

AD-A134 663

A PHOTACOUSTIC STUDY OF CHEMICALLY ACTIVE SYSTEMS(U)
PRINCETON UNIV NJ APPLIED PHYSICS AND MATERIALS LAB
B S ROYCE SEP 83 APML-150983 ARO-16865.13-CH

1/1

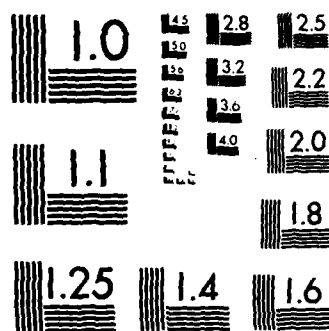
UNCLASSIFIED

DAGG29-80-C-0053

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ARO 16865.13-CH
(12)

AD-A134663

A Photoacoustic Study of Chemically Active Systems

FINAL REPORT APML 150983

Barrie S. H. Royce

September 1983

U.S. Army Research Office

Contract DAAG29-80-C0053

Materials Laboratory

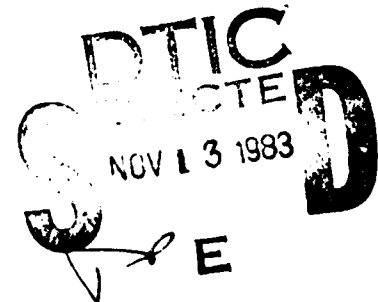
Department of Mechanical and Aerospace Engineering

Princeton University

Princeton, NJ 08544

Approved for Public Release

Distribution Unlimited



DTIC FILE COPY

83 11 07 038.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER APML 150983	2. GOVT ACCESSION NO. AD A1341663	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photoacoustic Study of Chemically Active Systems		5. TYPE OF REPORT & PERIOD COVERED Final
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Barrie S. H. Royce		8. CONTRACT OR GRANT NUMBER(s) DAAG29-80-C0053
9. PERFORMING ORGANIZATION NAME AND ADDRESS Applied Physics & Materials Laboratory School of Engineering & Applied Science Princeton University, Princeton, NJ 08544		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE September 1983
		13. NUMBER OF PAGES 22 pages
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photoacoustic, Spectroscopy, Photothermal Deflection, Mirage Effect, Fourier Transform Infrared, Catalytic Surfaces, Polymeric Cure, Electrochemical Interfaces.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → The method of gas-microphone photoacoustic spectroscopy and the related photothermal deflection spectroscopy have been developed for application to chemically active systems. Fourier Transform Infrared Photoacoustic Spectroscopy has been used to study surface reactions on zeolites and photopolymerization reactions in acrylates. In both cases the chemical reactions were initiated in the photoacoustic cell and followed in situ. The catalytic studies were carried out in a cell with a high temperature capability of 400°C		

20. ABSTRACT CONTINUED

and cell design permitted gas flows through the cell during data acquisition. The photopolymerization experiments were conducted at room temperature but employed control of the gas phase above the sample to evaluate the effects of oxygen radicals on surface photopolymerization.

Photothermal deflection spectroscopy has been applied to the study of electrode electrolyte interfaces during electrochemical or photoelectrochemical reactions. Surface spectroscopic studies made in situ have enabled corrosion processes to be followed and an extension of the technique using concentration gradient produced signals has permitted charge transfer to electrolyte ions and electrode dissolution processes to be followed.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Institution/	
Availability Codes	
Dist	Special
A-1	



TABLE OF CONTENTS

	<u>Page</u>
Title Page	i
Report Documentation Page	ii
Table of Contents	iv
Photoacoustic Studies of Chemically Active Systems	1
Fourier Transform Infrared Photoacoustic Spectroscopy	2
The Mirage Effect Probe for the in situ Study of Electrochemical Interfaces	6
References	19
Publications Resulting from the Contract	21
Participating Scientific Research Personnel	22

PHOTOACOUSTIC STUDIES OF CHEMICALLY ACTIVE SYSTEMS

Research on DAAG29-80-C0053 has been concerned with the application of Photoacoustic spectroscopy and the related Mirage Effect method to the study of systems in which reactions are taking place. The major experimental achievements of the research program include:

- i) The extension of the gas-microphone photoacoustic technique to the infrared spectral region between 4000 and 400 cm^{-1} using Fourier Transform Spectroscopic methods.
- ii) In situ studies of photopolymerization reactions in acrylic polymers and the influence of oxygen on these reactions using FTIR Photoacoustic methods.
- iii) Studies of Zeolite catalysts at atmospheric pressure and temperatures up to 400°C using a high temperature photoacoustic cell in conjunction with the FTIR spectrometer.
- iv) The development of Photothermal deflection spectroscopy to study photo-corrosion reactions taking place at electrode-electrolyte interfaces. These are also in situ measurements and involve highly light scattering polycrystalline samples as well as single crystals.
- v) The extension of the Photothermal method to the detection of refractive index gradients produced by electrode-electrolyte interactions. These include charge transfer to electrolyte redox species as well as the electrode dissolution reactions.

The following sections contain a brief review of each of these areas. The section dealing with the Mirage Effect is more extended since the results of these studies have only just started to appear in the archival journals. References to all published work are given.

Fourier Transform Infrared Photoacoustic Spectroscopy

The extension of the photoacoustic method into the spectral region between 4000 and 400 cm^{-1} has permitted this bond specific optical range to be probed for realistic catalyst surfaces and for chemically reacting systems such as acrylate polymers during photopolymerization. Dispersive techniques [1] were first employed in this interesting spectral range, however, the detector noise limited response of the photoacoustic method soon indicated the advantages of applying Fourier Transform techniques with a photoacoustic detector. Rockley [2], Vidrine [3], and Royce et al [4] developed this technique using commercial FTIR spectrometers. The Princeton group's initial measurements were made with a Nicolet spectrometer, however, later measurements were conducted with a Bomem FTIR spectrometer obtained through an NSF Equipment Grant [5]. Experience with the Nicolet indicated the importance of variable and slow mirror speeds and the need to acoustically isolate the interferometer from room vibrations. The Bomem spectrometer has computer controlled mirror speeds that provide lower mirror velocities than those available with other spectrometers. In order to minimize effects on the PAS measurements due to room vibrations the interferometer has been mounted on a massive marble table supported on Newport pneumatic laser table feet. The vibration isolation provided by this configuration has improved the signal to noise ratio by more than an order of magnitude over the unmodified configuration of the spectrometer. The photoacoustic cells used in the research were developed at Princeton. One is a non-resonant cell for use in room temperature measurements and the other, which can operate with sample temperatures up to 400°C, is of a Helmholtz resonance design but with a broad resonance peak. B+K microphones closely

coupled to acoustically isolated preamplifiers are used as signal detectors in both cases. A PAR 113 low noise amplifier is used for signal adjustment prior to its return to the FTIR A to D converter, signal levels being controlled to achieve maximum utilization of the digital range of the converter. A schematic diagram of the FTIR-PAS data acquisition path is shown in Figure 1.

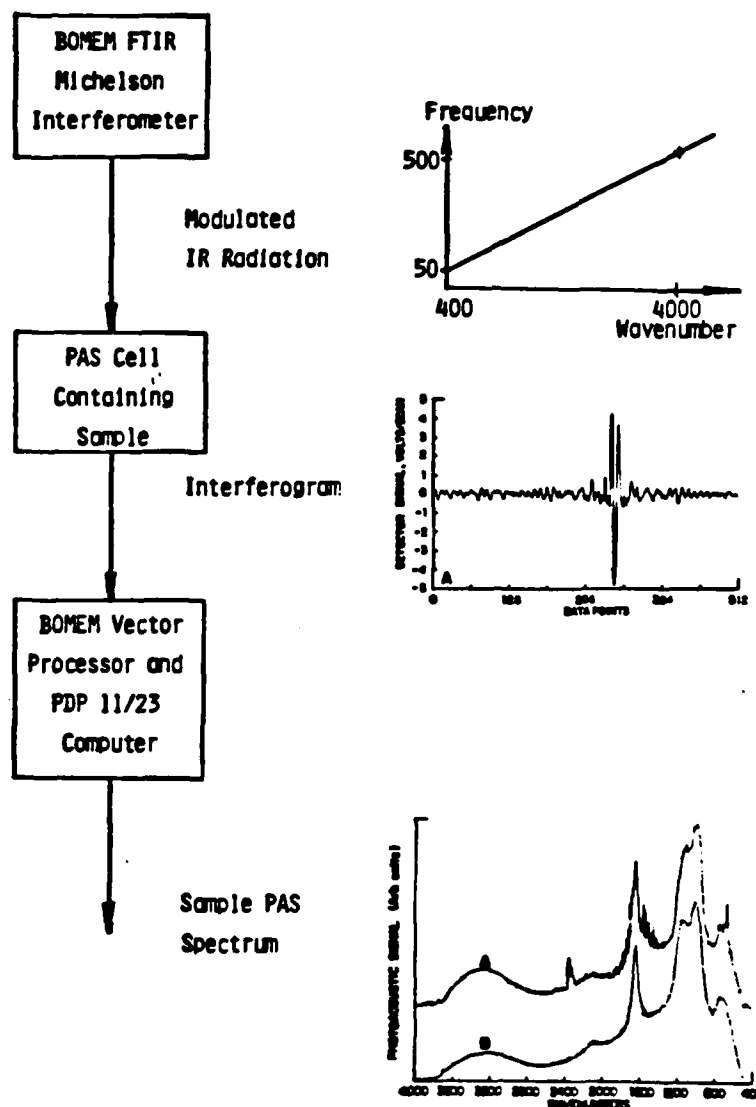


Figure 1.

Laufer et al [6] using this equipment provided an early demonstration of the advantages of the FTIR PAS approach for the elimination of dispersion induced artifacts in the IR absorption spectrum of powdered materials. Whereas the incorporation of such powders in mulls or other matrix materials may induce anomalous transmission due to the Christensen effect [7] the photoacoustic method which does not require sample encapsulation in this manner avoids these problems and provides unambiguous information about the location of spectral lines. Recently McClelland et al [8] have exploited this observation and have successfully applied FTIR PAS methods to obtain high quality spectra of coal free from this type of artifact.

Because of the wave number dependent modulation frequency associated with the FTIR PAS technique care must be taken in normalizing spectral data to account for both the intensity distribution of the spectrometer light source and the wave number dependence of the thermal diffusion length in the sample. Teng and Royce [9] extended their earlier absolute optical absorption coefficient measurements [10] using the photoacoustic method to this situation and demonstrated that measurements of the spectra made at different interferometer mirror velocities (and hence modulation frequency ranges) could be used to obtain quantitative spectral data over a wide spectral range.

The environment of the photoacoustic cell sample compartment can be controlled and used as an active participant in an in situ experiment rather than just a passive pressure transducer. Royce et al [11] exploited this fact to study the oxygen inhibition of photopolymerization in acrylic materials. The oxygen partial pressure in the photoacoustic cell was controlled and the UV induced photopolymerization of the Acrylate based material

was studied using the FTIR-PAS spectrum to follow the decrease in the number of C=C bonds by monitoring the CH bending vibration at 1407 cm^{-1} due to the CH_2 chromophore of the acrylate group. In order to compensate for any spectral changes produced in the PAS data by changed thermal parameters the nearby peak at 1509 cm^{-1} associated with the aromatic rings of the unchanged Bis-phenol A backbone molecule was used as an internal normalization standard. The effects of oxygen inhibition were clearly revealed by this data which is of technological importance since it applies to the surface condition of the curing sample.

It is highly desirable to be able to obtain spectroscopic data about the surfaces of real catalysts, such as zeolites or metals supported on silica, under conditions that approximate those of reactions of interest. Preliminary room temperature measurements by Royce et al [11,12] indicated that the FTIR-PAS method that they had developed was satisfactory for observing surface adsorbates on zeolites and chemical modifications produced on cab-o-sil surfaces when OH groups were chemically replaced by CH_3 groups. These results indicated the desirability of developing a cell that could operate at 400°C and in which in situ surface reactions could be followed. Such a cell was developed in conjunction with Benziger and McGovern of Princeton's Chemical Engineering department and is being used to study methanol reactions over zeolites [13].

The Mirage Effect Probe for the in situ Study of Electrochemical Interfaces

An important new spectroscopic and near interface electrochemical probe for the study of electrode-electrolyte interactions has been developed. The technique, the Mirage Effect, uses the deflection of a focused laser beam passing tangentially to the interface to provide both spectroscopic information about the sample surface and about interfacial reactions through their effect on the electrolyte. In this section the basic concepts of this method are briefly outlined and preliminary results of its application to some semiconducting samples are reviewed.

In the approximation of ray optics [14] a beam of light passing through a region of space containing refractive index inhomogeneities is expected to be deflected through some angle ϕ as indicated on the diagram below.

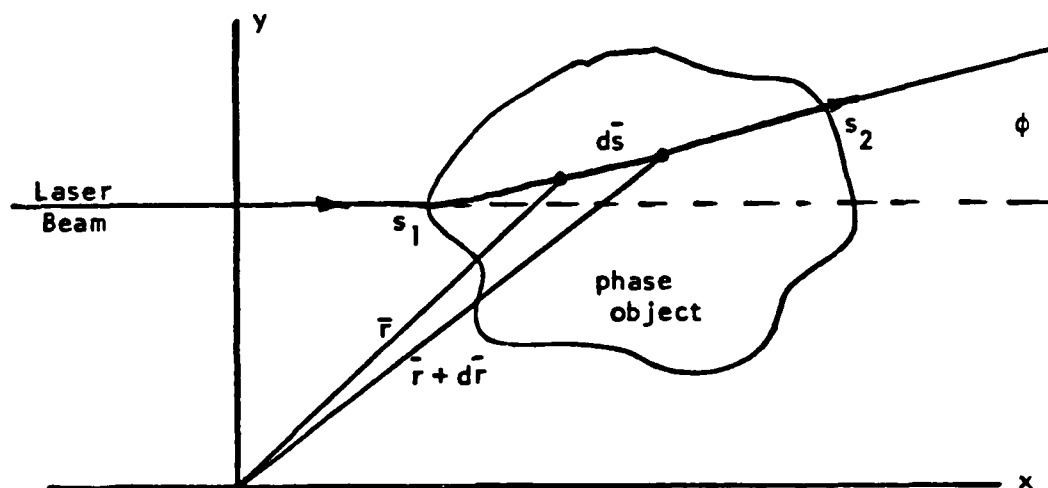


Figure 2. Beam deflection by a refractive index inhomogeneity.

Using the notation of the figure, with s the distance along the ray of light and $n(x,y,z)$ the refractive index at a point a distance $\vec{r}(x,y,z)$ from the

origin of the coordinate system, the beam path is described by the ray equation:

$$\frac{d}{ds} \left(n \frac{d\vec{r}}{ds} \right) = \nabla n$$

and the beam deflection is then given by:

$$\phi = A \int_{s_1}^{s_2} \left(\frac{\partial n}{\partial y} \right) \cdot ds \approx A \int_{x_1}^{x_2} \left(\frac{\partial n}{\partial y} \right) dx$$

for a paraxial ray for which ϕ is small.

For application to an electrochemical interface the beam considered is a focused Helium/Neon laser beam with a beam waist approximately 40 microns in diameter over a length of about 3 mm. This beam passes tangentially, across an electrode surface at a distance of 50 to 200 microns from the interface and the "phase object" is a refractive index profile that results from processes occurring in the solid electrode, at its surface or in the electrolyte with which it is in contact. These processes can frequently be treated in a one dimensional approximation and are associated with heat transfer occurring between the electrode and the electrolyte or a species concentration gradient in the electrolyte due to the electrochemical reactions occurring at the electrode. For these two cases:

$$\left(\frac{dn}{dy} \right) = \left(\frac{dn}{dT} \right) \cdot \left(\frac{dT}{dy} \right) \quad \text{or} \quad \left(\frac{dn}{dy} \right) = \left(\frac{dn}{dc} \right) \cdot \left(\frac{dc}{dy} \right)$$

The quantities (dn/dT) and (dn/dc) are properties of the electrolyte and the species involved, and can be separately measured, whereas (dT/dy) and (dc/dy) are related to the spectroscopic or electrochemical processes that are of interest. For an aqueous electrolyte (dn/dT) has a value of about 10^{-4} K^{-1} and (dn/dc) a value of about 10^{-2} per mole.

The use of the laser beam deflection method for highly sensitive spectroscopy is a development of photoacoustic spectroscopy and has a sound experimental and theoretical basis provided by the papers of Fournier et al [15], Murphy and Aamodt [16] and by Jackson et al [17]. Its application to electrochemical systems was first reported by Royce and coworkers [18,19,20] who realized that the configuration required for this spectroscopic method was directly compatible with that associated with in situ photoelectrochemical studies and did not require the thin electrodes needed for rear surface photoacoustic detection using gas microphones. More recently Roger et al [21] have used laser illumination and polarization modulation for similar in situ studies of electrode-electrolyte interfaces and have reported sub-monolayer detection sensitivity.

In the spectroscopic use of the method the sample to be investigated is the working electrode and is contained in a glass electrochemical cell having windows which permit the photochemical and probe radiation to be normally incident on the sample and the measuring laser beam to pass tangentially across the illuminated surface. A platinized platinum gauze and a saturated calomel reference electrode are also provided to form a standard three electrode electrochemical cell. The experimental configuration employed is shown in the following figure. When used in this mode, the laser probe beam responds to the temperature gradient generated at the interface due to the absorption of radiation by the electrode or the surface species. The incident spectroscopic radiation is modulated at approximately 50 Hz. The surface temperature of the sample fluctuates at the same frequency with an amplitude of circa 10^{-3} K due to non-radiative de-excitation processes which accompany the absorption of the radiation. This causes a

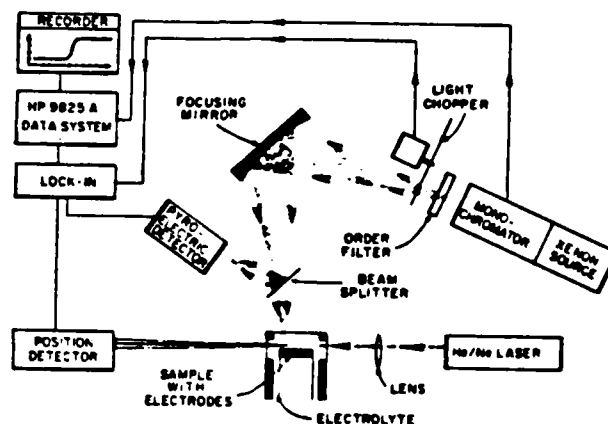
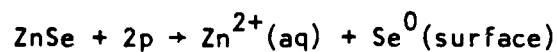


Figure 3. Schematic diagram of the photoelectrochemical Mirage Effect apparatus.

periodic deflection of the laser beam which can be detected using a sensitive position detector and a lock-in amplifier. The amplitude of the periodic beam deflection is directly proportional to the optical absorption coefficient of the sample, provided the film thickness or the bulk thermal diffusion length in the solid are short compared to the optical absorption depth of the spectroscopic radiation. Spectroscopic data may therefore be obtained by measuring the beam deflection amplitude as a function of the incident wavelength and normalizing it by the incident light intensity measured using the pyroelectric detector.

The method was first applied in this laboratory to study the photocorrosion [18,19] of the well understood ZnSe system [22,23] in electrolytes of controlled pH. Photoelectrochemical corrosion resulted from the reaction with photogenerated holes, viz:



and the growth of the selenium surface films was studied optically in situ.

Subsequent Auger measurements confirmed the interpretation of the spectroscopic data, showing a strong Se peak and the absence of Zn after the above treatment in an electrolyte of pH 4.

Similar studies [19] have also been made on thin polycrystalline film cadmium telluride samples produced by the gradient recrystallization growth technique [24] and electrochemically produced tellurium surface films have been spectroscopically identified. The highly light scattering nature of these polycrystalline thin (100μ) films made conventional transmission spectroscopy impossible as did the presence of an opaque electrode on the single crystal sample used to identify the absorption features in the polycrystalline films. The absorption spectra of these CdTe samples are displayed below and were measured with a resolution of 4 nm which was adequate for obtaining the desired spectral information.

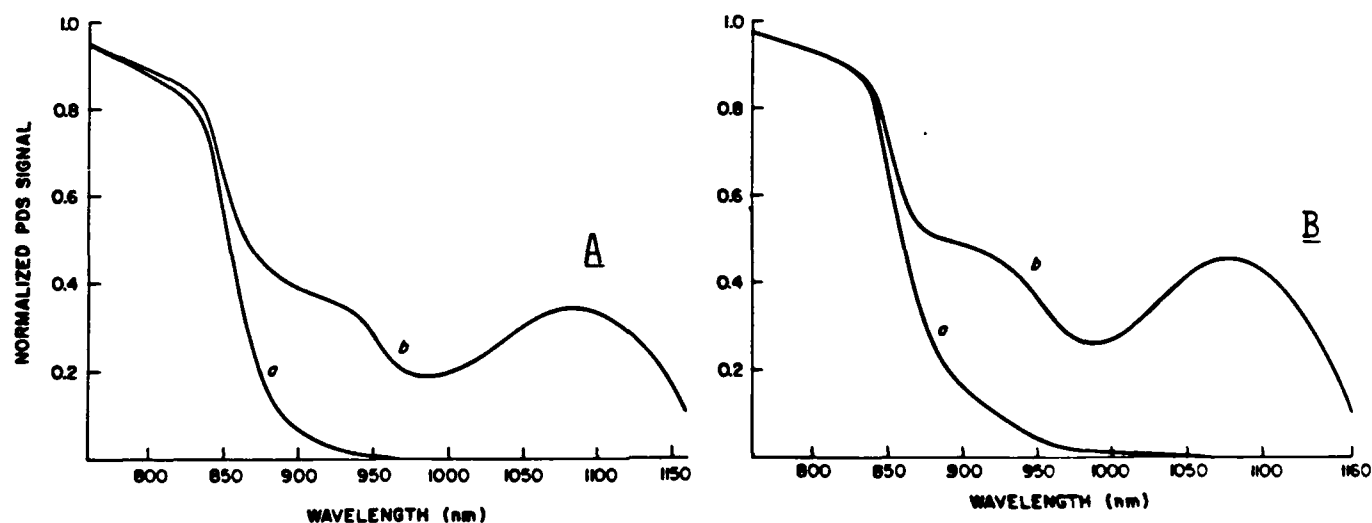


Figure 4. Mirage Effect Spectra for nCdTe thin films and a single crystal.

- | | |
|-------------------------|----------------------------------|
| A. Polycrystals | B. Crystal |
| a. Insulating substrate | a. Fresh crystal surface |
| b. Conducting substrate | b. Photocorroded crystal surface |

Curve B(a) is a spectrum of the single crystal prior to electrochemical photocorrosion and shows the band edge at its expected position. Curve B(b) is the spectrum obtained after the surface had been photocorroded in an acidified SnCl_2 electrolyte by exposure to circa 1 mw/cm^2 of 632.8 nm light for 15 mins. Vazquez-Lopez et al [24] have shown that this procedure generates a Te surface layer on the crystal and the Mirage Effect spectral clearly shows the additional absorption produced by this layer. Comparison of this spectrum with that of the polycrystalline thin films produced on a conducting substrate, A(b), indicates that these films are non-stoichiometric with excess Te. The polycrystalline films growth under the same conditions on an insulating substrate, A(a), are seen to be approximately stoichiometric.

These measurements have demonstrated the utility of this technique for obtaining spectral data in situ at electrode/electrolyte interfaces and, in particular, for following the growth of the thin surface films resulting from electrochemical decomposition. The method has important advantages over more conventional techniques in that it measured absorbed energy and consequently does not require transparent or reflecting electrodes. This means that polycrystalline samples can be easily studied and that these can be mounted on opaque substrates if required. It has also been demonstrated by Jackson et al [25] that the ultimate sensitivity of this method is approximately two orders of magnitude better than that of conventional transmission spectroscopy, a fact which will facilitate the detection of thin surface films or changes induced in surface species during an electrochemical reaction. The measurements of Roger et al [21] have indicated that with certain systems and polarization modulation, submonolayer coverages would be detectable.

When an electrode material, such as the ZnSe considered above, undergoes photochemical decomposition the concentration of solution species is

changed in the vicinity of the electrode with the major effect being realized in a region approximately 10^{-4} m in thickness. In general, the addition of chemical species to an electrolyte will change its refractive index and, as discussed above, this refractive index gradient can be detected using the same apparatus as that required for the Mirage Effect Spectroscopy.

When ZnSe undergoes photodecomposition in an acidic electrolyte (pH 4) zinc ions go into solution at the electrode surface and diffuse away from the electrode into the bulk electrolyte. These ions cause a negligible change in the optical absorption of the electrolyte but do change its refractive index. Under open circuit conditions, when photoelectrochemical reactions occur through local corrosion of the semiconductor surface, the zinc diffusion profile into the bulk electrolyte has the form of a complementary error function:

$$c(y,t) = c_s \operatorname{erfc} \left(\frac{y}{\sqrt{4Dt}} \right)$$

The deflection of the laser beam produced by this time dependent diffusion profile then is given by:

$$\phi(y,t) = A \left(\frac{dn}{dc} \right) \left(\frac{dc(y,t)}{dy} \right)$$

i.e.
$$\phi(y,t) = B \left(\frac{dn}{dc} \right) \frac{1}{\sqrt{\pi Dt}} \exp \left[-\frac{y^2}{4Dt} \right]$$

where y is the distance between the laser probe beam and the sample surface, D is the diffusion coefficient of zinc ions in the electrolyte and t is the time since the inception of the photocorrosion illumination period.

Figure 5 below shows the measured beam deflection as a function of time for a ZnSe single crystal being exposed to bandgap radiation (460 nm) with the laser probe beam at a distance of approximately 10^{-4} m from the sample surface. Similar curves were obtained for other beam locations, however, the

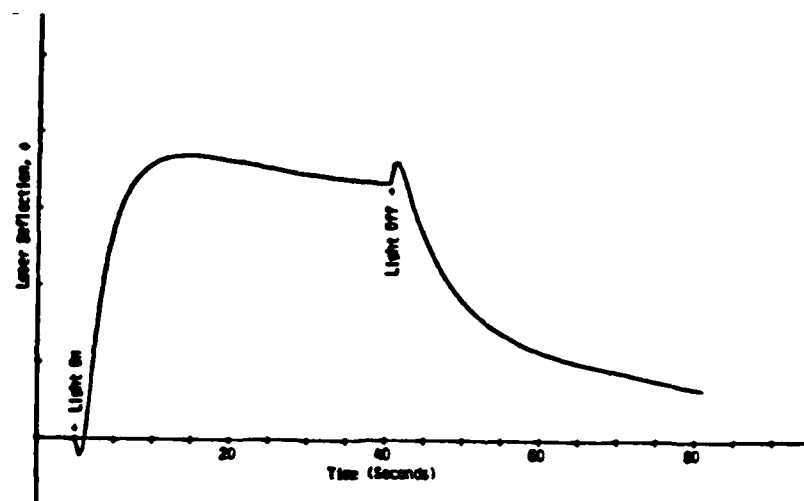


Figure 5. Thermal and concentration gradient associated beam deflection during the photodissociation of ZnSe.

time of maximum deflection and deflection amplitude are different. An additional feature, not included in the expression for ϕ given above, is seen in this data. When the band gap light is turned on to initiate the photocorrosion process some of the electron-hole pairs generated recombined non-radiatively rather than causing sample decomposition and produce a temperature increase at the sample surface of circa 10^{-3} K. [It is these non-radiative recombination processes that were responsible for the spectroscopic signal discussed above.] Thermal energy diffusion away from this surface causes a beam deflection through the temperature dependence of the refractive index and this is of opposite sign to that due to the concentration profile since a temperature increase reduces the refractive index of the electrolyte. Because of the much higher value of the thermal diffusion coefficient as compared to the matter diffusion coefficient for the zinc ions in solution and the relative values of (dn/dT) and (dn/dc) the thermal signal is the first to arrive at the laser probe whereas the ion diffusion profile dominates the beam deflection behavior at later times. When the photocorroding light

is turned off the sample surface temperature drops and additional zinc ions are no longer created. The deflection of the laser beam, therefore, returns to zero with the thermal contribution again being the most rapid and of opposite sign.

This behavior has been modeled in the ray approximation outlined above and the family of curves in Figure 6 below shows the expected laser beam deflection as a function of time for various locations of the probe beam when both thermal and matter diffusion occur from the electrode surface. It is

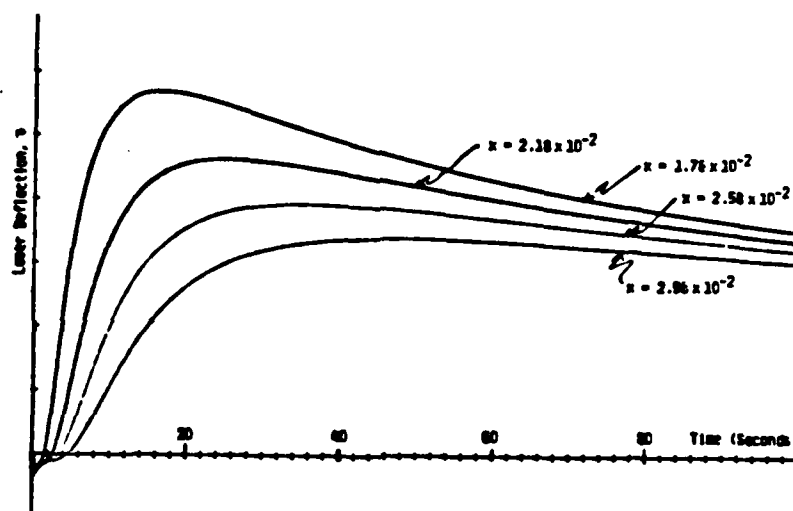


Figure 6. Theoretical model for laser beam deflection.

seen that these curves exhibit the same features as the experimental data with a matter diffusion coefficient some two orders of magnitude smaller than the thermal diffusion coefficient. Initial estimates of the matter diffusion coefficient to be used in the curve fitting procedure can be obtained from the position of the laser deflection maximum assuming that the concentration gradient alone is responsible for the beam deflection. Under these conditions $(d\phi/dt)$ is zero when:

$$t_{\max} = (x^2/2D)$$

By measuring $\phi(x,t)$ at two or more locations, the laser position with respect to the surface, x , the diffusion coefficient, D , can be calculated from the experimental data.

It is also possible to verify this deflection assignment experimentally by applying approximately -1.0 V vs. SCE to the ZnSe crystal and repeating the experiment. This bias yields the flat band condition for the n-type samples used and consequently non-radiative recombination processes are dominant. Under these conditions the photodissolution contribution to the deflection signal is negligible and only the thermal term remains. At other applied potentials the relative values of the Zn dissolution signal and the thermal signal are observed to vary in a systematic way. The probe method may therefore be employed to detect electronic characteristics of the electrode, such as its flat band potential, as well as to obtain data on the electrode decomposition reaction.

Diffusion equations similar to those for the zinc ions discussed above may be written to describe concentration profiles produced by charge exchange between a semiconducting electrode and redox couples in the electrolyte. The laser beam deflection is also sensitive to such gradients and may be used to provide detailed information about the rate of charge transfer to the redox couple. Due to the fact that the potential drop at the semiconductor-electrolyte interface is often totally confined to the space charge region this information is usually hard to obtain using standard electroanalytical techniques which rely on the interface potential being dropped across the double layer region. Fairly sophisticated (and experimentally complicated) electrochemical approaches such as photoelectrochemical rotating ring-disk voltammetry [26] may be used, however, surface spectroscopic data concomitantly available via the photothermal signal is then forfeited.

Mirage spectroscopy further offers the opportunity for gaining information about the semiconductor-electrolyte interface often inaccessible by purely electrochemical means. For example, irradiation related processes occurring under open circuit conditions can be observed. Previously such processes have been inferred from photovoltage measurements. The ability to carry out such studies is demonstrated by recent experiments on polycrystalline CdS in a sulphide electrolyte which indicate the photoinduced oxidation of solution sulphide species at open circuit, suggesting the occurrence of "short circuit" surface photoelectrochemistry.

The Mirage Effect can also be employed to interrogate the photophysics of semiconductor-liquid junction absorption. The overall quantum yield for this process can be expressed as:

$$\phi_{\text{Total}} = \phi_R + \phi_{\text{NR}} + \phi_D + \phi_E$$

where ϕ_R = Radiative processes

ϕ_{NR} = Nonradiative or thermal processes

ϕ_D = Semiconductor decomposition from an excited state

ϕ_E = Electron flow processes and associated interfacial chemistry.

The last two terms in this equation have been studied extensively using electrochemical and surface reflectance techniques. Recently, Streckert et al [27] have correlated radiative interfacial processes ϕ_R with ϕ_E by combining luminescence spectroscopy on appropriately doped semiconductors with electrochemical measurements. However, with the exception of the experiments of Fujishima et al [28] on thermistor mounted photoelectrodes, little experimental data associated with the second term, ϕ_{NR} , is available. Although yielding thermodynamic and photophysical data on the interfaces of interest, Fujishima et al's experiments have been limited by complex experimental

conditions (a thermistor must be attached at the site of irradiation such that it does not interfere with the photoelectrochemistry); the Mirage approach does away with this problem.

The Mirage Effect is of particular interest in studying the effects of a surface layer and competitive charge transfer processes that are occurring. The spectroscopic aspect of the probe may be employed to monitor changes in the surface layer and the concentration profile aspect may be used to monitor the charge transfer to the redox species.

Thermodynamic information about the charge transfer process may also be obtained by measuring the electrochemical Peltier heats of the redox reaction. For an electrochemical process the appropriate electrochemical Peltier coefficient has the form:

$$\pi = [T(S_{T,p}) + Q^* - \eta F n] / nF$$

where $S_{T,p}$ is the entropy of the reaction at a temperature T , Q^* is the transported heat per unit reaction and η the electrode overpotential. Passage of current through the interface gives rise to a heat release:

$$\left(\frac{dQ}{dt}\right) = \pi(I) + I^2 R$$

where the second term represents Joule heating of the electrolyte. The Peltier coefficient may be either positive or negative and so heat may be released or adsorbed at the interface depending upon the sign of the current and the nature of the redox couple involved. The interfacial polarization term is always exothermic.

The use of electrochemical calorimetry to study this process has been discussed by Sherfey and Brenner [29] and the measurement of Peltier heats using thermistor bridge methods has been reported by Tamamushi [30,31] and by Ozeki et al [32]. The laser beam technique is much more sensitive than

either of these probes and has been used in some initial measurements in our laboratory to detect the Peltier heat associated with the $\text{Fe}(\text{CN})_6^{4-/3-}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+/3+}$ couples at platinum electrodes. Because the thermal diffusion coefficient of the aqueous electrolyte is approximately two orders of magnitude greater than the matter diffusion coefficient of the redox species, the thermal term is temporally separable from the concentration term as was also indicated in the data shown in Figure 5.

References

1. M.J.D. Low and G.A. Parodi, Appl. Spect. 34 (1980) 76 and Spect. Lett. 13 (1980) 151.
2. M.G. Rockley, Chem. Phys. Lett. 68 (1979) 455 and Appl. Spec. 34 (1980) 405.
3. D.W. Vidrine, Appl. Spec. 34 (1980) 314.
4. B.S.H. Royce, J. Enns and Y.C. Teng, Bull. Am. Phys. Soc. 25 (1980) 408.
5. NSF Award Number CPE 8100183.
6. G. Laufer, J.T. Huneke, B.S.H. Royce and Y.C. Teng, Appl. Phys. Lett. 37 (1980) 517.
7. C. Christensen, Ann. Phys. Chem. 23 (1884) 298.
8. J.F. McClelland, R.N. Kniseley, P.R. Solomon and R.M. Carangelo, 3rd Int. Conf. on Photoacoustic and Photothermal Spectroscopy, Paris, France, 1983, Paper 2.7.
9. Y.C. Teng and B.S.H. Royce, Appl. Optics. 21 (1982) 77.
10. Y.C. Teng and B.S.H. Royce, J. Opt. Soc. Am. 70 (1980) 557.
11. B.S.H. Royce, Y.C. Teng and J.A. Ors, Proc. IEEE Ultrasonics Symposium (1981), p. 784.
12. B.S.H. Royce, Y.C. Teng and J. Enns, Proc. IEEE Ultrasonics Symposium (1980), p. 653.
13. S.J. McGovern, B.S.H. Royce and J.B. Benziger (submitted to J. Catalysis).
14. D. Marcuse, "Light Transmission Optics," Van Nostrand Reinhold Co., New York (1972) Chapter 3.
15. D. Fournier, A.C. Boccara and J. Bardo, App. Phys. Lett. 36 (1980) 130.
16. J.C. Murphy and L.C. Aamodt, J. App. Phys. 51 (1980) 4580 and 52 (1981) 4903.
17. W.B. Jackson, N.M. Amer, A.C. Boccara and D. Fournier, App. Optics 20 (1981) 1333.
18. B.S.H. Royce, S. Sanchez-Sinencio, R. Goldstein, R. Muratore, R. Williams and W.M. Yim, Bull. Am. Phys. Soc. 27 (1982) 243.
19. B.S.H. Royce, S. Sanchez-Sinencio, R. Goldstein, R. Muratore, R. Williams and W.M. Yim, J. Electrochem. Soc. 129 (1982) 2393.

20. J.G. Mendoza-Alvarez, B.S.H. Royce, F. Sanchez-Sinencio, O. Zelaya-Angel, C. Menzes and R. Triboulet, Thin Solid Films 102 (1983) 259.
21. J.P. Roger, D. Fournier and A.C. Boccara, Third International Conference on Photoacoustic and Photothermal Spectroscopy, Paris, April 1983.
22. R. Williams, J. Electrochem. Soc. 114 (1967) 1173.
23. J. Gaution, P. Lemasson, F. Rabago and R. Triboulet, J. Electrochem. Soc. 126 (1979) 1868.
24. C. Vazquez-Lopez, F. Sanchez-Sinencio, J.S. Helman, J.P. Pena, A. Lastras-Martinez, P.M. Racciah and R. Triboulet, J. App. Phys. 50 (1979) 5391.
25. W.B. Jackson and N. Amer. Phys. Rev. B25 (1982) 5559.
26. T. Inoue, T. Watanabe, A. Fujishima and K. Honda, Bull. Chem. Soc. Jap. 52 (1979) 1243.
27. H.H. Streckert, B.R. Karas, D.J. Morano and A.B. Ellis, J. Am. Chem. Soc. 84 (1980) 2332.
28. A. Fujishima, Y. Masada, K. Honda, G.H. Brilmeyer and A.J. Bard, J. Electrochem. Soc. 127 (1980) 840.
29. J.M. Sherfey and A. Brenner, J. Electrochem. Soc. 105 (1958) 665.
30. R. Tamamushi, J. Electroanal. and Int. Electrochem. 45 (1973) 500.
31. R. Tamamushi, J. Electroanal. Chem. 65 (1975) 263.
32. T. Ozeki, I. Watanabe and S. Ikeda, J. Electroanal. Chem. 96 (1979) 117.

Publications Resulting from the Contract

1. B.S.H. Royce, J. Enns and Y.C. Teng, *Fourier Transform Infrared Photoacoustic Spectroscopy of Solids*, Bull. Am. Phys. Soc. 25, 408 (1980).
2. G. Laufer, J.T. Huneke, B.S.H. Royce and Y.C. Teng, *Elimination of Dispersion Induced Distortion in Infrared Absorption Spectra by the Use of Photoacoustic Spectroscopy*, Appl. Phys. Lett. 37, 517 (1980).
3. B.S.H. Royce, Y.C. Teng and J. Enns, *Fourier Transform Infrared Photoacoustic Spectroscopy of Solids*, Paper H2. IEEE Symposium on Ultrasonics, Boston, (5-7 November 1980). 1980 Ultrasonics Symposium Proceedings, 652 (1980).
4. Y.C. Teng and B.S.H. Royce, *Quantitative Fourier Transform Infrared Photoacoustic Spectroscopy of Condensed Phases*, Paper TuA2. Second International Topical Meeting on Photoacoustic Spectroscopy, Berkeley (June 1981) and Appl. Optics 21, 77 (1982).
5. B.S.H. Royce and Y.C. Teng, *Fourier Transform Infrared Photoacoustic Spectroscopy of Condensed Phases*. International Conference on Acoustic Emission and Photoacoustic Spectroscopy, London (July 1981). Proceedings Institute of Acoustics (1982).
6. B.S.H. Royce, Y.C. Teng and J.A. Ors, *Reactions in Polymers Studied with FTIR-Photoacoustic Spectroscopy*. IEEE Symposium on Ultrasonics, Chicago (14-16 October 1981). 1981 Ultrasonics Symposium Proceedings, 784 (1981).
7. B.S.H. Royce, F. Sanchez-Sinencio, R. Goldstein, R. Muratore, R. Williams and W.M. Yim, *Optical Studies of the Photocorrosion of ZnSe*. Bull. Am. Phys. Soc. 27, 243 (1982) and J. Electrochem. Soc. 129, 2393 (1982).
8. J.G. Mendoza-Alvarez, B.S.H. Royce, F. Sanchez-Sinencio, O. Zelaya-Angel, C. Menezes and R. Triboulet, *Optical Properties of CdTe Thin Films Studied by Photothermal Deflection Spectroscopy*. Bull. Am. Phys. Soc. 28, 534 (1983) and Thin Solid Films 102, 259 (1983).
9. B.S.H. Royce, D. Voss and A.B. Bocarsly, *Mirage Effect Studies of Electrochemical Processes*. Third International Topical Meeting on Photoacoustic and Photothermal Spectroscopy, Paper 4.15, Paris (April 1983) and Les édition de Physique (in press).
10. B.S.H. Royce, A.B. Bocarsly and R. Muratore, *Mirage Effect Studies of Electrochemical Interfaces*. 164th Meeting--The Electrochemical Society, Washington, DC (October 1983).

Participating Scientific Research Personnel

Professor Barrie S. H. Royce, Principal Investigator.

Professor Feliciano Sanchez-Sinencio, Visiting Professor, Physics Department, Centro de Investigacion y de Estudios Avanzados del IPN, Mexico.

Professor Julio Mendoza-Alvarez, Visiting Professor, Physics Department, Centro de Investigacion del IPN, Mexico.

Dr. David Voss, Research Associate.

Dr. Sheela K. Ramasesha, Research Associate.

Dr. Peter B. Kelly, Research Associate.

Dr. Y. C. Teng, Received Ph.D. 1982.

Mr. R. Muratore, M.S.E. Candidate.

Ms. T. Deguchi, M.S.E. awarded 1983.

END

FILMED

12-10-1944

DTIC