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Surface Treatments and Modifications of Si Wafers Produced by Czochralski Method for Solar Cell Applications

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The objective of this work is to carry out surface treatments and modification of single-crystal silicon (Si) wafers produced by the Czochralski (Cz) method for solar cell applications. Lapping and polishing processes were performed on Si wafers for removing saw damages which occurred when sliced Si ingot was grown in the Cz system. The appropriate time and speed for the slicing process were determined as a result of parameter studies. The wet texturing process was generated with different durations on the surface of lapped and polished Si wafers to acquire square-based pyramidal structures for preventing losses from incoming sunlight which is necessary for solar cell applications. An x-ray diffractometer, scanning electron microscope, surface profilometer, and UV–Vis spectrophotometer were employed for characterizations of all processes. The results show that single-crystal Si wafers were successfully produced by the Cz method, and after the texturing process, roughness and reflectance values of the wafers significantly decreased. The wafers could be potential candidates for economical mass production.

Key words: Silicon, semiconductors, wafer preparation, surface modification

INTRODUCTION

Semiconductor technologies are essential for almost all devices that use electronic circuits and chips. Since the discovery of the semiconductor characteristics of Si, developments in this field have accelerated significantly and have achieved economical production because Si is the second most abundant element on Earth and suitable for use in transistors, solar cells, detectors, and other semiconductor devices.[1] Solar cells are a kind of semiconductor that detects sunlight whereby a difference of potential occurs by movements of electrons induced by photons from sunlight. This phenomenon takes place in the creation of the *p*-*n* junction which is formed by doping *p*-type Si wafers with group IV elements or *n*-type Si wafers with group IIIA elements, which are generally phosphorus (P) and boron (B), respectively.[2–4] For achieving a solar cell's maximum efficiency, it is indispensable to catch the maximum incoming sunlight while preventing reflection; this can be realized by texturing the wafers' surfaces with some operations.[5–9] In this study, Si wafers with a textured surface were produced starting with Si chunks as the precursor and the Cz method as a growing technique. Si ingot was sliced to obtain Si wafers. The produced wafers were lapped and polished for use for general purposes. The texturing operation was carried out with NaOH-based solution in a one-step and economical method which could be scaled for mass production.

EXPERIMENTAL DETAILS

All chemical components, sample names, and equipment used in the processing line are summarized in Table I and illustrated in Fig. 1. In Table I,

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Table I. Chemicals, sample names, and equipment used in the related processes

Types of process	Chemicals	Sample name	Equipment
Cz process	Polycrystalline Si chunks N gas		PVA TePla
Slicing	Boron oil	*X*1, *X*2, *X*3	STX 1202 precision slicing machine
Lapping	Colloidal alumina powder + DI water		Logitech lapping and polishing machine
Polishing	Colloidal cerium powder + DI water Colloidal silica powder + DI water		
Texturing	Sodium hydroxide + isopropyl alcohol + DI water	*X*2	Lab equipment

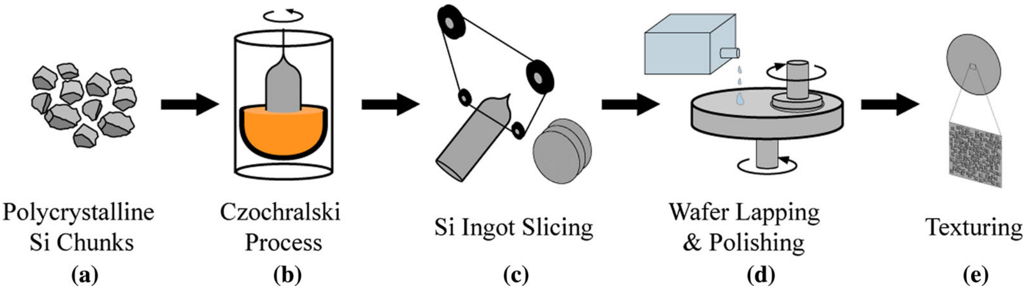

Fig. 1. All process steps; (a) Si chunks used in (b) the Cz process, (c) slicing of produced single-crystal Si ingot, (d) lapping and polishing of obtained Si wafers, (e) texturing of wafers.

the types of processes including equipment models and the chemical materials used in the processes are clearly defined, and three specimens were called *X*1, *X*2, and *X*3, according to process parameters. Figure 1 depicts all process steps utilizing Si chunks in the Cz process, slicing of produced single-crystal Si ingot, lapping and polishing of obtained Si wafers, and texturing of the wafers.

Single-crystal Si ingot was produced via the Cz method using a PVA-TePla approach. The desired orientated seed crystal was dipped into molten polycrystalline Si liquid slightly above the melting temperature in a quartz crucible and, afterwards, the seed crystal was hoisted with a specified pull and slew speed to ensure formation of the same orientated structure of the particles around the seed crystal, as illustrated in Fig. 1a and b.[10–12] Polycrystalline Si chunks (5 kg) were loaded into the system for production. The melting temperature was set at 1429°C, and when the system reached the specified temperature, the seed crystal was hoisted with a 1.1-mm/min pull speed and 10/10 rotations/min. The Ar gas flow rate was set to 25 L/min during the process. Single-crystal ingot production required approximately 19 h, producing an ingot of 200 mm in length and 90 mm in diameter at the end of process.

The ingot slicing process was carried out using an STX 1202 precision slicing machine with a 150-m long steel wire supported with diamond particles, as presented in Fig. 1c.[12] Boron oil was used as a coolant and lubricant. Slicing was performed by moving wire in x, y, and z axes. The x axis is the direction of steel wire perpendicular to the ingot, and the wire accelerates in this axis. The y axis is responsible for ingot thickness and is in the direction of the length of the ingot. The z axis is the direction from top to bottom of the ingot, and the steel wire slices the ingot when moving along this axis. The optimal operation condition was determined by parametric experiments. The slicing feed ratio defines the distance at which the steel wire descends in a minute along the z axis. The slicing feed ratio was varied at 1 mm/min, 2 mm/min, and 3 mm/min, while the wire feed speed was kept constant.

Lapping and polishing processes were respectively performed using a Logitech lapping and polishing machine as illustrated in Fig. 1d. Wafers must be fixed on the glass substrate to be subjected to lapping, polishing and cutting processes. For this purpose, the wafer was bonded by polymer binder on the glass surface, and a weight was placed on the materials for strong adhesion and avoidance of air space between glass and wafer.[12] The wafer's surface to be polished was placed on the rotating iron drum. Asperities on the surface of the material were removed, and the desired smooth surface was obtained via the incoming lapping and polishing solution. Alumina (Al_2O_3) powder (9 μm) was mixed with deionized (DI) water in a 1/10 ratio, and this mixture was used for rough lapping. This step was undertaken for 1 h with a 45-rpm speed. For precision lapping, ceria (CeO_2) powder (3 μm) was mixed with DI water in a 1/10 ratio, and this step was undertaken for the same duration and rpm speed as with the previous step. The polishing step utilized a velvet pad instead of an iron drum. The polishing process was performed using silica (SiO_2) suspension (40 nm) and was undertaken for 30 min with a 30-rpm speed.

The aim of texturing process is to avoid reflection at the same angle of photons coming from the sun and to ensure that reflected photons move forward towards to the material surface, thereby creating square-based pyramidal structures on the wafer surface.[5–9,13] The solution of wt. 2% NaOH, wt. 6% IPA, and wt. 92% DI water was prepared by stirring in a magnetic stirrer at room temperature for 5 min in air.[14] Afterward, the solution was heated to 80°C, and four pieces of wafers were placed inside. The samples were taken after 20, 30, 40, and 50 min to observe the effect of process time on the reflection, as illustrated in Fig. 1e.

X-ray diffraction (XRD) was used to identify whether the produced Si ingot was single crystal or not. Si wafers from the produced ingot were characterized through XRD including a grazing angle attachment and an incident angle of 1° (Thermo-Scientific, ARL-K_α). X-ray radiation of Cu-K_α was set to run the system at 45 kV and 44 mA with a scanning speed of 2°/min. As in the case of the microstructure of the samples, the surfaces of texturing wafers were examined by means of a scanning electron microscopy (SEM, Coxem Em 30+) instrument operating at an accelerating voltage of 20 kV with several magnifications. The wafer surface profiles were scrutinized with a Mitutoyo SJ-301 surface profilometer. The surface roughness profile was procured using an XP-2 surface profilometer to specify surface differences between slicing, lapping, and polishing. Peak-to-valley roughness (R_t) and mean roughness height/depth (R_z) values of the specimens were measured and also compared. UV–Vis spectroscopy was utilized to identify reflection characteristic of Si wafers and for comparison of before and after texturing with different durations. The logic of the system is that light in predetermined wavelengths is sent to the material surface, and reflection light from the surface is collected and measured by a sensor; a percent reflectance value is given as a result. Measurements were performed within the range of 230–810-nm wavelengths using Thermo-Scientific Evolution 600 UV–Vis equipment to analyze reflection characteristic in near-UV, visible light, and near-IR regions.

RESULTS AND DISCUSSION

Figure 2 indicates the main and zoomed-in image in the range around the 68–71° XRD pattern of the Si wafer prepared from the produced Si ingot with the Cz method using (100) seed crystal. More specifically, the XRD pattern is associated with Si wafer obtained from Si ingot without any operation. It was denoted that the material gave only unique peaks around 69.56°, which provides Si wafer with only (400) planes. It should be noted that when Si (100) seed crystal rod was used, the ingot was produced, and thus this result confirmed that ingot was manufactured as a single crystal.[15–17]

The surface roughness profile specifies surface differences among slicing, lapping, and polishing processes. Regarding these results, R_t and R_z values of the specimens were measured and also compared in detail. As listed in Tables I and II, three specimens were sliced with different slicing feed rates (moving along the z axis) of 1 mm/min, 2 mm/min, and 3 mm/min, and they were called as $X1$, $X2$, and $X3$, respectively; wire speed was determined as 5 m/s for all operations. Lapping process parameters were 2-drops/s abrasive solution feed speed (colloidal alumina solution of 9-micron particle size) and 45-rpm table rotation speed. Slicing was conducted for 120 min for $X1$, 60 min for $X2$, and 40 min for $X3$. In order to compare them, the first surface roughness measurements were generated. As expected, owing to a more precise slicing feed rate, the most frequent fluctuations and fewer peak-to-valley heights were observed in the $X1$ sample; there was an opposite situation in the $X3$ sample, while the $X2$ sample contained values between $X1$ and $X3$, as shown in Fig. 3. The first lapping processes were performed for 30 min. Once the visual inspection was performed on the samples, flat and peak-to-valley surfaces were seen, as shown in Fig. 4. For this reason, it was decided that the second roughness measurement was generated on both flat and peak-to-valley (non-flat) surfaces. The objective of the second lapping process was to make

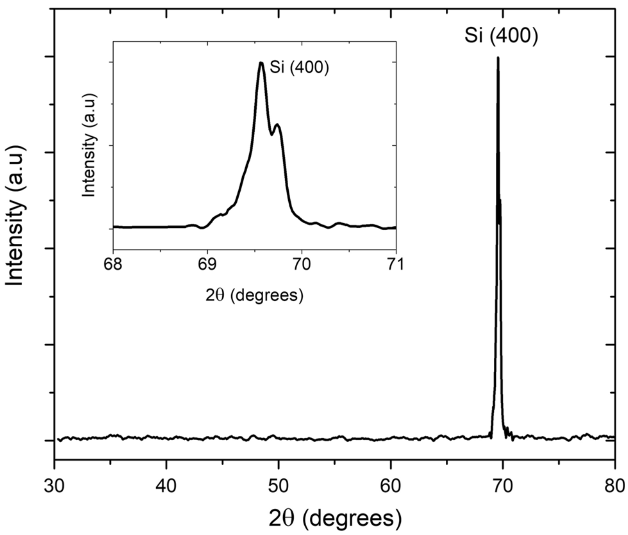

Fig. 2. The main and zoomed-in image in the range around the 68–71° XRD pattern of the Si wafer prepared from the produced Si ingot using (100) seed crystal.

Table II. Slicing and lapping parameters

				Profilometer result (μm)			
Process	**Sample**	**Slicing feed rate**	**Time (min)**	***R_t***		***R_z***	
Slicing	*X*1	1 mm/min	120	21.07		20.35	
	*X*2	2 mm/min	60	31.80		27.80	
	*X*3	3 mm/min	40	42.76		38.20	
				Flat	Non-flat	Flat	Non-flat
1st lapping	*X*1		30	1.61	5.91	1.35	5.22
	*X*2		30	1.78	12.37	1.57	9.48
	*X*3		30	1.85	21.72	1.49	18.07
2nd lapping	*X*1		30	1.59		1.30	
	*X*2		30	1.73		1.52	
	*X*3		60	1.82		1.45	
				Sample		Time (min)	
Total process time (min)				*X*1		180	
				*X*2		120	
				*X*3		130	

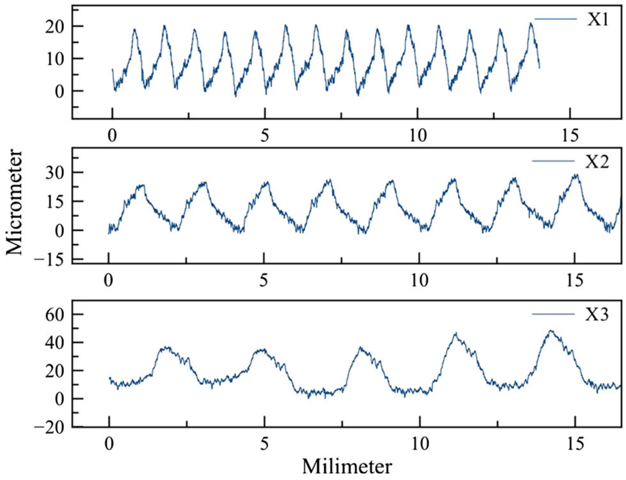

Fig. 3. Surface roughness measurements of (a) *X*1, (b) *X*2, and (c) *X*3 samples after ingot slicing process with 1 mm/min, 2 mm/min, and 3 mm/min slicing, respectively.

completely flat surfaces on the samples. For this reason, the process time was determined by visual inspection, as given in Table II. After all studies, the *X*2 sample process provided the optimum values for combination of duration and roughness when compared to others.

As a note of microstructures, SEM observation (see Fig. 5 for details) attempts to survey surface characteristics for solar cell applications. SEM micrographs of the optimum Si wafer sample, called *X*2, is obviously presented in Fig. 5. The optimum results were accomplished with the *X*2 sample in a complete production/slicing/lapping/polishing process. This is why texturing studies were continued with the same sample. The *X*2 sample was divided into smaller pieces (15 mm × 15 mm) to assess texturing parameters in Si wafers. More specifically, the textured surfaces of Si wafer (*X*2 sample) prepared by etching along with the faces of the crystal planes using the solution having wt. 2% NaOH, wt. 6% IPA, and wt. 92% DI water were characterized with respect to their microstructure by SEM. In these applications, surface texturing can be employed to minimize reflection characteristics. Any roughening of the surface reduces reflection by augmenting the variations of reflected light bouncing back onto the surface, rather than out to the surrounding air. The crystalline structure of silicon wafer results in a surface made up of rough pyramids if the surface is appropriately aligned with respect to the internal atoms. The objective is to create square-based four-sided pyramids reported in the literature,[14] and the images on the SEM analysis results confirmed that similar structures were obtained, as shown in Fig. 5. Moreover, in spite of the fact that the bases of the pyramids in SEM images in Fig. 5 seem to be round, in fact, they are observed to have an asymmetric cornered structure. The SEM images could be observed with a tilt mode to see the pyramids better. In another report,[18] Sing et al. used the same solution with different ratios for the texturing process and had nearly the same results obtained herein. As will be explained later, UV–Vis spectrophotometer results supported the effect of the texturing surface on the reflection.

UV–Vis spectroscopy results identify reflection characteristics of silicon wafers in order to compare before and after texturing and anti-reflection

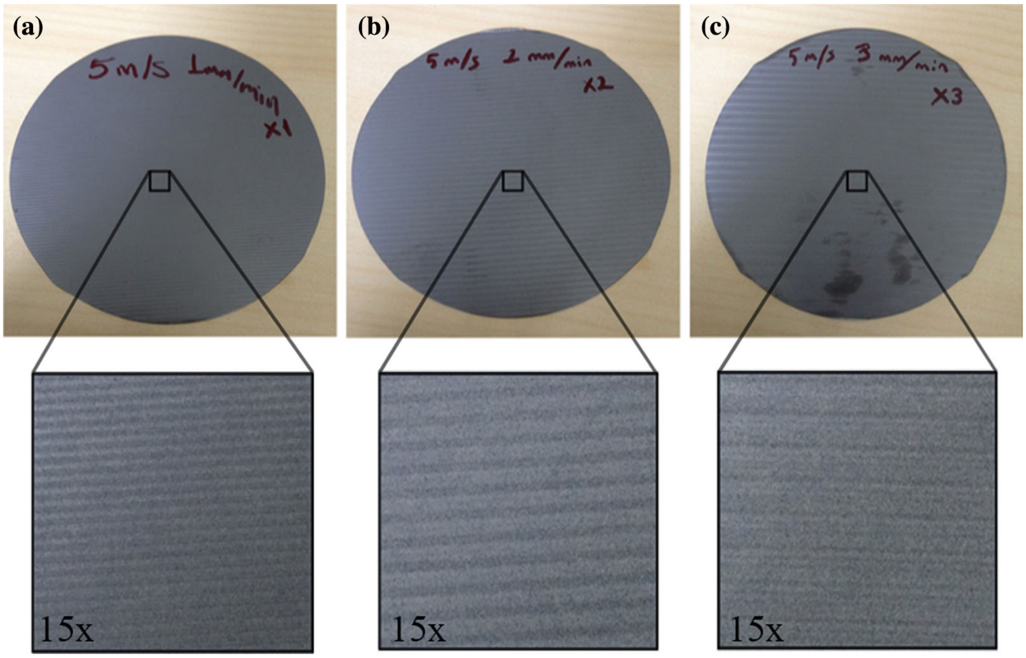

Fig. 4. Visual inspection of (a) $X1$, (b) $X2$, and (c) $X3$ samples after the lapping process for 30 min with 2-drops/s abrasive solution feed speed and 45-rpm table rotation speed.

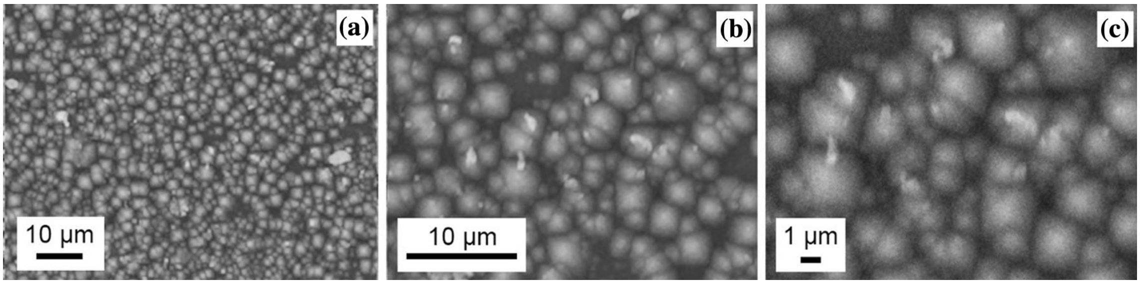

Fig. 5. SEM images of Si wafer ($X2$ sample) texturing with 2% NaOH solution at 50 min with (a) 2 kx, (b) 5 kx, and (c) 8 kx magnifications.

coating processes for use as solar cells.[5–8] The reflection of the upcoming photons from the material surface is an undesirable situation. As such, texturing and anti-reflection processes are carried out in solar cell applications. In this research, the texturing process was performed using NaOH-based solutions at different times, and the results were analyzed by generating reflectance (%) – wavelength (nm) graphics using UV–Vis equipment. It is clear that the reflectance values were increased with increasing process time, and better results were generated in a 50-min process time, as shown in Fig. 6; this is explained by the created pyramidal structure's size increasing with duration, which refracts incoming photons better and prevents reflection from the surface.[5,6] It is fair to point out that there are no whole studies about Si ingot production, slicing of ingots, and lapping/polishing of the Si wafers.[14] In our work, especially, production, slicing, lapping/polishing, and texturizing

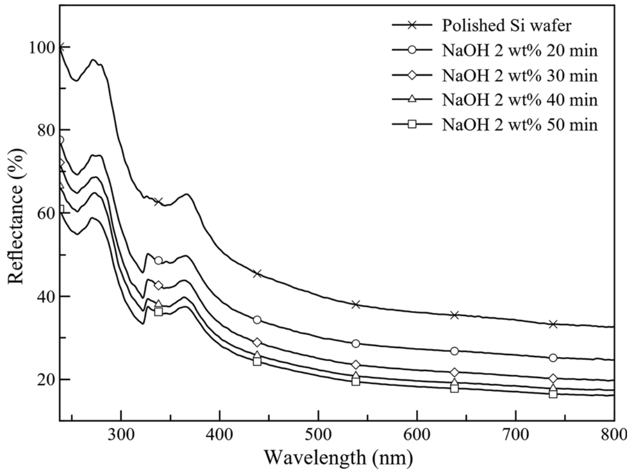

Fig. 6. Comparison of the effect of different texturing process times on reflection.

processes are able to be suited and scaled for mass production. Notably, texturing with 2 wt.% NaOH solution is a one-step and economical method as compared to other methods,[7] and in 50 min, reflection was decreased by about 35% in the range of 300–400-nm wavelength from approximately 62%. Even though NaOH + IPA + DI water solution is preferred for the texturing process in Refs. 6 and 14, we shared reflectance (%) – wavelength (nm) results to further elucidate the outcome.

CONCLUSION

In summary, the production of Si wafer was successfully carried out by the production of single-crystal Si ingot using the Cz method with (100) seed crystal. This was evidenced by the XRD pattern of produced Si wafer which gave only characteristic peaks associated with (400) planes of the silicon structure. Some parameter studies were generated about slicing of Si ingot, and lapping and polishing of produced wafers to be ready for use as devices or substrates for many applications. The optimum parameters were found for the $X2$ samples with a 2-mm/min slicing feed rate and 120 min of total slicing, lapping, and polishing. Texturing studies were carried out for application as solar cells with 2 wt.% NaOH, 6 wt.% IPA, and 92 wt.% DI water solution. The highest reduction in reflectance was seen after 50 min, which is about 35% in the wavelength range of 300–400 nm from approximately 62%. Thus, it is shown this solution can be used for texturing Si wafers in a one-step, economical, and scalable method for mass production.

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