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ARTICLE

Effects of Etching Solution Concentration on Silicon Surface Reflectivity as a Solar Cell Surface Modifier

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Abstract: The surface structure of single-crystal silicon is known to be one of the best ways to reduce reflection, increase light trapping ability, and increase light absorption. The hierarchical surface structure plays an important role in reducing the reflectivity of single-crystalline silicon surfaces. Through this research, the size and density of the pyramids formed on the silicone surface, as well as their dependence on the concentration of the etching solution during silicone processing, were studied and evaluated. The pyramids etched on the silicon surface formed photo-traps that increased the efficiency of light absorption. The effects of hydroxylamine (NH_2OH) on a 20 wt.% KOH and 20 wt.% NaOH solutions were investigated. The concentration of NH_2OH varied from 6 to 18 wt.% while the etching temperature was kept at 70 °C and the etching time was 40 minutes. Optimal etching conditions were identified, with the 20 wt.% KOH + 18 wt.% NH_2OH solution yielding better results than the 20 wt.% KOH solution. The normal incidence percent reflectivity was 6.5%, at 640 nm wavelength for Si {100} surfaces etched in a 20 wt.% NaOH + 18 wt.% NH_2OH solution. This normal incidence percent reflectivity value was slightly higher than that achieved by the 20 wt.% pure NaOH solution, where a percent reflectivity of 6.0% was measured at the same wavelength. Moreover, the addition of NH_2OH significantly increased the size of the etched pyramid structures.

Keywords: Micro-Pyramid, Surface morphology, Percent reflectivity, Solar cell, NH_2OH.

1. Introduction

Silicone substrates with different surface structures of different sizes and shapes are very popular in industrial and research applications, since silicon is one of the most abundant elements in nature, and it is a relatively safe element for the environment. Silicon is also one of the leading materials in solar cell technologies, thanks to its relatively high efficiency and the well-established processing techniques. Surface texture plays a major role in improving solar cell efficiency, and it is beneficial for cost-effective crystalline silicon solar cells [1–3]. A textured surface can effectively reduce the light reflection of the surface of cells by enhancing appropriate light absorption via multiple intra-shape reflections when compared to a flat surface, thus increasing cells' efficiency [4–6]. Large-scale photovoltaic production uses potassium hydroxide (KOH) or sodium hydroxide (NaOH) as aqueous etching solutions. These alkaline solutions are anisotropic etchants for Si and produce randomly distributed pyramid structures on the Si surface [5–10].

In this study, the surface structure of silicon was studied based on free alkali profiling by mixing potassium hydroxide (KOH) with different concentrations of NH_2OH, and by mixing sodium hydroxide (NaOH) with different concentrations of NH_2OH. The resulting pyramid structures exhibited different sizes and shapes,

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depending on the composition and concentration of the etching solutions. These variations in surface morphology have significant implications for reflectivity and are of great interest to the solar cell industry [11-17]. Therefore, to reduce the cost of solar cells, improve cell performance, and distribute the size of the pyramids more uniformly, the etching process must be carefully optimized and evaluated [18]. The goal of this study was to improve the surface structure of silicon to achieve lower reflectivity by controlling the properties of the pyramids pattern on the etched silicon surface. The shape, structure, and size of the pyramid are important factors that determine the interactions of the surface with incident light [7].

2. Experimental Procedure

In this work, 8 small pieces (1.5 cm^2 each) of p-type {100} single-crystalline silicon with a resistivity of 3–30 Ω.m and a thickness of 675 µm were used. Prior to mounting the samples on the etching stage, all samples were cleaned in an ethanol bath, and after that, they were rinsed in deionized water several times. The silicon wafers were then immersed in a 25 wt.% NaOH solution for 2 minutes to remove the oxide, and then rinsed in deionized water several times. After completing the cleaning process, the samples were placed in a drying oven (hot air) for 20 seconds at a temperature of 60°C to remove moisture, then these samples were etched with different concentrations of solutions of KOH, NaOH, and NH_2OH. In the first stage, 20 wt.% KOH was mixed with varying concentrations of NH_2OH (6, 12, and 18 wt.%). In the second stage, 20 wt.% NaOH was mixed with different concentrations of NH_2OH (6, 12, and 18 wt.%). During the experiment, the reaction temperature and the reaction time were kept constant at 70.0 ± 0.1°C and 40 minutes, respectively. At the end of the reaction, all treated wafers were washed again in ethanol and deionized water baths for 5 minutes, and then they were dried in a drying oven (hot air) for 20 seconds at a temperature of 60°C and prepared for testing. The morphology of all textured samples was studied using an FEI Inspect F50 scanning electron microscope (SEM). The reflectance ratio spectra of the etched surfaces were measured using a FilmTek 3000 spectrophotometer (SCI, USA) within the wavelength range of 240-840 nm. All percent reflectivity measurements were performed at normal incidence. Through the SEM images, the pyramidal number density and average pyramidal volume were evaluated. SEM images were analyzed using ImageJ software [7].

3. Results and Discussion

In anisotropic wet etching, the microscopic surface roughness is controlled by many factors. Among these factors are: 1) The formation of hydrogen bubbles, which hinder surface interactions and act as a mask on the surface. 2) The redeposition of etching byproducts, such as SiO_2 deposits resulting from etching the Si crystal and other contaminants above the surface, on the surface during the etching process. Microscopic roughness appears during the etching process in the form of micro pyramids. The size and density of these pyramids depend on various parameters, including etching time, solution concentration, temperature, and the crystalline orientation of the Si wafers.

In this study, the etching characteristics of Si{100} surfaces were investigated using different concentrations of KOH, NaOH, and NH_2OH mixtures. These solutions were used to pattern the silicon substrates at a temperature of 70 °C for 40 minutes. The surface morphology, pyramid size, pyramid density, and optical reflectivity of all samples were examined. Optical measurements confirmed that the applied etching treatments led to a significant reduction in surface reflectivity.

Figure 1 presents SEM images illustrating the surface morphology of four samples etched with varying NH_2OH concentrations (6 to 18 wt.%), while maintaining a constant KOH concentration of 20 wt.%. As shown in Fig. 1(a), samples etched with KOH alone exhibit small pyramids. In contrast, Fig. 1(b) shows that the addition of 6 wt.% NH_2OH to the KOH solution results in noticeably larger pyramids. Figs. 1(c) and 1(d) reveal that further increasing the NH_2OH concentration to 16 wt.% and 18 wt.%, respectively, leads to the formation of even larger pyramids. However, these higher concentrations also cause a nonuniform pyramid size distribution and the emergence of irregularly shaped pyramids.

This irregularity is likely due to enhanced anisotropic etching effects, which may result from increased hydrogen bubble formation and the inherent crystalline orientation of the silicon surface, as discussed earlier.

A closer look at Fig. 1(d) shows that the higher NH_2OH concentration enhances the formation of larger distorted pyramids with truncated apexes and with smaller pyramid formations on these apexes. This can be useful for suppressing reflection and can increase the light-trapping efficiency of the textured surface [19-22]. It is also worth mentioning that a native silicon oxide thin film forms on the surface immediately after taking the samples out of the etching solution. However, this rather thin layer is not visible in the SEM images, as it is transparent to the SEM technique.

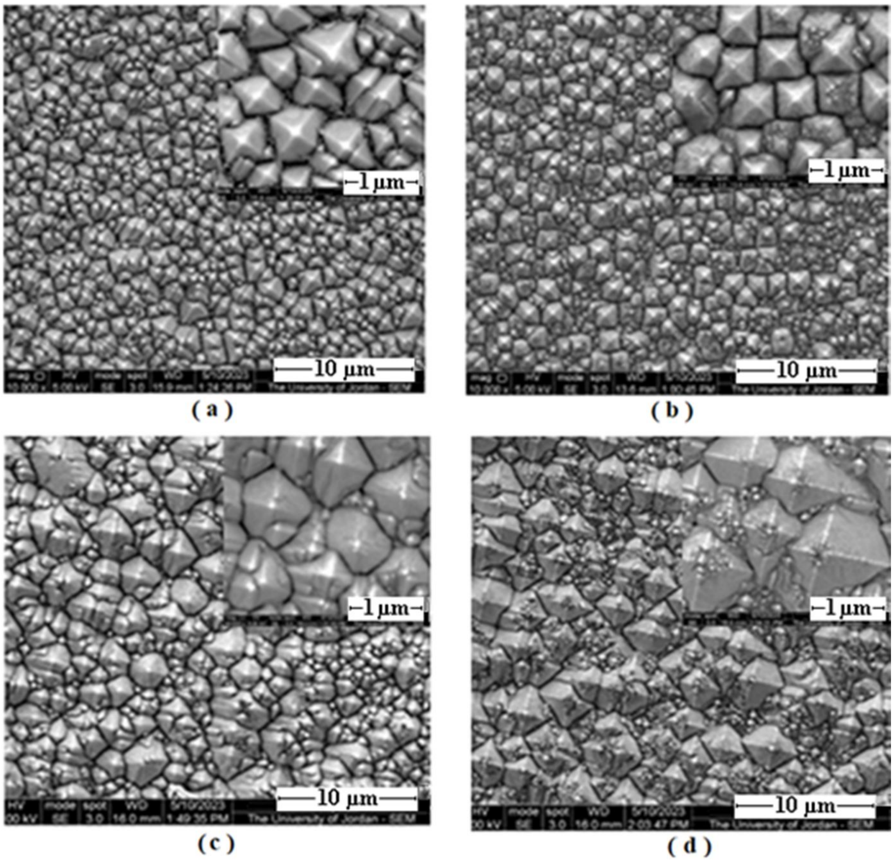

FIG. 1. SEM images of silicon surfaces etched using 20 wt.% KOH mixed with different NH_2OH concentrations at 70 °C for 40 minutes: (a) 0 wt.%, (b) 6 wt.%, (c) 12 wt.%, and (d) 18 wt.% NH_2OH.

The effect of NaOH mixed with different concentrations of NH_2OH on the etching process was also studied. NH_2OH at concentrations of 6, 12, and 18 wt.% was mixed with 20 wt.% NaOH at 70 °C for 40 minutes, and the solutions were used to etch the previously cleaned Si surfaces.

Figure 2 shows SEM images of the studied patterned substrates. The shape and density of the pyramids are directly related to the concentration of NH_2OH solution. At the NH_2OH solution concentration of 18 wt.%, the surface coverage of these pyramids covers the entire surface, and the size of the pyramids is large. As the concentration of NH_2OH increases and as it is added to the 20 wt.% NaOH solution, the dissolution kinetics is changed so that the removal of silicon atoms from the surface of the silicon crystal is very large. This change hinders the formation of orthosilicic acid, Si $(OH)_4$, which cannot keep up with the large Si dissolution rate. As the concentrations of these complexes also increase, a protective layer forms on the silicon surface, preventing etchants from reaching the surface of the silicon substrate [23].

Based on the results shown in Figs. 1 and 2, it can be said that modified etching is the best option for creating microstructures that require relatively low surface roughness. Surface roughness at the microscopic level is a direct result of irregular removal of atoms from the surface and their extension into the crystalline mass, and is the property of the formation of pyramids on the surface. In the case of wet etching, the surface roughness is strongly influenced by hydrogen bubble formation, which interferes with surface interactions and acts as a micro-mask, as well as by the redeposition of etching byproducts [24].

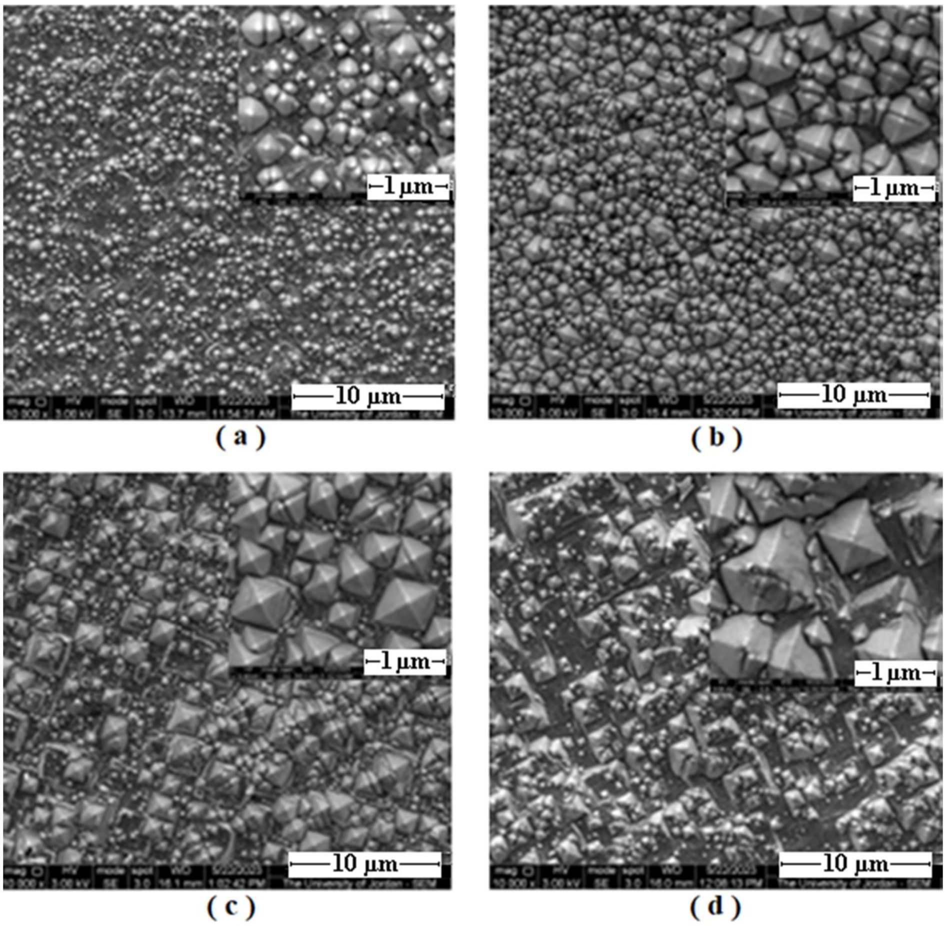

FIG. 2. SEM images of silicon surfaces etched using 20 wt.% NaOH mixed with different NH_2OH concentrations at 70 °C for 40 minutes: (a) 0 wt.%, (b) 6 wt.%, (c) 12 wt.%, and (d) 18 wt.% NH_2OH.

Figure 3 shows the number density distributions and sizes of the pyramids as a function of the concentration of KOH mixed with different NH_2OH concentrations. This figure clearly shows that increasing NH_2OH concentration leads to larger pyramid sizes and a lower average number density of pyramids compared to etching without NH_2OH. The average size of the pyramids increases with increasing concentration of NH_2OH. The average size of the pyramids is 0.940 ± 0.160 μm at 20 wt.% KOH mixed with 18 wt.% NH_2OH concentration, and it decreases to 0.530 ± 0.078 when no NH_2OH is added to the solution. The pyramids' number density decreases from 1.13 to 0.610 μm^{-2} with increasing NH_2OH concentration from 0 to 18 wt.%.

Figure 4 presents the size distribution of pyramids as a function of NaOH mixed with different NH_2OH concentrations. The largest pyramids were obtained using 20 wt.% NaOH mixed with 18 wt.% NH_2OH. Pyramid sizes increased from 0.280 ± 0.040 to 0.970 ± 0.110 μm (mean ± s.d.), and pyramid number density decreased from 2.60 to 0.600 μm^{-2} with the increase in NH_2OH concentration from 0 to 18 wt.%. The concentration of NH_2OH added to KOH or NaOH has an obvious effect on both the pyramid sizes and the average number density of pyramids. This is especially important for their application in solar cells.

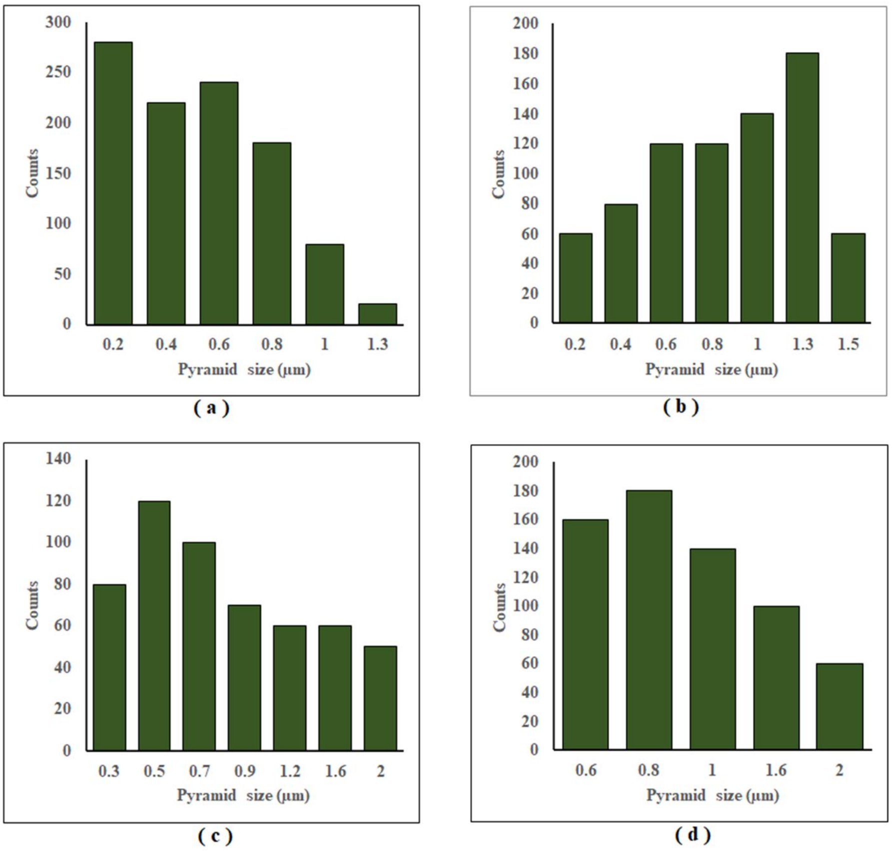

FIG. 3. Pyramid size distribution obtained using ImageJ software for 20 wt.% KOH mixed with different NH_2OH concentrations. (a) 0 wt.%, (b) 6 wt.%, (c) 12 wt.%, and (d) 18 wt.% NH_2OH.

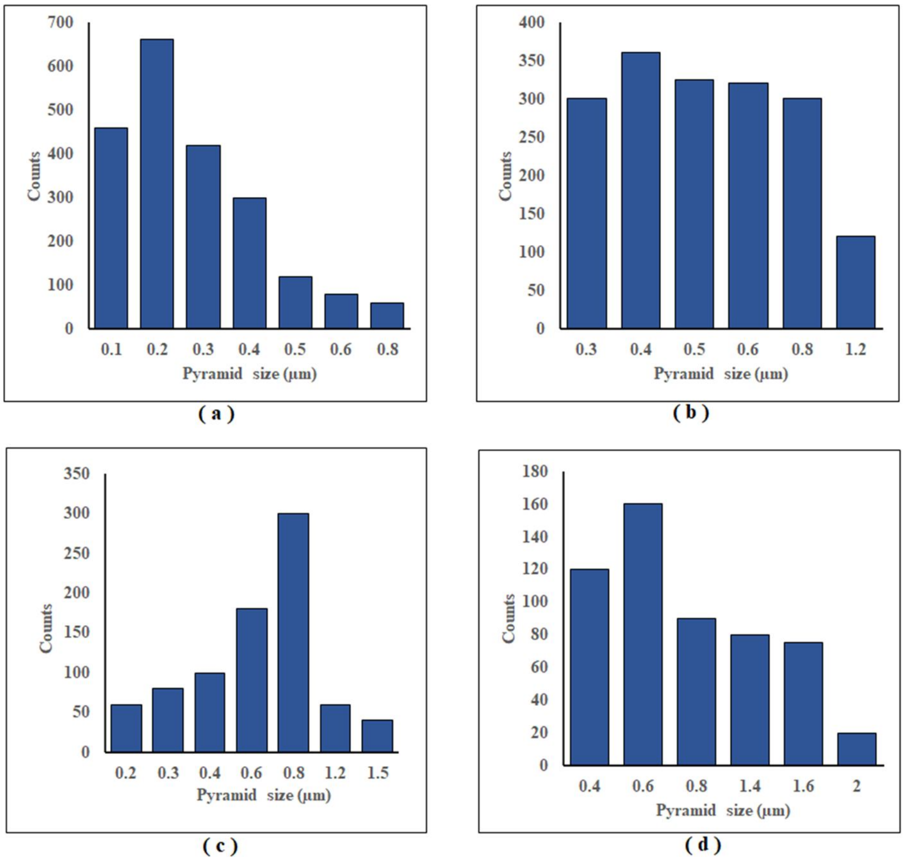

FIG. 4. Pyramid size distribution obtained using ImageJ software for 20 wt.% NaOH mixed with different NH_2OH concentrations. (a) 0 wt.%, (b) 6 wt.%, (c) 12 wt.%, and (d) 18 wt.% NH_2OH.

Figure 5(a) shows the optical reflectivity spectra of etched silicon wafers for different concentrations of NH_2OH mixed with 20 wt.% KOH. These spectra, as recorded in the wavelength range of 240-840 nm, show lower percent reflectivity values in the visible spectrum as well as in the near infrared region [21]. A lower reflectivity in the near infrared region ensures photon absorption, resulting in improved performance of solar cell devices. The percent reflectivity values of all samples remain almost constant in the visible wavelength range (440-600 nm) and begin to decrease with an increasing NH_2OH ratio until a minimum value of 6.5%, at 650 nm wavelength is reached at a concentration of 18 wt.% NH_2OH mixed with 20 wt.% KOH. A similar trend is observed for mixing different concentrations of NH_2OH with 20 wt.% NaOH, as can be seen in Fig. 6(a), where the percent reflectivity value reached 6.0% at a concentration of 18 wt.% NH_2OH mixed with 20 wt.% NaOH. Fig. 5(b) zooms in on the two peaks observed in the percent reflectivity spectra of the samples studied. These peaks are attributed to the crystalline silicon direct band gap [25]. The peak at around 272 nm does not show any appreciable shift, while the peak at around 364 nm for the polished silicon shifts toward 370 nm for the etched samples. This small shift may be related to changes in the stress in the etched samples. In Fig. 6(b), a similar behavior is observed but with the 364 nm peak shifting to a lower wavelength of 361 nm. This shift can also be associated with the changes in stress.

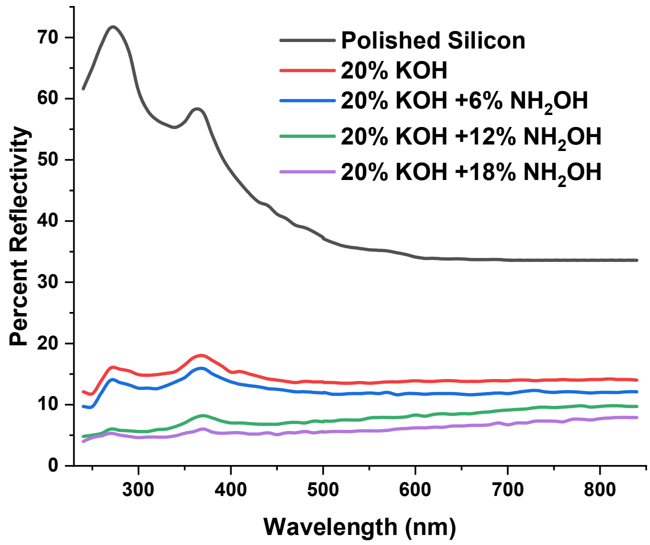

FIG. 5(a). Percent reflectivity of patterned silicon as a function of the wavelength for samples etched in 20 wt.% KOH mixed with different NH_2OH concentrations.

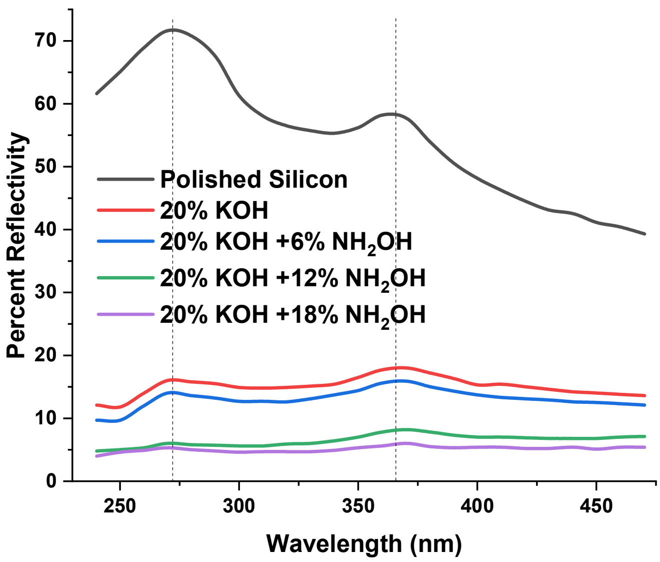

FIG. 5(b). A zoom in on the observed peaks in the percent reflectivity as a function of wavelength for samples etched in 20 wt.% KOH mixed with different NH_2OH concentrations.

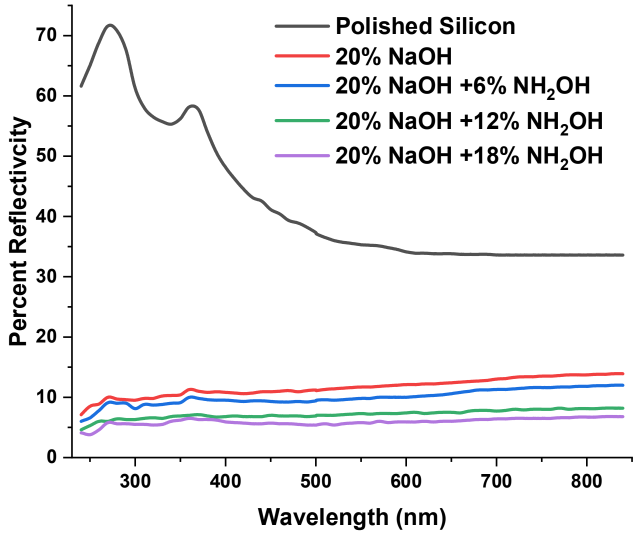

FIG. 6(a). Percent reflectivity of patterned silicon as a function of wavelength for samples etched in 20 wt.% NaOH mixed with different NH_2OH concentrations.

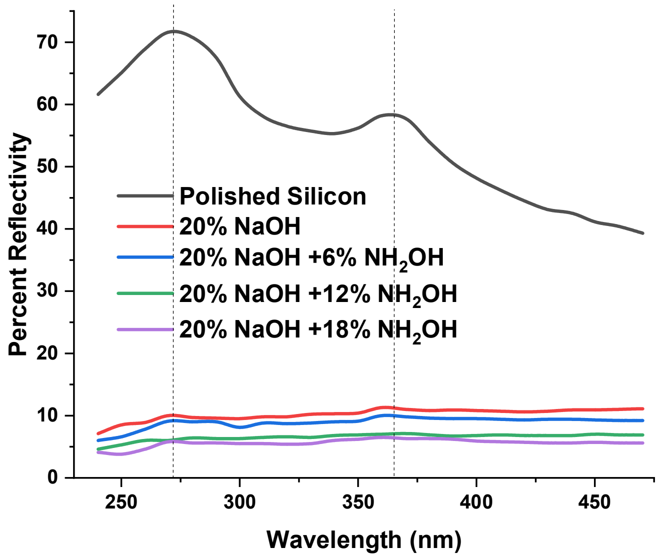

FIG. 6(b). A zoom in on the peaks observed in the percent reflectivity of silicon as a function of wavelength for samples etched in 20 wt.% NaOH mixed with different NH_2OH concentrations.

The percent reflectivity decreases from 13.8% to about 6.5% as the concentration of NH_2OH changes from 0 to 18 wt.% mixed with 20 wt.% KOH for samples measured at a wavelength of 640 nm, as shown in Fig. 7. A decrease in reflectivity from 12.4% to 6.0% is also observed as the concentration of NH_2OH increases from 0 to 18 wt.% mixed with 20 wt.% NaOH for the samples measured at a wavelength of 640 nm, as shown in Fig. 8. These differences in percentage reflectivity are due to changes in surface roughness resulting from the changes in the size and number density of the pyramids formed on the surface of the patterned silicon sample. The drop in the percent reflectivity indicates better light trapping properties, and it can lead to improvements in light harvesting properties of the modified surfaces and solar cells.

Table 1 summarizes the results for all the samples studied. This table shows the extent to which the percent reflectivity of light depends on the number density and the size of the pyramids resulting from changing the concentration of the NH_2OH solution mixed with 20 wt.% KOH or 20 wt.% NaOH solutions. Increasing the NH_2OH concentration leads to larger pyramid structures and a corresponding decrease in their number density [26].

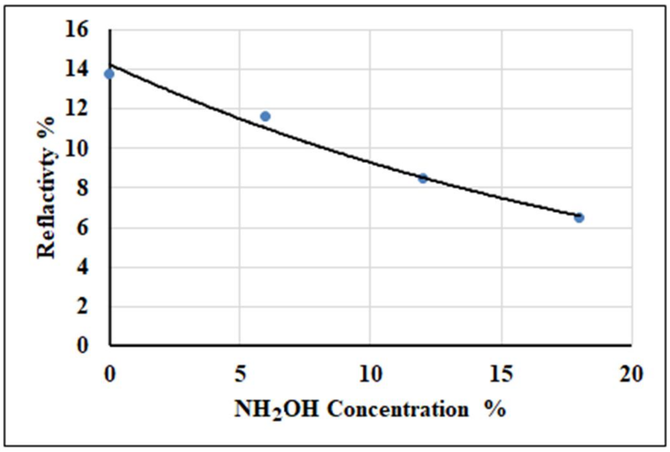

FIG. 7. Percent reflectivity of silicon surfaces etched with 20 wt.% KOH mixed with different NH_2OH concentrations at a wavelength of 640 nm.

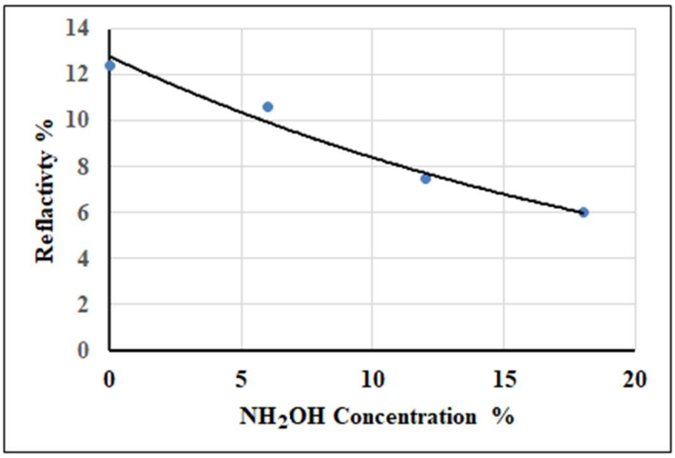

FIG. 8. Percent reflectivity of silicon surfaces etched with 20 wt.% NaOH mixed with different NH_2OH concentrations at a wavelength of 640 nm.

TABLE 1. Number of pyramids per mm^2, pyramids density, pyramid size (average ± s.d.), and average reflectivity (at λ = 640 nm) for eight samples prepared at 70 °C with an etching time of 40 minutes under different concentration texturing conditions.

Texturing conditions	Number of pyramids for each 1 mm^2	Density (μm^{-2})	Average pyramid size (µm)	Average reflectivity (λ = 640 nm) (%)
20 wt.% KOH	1020	1.130	0.530 ± 0.078	13.8
20 wt.% KOH + 6 wt.% NH_2OH	760	0.840	0.800 ± 0.111	11.7
20 wt.% KOH + 12 wt. % NH_2OH	640	0.650	0.930 ± 0.172	8.5
20 wt.% KOH + 18 wt.% NH_2OH	545	0.610	0.940 ± 0.160	6.5
20 wt.% NaOH	2100	2.600	0.280 ± 0.040	12.4
20 wt.% NaOH+ 6 wt.% NH_2OH	1725	2.010	0.570 ± 0.044	10.6
20 wt.% NaOH+ 12 wt.% NH_2OH	820	0.920	0.680 ± 0.108	7.5
20 wt.% NaOH+ 18 wt.% NH_2OH	540	0.600	0.970 ± 0.110	6.0

4. Conclusions

The effect of changing the concentration of hydroxylamine (NH_2OH) in solutions of 20 wt.% KOH and 20 wt.% NaOH on producing a homogeneous pyramidal pattern on the surface of single-crystal silicon was studied to obtain lower percent reflectivity values that enable the production of solar cells with higher efficiency. A percent reflectivity of 6.5% was obtained when mixing 20 wt.% KOH with 18 wt.% NH_2OH, while a percent reflectivity of 6.0% was obtained when mixing 20 wt.% NaOH with 18 wt.% NH_2OH. These low reflectivity values can be very useful for solar cells and photovoltaic applications.

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