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EXPERIMENTAL OPTIMIZATION OF AN ANISOTROPIC ETCHING PROCESS FOR RANDOM TEXTURIZATION OF SILICON SOLAR CELLS

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ABSTRACT

A multifactor experimental investigation of silicon surface texturing was conducted in Sandia's Photovoltaic Device Fabrication Laboratory using aqueous potassium-hydroxide (KOH) solutions with isopropyl alcohol (IPA) added as a complexing agent. Czochralski, magnetic-Czochralski, and float-zone silicon wafers of different resistivities with both polished and lapped surfaces were included in the experiment. Process variables considered were solution temperature, time in solution, degree of mechanical mixing, KOH concentration, and IPA concentration. Using hemispherical reflectance as the primary gauge of success, process variables were identified that resulted in an effective surface texture with reflectance less than 12% prior to anti-reflection coating. Of particular interest was a low temperature (70 °C) process with less than 2% concentration of both KOH and IPA and wide process variable tolerances.

INTRODUCTION

Anisotropic etching using concentrated alkaline solutions at elevated temperatures is often done in the semiconductor industry to thin or pattern single-crystal silicon wafers. These etching processes have been thoroughly characterized for silicon wafers of different crystalline orientations and different doping densities [1,2].

Relatively mild alkaline solutions with low concentrations (less than 5%) of either potassium hydroxide (KOH) or sodium hydroxide (NaOH) are also used to etch a textured surface of microscopic pyramids on silicon wafers with <100>-oriented surfaces. For solar cells, this textured surface is used to minimize reflection losses from the front surface and to enhance optical light-trapping within silicon cells that have a reflective back surface [3]. Unfortunately, the chemical processes used for surface texturing of silicon are not as well characterized or documented as those used for thinning and etching in the semiconductor industry. Research laboratories and many industrial firms that use surface texturing processes typically haven't had the opportunity to optimize the process for optical effectiveness, cost, and safety [4,5].

The Photovoltaic Device Fabrication Laboratory (PDFL) is actively involved in collaborative research with the U.S. photovoltaic industry to identify optimized silicon processing procedures that increase the efficiency and lower the cost of silicon solar cells. In order to implement a well-characterized surface texturing process in the PDFL, we conducted a multifactor experimental investigation of silicon texturing using aqueous KOH solutions. Our objective was to identify a process that provides a repeatable and uniform surface texture with low chemical usage, low chemical disposal costs, and with minimal vapor effluent.

EXPERIMENT DESIGN

An experimental strategy based on response surface methodology was used to design an 18-trial surface texturing experiment using aqueous KOH solutions with isopropyl alcohol (IPA) added as a complexing agent. The details of the chemical reactions that occur during the etching process were not investigated, but other work has indicated that the addition of the IPA facilitates the texture etching process by dissolving hydrous silica formed at the reaction interface [2]. Czochralski (Cz), magnetic-Czochralski (MCz), and float-zone (FZ) silicon wafers of different resistivities and with both polished and lapped surfaces were included in the experiment. Table 1 describes the types of wafers used in the experiment. Two wafers of each type were included in each trial of the experiment.

The five process variables (factors) evaluated were solution temperature, time in solution, degree of mechanical agitation, KOH concentration, and IPA concentration. Table 2 gives the ranges considered for each process variable. The ranges chosen were believed to include most conditions evaluated by other researchers. With the exception of three

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trials run at mid-range for all variables, all trials were run using combinations of the extremes of the ranges given in Table 2.

The responses measured during this experiment were the hemispherical spectral reflectance of the textured surface, pyramid-base width, texture uniformity, and etch rate. Measured results were analyzed using a program called STRATEGY designed for statistically analyzing the results of multifactor experiments [6].

Subsequent to this initial 18-trial experiment, several additional trials have been conducted in the PDFL that helped refine the resolution of the results. The results from these additional trials were included in the regression analysis performed by STRATEGY.

Table 1: Silicon wafer types included in surface texturing experiment. All wafers are 100-mm diameter and <100>-oriented.

Supplier	Type	Resistivity (Ωcm)	Surfaces
Monsanto	n-type, Cz	7-21	Polished/Lapped
Monsanto	p-type, Cz	14-25	Polished/Lapped
Wacker	n-type, FZ	0.25	Lapped/Lapped
Unisil	p-type, MCz	0.30	Lapped/Lapped

Table 2: Process variables (factors) and ranges used in surface texturing experiment.

Factor	Lower Limit	Upper Limit
Solution temperature (°C)	70	90
Time in solution (min)	10	30
Mechanical mixing	None	High
KOH concentration (%)	1	5
IPA concentration (%)	1	20

TEXTURING PROCESS DESCRIPTION

The initial 18-trial experiment was conducted using a 4000-ml quartz vessel to contain the KOH solution. The quartz vessel and chemical solution were heated on a Corning hotplate, Model PC-351, equipped with a large (5 cm) magnetically-driven stirring bar. A flat, loose fitting, glass cover was used to cover the vessel during the etching process. The temperature of the solution was maintained within ±2 °C of the desired value using this apparatus. The chemical solutions consisted primarily of high-purity deionized water (18 MΩcm), so the standard procedure involved heating just the water to a temperature near the desired level prior to adding KOH and IPA.

Note that the boiling point of IPA at sea-level is 82.5 °C; IPA should never be added to the solution if the temperature is at or above this level. For additional safety, it is also prudent to add the IPA to the water prior to adding the KOH. In case the water is hotter than anticipated, this avoids the possibility of spitting alkaline solution if the IPA boils on contact.

Eight silicon wafers (two of each type) were used for each trial of the experiment. Wafers were held in adjacent slots in a Teflon wafer carrier (Fluoroware, Model A182-39M) when submersed in the KOH solution. The wafer carrier rested above the magnetic stir-bar on a 10-cm diameter quartz ring about 2 cm in height. The range of mechanical mixing varied from none to the highest rotational rate that could be achieved without the stir-bar losing magnetic coupling.

Prior to each trial, and in order to provide a common initial condition for each wafer type, new wafers were first etched for 60 seconds in buffered-oxide-etch (BOE). After the BOE, a surface-damage removal etch in a 1:1 solution of KOH:H20 at 85 °C for 30 minutes was used to thin the wafers by approximately 30 μm. The wafers were then stored in isopropyl alcohol for at least 10 minutes to prevent surface oxidation while waiting for the texturing solution to reach the desired temperature. The wafers were then immersed in the texturing solution for the desired period of time, removed, and rinsed with deionized water.

Fresh solutions of ultrapure deionized water and semiconductor-grade KOH and IPA were mixed for each trial. The KOH was a 45% concentrated solution from General Chemical and the IPA was from the same supplier.

Subsequent to the initial 18-trial experiment conducted in the quartz vessel, additional texture-etch trials were run in the PDFL using a commercial etch bath. The FilterChem etch bath, Model EDM-4SHR, has a chemical capacity of about 10 liters and is equipped with a chemical circulation pump (22 lpm) that fills the etch tank from the bottom and cascades the solution over the top of the tank. The bath is made of Halar^{TM} to be compatible with high temperature alkaline solutions. A microprocessor controlled heating system maintains the chemical solution within ±0.5 °C of the desired setpoint, but the system is limited to a maximum temperature of approximately 80 °C. The bath is also equipped with a hinged cover that was closed after the wafer carrier was placed in the etch tank. The cover was not air-tight and was opened at 5-min intervals in order to manually agitate the wafer carrier. Additional tests are planned to determine if this manual agitation is necessary.

After each trial, the wafers were rinsed and dried and a number of measurements were performed on both surfaces of each wafer. Wafer thickness was measured before and after etching, a NIKON optical micrometer at 400X magnification was used to measure typical pyramid base dimensions, hemispherical spectral reflectance was measured with a Beckman spectrophotometer, photographs were taken at 400X magnification, and in many cases a scanning electron microscope (SEM) was used to photograph the surface at 2000X magnification.

EXPERIMENTAL RESULTS

The surface textures resulting from the different trials varied from no texture, to very large (30 μm base dimension) individual pyramids that sparsely populated the surface, to a near ideal texture with uniform coverage of intermingled pyramids with base dimensions from about 1 to 5 μm. Figure 1 illustrates the case with large individual pyramids and Figure 2 illustrates the result of an effective surface texturing process. In general, pyramids with base dimensions larger than about 10 μm are undesirable from a cell fabrication standpoint. Such large pyramids can protrude through photoresist or interfere with other cell processing procedures.

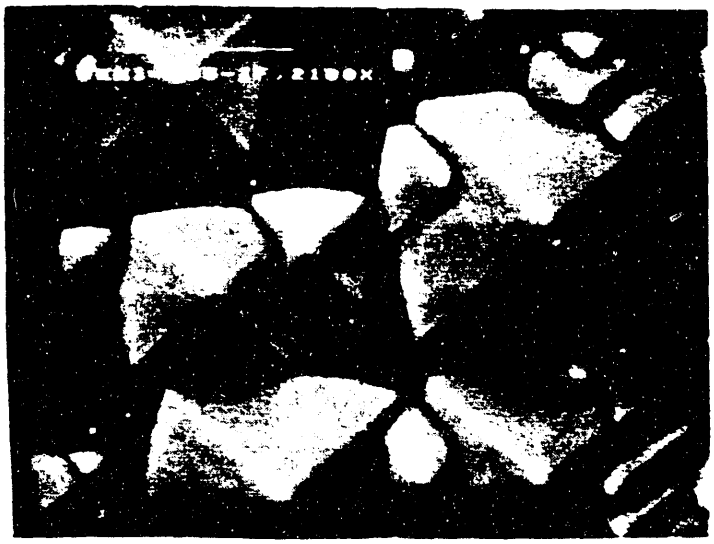

Figure 1: SEM photograph at 2100X magnification for trial at 90 °C for 30 minutes with 5% KOH, 20% IPA, and mechanical mixing.

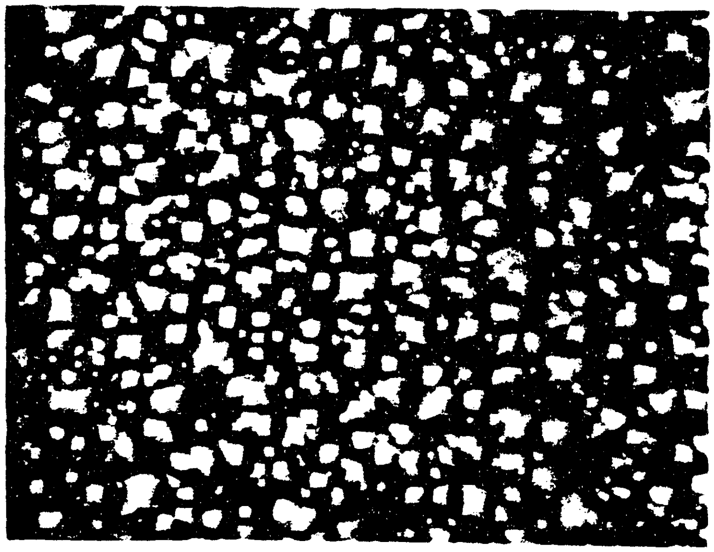

Figure 2: SEM photograph at 2200X magnification for trial at 70 °C for 30 minutes with 1.5% KOH, 3.8% IPA, and mechanical mixing.

Figure 3 shows the hemispherical spectral reflectance for an untextured wafer, and for a wafer with surface texture similar to that in Figure 2. Addition of a 110-nm silicon dioxide antireflection coating resulted in the bottom curve shown in Figure 3, with less than 2% reflectance over most of the useful spectrum.

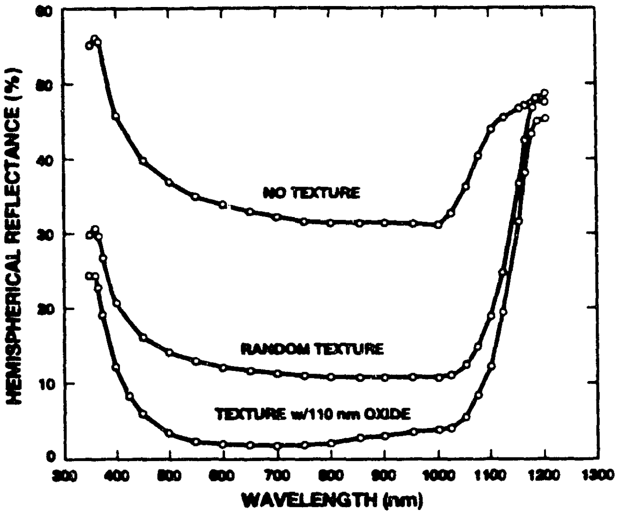

Figure 3: Hemispherical reflectance for silicon wafers with and without surface texture.

MULTIFACTOR RESPONSE SURFACE

Using the measured results from twenty trials conducted during the initial series of experiments in the quartz vessel and from an additional twelve trials in the commercial etch bath in the PDFL, the STRATEGY program was used to "fit" the results with respect to the five process variables considered. A "five-factor interaction model" was used, allowing linear variation with each parameter as well as first order interactions between parameters. The hemispherical reflectance of the textured wafer at a 1000-nm wavelength was the measured response used for analysis. All reflectance measurements used in the regression analysis were made without antireflection coatings on the wafers.

Figures 4, 5, and 6 show selected "slices" through the 5-dimensional response surface associated with hemispherical reflectance measurements on the p- and n-type wafers used. Our measurements indicated no significant difference between the p- and n-type Cz wafers used, so the measured results were combined prior to regression analysis. The surface textures achieved on these Cz wafers were also independent of the initial surface smoothness; the polished side of each wafer had a resulting texture and reflectance identical to the lapped side. As indicated by the contours in the figures, there was a high degree of interaction between the process variables considered; no single variable had a dominant affect on the quality of the surface texture. This high degree of interaction is consistent with the difficulty others have had in identifying a repeatable texturing process.

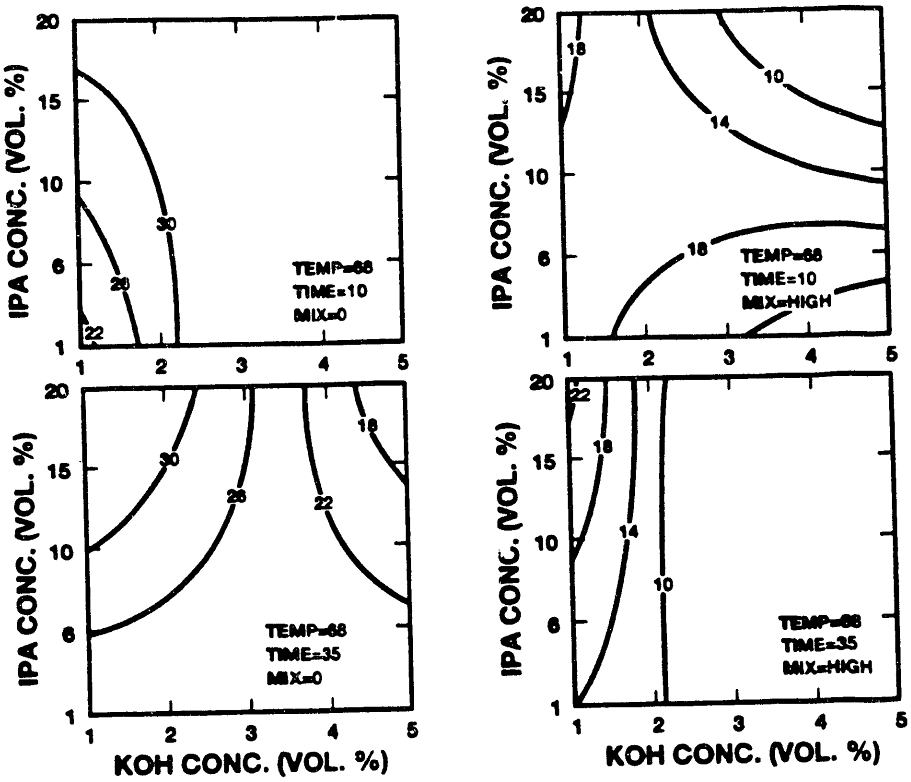

Figure 4: Results of regression fit to data from all texturing trials for Cz wafers for solution temperature of 68 °C. Contours are hemispherical reflectance (%) at 1000 nm. (Vol. % for KOH is volume percent of 45% KOH liquid solution. Time is in minutes.)

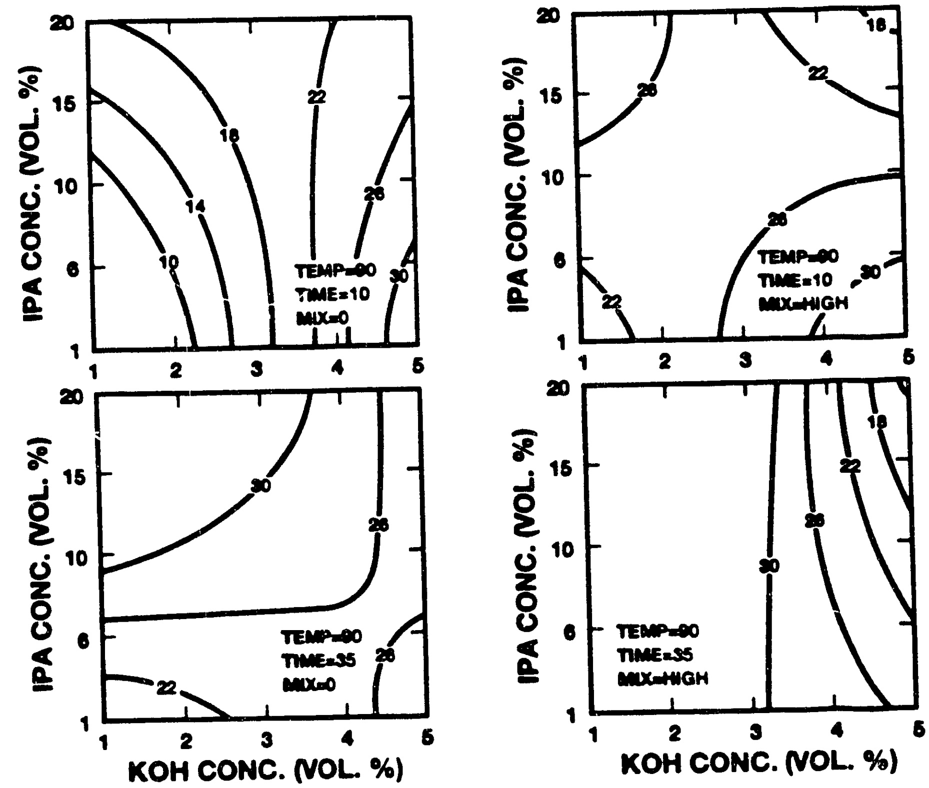

Figure 5: Results of regression fit to data from all texturing trials for Cz wafers for solution temperature of 90 °C. Contours are hemispherical reflectance (%) at 1000 nm

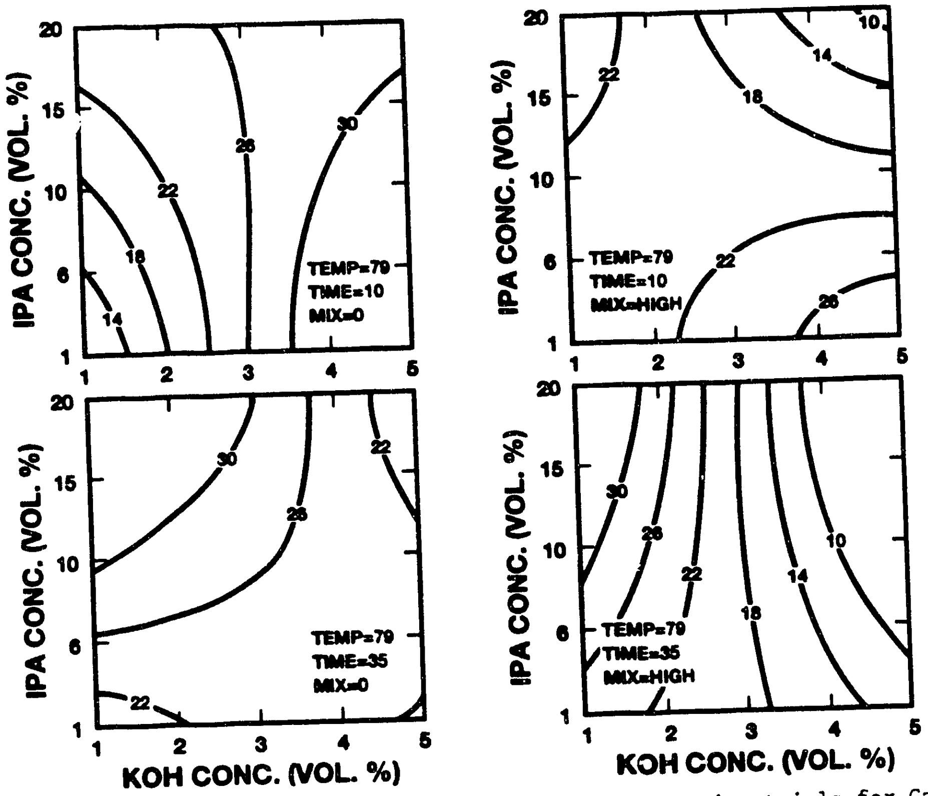

Figure 6: Results of regression fit to data from all texturing trials for Cz wafers for solution temperature of 79 °C. Contours are hemispherical reflectance (%) at 1000 nm.

The confidence limits associated with the contours in these figures vary with the magnitude of each parameter. However, evaluation of the residuals from the regression analysis indicated that the contours fit the measured data within less than 5% reflectance for all but five of the thirty one trials conducted to date. As additional trials are run at different variable levels, the results will be used to improve our resolution of the response surface. Nonetheless, the results now available give a reasonably clear indication of the process variables that give an effective surface texture.

Analysis of the reflectance measurements for FZ and MCz wafers indicated a response surface similar to that for the Cz wafers. However, both FZ and MCz wafers had a slightly wider range of process variables that resulted in an effective surface texture.

Other measured results such as silicon etch rates have not yet been thoroughly analyzed. However, the high temperature solutions with high KOH concentration clearly had the fastest etch rates, but typically did not result in the most desirable surface textures.

DISCUSSION

Minimizing the reflection loss from the front surface of a solar cell is the primary motivation for surface texturing. However, several other things must be considered to ensure that the texturing process is compatible with other cell fabrication processes and is achievable at an acceptable cost. As mentioned previously, pyramid dimensions must be compatible with cell processing procedures such as photolithography. In addition, chemical cost, vapor effluent during processing, the number of times a chemical solution can be reused, and chemical disposal cost are important considerations.

Perhaps the most important result from our work is the identification of an effective texturing process at a reasonably low temperature (70 °C) and with low concentrations of both KOH and IPA. Although additional trials are required to fully confirm the results, Figure 4 indicates that with mechanical mixing at about 70 °C a large range for both KOH and IPA concentration will result in an effective surface texture. Due to this broad range of acceptable KOH and IPA concentration, the contours in Figure 4 also suggest that it may be possible to reuse the texture solution several times by starting with low concentrations of both chemicals and then replenishing the solution with fresh chemicals prior to each use. The relatively low temperature and low IPA concentration also significantly reduce the quantity of IPA vapor released to the atmosphere during processing.

This low-temperature KOH solution also has a relatively slow etch-rate for silicon dioxide, making it possible to use an oxide mask to limit the texturing to selected areas, or to texture only one side of the wafer.

CONCLUSION

Although additional experimental trials are required to improve the confidence limits associated with our results, process variables have been identified that result in a repeatable, low-reflectance, surface texture compatible with photolithography and other cell fabrication processes used in the Photovoltaic Device Fabrication Laboratory at Sandia.

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