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CADMIUM SULFIDE/COPPER SULFIDE HETEROJUNCTION CELL RESEARCH

Technical Progress Report, February 26—May 31, 1979

By
W. W. Anderson

June 1979

Work Performed Under Contract EG-77-C-03-1459

Lockheed Missiles & Space Company, Inc.
Palo Alto Research Laboratory
Palo Alto, California

U.S. Department of Energy

Solar Energy

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LMSC-D676741

DSE-1459-T1

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LOCKHEED MISSILES & SPACE COMPANY, INC.
PALO ALTO RESEARCH LABORATORY
3251 HANOVER ST.
PALO ALTO, CA 94304

PREPARED FOR THE
SOLAR ENERGY RESEARCH INSTITUTE
UNDER CONTRACT XJ-9-8033-1

ABSTRACT

All vacuum deposition process $Au/Cu_2S/Cd_{1-x}Zn_xS/Nb$ photovoltaic cells have been fabricated by sequentially sputtering (1) Nb in Ar, (2) $Cd_{1-x}Zn_x$, and then (3) Cu in H_2S and Ar gas mixtures, and finally, in a separate operation, (4) Au in Ar. Photovoltaic response of as-deposited junctions (i.e., without subsequent heat treatment) is obtained with appropriate deposition parameters.

Resistivity of CdS or $Cd_{0.9}Zn_{0.1}S$ films is controlled by sputtering from In-doped metal cathodes. Junction characteristics are strongly influenced by deep trap levels on the $Cd_{1-x}Zn_xS$ side of the heterojunction. A trap level at $E_t \approx 0.37$ eV below the conduction band edge has been identified in sputter deposited CdS by admittance spectroscopy.

CONTENTS

ILLUSTRATIONS

Section 1
INTRODUCTION

The program objective is to investigate and evaluate the application of cylindrical-post-magnetron reactive sputtering to the production of solar-cell quality thin films of CdS/Cu_2S for large-scale terrestrial photovoltaic energy conversion. All-vacuum solar-cell structures were formed by using four cylindrical-post-magnetron sputtering sources surrounding a rotatable substrate holder (Ref. 1). Devices are prepared on glass substrates by sequentially sputtering Nb in Ar, Cd (or a Cd/Zn alloy) in an Ar-H_2S mixture and, finally, Cu in an Ar-H_2S mixture. A Au grid pattern is sputtered onto the Cu_2S in a separate operation.

Under the preceding DOE contract (Ref. 1), deposition parameters were determined for requisite resistivity of CdS and/or $Cd_{0.9}Zn_{0.1}S$ and the desired Cu_2S phase:

- A $Cd_{0.9}Zn_{0.1}$:(2 at.% In) cathode was installed to deposit 30 Ω-cm films of $Cd_{0.9}Zn_{0.1}S$ and a Cd:(1 at.% In) cathode for 3 Ω-cm C_dS. $Cd_{0.9}Zn_{0.1}S$:In and CdS:In films from the doped cathodes exhibited the expected resistivities.
- During Cu_2S deposition onto glass, a high substrate temperature was found to favor chalcocite formation while a low substrate temperature was found to favor djurleite formation. Cu_2S deposited onto CdS films exhibited a similar substrate temperature dependence if other deposition parameters were properly controlled.

Cu_2S/CdS and $Cu_2S/Cd_{0.9}Zn_{0.1}S$ junctions are rectifying and photovoltaic when the Cu_2S is deposited at 140 to 150°C substrate temperature. Some device improvement is obtained upon heat treatment, but the optimum sequence has yet to be determined. Gridded structures are now being prepared wherein only the fine finger grids are deposited, the interconnect bus being omitted. A pinhole problem in the CdS film was identified and traced to substrate cleaning and handling procedures. In the meantime, unshorted grid fingers may be interconnected to obtain representative device characteristics. An initial conversion efficiency of 0.4 percent has been obtained in natural insolation at 83 mW/cm^2.

Section 2
(Cd,Zn)S CHARACTERIZATION

Resistivity of CdS and $Cd_{0.9}Zn_{0.1}S$ films as a function of In concentration had been investigated by co-sputtering of an In cathode adjacent to the primary Cd or $Cd_{0.9}Zn_{0.1}$ cathode (Ref. 1). The Cd or $Cd_{0.9}Zn_{0.1}$ cathode was operated at 1 A while current to the In cathode was varied. The calculated In concentration (obtained from the In deposition rate as a function of In cathode current) was in reasonable agreement with the In concentration as measured in the films by an electron beam microprobe. Based on this work a cathode of $Cd_{0.9}Zn_{0.1}$:(2 at.% In) was installed to deposit 30 Ω-cm resistivity films of $Cd_{0.9}Zn_{0.1}S$:In. Film resistivity from the doped cathode could be varied from 30 to 600 Ω-cm by varying substrate temperature.

Carrier concentration in the $Cd_{0.9}Zn_{0.1}S$ films was measured by the van der Pauw technique and checked by $1/C^2$ versus V analysis of $Cu_2S/Cd_{0.9}Zn_{0.1}S$ devices. Considerable dispersion of junction admittance was found as shown in Fig. 1 for a typical device. This was tentatively ascribed to deep trap levels in the film. At high measurement frequencies (f = 1 MHz), good agreement between $1/C^2$ versus V and van der Pauw measurements were obtained as shown in Fig. 2. Another indication of the presence of deep traps was the significant hysteresis in device I-V characteristics obtained at rapid sweep rates as shown in the insert to Fig. 3. Similar results were obtained on CdS films and analyzed by admittance spectroscopy.

Measurements of the complex admittance of Schottky barrier diodes as a function of temperature and frequency provide a spectroscopy of deep trapping levels (Ref. 2). Measurements on a Au/CdS Schottky diode are shown in Fig. 4. The peak in conductance occurs for $\omega_p \langle\tau\rangle = 1$ where $\langle\tau\rangle$ is the inverse of the trap emission rates.

$$\langle\tau\rangle^{-1} \approx 2\, C_n N_c \exp(-E_T/kT)/\beta \qquad (1)$$

where β is the trap degeneracy factor and C_n is the capture rate. For an energy independent capture rate,

$$\omega/T_p^{3/2} = 4.31 \times 10^{14}\, C_n \exp(-E_T/kT_p) \qquad (2)$$

where T_p is the temperature of peak conductance at frequency $f = \omega/2\pi$. For an energy independent capture cross section

$$C_n = \sigma_n v_{th} = \sigma_n \sqrt{\frac{3kT_p}{m_n^*}} \qquad (3)$$

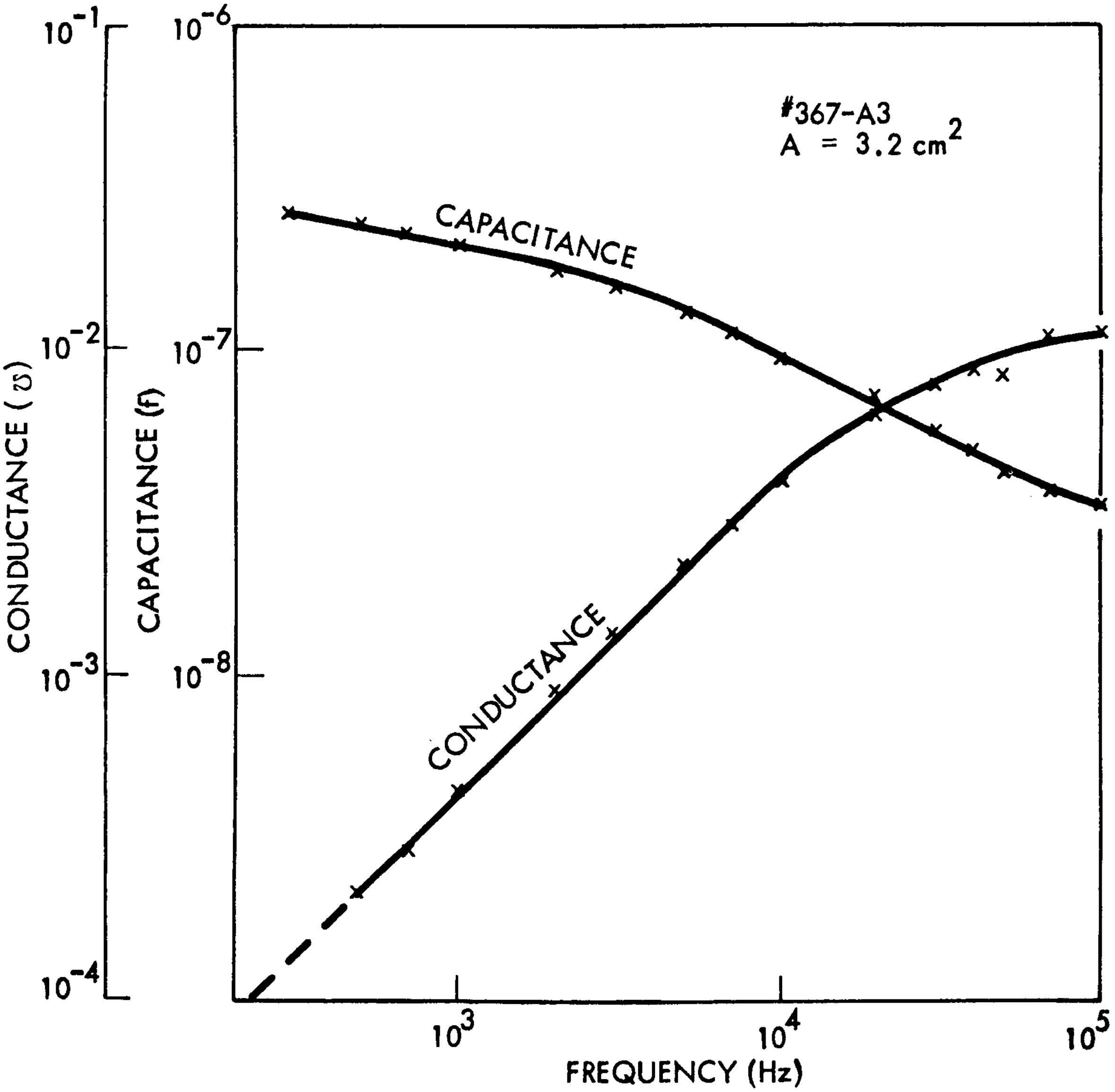


Fig. 1 Zero Bias $Cu_2S/Cd_{0.9}Zn_{0.1}S$ Admittance

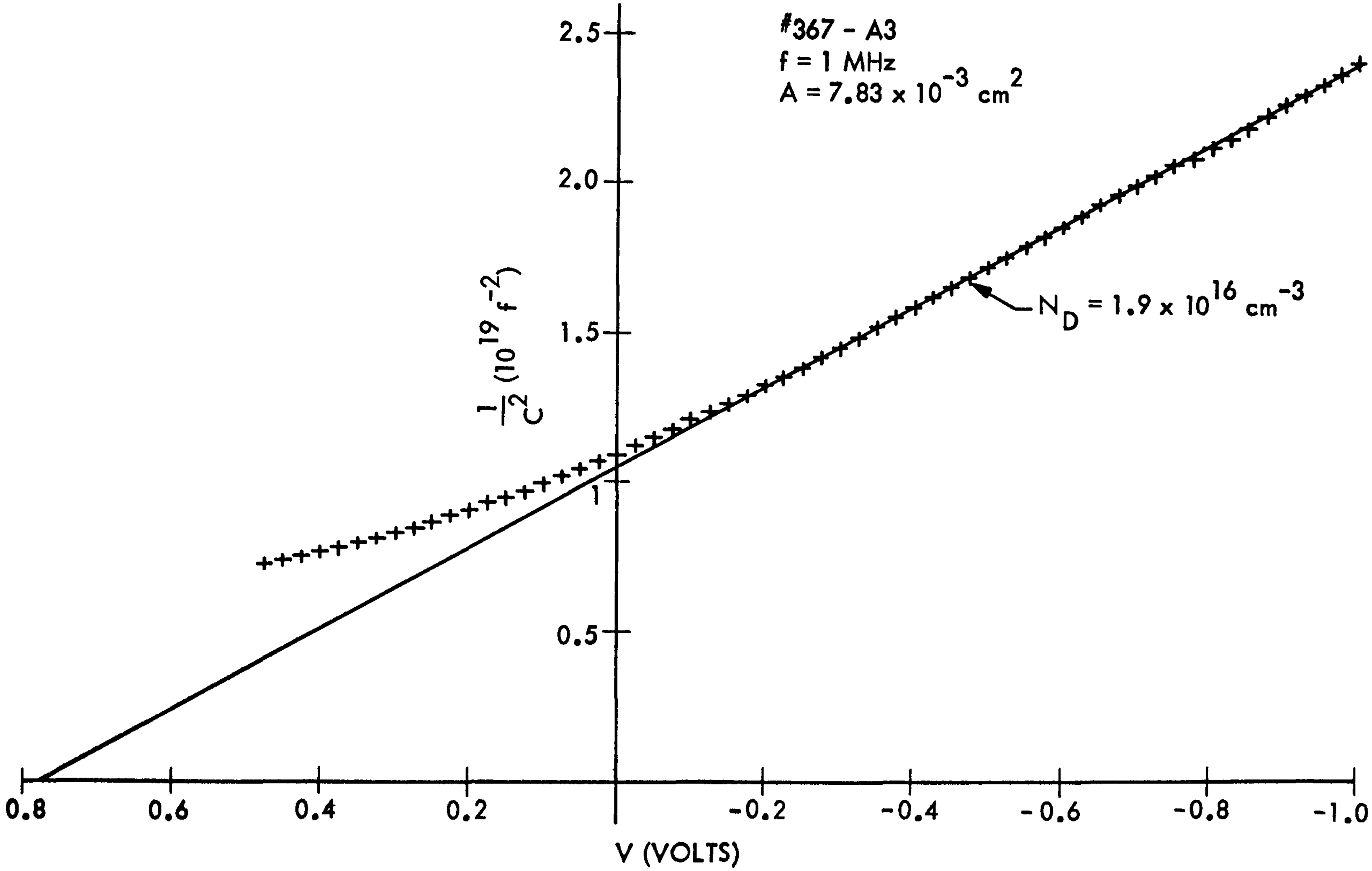
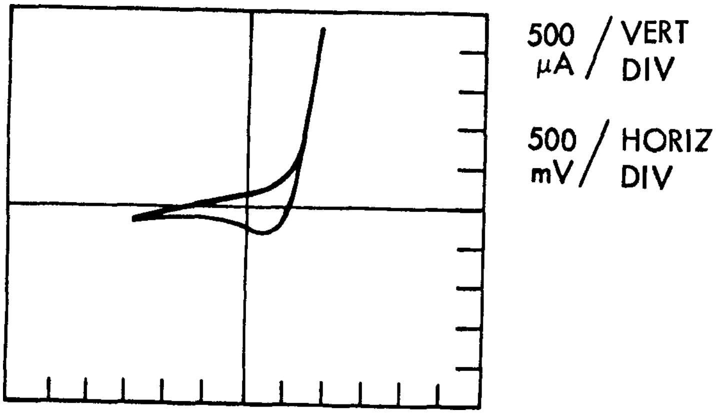
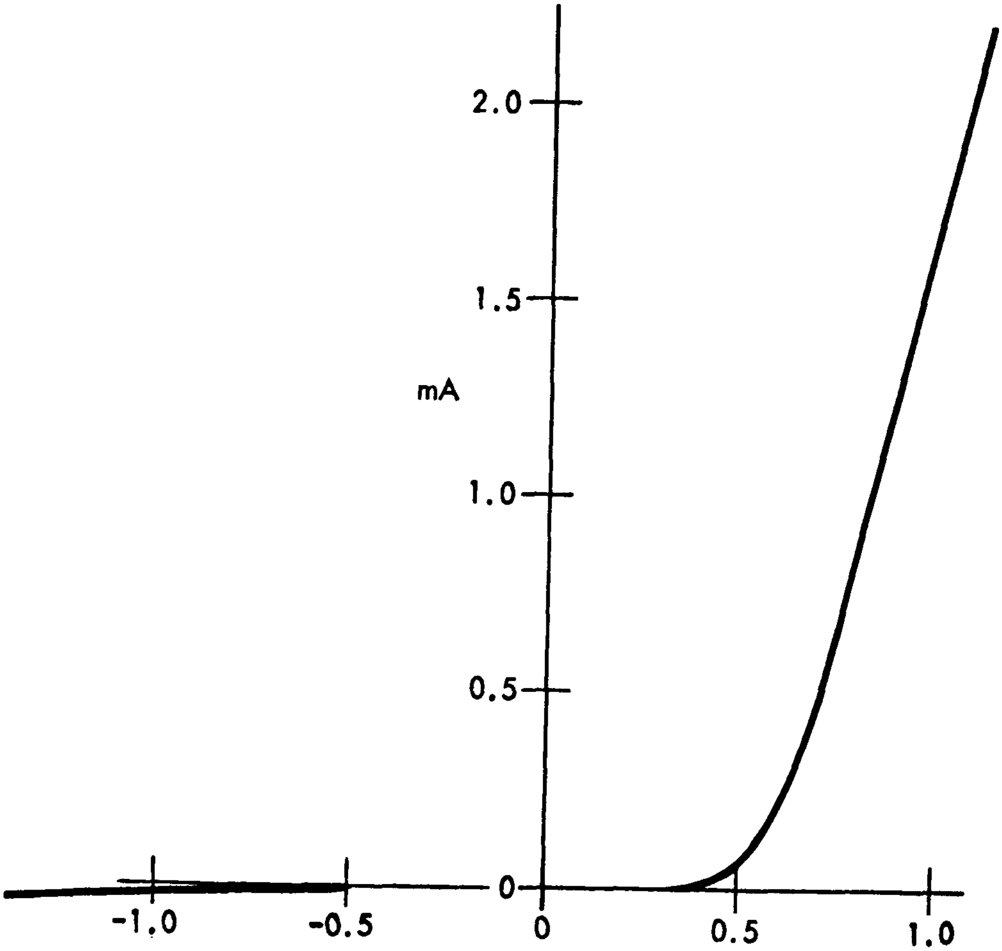


Fig. 2 $1/c^2$ Versus V for $Cd_{0.9}Zn_{0.1}S/Cu_2S$ Diode at 1 MHz



(a) Fast Sweep



(b) Slow Sweep

Fig. 3 $Cu_2S/Cd_{0.9}Zn_{0.1}S$ Current-Voltage Characteristic Influenced by Deep Traps

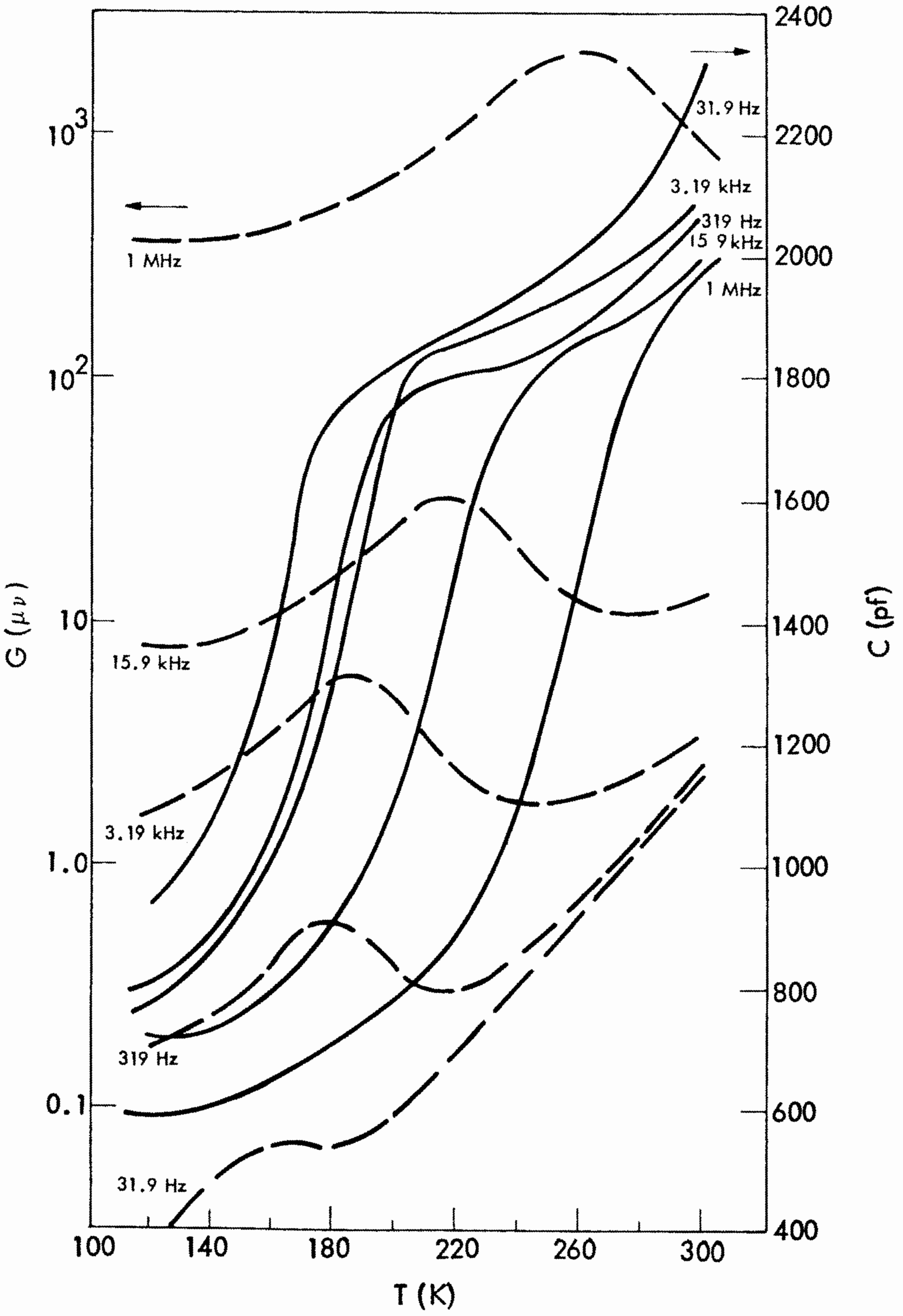


Fig. 4 Admittance of Au/CdS Diode Due to Deep Traps

and

$$\omega/T_p^2 = 6.51 \times 10^{20} \sigma_n \exp(-E_T/kT_p) \qquad (4)$$

The data of Fig. 4 were analyzed according to both Eqs. (2) and (4) and plotted in Fig. 5. The results from Eq. (2) were $E_T = 0.374$ eV with $C_n = 7 \times 10^{-5}$ cm^3/s, while Eq. (4) resulted in $E_T = 0.365$ eV with $\sigma_n = 2 \times 10^{-12}$ cm^2. In both cases, the standard deviation in slope estimate for E_T was 0.05 eV. The trap activation energy is only weakly dependent on the temperature dependence of N_c and v_{th}. Both linear approximations to the data points are characterized by a Coefficient of Determination of $r^2 = 0.95$, which is strongly indicative of a linear relation, but the data do not permit a choice between Eqs. (2) and (4). Of particular interest is the fact that $E_T \approx 0.37$ eV does not correspond to any of the established trap energies in evaporated CdS films (Ref. 3).

A new cathode, identified as Cd:(1 at.% In), was installed to deposit 3 Ω-cm CdS:In at a substrate temperature of 300°C. The resistivity of films deposited from this cathode was a function of substrate temperature as shown in Fig. 6. The resistivity is a stronger function of substrate temperature than had been anticipated. The samples used in Fig. 6 had been supplied with a 500 Å In contact layer over the substrate. When the 500 Å In contact layer was omitted, the CdS films had high resistivity and were highly photosensitive. Subsequent to these observations, it was found that the high-purity Cd cathode vendor had inadvertently reversed cathode identifications, so an undoped Cd cathode (In = 0%) was in fact being used. This is presumably the cause of high series resistance obtained in Cu_2S/CdS cells deposited from this cathode.

The electrical properties of CdS or CdS:In over glass are significantly different from the properties over Nb coated substrates. This was first noted by observation of the electrical characteristics of In contacts pressed onto CdS over Nb metallized and unmetallized regions of a substrate as indicated in Fig. 7. The In contacts located over Nb were blocking in one polarity while contacts over glass were ohmic. The effect is also present in $Cd_{0.9}Zn_{0.1}S$:In films as shown in Fig. 8. In Fig. 7, the Nb substrate metallization was used as a second contact, whereas in Fig. 8 an In contact was used. The effect is present in In doped and undoped films. SIMS analysis for oxygen showed no significant difference in oxygen at the CdS surface over glass and over Nb. The oxygen content peaks at the surface as shown in Fig. 9, with a slight difference in the region over Nb vis á vis that over glass. However, the intersample differences in surface oxygen were greater than the intrasample differences, whereas the intersample differences in contact characteristics were negligible. Since a Cs^+ ion source was used in this initial experiment, the sensitivity to electropositive elements such as Nb was inadequate for detection of small concentrations at the surface. The specific, electrically active species coming from the Nb metallization and influencing the CdS surface is yet to be identified.

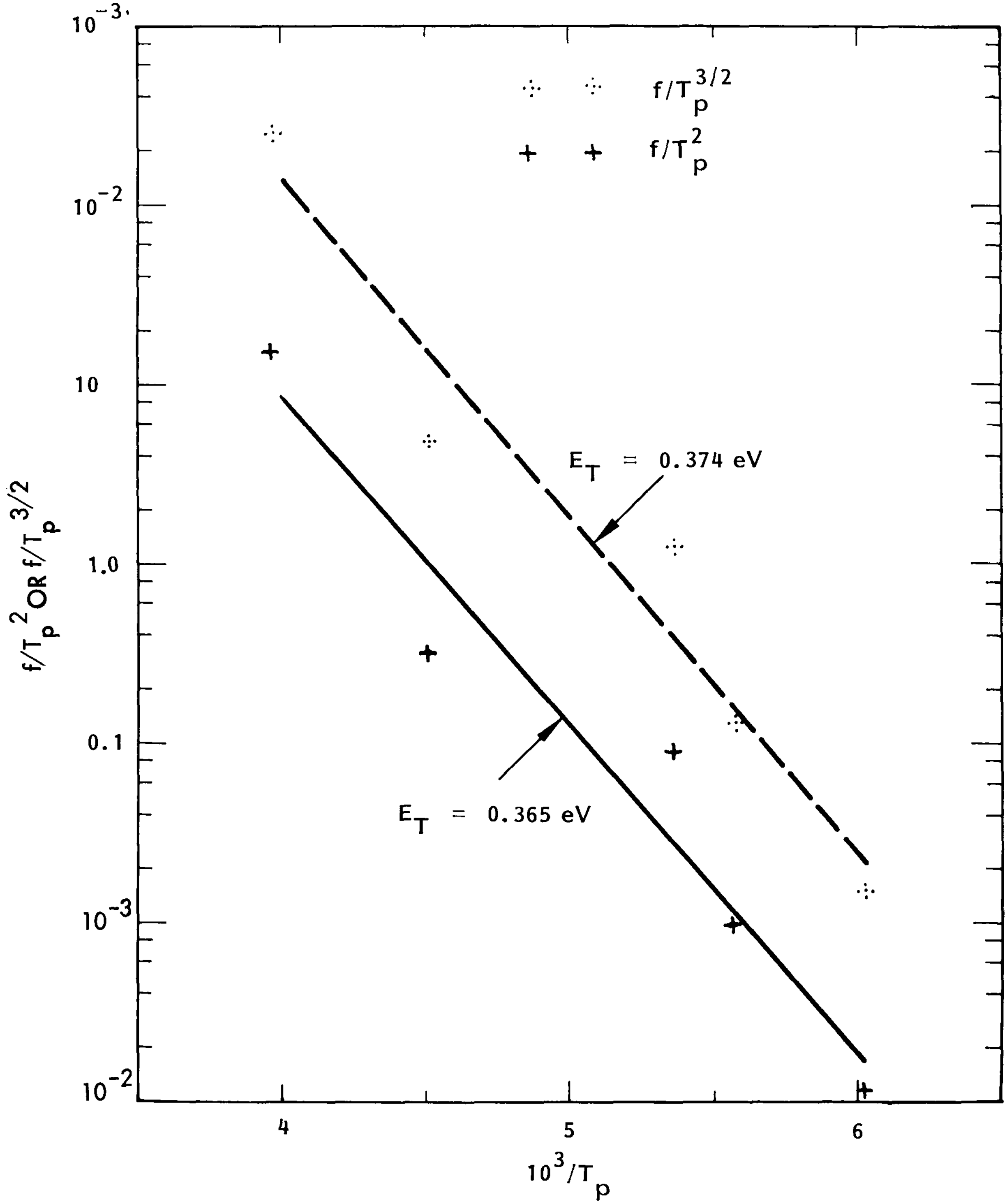


Fig. 5 Trap Activation Energy Analysis for Two Different Models of Carrier Capture Rate (see text for details)

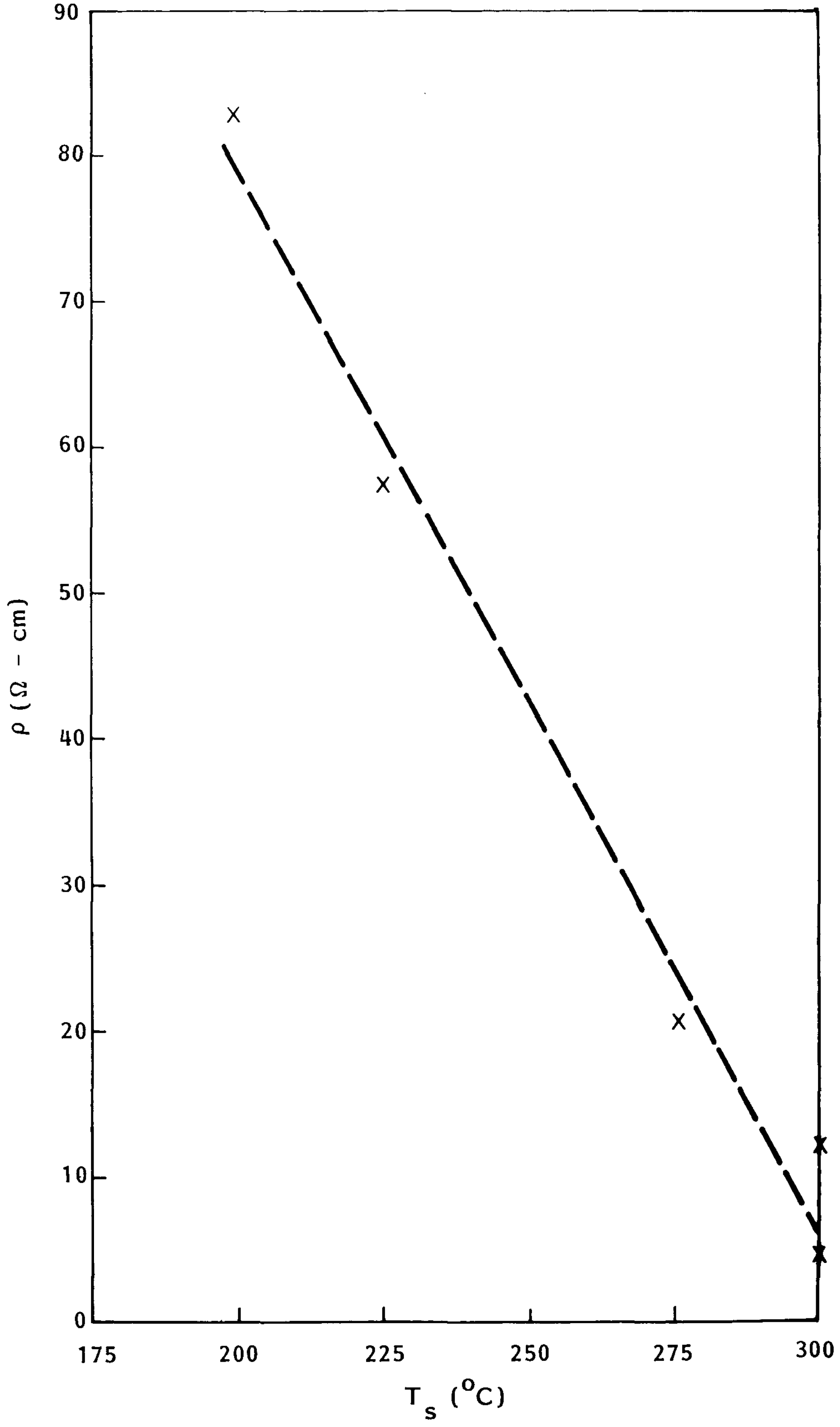
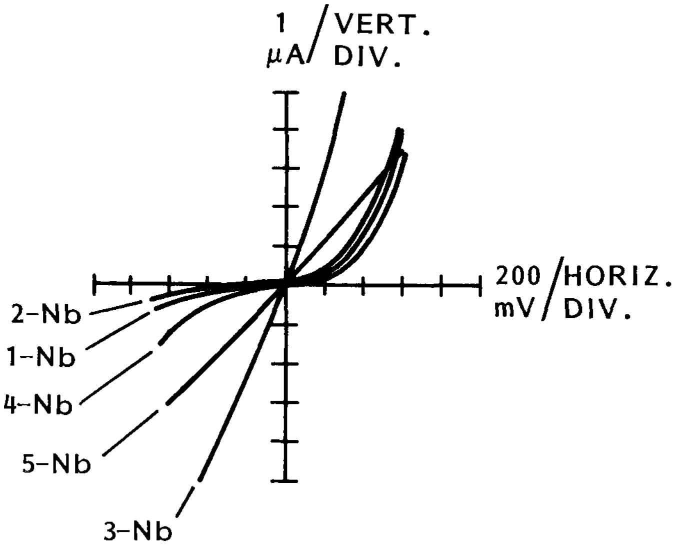
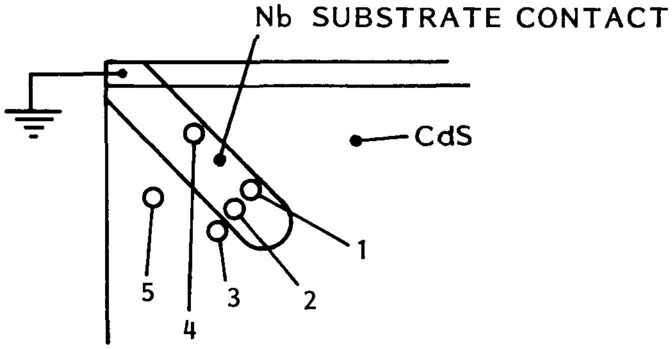


Fig. 6 CdS:In Film Resistivity as Function of Substrate Temperature

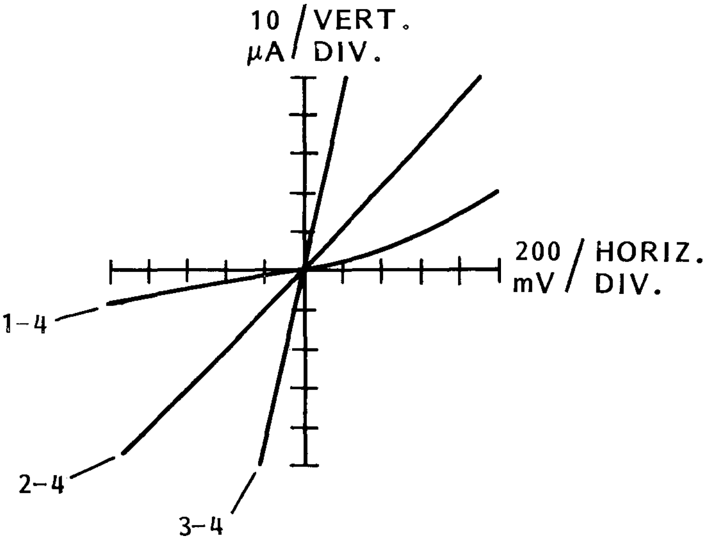


(a) I-V contact characteristic

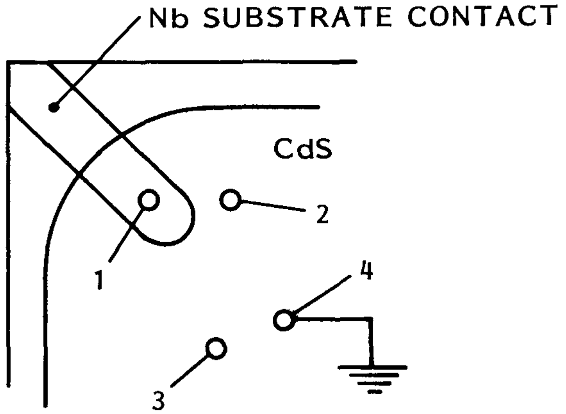


(b) 1-5, In contacts on CdS

Fig. 7 I-V Characteristics of In/CdS/Nb Contact, Illustrating Effect of Substrate Material on In/CdS Contact Characteristic

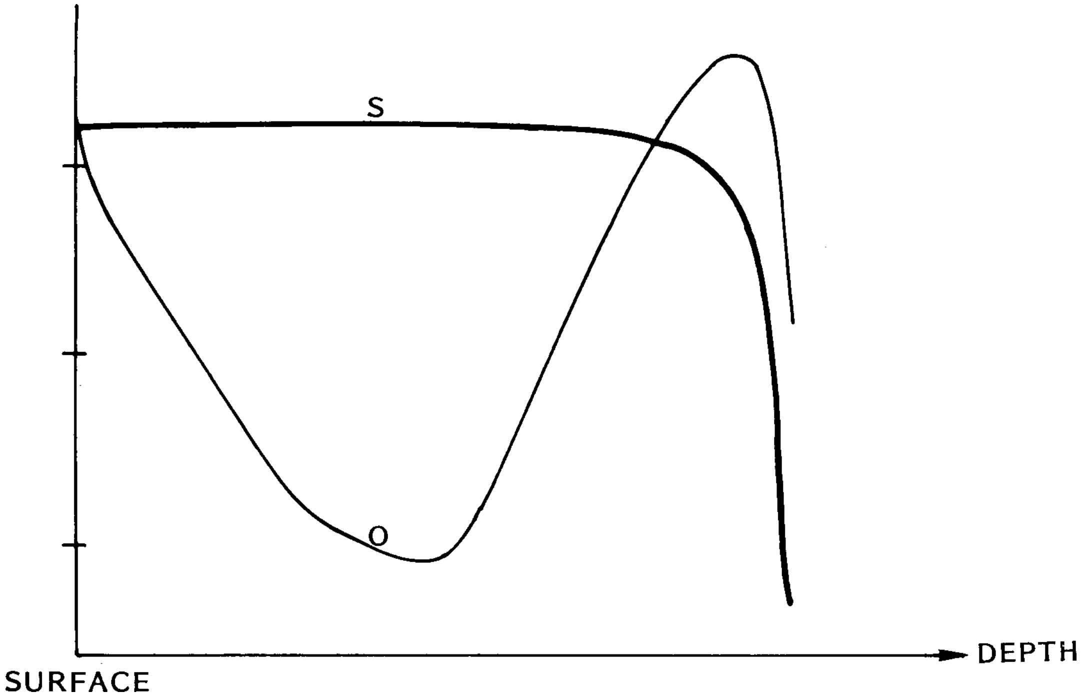


(a) I-V contact characteristic

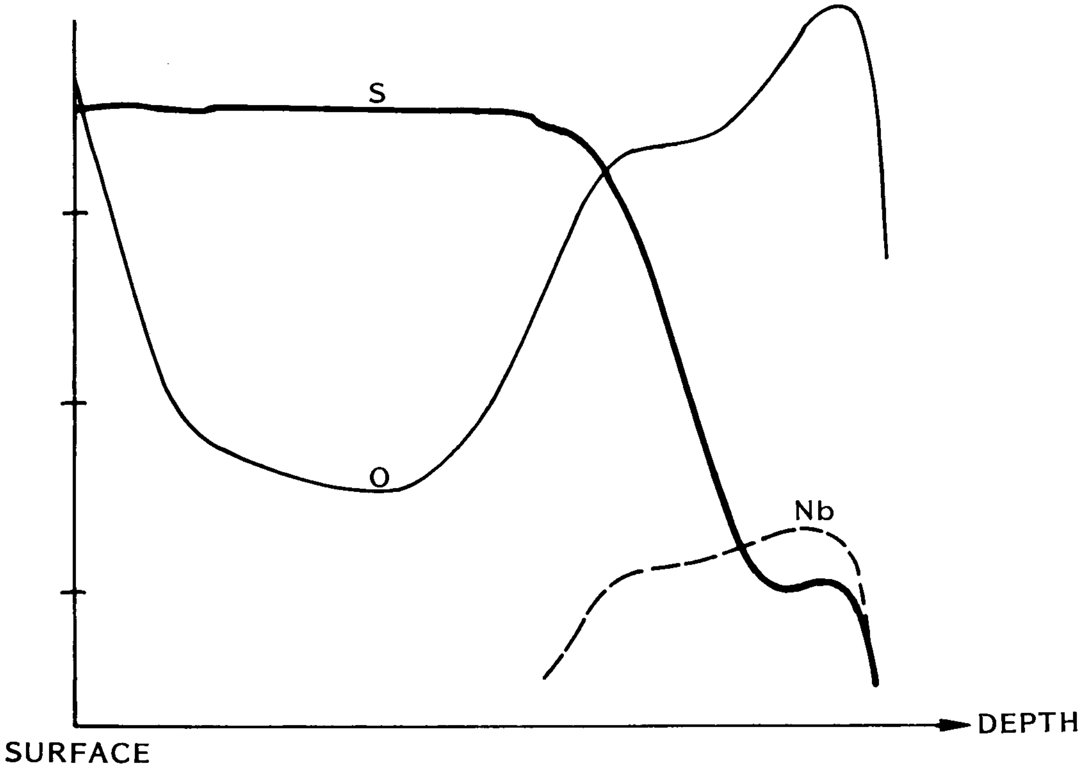


(b) 1-4, In contacts on $Cd_{0.9}Zn_{0.1}S$:In

Fig. 8 I-V Characteristics of In/$Cd_{0.9}Zn_{0.1}S$/In Contact, Illustrating Effect of Substrate Material on In/$Cd_{0.9}Zn_{0.1}S$ Contact Characteristic



(a) CdS over glass substrate



(b) CdS over Nb metallization

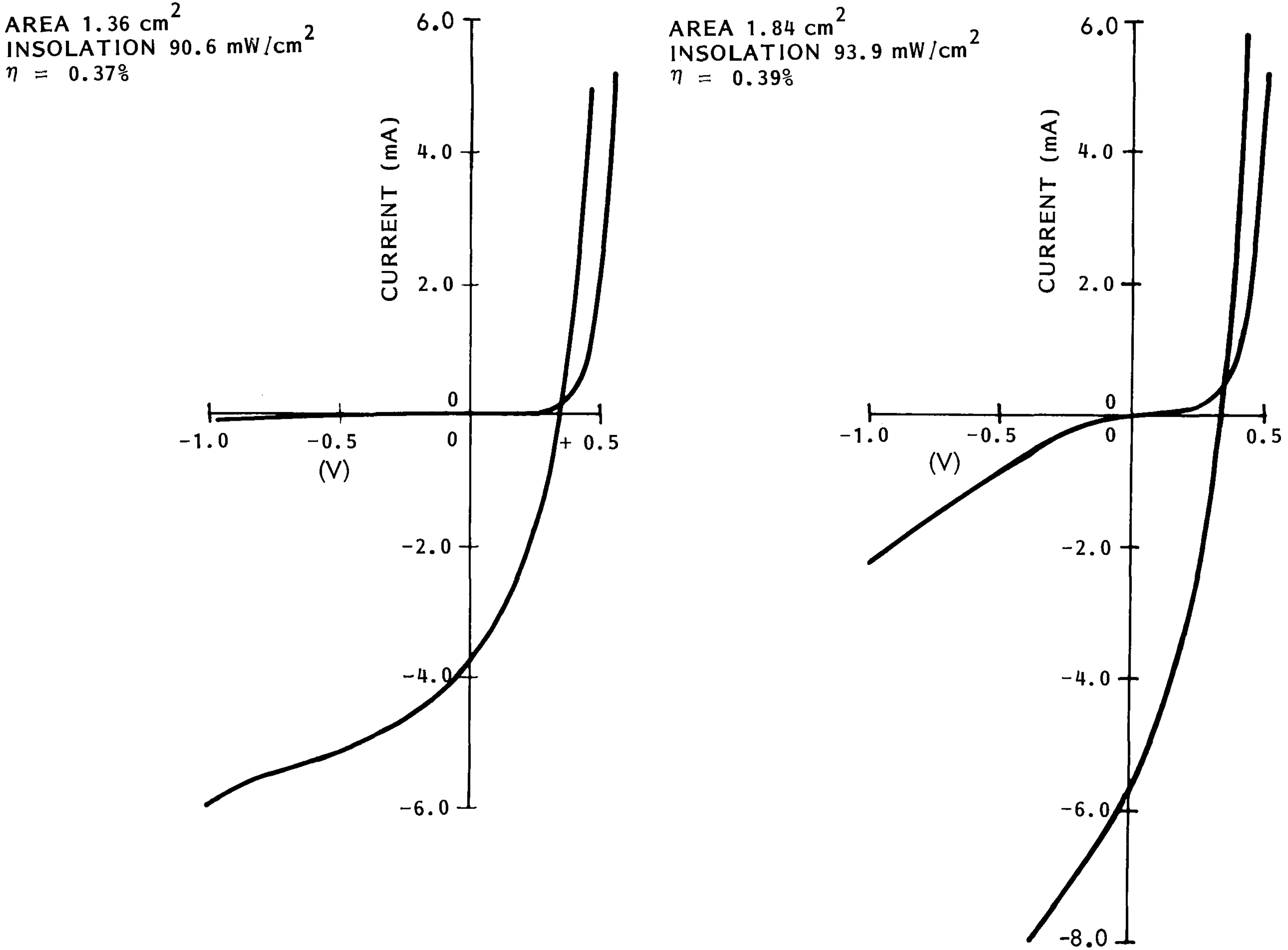
Fig. 9 SIMS Profile of Electronegative Elements (Primarily S and O) in CdS Deposited Over Nb Metallized and Uncoated Glass Substrate Regions

Section 3
DEVICE-MATERIAL PARAMETER CHARACTERIZATION

Photovoltaic response had been observed in $Cu_2S/Cd_{0.9}Zn_{0.1}S$ devices prepared by reactive sputtering (Ref. 1). The fine finger grid pattern has now been sputtered onto a number of cells. I-V characteristics of individual grid lines ($Au/Cd_{0.9}Zn_{0.1}S/Nb$) showed random shorts. The problem was traced to pinholes associated with substrate handling and cleaning procedures. Corrective action is being undertaken to eliminate particulate contamination of the substrate. In the meantime, useful information has been obtained on large area cell performance by interconnecting unshorted grid lines.

The V-I characteristics of two regions of a $Cu_2S/Cd_{0.9}Zn_{0.1}S$ device are shown in Fig. 10. This device had one grid short which was removed, and the cell operated as two unequal area segments. The conversion efficiencies of 0.37 and 0.39 percent were measured under natural insolation. The poor fill factors ($FF \approx 0.35$) were due to a high series resistance in combination with an apparent photosensitive shunt conductance.

Cu_2S/CdS devices were also deposited, but series resistance was inordinately large because of the use of undoped CdS. The CdS was photoconductive so that a diode characteristic was only observed under illumination.



(a) Small section of device 401

(b) Large section of device 401

Fig. 10 Current-Voltage Characteristic of All Sputter Deposited $Cu_2S/Cd_{0.9}Zn_{0.1}S$ Cell

Section 4

SUMMARY STATUS

All steps in the sputter deposition of Au/$Cu_2S/Cd_{1-x}Zn_xS$/Nb cells have been demonstrated. Preliminary efficiency measurements were made on nonoptimized $Cu_2S/Cd_{0.9}Zn_{0.1}S$ cells. A problem of pinhole shorts on the Au gridded cells was identified, and remedial action was instituted. Emphasis was shifted from the $Cu_2S/Cd_{0.9}Zn_{0.1}S$ cell to the Cu_2S/CdS cell. However, the cathode vendor had mislabeled the pure Cd and Cd:In cathodes so that most of the work this reporting period was performed with the wrong cathode. Analysis of the results obtained with the pure Cd cathode enabled us to identify the problem, so work during the next quarter will concentrate on the Cu_2S/CdS:In cell and its optimization.

A significant result of this quarter's work was identification of the influence of the Nb substrate contact on the electrical properties of the CdS or $Cd_{0.9}Zn_{0.1}S$ films deposited over the contact metal.

Section 5
REFERENCES

1. Final Report on Contract EG-77-C-03-1459, Nov 1978
2. D. L. Losee, J. Appl. Phys. Vol. 46, 1975, pp. 2204
3. Institute of Energy Conversion, Progress Report DSE/2538-3, Jul 1977 (Note that we erroneously reported $E_T = 0.23$ eV at the In-Depth Review Meeting, Univ. of Delaware, 28 Feb - 2 Mar 1979)

☆U.S. GOVERNMENT PRINTING OFFICE: 1979-640-258-1581