

N76 12494

APPLIED RESEARCH ON II-VI COMPOUND MATERIALS
FOR HETEROJUNCTION SOLAR CELLS

NSF Grant GI-38445X

July 1, 1974 - June 30, 1975

\$ 53,954

Richard H. Bube

Department of Materials Science and Engineering
Stanford University
Stanford, California 94305

Professor Richard H. Bube, Principal Investigator

National Solar Photovoltaic Program Review Meeting
July 22-25, 1975
Los Angeles, California

ABSTRACT

The objective of this grant is the investigation of heterojunction solar cells based on several II-VI compound systems suitable for large-scale terrestrial utilization.

Several II-VI heterojunctions show promise for photovoltaic conversion of solar energy. The three of greatest interest are p-CdTe/n-CdS, p-CdTe/n-ZnSe, and p-ZnTe/n-CdSe. The last of these three is of interest primarily as an opportunity to determine the effects of very small lattice mismatch rather than as an actual solar cell. p-CdTe/n-CdS heterojunction cells have been prepared by close-spaced transport deposition of p-CdTe on single crystal n-CdS, and by two-source vacuum evaporation of n-CdS on single crystal p-CdTe. Both types of cells, in an experimental stage, are quite comparable, exhibiting values of quantum efficiency between 0.5 and 0.9, open-circuit voltages between 0.50 and 0.66 V, fill factors between 0.4 and 0.6, and solar efficiencies up to 4 percent. Cells of p-ZnTe/n-CdSe have also been made by close-spaced vapor transport deposition of n-CdSe on single crystal p-ZnTe.

A detailed program of heterojunction evaluation has been initiated, involving (1) J-V characteristics in the dark vs temperature to determine diode properties in the absence of illumination, (2) J-V characteristics in the light using the solar simulator, (3) V_{oc} vs J_{sc} as a function of light intensity at different temperatures to determine magnitudes and temperature dependence of key diode parameters, (4) junction capacitance vs voltage in light and dark, (5) SEM determination of minority carrier diffusion lengths, (6) optical transmission to determine exact variation of absorption constant with photon energy, and (7) spectral response of J_{sc} to determine dependence of quantum efficiency on photon energy.

Measurement of J-V curves in the dark as a function of temperature for evaporated n-CdS on p-CdTe heterojunctions reveals two ranges of behavior: above 250°K, the current is thermally activated, $\eta = 2.4$ and is independent of temperature, and $J_0 = 1.9 \times 10^2 \exp(-0.54 \text{ eV}/kT) \text{ A/cm}^2$; below 250°K, tunneling dominates, $\eta = 21 \text{ V}^{-1}$ and is independent of temperature, and $J_0 = 5.7 \times 10^{-10} \text{ A/cm}^2$ independent of temperature. J_0 and/or η may be light-dependent, as evidenced by the crossover of light and dark J-V curves. Low fill factors may be associated with a bias-dependent quantum efficiency. No transient or quenching effects have been observed in this system at room temperature.

Making ohmic, low-resistance contacts to p-CdTe has been a major problem. Such contacts can be made with Ni to a surface etched with $\text{K}_2\text{Cr}_2\text{O}_7:\text{H}_2\text{SO}_4:\text{H}_2\text{O}$, after heat treatment, if the CdTe resistivity is less than 10 ohm-cm. Ohmic, low-resistance contacts have been made with Ni to 133 ohm-cm p-CdTe after implantation of the CdTe with As. Evidence is conclusive from a variety of sources that the contact consists of a thin Schottky bar or with current transport dominated by tunneling.

p-ZnTe/n-CdSe heterojunctions show quantum efficiencies between 0.18 and 0.30, open-circuit voltages between 0.55 and 0.68 V, fill factors between 0.38 and 0.49, and solar efficiencies up to about 1 percent. A bias-dependent quantum efficiency is indicated due to short diffusion length of photoexcited holes in CdSe. V_{oc} vs $\ln J_{sc}$ measurements indicate that between 74°C and 221°C η changes from 10.2 to 15.6 V^{-1} (η from 3.25 to 1.49) and $J_0 = 1.3 \times 10^{-3} \exp(-0.33 \text{ eV}/kT)$, suggesting thermally assisted tunneling as the current transport mode.

Future work includes detailed correlation of diode parameters in p-CdTe/n-CdS and p-ZnTe/n-CdSe with preparation variables, investigation of methods to increase the conductivity of both surface and bulk p-CdTe, determination of the properties of p-ZnTe/n-CdSe junctions made on (111) oriented ZnTe to achieve minimum lattice mismatch condition, and evaluation of p-CdTe/n-ZnSe heterojunctions.

**APPLIED RESEARCH ON II-VI COMPOUND MATERIALS
FOR HETEROJUNCTION SOLAR CELLS
NSF Grant GI-38445X**

Stanford University

July 1, 1974 - June 30, 1975

\$ 53,954

**Professor Richard H. Bube
Principal Investigator**

PROJECT OBJECTIVES

**INVESTIGATION OF HETEROJUNCTION SOLAR CELLS BASED
ON SEVERAL II-VI COMPOUND SYSTEMS SUITABLE FOR
LARGE-SCALE TERRESTRIAL UTILIZATION.**

PLANNED ACTIVITY LAST 6 MONTHS

- * PREPARE AND INVESTIGATE ALL FILM p-CdTe/n-CdS CELLS
- * OPTIMIZE ELECTRICAL CONTACTS TO p-CdTe
- * BRING NEW VACUUM SYSTEM TO FULL OPERATING POTENTIAL
- * BEGIN EVALUATION OF OTHER II-VI HETEROJUNCTION SYSTEMS:
p-ZnTe/n-CdSe, p-CdTe/n-ZnSe, p-ZnTe/n-CdTe

HETEROJUNCTION EVALUATION

- * J-V CHARACTERISTICS IN DARK vs TEMPERATURE
Diode properties in absence of illumination
- * J-V CHARACTERISTICS IN LIGHT
Using solar simulator, determine J_{sc} , V_{oc} , fill factor, collection efficiency, solar efficiency
- * V_{oc} vs $\ln J_{sc}$ PLOTS AS A FUNCTION OF LIGHT INTENSITY AT DIFFERENT TEMPERATURES
Diode constant at different temperatures, $J_0(T)$, and effective barrier height for forward currents in light
- * JUNCTION CAPACITANCE vs V IN DARK AND LIGHT
Width and variation of depletion layer
- * SEM DETERMINATION OF MINORITY CARRIER DIFFUSION LENGTHS
- * OPTICAL TRANSMISSION
Absorption constant vs photon energy
- * SPECTRAL RESPONSE OF J_{sc}
Variation of quantum efficiency on photon energy

EVAPORATED n-CdS ON SINGLE CRYSTAL p-CdTe

* HEAT TREATMENT TO ABOUT 430°C REQUIRED FOR OPTIMUM PERFORMANCE

* DIODE CHARACTERISTICS IN THE DARK vs TEMPERATURE

$$T > 250^{\circ}\text{K} \quad J = J_0 \left[\exp \left(\frac{qV}{\eta kT} \right) - 1 \right]$$

$$J_0 = J_0^{\circ} \exp \left(-E^*/kT \right)$$

$$\eta = 2.4 \quad E^* = 0.54 \text{ eV}$$

$$T < 250^{\circ}\text{K} \quad J = J_0 \left[\exp(\alpha V) - 1 \right]$$

$$J_0 = 5.7 \times 10^{-10} \text{ A/cm}^2$$

$$\alpha = 21 \text{ V}^{-1}$$

* J AND/OR η ARE LIGHT DEPENDENT AS EVIDENCED BY THE CROSSOVER OF LIGHT AND DARK J-V CURVES

* A BIAS-DEPENDENT COLLECTION EFFICIENCY MAY CONTRIBUTE TO LOW FILL FACTORS

* NO TRANSIENT OR QUENCHING EFFECTS OBSERVED AT ROOM TEMPERATURE

ELECTRICAL CONTACTS TO p-CdTe

- * OHMIC, LOW-RESISTIVITY CONTACT TO SURFACE OF p-CdTe ETCHED WITH $K_2Cr_2O_7:H_2SO_4:H_2O$ FOR RESISTIVITY < 10 OHM-CM
- * OHMIC, LOW-RESISTIVITY CONTACT TO SURFACE OF p-CdTe IMPLANTED WITH As FOR RESISTIVITY OF 133 OHM-CM
- * DEVELOPMENT OF A "3-POINT" MEASURING TECHNIQUE THAT ALLOWS CELL EVALUATION EVEN IF CONTACTS NOT IDEAL
- * EVALUATION OF OHMIC TO NON-OHMIC TRANSITION BY MEASURING CONTACT PROPERTIES vs TEMPERATURE
- * MODEL FOR CONTACT INVOLVING A THIN SCHOTTKY BARRIER WITH CURRENT TRANSPORT DOMINATED BY TUNNELING
 - Chemical effect of etching
 - Auger analysis of contact
 - Low-temperature capacitance
 - Quantitative shape of temperature dependence

OTHER II-VI SYSTEMS: p-ZnTe/n-CdSe

* 11 HETEROJUNCTIONS MADE BY CLOSE-SPACE VAPOR TRANSPORT OF CdSe ONTO SINGLE CRYSTAL ZnTe

* OHMIC LOW-RESISTANCE CONTACTS POSSIBLE TO ETCHED p-ZnTe

* TYPICAL CELL PARAMETERS

V_{oc}	0.55 - 0.68 V	Fill Factor	0.38 - 0.49
Quantum Efficiency	0.18 - 0.30	Solar Efficiency	0.55 - 0.85 percent

* DIODE CHARACTERISTICS AT 22°C

$$\begin{aligned} \eta_{dark} &= 2.38 & \eta_{light} &= 2.41 \\ J_{o, dark} &= 4.2 \times 10^{-9} \text{ A/cm}^2 & J_{o, light} &= 1.2 \times 10^{-8} \text{ A/cm}^2 \end{aligned}$$

* TEMPERATURE DEPENDENCE OF DIODE CHARACTERISTICS IN LIGHT

$$\begin{aligned} \eta \text{ at } 74^\circ\text{C} &= 3.25 & \eta \text{ at } 221^\circ\text{C} &= 1.49 \\ J_o &= 1.3 \times 10^{-3} \exp(-0.33 \text{ eV/kT}) \text{ A/cm}^2 \end{aligned}$$

SUMMARY OF KEY RESULTS

- * CONTACTS TO p-CdTe ARE UNDERSTOOD; OHMIC, LOW-RESISTANCE CONTACTS CAN BE MADE; CELLS CAN BE EVALUATED EVEN IN THE ABSENCE OF IDEAL CONTACTS
- * TWO MECHANISMS DETECTED FOR J_0 FOR p-CdTe/n-CdS: HIGH-TEMPERATURE THERMALLY ACTIVATED WITH $E^* = 0.54$ eV, AND LOW-TEMPERATURE TUNNELING
- * J_0 FOR p-ZnTe/n-CdSe IS THERMALLY ACTIVATED AT HIGH TEMPERATURES WITH $E^* = 0.33$ eV
- * EVIDENCE FOR A BIAS-DEPENDENT COLLECTION EFFICIENCY CONTRIBUTING TO POOR FILL FACTORS
- * DEVELOPMENT OF VACUUM EVAPORATOR SYSTEM
- * IMPORTANCE OF LIGHT AND PREPARATION VARIABLES ON J_0 AND η

PLANNED ACTIVITY FOR NEXT 6 MONTHS

* **p-CdTe/n-CdS HETEROJUNCTIONS**

Correlation of E^* with preparation variables
Determine presence and extent of bias-dependent collection efficiency
Transient measurements at low T to determine effect of light on J_0 and
Optimization of CdS film deposition

* **ELECTRICAL CONTACTS TO p-CdTe**

Evaluations for other metals with different work functions
Investigation of methods to make surface high conductivity
Contacts to p-CdTe films

* **p-ZnTe/n-CdSe HETEROJUNCTIONS**

Properties of junctions on (111) oriented ZnTe to achieve minimum lattice mismatch (0.35 percent)
Full characterization of junction properties

* **OTHER SYSTEMS**

The system of principal interest is p-CdTe/n-ZnSe
Larger "window"
Larger diffusion voltage
Susceptible of extension to p-CdZnTe/n-ZnSSe
If results with p-CdTe/n-CdS warrant, then p-CdTe/n-CdZnS