1.0

1.1

1.25   1.4   1.6

4.5
50
56

2.8   2.5
3.2   2.2
36
40   2.0

1.8

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Polished (111), (100), and textured (100) single crystal, n-Si surfaces have been studied in relation to their use as photoanode materials in a photoelectro-chemical device. Textured (100) Si is prepared by chemically etching the polished (100) surface. The textured surface consists of pyramids having (111) sides, necessitating the study of polished (111) Si as a comparison. Electron microscopy and Auger spectroscopy have been employed to characterize textured and polished surfaces functionalized with the electroactive reagents (1,1'-ferrocenediyl)dimethylsilane and (1,1'-ferrocenediyl)dichlorosilane. (over)

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Electrochemical techniques have been used to determine coverage of electro-active material, and the textured surface is found to bind about twice as much material as the polished surfaces. The charge transfer properties of the surface-confined material on the polished (100) and (111) Si are virtually identical: the position of the photoanodic wave corresponding to uphill ferro-cene oxidation is within 30 mV and the ferricenium reduction peak is also at the same potential. The textured (100) Si surface shows a slightly more positive (100 mV) photoanodic and dark cathodic peak. Photoelectrochemical cells based on textured (100) Si vs. polished (100) Si are about 20% better in overall efficiency due to lower reflection losses associated with the textured surface.

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TECHNICAL REPORT NO. 23

Study of Textured n-Type Silicon Photoanodes: Electron

Microscopy, Auger, and Electroanalytical Characterization

of Chemically Derivatized Surfaces

by

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Prepared for Publication in the

Journal of Electroanalytical Chemistry

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Study of Textured n-Type Silicon Photoanodes: Electron Microscopy, Auger,

and Electroanalytical Characterization of Chemically Derivatized Surfaces

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<u>Abstract:</u> Polished (111), (100), and textured (100) single crystal, n-Si surfaces have been studied in relation to their use as photoanode materials in a photoelectrochemical device. Textured (100) Si is prepared by chemically etching the polished (100) surface. The textured surface consists of pyramids having (111) sides, necessitating the study of polished (111) Si as a comparison. Electron microscopy and Auger spectroscopy have been employed to characterize textured and polished surfaces functionalized with the electroactive reagents (1,1'-ferrocenediyl)dimethylsilane and (1,1'-ferrocenediyl)dichlorosilane. Electrochemical techniques have been used to determine coverage of electroactive material, and the textured surface is found to bind about twice as much material as the polished surfaces. The charge transfer properties of the surface-confined material on the polished (100) and (111) Si are virtually identical: the position of the photoanodic wave corresponding to uphill ferrocene oxidation is within 30 mV and the ferricenium reduction peak is also at the same potential. The textured (100) Si surface shows a slightly more positive (100 mV) photoanodic and dark cathodic peak. Photoelectrochemical cells based on textured (100) Si vs. polished (100) Si are about 20% better in overall efficiency due to lower reflection losses associated with the textured surface.

Semiconductor-based devices depend on interfacial structural and electronic properties. Performance of semiconductor/liquid junction devices for the conversion of light to electricity and/or fuels have been shown to depend on semiconductor surface treatments such as etching and chemical modification.[1-5] In this article we wish to report the results of a study of single crystal, n-type Si photoanodes that have been purposely etched to improve surface area and to reduce reflectivity. The resulting etched surface will be referred to as "textured".
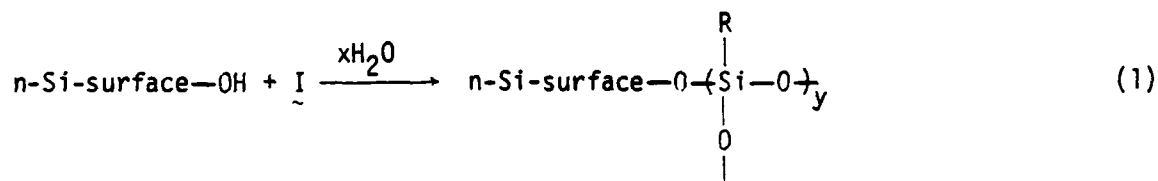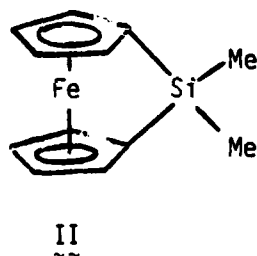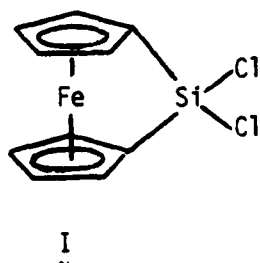
It is known that the (100) face of single crystal Si can be chemically etched to reveal (111) planes resulting in a textured (100) Si surface consisting of pyramids having (111) sides.[6,7] Texturing the (100) surface is a sort of anti-reflection technique that has been proposed as a way to improve the efficiency of p-n Si solar cells.[6,7] We undertook a study of the textured Si surface in connection with semiconductor photoelectrochemistry, in part to demonstrate that the anti-reflection properties can be exploited in a liquid junction device. An important difference between the p-n device and the liquid junction is that the p-n device does not crucially depend on the surface properties for the photovoltaic effect whereas the surface is the essential aspect in the photovoltaic effect in the liquid junction. Thus, surface texturing is not obviously extended to semiconductor/liquid junctions.

The textured surface also results in an increase in surface area and this may be useful when the surfaces are to be chemically derivatized with redox reagents that mediate electron transfer to or from solution species.[5,8] Increased surface area for chemically derivatized electrodes would seemingly be useful in two respects. First, the increased surface area would result in a lower turnover rate at a given photocurrent for the surface-confined redox mediator. Second, the total number of turnovers needed would be lower for the higher surface area. Finally, when the rate of the mediated redox reaction is rate (current) limiting, increasing

the surface area would aid in realizing a situation where current
is limited only by light intensity.

Since texturing the (100) surface of Si reveals (111) planes, we have
made careful comparisons of polished and textured (100) surfaces with
polished (111) surfaces of single crystal Si. It is possible that different
crystal faces will give a different output photovoltage.[9] Further, surface
states may differ to an extent that interfacial charge transfer kinetics could
be altered.

Electron microscopy, Auger spectroscopy, and electrochemical
techniques have been employed to characterize n-type Si surfaces. Redox
reagents I and II have been used to derivatize the surface of n-type Si
by exploiting chemistry represented by equations (1)[10-12] and (2).[13] Auger studies have

I

II

$$\text{n-Si-surface—OH} + I \xrightarrow{\ xH_2O\ } \text{n-Si-surface—O} \left(Si\text{—O} \right)_y \qquad (1)$$

R = ferrocenyl—

$$\text{n-Si-surface—OH} + II \longrightarrow \text{n-Si-surface—O—Si—R} \qquad (2)$$
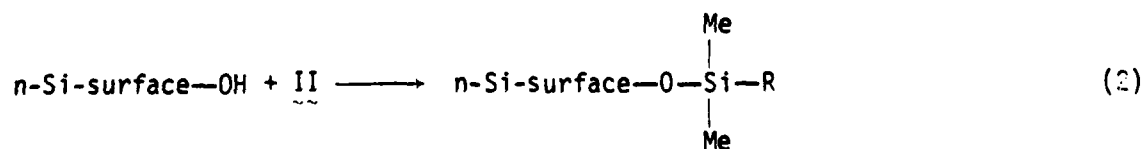
R = ferrocenyl—

been carried out on hydrolyzed samples of $\underline{I}$ and Pt/Pt-oxide and Au/Au-oxide surfaces

derivatized with $\underline{I}$ as a comparison to Si derivatized with $\underline{I}$.

Electrochemical behavior of the n-type Si photoanodes has been examined

in non-aqueous (EtOH) electrolyte solutions containing

added ferrocene, since it has previously been shown that this medium can

yield constant output parameters when the n-type Si is illuminated.[14]

Derivatized photoanodes have been characterized in EtOH electrolyte

solution containing no electroactive material.

Experimental

Materials. Single-crystal, P-doped, n-type Si wafers (both (100) and
(111) face exposed) were obtained from Monsanto Co. The polished wafers
were 0.35 mm thick with resistivities between 3-6 Ωcm for the (100) face and
between 3-7 Ωcm for the (111) face. Absolute EtOH, spectroquality isooctane,
reagent grade KOH, $Fe(\eta^5-C_5H_5)_2$, and ethylene glycol were used as received from
commercial sources. Electrometric grade [n-Bu$_4$N]ClO$_4$ (Southwestern Analytical Chemical)
was dried under vacuum (353°K) for 12 hours, and stored in a dessicator until
used. Hexane was distilled from sodium benzophenoneketyl under Ar.
Ferricenium as the PF$_6^-$ salt was prepared according to the literature.[15]
(1,1'-ferrocenediyl)dichlorosilane, I, and (1,1'-ferrocenediyl)dimethylsilane, II,
were prepared according to the published procedures.[10,13] Hydrolysis of I to
produce polymeric material was done according to the literature procedure.[12]

Electrode Fabrication. Electrodes were made by cutting the wafers into
pieces ~20 mm^2 and mounting as previously reported.[14] The electrode was
rubbed on the back with Ga-In and secured with conducting Ag epoxy to a coiled
or flattened Cu wire. The Cu wire lead was passed through 4 mm Pyrex tubing
and all surfaces were insulated with ordinary epoxy so as to leave only the front
surface exposed.

Just prior to use naked Si electrodes were etched in concentrated HF for 60 s
to remove SiO$_x$ and rinsed in distilled H$_2$O and EtOH. Electrodes to be derivatized
were treated in 10 M NaOH for 60 s after the HF etch, then rinsed with
distilled H$_2$O and acetone. For derivatization the electrodes were exposed
for 1-15 h to an Ar-purged isooctane solution of (1,1-ferrocenediyl)-
dichlorosilane in an Ar atmosphere at 298°K, or for 3-5 h to a hexane
solution of (1,1'-ferrocenediyl)dimethylsilane in a Vacuum Atmospheres
N$_2$ dry box. For derivatization with (1,1'-ferrocenediyl)dimethylsilane
the HF/NaOH pretreatment was carried out in an ultrasonic bath. The
process was completed by rinsing the electrode first with isooctane or hexane
and then with acetone. Pt and Au electrodes were mounted, pretreated, and
derivatized with (1,1'-ferrocenediyl)dichlorosilane as previously described.[10-12]

Etching of (100) Silicon. Silicon with the (100) face exposed was etched according to the procedure given in the literature.[6,7] The silicon was first etched in concentrated HF for 60 s, rinsed with distilled water, and then placed into a solution which was 19% KOH and 1% ethylene glycol in water. The silicon was etched for 5-30 min at 78-80°C in an ultrasonic bath, then rinsed with distilled H_2O. The etching solution could not be consistently reproduced. The half-polished/half-textured electrodes were prepared by covering approximately half of the front face of a 1 cm x 4 cm piece of silicon with ordinary epoxy. Then the half-epoxied strip was treated as above, etching for 15 min. After the etching process, the epoxy was removed by soaking in CH_2Cl_2 for several hours. The strip was cut into smaller strips, ~0.5 cm by 1 cm, and these were made into electrodes as described above.

Electrochemical Studies. All experiments were performed in single compartment Pyrex cells, equipped with a saturated calomel (SCE) reference electrode, Pt wire counterelectrode, and Si working electrode. Electrodes were characterized electrochemically in 0.1 $\underline{M}$ [$\underline{n}$-Bu4N]ClO_4 in EtOH using a PAR Model 173 potentiostat and a PAR 175 universal programmer. Scans were recorded on a Houston Instruments X-Y recorder. Irradiation was supplied with a He-Ne laser emitting ~5.6 mW at 632.8 nm. Laser intensity was varied with Corning colored glass filters and monitored with a beam splitter and a Tektronix J16 digital radiometer equipped with a J6502 probe.

Stirred, Ar purged solutions of 5 x $10^{-2}\underline{M}$ $Fe(\eta^5-C_5H_5)_2$, 1.5 m$\underline{M}$ $Fe(\eta^5-C_5H_5)_2^+$, and 0.1 M [$\underline{n}$-Bu$_4$N]ClO_4 in EtOH were used for steady state current potential curves. The E_{redox} of the solution was measured with a digital voltmeter by determining the potential difference between a Pt electrode and an SCE. A jack was used to raise and lower the entire cell assembly when using the half-polished/half-textured electrode in order to move the unexpanded laser beam between the textured and polished parts of the electrode.

Auger Electron Spectroscopy. Auger spectra were obtained on a Physical Electronics Model 590A Scanning Auger Spectrometer, equipped with a sample introduction system. A 5 keV electron beam with beam currents of 0.1-3 µA was used as the excitation source. Electrode samples were mounted by clipping the electrode Cu wire lead to the sample holder. Pretreated Si samples were either clipped down or mounted with conducting Ag paint, and the solid obtained by hydrolyzing (1,1'-ferrocenediyl)dichlorosilane was pressed into In for study to avoid problems with sample charging.

Scanning Electron Microscopy. SEM's were taken on a Cambridge Mark 2A Stereoscan, with a resolution of 200 Å. The microscope used is equipped with a Kevex energy dispersive X-ray analyzer. Samples were mounted with conducting Ag paint. Generally, the samples were not gold coated since charging was not a problem at the magnifications used.

Results

a. Electron Microscopy of Electrode Surfaces. Electron microscopy has been employed to examine the nature of derivatized and textured surfaces. Electron microscopy has been particularly useful in establishing that the textured (100) Si surface actually consists of pyramids.

Chemical etching of (100) Si generally produces a rough surface, but there is irreproducibility in the extent to which the chemical etching produces a textured surface consisting of pyramids. In some cases, etching solutions prepared in the same way did not yield the same results. In fact, the best etching solution was not easily reproduced and virtually all textured surfaces studied in detail were prepared using a single solution.[16]

Figure 1 shows a comparison of the smooth (100) Si surface and the textured (100) Si surface. The ~4 mm x 12 mm exposed surface is half-polished and half-textured according to the procedure used in the Experimental. The half-polished/half-textured material was subsequently fashioned into a photoelectrode so that the polished and textured electrode surface could be compared by illuminating one part or the other using a masked illumination source. The photograph shows that the polished part is in fact smooth at magnification 10,000X; though not shown, the polished (100) surfaces used were shown to be smooth at ~200 Å resolution. The micrograph of the textured portion does show sharp, well-developed pyramids, while the region between the polished and fully textured portions shows the beginnings of the growth of the pyramids. Polished (111) Si surfaces are smooth at ~200Å resolution.

The low magnification portion of Figure 1 illustrates the difference in specular reflection of the polished and textured (100) Si surface. The polished surface clearly reflects the image of the object in the photograph, whereas the textured surface does not.

Chemical etching to produce the textured (100) Si surface is irreproducible as mentioned above. Variation in the textured surfaces is represented by the scanning electron microscopy data shown in Figure 2. These surfaces were produced, ostensibly, by the same procedure used to prepare the textured surface in Figure 1. But clearly there are differences. However, increase in surface area and decrease in specular reflection are common to all (100) surfaces etched according to the procedure used. Just what gives rise to the variations in surface morphology is not known. All electrochemical studies of textured (100) Si were for surfaces for which the photograph in Figure 1 is representative.

Electron microscopy was also used to examine polished (111) and (100) Si, Au, and Pt surfaces that were derivatized with I and II. At coverages of I in the range 3×10^{-10} to 5×10^{-9} mol/cm^2 or of II in the range $3-8 \times 10^{-10}$ mol/cm^2 we were unable to reproducibly observe anything other than smooth surfaces at a resolution of ~200 Å. These coverages are the number of moles of ferrocenyl-units per cm^2 of projected surface area determined by cyclic voltammetry. The electron microscopy sometimes reveals globules, splotches, particles, or what appear to be blisters on the surface but energy dispersive X-ray analysis (EDAX) of these particular places does not reveal Fe. For coverages below 5×10^{-9} mol/cm^2>95% of the electrode surface is smooth at 200 Å resolution. Gross deposition of samples of I onto electrodes does give structures and EDAX can be used to detect Fe, but smooth surfaces can be generally found even for electrochemical coverages of >5×10^{-9} mol/cm^2. Gross deposition of I to give visibly detectable material can be accomplished by dropwise addition of solutions of I onto the electrode surface followed by solvent evaporation. Electroactive material exceeds 10^{-8} mol/cm^2. The structures (particle, globules, splotches, blisters) that sometimes appear at this, and lower, coverage are apparently not uniquely related to the derivitization procedure. Thus, we find that derivatization of smooth surfaces with I or II results in uniform coating at a resolution of ~200 Å. Electron microscopy of textured (100) Si that has been derivatized with I or II shows no differences compared to the textured, but non-derivatized surfaces.

b. Auger Electron Spectroscopy of Electrode Surfaces. We undertook Auger electron spectroscopy studies of Si, Au, and Pt surfaces functionalized with I and II to add to our characterization of the interface. Previous studies of electrode surfaces have shown that ferrocene-centered redox material derived from I is deficient in Fe.[12] Figure 3 shows Auger spectra for Si before and after functionalization with I and for hydrolyzed I and for Pt functionalized with I. Though much data were collected, little in the way of quantitative information has been gained. Generally, functionalized Au and Pt show significantly different Si/Fe ratios from electrode to electrode suggesting a variable and non-reproducible degree of decomposition in the functionalization reaction,[12] even when electrochemical coverage is similar. Three qualitative conclusions can be drawn: (i) functionalized electrodes show Fe everywhere at the ~10 μm resolution used in these experiments; (ii) for Si electrodes the coating of oxide and electroactive material is sufficiently thick that no pure Si is observable;[17] and (iii) the Auger of material derived from hydrolysis of I is similar to the spectrum for the material on the surface of Pt or Au derivatized with I. Conclusions regarding the quantitative aspects of elemental composition of the surface-confined material cannot be made. Damage of the organometallic material in the Auger is a possible source of problems in reproducibility,[18] but we believe that the main source of irreproducibility lies in the derivatization reaction itself. We note that hydrolysis of I gives material having a different elemental analysis from preparation to preparation. Further, we have obtained very reproducible, quantitative results from the Auger using other derivatizing reagents. For now, the Auger clearly shows that Fe is present on surfaces after exposure to I or II. In the future we will focus effort on the quantitative aspects of this problem by first concentrating on reagent II, since it should be present only in monolayer coverage.[13]

c. Electrochemical Characterization of Polished vs. Textured (100) Si.

Several experiments have been carried out to characterize the photoelectro-chemical behavior of polished and textured (100) Si surfaces. Also, polished (111) Si has been compared to the (100) Si surfaces, since the (111) planes are revealed in the textured (100) surface. Electro-chemical characterization of chemically derivatized surfaces using reagents I and II to modify the surface has been performed, in order to determine whether the textured surface will bind more reagent than the polished surface. Table I and Figure 4 summarize the essential results. The textured surface does bind more reagent per unit of projected area. The enhancement in coverage using reagent II is most reliable, since this reagent has no tendency to form polymer on the surface, under the conditions used.[13] We find that the enhancement in coverage is about a factor of two for the textured surface compared to the polished Si. Surprisingly, the average coverage for reagent I is also about a factor of two greater for the textured surface.

After examining the very rough surface in the textured case compared to the polished (100) Si, Figure 1, the rather small enhancement factor in surface coverage is surprising. However, geometrical considerations suggest that the available area should increase by only a small factor (<4) if pyramids of (111) sides are revealed upon texturing the (100) surface. A definite increase in surface coverage of the reagent II does occur. Data for derivative I, where polymerization is possible, is less convincing, since the overlap of coverages obtained for textured and polished surfaces is considerable.

The position of the photoanodic current peak for the oxidation of the surface-confined reagent is a measure of the extent to which the oxidation can be driven uphill with light of a given intensity. The peak on a reversible electrode such as Pt or Au gives the formal potential of the surface-confined ferrocene reagents and it is about +0.50 V vs. SCE.[10] The

peak at 0.0 - +0.1 V vs. SCE on the illustrated Si indicates that ferrocene

is oxidized in an uphill sense by about 400-500 mV. There appears to be a

small, but definite, effect upon texturing the surface that results in a

more positive photoanodic current peak (70-100 mV) compared to the polished

surface. The effect on peak position is not simply due to the (111) surfaces

that are exposed. This conclusion is firm because polished (111) and polished

(100) give nearly the same average peak position and the same average

coverage of electroactive material. Texturing the surface apparently

alters the interface properties in such a way that the surface confined

molecule is less easily driven uphill under the conditions employed.

Data for the dark reduction of low concentration of ferricenium in

solution are given in Table II. A comparison of the position of the

cathodic current peak and the peak cathodic current density is given for

textured (100) and polished (100) and (111) Si. The cathodic current peak

occurs ~25-30 mV more positive at the textured electrodes. This

result suggests that the textured (100) surface has a slightly worse back

reaction problem compared to the polished surfaces. The ability to reduce

the ferricenium at the more positive potential indicates that the textured

surface will have more back electron transfer when ferrocene is photooxidized.

However, the effects on back reaction rates appear to be modest. Even fast

scan rates in the cyclic voltammetry reveal little difference between the

polished and textured surfaces.

The cathodic peak height and the shape of the wave for textured and

polished Si surfaces are quite similar. The fact that the integrated area

under the cathodic wave for textured and polished surfaces is nearly the same

indicates that the increased area is not important; the roughness is low

compared to the thickness, d, of the electrolyte solution layer that is

important in the cyclic voltammetry. The two possible extremes are sketched

in Scheme I. Electron microscopy shows that the textured (100) Si surface

is rough on the 1 - 5 ⊥ scale.[6,7] By knowing the area under the cathodic wave,

the electrode area, and the bulk solution concentration of ferricenium, the thickness, d, for the polished surfaces can be approximated. At 100 mV/s scan rates, we find d to be ~20 μ, or several times larger than the roughness of the textured (100) Si surface. The value of d ≈ 20 μ accords well with theory.[19] Thus, we would expect nearly the same area under cyclic voltammetry waves for the polished and textured (100) Si, as found.
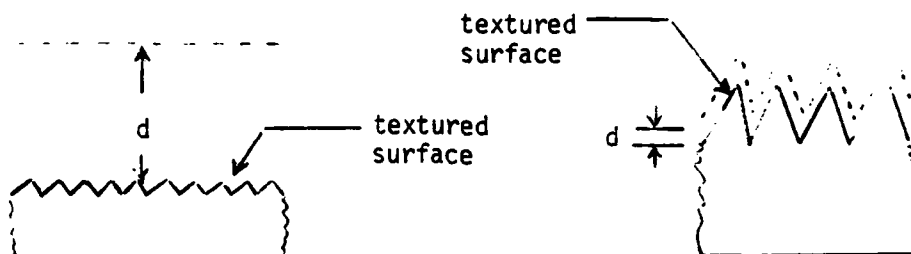
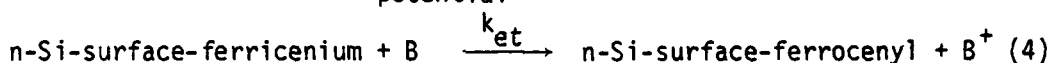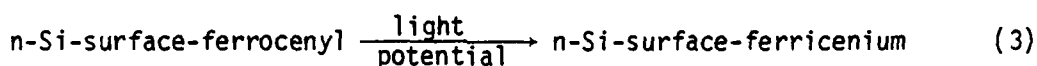Scheme I. Representation of two extremes for relation of textured surface to thickness, d, of electrolyte solution that contains accessible electroactive material in a cyclic voltammetric scan. In (a) the textured surface and a smooth surface would give the same cyclic voltammetry, whereas in (b) the textured surface would give a larger integrated area under the wave.

Scheme I is also useful in understanding the difficulty in interpreting the derivatized surfaces. When using a derivative that can polymerize and form a thick coating of thickness, d, the question is again whether the roughness is of the same order as d. Obviously, when using a material that does not polymerize and forms covalent bonds only to the surface —OH groups, II (equation (2)), the value of d is low compared to the physical scale of the roughness. When the polymer from I (equation (1)) is significantly thicker than the scale of roughness, textured and polished surfaces again become indistinguishable. However, when the polymer coating has a thickness less than the height of the pyramids then even a polymeric coating of electroactive material will reveal the roughness. From the coverages actually found, Table I , we would conclude that the average value of d for surface derivatives with I to be well below 1 ..

Auger and electron microscopy are consistent with this finding. We find in the Auger, for example, that not even the highest coverage, 1.8×10^{-8} mol/cm^2, for $\underline{I}$ on Au completely attenuates the Auger signal characteristic of the underlying Au. The electron microscopy of textured (100) Si surfaces does not show less definition of the pyramids when the surface has polymeric coverage of electroactive material. We conclude that for typical coverages of $\underline{I}$ or for the ~monolayer coverages of $\underline{\underline{II}}$ there is an important increase (~2) in the amount of attached electroactive material per unit of projected electrode area.

The improved surface coverage on textured surfaces means that current density for mediated oxidation of solution species, B, according to equations (3) and (4) can be a factor of ~two greater under conditions where

$$\text{n-Si-surface-ferrocenyl} \xrightarrow[\text{potential}]{\text{light}} \text{n-Si-surface-ferricenium} \qquad (3)$$

$$\text{n-Si-surface-ferricenium} + B \xrightarrow{k_{et}} \text{n-Si-surface-ferrocenyl} + B^+ \quad (4)$$

neither light intensity nor mass transport of B are current limiting. Under these conditions current density is directly proportional to surface coverage of the mediation system (ferricenium/ferrocene).[20] Preliminary results do show an average increase of about two in the photocurrent density for the mediated $I^- \rightarrow I_3^-$ process at textured vs. polished surfaces using reagent $\underline{\underline{II}}$ as the surface-confined mediator system.

d. Comparison of Energy Conversion Efficiency for Textured and Polished (100) Si Photoanodes. Figure 5 and Table III summarize data for the conversion of 632.8 nm light to electricity using textured and polished (100) Si surfaces as the photoanode in a photoelectrochemical cell. The counterelectrode used was Pt and the cell chemistry is that represented by equations (5) and (6) in a 0.1 $\underline{M}$ [$\underline{n}$-Bu$_4$N]ClO$_4$/EtOH electrolyte solution.

$$\text{Photoanode Reaction:} \quad \text{Ferrocene} \longrightarrow \text{Ferricenium} + e^- \qquad (5)$$

$$\text{Cathode Reaction:} \quad \text{Ferricenium} + e^- \longrightarrow \text{Ferrocene} \qquad (6)$$
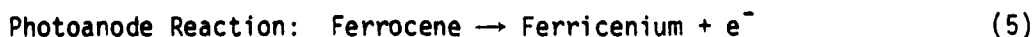
The comparison was made using a half-polished/half-textured (100) Si electrode like that shown in Figure 1. The only difference was that the polished or the textured portion was illuminated by suitable manipulation of the incident He-Ne laser beam used as the input optical source. In such an experiment the contribution of the polished and the textured (100) Si surface to reduction of the solution ferricenium is constant, and we have a true test of the relative photoeffects.

The data show that the textured portion of the photoanode results in improved energy conversion properties, except at the highest intensity used. There is a slight improvement in open-circuit photovoltage and the voltage at the maximum power point. But the main improvement is in the photo-current. There is about a 20% improvement in short-circuit current. This improvement is very likely the consequence of lowered specular reflection from the textured surface. The improvement is significant and reproducible but we still find overall low efficiency for the n-Si based cell. The textured surface does not significantly affect parameters other than the photocurrent.

Conclusions

A comparison of the photoanode properties of polished (100), (111), and textured (100) Si surfaces reveals only minor differences with respect to inherent properties. There does appear to be a small loss in output voltage for surface-ferrocene oxidation for the textured (100) surface and this appears to be due to better kinetics for ferricenium reduction than at the polished (100) or (111) surface. The textured surface is rough (1 - 5 μ pyramids) on a scale that results in a factor of two greater coverage of electroactive material compared to polished surfaces that appear smooth at ~200 Å resolution. Even for a surface derivatizing reagent that can polymerize, the textured surface is rough enough to enhance coverage per unit of projected area. Auger

spectroscopy and electron microscopy suggest uniform coverage of electro-
active reagent but the resolution is only ~10 μ for Auger and
~200 Å for electron microscopy. The textured surface does appear to
lower reflection losses compared to polished surfaces and improvement
of ~20% in energy conversion efficiency is possible by texturing the
(100) Si surface. However, overall efficiency of the n-Si-based cell
employing the ferricenium/ferrocene redox couple is still low.

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16. After completing the bulk of the work described herein we have obtained a more reproducible texturing procedure used by the Jet Propulsion Laboratory: 15% NaOH at 85°C for 5-10 min followed by transfer (without rinsing) to 1% NaOH, 3½% 2-propanol at 85° C for 5-10 min. Results with textured surfaces prepared in this manner are similar to those reported here.

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Table I. Photoelectrochemical Characterization of Derivatized n-Type Si.

Sample[a]	Derivative[b]	E_{PA}, V vs. SCE[c]	Coverage, $mol\,cm^{-2} \times 10^{10}$[d]
Polished (100) Si			
#12	II	-0.03	5.4
#13	II	-0.03	3.5
#14	II	+0.10	4.4
#15	II	+0.01	7.6
#11	II	-0.03	3.6
		Avg. 0.00	Avg. 4.9
Textured (100) Si			
#16	II	+0.07	8.1
#17	II	+0.05	11
#18	II	+0.17	15
#19	II	+0.17	11
#20	II	+0.05	12
#21	II	+0.05	5.9
#10	II	+0.18	7.8
#22	II	+0.10	14
		Avg. +0.11	Avg. 10.6
Polished (111) Si			
# 9	II	-0.03	5.9
#23	II	0.00	3.2
#24	II	-0.01	7.2
#25	II	0.00	3.3
#26	II	-0.02	4.1
#27	II	+0.10	6.7
		Avg. +0.01	Avg. 5.1
Polished (100) Si			
#28	I	+0.04	36
#29	I	+0.11	100
#30	I	0.00	46
#31	I	+0.02	22
# 8	I	+0.01	7.4
#32	I	+0.08	33
#33	I	+0.05	78
#34	I	+0.05	29
		Avg. +0.05	Avg. 44
Textured (100) Si			
#36	I	+0.22	190
#37	I	+0.22	260
#38	I	+0.20	160
#39	I	+0.08	12
# 5	I	+0.05	78
# 6	I	+0.12	31
# 7	I	+0.04	22
		Avg. +0.12	Avg. 115

Table I. (continued)

Sample[a]	Derivative[b]	E_{PA}, V vs. SCE[c]	Coverage, molcm^{-2} xl0^{10}[d]
Polished (111) Si			
# 1	I	+0.14	94
#40	I	+0.06	46
#41	I	+0.06	9.3
#42	I	-0.06	10
#43	I	-0.06	10
#44	I	+0.02	20
#45	I	-0.06	3.8
#46	I	+0.06	15
#47	I	-0.01	15
#48	I	+0.02	13
# 4	I	+0.02	21
		Avg. +0.02	Avg. 23

[a]Face of silicon exposed ((100) or (111)) and whether or not the electrode was textured.

[b]The derivatives used. I = (1,1'-ferrocenediyl)dichloroylsilane and II = (1,1'-ferrocenediyl)dimethylsilane.

[c]The potential of the peak of the photoanodic wave with a scan rate of 0.1 V/sec; 632.8 nm illumination, ~50 mW/cm^2.

[d]The coverage of electroactive material on the surface calculated by integrating the area under the anodic wave and dividing by the projected surface area.

Table II. Comparison of Dark Reduction of Ferricenium at Textured and Polished n-Type Si.[a]

Electrode		i_{pc}, $\mu A/cm^2$ [b]	E_{pc}, V vs. SCE [c]
Polished (100) Si	#156	11.0	-0.03
	#155	10.5	+0.06
	#157	9.5	+0.02
	#158	11.0	-0.05
	Av.	10.5	0.00
Polished (111) Si	#69	11.2	0.00
	#68	10.7	+0.01
	#66	9.5	+0.08
	#64	---	-0.07
	Av.	10.5	+0.005
Textured (100) Si	#168	12.2	+0.05
	#169	11.7	+0.11
	#170	9.6	-0.04
	#163	---	0.00
	Av.	11.2	+0.03

[a] Data for 100 mV/sec cathodic sweep from +0.6 V vs. SCE in quiet solutions of $[Fe(\eta^5-C_5H_5)_2]PF_6$ in EtOH solvent containing 0.1 $\underline{M}$ $[\underline{n}-Bu_4N]ClO_4$.

[b] Current density at cathodic current peak for $[Fe(\eta^5-C_5H_5)_2^+]$ reduction.

[c] Potential for cathodic current peak.

Table III. Output Characteristics for a Polished vs. Textured (100) n-Type Silicon Photoelectrode.[a]

Pretreatment[b]	Input, mW[c]	Φ_e[d]	Max. Pwr. Out, μW	(Φ_{mp})[e]	Max, V, mv[f]	V@η_{max}, mv[g]	η_{max},%[h]	Fill Factor[i]
Polished	0.28	0.37	8.8	(0.28)	355	220	3.2	0.47
	0.59	0.35	15.3	(0.23)	380	220	2.6	0.38
	0.93	0.34	20.9	(0.19)	400	230	2.2	0.32
	5.52	0.10	33.4	(0.05)	440	230	0.6	0.26
Textured	0.28	0.43	10.6	(0.33)	365	230	3.8	0.48
	0.59	0.40	17.3	(0.28)	390	210	3.0	0.38
	0.93	0.36	21.8	(0.20)	400	230	2.3	0.32
	5.52	0.10	32.8	(0.05)	435	230	0.6	0.26

[a]Data are from the curves shown in Figure 5. The solution in the cell was 5×10^{-2} M ferrocene, 1.5×10^{-3} M ferricenium (E_{redox} = +0.34 V vs. SCE), 0.1 M [n-Bu$_4$N]ClO$_4$ in EtOH.

[b]Region of electrode illuminated.

[c]Input power is from a 632.8 nm He-Ne laser. For power density multiply by 354 cm^{-2}.

[d]Quantum yield for electron flow at E_{redox}; this corresponds to the short-circuit quantum yield measured as the number of electrons passed per incident photon.

[e]Quantum yield for electron flow at the maximum power point.

[f]Maximum voltage is the open-circuit photopotential.

[g]Output voltage at the maximum power point.

[h]Efficiency for conversion of 632.8 nm light to electricity.

[i]Fill factor is the ratio $\dfrac{(\phi_{mp})(V @ \eta_{max})}{(\Phi_e)(Max. V)}$.

Figure 1. This photograph depicts a half-polished/half-textured sample of (100) Si. The left hand portion shows good specular reflection of the ruled object (0.5 mm/div) for the polished portion while the textured portion shows no specular reflection. The three scanning electron micrographs show the polished (top) partially textured (middle) and fully textured (bottom) regions of the (100) Si sample at the same magnification.

Figure 2. Scanning electron micrographs showing representative results from chemical etching of four different samples of (100) Si according to the procedure given in the Experimental. The magnification is the same in each case.
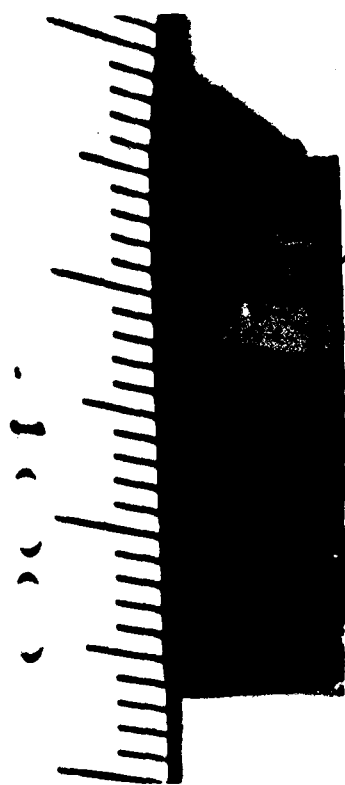
polished
100 silicon
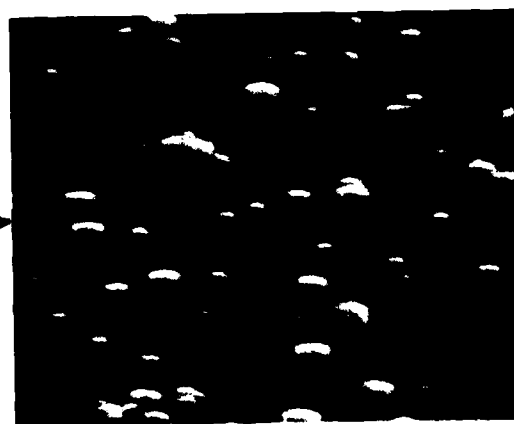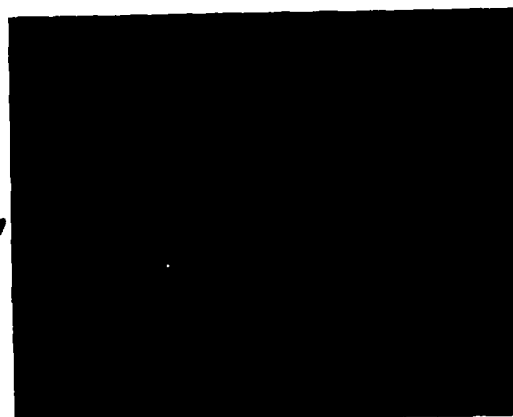
textured
100 silicon

1 µm

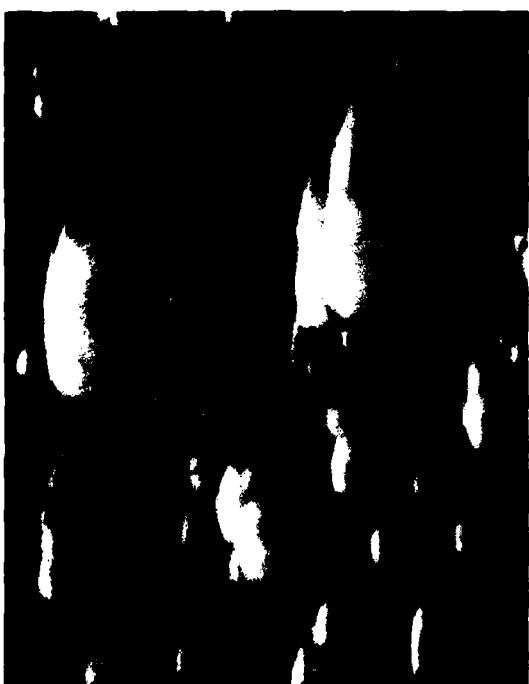Figure 3. Auger spectra of (a) pretreated, polished (100) Si;

(b) polished (100) Si derivatized with (1,1'-ferrocenediyl)-

dichlorosilane at 7.4×10^{-10} mol/cm^2; (sample #8 in Table I);

(c) pretreated Pt derivatized with (1,1'-ferrocenediyl)-

dichlorosilane at 1.8×10^{-9} mol/cm^2; and (d) product from

hydrolysis of (1,1'-ferrocenediyl)dichlorosilane pressed

into In.
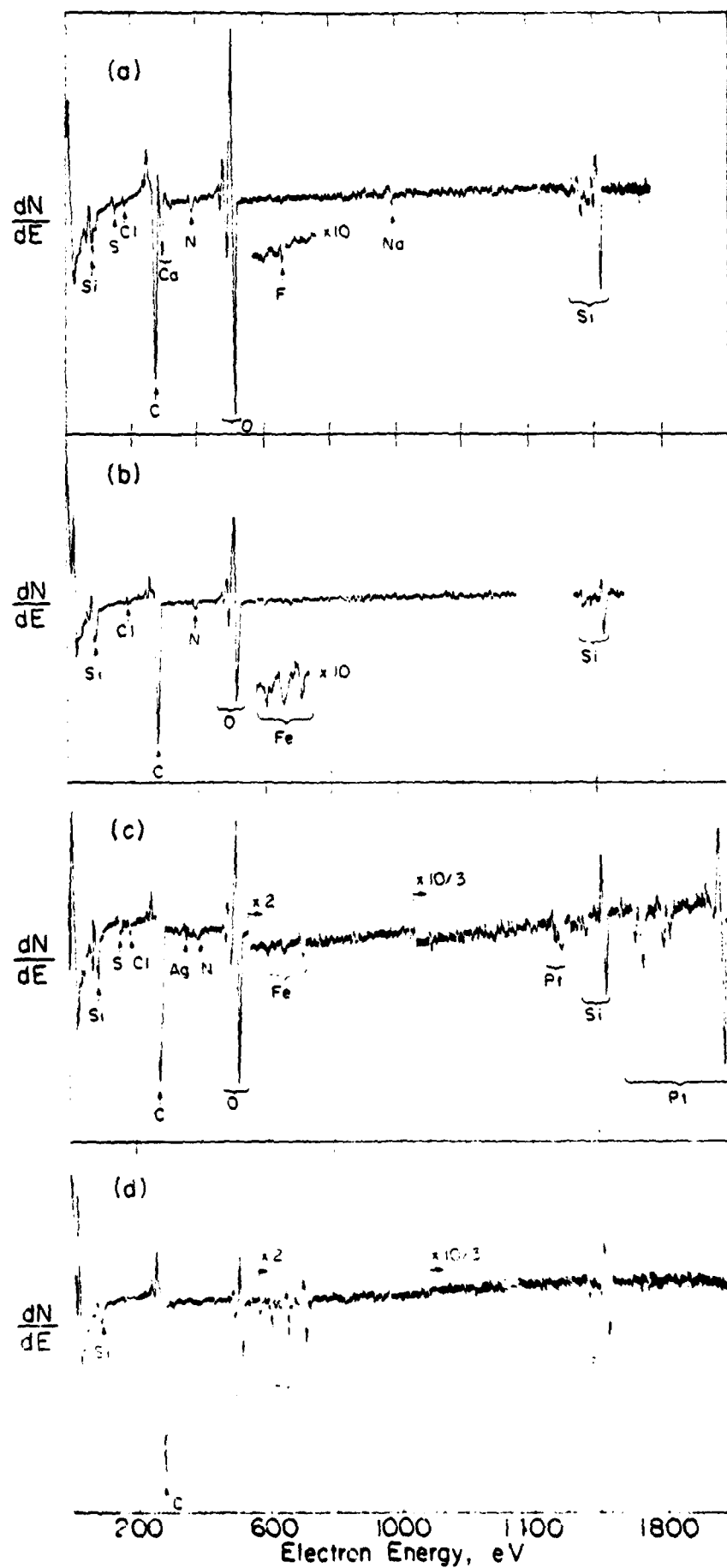
<u>Figure 4.</u> Cyclic voltammograms (100 mV/sec) for n-type Si surfaces

derivatized with (1,1'-ferrocenediyl)dimethylsilane under 632.8 nm

illumination ($\sim$50 mW/cm^2) in 0.1 $\underline{M}$ [$\underline{n}$-Bu$_4$N]ClO$_4$/EtOH electrolyte

solution: (a) polished (111) Si, sample #9 in Table I and

Table II; (b) polished (100) Si, sample #12 in Table I and

Table II; and (c) textured (100) Si, sample #20 in Table I .   -

Current, μA/cm²

Potential, V vs. SCE
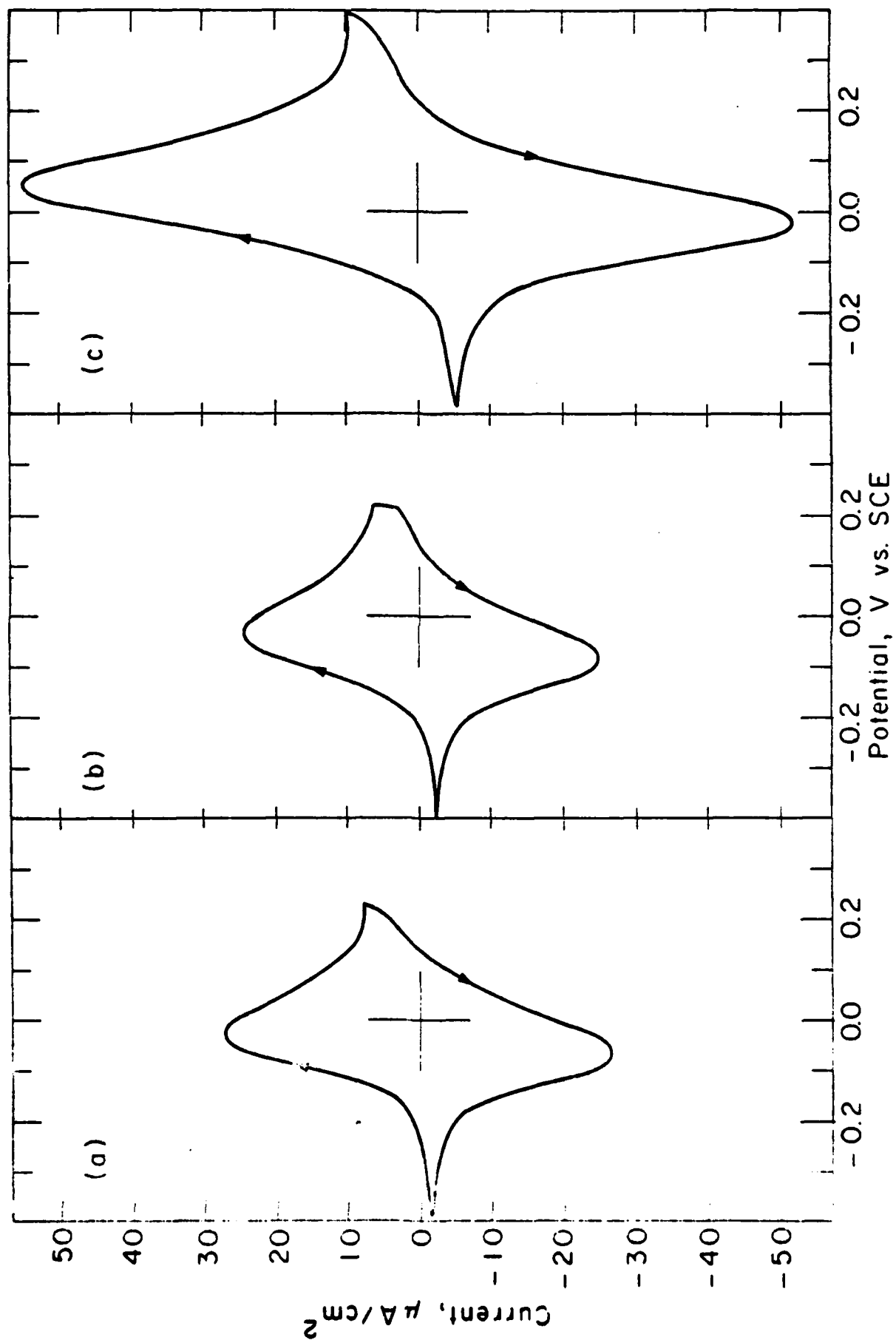
Figure 5. Steady state current-voltage curves for half-polished/half-textured n-type (100) Si photoelectrode in stirred EtOH solution of 5×10^{-2} $\underline{M}$ $Fe(\eta^5-C_5H_5)_2$, 1.5×10^{-3} $\underline{M}$ $Fe(\eta^5-C_5H_5)_2PF_6$, and 0.1 $\underline{M}$ $[\underline{n}-Bu_4N]ClO_4$, E_{redox} = +0.34 V vs. SCE. Irradiation with 632.8 nm light at the indicated power. The area illuminated in all cases was 2.8×10^{-3} cm^2. "Polished" and "textured" refer to the portion of the electrode that was actually illuminated.
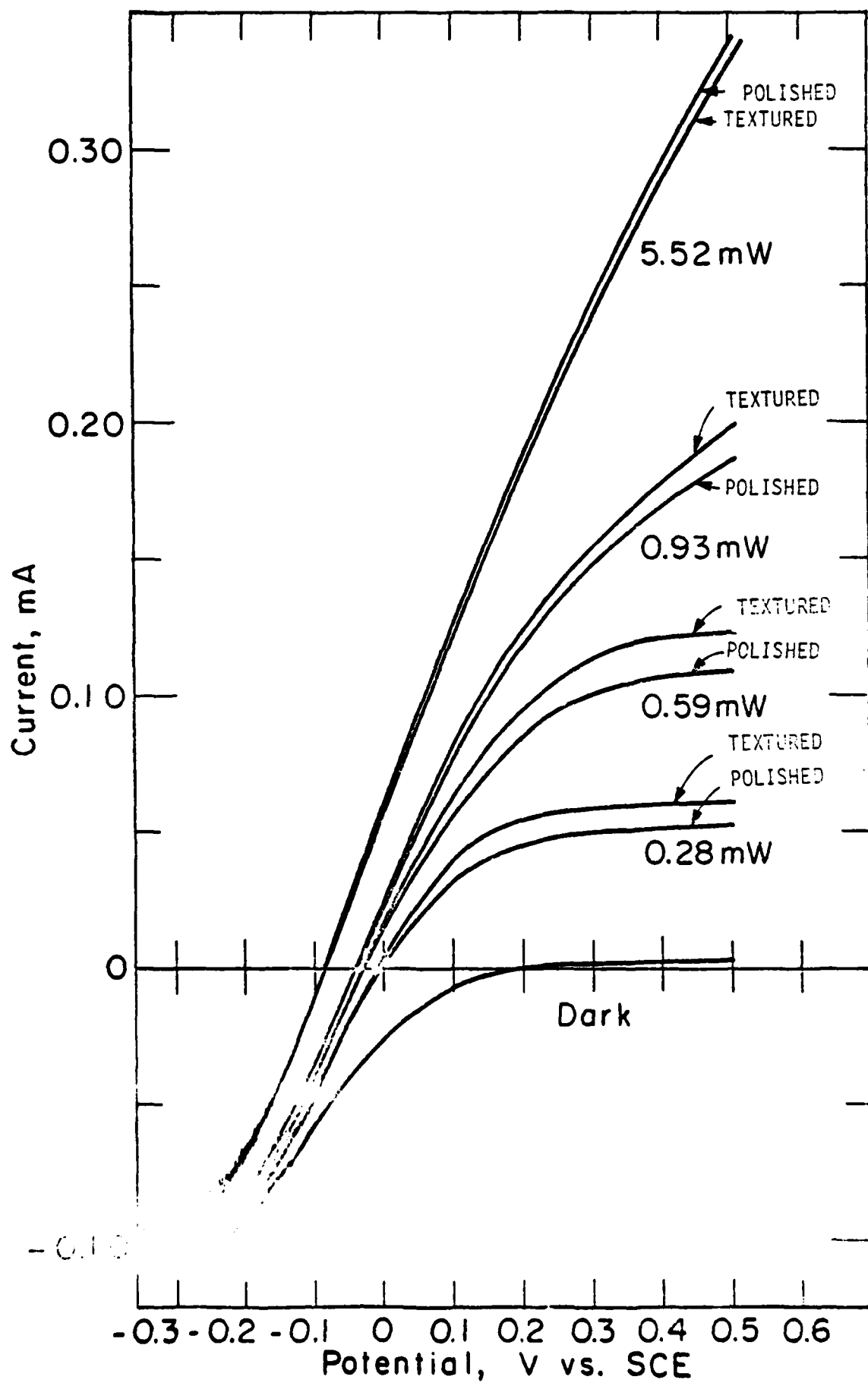
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