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"In Situ Characterization of the Illuminated Silicon/ Electrolyte Interface by Fourier Transform Infrared Spectroscopy

by

L. M. Peter, D. Blackwood, and S. Pons

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Department of Chemistry
University of Utah
Salt Lake City, UT 84112

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Henry Eyring Building
Salt Lake City, UT 84112

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22a. NAME OF RESPONSIBLE INDIVIDUAL
Stanley Pons

22b. TELEPHONE *(Include Area Code)*
(801)581-4760

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ABSTRACT

[illegible] Silicon [illegible] Fluoride

The illuminated n-Si/aqueous NH_4F interface has been studied by attenuated reflectance infrared spectroscopy under conditions in which photoetching occurs. An anomalously strong Si-H stretch band was observed to develop in the region of 2100/cm when the silicon was illuminated. The intensity of the band was found to increase linearly with time under steady illumination, rapidly exceeding values corresponding to monolayer hydrogen coverage. The absorbance decayed slowly in the dark. The results indicate that the etching process involves a Si(II) intermediate which can disproportionate to form a hydrogenated amorphous silicon overlayer which builds up progressively as photoetching proceeds.

[illegible]

Semiconductors.

IN-SITU CHARACTERIZATION OF THE ILLUMINATED SILICON/ELECTROLYTE INTERFACE BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

Laurence M. Peter
University of Southampton
Southampton SO9 5NH
ENGLAND

Daniel. J. Blackwood and Stanley Pons*
Department of Chemistry
University of Utah
Salt Lake City, UT 84112
USA

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*To whom correspondence should be addressed.

In-situ spectroscopic measurements have made important contributions to our understanding of the solid/solution interface. The application of electrochemically modulated infrared spectroscopy has been particularly rewarding in the case of the metal/electrolyte interface ~~(1-4)~~, but there have been surprisingly few attempts to extend the method to the semiconductor/ electrolyte interface ~~(5-8)~~. Palik and Holm (5) showed that electric field modulation of the internal reflection response of the Si-electrolyte interface gives information about free carriers, interface states and molecular species at the interface, and this approach has been refined by Rao and co-workers ~~(6,7)~~, who have studied the n-Si/acetonitrile surface and identified bands due to surface bound hydrogen species.

Electrochemical modulation of the infrared absorbance of the semiconductor solution interface is usually achieved by stepping the potential between two values, which can either lead to changes in surface coverage of absorbing species or to the perturbation of vibrational absorption bands by the electric field. We have taken a ~~different~~ approach which exploits the fact that in the case of a semiconductor the surface density of minority carriers can be perturbed at constant potential by illumination. In this way it should be possible to modulate the rate of the surface reactions involved in photoetching and hence to detect the vibrational spectra of intermediate species. This powerful new approach has been applied for the first time to examine the photoetching of silicon in aqueous ammonium fluoride solutions since this reaction is of considerable theoretical and practical significance.

Measurements were made using a 3 mm thick 5 cm long silicon plate mounted in a total attenuated reflectance configuration in an Bruker/IBM model IR/98 Fourier transform spectrometer. The spectral resolution was either 8 or 2 cm^{-1}. The silicon was n-type with a donor density of about 10^{15} cm^{-3}, and was cut to expose the 110 surface. The optical geometry resulted in five reflections of the infrared beam at the surface exposed to the electrolyte. The front surface of the plate was in contact with a solution of ammonium fluoride contained in a

PTFE cell equipped with a platinum counter electrode and a saturated calomel reference electrode. Ohmic contacts to the silicon plate were made with indium-tin solder. The electrode was illuminated with a 50 Watt tungsten halogen lamp controlled by a stabilized dc power supply, and the incident light passed through a PTFE plate to ensure diffuse and uniform illumination of the electrode. The electrode potential was controlled by a potentiostat, which also registered the photocurrent.

Subtractively normalized difference spectra were obtained at constant potential by collecting 64 scans in the dark followed by 64 scans either during illumination or following a defined period of illumination. The output power of the lamp was controlled to give the desired photocurrent in the range 0.05 - 1 mA cm^{-2}.

Figure 1 shows the photocurrent-voltage curve obtained when the silicon plate was illuminated. The well formed saturation photocurrent regime indicates that the rate of surface reaction is controlled by the hole flux so that photoetching is expected to proceed at a constant rate. The photocurrent was found to be stable over long periods for NH_4F concentrations in the range 0.05 - 0.5 mol dm^{-3} and pH values between 3.5 and 5.6. Passivation of the silicon (9) was only observed at low fluoride concentrations when the photocurrent exceeded about 1 mA cm^{-2}.

Initial experiments in which spectra were recorded during illumination of the silicon in the saturation photocurrent region resulted in the appearance of a band at 2100 cm^{-1} which was identified as due to Si-H stretch (10). The experimental procedure was then changed so that spectra were recorded immediately after a period of illumination in order to find out whether a stable or transient species was involved. The results showed that the decay of the Si-H band in the dark occurred over a timescale of several minutes, and the band intensity was unaffected when the solution was stirred. It is clear from these observations that a relatively stable surface species is involved.

The existence of surface bound hydrogen on HF etched silicon has been established by Yablanovitch et al (11), who observed unusually low surface recombination velocities on HF treated Si and Ge. Initially we concluded that a similar surface species was formed by photoetching in fluoride solutions, but further experiments led to the surprising conclusion that the intensity of the Si-H band increased linearly with illumination time with no sign of the saturation expected for monolayer coverage. Figure 2 illustrates the intense band recorded after illuminating for 60 seconds at a photocurrent density of 0.5 mA cm^{-2}, and Figure 3 demonstrates the linear dependence of the peak height on illumination time. The position and half width of the absorbance band still correspond closely to those reported by Yablanovitch et al for HF etched silicon, but the integrated absorbance is much larger. The maximum intensity of the absorption band that could be achieved was found to be limited only by the surface roughening of the silicon surface which occurred after prolonged illumination.

Figure 4 shows that the absorbance was also found to be an approximately linear function of the photocurrent when the silicon was illuminated for a fixed period at different intensities, and it appears that the intensity of the Si-H stretch band is proportional to the total charge passed.

The stability of the photogenerated Si-H was investigated by collecting spectra at intervals after illuminating the silicon for 60 seconds. Figure 5 shows the decay of the band intensity which was observed and Figure 6 shows that the absorbance fell to half of its original value in about 300 seconds.

The number of Si-H oscillators was estimated from the integrated absorbance using an absorption cross section of 5×10^{-20} cm^2 calculated from the absorption strengths for silanes given by Brodsky et al (10). The maximum absorbance observed experimentally was found to correspond to about 40 monolayers of hydrogen. A calculation based on the absorption spectrum given by Yablanovitch et al yielded a similar value of the coverage. Such high values of coverage are implausible, even if surface roughening is taken into account, and it is clear that the Si-H species cannot be located at the surface of the silicon. At the same time, the half width (60 cm^{-1}) of the Si-H band is considerably larger than the values measured by Chabal (12) for hydrogen and water adsorption on vicinal Si (100) 2x1 surfaces, suggesting that a different explanation of the band is required.

These observations led us to consider the possibility that the photoetching of silicon in fluoride solutions results in the formation of an amorphous silicon overlayer. Whilst there is evidence that such a layer is formed by the chemical or electrochemical dissolution of silicon in concentrated HF, it has been reported that no such film is formed at low HF concentrations (13). The vibrational spectra of Si-H species in hydrogenated amorphous silicon have been widely studied by infrared (10) and high resolution electron energy loss spectroscopy(14). The Si-H stretch band is located between 2080 and 2120 cm^{-1}, and typical half widths are consistent with those observed in the photoetching experiment. The integrated absorption strength of the bands in amorphous Si has been used by Brodsky et al (10) to calculate the hydrogen content of the material. The calculation uses the Maxwell Garnett local effective medium theory to account for the local field in the solid, and when applied to our data it gives an equivalent density of Si-H oscillators of 7×10^{17} cm^{-2}, in good agreement with the value estimated directly by comparing the integrated absorption with the results of Yablanovitch et al.

The infrared absorption of stain films on silicon has been investigated by Beckmann (15), who concluded that etching in HNO_3/HF mixtures gave films with a composition between H_2SiO and $HSiO_{1.5}$. Beckmann estimated that these films contained as many as 4×10^{18} Si-H groups cm^{-2}, and it seems likely that the mechanism of formation of these films is the same as that operating under photoetching conditions. If we assume that the hydrogen content of our surface films is around 20%, the maximum thickness of the amorphous silicon layers produced in our experiments would be of the order of 50 nm.

The slow buildup of an amorphous silicon overlayer during photoetching probably results from a disproportionation reaction involving a soluble Si(II) species. There is good evidence that divalent silicon species and hydrogen are produced by the electrochemical etching of silicon in fluoride solutions at low current densities (13). It is also known that the quantum yield for photodissolution exceeds 2 (16), so that hole capture must be followed by electron injection. We therefore postulate the following reaction sequence

$$Si + h + HF + 2\,F^- \longrightarrow SiHF_3 + e$$

$$2\,SiHF_3 \longrightarrow Si + H_2SiF_6$$

This reaction will compete with

$$SiHF_3 + 3\,HF \longrightarrow H_2SiF_6 + H_2$$

leading to the incorporation of hydrogen in the amorphous silicon layer.

It is clear that the overlayer does not hinder the photodissolution process, which is limited by the supply of photogenerated holes to the surface. It should be possible to detect the transient SiHF3 intermediate and further infrared measurements with higher time resolution are planned.

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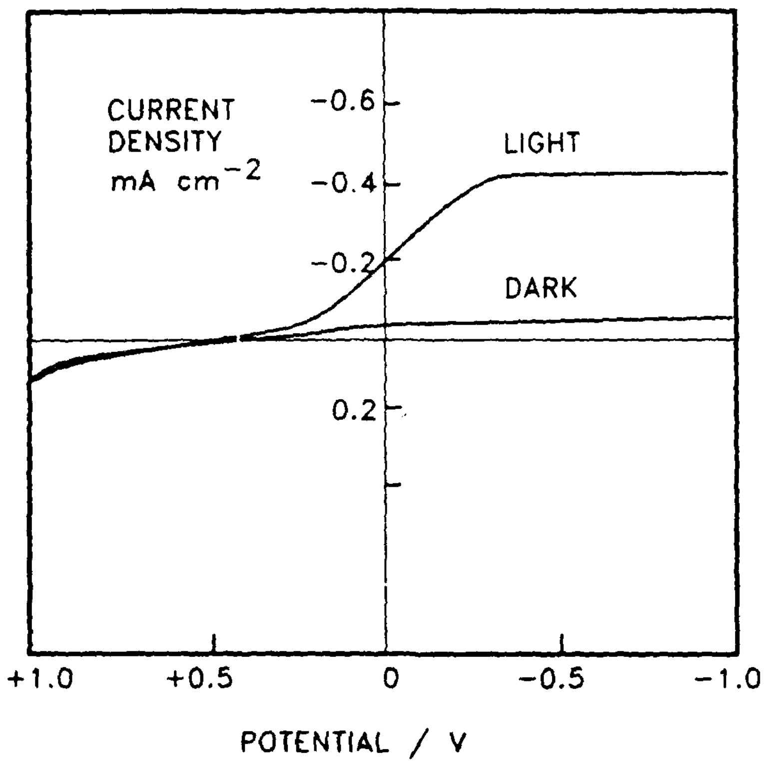
FIGURE LEGENDS

Figure 1	Photocurrent-voltage curves for the silicon sample in 0.5 mol dm^{-3} NH_4F at pH 4.5 under illumination and in the dark.
Figure 2	Infrared difference spectra obtained by ratioing the spectra obtained immediately after 60 seconds of illumination at a photocurrent density of 0.5 mA cm^{-2} to that obtained before illumination had occurred. Resolution = 2 cm^{-1}.
Figure 3	Plot of the height of band shown in Figure 2 against the time for which the silicon sample was illuminated.
Figure 4	Plot of the relative absorption at 2100 cm^{-1} against photocurrent density. Data taken from spectra obtain during 30 second illumination periods.
Figure 5	As Figure 2 with the addition of difference spectra obtained 180 and 360 seconds after the termination of the illumination. Resolution = 8 cm^{-1}.
Figure 6	Plot of the fraction of the initial absorbance remaining against the time since the termination of the illumination.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DENSITY
mA cm^{-2}
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-0.4
-0.2
0.2
LIGHT
DARK
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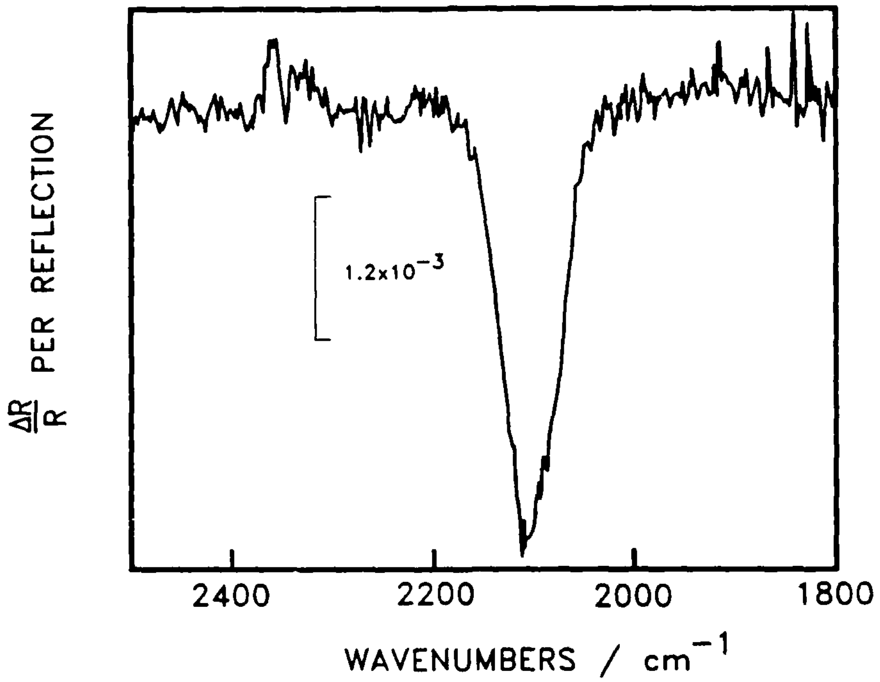
+0.5
0
-0.5
-1.0
POTENTIAL / V

Fig 1



$\frac{\Delta R}{R}$ PER REFLECTION
1.2×10^{-3}
2400
2200
2000
1800
WAVENUMBERS / cm^{-1}

Fig 2

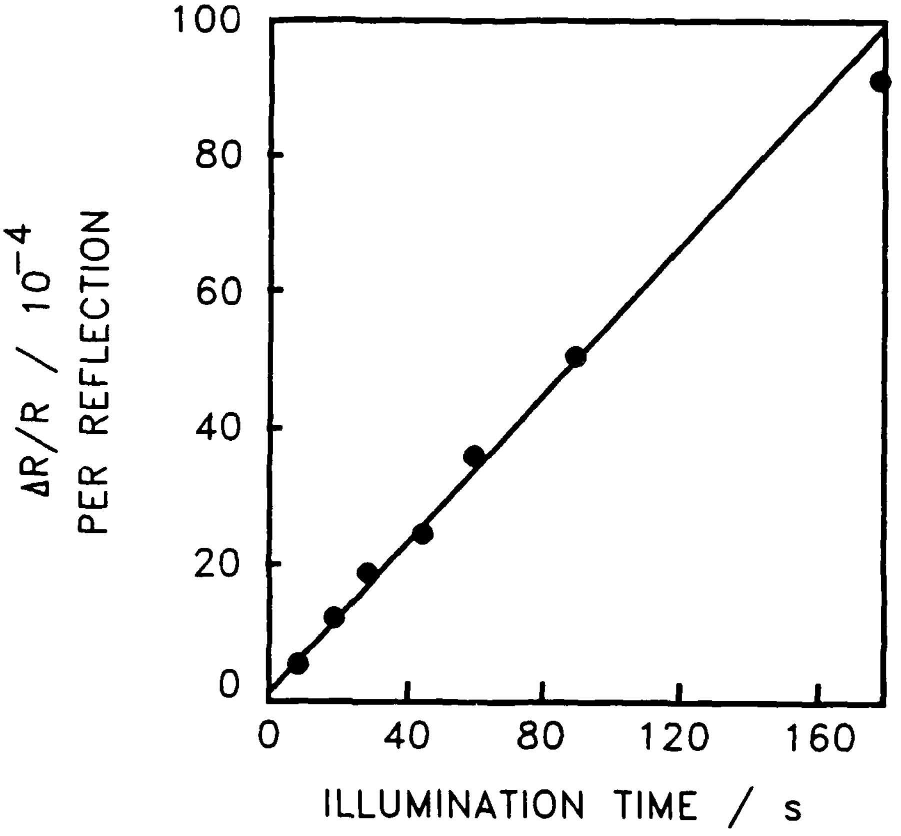
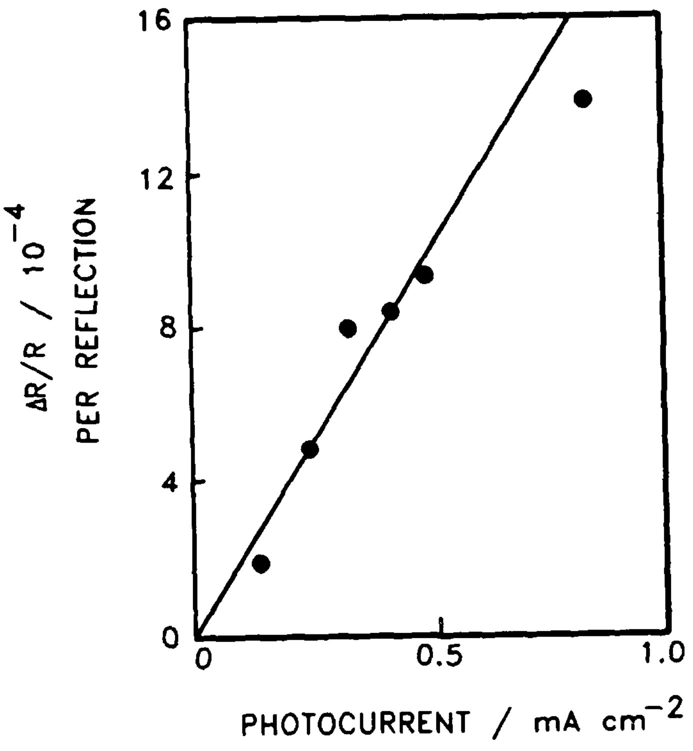

100
80
60
40
20
0
0
40
80
120
160
ΔR/R / 10^{-4}
PER REFLECTION
ILLUMINATION TIME / s

Fig3



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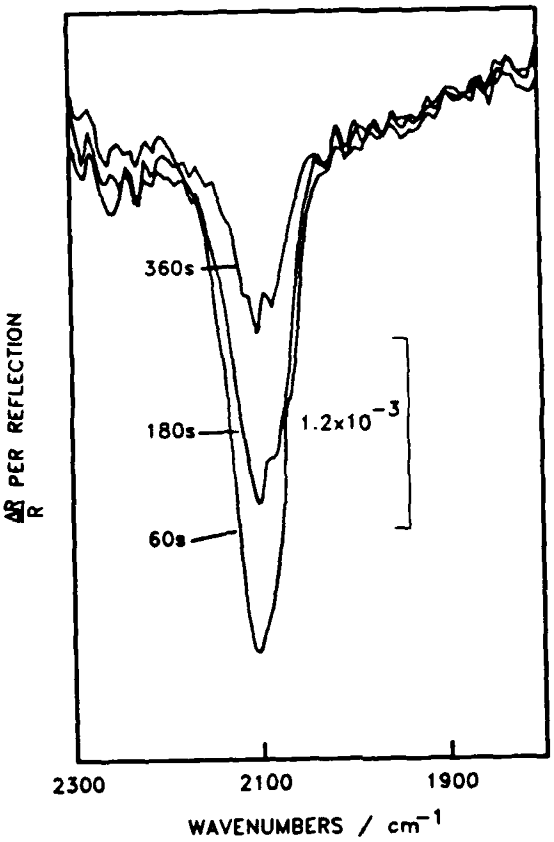
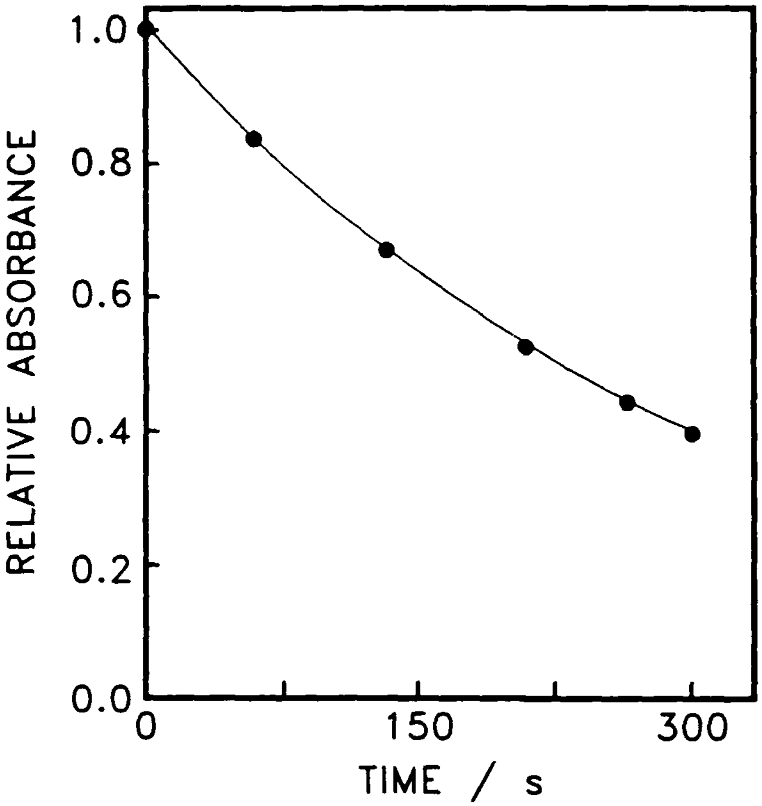


$\frac{\Delta R}{R}$ PER REFLECTION
360s
180s
60s
1.2×10^{-3}
2300
2100
1900
WAVENUMBERS / cm^{-1}

Fig 5



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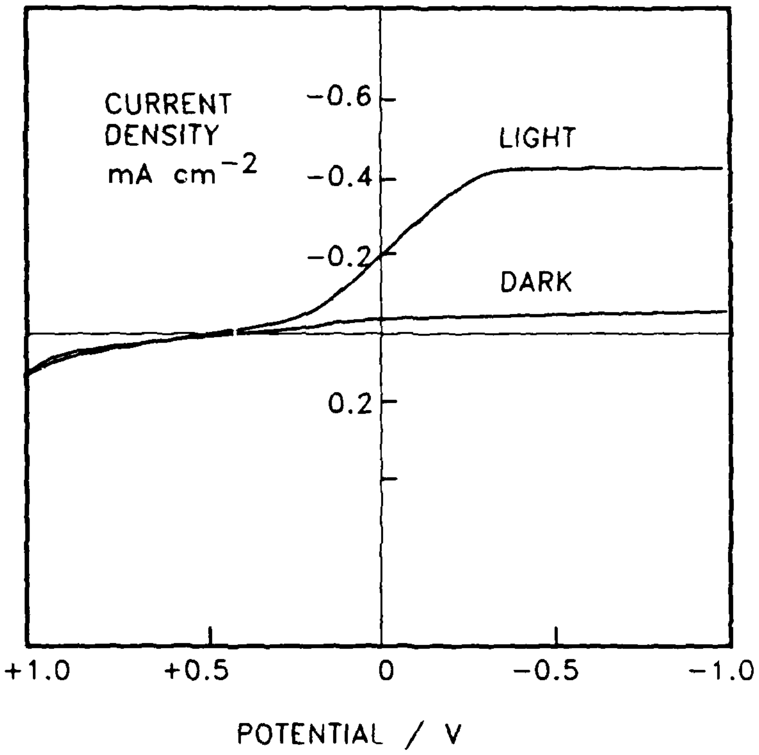
CURRENT
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mA cm^{-2}
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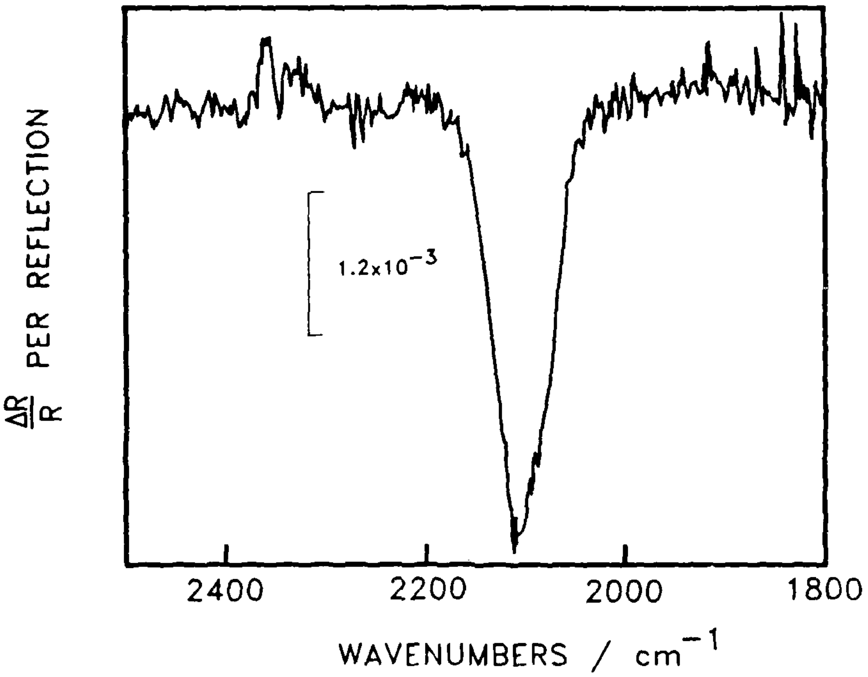
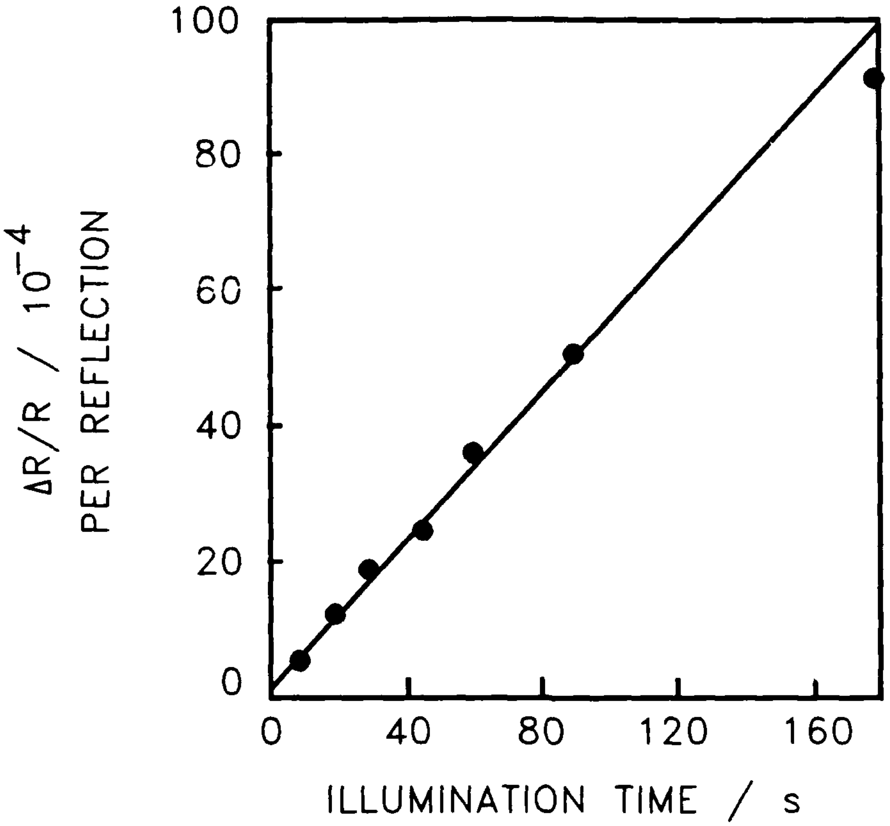
−0.4
−0.2
0.2
LIGHT
DARK
+1.0
+0.5
0
−0.5
−1.0
POTENTIAL / V

Fig 1



$\frac{\Delta R}{R}$ PER REFLECTION
1.2×10^{-3}
2400
2200
2000
1800
WAVENUMBERS / cm^{-1}

Fig 2


100
80
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20
0
0
40
80
120
160
ΔR/R / 10⁻⁴ PER REFLECTION
ILLUMINATION TIME / s

Fig3

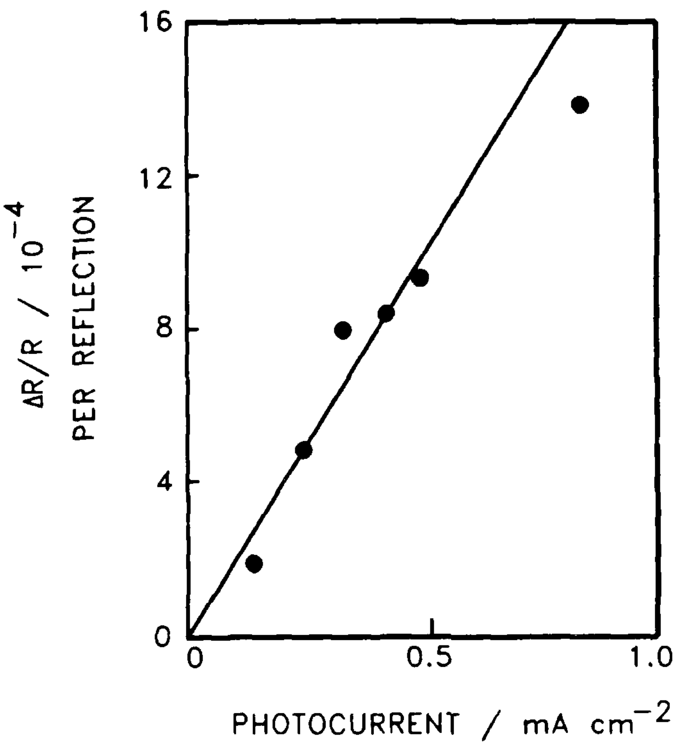
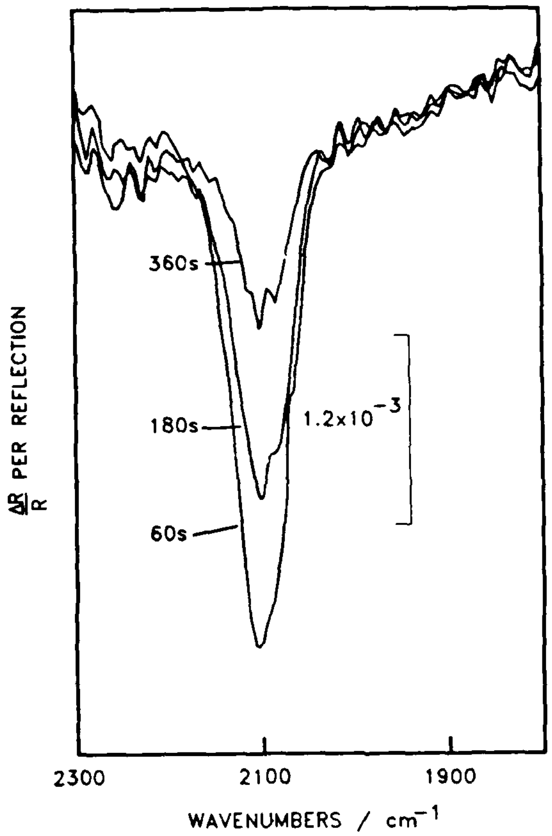


Fig 4



$\frac{\Delta R}{R}$ PER REFLECTION
360s
180s
60s
1.2×10^{-3}
2300
2100
1900
WAVENUMBERS / cm^{-1}

Fig 5

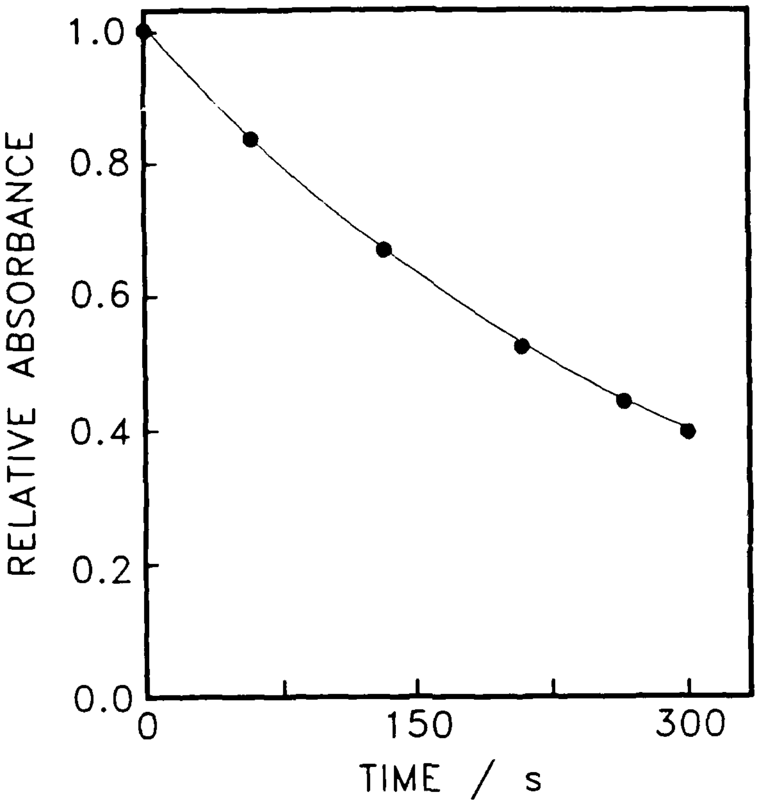


Fig 6

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Dr. Robert A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Douglas N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, UT 84602

~~Dr. Stanley Pons~~
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EIC Laboratory Inc.
111 Downey Street
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Dr. Joseph S. Foos
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Donald M. Schleich
Department of Chemistry
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 01

Dr. Stan Szpak
Code 633
Naval Ocean Systems Center
San Diego, CA 92152-5000

Dr. George Blomgren
Battery Products Division
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Dr. Ernest Yeager
Case Center for Electrochemical
Science
Case Western Reserve University
Cleveland, OH 44106

Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, CA 93555

Dr. Ashok V. Joshi
Ceramatec, Inc.
2425 South 900 West
Salt Lake City, Utah 84119

Dr. W. Anderson
Department of Electrical &
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SUNY - Buffalo
Amherst, Massachusetts 14260

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Dr. V. R. Koch
Covalent Associates
52 Dragon Court
Woburn, MA 01801

Dr. Randall B. Olsen
Chronos Research Laboratories, Inc.
4186 Sorrento Valley Blvd.
Suite H
San Diego, CA 92121

Dr. Alan Hooper
Applied Electrochemistry Centre
Harwell Laboratory
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Dr. John S. Wilkes
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Dr. Gary Bullard
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Ementech, Inc.
Route 5, Box 946
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Dr. Michael Binder
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Professor Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton, Hants, SO9 5NH UK