and Sample (b1) are in different time under 60˚C. Sample (c1) and Sample (d1) are in different time under 70˚C.

Conclusions

In this paper, we study the texture of monocrystalline silicon wafers with a potassium hydroxide solution. We investigated the changes of pyramid size with the etching time, the concentration of KOH and temperature. First, in this study, we considered the KOH in concentrations (15wt%, 20wt%, 25wt% and 30wt%) with the addition of 5% IPA and investigated the reflectance. According to previous studies, the concentration of KOH was fixed at 20wt% and 25wt% because their reflectance is relatively low, 12.049% and 14.593%. Our optimized (to obtain the smallest size) for etching process was determined to be: 20wt% KOH, 3wt% IPA, solution temperature =60˚C and etching time = 5min where the average size of the silicon wafer was 1.292μm. Meanwhile, to obtain the dense and uniformly distributed pyramid structures from the SEM images, the optimized condition is 20wt% KOH, 3wt% IPA, 70˚C and 15mins.

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