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SEMICONDUCTOR-ELECTROLYTE PHOTOVOLTAIC ENERGY CONVERTER

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The goal of this work is the evaluation of the feasibility and practicality of a solar cell consisting of a semiconductor surface in contact with an electrolyte. Preliminary experimental and theoretical work, as well as a literature search, indicates the system merits further study.

Specific semiconductor electrodes and promising electrolytes have been identified for further study. The systems will first be evaluated for efficient energy conversion at typical solar photon irradiances. They will then be evaluated for stability, and finally, for economical and practical solar cell construction.

In Fig. 1 we show the basic components and processes for photovoltaic energy conversion at the surface of an n-type semiconductor in contact with an electrolyte which is oxidizing to conduction band electrons. To date, we have studied characteristics of single crystal CdS, GaAs, CdSe, CdTe and thin film CdS in contact with aqueous and methanol based electrolytes. We have measured open circuit voltages from Mott-Schottky plots and open circuit photovoltage. We have measured short circuit current and quantum efficiency as a function of λ at low photon irradiances and as a function of photon irradiance up to 20 mW/cm². Electrode corrosion as a function of current and electrolyte composition has been studied by drift of V_{OC} and I_{SC} with time, by microscopic examination of electrode surfaces and by electrochemical analysis of electrode decomposition products.

The quantum efficiency for short circuit photo current of a CdS crystal and a 20 μ m film is shown in Fig. 2 while the electrical and photovoltaic properties are shown in Fig. 3. The highest photon irradiances we have used to date were with the GaAs cell shown in Fig. 4. Significantly higher conversion efficiencies were obtained with a different electrolyte and at low photon irradiances on GaAs as shown in Fig. 5. From an analysis of the short circuit current spectral response shown in Fig. 6, it appears that a significant diffusion contribution to I_{SC} occurs as well as the drift component due to photogeneration of carriers in the space charge region.

As shown in Fig. 1, charge may be transferred from the semiconductor surface to the electrolytic solution in contact with this surface either by simple electron transfer or by deposition on or dissolution from the semiconductor of ionic species. The latter modes are basically undesirable because they inevitably result in changes in the composition and/or dimensions of the electrode. For example, in cadmium sulfide in contact with aqueous solutions, charge appears to be transferred in part by deposition of molecular sulfur and concomitant dissolution of cadmium ion



In methanol solvent, on the other hand, electrolysis of the solvent apparently accounts for a substantial fraction of the current observed.

As a first step in solving the problems of electrode dissolution, we are developing analytical methods suitable for detecting dissolution of CdS, CdSe, CdTe, and GaAs. To do this, it is only necessary to analyze for the level of Cd²⁺ or Ga³⁺ in the photovoltaic cell solution. Anodic stripping analysis is ideally suited for determination of these two metals, and apparatus suitable for this determination is readily available to us. The steps in this procedure are shown in Fig. 7. Analysis of 1×10^{-6} , (0.1 ppm) Cd²⁺ is routine by this technique with a precision of 5%. A typical replicate analysis is shown in Fig. 8.

Suppression of photo-initiated dissolution of the semiconductor electrode will be attempted. Addition of various redox couples capable of donating electrons to holes at the semiconductor surface will be investigated



(2)

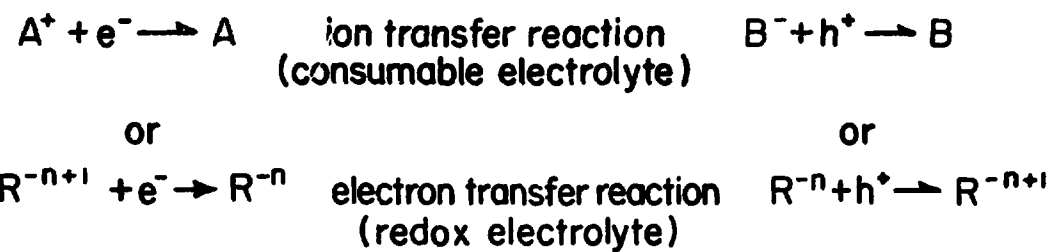
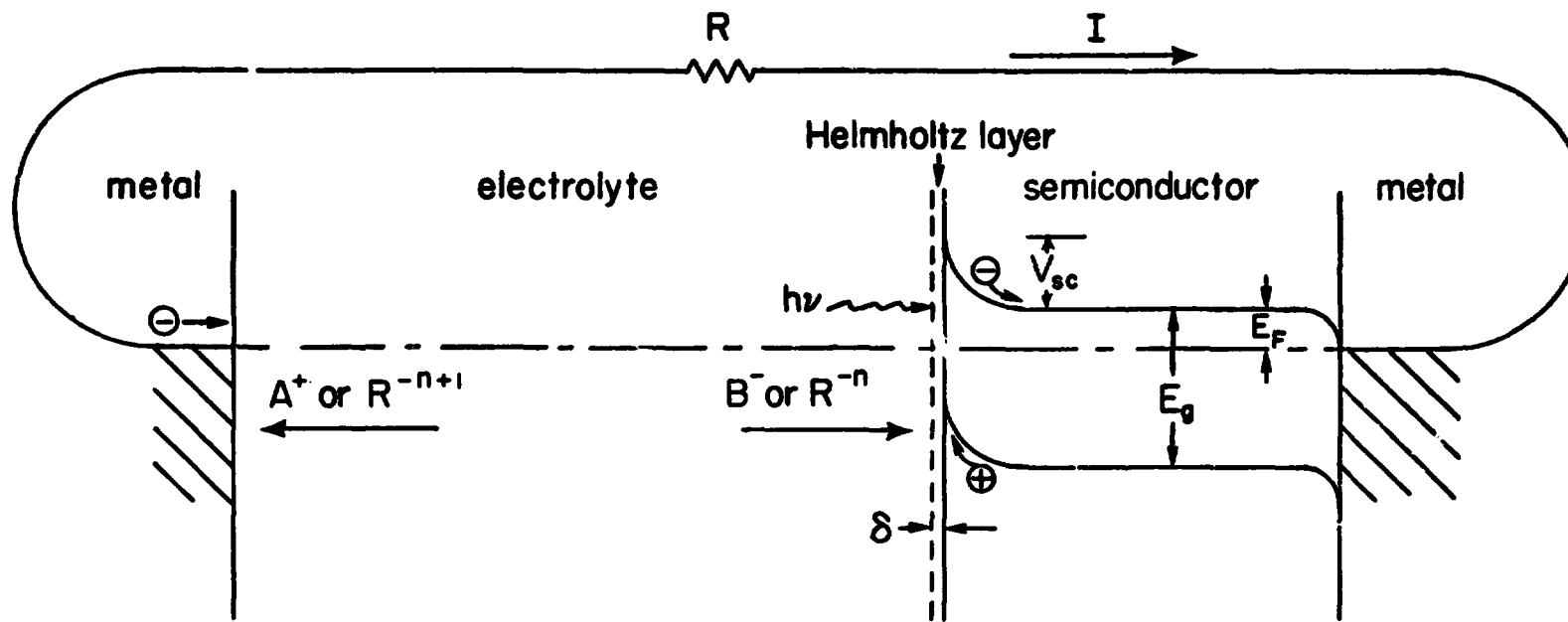
When this reaction is more rapid than reaction (1) above, electron transfer will suppress anodic dissolution. This is apparently the case when the electron donor is methanol. However, the oxidation of methanol to formaldehyde is irreversible and causes destruction of the solvent. We are seeking couples R/O which are reversible and may be reduced at the counter electrode, making the solvent-electrolyte system simply an ionic conductor with no permanent change occurring with time.

An attempt to demonstrate comparable photovoltaic energy conversion efficiency in polycrystalline thin film devices will be made. A system for vacuum evaporation of CdS and other II-VI compounds has been set up.

We will obtain a quantitative measure of the electrode dissolution problem for CdS. Cd²⁺ ion concentration in the cell electrolyte will be measured as a function of "exposure", i.e., short circuit current multiplied by time of current flow during illumination at constant intensity. The quantity of interest is in the number of Cd²⁺ ions going into solution for each charge transfer event across the semiconductor-electrolyte interface.

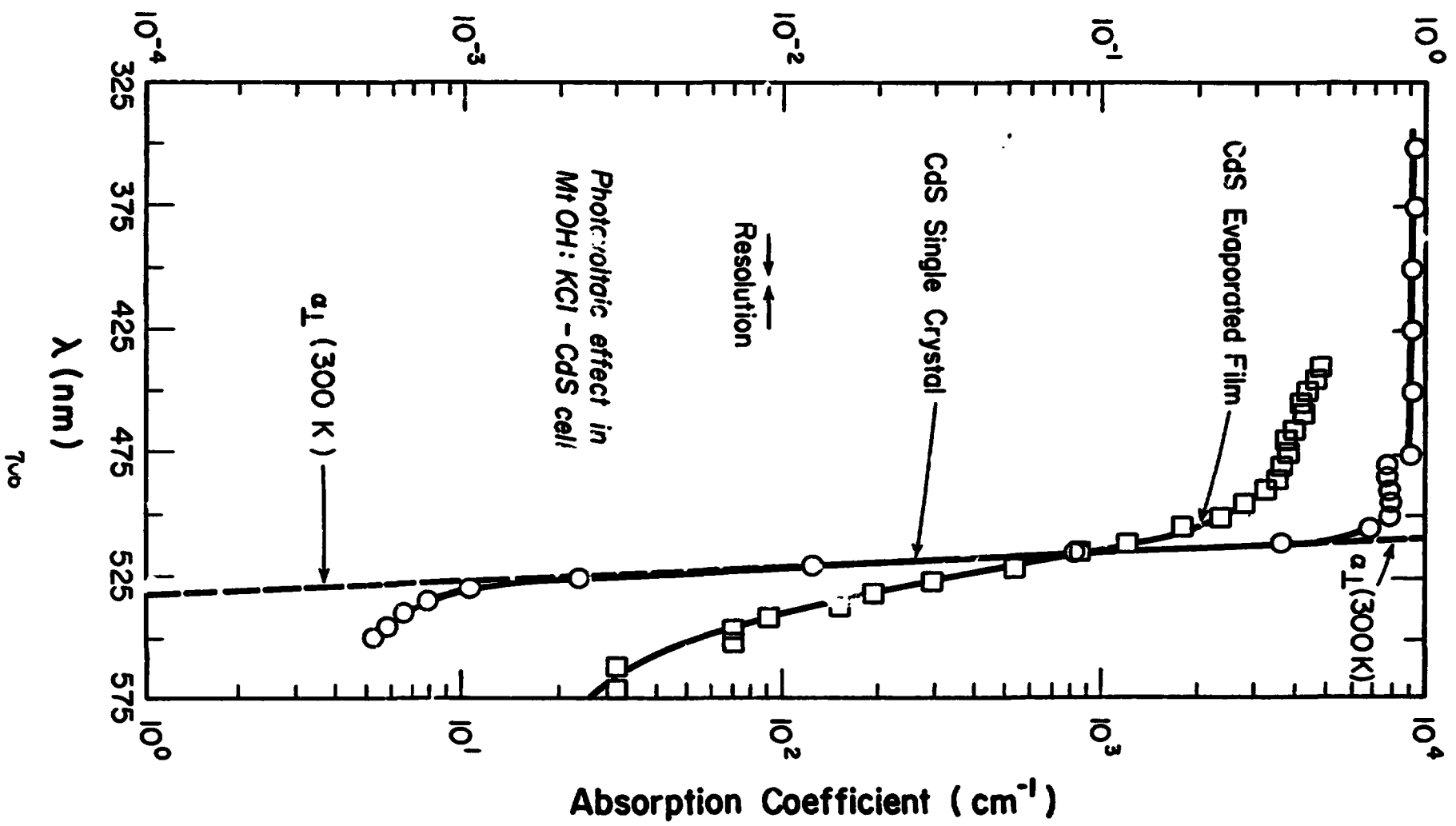
To date, CdS and GaAs have been studied since they were available. Samples of CdTe and CdSe have been obtained which will be evaluated for efficient photovoltaic energy conversion.

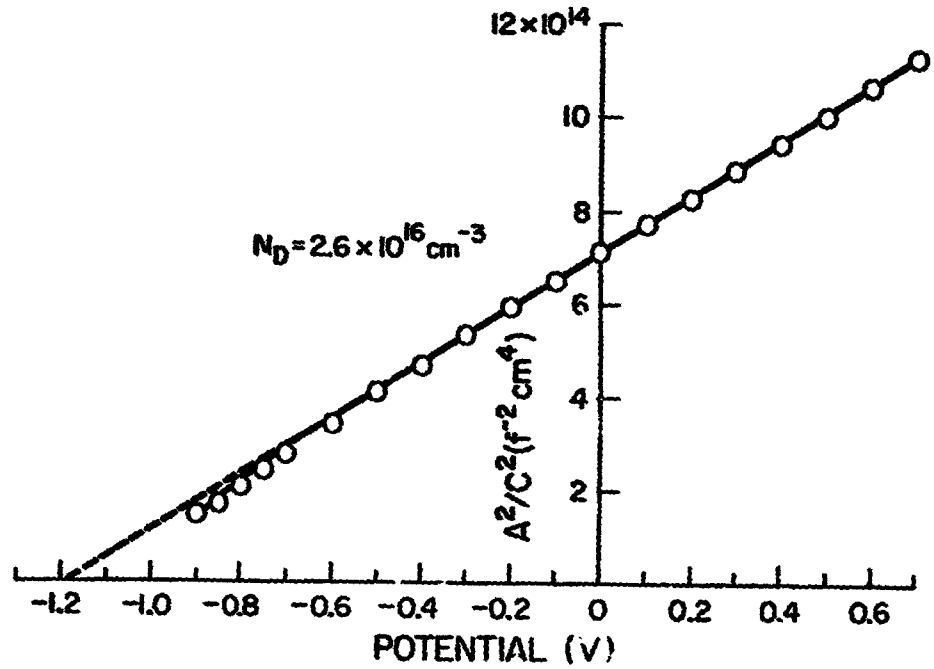
It appears that a Becquerel effect solar cell is capable of conversion efficiencies of technological significance. Our measured external conversion efficiency of 30% was for low intensity, almost monochromatic radiation, and so is not directly comparable to commercial state-of-the-art solar cells. However, these are preliminary experiments with the simplest electrolytes on a nonoptimum semiconductor. Use of a semiconductor such as CdTe would optimize the device spectral response to the solar source and comparable efficiencies would then be highly significant. GaAs, which is also well matched to the solar spectrum, gave a 20% conversion efficiency for monochromatic excitation.



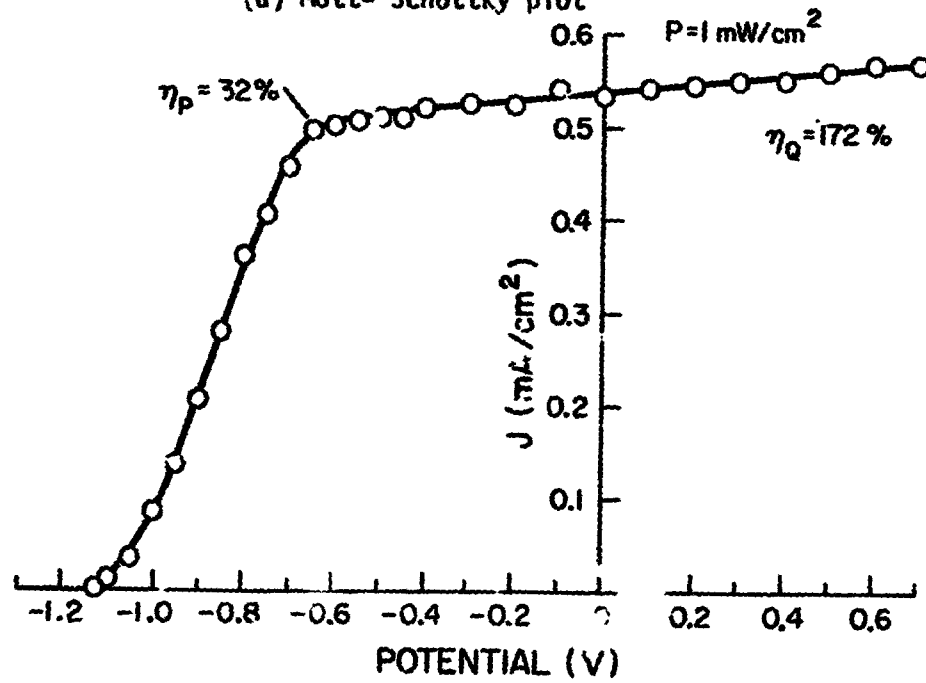
Processes in electrolyte-semiconductor photovoltaic cell.

Short Circuit Current Collection Efficiency



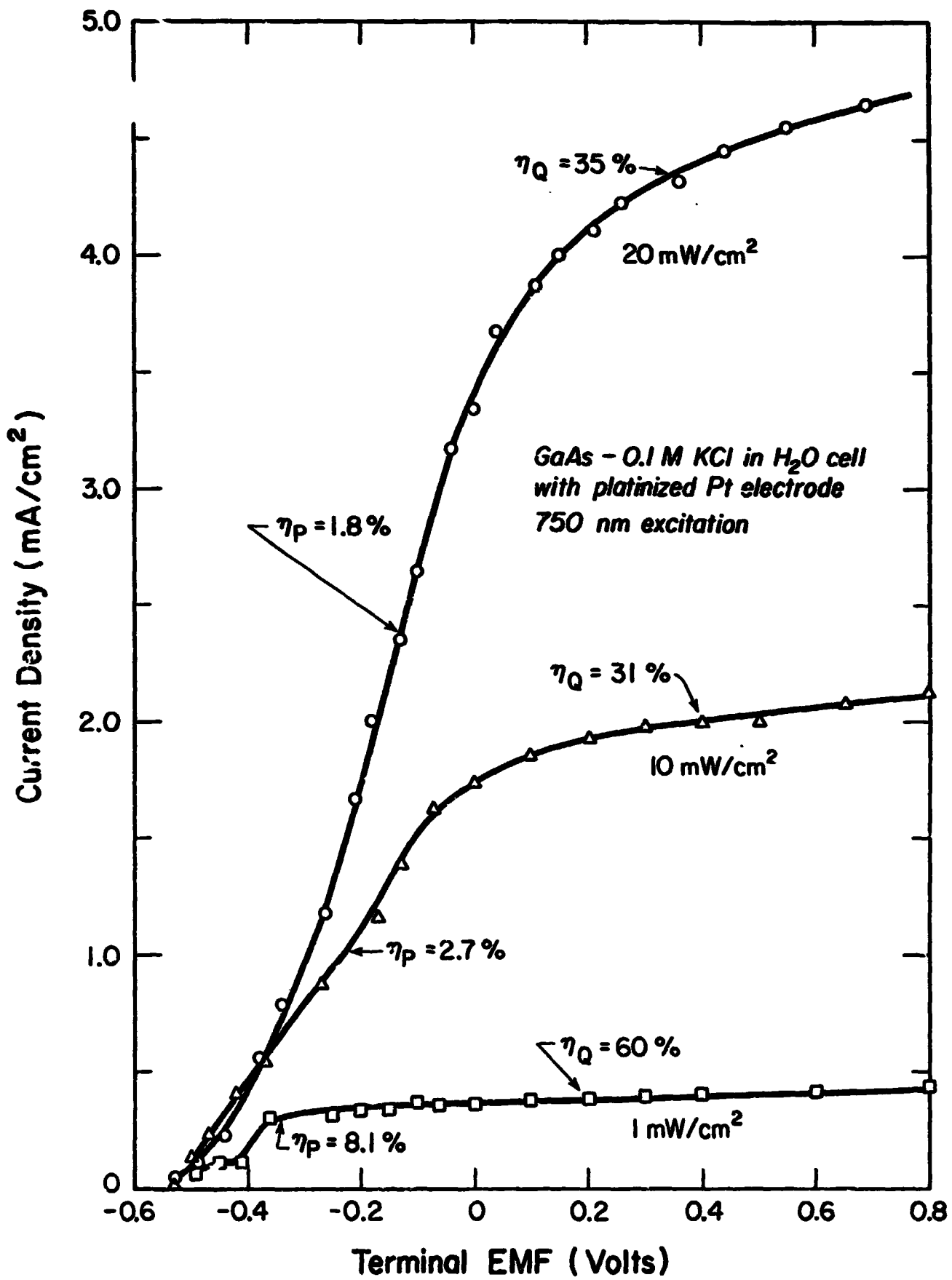


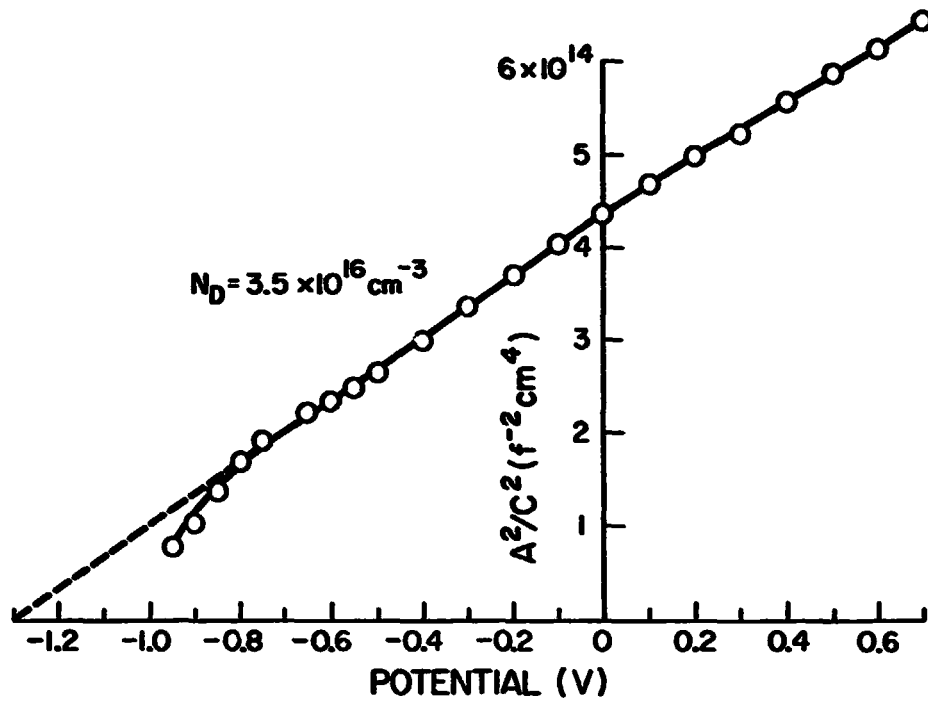
(a) Mott-Schottky plot



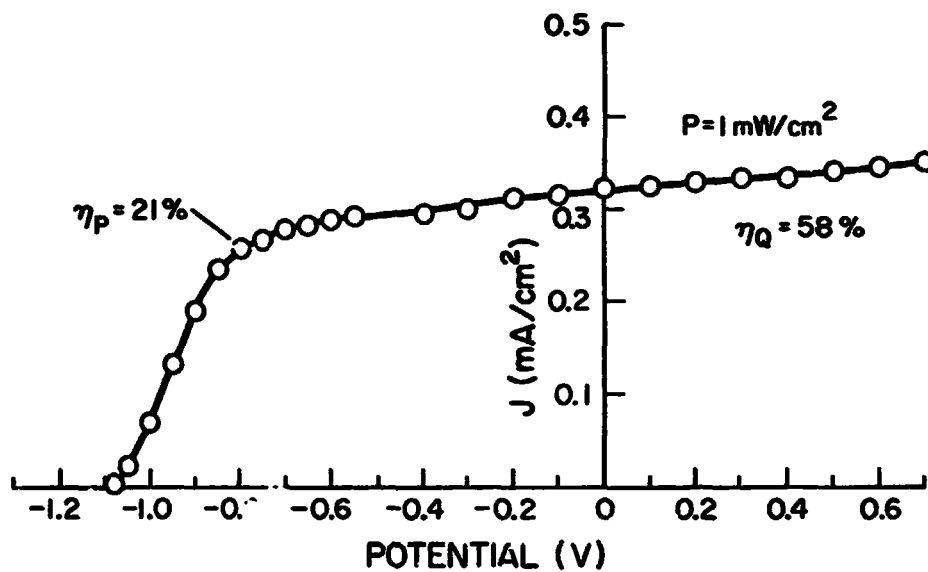
(b) Current - voltage characteristics under 400 nm excitation

Electrical and photovoltaic characteristics of CdS - 0.1M CH₃COOH cell



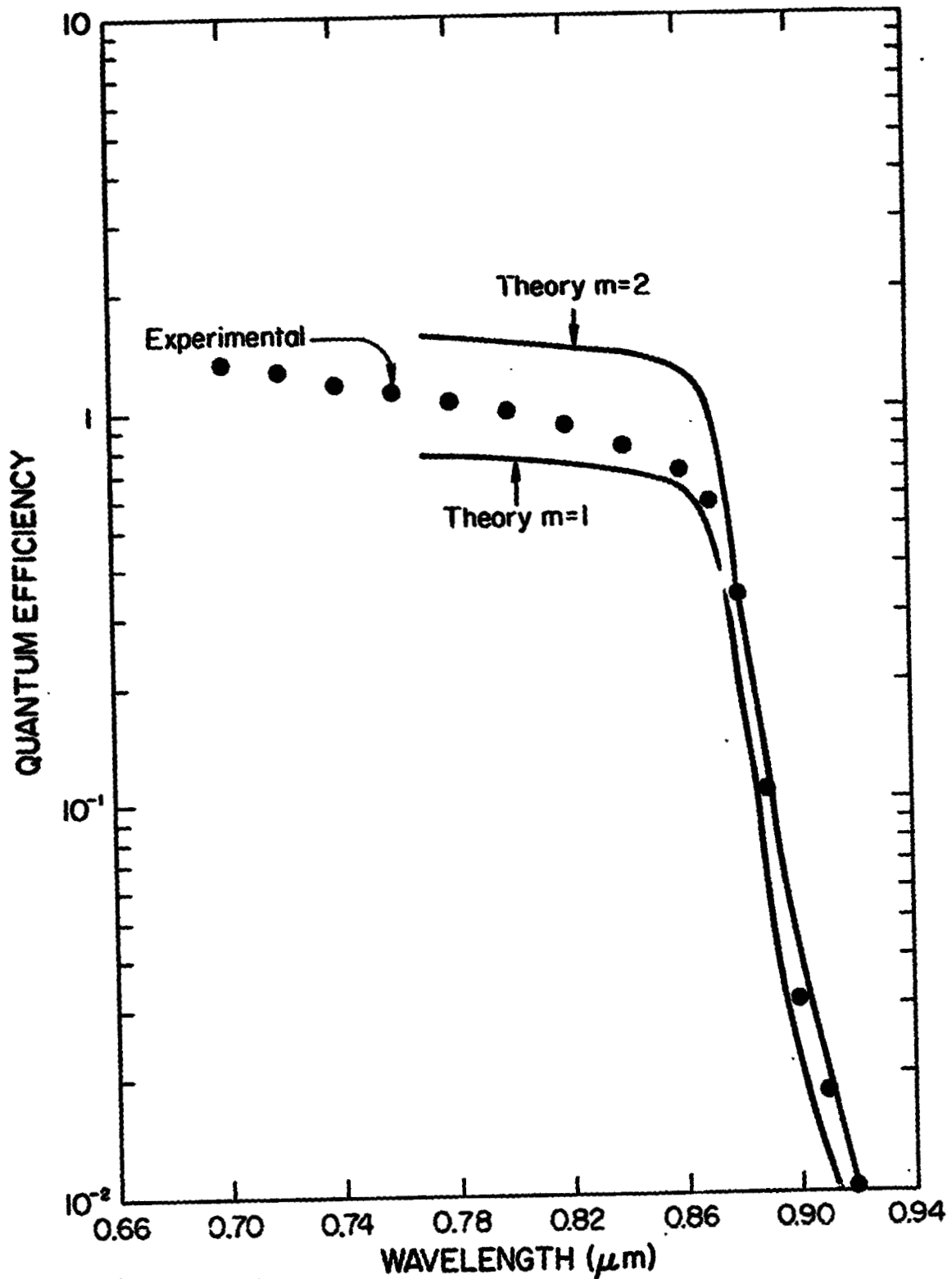


(a) Mott- Schottky plot



(b) Current - voltage characteristic under 740 nm excitation

Electrical and photovoltaic characteristics of GaAs - 0.1M HCl cell



Short circuit quantum efficiency of GaAs-0.1M HCl cell.

Experimental points are shown along with theoretical curves for

$L_p = 2\mu\text{m}$ with and without current doubling.

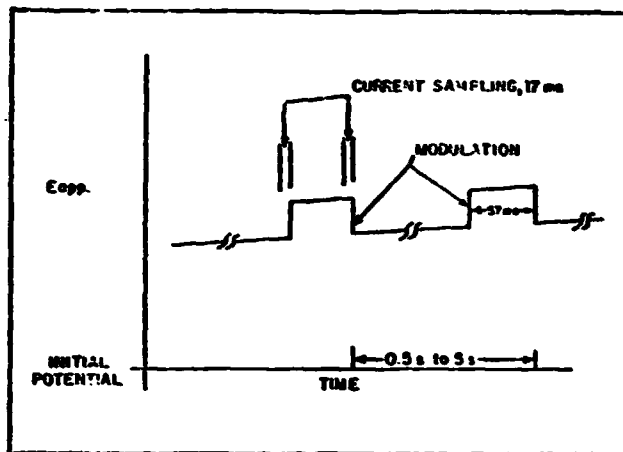


Figure V-9. EXCITATION POTENTIAL WAVEFORM FOR DIFFERENTIAL PULSE POLAROGRAPHY

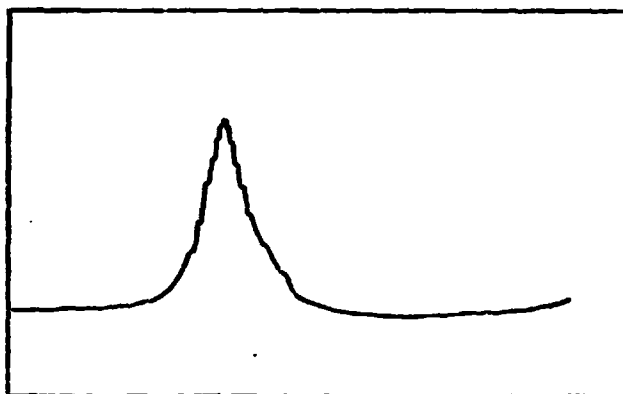


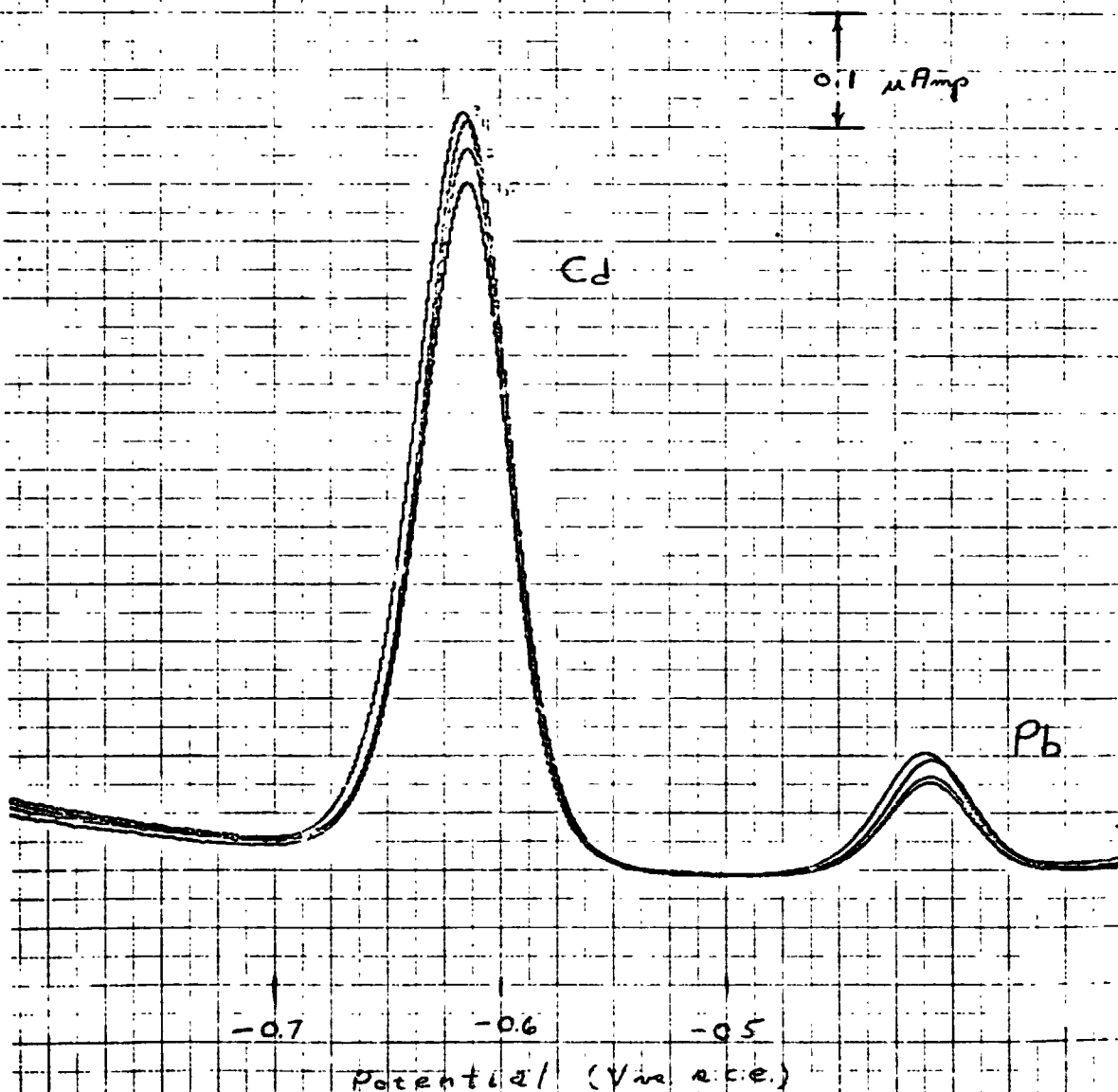
Figure V-10. TYPICAL DIFFERENTIAL PULSE POLAROGRAM

V-5

Differential Pulse Stripping

Replicate Analysis of

$1.0 \times 10^{-6} \text{ M Cd}^{2+}$



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