AD-A106 382 MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/G 20/12
DELIBERATE MODIFICATION OF THE BEHAVIOR OF N-TYPE CADMIUM TELLU--ETC(U)
SEP 81 S TANAKA, J A BRUCE, M S WRIGHTON N00014-75-C-0880
UNCLASSIFIED TR-29 NL

[illegible]

END
DATE
FILMED
11-81
DTIC

AD A106382

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: ONR/TR-29

2. GOVT ACCESSION NO.: AD A106382

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): "Deliberate Modification of the Behavior of n-Type Cadmium Telluride/Electrolyte Interfaces by Surface Etching: Removal of Fermi Level Pinning"

5. TYPE OF REPORT & PERIOD COVERED: Interim Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): Shinichi Tanaka, James A. Bruce and Mark S. Wrighton

12

8. CONTRACT OR GRANT NUMBER(s): N00014-75-C-0880

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Department of Chemistry, Rm. 6-335
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 051-579

11. CONTROLLING OFFICE NAME AND ADDRESS:
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

12. REPORT DATE: September 2, 1981

13. NUMBER OF PAGES: 44

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; reproduction is permitted for any purpose of the United States Government; distribution unlimited.

DTIC
OCT 30 1981
H

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Distribution of this document is unlimited.

18. SUPPLEMENTARY NOTES

Prepared and accepted for publication in the Journal of Physical Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Etching, Fermi level pinning, cadmium telluride, Auger/XPS

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Single crystal, n-type CdTe (E_g = 1.4 eV) has been studied with respect to barrier height, E_B, when contacting a liquid electrolyte solution containing a fast, one-electron, outer-sphere redox reagent. We approximate E_B as equal to the photovoltage measured by cyclic voltammetry of various redox couples at illuminated n-CdTe vs. a reversible electrode. N-CdTe surfaces pretreated with an oxidizing etch give an E_B of 0.5 V ± 0.1 V in H_2O/0.1 M $NaClO_4$ or CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ that is independent of the $E_{1/2}$ of the added redox couple. A reducing etch pretreatment gives an E_B in either of the electrolyte solutions

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

FILE COPY

that depends on E of the redox couple in a manner consistent with a nearly ideal semiconductor. The reduced CdTe exhibits an E_B of up to 0.9 V for a redox couple having E near 0.0 V vs. SCE, whereas couples having E negative of -1.0 V vs. SCE give zero photovoltage. Auger and X-ray photoelectron spectroscopy of the reduced and oxidized surfaces are qualitatively different. The reduced surface exhibits signals for Cd and Te in relative intensities that are consistent with a close to stoichiometric (1/1) surface. The oxidized surface exhibits little or no detectable Cd signal and the Te signal is consistent with a thick overlayer of elemental Te. The data are consistent with the conclusion that the CdTe/Te interface is Fermi level pinned (E_B independent of contacting medium), the semimetallic Te overlayer behaves as a metal contacting CdTe and the CdTe/Te interface energetics are therefore not influenced by changes in the contacting medium.

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-75-C-0880

Task No. NR 051-579

TECHNICAL REPORT NO. 29

"DELIBERATE MODIFICATION OF THE BEHAVIOR OF N-TYPE CADMIUM TELLURIDE/ELECTROLYTE INTERFACES BY SURFACE ETCHING: REMOVAL OF FERMI LEVEL PINNING"

by

Shinichi Tanaka, James A. Bruce and Mark S. Wrighton

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Prepared for publication in the Journal of Physical Chemistry

September 2, 1981

Deliberate Modification of the Behavior of N-Type Cadmium Telluride/Electrolyte Interfaces by Surface Etching: Removal of Fermi Level Pinning

Shinichi Tanaka,[1] James A. Bruce, and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Abstract: Single crystal, n-type CdTe (E_g = 1.4 eV) has been studied with respect to barrier height, E_B, when contacting a liquid electrolyte solution containing a fast, one-electron, outer-sphere redox reagent. We approximate E_B as equal to the photovoltage measured by cyclic voltammetry of various redox couples at illuminated n-CdTe vs. a reversible electrode. N-CdTe surfaces pretreated with an oxidizing etch give an E_B of 0.5 V ± 0.1 V in H_2O/0.1 M $NaClO_4$ or CH_3CN/0.1 M [n-Bu_4N]ClO_4 that is independent of the $E_{1/2}$ of the added redox couple. A reducing etch pretreatment gives an E_B in either of the electrolyte solutions that depends on $E_{1/2}$ of the redox couple in a manner consistent with a nearly ideal semiconductor. The reduced CdTe exhibits an E_B of up to 0.9 V for a redox couple having $E_{1/2}$ near 0.0V vs. SCE, whereas couples having $E_{1/2}$ negative of -1.0 V vs. SCE give zero photovoltage. Auger and X-ray photoelectron spectroscopy of the reduced and oxidized surfaces are qualitatively different. The reduced surface exhibits signals for Cd and Te in relative intensities that are consistent with a close to stoichiometric (1/1) surface. The oxidized surface exhibits little or no detectable Cd signal and the Te signal is consistent with a thick overlayer of elemental Te. The data are consistent with the conclusion that the CdTe/Te interface is Fermi level pinned (E_B independent of contacting medium); the semimetallic Te overlayer behaves as a metal contacting CdTe and the CdTe/Te interface energetics are therefore not influenced by changes in the contacting medium.

Results from this laboratory were recently reported[2] showing that n-type CdTe photoanodes give an open-circuit photovoltage, E_V, of ~0.5 V independent of the electrochemical potential, E_{redox}, of the contacting electrolyte solution. Certain aspects of the results were independently reported.[3] A nearly constant barrier height, E_B, has been found[4] for n-CdTe contacted by metals having different work functions, ϕ. The value of E_V is generally close to E_B at high illumination intensity. The finding of a constant E_B for n-CdTe, independent of E_{redox} or ϕ, leads to the conclusion that n-CdTe is Fermi level pinned.[2,5]

We take the term "Fermi level pinned" to refer to a semiconductor that is measured to have a constant E_B, independent of the contacting medium for a wide range of E_{redox} or ϕ. The origin of a constant E_B can be attributed to surface states situated between the top of the valence band, E_{VB}, and the bottom of the conduction band, E_{CB}. The density and distribution of surface states can control the value of E_B as a function of E_{redox} or ϕ.[5,6] When the region between E_{CB} and E_{VB} is free of surface states, E_B of an n-type semiconductor is expected to vary with E_{redox} according to equation (1)[7] for E_{redox} situated between E_{VB} and E_{CB} where

$$E_V \approx E_B = |E_{redox} - E_{FB}| \qquad (1)$$

E_{FB} is the electrochemical potential of the semiconductor, E_f, when there is no band bending. When $E_f = E_{FB}$ there is no accumulation or depletion of the majority charge carrier at the surface and $E_B = 0$. But even for surface-state-free semiconductors, equation (1) may not apply for all E_{redox} between E_{CB} and E_{VB}. It is possible that for E_{redox} sufficiently close to E_{VB} for an n-type semiconductor that the charge carrier distribution at the surface can be "inverted" giving more holes than electrons in the surface region. This results in a situation like that for a semiconductor having surface states: additional positive movement of E_{redox} will not cause variation in E_B, rather additional potential drop across the interface will occur in the Helmholtz double layer in the electrolyte solution.[8,9]

For n-CdTe the origin of the constant E_B is most consistent with surface states rather than carrier inversion, since the range of E_{redox} where E_B is constant includes redox couples with $E_{\frac{1}{2}}$ as negative as -2.0 V vs. SCE where carrier inversion would be very unlikely.[2] We use measured $E_{\frac{1}{2}}$ values to approximate the formal potential of redox couples used in this study. When surface states are invoked it should be possible to manipulate the surface properties by surface chemical treatments.[5,10,11] Such treatments could include oxide formation, reversible adsorption of chemical species, covalent attachment of reagents, and other surface chemistry. We show in this paper that we can alter the behavior of n-CdTe from the Fermi level pinned situation to one where nearly ideal behavior, equation (1), is found by using a different surface pretreatment than used in the earlier studies of n-CdTe.

Experimental Section

CdTe and Electrode Fabrication. Oriented single crystals of n-CdTe, (111) plane exposed, 0.2 - 30 Ω cm, were obtained from Cleveland Crystals, Inc., Cleveland, Ohio. The crystals were polished first with 20 μm alumina and then with 10 μm alumina on a polishing glass. The crystals were finished with 0.3 μm alumina on a polishing cloth (Politex Supreme PS, Gros Corp., Stamford, CT), fixed onto the glass. Ohmic contact was made to the CdTe by rubbing Ga-In eutectic onto the back of the crystal. A Cu wire was attached using conducting Ag epoxy. The Cu wire was encased in a 4 mm Pyrex tube and all surfaces but the exposed front surface of CdTe were sealed with ordinary epoxy. The exposed surface of the CdTe was the (111) face. Just prior to use all electrodes were etched and cleaned as described below.

Etching Procedures. Two different types of etchants were used, oxidizing and reducing. An oxidizing etch was one of the following: (i) 4 g $K_2Cr_2O_7$, 10 ml concentrated HNO_3, and 20 ml H_2O;[12] (ii) 1/1/1 by volume saturated solution of $K_2Cr_2O_7$, concentrated HCl, and concentrated HNO_3;[13] (iii) 3/2/1 by volume solution of 48% HF, 30% H_2O_2, and H_2O and then briefly rinsed with concentrated HCl;[14] (iv) 3/2/1/0.01 by volume of concentrated HNO_3, concentrated H_2SO_4, glacial acetic acid, and concentrated HCl; (v) 2/1/1 by volume solution of 48% HF, concentrated HNO_3, and glacial acetic acid.[15] For an oxidizing etch the CdTe electrode was immersed in the etchant for 30 s at 25°C. After etching the electrode was rinsed liberally with distilled H_2O.

For a reducing etch the electrode was first etched with oxidizing etchant (i) above for 30 s, rinsed with distilled H_2O and then immersed into a boiling solution of 2.5 M NaOH and 0.6 M $Na_2S_2O_4$ for 3 min. The electrode was then rinsed liberally with distilled H_2O.

Chemicals. Spectrograde CH_3CN was freshly distilled from P_2O_5 prior to use. [n-Bu_4N]ClO_4 from Southwestern Analytical Chemicals was vacuum dried at 70°C for 24 h prior to use, and $NaClO_4$ was obtained from commercial sources and used without further purification. Triply distilled H_2O was used for solvent in aqueous electrolyte systems.

Redox reagents were generally obtained from commercial sources; TMPD was purified by sublimation; $K_4Fe(CN)_6$, $[Ru(NH_3)_6]Cl_3$, $Fe(\eta^5-C_5H_5)_2$, $EuCl_3$, and 9,10-anthraquinone-2-SO_3^- were used as received. Other redox couples are those used and purified in this laboratory previously.[2,16] Abbreviations for redox couples are MV^{2+} ≡ N,N'-dimethyl-4,4'-bipyridinium; TQ^{2+} ≡ N,N'-trimethylene-2,2'-bipyridinium; TMPD ≡ N,N,N',N'-tetramethyl-p-phenylenediamine; and AQ ≡ 9,10-anthraquinone-2-SO_3^-. The $E_{1/2}$ values are from cyclic voltammograms at Pt or Hg electrodes. The $E_{1/2}$ value was taken to be the average position of the anodic and cathodic peaks.

Electrochemical Equipment and General Procedures. Electrolyte solutions were generally H_2O/0.1 M $NaClO_4$ or CH_3CN/0.1 M [n-Bu_4N]ClO_4. The non-aqueous electrolyte solution was passed through anhydrous neutral Al_2O_3 just prior to use to insure dryness. In the case of $[Ru(NH_3)_6]Cl_3$ the supporting electrolyte was 0.1 M KCl because $Ru(NH_3)_6{}^{3+}$ is not sufficiently soluble in 0.1 M $NaClO_4$. AQ in aqueous solution was studied in H_2O buffered to pH = 8.6 using borax/HCl. All electrochemistry was carried out under a positive pressure of pure Ar.

Cyclic voltammograms were obtained using a PAR model 173 potentiostat driven by a PAR model 175 programmer. Data were recorded on a Houston Instruments X-Y recorder. The electrochemical cell was a single compartment cell consisting of a working electrode of n-CdTe, Pt, or Hg, a Pt counterelectrode, and a reference electrode. For aqueous electrolytes the saturated calomel reference electrode (SCE) was used. A 0.1 M $AgNO_3$/Ag/0.1 M [n-Bu_4N]ClO_4/ CH_3CN reference (+0.35 V vs. SCE) was used in CH_3CN solutions. All E_B determinations are from cyclic voltammograms at 100 mV/s.

For cyclic voltammograms redox reagents were added to solution at ~1 m*M* concentration in all cases. The n-CdTe electrodes were illuminated using a beam expanded He-Ne laser from Coherent Radiation, providing ~50 mW/cm^2 at 632.8 nm. This is sufficient light intensity to insure that photocurrent for ~1 m*M* solutions of redox reagent is limited by diffusion, not excitation rate (light intensity).

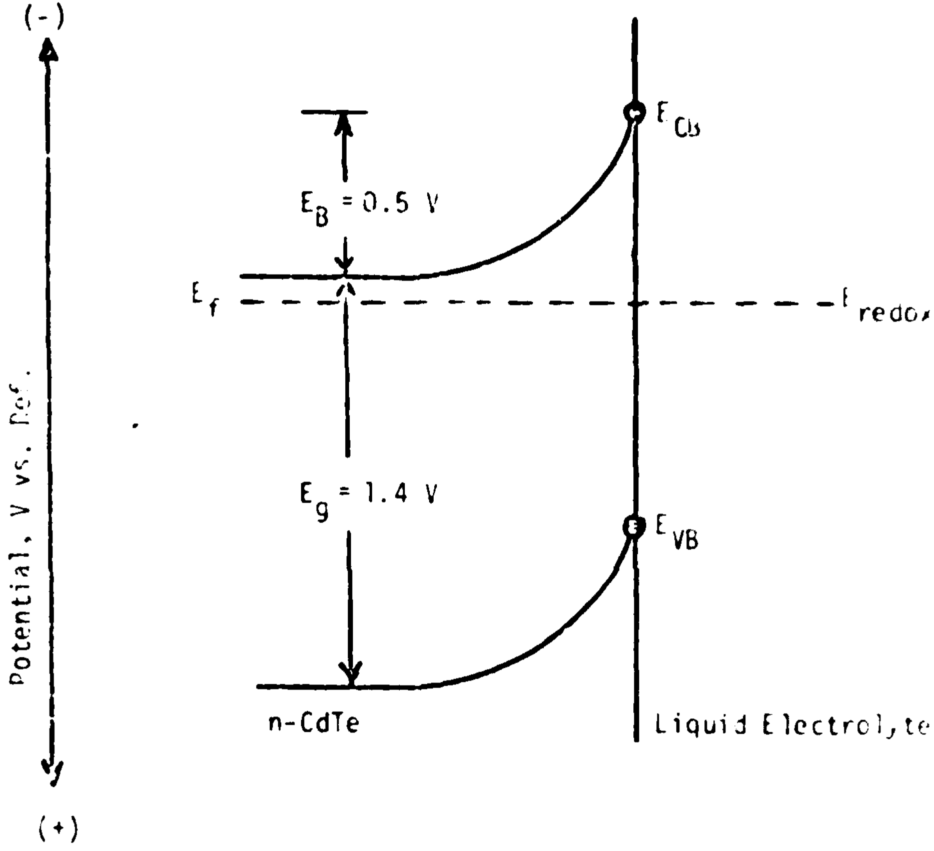
XPS and Auger Studies. Auger spectra were obtained on a Physical Electronics model 590A scanning Auger spectrophotometer. A 5 KeV electron beam with a beam current of 0.6 to 1 μA was used as the excitation source. The samples were mounted by attaching the Cu wire lead to the sample holder to insure electrical grounding. A Physical Electronics model 04-303 differential ion gun was used to produce a 2 keV Ar$^+$ ion beam for sputtering. The pressure was maintained at ~3 x 10^{-8} torr in the main vacuum chamber and 1.5 x 10^{-4} torr of Ar in the ionization chamber, while sputtering.

X-ray photoelectron spectra (XPS) were obtained on a Physical Electronics model 548 spectrometer with a magnesium anode. The broad scans (0-1000 eV) were recorded with a pass energy of 100 eV and the narrow scans with a pass energy of 25 eV. The peak energies at the Cd and Te peaks were referenced to the C 1s binding energy (284.6 eV) to correct for charging. Samples were mounted as above and sputtering was done with a 5 keV Ar$^+$ beam, after introducing Ar into the vacuum chamber to bring the pressure to ~7 x 10^{-5} torr.

Elements detected by Auger and XPS were identified by reference to data previously reported using these techniques.[17,18]

Results

a. Determination of E_V vs. E_{redox} for n-CdTe. Scheme I illustrates the interface energetics for n-type CdTe in equilibrium with a redox couple in an electrolyte solution where $E_B = 0.5$; E_g is the band gap for CdTe, 1.4 eV.



Scheme I. Representation of n-CdTe/liquid electrolyte interface energetics when the barrier height, E_B, is 0.5 V.

In the previous studies,[2,3] the value of E_B was determined for CH_3CN electrolyte solutions and for CdTe etched with an oxidizing etch. We have extended these studies to aqueous solution and to CdTe etched with a reducing etch. The important finding is that the reducing etch results in an E_B that depends strongly on E_{redox} whereas the oxidizing etch gives an E_B that is independent of E_{redox} in either H_2O or CH_3CN. We now detail the procedure used to determine E_B vs. E_{redox} and the data that have been collected in CH_3CN and H_2O for "oxidized" surfaces and "reduced" surfaces of n-CdTe.

1. Procedure for Determining E_B and the Classification of Redox Couples. Referring to Scheme I and equation (1), the maximum photovoltage, E_V, from the photoanode is equal to E_B. That is, when the $E_f = E_{FB}$ the bands are no longer bent and E_f is E_B away from E_{redox}. We[2,16] and others[9,19] have used cyclic voltammetry of redox reagents at low concentration to measure E_B conveniently and rapidly for a wide range of redox couples. Generally, we choose fast, one-electron, outer-sphere redox reagents to avoid complications from adsorption, such as S^{2-} on CdS[20] or I^- on $MoSe_2$,[21] and to insure that the energetics, not kinetics, dominate the measurement of the E_B. The procedure involves comparing the position of the peak of the photoanodic current, E_{PA}, in a cyclic voltammogram for the illuminated anode relative to the anodic current peak at a reversible electrode, e.g. Pt, for the redox couple under consideration. The anodic current peak gives the approximate electrode potential, E_f, where there is a 1/1 ratio of oxidized and reduced forms of the redox couple. The extent to which the peak at illuminated electrodes is more negative than at the reversible electrode is the photovoltage, E_V. And for sufficiently high light intensity this approximates the maximum open-circuit voltage possible. Thus, we take equation (2) to give the value of E_B within 100 mV.

$$E_B \simeq E_V = |E_{PA,Pt} - E_{PA,n\text{-}CdTe\ illum.}| \qquad (2)$$

At the very least, the procedure gives excellent relative values of E_V vs. $E_{1/2}$ values for the redox couples when the reduced form is added at the same concentration and the light intensity is the same.

Depending on the observed behavior of the redox couple at the semiconductor, we class the redox couples into one of five classes according to the following criteria:[16a]

Class I - $E_{1/2}$ is sufficiently negative that reversible behavior is observed at the semiconductor; $E_{1/2}$ is more negative than E_{CB} and there is no photoeffect.

Class II - $E_{1/2}$ is near E_{CB} but slightly positive of it so that dark oxidation is observed but rate is poor and is improved by irradiation with a small negative shift of the anodic current peak.

Class III - no dark oxidation of the reduced form of the couple; E_B depends on E_{redox} such that E_B is proportional to $E_{1/2} - E_{FB}$ for $E_{1/2}$ between E_{FB} and E_{VB}.

Class IV - no dark oxidation of the reduced form of the couple but E_B independent of $E_{1/2}$.

Class V - redox couples having $E_{1/2}$ sufficiently negative or positive that decomposition current for electrode is too great to allow study of the redox couple.

2. E_B in CH_3CN and H_2O vs. E_{redox} for Oxidized CdTe. Figure 1 and Table I summarize E_V determinations for a number of redox couples in H_2O and in CH_3CN for n-CdTe that was etched using an oxidizing etch. Generally, the oxidizing etches (i), (ii), or (iv) (see Experimental) give a value of E_V that is roughly independent of $E_{1/2}$ for the redox couples used. The data in Figure 1 and Table I for CH_3CN solution are from the previous work in this laboratory[2] and results for other oxidizing etches accord well with these data. The data for H_2O solutions represent new information and illustrate that E_B is essentially independent of $E_{1/2}$ for a wide range of $E_{1/2}$'s. Study of redox couples in H_2O with $E_{1/2}$ more positive than +0.3 or more negative than -1.4 V vs. SCE is precluded by photoanodic or cathodic decomposition currents, respectively. In CH_3CN the range is somewhat greater, consistent with the fact that it is well known that solvent can profoundly change the energetics for anodic and cathodic decomposition processes.[22] Except for the Class V couples, all of the redox couples studied at n-CdTe treated with the oxidizing etch belong to Class IV.

As reported previously,[2,3] the n-CdTe surface is not durable and the data given in Table I are for freshly etched surfaces for the first one to three cyclic voltammograms (100 mV/s) for a given redox couple. The positive potential limit was generally no further than 100 mV beyond the photoanodic current peak. Nonetheless, the photoanodic decomposition is a serious contributor to error and the values in Table I and Figure 1 represent the average of results of a number of determinations. The cyclic voltammetry of 1 m$\underline{M}$ $Fe(CN)_6^{4-}$ in H_2O/0.1 $\underline{M}$ $NaClO_4$ is illustrative of the quality of the data, Figure 2. The $Fe(CN)_6^{3-/4-}$ couple is durable and fairly reversible in H_2O at Pt, but the oxidation of $Fe(CN)_6^{4-}$ is blocked in the dark at n-CdTe. Upon illumination of the n-CdTe with $\geq E_g$ light $Fe(CN)_6^{4-}$ is oxidized and the $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-}$ current peak is ~0.6 V more negative than at Pt. Note the large amount of photoanodic current just beyond the peak for the $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-}$; this current is attributable to the decomposition represented by equation (3).[23a,b]

$$CdTe + 2h^+ \longrightarrow Cd^{2+} + Te \qquad (3)$$

Such decomposition can likely lead to sufficiently thick layers of elemental Te that the surface properties are significantly altered, vide infra. The main point is that the data regarding E_B need to be obtained within one to three cyclic voltammetry scans after etching to insure that the data reflect the properties of the freshly etched surface. At the deliberately low redox reagent concentrations needed to obtain mass transport limited oxidation currents there is simply not enough reducing agent to completely suppress the photoanodic decomposition. In order to exploit the n-CdTe in sustained photoelectrochemical energy conversion applications high concentrations of the redox reagent would be employed.

3. E_B in CH_3CN and H_2O vs. E_{redox} for Reduced CdTe. Figure 1 and Table II summarize the E_B determinations for n-CdTe that has been treated using the reducing etch. There is a remarkable difference in the set of data for the reduced CdTe vs. the oxidized CdTe. For reduced n-CdTe, unlike oxidized n-CdTe, the E_B depends on the $E_{1/2}$ of the contacting redox couple. The dependence is nearly that expected for an ideal semiconductor, equation (1), where $E_{FB} \approx -1.0$ V vs. SCE + 0.1 V in CH_3CN or in H_2O, in accord with an E_{FB} value determined from capacitance measurements in CH_3CN.[3] Importantly, the CdTe that has been treated with the reducing etch is essentially a reversible electrode in the dark for sufficiently negative redox couples unlike CdTe that has been treated with the oxidizing etch. No available redox couple is reversible in the dark at n-CdTe that has been etched with the oxidizing etch.

Figure 3 shows the cyclic voltammetry for the $TQ^{2+/+}$ and $TQ^{+/0}$ couples in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ for the reduced CdTe surface. The more positive $TQ^{2+/+}$ wave is shifted negative (relative to the position at Pt) at the illuminated CdTe to a larger extent than is the $TQ^{+/0}$ wave. For an oxidized CdTe each wave is shifted negative by 0.5 V relative to their positions at Pt. The small shift for the $TQ^{+/0}$ wave is consistent with the fact that the $E_{1/2}(TQ^{+/0})$ is close to E_{FB} -1.0 V vs. SCE. Couples having $E_{1/2}$ more negative than -1.0 V vs. SCE can be in Class I at the reduced CdTe but cathodic decomposition, equation (4) limits the negative range that can

$$CdTe + 2e^- \rightarrow Cd + Te^{2-} \qquad (4)$$

be examined, *vide infra*. Couples such as $TQ^{2+/+}$ and $TQ^{+/0}$ where E_B varies with $E_{1/2}$ are in Class III. All redox couples in the region positive of ~ -0.9 V appear to belong to Class III but the positive limit to the range of $E_{1/2}$'s that can be tested is again determined by the potential onset for photoanodic decomposition, equation (3).

Figure 4 illustrates the difficulty that results from the competing photoanodic decomposition. A freshly etched (reduced) n-CdTe photoelectrode exhibits a photoanodic current peak for $Fe(\eta^5-C_5H_5)_2 \rightarrow Fe(\eta^5-C_5H_5)_2^+$ at ~-0.3 V vs. SCE and when the scan is not extended too far beyond the peak the scan is fairly reproducible. However, when the first scan is extended to a positive limit of +0.6 V vs. SCE, the second scan reveals a photoanodic current peak that is shifted 0.3 V more positive. Apparently, the photoanodic decomposition current results in surface chemistry that alters the value of E_B. Interestingly, it appears that the photoanodic decomposition of the reduced n-CdTe results in a surface that gives a value of E_B that is similar to that for the oxidized n-CdTe from the oxidizing etch. In fact, it appears that the E_B that can be obtained for reduced n-CdTe using the $TMPD^{2+/+}$ couple is controlled by the photoanodic decomposition that occurs, since the $E_{1/2}(TMPD^{2+/+})$ is so positive. When scanning the reduced n-CdTe in a CH_3CN/0.1 M $[n-Bu_4N]ClO_4$/TMPD solution the E_B with respect to the $TMPD^{+/0}$ couple is larger than with respect to the $TMPD^{2+/+}$ couple on the first scan, but on the second scan the E_B is found to be the same, within 100 mV, for the two couples, Figure 5. Accordingly, the two most positive redox couples used in CH_3CN give smaller than expected photovoltages. Further, the E_B on the second scan is the same as that found for the oxidized n-CdTe from the oxidizing etch. The point is that E_B is very sensitive to the extent to which n-CdTe is oxidized after the reducing etch. Redox couples that have $E_{1/2}$ more positive than +0.4 V vs. SCE clearly suffer from the photoanodic decomposition and are borderline Class V couples. Photoanodic decomposition is even more severe in H_2O than in CH_3CN and couples positive of +0.1 V vs. SCE are Class V.

Figure 6 illustrates the behavior of the $TMPD^{+/0}$ system at the reduced n-CdTe in H_2O/0.1 M $NaClO_4$ solution. This redox couple gives the largest observed value of E_B, 0.9 V. This large value of E_B compared to that for the oxidized n-CdTe and the establishment of redox couples that give zero and near-zero values of E_B establish a clear difference between the oxidized and reduced n-CdTe prepared via the etching procedures. For either surface it appears that the E_B vs. $E_{1/2}$ is independent of whether the solvent is CH_3CN or H_2O. However, in H_2O the potential onset for photoanodic decomposition current is more negative than in CH_3CN, consistent with previous findings for CdS and other photoanode materials.[22]

b. Cyclic Voltammetry of n-CdTe in the Absence of Redox Couples. The n-CdTe electrodes exhibit current-potential properties that are consistent with an important influence from a redox labile CdTe surface in the E_B determinations. Figure 7 shows the cathodic current in H_2O/0.1 M $NaClO_4$ for n-CdTe electrodes pretreated in various ways. As illustrated, an oxidized n-CdTe from the oxidizing etch exhibits a large cathodic current in a potential region where the reduced n-CdTe exhibits none. For all five oxidizing etchants we find dark cathodic currents where the reducing etchant gives none or little. However, a reduced n-CdTe electrode that has been photoanodized in one positive scan does exhibit a large cathodic current. These data illustrate that the oxidized surfaces do behave in a manner that is different compared to the reduced surfaces. However, the nature of the reducible surface species is not clear. It is attractive to conclude that the reduction current is attributable to processes such as that represented by equation (5), since

$$CdTe_n + 2e^- \longrightarrow CdTe_{n-1} + Te^{2-} \qquad (5)$$

it appears that oxidation of Te^{2-} is the process that occurs in photoanodic decomposition, equation (3).

The reduction according to equation (4) appears to occur at ~-1.6 V vs. SCE, Figure 7. The reduced n-CdTe exhibits a large cathodic current at sufficiently negative potentials and a return sweep shows surface oxidation presumably corresponding to the oxidation of Cd back to Cd^{2+} and/or Te_x^{2-} to a higher oxidation state. Similar processes have been observed for CdS.[23c,d]

The irreversible oxidation and reduction of the n-CdTe in the potential range where CdTe has been evaluated with respect to E_B is clearly responsible for the changes in E_B that occur with successive cyclic voltammetry scans. Unfortunately, it does not appear that it is possible to electrochemically repair damage that results from photoanodic decomposition. Nor does electrochemical reduction of oxidized n-CdTe from the oxidizing etch change the surface to that generated by the reducing etch procedure. Both the surface electrochemistry and the surface redox chemistry involving the etch solutions is complicated and it does not appear that complete characterization is possible by using only electrochemical techniques. In the section below, we describe surface analyses by XPS and Auger that confirm the rough chemical expectations from an oxidizing vs. reducing pretreatment of CdTe.

c. X-Ray Photoelectron Spectra and Auger Analysis of n-CdTe. Figures 8 and 9 show the XPS and Auger spectra for representative samples of reduced and oxidized CdTe. The spectra show qualitative differences for the oxidized and reduced CdTe. From the oxidizing etch it is logical to conclude that the surface is rich in some form of Te. Previous workers have shown that a Te film can be formed on the surface, and Auger and XPS spectra of CdTe surfaces treated with $HNO_3/H_2O/K_2Cr_2O_7$ solutions are consistent with the formation of a rather thick, Te-rich overlayer.[24-26] As the earlier workers found, we find that the oxidizing etch yields a surface that does not exhibit a significant signal for Cd. A surface that has been reduced exhibits a strong Cd signal in both the Auger and XPS spectra. Other important features of the spectra are given below.

The reducing etch yields a surface that has a number of impurities that would appear to derive from the etch solution: S, Na, and Cl are present in addition to the ubiquitous C and O. The expected signals for the elements Cd and Te are easily detected and appear as important features in Auger and XPS. Sputtering the surface of either the oxidized or reduced CdTe yields a clean spectrum for CdTe which, excepting for selective sputtering, is probably the spectrum of Cd and Te very close to the 1/1 stoichiometry of CdTe. The XPS of the reduced CdTe in the Cd region, Figure 9, show the Cd signals to be at nearly the same binding energy as for the sputtered surface. However, the signals in the Te region provide evidence for at least two types of Te. One of the sets of signals in the Te region is likely due to Te^{2-}, matching the binding energy for the sputtered surface. The higher binding energy set of Te peaks is logically due to an oxidized form of Te. In fact, the samples are exposed to air and it is likely that the Te signals are the same as those obtained from air oxidation of a cleaved crystal. Others have assigned the air oxidation product to TeO_2[25] and the observation of an O signal is consistent with such a conclusion. But the main point is that both Cd^{2+} and Te^{2-} are easily detectable from the reducing etch.

Use of Ar^+ sputtering can result in surface chemistry to change the oxidation level of the surface species.[27] However, the Cd signals for reduced CdTe are at the same position as for the sputtered sample suggesting that Ar^+ does not affect the Cd^{2+} presumably present. Further, sputtering the reduced surface removes the set of higher binding energy Te signals consistent with the removal of the more oxidized Te material leaving Te^{2-}. Thus, we believe that surface damage due to the sputtering technique is relatively unimportant.

The oxidizing etch of CdTe shows impurity signals C, O, and Cr in the electron spectroscopies. The C and O are omnipresent; the Cr logically comes from the use of $K_2Cr_2O_7$ in the etch solution. The Cr is unequivocally detected in the Auger spectrum, Figure 8; the XPS spectrum is equivocal because the Te and Cr binding energies are very similar. The ~580 eV binding energy region for the oxidized CdTe, Figure 9, is very different than the reduced CdTe. Two, relatively broad signals are observed whose peak positions do not match any of the signals for reduced CdTe. Inasmuch as Cr is detectable in the Auger of the same sample and the Cr XPS signals are about as intense as those for Te,[18] it is likely that some of the intensity in the ~580 eV region is due to some form of Cr. But, since Te is observable in the Auger, some of the intensity is due to some form of Te. Photooxidation of the reduced CdTe or treatment of CdTe with Br_2/MeOH yields a high ratio of the lower energy to the higher energy Te peaks than the ratio observed for reduced CdTe. Thus, the pair of lower binding peaks are logically a combination of Te_x^{2-} and Te^{2-} consistent with the insensitivity of the binding energy to changes in x in Te_x^{2-}.[18] The higher binding energy Te peaks are likely due to TeO_2.[25] Interestingly, the oxidizing etch of Br_2 in CH_3OH does not yield a surface that is as Te-rich as we find for etch (i).[24,25] In fact, the Br_2/CH_3OH etch appears to yield a Cd/Te element ratio that is close to that for the sputtered surface. The Br_2 must be capable of oxidatively removing elemental Te that is initially formed by the oxidation of the surface such that the Te_x^{2-} layer is qualitatively thinner than with etch (i). The oxidizing etch used for most of our work produces a very Cd-deficient surface, and we associate the difference in photovoltaic response of reduced and oxidized CdTe with the difference in the amount of Te^{2-} at the surface.

Discussion

In electronic device applications and energy conversion applications the surface chemistry of materials can be an important limiting parameter. For CdTe, a material having nearly optimum response to the solar spectrum, photovoltaic devices could give high efficiency. However, the Fermi level pinning yields a relatively low output photovoltage. We have demonstrated that the surface pretreatment associated with the use of several oxidizing etchants results in a Te-rich (Cd-deficient) surface. We associate the Fermi level pinning with the overlayer of Te-rich material. A reducing etch for the CdTe generates a surface that is close to the expected Cd/Te stoichiometry, and in this case the CdTe behaves as a nearly ideal semiconductor with an output photovoltage of up to ~0.9 V using the $TMPD^{+/0}$ redox couple. The ~0.9 V output photovoltage exceeds the photovoltage from the Fermi level pinned system by 0.3 - 0.4 V. However, the removal of Fermi level pinning results in zero photovoltage for redox couples that have $E_{\frac{1}{2}}$ more negative than ~-1.0 V vs. SCE, while the Fermi level pinned CdTe gives ~0.5 V for such couples.

The demonstration that Fermi level pinning can be manipulated by surface chemistry is an important finding inasmuch as the phenomenon of Fermi level pinning seems to be fairly common for small band gap materials. If the pinning results in a large photovoltage relative to E_g as in the case of p-InP[28] there may be no advantage in removing pinning, but when the photovoltage is a small fraction of E_g the pinning is a serious drawback. The removal of Fermi level pinning for n-CdTe does not alter the extreme susceptibility of n-CdTe to photoanodic decomposition at sufficiently positive potentials. However, our results suggest that examination of the Schottky barrier, n-CdTe/metal, behavior using the reducing etch to pretreat the CdTe would be worthwhile. It may be possible to prepare durable n-CdTe/metal interfaces that give good photovoltages. Previously, it was determined that a photovoltage of 0.68 V could be obtained for Schottky barriers using CdTe;[4a] our data suggest that the reducing etch pretreatment could improve this value.

If we take the Te-rich overlayer on oxidized CdTe to be a layer of elemental Te we can understand the Fermi level pinning of the CdTe to be due to the contact of the underlying CdTe by the Te layer. Support for the conclusion that the overlayer is in fact elemental Te comes from the original literature concerning the oxidizing etch.[12b] Elemental Te is known to have significant conductivity and can be regarded as semimetallic.[29] Contacting the outer Te layer with either metals or a liquid electrolyte will not alter the CdTe/Te interface energetics.[5] Thus, the photovoltage is fixed to the value associated with the CdTe coated by a relatively thick Te overlayer. We should emphasize that this may not be the only mechanism for Fermi level pinning of CdTe. For example, the CdTe/metal barrier height changes by only ~0.2 V for a 1.5 V change in ; for the contacting metal[4] where CdTe is pretreated with the Br_2/CH_3OH etch that yields a near stoichiometric Cd/Te surface.[24-26] The pinning in this instance may be due to interface states associated with a much thinner layer of Te on the surface. If a sufficient density of interface states results from reaction with a metal contact the prospects are not good for improving photovoltage for the CdTe/metal system by using a reducing pretreatment for CdTe. In this connection it is noteworthy that two earlier studies[3] of n-CdTe/liquid interfaces report the use of the Br_2/CH_3OH pretreatment and claim some results that parallel our findings for the reducing etch. However, photovoltages were not as high as those obtained here and greater difficulty with reproducibility was apparently encountered. It may be that the most efficient devices would then be those based on liquid electrolyte contacts, but the lack of durability remains a major hurdle to the achievement of any useful photoelectrochemical device from exploitation of a reducing etch procedure for n-CdTe. The results, though, do establish that a reproducible surface pretreatment can yield reproducible photovoltage measurements. Further, the finding that Fermi level pinning can be removed establishes that the extent of ionic vs. covalent bonding in the series CdS, CdSe, and CdTe does not control the value of E_B or its dependence on ϕ or E_{redox}.[4b] Rather, the presence of a layer of semimetallic Te on CdTe can rationalize the earlier observation[2] of a constant E_B vs. E_{redox} for n-CdTe. This work thus establishes one mechanism for Fermi level pinning. Preserving the integrity of the reduced CdTe surface is now the object of our future studies using n-CdTe photoanodes.

Acknowledgements. We thank the Office of Naval Research for partial support of this research. Partial support of the research activities of Shinichi Tanaka from the M.I.T. Center for Advanced Engineering Studies and from the Toyobo Co. Ltd. is gratefully acknowledged.

References

1. Participant in programs of the Center for Advanced Engineering Studies at M.I.T. while on leave from Toyobo Co., Ltd., Osaka, Japan, 198[illegible]

2. Aruchamy, A.; Wrighton, M.S. J. Phys. Chem., 1980, 84, 2848.

3. (a) Nadjo, L. J. Electroanal. Chem., 1980, 108, 29; (b) Sculfort, [illegible] Baticle, A.M. Revue Phys. Appl., 1980, 15, 1209.

4. (a) Ponpon, J.P.; Siffert, P. Rev. Phys. Appl., 1977, 12, 42[illegible] (b) McGill, T.C. J. Vac. Sci. Technol., 1974, 11, 935; (c) Mead, [illegible] Spitzer, W.G. Phys. Rev., 1964, 134, A713.

5. Bard, A.J.; Bocarsly, A.B.; Fan, F.-R. F.; Walton, E.G.; Wrighton, M.[illegible] J. Am. Chem. Soc., 1980, 102, 3671.

6. Lin, M.S.; Hung, N.; Wrighton, M.S., to be submitted.

7. Gerischer, H. J. Electroanal. Chem., 1975, 58, 263.

8. Turner, J.A.; Manassen, J.; Nozik, A.J. Appl. Phys. Lett., 198[illegible]

9. Kautek, W.; Gerischer, H. Ber. Bunsenges. Phys. Chem., 1980, 84, 64[illegible]

10. Heller, A.; Parkinson, B.A.; Miller, B. Appl. Phys. Lett., [illegible], 3[illegible], 521.

11. Heller, A.; Lewerenz, H.J.; Miller, B. Ber. Bunsenges. Phys. Chem., 1980, 84, 592.

12. (a) Warekois, E.P.; Lavine, M.C.; Mariano, A.N.; Gatos, H.C. J. Appl. Phys., 1962, 33, 690; (b) Ichimiya, T.; [illegible], T.; Mizuma, K.; [illegible], J.; Kamiya, Y.; Ono, K. "Solid State Physics in Electronics and Telecommunications", Vol. 2, Academic Press, 1960, p. 845.

13. Heller, A.; Chang, K.C.; Miller, B. J. Electrochem. Soc., 197[illegible]

14. Gerischer, H. J. Electrochem. Soc., 1977, 82, 133.

15. Inoue, M.; Teramoto, I.; Takayanagi, S. J. Appl. Phys., 1961, [illegible]

16. (a) Schneemeyer, L.F.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 10[illegible], [illegible] and 1979, 101, 6496; (b) Bocarsly, A.B.; Bookbinder, D.C.; Dominey, [illegible] Lewis, N.S.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3683

17. Davis, L.E.; MacDonald, N.C.; Palmberg, P.W.; Riach, G.E.; Weber, G.E. "Handbook of Auger Electron Spectroscopy", 2nd ed., Perkin-Elmer Corporation, Eden Prairie, MN, 55343, 1976.

18. Wagner, C.D.; Riggs, W.M.; Davis, L.E.; Moulder, J.F.; Muilenberg, G.E. "Handbook of X-Ray Photoelectron Spectroscopy", Perkin-Elmer Corp., Eden Prairie, MN, 55343, 1979.

19 (a) Frank, S. N.; Bard, A. J. J. Am. Chem. Soc., 1975, 97, 7427.
(b) Kohl, P. A.; Bard, A. J. J. Am. Chem. Soc., [illegible].
(c) Laser, D.; Bard, A. J. J. Phys. Chem., [illegible], 459.

20 (a) Ellis, A. B.; Kaiser, S. W.; Bolts, J. M.; Wrighton, M. S.
J. Am. Chem. Soc., 1977, 99, 2839. (b) Minoura, H.; Watanabe, T.;
Oki, T.; Tsuiki, M. Japan. J. Appl. Phys., 1977, 16, 865.
(c) Minoura, H.; Tsuiki, M.; Oki, T. Ber. Bunsenges. Phys. Chem.,
1977, 81, [illegible]. (d) Ginley, D. S.; Butler, M. A. J. Electrochem. Soc.,
19[illegible], 12[illegible], [illegible].

21 [illegible] Tributsch, H.; Gerischer, H. J. Electrochem. Soc.,
[illegible].

22 (a) [illegible], A. [illegible]; Wrighton, M. S. J. Electrochem. Soc., 1977, 124, [illegible].
[illegible] J. Electroanal. Chem., 1977, [illegible].
[illegible] Tsubomura, H. J. Electrochem. [illegible],
[illegible] Schneemeyer, L. F.; Wrighton, M. S.; Stacy, A.;
Sienko, M. J. Appl. Phys. Lett., 1980, 36, 701.

23 [illegible] Kaiser, S. W.; Wrighton, M. S. J. Am. Chem. Soc., [illegible],
[illegible] Gerischer, H.; Mindt, W. Electrochim. Acta, [illegible],
[illegible] Gerischer, H. Electrochim. Acta, [illegible],
[illegible] Fujishima, A.; Honda, K. Chem. Lett., [illegible].

24 [illegible] J. Electrochem. Soc., [illegible], 424

25 [illegible] Phys. [illegible] J. Appl. Phys., [illegible].

26 [illegible] Saxena, A. N.; Siffert, P. Appl. Phys. [illegible].

27 [illegible] Wandelt, K. Thin Solid Films, [illegible].

28 [illegible] Lewis, N. S.; Wrighton, M. S. J. Am. Chem. Soc., [illegible],
[illegible].

29 [illegible] Advanced Inorganic Chemistry, 4th ed.,
[illegible].

Table I. Barrier Height Determinations for Oxidized n-CdTe by Cyclic Voltammetry for Various Redox Couples in CH_3CN or H_2O.[a]

Redox Couple (Class), #[b]	$E_{1/2}$	Solvent	$E_{PA,Pt}$	$E_{PA,n\text{-}CdTe,illum.}$	E_V, V (±100 mV)
$TMPD^{2+/+}$ (IV), 1	+0.70	CH_3CN	+0.72	+0.13	0.59
$TMPD^{+/0}$ (IV), 2	+0.10	CH_3CN	+0.14	-0.45	0.59
$Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$ (IV), 3	+0.40	CH_3CN	+0.43	-0.19	0.62
$Fe(\eta^5\text{-}C_5Me_5)_2^{+/0}$ (IV), 4	-0.12	CH_3CN	-0.07	-0.62	0.55
$MV^{2+/+}$ (IV), 5	-0.45	CH_3CN	-0.41	-0.93	0.52
$MV^{+/0}$ (IV), 6	-0.85	CH_3CN	-0.82	-1.32	0.50
$Ru(bpy)_3^{2+/+}$ (IV), 7	-1.34	CH_3CN	-1.29	-1.77	0.48
$Ru(bpy)_3^{+/0}$ (IV), 8	-1.49	CH_3CN	-1.48	-1.99	0.51
$Ru(bpy)_3^{0/-}$ (IV), 9	-1.73	CH_3CN	-1.71	-2.32	0.61
$Anthracene^{0/-}$ (IV)	-1.99	CH_3CN	-1.95	-2.24	0.29
$Fe(CN)_6^{3-/4-}$ (IV), 1	+0.21	H_2O	+0.30	-0.31	0.61
$TMPD^{+/0}$ (IV), 2	+0.02	H_2O	+0.06	-0.43	0.49
$Ru(NH_3)_6^{3+/2+}$ (IV), 3	-0.19	H_2O	-0.12	-0.64	0.52
$AQ^{0/2-}$ (IV), 4	-0.56	H_2O	-0.40[c]	-0.93	0.53
$MV^{2+/+}$ (IV), 5	-0.61	H_2O	-0.54[c]	-1.07	0.53
$TQ^{2+/+}$ (IV), 6	-0.81	H_2O	-0.77[c]	-1.15	0.38

---

[a] Conditions for etching and cyclic voltammetry are given in the Experimental unless otherwise noted. Data for CH_3CN are from ref. 2. All potentials, $E_{1/2}$, $E_{PA,Pt}$, $E_{PA,n\text{-}CdTe,illum.}$, are given in volts vs. SCE.

[b] # refers to data points on plots in Figure 1. For Class definitions see text.

[c] Measured at Hg working electrode.

Table II. Barrier Height Determinations for Reduced n-CdTe by Cyclic Voltammetry for Various Redox Couples in CH_3CN or H_2O.[a]

Redox Couple (Class), ≠[b]	$E_{1/2}$	Solvent	$E_{PA,Pt}$	$E_{PA,n\text{-}CdTe,illum.}$	E_B, V (±100 mV)
$TMPD^{2+/+}$ (III,V), 1	+0.70	CH_3CN	+0.79	+0.22	0.57
$Fe(\eta^5\text{-}C_5H_5)_2{}^{+/0}$ (III,V), 2	+0.40	CH_3CN	+0.48	-0.26	0.74
$TMPD^{+/0}$ (III), 3	+0.10	CH_3CN	+0.19	-0.53	0.72
$Fe(\eta^5\text{-}C_5Me_5)_2{}^{+/0}$ (III), 4	-0.12	CH_3CN	-0.07	-0.69	0.62
$TQ^{2+/+}$ (III), 5	-0.59	CH_3CN	-0.52	-0.76	0.24
$TQ^{+/0}$ (III), 6	-0.89	CH_3CN	-0.82	-1.00	0.18
$Ru(bipy)_3{}^{2+/+}$ (I)	-1.34	CH_3CN	-1.29	-1.29 (dark or light)	0.00
$Ru(bipy)_3{}^{+/0}$ (I)	-1.49	CH_3CN	-1.48	-1.48 (dark or light)	0.00
$TMPD^{+/0}$ (III), 1	+0.02	H_2O	+0.07	-0.79	0.86
$Ru(NH_3)_6{}^{3+/2+}$ (III), 2	-0.19	H_2O	-0.14	-0.70	0.56
$Eu^{3+/2+}$ (III), 3	-0.64	H_2O	-0.54	[illegible]	0.48
$TQ^{2+/+}$ (III), 4	-0.81	H_2O	-0.77[c]	-1.03	0.26

[a] Conditions as in Table I and Experimental.

[b] ≠ refers to data entries on plots in Figure 1. For Class definition see text

[c] Measured at Hg working electrode.

Figure Captions

Figure 1. Plots of photovoltage for n-CdTe treated with either the reducing or oxidizing etch as a function of the E_{redox} of the solution. Data are determined by cyclic voltammetry as described in the text and in the Experimental. The numbers for the individual data points are keyed to the redox couples in Tables I and II.

Figure 2. Representative data for cyclic voltammetry of the $Fe(CN)_6^{3-/4-}$ couple at a Pt electrode and an oxidized n-CdTe electrode.

Figure 3. Cyclic voltammetry for the $TQ^{2+/+\cdot}$ and for the $TQ^{+\cdot/0}$ couples at Pt and at reduced n-CdTe.

Figure 4. Cyclic voltammetry on the left compares the response of $Fe(\eta^5-C_5H_5)_2^{+/0}$ at Pt and reduced n-CdTe. The data on the right illustrate the consequences of photoanodic decomposition of n-CdTe by a positive excursion beyond the photoanodic current peak for the $Fe(\eta^5-C_5H_5)_2^{+/0}$ couple. Scan 1 is the first scan and scan 2 is the second scan under the same conditions as the data on the left for n-CdTe.

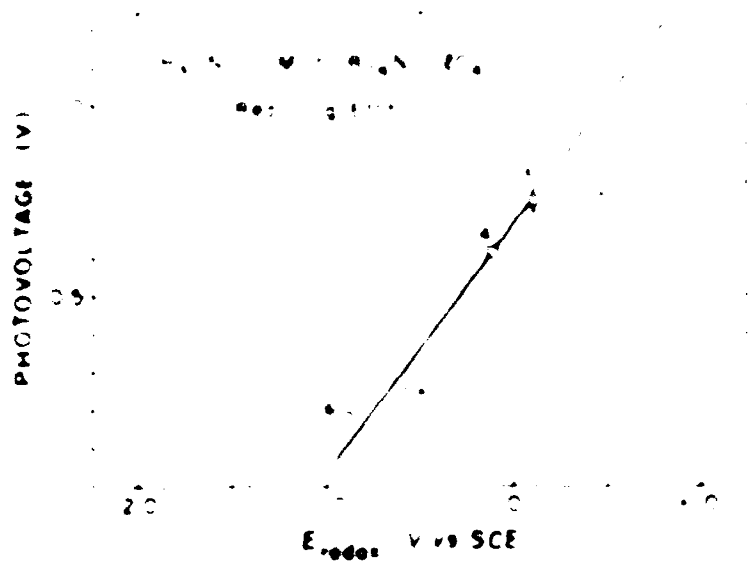
Figure 5. Cyclic voltammetry for $TMPD^{2+/+}$ (positive peak) and $TMPD^{+/0}$ (negative peak) at illuminated (reduced) n-CdTe on the first scan, 1 (——), and second scan, 2 (----), from an initial potential of -1.0 V vs. SCE.

Figure 6. Comparison of cyclic voltammetry for TMPD at Pt and reduced n-CdTe showing almost 0.9 V more negative $TMPD \rightarrow TMPD^{+\cdot}$ peak at illuminated n-CdTe compared to Pt. The dashed curve for n-CdTe is the dark response.

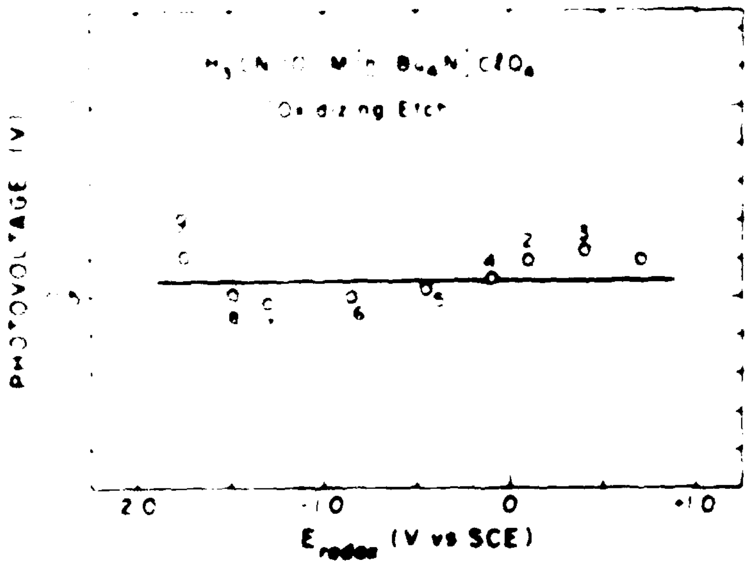
Figure 7. (Left) Dark cathodic current of n-CdTe in H_2O/0.1 M $NaClO_4$ at 5 mV/s. (a) n-CdTe etched with etchant (i) in the Experimental, (b) n-CdTe etched with the reducing etch; (c) reduced n-CdTe scanned once from -1.4 to +0.35 V vs. SCE at 100 mV/s under illumination (50 mW/cm^2) in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ to oxidize the surface. In each case the initial potential is 0.0 V vs. SCE. (Right) Dark current voltage curve of n-CdTe etched with the reducing etch in H_2O/0.1 M $NaClO_4$ at [illegible]. The cathodic limit for (a) (——) is -1.9 V vs. SCE and significant oxidation current results on the return sweep. A freshly reduced electrode scanned to -1.4 V vs. SCE, (b) (----), shows neither [illegible] oxidation nor reduction current. The initial potential [illegible] 0.0 V vs. SCE.

Figure 8. Left three spectra are XPS spectra (scale [illegible] the right three spectra are Auger spectra. The top spectra are [illegible] etched using reducing etch; the middle spectra are for n-CdTe [illegible] the oxidizing etch (i), and the bottom spectra are for n-CdTe [illegible] with Ar$^+$ until no changes in the Cd/Te signal ratios are observed. The sensitivity for the Auger spectrum of the sputtered sample [illegible] the other two.

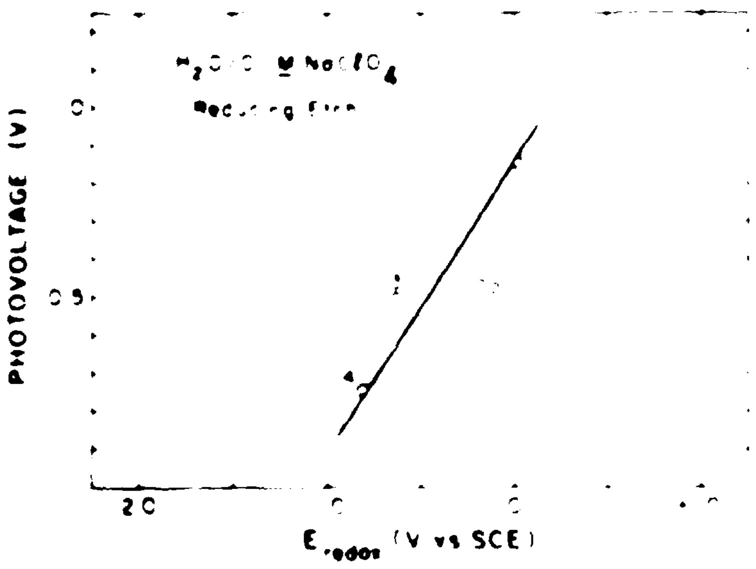
Figure 9. XPS spectra of Te, $3d_{3/2}$ and $3d_{5/2}$ signals for (a) [illegible] CdTe (scale = 1000 counts/div); (b) n-CdTe etched using reducing [illegible] (scale = 300 counts/div); (c) n-CdTe etched using oxidizing etch [illegible] (scale = 300 counts/div). XPS spectra of Cd, $3d_{3/2}$ and $3d_{5/2}$ [illegible] (d) Ar$^+$ sputtered n-CdTe (scale = 1000 counts/div) and (e) n-CdTe etched using the reducing etch (scale = 300 counts/div). The samples [illegible] are the same used for the spectra shown in Figure 8



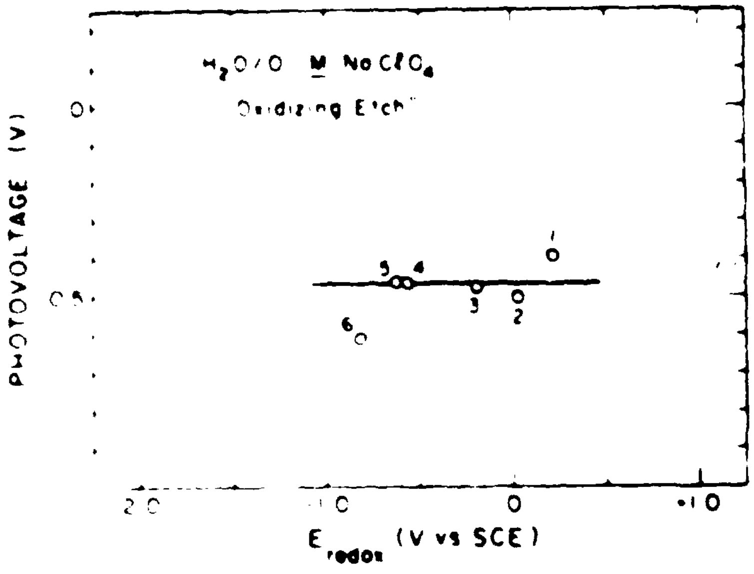
M n-Bu₄N ClO₄
Reducing Etch
PHOTOVOLTAGE (V)
0.5
2.0
1.0
0
+1.0
E_redox (V vs SCE)



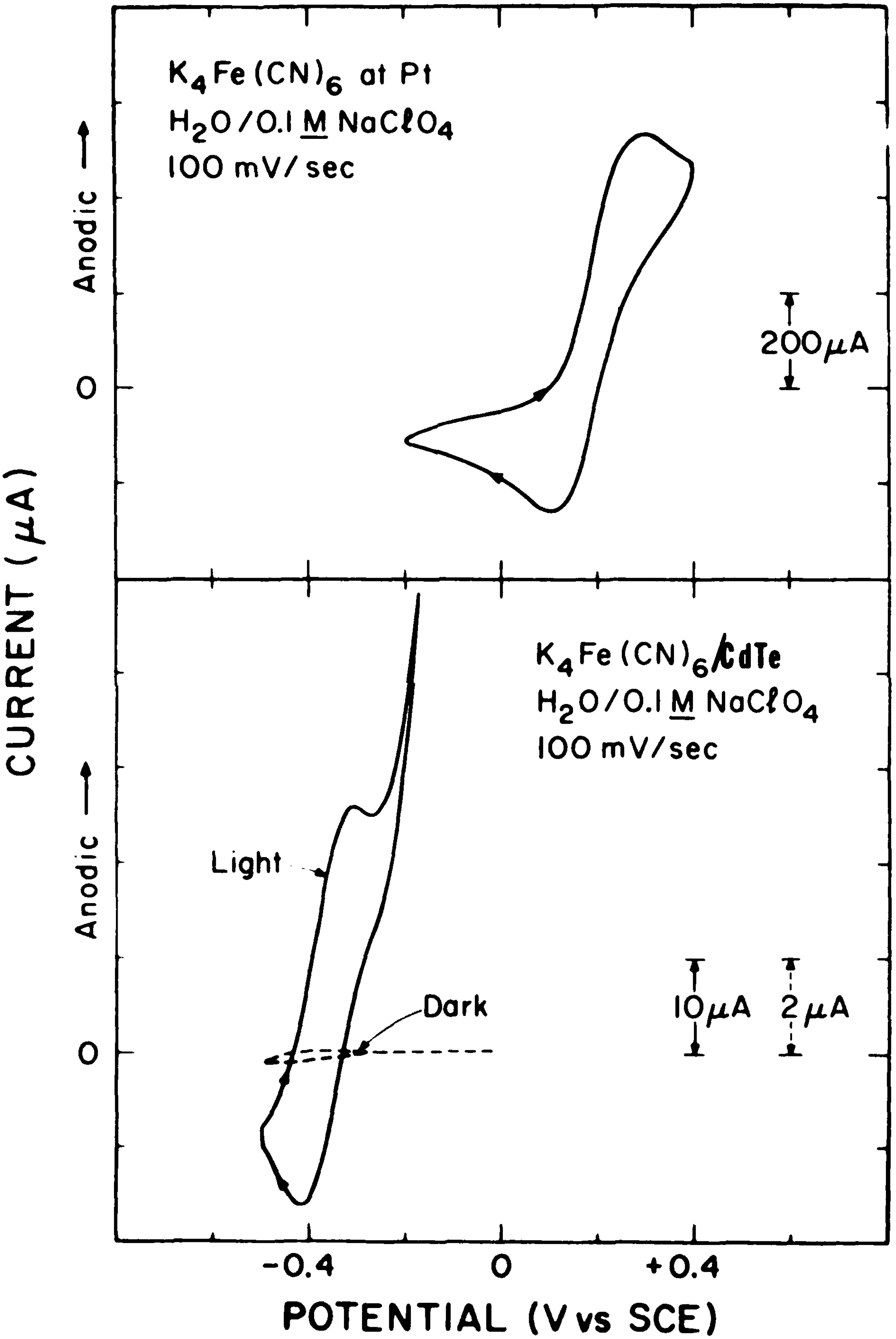
H₃CN/0 M n-Bu₄N ClO₄
Oxidizing Etch
PHOTOVOLTAGE (V)
0.5
2.0
1.0
0
+1.0
E_redox (V vs SCE)

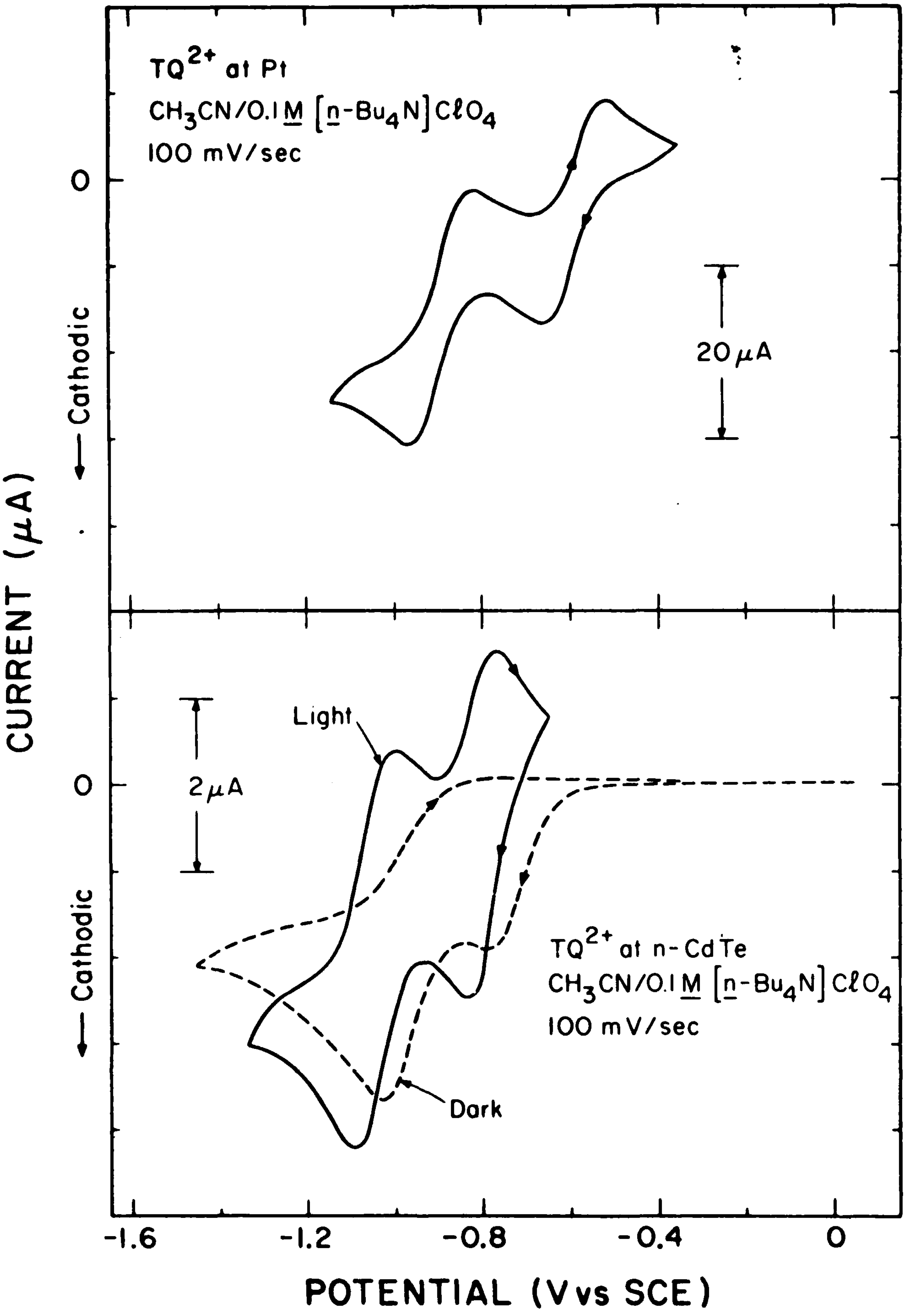


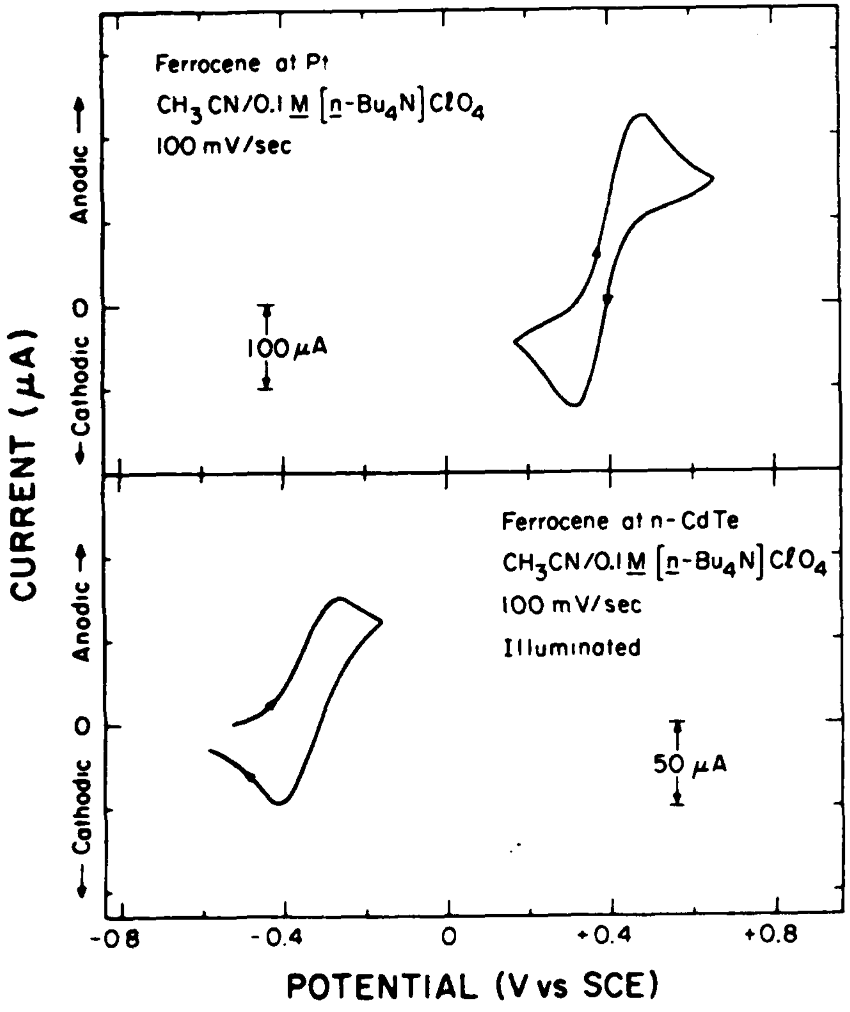
H₂O/0 M NaClO₄
Reducing Etch
PHOTOVOLTAGE (V)
0
0.5
2.0
1.0
0
+1.0
E_redox (V vs SCE)

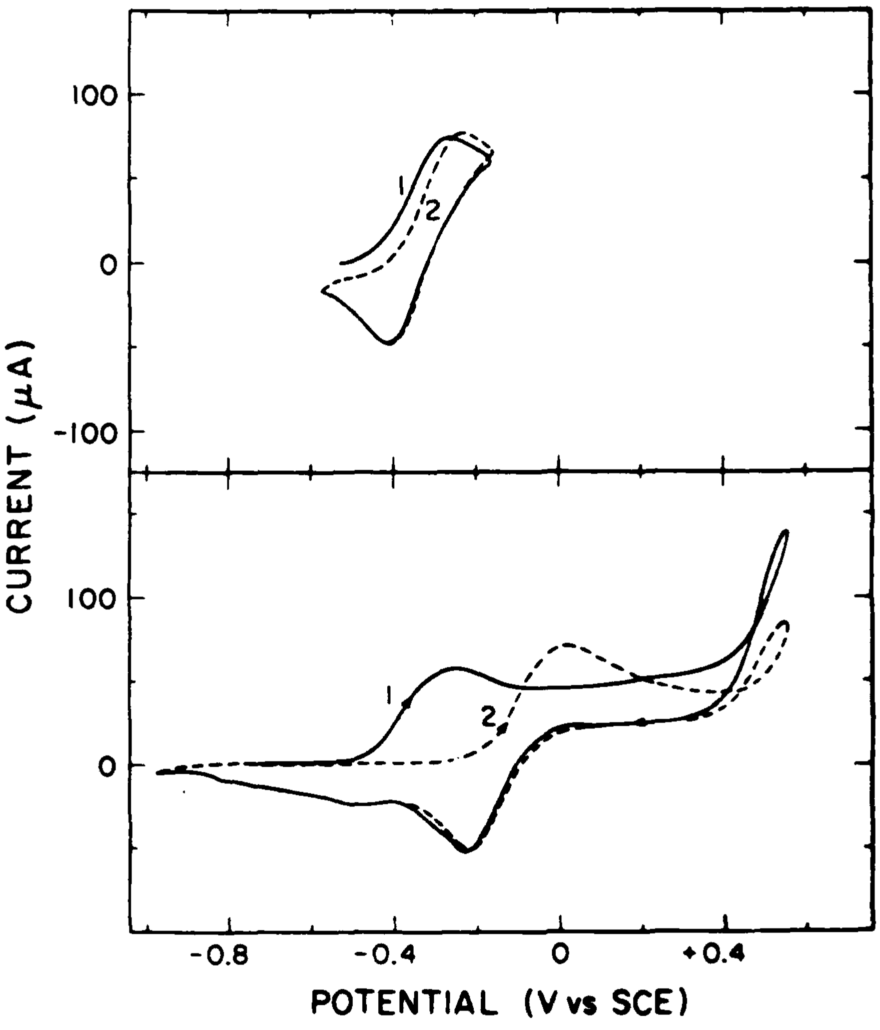


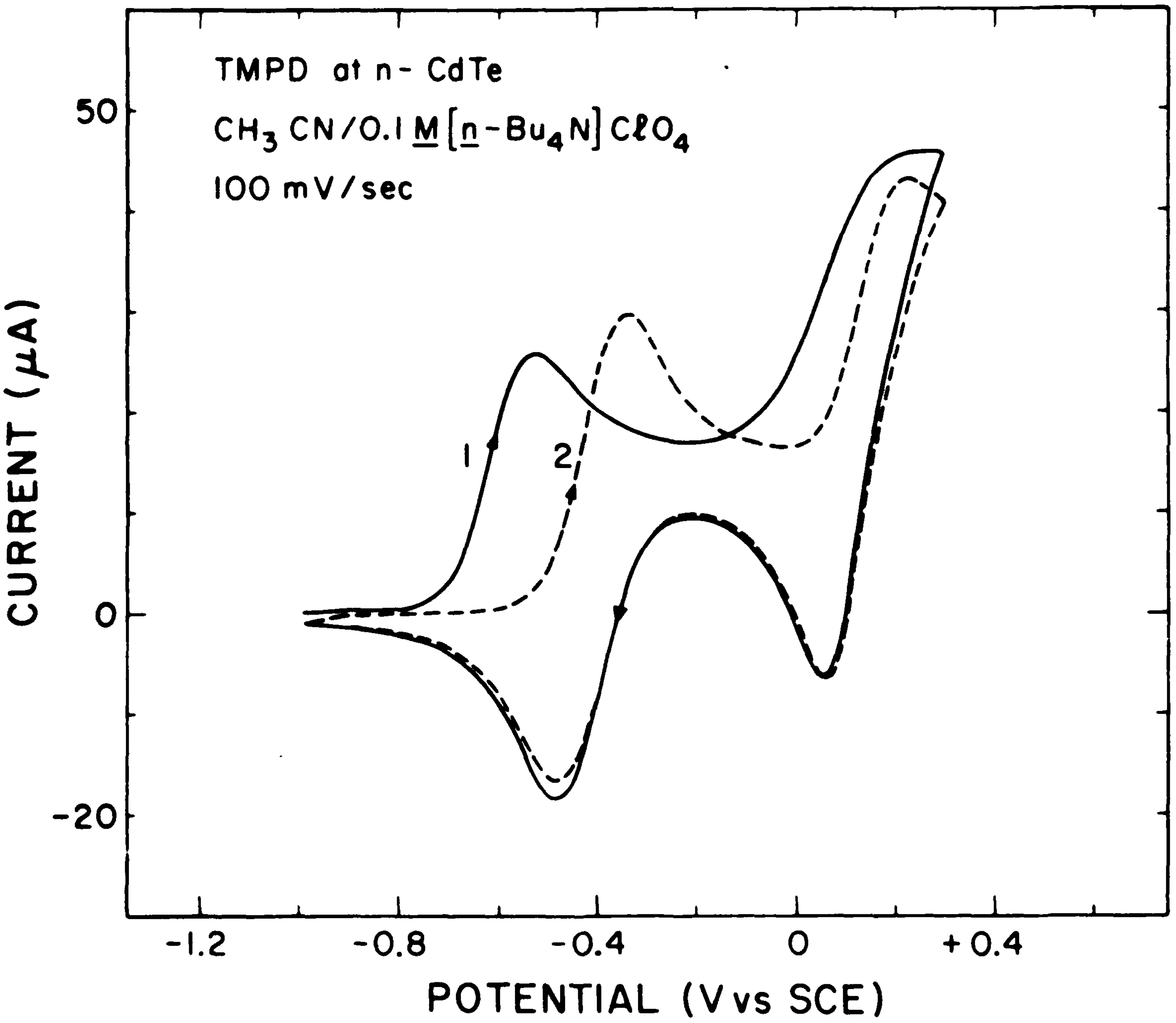
H₂O/0 M NaClO₄
Oxidizing Etch
PHOTOVOLTAGE (V)
0
0.5
2.0
1.0
0
+1.0
E_redox (V vs SCE)

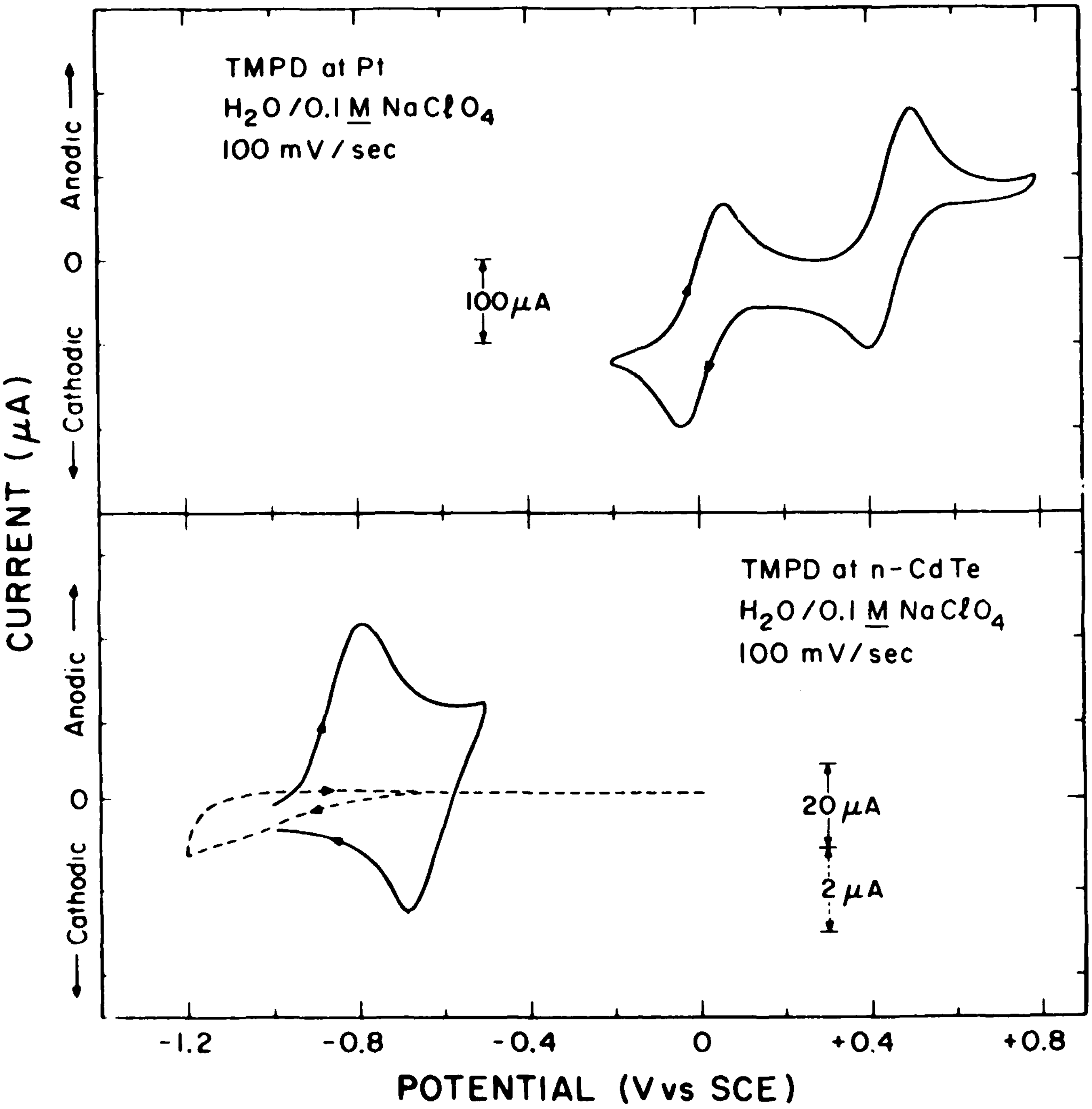

K4Fe(CN)6 at Pt
H2O/0.1 M NaClO4
100 mV/sec
Anodic →
0
200μA
K4Fe(CN)6/CdTe
H2O/0.1 M NaClO4
100 mV/sec
Anodic →
Light
Dark
0
10μA
2μA
-0.4
0
+0.4
CURRENT (μA)
POTENTIAL (V vs SCE)


TQ^{2+} at Pt
CH$_3$CN/0.1 M [n-Bu$_4$N]ClO$_4$
100 mV/sec
20 μA
0
← Cathodic
CURRENT (μA)
Light
2 μA
0
← Cathodic
TQ^{2+} at n-CdTe
CH$_3$CN/0.1 M [n-Bu$_4$N]ClO$_4$
100 mV/sec
Dark
-1.6
-1.2
-0.8
-0.4
0
POTENTIAL (V vs SCE)

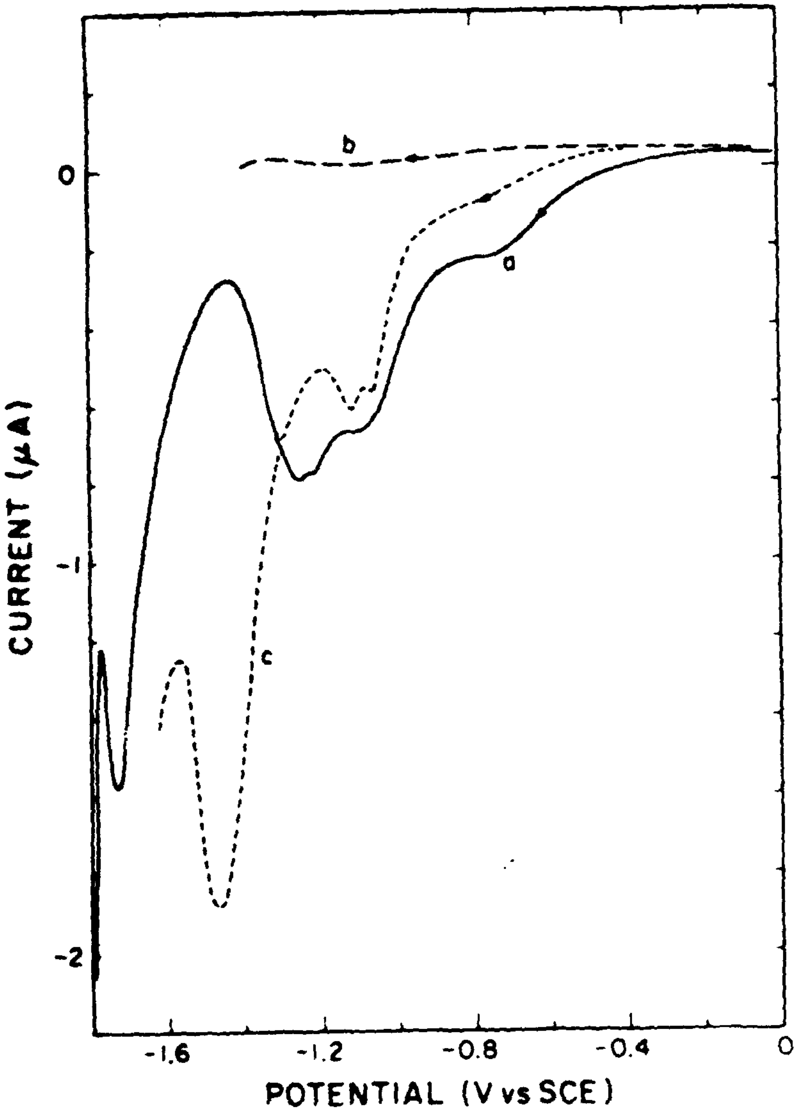

Ferrocene at Pt
$CH_3CN/0.1\,\underline{M}\,[\underline{n}\text{-}Bu_4N]ClO_4$
100 mV/sec
100 μA
Ferrocene at n-CdTe
$CH_3CN/0.1\,\underline{M}\,[\underline{n}\text{-}Bu_4N]ClO_4$
100 mV/sec
Illuminated
50 μA
CURRENT (μA)
Anodic
0
Cathodic
-0.8
-0.4
0
+0.4
+0.8
POTENTIAL (V vs SCE)

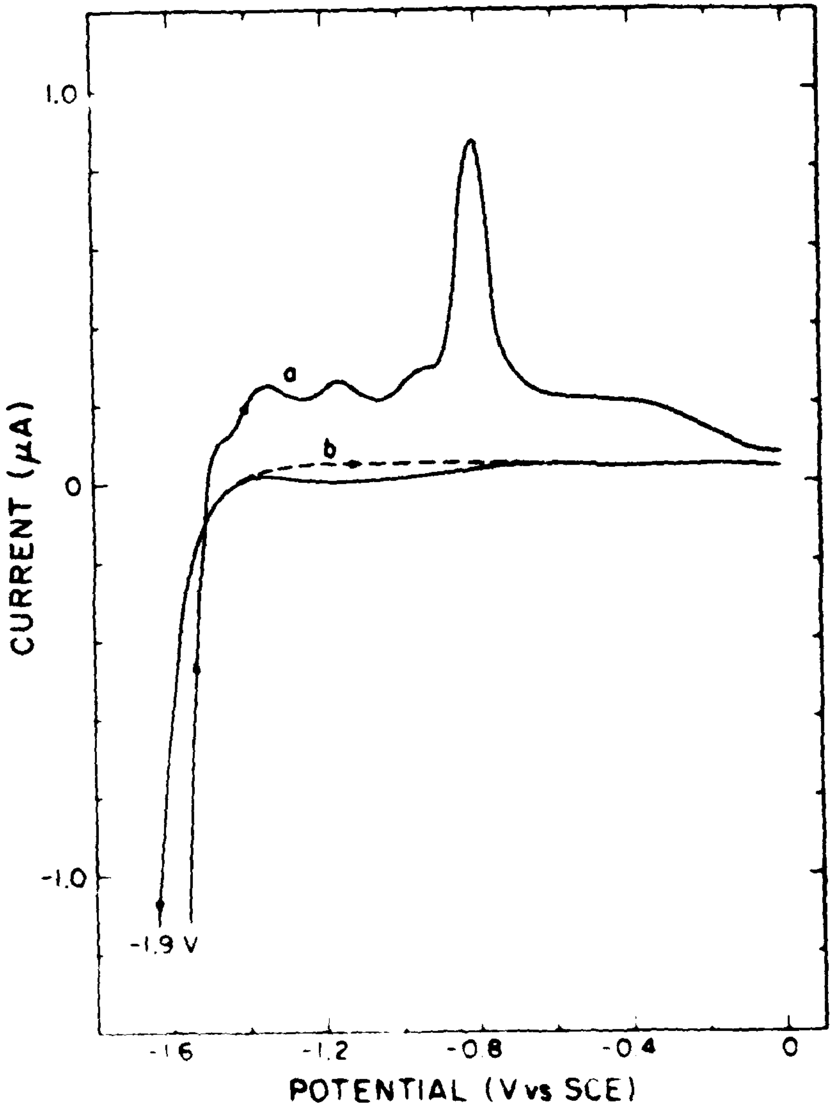

CURRENT (μA)
100
0
-100
1
2
-0.8
-0.4
0
+0.4
POTENTIAL (V vs SCE)

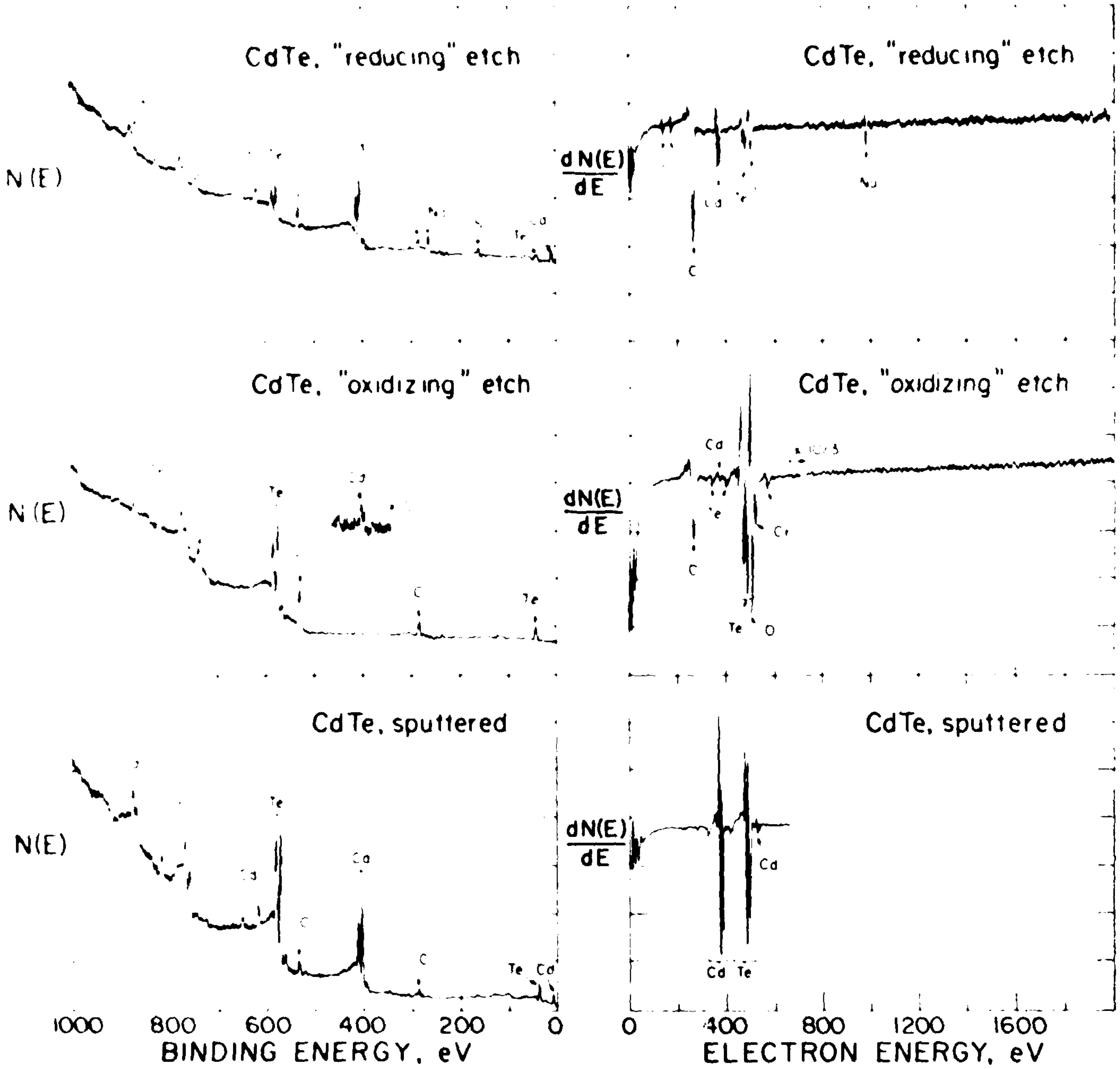

TMPD at n- CdTe
$CH_3CN/0.1\,\underline{M}\,[\underline{n}\text{-}Bu_4N]Cl O_4$
100 mV/sec
1
2
CURRENT (μA)
50
0
-20
-1.2
-0.8
-0.4
0
+0.4
POTENTIAL (V vs SCE)

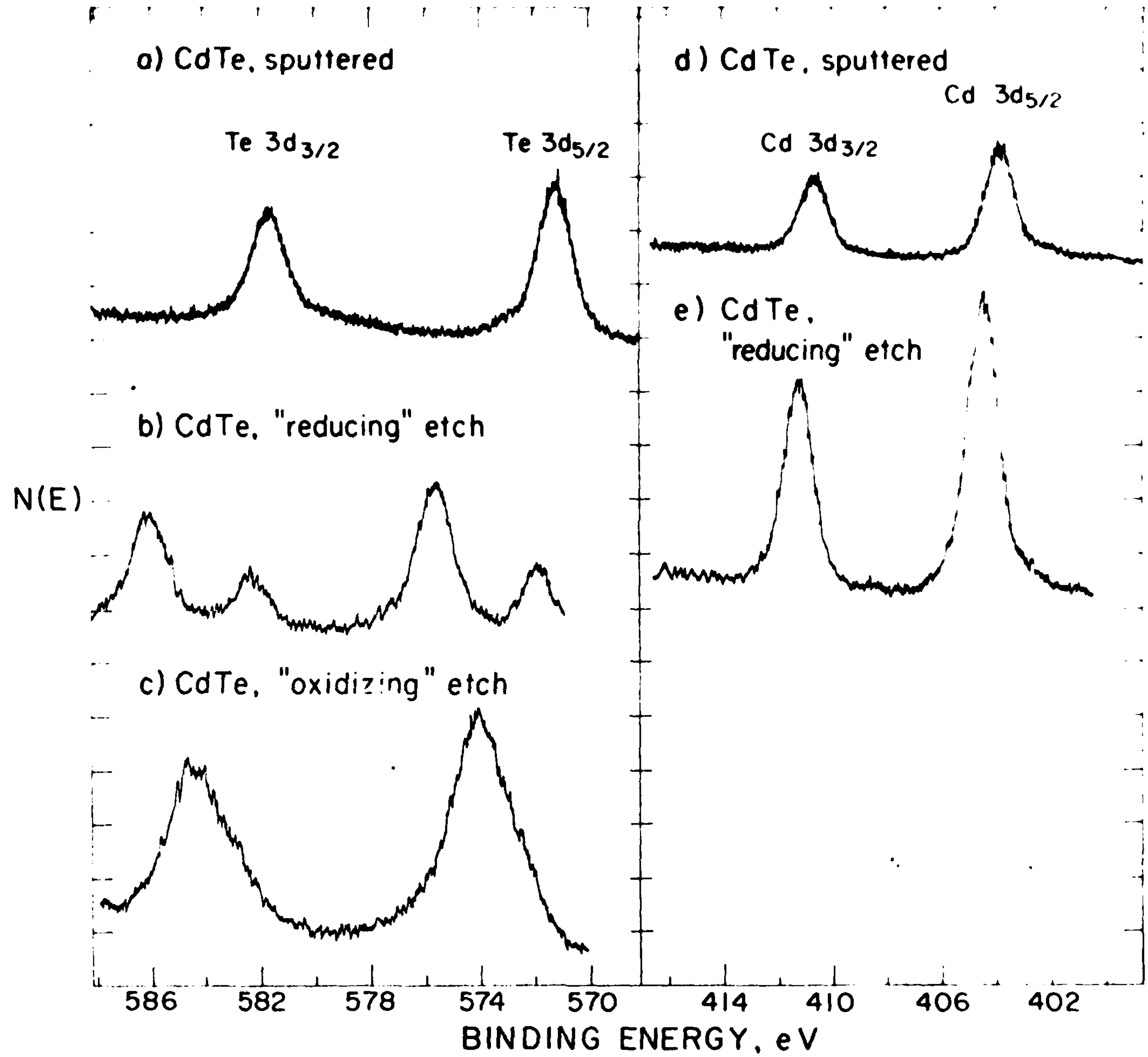


TMPD at Pt
$H_2O/0.1\ \underline{M}\ NaClO_4$
100 mV/sec
100 μA
TMPD at n-CdTe
$H_2O/0.1\ \underline{M}\ NaClO_4$
100 mV/sec
20 μA
2 μA
CURRENT (μA)
← Cathodic
Anodic →
0
← Cathodic
Anodic →
0
-1.2
-0.8
-0.4
0
+0.4
+0.8
POTENTIAL (V vs SCE)


CURRENT (μA)
0
-1
-2
POTENTIAL (V vs SCE)
-1.6
-1.2
-0.8
-0.4
0
a
b
c


CURRENT (μA)
1.0
0
-1.0
POTENTIAL (V vs SCE)
-1.6
-1.2
-0.8
-0.4
0
a
b
-1.9 V


CdTe, "reducing" etch
N(E)
Te
Na
Te
Cd
CdTe, "reducing" etch
dN(E)/dE
C
Cd
Te
Na
CdTe, "oxidizing" etch
N(E)
Te
Cd
C
Te
CdTe, "oxidizing" etch
dN(E)/dE
Cd
C
Te
Te
O
Cr
CdTe, sputtered
N(E)
Te
Cd
Cd
C
C
Te
Cd
CdTe, sputtered
dN(E)/dE
Cd
Cd
Te
1000
800
600
400
200
0
BINDING ENERGY, eV
0
400
800
1200
1600
ELECTRON ENERGY, eV


a) CdTe, sputtered
Te 3d3/2
Te 3d5/2
b) CdTe, "reducing" etch
c) CdTe, "oxidizing" etch
d) CdTe, sputtered
Cd 3d5/2
Cd 3d3/2
e) CdTe, "reducing" etch
N(E)
586
582
578
574
570
414
410
406
402
BINDING ENERGY, eV

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Office of Naval Research
Attn: Code 472
800 North Quincy Street
Arlington, Virginia 22217 2

ONR Branch Office
Attn: Dr. George Sandoz
536 S. Clark Street
Chicago, Illinois 60605 1

Disestablished
~~New York, New York 10003~~ 1

ONR Western Regional Office
1030 East Green Street
Pasadena, California 91106 1

ONR Eastern Central Regional Office
Attn: Dr. L. H. Peebles
Building 114, Section D
666 Summer Street
Boston, Massachusetts 02210 1

Director, Naval Research Laboratory
Attn: Code 6100
Washington, D.C. 20390 1

The Assistant Secretary
of the Navy (RE&S)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350 1

Commander, Naval Air Systems Command
Attn: Code 310C (H. Rosenwasser)
Department of the Navy
Washington, D.C. 20360 1

Defense Technical Information Center
Building 5, Cameron Station
Alexandria, Virginia 22314 12

Dr. Fred Saalfeld
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375 1

No.
Copies

U.S. Army Research Office
Attn: CRD-AA-IP
P. O. Box 1211
Research Triangle Park, N.C. 27709 1

Naval Ocean Systems Center
Attn: Mr. Joe McCartney
San Diego, California 92152 1

Naval Weapons Center
Attn: Dr. A. B. Amster,
Chemistry Division
China Lake, California 93555 1

Naval Civil Engineering Laboratory
Attn: Dr. R. W. Drisko
Port Hueneme, California 93401 1

Department of Physics & Chemistry
Naval Postgraduate School
Monterey, California 93940 1

Dr. A. L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps
Code RD-1
Washington, D.C. 20380 1

Office of Naval Research
Attn: Dr. Richard S. Miller
800 N. Quincy Street
Arlington, Virginia 22217 1

Naval Ship Research and Development
Center
Attn: Dr. G. Bosmajian, Applied
Chemistry Division
Annapolis, Maryland 21401 1

Naval Ocean Systems Center
Attn: Dr. S. Yamamoto, Marine
Sciences Division
San Diego, California 91232 1

Mr. John Boyle
Materials Branch
Naval Ship Engineering Center
Philadelphia, Pennsylvania 19112 1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
[illegible] Marcus [illegible] Research [illegible] [illegible] San Francisco [illegible]	1
[illegible] [illegible] [illegible], Maryland 21[illegible]	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

No.
Copies

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003 1

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 41106 1

Dr. D. N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, Utah 84602 1

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125 1

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974 1

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974 1

Dr. T. Katan
Lockheed Missiles & Space
Co, Inc.
P.O. Box 504
Sunnyvale, California 94088 1

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135 1

Dr. B. Brummer
EIC Incorporated
55 Chapel Street
Newton, Massachusetts 02158 1

Library
P. R. Mallory and Company, Inc.
Northwest Industrial Park
Burlington, Massachusetts 01803 1

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southhampton SO9 5NH
United Kingdom

Dr. Sam Perone
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Naval Ocean Systems Center
Attn: Technical Library
San Diego, California 92152

Dr. C. E. Mueller
The Electrochemistry Branch
Materials Division, Research
& Technology Department
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910 1

Dr. G. Goodman
Globe-Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201 1

Dr. J. Boechler
Electrochimica Corporation
Attention: Technical Library
2485 Charleston Road
Mountain View, California 94040 1

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063 1

Dr. H. Richtol
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181 1

TECHNICAL REPORT DISTRIBUTION LIST, [illegible]

No.
Copies

[illegible]
Department [illegible]
Northwestern [illegible]
[illegible]

[illegible]
Department [illegible]
University [illegible]
[illegible]
CANADA [illegible]

[illegible]

[illegible]

[illegible]
Department [illegible]
University [illegible]
Southampton [illegible] England

[illegible]
University of Texas
Department of Chemistry
Austin, Texas [illegible] 1

Dr. Janet [illegible]
Department [illegible]
State University of New
York at Buffalo
Buffalo, New York [illegible]

[illegible]
[illegible] Science Center
[illegible] International
[illegible] Avenue
[illegible], California 1

Dr. R. A. Osteryoung
Department of Chemistry
State University of New
York at Buffalo
Buffalo, New York 14214

[illegible]
[illegible] Weapons Center
[illegible]
[illegible]
[illegible], Maryland 20910 1

Mr. James R. Moden
Naval Underwater Systems
Center
Code 3632
Newport, Rhode Island [illegible]

[illegible] AN [illegible]
[illegible]

TECHNICAL REPORT DISTRIBUTION LIST, [illegible]

No. Copies

[illegible]

[illegible] England

[illegible] Davis Highway
[illegible] Virginia 20362

1

[illegible]
[illegible]
[illegible]
Room [illegible]
Washington [illegible]

[illegible]
Manager [illegible]
Power [illegible]
Naval Weapons [illegible] Center
Crane, Indiana [illegible]

Dr. [illegible]
Energy [illegible]
Lawrence Berkeley Laboratory
University of California
Berkeley, California [illegible]

Dr. Bernard [illegible]
U.S. Army Research Office
P.O. Box [illegible]
Research Triangle Park, NC [illegible]

Dr. Denton [illegible]
Air Force Office of
Scientific Research
Bldg. [illegible]
Bolling AFB
Washington, DC [illegible]

TECHNICAL REPORT DISTRIBUTION LIST, 051A

No.
Copies

[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

[illegible]
[illegible]
[illegible]
[illegible]

[illegible]
[illegible]
[illegible]
[illegible]

[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

[illegible] Schuster
[illegible]
[illegible] Illinois
[illegible]

[illegible]son
Department of Chemistry
University of Southern
California
Los Angeles, California 900[illegible] 1

~~Dr. M. S. Wrighton~~
~~Department of Chemistry~~
~~Massachusetts Institute of~~
~~Technology~~
~~Cambridge, Massachusetts 02139~~ 1

Copies

Dr. M. Rauhut
Chemical Research Division
American Cyanamid Company
Bound Brook, New Jersey [illegible]

Dr. [illegible]
Department of Chemistry
University of California,
Los Angeles
Los Angeles, California [illegible]

Dr. D. Haarer
IBM
San Jose Research Center
[illegible]
San Jose, California [illegible]

Dr. John [illegible]
Code 61[illegible]
Naval Research Laboratory
Washington, D.C. [illegible]

Dr. William M. Jackson
Department of Chemistry
Howard University
Washington, DC 20059

Dr. George E. Walrafen
Department of Chemistry
Howard University
Washington, DC 20059

DA

FILM