EFFECT OF VARIOUS OPTICAL RADIATIONS AND WATER VAPOR ON TRAPPING SPECTRUM OF CADMIUM SULFIDE

by Paul A. Faeth
Lewis Research Center
Cleveland, Ohio
EFFECT OF VARIOUS OPTICAL RADIATIONS AND WATER VAPOR
ON TRAPPING SPECTRUM OF CADMIUM SULFIDE

By Paul A. Faeth

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – CFSTI price $3.00
EFFECT OF VARIOUS OPTICAL RADIATIONS AND WATER VAPOR
ON TRAPPING SPECTRUM OF CADMIUM SULFIDE*

by Paul A. Faeth
Lewis Research Center

SUMMARY

Trapping levels in a single cadmium sulfide crystal were studied by the thermally stimulated current method. In all, six trapping levels were detected in the crystal. A study of the shallow traps, which occurred at 0.04, 0.12, and 0.13 electron volt below the conduction band edge, indicated that these traps could be filled preferentially by matching the photon energy to the energy height of the trap above the valence band edge. Also, filled traps could be emptied by light with sufficient energy per photon. Cooling of the crystal during illumination with white light populated a previously unreported trapping level. Water vapor which was adsorbed on the crystal surface produced a thermally stimulated current at 80° to 100° C in the absence of any treatment of the crystal by light. This peak was ascribed to the break up of water ions on the crystal surface. Pumping on the crystal with adsorbed water present also stimulated currents believed due to desorption of water ions.

INTRODUCTION

Cadmium sulfide is a material of considerable interest because of its photoelectric properties. It has found wide use as a photoconductor, and more recently has shown promise as a solar cell material (ref. 1). The photoelectric properties of cadmium sulfide are modified by the presence of electron and hole traps in the crystal (refs. 2 and 3) and by adsorbed gases, which may produce electrical effects similar to traps (refs. 4 to 6). It is reasonable to suppose that the operation of devices such as the cadmium sulfide solar cell will be affected by the presence of traps and adsorbed gases. Indeed, adsorbed water vapor seriously damages cadmium sulfide solar cells and photoconductors. Consequently, trapped carriers were studied in a single crystal of high-resistivity

cadmium sulfide, by using the thermally stimulated current (TSC) technique. The trapping levels observed in this research occur at energies which correspond approximately to those previously reported for electron traps, and it is assumed that only electron traps were observed.

Various wavelengths of light were used singly and in combination with other wavelengths to populate the trapping levels. The purpose of this procedure was to make qualitative observations on the manner in which radiation filled and emptied the traps. In another series of experiments, water vapor was allowed to adsorb on the crystal surface. The effect on the thermally stimulated current was observed in order to determine the effect of absorbed water vapor on the electrical properties of the crystal.

EXPERIMENTAL APPARATUS AND PROCEDURE

The determination of trap depths in cadmium sulfide by measuring the TSC is a most informative technique. The TSC is that additional current produced in the crystal when mobile carriers are released from trapping centers by thermal energy. The mobile carriers are usually excited into the trapping centers by illumination with optical radiation at low temperatures. Recent reviews of this subject for cadmium sulfide have been given by Nicholas and Woods (ref. 7) and Dittfeld and Voigt (ref. 8).

The measuring system that was used is similar to the one described by Bube (ref. 9). A beam splitter was provided so that the sample could be exposed to two different water-filtered radiations, either simultaneously or separately. Intensity estimations only were made. Specific radiations or bands were obtained by using narrow band interference filters and/or Wratten (W-) filters and a quartz-iodine light source (ref. 10). The sample was exposed to light through a photographic shutter.

The sample was contained in a vacuum-jacketed Dewar and could be exposed to various gaseous atmospheres. Helium was used as the heat-transfer medium. Oxygen, nitrogen, and helium were introduced through a liquid-nitrogen cold trap. Water vapor was carried into the system by passing helium through a bubbler.

The specimen of cadmium sulfide was obtained from a commercial supplier. The crystal was sulfur compensated and had an initial dark resistivity of about $10^{10}$ ohm-centimeters. The crystal had been grown by evaporating pure cadmium sulfide in an inert atmosphere. Indium contacts were used in conjunction with platinum leads. In most cases a potential of 180 volts was applied across the sample. A low-order external variable resistor ($2.9 \times 10^4$ ohms) in series with the sample was used as a current detector. The voltage change across this resistor was monitored with a millimicrovoltmeter, and was recorded.

Only minor difficulty was encountered in obtaining reproducible TSC dark current
measurements from day to day. In general, the dark current which was measured without optical stimulation at liquid-nitrogen temperature was reproducible, but it was observed that the previous history (ref. 11) of the sample was important to the reproducibility of the TSC dark current obtained. Repeated measurements of the dark current showed only slight displacements if the sample was consistently stored in the dark. It was further observed that infrared radiations at liquid-nitrogen temperatures caused the equilibrium dark current to be suppressed. Subsequent experiments of white-light-excited TSC curves always resulted in peak suppression (refs. 12 and 13) after an infrared radiation and indicated a residual effect of the infrared radiation that was not easily dissipated between cycles.

Trap depths were determined by using various constant heating rates according to established techniques (refs. 3 and 7). A constant heating rate was not used for the other TSC experiments, since a relatively fast rate improved peak resolution but was unsatisfactory for trap depth calculations. Because of the rather transient nature of traps III to VI (described in the stimulation sequences in the section EXPERIMENTAL RESULTS), no attempt was made to maintain a constant rate but only a reproducible rate.

EXPERIMENTAL RESULTS

The observation of a specific trap emptying and the relative concentration of trapped carriers depended on (1) the previous history of the sample; (2) the radiation used as stimulation (including radiation combinations); (3) the temperature at which the radiation took place; and (4) the ambient atmosphere and its effect on (1), (2), and (3).

A typical thermally stimulated current curve is shown in figure 1. This curve was generated by cooling the crystal in the dark, illuminating it with white light, and then warming it. Figure 1 shows the current peaks produced from the trapping levels designated as I, II_A, II_B, IV, V, and VI. Trap III could not be filled by the technique used to fill the other traps and will be discussed in the section Cooling During Illumination. The two peaks, II_A and II_B, appeared as one if the illumination time or light intensity was excessive. The low-temperature traps, I, II_A, and II_B, had energy depths below the conduction band edge of 0.042, 0.125, and 0.131 electron volts, respectively. These values are the least squares average of 12 determinations using heating rates in the range 0.04^0 to 0.3^0 C.

Traps IV, V, and VI found at higher temperatures were not as reliably reproduced as those occurring at low temperatures. They could occasionally be induced to appear by subjecting the crystal to special treatments described in the section Wavelength-Dependent Trap Filling. However, reliable data could not be obtained which would permit significant trap depth calculations.
The dependence of the particular traps filled on the excitation wavelength is illustrated in a general way in figure 2. Helium is assumed to be the only gas present and not to interact with the surface. The solid curve represents the TSC obtained after illumination for 30 seconds with white light at liquid-nitrogen temperature and indicates that the low-temperature as well as the high-temperature traps participate. The long-dash curve was obtained when only infrared radiation (W-87, wavelengths $> 0.8 \mu$) were used at liquid-nitrogen temperature. The low-temperature traps I and II were not filled and only that trap (V) or group of traps (IV and V) in the vicinity of 60°C were occupied. A similar curve resulted if first white light or 533-millimicron illumination followed by infrared illumination was used. The short-dash curve was obtained when the following illumination scheme was used: At room temperature the sample was illuminated for 5 minutes with 899-millimicron light followed by 10 minutes with white light. The sample was then cooled to liquid-nitrogen temperature in helium and illuminated for 2 minutes with white light. The low-temperature traps were filled by this treatment. Figure 2 indicates that radiation sequences can be used to fill specific traps and exclude others if the proper sequences are known.
Other monochromatic wavelengths (30 sec at liquid-nitrogen temperature) were used as stimulating illumination, and the traps that were filled were observed. Only minor filling of traps IV and V was observed after these treatments: (1) stimulation using 533-millimicron light populated traps I and II extensively (trap II not resolved); (2) stimulation with 501-millimicron light showed lesser general trap occupancy, the peak height of trap I being 2.5 times that of traps II (no resolution); (3) 578-millimicron light showed average filling intermediate between that for items (1) and (2), with the peak height of trap II greater than that of trap I (trap II not resolved). Illumination with 697-millimicron light showed no filling of traps I and II. Evidently, as the energy used for illumination became less than the band energy (2.4 eV, wavelength = 515 m\(\mu\)), the traps close to the conduction band showed smaller trap populations. Since all except perhaps the 501-millimicron radiation were less than the band energy, these traps must have been filled directly from the valence band.
A series of experiments was performed during which time the irradiation was applied to the sample continuously during the cooling process. Woods and Nicholas (ref. 13) have performed a similar experiment with white light. The photocurrent decreased as the temperature was lowered from 100°C, leveled near room temperature, reached a maximum near -80°C, and then decreased steadily until liquid-nitrogen temperature was reached. In the presence of white light (heat filter passing wavelength less than 800 mμ), the resultant TSC curve (solid curve of fig. 3) showed the presence of a new peak III occurring at about 0°C. Traps I and II were well filled, and trap II showed no resolution. A similar experiment that was conducted by using only 533-millimicron illumination resulted in the long-dash curve, which shows the exclusion of the new peak. (Traps I and II were filled as shown by the solid curve but are excluded from the drawing for clarity.) A detail of the area around 0°C is shown in the inset of figure 3. The behavior of the solid- and long-dash curves indicated the necessary participation of at least a
second wavelength to achieve the filling of trap III. To test this hypothesis the specimen was exposed to two illuminations simultaneously as the sample was cooled. The primary illumination was 533-millimicron light; the secondary illumination was a band of light formed by the heat filter and various Wratten filters. The Wratten filters were changed between experiments and were such that additional increments of shorter wavelengths could be passed with each succeeding filter in the series. This procedure revealed that the secondary wavelength needed to allow trap III to fill lay in the region 610 to 650 millimicrons. The short-dash curve (fig. 3) illustrates the results. Secondary wavelengths greater than 650 millimicrons did not produce filling of trap III. Further qualitative support for direct filling of traps is found in these results, since the energy complement needed to fill the reported trap at 0.41 electron volt (ref. 7) would correspond to a wavelength of about 621 millimicrons. In this case, the induced trap III was not positively identified with an energy of 0.41 electron volt.

Of particular interest is the relation between the peak heights for traps I and II. Generally, the relative heights were $I > \Pi_A > \Pi_B$; the trend was reversed with the treatment described on page 3. In particular, the filling of trap I was greatly suppressed and indicated the need for the participation of yet other wavelengths to achieve trap filling. On the other hand, the presence of additional wavelengths may have been the factor that suppressed the filling of trap I.
Effect of Water on Thermally Stimulated Current

An interesting effect on the TSC was produced by water vapor. Since Bube (ref. 14) has shown that water vapor produces a reduced photoeffect for cadmium sulfide, it was pertinent to determine whether water vapor would affect the TSC. Consequently, a series of experiments was performed in which water vapor was purposely introduced into the system at or above room temperature. The sample was then cooled to liquid-nitrogen temperature, and the TSC was measured without illumination of the sample at any time. Without exception, a complex peak appeared in the vicinity of 80° to 100° C. The partial pressure of water vapor in the system was subsequently decreased by reducing the total pressure to 1/6 atmosphere. The pressure was then restored to 1 atmosphere with dry helium. The results of a series of such manipulations are shown in figure 4. The results indicate that water vapor produces simulated TSC peaks, the areas of which are a function of the partial pressure of water in the system.

After prolonged pumping, the normal dark current curve could be obtained. However, infrared illumination (W-87) at room temperature followed by cooling to liquid-nitrogen temperature (no illumination) and subsequent heating caused the 80° to 100° C peak to reappear. A similar experiment with white light at room temperature revealed a very broad peak which crested in the 80° to 100° C region. This may be attributed to photosorption of water since small amounts of water undoubtedly were still present.

Illumination with white light at liquid-nitrogen temperatures showed that the peaks at 60° and 100° C were separate and building. After three temperature cycles without changing the charge of helium, a broad peak crested near 80° C was produced. This indicated that the amount of water on the surface was increasing. The low-temperature traps remained relatively empty during these water treatments, although their presence could be detected. A subsequent TSC experiment (533-mu illumination for 2 min at liquid-nitrogen temperature) showed the strong reappearance of traps I and II and the disappearance of the 80° to 100° C peaks. Further pumping on the system again reduced the peaks in the region 80° to 100° C.

Effect of Pumping on Thermally Stimulated Current

Evacuation of the helium in the system between experiments frequently produced a current spike as the pressure decreased below approximately 1 millimeter. This peculiar effect was reproducible and was observed at room and at liquid-nitrogen temperatures (fig. 5). After a dark current determination, if the sample was returned to liquid-nitrogen temperature in the dark and was pumped and a spike was obtained, a subsequent TSC dark current measurement would show a peak at 60° C. This result indicates that
(a) No illumination.

(b) 501-Millimicron light on crystal that had been stored in dark at liquid nitrogen temperature. Photocurrent, 8x10^-6 ampere; dark current, 2x10^-8 ampere.

Figure 5. - Variation of current in cadmium sulfide crystal resulting from cyclic evacuation of helium from system.
TABLE I. - COMPARISON OF TRAP DEPTHS OF THIS RESEARCH WITH LITERATURE VALUES

<table>
<thead>
<tr>
<th>Trap</th>
<th>This research</th>
<th>Nicholas and Woods (ref. 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.042</td>
<td>155</td>
</tr>
<tr>
<td>II A</td>
<td>0.125</td>
<td>200</td>
</tr>
<tr>
<td>II B</td>
<td>0.131</td>
<td>215</td>
</tr>
<tr>
<td>III</td>
<td>-----</td>
<td>270</td>
</tr>
<tr>
<td>IV</td>
<td>-----</td>
<td>310</td>
</tr>
<tr>
<td>V</td>
<td>-----</td>
<td>330</td>
</tr>
<tr>
<td>VI</td>
<td>-----</td>
<td>400</td>
</tr>
</tbody>
</table>

traps may possibly be filled by using stimulations other than light and may be associated with the desorption of a gas (water vapor) from the surface. The effect was not observed with oxygen or nitrogen. Pumping between cycles of a normal white-light TSC determination indicated that the area of the 60° peak (fig. 1) first increased and then decreased with pumping time. This result may be similar to the heating-vacuum treatment noted by Woods and Nicholas (ref. 13).

At room temperature the pumping spikes could only be obtained after white-light or 533-millimicron illumination. Infrared (W-87) illumination occasionally produced the spike, but not always. The areas under the curves of figure 5(a) for room temperature and liquid-nitrogen temperature correspond to the participation of $6.5 \times 10^{13}$ and $1.2 \times 10^{11}$ electrons per square centimeter, respectively.

The curve illustrated in figure 5(b) is typical of the curve obtained immediately after the crystal had been stored in the dark for several weeks (a "rested" crystal). The curve was obtained under continued illumination with 501-millimicron light. After continued use of the pumping sequences, the curves illustrated in figure 5(a) were typical of the results obtained. It is tempting to associate the six current spikes of figure 5(b) with the six trap peaks observed in this study and those reported in the literature. However, further work is needed before such a correlation can be established.

**DISCUSSION**

**Energy Depth of Trapping Levels**

Nicholas and Woods (ref. 7) have made a critical survey of trapping levels in cadmium sulfide. The present results are compared with their mean values in table I. This table shows both the energy depth of the trapping levels and the temperature of maximum conductivity $T^*$ associated with each level.
Wavelength-Dependent Trap Filling

The experimental observations concerning wavelength-dependent trap filling were as follows:

1. White light fills traps I, II, IV, and V.
2. Infrared light fills traps IV and V only.
3. White light followed by infrared light fills traps IV and V only.
5. 533-Millimicron light fills traps I, II, IV, and V (with I and II enhanced and IV and V much diminished).
6. 578-Millimicron light fills traps I, II, IV, and V (with II enhanced and IV and V much diminished).
7. 697-Millimicron light fills only traces of traps IV and V.

These observations lead to the following deductions concerning the traps:

1. Traps can be filled directly from the valence band by light having energy sufficient to raise an electron from the valence band to the trap level. This is supported by the fact that light of an energy less than the band gap energy can populate trapping levels (items (2), (5), (6), and (7)). The efficiency of this process seems to be highest when the photon energy is close to that required to promote an electron into the trap. This is shown by items (5) and (6), where the shallow traps (I and II) were populated preferentially to the deeper traps (IV and V) by light of wavelengths close to the energy height of I and II from the valence band.

2. Traps can also be emptied by light of energy sufficient to promote the trapped electron to the conduction band. This is demonstrated by the absence of electrons in traps I and II (item (3)), where it is shown that infrared light removed them.

Cooling During Illumination

The detection of a new trapping center III, when the sample was cooled during irradiation, is difficult to understand. No explanation can be offered at this time. The wavelength-dependent filling of this trap, however, suggests that this level can also be filled from the valence band.

Effect of Water Vapor on Thermally Stimulated Current Spectrum

The effect of water vapor on the TSC spectrum was the occurrence of a broad peak
at 80° to 100° C. This peak appeared without any illumination of the crystal and, therefore, must have been due only to the interaction of water vapor with the crystal. The size of the water-vapor peak could be increased or decreased by increasing or decreasing the partial pressure of the water vapor. This indicates that the size of the peak depended on the amount of water vapor adsorbed on the surface of the crystal. It is reasonable to suppose that this peak is associated with the desorption of water from the crystal surface.

The work of Sébene and Balkanski (ref. 15) has shown that water is adsorbed by cadmium sulfide surfaces, where it attaches an electron to form water ions. Desorption of this water by heating the crystal must release electrons to the bulk of the crystal from the breakup of the ions. A peak in the TSC will result. In this way, the adsorbed water could act to simulate a trapping center in the TSC experiment.

**Effect of Pumping on Thermally Stimulated Current**

It is reasonable to explain the effect of pumping on the dark current through the crystal in a way similar to the effects of water vapor on the TSC. A decrease in pressure will cause desorption of water from the surface and a corresponding release of electrons to the crystal from breakup of the water ions. Thus, pumping alone may produce a current pulse resulting from desorption of water vapor. Some of the electrons released by desorption may be trapped and subsequently detected in the TSC measurement.

At room temperature, pumping would not produce a current pulse unless the crystal was first illuminated. This suggests (1) that, at room temperature, adsorption of water vapor to form water ions does not occur to any great extent unless the free electron concentration is increased by illumination, and (2) that photosorption of water vapor probably occurs on cadmium sulfide.

**Correspondence Between Trap Depths and Absorption Spectrum of Water**

It is interesting that the trapping spectrum of cadmium sulfide, within present experimental error, exhibits a reasonably close correspondence to the vibrational absorption spectrum of water vapor (fig. 6). The capped lines of the cadmium sulfide line indicate the trap values and error reported by Woods and Nicholas (ref. 7). The nonoptical vibrational energy transitions of the $^3\Sigma_g^-$ state of oxygen are also given. These observations and the fact that the deeper traps of cadmium sulfide are affected by water
vapor and oxygen (ref. 6) might lead to the conclusion that some of the traps in cadmium sulfide measured by the TSC technique are associated with these energy transitions. The other gases exhibit a similar correspondence, and in some respects hydrogen sulfide, which adsorbs strongly on cadmium sulfide, is a closer fit and may be expected to show similar effects.

Such a hypothesis is further supported, in a general way, by the work initiated by Eischens and Pliskin (ref. 16) on the spectroscopy of adsorbed gases. Their work, in general, indicates frequency shifts of gaseous adsorbate absorption bands upon adsorption (ref. 17). These shifts are thought to reflect changes in relative levels of the energy states of the transition whether rotational, vibrational, or electronic. Furthermore, a simultaneous change in a measured electronic property of the solid, such as the TSC, might be expected.

**CONCLUSIONS**

The following conclusions have been drawn from a study of the effect of various optical radiations and water vapor on the trapping spectrum of cadmium sulfide:

1. Light of specific wavelengths, the energy of which is less than the band edge, can
be used to excite electrons directly from the valence band into electron trapping levels near the conduction band.

2. Populated electron trapping levels near the conduction band can be emptied selectively with optical radiation. It is concluded, therefore, that white light probably fills and empties traps simultaneously.

3. The presence of water vapor on the surface of cadmium sulfide during a thermally stimulated current experiment can be detected and produces a nonoptically induced thermally stimulated current.

4. Pumping over the surface of a cadmium sulfide crystal removes adsorbed gases (water ions), which can be detected electrically as current spikes.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 10, 1966.
REFERENCES


"The aeronautical and space activities of the United States shall be conducted so as to contribute ... to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—National Aeronautics and Space Act of 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546