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Progress Report No. 7

MECHANISM OF THE PHOTOVOLTAIC EFFECT IN II-VI COMPOUNDS

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

October 1 - December 31, 1969

School of Engineering
Department of Materials Science
Stanford University
Stanford, California

Grant NGL-05-020-214 S-1

Principal Investigator
Richard H. Bube, Professor

Report Prepared By:
R. H. Bube
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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

The nature and interrelationship of electronic transitions involved in the photocapacitance effects at a Cu₂S-CdS non-heated heterojunction were investigated in a detailed study involving measurements of spectral response, optical quenching in different wavelength ranges, forward and reverse bias effects on quenching, and the influence of the photocapacitance on the short-circuit current, open-circuit voltage, and forward current of a photovoltaic cell. The electronic transitions involved in these processes afford a unique opportunity to investigate the properties and the role played by extrinsic states at the heterojunction, such effects being related to the final operational characteristics of a heat-treated cell.

A persistent increase in capacitance of a Cu₂S-CdS heterojunction occurs after photoexcitation at any temperature below room temperature. At 110°K, this persistent capacitance increment can be as high as 50 percent of the value of the dark capacitance. This persistent capacitance can be quenched by heating, applying forward bias in the dark, or by irradiating with suitable wavelengths. The electronic transitions responsible for these effects can be described in terms of a band diagram for the junction involving a narrow conduction band spike, a set of high-lying imperfection levels in the CdS at the junction, and a set of deep-lying imperfection levels in the CdS at the junction.

Investigation of these effects as a function of cell dipping time in junction formation, crystallographic orientation of the crystal face, and heat treatment after formation is to be followed up. Such studies will also form part of our larger program on the effect of methods of junction formation on the photovoltaic properties of the resulting cells.
1. INTRODUCTION

In our previous report (Progress Report: No. 6), we described the results of some preliminary investigations of photocapacitance effects at non-heat-treated Cu$_2$S-CdS heterojunctions. It was found that there was a persistent increase in capacitance of the junction after photoexcitation at any temperature below room temperature, increasing in magnitude with decreasing temperature of the photoexcitation. At a temperature of about 110$^\circ$K this persistent capacitance increment can be as high as 50 percent of the value of the dark capacitance. Three methods of "quenching" this photocapacitance increment were discussed: (a) heating the cell in the dark (thermal quenching), (b) applying forward bias at low temperature in the dark (forward bias quenching), and (c) illuminating the junction at low temperature with near-infrared radiation in the wavelength range 0.7 to 1.0 micron (1.2 to 1.8 ev) (optical quenching). Because it is evident that the electronic transitions involved in these processes afford a unique opportunity to investigate the properties and role played by extrinsic states at the heterojunction, such effects being related to the final operational characteristics of the heat-treated cell, the nature of these phenomena has become a subject for concentrated investigation.

This report describes the results of a complete series of measurements of the photocapacitance effect performed on a single sample (3-B(P-E)-1; i.e., B-face CdS sample, polished and etched before junction formation). A tentative interpretation of these effects in terms of electronic transitions at the junction is developed.
II. MEASUREMENT OF THE PHOTOCAPACITANCE EFFECTS

The basic experimental procedures are the same as those described in Progress Report No. 6. All capacitance data were obtained with a Boonton 75-D Capacitance Bridge with a 77-2A Range Extender. The operating frequency is 1 MHz, and the amplitude was fixed at about 30 mv peak-to-peak. Independent measurements show that the magnitude of both the dark capacitance and the photocapacitance increment are only weak functions of the frequency at which the capacitance measurement is made.

Excitation Spectrum

The excitation spectrum for the photocapacitance at 106°K is given in Figure 1. (This is a more complete and accurate representation of the effect than Figure 2 of Report No. 6.) Below 0.8 micron, the solid curve indicates the value of the capacitance with the exciting monochromatic excitation on, and the dashed curve is the value reached after the excitation is turned off; thus the difference represents the contribution to the capacitance from free or shallowly trapped carriers. For wavelengths longer than 0.8 microns, there is no difference between the two curves.

A wavelength of 0.5 micron, near the band edge of CdS, produces a photocapacitance increment of about 350 pf, which is more than half the value of the dark capacitance at that temperature. The excitation spectrum of Figure 1 can be interpreted as being composed of the following processes: (a) excitation of photocapacitance by intrinsic radiation (0.5 micron and less); (b) excitation of photocapacitance by extrinsic radiation (0.6 - 0.8 micron); (c) quenching of photocapacitance by extrinsic radiation (0.8 - 1.0 micron); and (d) low-level excitation of photocapacitance by extrinsic radiation out to about 1.4 micron.
Figure 1. Excitation Spectrum of Photocapacitance at 105°K.
Optical Quenching of Photocapacitance

Optical quenching spectra for the photocapacitance, measured in different ways, are given in Figure 2. This experiment is performed by first establishing the photocapacitance increment, then shining on monochromatic light for a fixed time and recording the change in capacitance.

Three quenching curves are given in Figure 2. Two were obtained at 110K and indicate the effect of doing the primary excitation with white light rather than monochromatic (0.5 micron) light. The third curve is obtained at 250K after excitation by 0.52 micron light.

Since, as noted above, the total photocapacitance increment excited by 0.5 micron light at 105K is about 350 pF, Figure 2 shows that 0.85 micron light quenches about 2/3 of this photocapacitance. With white light primary photoexcitation, the total photocapacitance increment is smaller, about 250 pF, and Figure 2 indicates that subsequent 0.85 micron light quenches only about 40 percent of this. It may also be noted that with 0.5 micron pre-excitation at 110K, some quenching is found for wavelengths as far out as 2.3 micron; for white light pre-excitation, however, all quenching beyond 1.1 micron is absent. Indeed, for white light pre-excitation, a small increase in capacitance is found for wavelengths between 1.2 and 1.4 micron. It can only be concluded that white light pre-excitation involves strong self-quenching, particularly in the wavelength range beyond 1.1 micron.

At 250K, pre-excitation by 0.52 micron light produces a photocapacitance of 90 pF. Two resolved quenching bands with maxima at about 0.9 micron and at 1.4 micron are measured.

It is evident from Figure 2 that quenching in the short and long wavelength ranges has a quite different temperature dependence. This temperature dependence is shown explicitly in Figure 5, where the magnitude of the quenching by 0.85 micron and 1.35 micron light is plotted as a
Figure 2. Optical Quenching Spectra of Photocapacitance at 110° and 250°K.
function of temperature. The decrease in photocapacitance caused by 1.35 micron light is independent of temperature, whereas the decrease caused by 0.85 micron light decreases with increasing temperature. The fraction of the total photocapacitance quenched by 0.85 micron light also decreases with increasing temperature, from about 2/3 at 110°K to about 1/2 at 250°K.

Applied Bias Effects

The effects of applied bias and of optical quenching can be displayed in a unique diagram at a given temperature, such as is shown in Figure 4 at 110°K and Figure 5 at 250°K. These diagrams summarize the effect of forward and reverse bias on the photocapacitance under three conditions: (a) in the dark, (b) quenched first with 1.35 micron light and exposed to 1.35 micron light during the bias measurements, and (c) quenched first with 0.85 micron light and exposed to 0.85 micron light during the bias measurements.

The results may be conveniently summarized as follows:

1. Reverse bias in the dark or with 1.35 micron light has only a very small effect on the photocapacitance.

2. Reverse bias with 0.85 micron light causes a significant decrease in the part of the photocapacitance remaining after optical quenching by 0.85 micron light only. At 110°K, the photocapacitance can be almost entirely removed by the combination of 0.85 micron light and reverse bias.

3. Forward bias in the dark causes a large decrease in photocapacitance, which is initially linear with applied voltage. Above about 0.6 V, the decrease in photocapacitance becomes relatively insensitive to increasing forward bias.

4. Forward bias with 1.35 micron light produces an effect similar to that caused by forward bias in the dark alone.

5. Forward bias with 0.85 micron light (after the full extent of optical quenching by this wavelength light) causes only a small additional
Figure 4. Effect of Applied Bias Voltage and Quenching Light on Photocapacitance at 110°K.
Figure 5. Effect of Applied Bias Voltage and Quenching Light on Photocapacitance at 250°K.
decrease in photocapacitance.

**Thermal Quenching of Photocapacitance**

The effect of heating on the photocapacitance established by photostimulation at a low temperature (like Figure 1 of Report No. 6) is shown in Figure 6. Four curves are shown: (a) the full photocapacitance with no other quenching process before heating; (b) partially quenched by forward bias before heating; (c) partially quenched by 0.85 micron light before heating; and (d) partially quenched by heating to 180°K, recooled to 110°K, and then reheated.

The various curves are quite similar and share the following characteristics. (The fact that the partially thermally-quenched curve lies above the full photocapacitance curve is attributable to the experimental fact that the measured dark capacitance on cooling was lower for this case than for the others for an unknown reason, and probably should not be ascribed basic significance.) A broad maximum in the photocapacitance vs. T curve characterizes the partially-quenched measurements, being most pronounced in the partially thermally-quenched case. The photocapacitance over the low-temperature range of 110°- 200°K is reduced much more in each case than the photocapacitance at higher temperatures.

**Relationship Between 0.85 and 1.35 Micron Quenching**

Capacitance as a function of time is shown in Figure 7 for two cases: (a) optical quenching in the order, 1.35 micron first and then 0.85 micron; and (b) for the reverse order. The 0.5 micron pre-excitation light is turned off at t=0, and the initial drop up to 1200 seconds is due to the decay of free or shallowly trapped carriers.

Two observations may be made from Figure 7. (1) When the 1.35 micron quenching light is turned off, there is an additional drop in capacitance. This effect is not observed for the 0.85 micron light. (2) Complete
Figure 6. Thermal Quenching of Full Photocapacitance and of Partially Quenched Photocapacitance
Figure 7. Capacitance vs. Time at 110°K, Showing Sequential Optical Quenching by 0.85 and 1.35 Micron Light
quenching with 0.85 micron light followed by 1.35 micron light results in a capacitance increase.

Both of these results show a significant photoexcitation of photocapacitance associated with 1.35 micron light.

It may also be noted from Figure 7 that initial quenching with 1.35 micron light has no effect on the level finally reached by quenching with 0.85 micron light.

**Effect of Previous Partial Quenching on 1.35 Micron Quenching**

Figure 8 shows the effect of initial partial quenching of photocapacitance by 0.85 micron light, forward bias, or heating, on the subsequent quenching by 1.35 micron light. To first order the manner of the partial quenching is irrelevant to the effect caused.

The magnitude of the quenching by 1.35 micron light decreases linearly with the magnitude of the initial partial quenching until quenching by 1.35 micron light disappears completely. This happens at a point corresponding to about 1/3 of the total photocapacitance removed by initial partial quenching. When more than this fraction of the photocapacitance is removed by the initial partial quenching, irradiation with 1.35 micron light produces excitation of photocapacitance.

**Effect of Photocapacitance Increment on Photovoltaic Properties of the Cell**

We have reported previously simply that the presence or absence of the photocapacitance in the non-heat-treated cells is vastly less significant for the properties of the photovoltaic cell than it is for the heat-treated cells. The effect in non-heat-treated cells is not completely negligible, however, and in general can be seen as (a) an increase in short-circuit current, (b) a decrease in open-circuit voltage, and (c) an increase in low-voltage forward current.
Figure 8. Effect of Previous Partial Quenching of Photo-
Capacitance on Subsequent Optical Quenching by
1.35 Micron Light
The spectral response of the cell at 105°K is shown in Figure 9 with and without the photocapacitance increment present, together with the spectral response at 300°K for reference. (The discontinuities in the curves are simply the result of changing gratings and will be removed by later calibration.) In order to obtain the data of Figure 9, the values of short-circuit current were measured at each wavelength as a function of time. For each of the two curves, with and without the photocapacitance, only the initial value is plotted. With no photocapacitance initially, the capacitance increases with time in the monochromatic light in accordance with the excitation spectrum of Figure 1; this in turn causes an increase in the short-circuit current with time. Similarly, beginning with the total photocapacitance as excited by 0.5 micron light, the capacitance decreases with time in the monochromatic light according to the quenching spectrum indicated in Figure 2. It is evident that the presence of the photocapacitance enhances the short-circuit current considerably over the entire response range at this temperature.

Figure 10 gives the spectral response of open-circuit voltage with and without photocapacitance, compared to the 300°K curve. The same remarks apply as in the case of Figure 9. The presence of the photocapacitance decreases the open-circuit voltage over the entire response range, although it is still higher than at 300°K for wavelengths less than 0.9 microns.

Figure 11 shows that the presence of the photocapacitance causes a significantly higher forward current flow in the dark. Since forward bias causes a decrease in photocapacitance, it was necessary to re-excite the photocapacitance several times in order to obtain these data.
Figure 9. Effect of Photocapacitance on Spectral Response of Short-Circuit Current at 105°K. Response Also Shown for 300°K.
Figure 10. Effect of Photocapacitance on Spectral Response of Open-Circuit Voltage at 105°K. Response Also Shown for 300°K.
Figure 11. Effect of Photocapacitance on the Forward I-V Characteristic in the Dark at 105°K.


***III. DISCUSSION OF RESULTS***

When all of the preceding results are considered together, certain coherent characteristics emerge. It is most convenient to discuss these patterns in terms of electronic processes taking place at or near the junction. Seven major electronic processes involving a minimum of assumptions or ad hoc mechanisms are summarized in the various parts of Figure 12.

(a) **Excitation of Photocapacitance by Intrinsic Radiation**

When an electron-hole pair is created in the vicinity of the junction, the electron drifts into the CdS and the hole is captured near the junction in an imperfection level, probably due to Cu impurity in the CdS. The trapped positive charge is responsible for the photocapacitance.

(b) **Excitation of Photocapacitance by Extrinsic Radiation, 0.5 - 0.8 Micron**

Direct excitation from the impurity levels produces a trapped hole with the same effects as (a).

(c) **Excitation of Photocapacitance by Extrinsic Radiation out to 1.4 Micron**

Several of the processes to be described, of which this is the first, indicate the importance of a level closer to the conduction band of CdS than the imperfections referred to in (a) and (b). Two processes are possible by which long wavelength excitation could proceed through such a higher-lying level. (1) Excitation of electron out of the deep impurity level to the higher-lying level, followed by tunneling of the electron out into the CdS, leaving the trapped hole on the deeper level. (2) Excitation of electron from the valence band of Cu$_2$S to the higher-lying level, followed by tunneling of the electron from the higher-lying level into the conduction band of the CdS, and by tunneling of the hole in the Cu$_2$S valence band into the impurity level.
Figure 12. Band Diagrams Illustrating Electronic Processes in
Excitation and Quenching of Photocapacitance (See Text)
Figure 12. Band Diagrams Illustrating Electronic Processes in Excitation and Quenching of Photocapacitance (See Text)
(d) Quenching of Photocapacitance by Forward Bias in the Dark

It is known that the forward bias current is primarily a tunneling current, tunneling proceeding through an intermediate imperfection level at the junction. Suggested here is that the forward tunneling current passes through the higher-lying level introduced in (c) and then recombines with the trapped holes in the lower-lying level. An immediate corollary is the conclusion that the greater the density of trapped holes (i.e., the larger the photocapacitance) the greater the forward tunneling current, as observed.

(e) Optical Quenching of Photocapacitance with Wavelengths Near 0.85 Micron

Radiation with this photon energy (greater than 1.2 eV) can either optically excite holes trapped in the deeper-lying imperfection levels to the valence band where they can diffuse out into the Cu$_2$S, as in the normal optical quenching of photoconductivity, or can excite electrons in the Cu$_2$S which recombine with these trapped holes after passing through into the CdS, as in the decay of enhancement with operation time in the heat-treated cells. Insofar as a competing process exists for optically freed holes between diffusing out and being recaptured at the imperfection levels, reverse bias should enhance quenching, as observed.

(f) Optical Quenching of Photocapacitance with Wavelengths Near 1.35 Micron

Quenching by long wavelength radiation is caused by excitation of an electron from the valence band of Cu$_2$S to the higher-lying imperfection level at the junction, followed by recombination of the electron in the higher-lying imperfection level with a hole in a deeper-lying level. Since this quenching process has to compete with return of the electron in the higher-lying level to the valence band of Cu$_2$S by recombination, or the loss of this electron to the CdS by tunneling, it is expected that its magnitude would be relatively small, as observed. Furthermore, since the net effect of 1.35 micron radiation, whether excitation or quenching, depends
on the instantaneous occupancy of the deeper-lying levels, due to competition between \((c)\) and \((f)\), it is expected that the actual effect of 1.35 micron radiation will depend critically on this occupancy, as observed. Also since the diffusion away of free holes is not involved in the 1.35 micron quenching, no effect of reverse bias should be found, again as observed.

\((g)\) Thermal Quenching of Photocapacitance

In many ways the thermal quenching of photocapacitance poses the greatest problem for interpretation: how are holes which require over a volt of energy to be removed optically to the valence band, removed thermally over a temperature range corresponding to thermal activation energies of a few tenths of a volt? The answer must be that this thermal energy is sufficient to produce electrons that are able to recombine with these holes. But then, what is the source of these electrons? Figure 12g shows one possibility, i.e., that the electrons come from the valence band of Cu$_2$S, are thermally excited to a higher-lying unoccupied level a few tenths of a volt above the valence band at the junction, and then recombine with the holes trapped in the CdS.

Another possibility, not shown, is that the electrons are somehow freed from shallow electron traps, previously filled by photoexcitation, and recombine with the trapped holes in the CdS. That the nature of the non-heat-treated interface enters this problem critically is shown by our previous experiments proving that optical and thermal hole-freeing energies for quenching in heat-treated cells were comparable. We predict a large increase in the thermal quenching energy when we heat-treat the present cells.

Effect on Photovoltaic Properties of Photocapacitance

If a small conduction band spike remains in the non-heat-treated cells,
as previously shown for the heat-treated cells, and as indicated schematically in Figure 12, the presence of the photocapacitance could increase the short-circuit current by narrowing this spike and increasing the tunnelling probability. The corresponding decrease in open-circuit voltage is an automatic consequence of the increase in short-circuit current and in \( I_o \) as shown in Figure 11. These three quantities are related by

\[
I_{sc} = I_o \left( e^{\frac{V_{oc}}{\alpha}} - 1 \right)
\]

or

\[
\frac{I_{sc}}{I_o} = e^{\frac{V_{oc}}{\alpha}}
\]

for \( \alpha V_{oc} > 1 \). For a finite change \( \Delta \) in both \( I_{sc} \) and \( I_o \),

\[
\Delta V_{oc} = \ln \left( \frac{I_{sc}(\Delta C)}{I_{sc}(0)} \right) \frac{I_o(0)}{I_o(\Delta C)}
\]

where \( I_{sc}(\Delta C) \) represents the short-circuit current at a given wavelength with the photocapacitance, and \( I_{sc}(0) \) is the same without the photocapacitance. For a wavelength of 6.8 microns, we have from Figs. 9-11,

\[
\frac{I_{sc}(\Delta C)}{I_{sc}(0)} = 3.14, \quad \frac{I_o(\Delta C)}{I_o(0)} = 6.29, \quad \text{and} \quad \alpha = 1.58 \times 10^{-2} \text{ mV}^{-1}
\]

giving a predicted value of \( \Delta V_{oc} = -48 \text{ mV} \), to be compared with the experimental value of \( \approx 20 \text{ mV} \).

**IV. FUTURE WORK**

The deep centers which act as hole traps to produce the photocapacitance effect are thought to be due to Cu diffused into the CdS. If this is true, then the magnitude of the photocapacitance should depend on the time of dipping in the CuCl solution to form the cell. This kind of effect will be investigated.
Photocapacitance data will also be obtained for several other cells, covering the range of fabrication variables used, as given in Report No. 5. The effect of short-time heat treatment on the photocapacitance properties of the cell will also be investigated.

A recent paper by Sullivan (C.A.Sullivan, Phys.Rev. 164, 706 (1967)) gives low-temperature diffusion data for electrically active Cu in CdS. By adjusting Sullivan’s data to 75°C, the dipping temperature of the cells, doping profiles can be calculated. From these, theoretical values of maximum photocapacitance can be derived for comparison with the experimental values.

Other aspects of our work, i.e., the effect of mode of junction formation, surface properties etc. on the photovoltaic cell, will of course also be continued and expanded.