Photoconductivity and Photovoltaic Studies on Some II-VI Compounds

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PHOTOCONDUCTIVITY AND PHOTOVOLTAIC STUDIES
ON SOME II-VI COMPOUNDS

by

Challa Nagesh

A Thesis
Submitted to the
Faculty of the Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
April 1979
The photoconductivity spectra of ultra-pure single crystals of CdS in the range 500-575 nm, CdSe in the range 700-900 nm, ZnSe in the range 420-570 nm and ZnS in the range 300-450 nm have been studied using an improved A. C. method of detection. The sensitivity of the apparatus is high enough to study weak photoconductors like ZnS. The photoconductivity spectrum of each substance showed a peak at the wavelength corresponding to the energy band gap of the substance. The energy band gaps obtained from the spectra are 2.35 eV for CdS, 1.6 eV for CdSe, 2.7 eV for ZnSe and 3.6 eV for ZnS, and are in excellent agreement with the values reported in the literature. A photovoltaic cell was made using a CdS-Cu$_2$S heterojunction. The V-I characteristic and the short circuit photoconductivity spectrum of this cell were studied. An attempt has been made to automate the experiment using an M6800 D2 microcomputer.
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Challa Nagesh
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SOME II-VI COMPOUNDS.

WESTERN MICHIGAN UNIVERSITY, M.A., 1979
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1. INTRODUCTION

Photoconductivity is a well known phenomenon, observed about a hundred years ago. It has been studied in great detail in recent years due to its vast potential in the photovoltaic effect, the conversion of light energy into electrical energy.

Photoconductivity is a phenomenon which occurs when electromagnetic radiation, especially light, is absorbed by a semiconductor and changes its conductivity. The theory of this phenomenon has been well established in the literature. (Bube 1960, Gorlich 1967, Rose 1963 and Mort and Pai 1976.) Energy from the light radiation is absorbed by the charge carriers in the semiconductor, which are excited from a non-conducting ground state to a higher energy state where they contribute to the conductivity. This is observed primarily in crystalline solids and can be attributed to the band structure of these solids.

Crystalline solids are those in which the atoms form an ordered periodic array. The periodicity of the atoms and their close proximity to one another are sufficient to cause the quantum mechanical exchange forces to come into play and to modify the energy levels of the individual atoms into energy bands. The way the energy bands are formed can be looked at as follows: the crystal can be thought of as being constructed from isolated atoms, and in the process, the one-to-one correspondence between a particular electron and its atom is lost.
In other words, we can no longer think of an electron as belonging to a particular atom; instead, it belongs to many atoms. This holds for all the electrons in the crystal and is more evident for those electrons which are loosely bound to the nucleus. As a result, many electrons in the crystal would have the same energy if not for the Pauli exclusion principle, which forbids any state to be occupied by more than one electron. Therefore an energy level of an electron in an isolated atom is now split into as many levels as there are atoms in the crystal. These levels are very closely spaced about the original energy level and, due to the large number of atoms in the crystal, they form a quasi-continuous band of allowed energies.

These bands are separated by forbidden bands in which the quantum mechanical selection rules forbid the electrons to exist. The allowed energy bands are filled up to some highest energy band, which is determined by the number of electrons available. The highest energy band is occupied by the valence electrons, or the loosely bound electrons, of the element. Each energy state can be filled with two electrons, one with spin up and the other with spin down. Hence an element with an odd number of valence electrons has a highest filled energy band only half full. Such an element with a partially filled valence band behaves as a metal. Here only a very small amount of energy is required, usually obtained from an applied field or crystal vibrations, to raise an electron to the empty portion of the band to bring about conduction.

When the number of valence electrons in an element is even, the highest filled energy band will be filled completely. Depending on
the width of the forbidden energy band (energy gap), the element will be either an insulator or a semiconductor. In an insulator the band gap is usually of the order of several electron volts and the electrons are not generally excited to the conduction band at room temperature. In semiconductors, the band gap is small (usually of the order of an electron volt) and the electrons can be easily excited to the conduction band. The electrons thus freed to add to the conductivity in semiconductors are less in number than for metals but more than in insulators.

The electrons, when excited to the conduction band, leave behind a hole, which is actually an electron deficiency. In an applied field, the electrons drift toward the positive electrode and the holes toward the negative electrode, thus the conductivity is a function of the number and mobility of electrons and holes.

Wherever the perfect periodicity of the crystal is disturbed, imperfections are formed. When this happens, the electrons in the crystal can take on energies which are normally forbidden in perfect crystals. This results in additional intermediate energy levels lying between the valence and the conduction bands. However, these imperfection levels are not spread over the whole crystal but are found in the vicinity of the imperfection. Some examples of imperfections are: (1) vacancies, (2) occupation of interstitial positions, (3) 1 and 2 together, (4) dislocations and (5) foreign atoms in either interstitial or substitutional sites.

Due to the imperfection levels in the crystal, there are several types of electronic transitions that can take place. When a photon
is absorbed by a crystal, any of the three types of absorption transitions which will produce free charge carriers can occur, namely:

1. the photon could be absorbed by an atom in the crystal resulting in an electron transition from the valence band to the conduction band;
2. the photon could also excite an electron from the valence band to a localized imperfection level, producing a free hole and an electron bound in the neighborhood of the imperfection; or
3. an electron is excited by a photon, from a localized imperfection level to the conduction band producing a free electron and a hole bound to the imperfection. These three processes are shown in Fig. 1.1(a). In a pure crystal, there is a minimum photon energy which is required to produce a transition from the valence to the conduction band. This minimum energy is equal to the band gap of the crystal and the corresponding wavelength is called the absorption edge.

Once the free holes and the electrons have been produced, they will remain free until they are either trapped, recombine or pass out of the crystal at the electrodes. The three ways of recombination which are opposite to the three types of excitation are shown in Fig. 1.1(b). Trapping occurs when an electron or a hole is captured at an imperfection and the recombination occurs when it recombines with a carrier of the opposite sign. In both cases the charge carriers do not contribute to the photoconductivity. The formation of bound electron-hole pairs, called excitons, also decrease the number of charge carriers contributing to the photocurrent. The generation of secondary electrons and holes by the primary electrons and holes increase the number contributing to the photocurrent.
Fig. 1.1(a) Types of Absorption of Light by the Electrons in a Semiconductor

Fig. 1.1(b) Types of Recombination of Holes and Electrons in a Semiconductor
In a photoconductor, photoconductivity results when absorbed radiation increases the conductivity. This is essentially achieved by the increase in the number of free electrons (n) and holes (p). In an intrinsic semiconductor, the number of free electrons is the same as the number of free holes (n_i). By doping the semiconductor with various impurities, these can be changed. In an n-type material, the number of electrons are far greater than the number of holes and in such a material electrons are called the majority carriers and the holes minority carriers. The reverse is the case in a p-type material.

One of the important parameters in the photoconductivity process is the lifetime of the carriers. The following are some of the several types of lifetimes that are used in characterizing the process. Free lifetime is the time during which charge carriers are free to contribute to the conductivity of the photoconductor. This is terminated by trapping, recombination or passing out of the photoconductor at the electrodes. The excited lifetime is that time during which the charge carrier remains in an excited state, including the time it spends in traps. Thus this would generally be longer than the free lifetime. The majority carrier lifetime is the free lifetime of the majority carriers and similarly the minority carrier lifetime is defined.

If the majority carrier lifetime is increased and the minority carrier lifetime is decreased then the probability for recombination will be very small and this increases the photoconductivity. This can be done by incorporating a material in the photoconductor which will create centers for the rapid recombination of the minority
carriers with traps and not affect the majority carriers. The majority carrier lifetimes in II-VI compounds vary from a fraction of a microsec in the insensitive pure crystal to a few millisec in the photosensitive crystals. In pure cadmium sulphide, the lifetimes of both the electrons and holes are about 1 µsec. However in the sensitized crystals, in which halogen donor impurities are incorporated, the electron lifetime can be increased to about 10 msec and the hole lifetime is decreased to 0.01 µsec. (Bube 1960, Ray 1969.)

If the free electron-hole pair produced by a single photon contributes completely to the photocurrent in the external circuit, then the sample is designated to have unity photoconductive gain (photoresponse). Various solids exhibit a wide range of photoconductive gains, some having photoconductive gains much greater than unity. The measurement of photoconductivity with respect to the wavelength of radiation is termed the spectral response of the photoconductor. A peak in the response occurs when the incident energy is about the same as the band gap of the material. At higher energies (or shorter λ) the excitation of the charge carriers takes place only in the surface regions of the material, because the absorption length is small and the photoconductivity is less than the maximum. At lower energies (or longer λ), the light is only partially absorbed and hence the photoresponse is once again less than the maximum. Thus in the spectral response of a pure photoconductor, we see a peak when the incident light has the energy almost equal to the band gap of the material and it falls off on either side.
Since the excitation from an imperfection level to the conduction band requires less energy (Fig. 1.1(a)), the spectral response can be increased at longer wavelengths if suitable imperfections are present in appreciable concentrations. In pure cadmium sulphide the peak in spectral response occurs at 2.3 eV. The incorporation of silver or gold extends the range of the spectral response to about 2.0 eV and with copper to about 1.7 eV (Bube 1962).

In this project the photoconductivity spectra of some II-VI compounds have been studied covering the range 300-900 nm (the near ultraviolet, visible and the near infrared regions). The compounds studied were CdS, CdSe, ZnS, and ZnSe. These compounds were obtained from Eagle Picher Industries Inc. in the form of ultra-high pure melt-grown single crystals. The compound cadmium sulphide has the highest photosensitivity among all the known materials. Its response as a function of the wavelength of the incident light was observed directly by measuring the photocurrent by an electrometer. The other three materials are at least two orders of magnitude less sensitive than CdS and the photocurrent could not be observed directly using an electrometer. An improved alternating current method (A. C. method) was developed to observe these spectra.

A photovoltaic cell is made using a CdS-Cu$_2$S heterojunction. The rectifying voltage-current characteristic of the cell and its spectral response was observed.

An attempt has been made to automate the experiment using an M6800 D2 microcomputer. This is programmed to control the monochromator, take the data, analyze it, and plot the response. The
results from the photoconductivity experiment are described in Chapter II. The photovoltaic effect and the results from CdS photovoltaic cell are described in Chapter III. The microcomputer instrumentation aspects of the project are given in Chapter IV. The summary and conclusions are given in Chapter V.
II. PHOTOCONDUCTIVITY STUDIES ON SOME II-VI COMPOUNDS

1. Electrometer Method of Detection: Results for CdS

The experimental apparatus consisted of a Jobin-Yvon optical system's H-20 monochromator with a 60W tungsten-halogen light source. The spectral range of this source and the monochromator was 200 to 900 nm, and the wavelength could be read off on a digital readout. The slit width used was 0.5 mm. The sample chamber was made of aluminum and had a removable top and screws at the bottom to adjust the height. The sample was mounted on a carriage made of plastic which in turn was attached to a strip of aluminum fixed to the bottom of the chamber. The carriage could be moved along this strip, up and down. A hole was made in the chamber wall in front of the carriage so that the light from the monochromator could be focused onto the crystal mounted on it. A funnel was welded to the hole to fit over the monochromator lens, so that the extraneous light was excluded and the crystal was exposed only to the light from the monochromator.

To measure the photoconductivity of a material, it is necessary to have electrical contacts by means of electrodes. An ideal electrical contact would be an 'ohmic contact' which would not hinder the photoconductivity mechanism of the material. Also, it will replenish the carriers drawn out of one electrode at the other end hence keeping the material electrically neutral. Let us consider the contacts in terms of the work functions of the metal and the photoconductor.
involved. When the work function of the metal is greater than that of the photoconductor, there is a barrier in the region of the contact. Rectification occurs at this junction with easy current flow when the metal is positive. A barrier is formed at the metal-photoconductor junction and any increase in the voltage is concentrated across this barrier and not across the whole volume of the crystal. When metals whose work functions are less than that of the photoconductor are used, no barrier forms when the contacts are made and an ohmic contact is formed. For n-type II-VI compounds, indium and gallium have been found to make good ohmic contacts. A general test for the ohmic contact is to study the voltage-current (V-I) characteristic to see if the current flow through the photoconductor is linear with the applied voltage.

Contacts were made to the cadmium sulphide crystal by evaporating indium onto it. The evaporation was done at a pressure of about $10^{-5}$ torr on a Kinney KDTG-3 vacuum evaporator. On one face of the crystal, a small indium dot was evaporated and on the opposite side a large area was covered with indium by evaporation. The contacts were made opposite each other across the crystal, to ensure that the volume photoconductivity was being observed. Copper leads were connected to the contacts using quick-drying silver paint.

The V-I characteristics were observed by connecting a Wavetek model 144 signal generator across the crystal and a 1 MΩ resistor. The output was measured across the combination and was fed to an x-y recorder. The signal from the Wavetek was set at 8V pp and the frequency was set very low. First the characteristic in the dark was
plotted. However, there was some ambient light falling on the crystal and the dark characteristic was not for a crystal in perfect darkness. The light used to illuminate the crystal was a 100W bulb placed at about 3" from the crystal. Fig. 2.1 shows the V-I characteristics of the CdS crystal with and without illumination. The figure shows that the contacts are ohmic and the differing slopes indicate a change in the resistance. The resistance without the light was observed to be about 1.4 MΩ and with the light it was about 380 KΩ. The conductivity with light was about four times the value without light. If the dark characteristic had been measured in total darkness, this ratio would have been greater.

Once the ohmic contacts have been made to the crystal, the photocurrent can be measured using an electrometer. The electrometer used was a Keithly Instruments model 610C solid state electrometer. The current was measured as the monochromator scanned from 500 nm to 575 nm. A peak was observed at about 525 nm, which is shown in Fig. 2.2. The current at the peak was about 2.5 x 10^{-8} A. This was plotted on an x-y recorder. The scanning interval was divided into ninety points and the current was noted at each point on the graph.

To measure the incident light intensity a 1P21 photomultiplier tube was fixed to the monochromator in place of the sample chamber. The power supply for the photomultiplier was a Hammer model NV-13 regulated power supply and the voltage was -530V. The incident light intensity was plotted in the same wavelength interval, and this is shown in Fig. 2.3.
Fig. 2.1 V-I Characteristics for Intrinsic Cadmium Sulphide Single Crystal
Fig. 2.2 The Photocurrent Spectrum of Cadmium Sulphide Single Crystal Using the Electrometer
Fig. 2.3 The Incident Light Intensity Falling on the Crystal in the Range 500-575 nm
A point-by-point ratio was then taken of the photocurrent and the incident light intensity to get the photoresponse spectrum of the substance. This is shown in Fig. 2.4. This is the absolute photoresponse spectrum of the substance in arbitrary units since the incident light intensity is not converted into standard units. The above three graphs and the rest of the spectra in the project were drawn using the DATPLT program of J. E. Herman on the PDP-10 computer.

ii. A. C. Method of Detection: Results for CdS

The photoconductivity was monitored using a fairly simple A. C. technique which essentially involved comparing a reference signal to the current through the photoconductor and amplifying the difference. The circuit diagram is given in Fig. 2.5. The signal from a signal generator with frequency of about 3 KHz is fed to the crystal and is amplified using an operational amplifier. This is then fed to a filter which is used to filter out the 60 Hz noise and through a buffer to a difference amplifier. The same signal from the signal generator was also fed to an amplifier (level changer) whose amplification can be varied by means of a potentiometer across it. The next stage is a phase shifter by means of which the phase of the reference signal can be changed at will. This output is also fed through a buffer to the other input of the difference amplifier.

With the crystal first in a light-tight box, the signal immediately after the high pass filter and the reference signal after the phase shifter are compared. The phase and the amplitude of the reference signal are adjusted to equal that of the signal from the
Fig. 2.4. The Photoresponse Spectrum of CdS Single Crystal in Arbitrary Units Using the Electrometer.
Fig. 2.5 The Circuit Diagram for A. C. Method of Measuring Photocurrent
crystal. At this point we have two identical signals going through the difference amplifier. When the crystal is exposed to light, the increase in the conductivity is seen and amplified by the difference amplifier (Lambe 1955). The greatest sensitivity of the circuit is achieved if the balancing is done with care to match the two signals perfectly. To increase the signal to ratio further, the output of the difference amplifier is fed to a narrow band filter which only passes a band of frequencies around 3 KHz. This final signal can be amplified further if necessary and then rectified and fed to a recorder.

For cadmium sulphide, the resistance $R_1$ in the circuit was $4.7 \, \text{M}\Omega$ and $R_2$ was $10 \, \text{K}\Omega$. The resulting photocurrent was plotted on the x-y recorder and is shown in Fig. 2.6. This was normalized by the method outlined in the previous section and the photoresponse spectrum in arbitrary units is shown in Fig. 2.7. This is the relative photoconductivity spectrum of the substance since the circuit cancels the signal due to the dark conductivity. At about 515 nm, there is a small step in the response curve which was not as pronounced when observed using the electrometer. The peak at 525 nm can be seen to correspond with the photon energy of about 2.35 eV which is in excellent agreement with the band gap of 2.4 eV for CdS (Ray 1969).

iii. Results for CdSe, ZnS and ZnSe

The photoresponse for the other II-VI compounds (CdSe, ZnS and ZnSe) could not be observed using the electrometer. Since the photosensitivity of these materials is at least two orders of magnitude less
Fig. 2.6 The Photocurrent Spectrum of CdS Single Crystal by the A. C. Method
Fig. 2.7 The Photoresponse Spectrum of CdS Single Crystal in Arbitrary Units by the A. C. Method
than CdS, the electrometer would give unreliable results, since the photocurrents are of the order of $10^{-10}$ A. Severe problems with the stray capacitances from the wiring and the electrical noise from the motor of the monochromator were encountered. However, the A. C. method is still applicable; it was used to observe the photoresponse of these materials. The contacts were made using indium which was evaporated onto the single crystals.

For cadmium selenide (CdSe), the resistance $R_I$ was 20 K$\Omega$, $R_S$ was 220 K$\Omega$, and the reference signal had to be attenuated to match that of the crystal. The signal was plotted as the monochromator scanned from 700 to 900 nm. The current from the crystal was shown in Fig. 2.8 and the incident light intensity is shown in Fig. 2.9. The photoresponse spectrum is shown in Fig. 2.10. The peak is at about 780 nm and this corresponds to a photon energy of 1.6 eV. The band gap of CdSe is known to be 1.7 eV.

For zinc selenide (ZnSe) and zinc sulphide (ZnS), the resistance $R_I$ was 4.7 M$\Omega$, $R_S$ was 20 K$\Omega$, and the reference signal was attenuated. An amplifier with a variable gain of 20 to 200 was inserted between the difference amplifier stage and the narrow band filter stage of the circuit. The photocurrent for ZnSe is shown in Fig. 2.11 and shows two peaks, one at about 460 nm and another peak at about 520 nm. The incident light intensity in the same spectral region is shown in Fig. 2.12. The resulting photoresponse spectrum is shown in Fig. 2.13. The second peak at 520 nm in the photocurrent disappeared in the photoresponse spectrum as it was not a characteristic of the substance but a reflection of the peak in the incident light intensity. The peak
Fig. 2.8  The Photoresponse Spectrum of CdSe Single Crystal by the A.C. Method
Fig. 2.9 The Incident Light Intensity Falling on the Crystal in the Range 700-900 nm
Fig. 2.10 The Photoresponse Spectrum of CdSe Single Crystal in Arbitrary Units by the A. C. Method
Fig. 2.11 The Photocurrent Spectrum of ZnSe Single Crystal by the A. C. Method
Fig. 2.12 The Incident Light Intensity Falling on the Crystal in the Range 420-570 nm
Fig. 2.13 The Photoresponse Spectrum of ZnSe Single Crystal in Arbitrary Units by the A. C. Method
of the photoresponse curve is at about 460 nm and corresponds to a photon energy of 2.7 eV. The band gap of ZnSe is 2.6 eV.

For ZnS, with slits of 0.5 mm, the signal was not seen when the wavelength was scanned from 300 nm to 500 nm. It was found that in order to observe any photoresponse from the sample, the slits had to be wide open so that the light fell on almost the entire area of the crystal. This could have been the reason that the ZnS forward response was unusual. However, when the wavelength was scanned from the longer wavelength side, i.e., from 500 nm to 300 nm, the response shown in Fig. 2.14 was observed. The incident light intensity in the same spectral region is shown in Fig. 2.15. The resulting photoresponse spectrum is shown in Fig. 2.16. The peak is seen to occur at about 345 nm corresponding to a photon energy of 3.6 eV. The band gap of ZnS is 3.7 eV.
Fig. 2.15 The Incident Light Intensity Falling on the Crystal in the Range 300-500 nm
Fig. 2.16 The Photoresponse Spectrum of ZnS Single Crystal in Arbitrary Units by the A.C. Method
III. PHOTOVOLTAIC EFFECT IN CdS

When the metal-crystal contact is not an ohmic one but a rectifying one, the photovoltaic effect is observed. Unlike the case with ohmic contacts, the electrons passing from the metal and the holes from the crystal must overcome a barrier produced by the rectifying contact. Also unlike the photoconductivity phenomenon, which is a majority carrier effect, the photovoltaic effect is a minority carrier phenomenon. In terms of the band structure, the effect can be explained as follows: in Fig. 3.1(a) the band structure for the metal and the crystal are shown before contact. The Fermi levels are located differently and there is a voltage difference $V$ between them. When they come into contact as in Fig. 3.1(b), the two Fermi levels are equalized. Under illumination the electrons from the metal flow across to the crystal and the holes, which are minority carriers in the crystal, flow toward the metal, both setting up a current in the same direction. Under open circuit conditions, this current produces a voltage across the junction and the maximum value for this voltage is $V$, the difference in the Fermi levels before contact. Thus with a rectifying contact, the $V$-$I$ characteristic of the device is like that of a diode.

A solar cell is a photovoltaic device which converts solar energy into electrical energy. There have been several different types of solar cells made, but the only types which are being extensively used so far are the silicon single-crystal cells. Although
Fig. 3.1 Energy Band Diagram of Cu-CdS Interface
they are very expensive, they have the advantage of being rugged, with efficiencies of about 11-12%. Recently, quite a few other types of solar cells have been studied and one of the more promising ones is the CdS solar cell. It can be mass produced quite inexpensively by evaporating CdS onto a copper substrate and dipping this in a hot cuprous ion solution to form a layer of Cu$_2$S on the CdS surface (Hovel 1975, Barnett 1978). This has been attempted here but could not be achieved, probably due to unsatisfactory vacuum conditions (Chopra 1969).

The photovoltaic cell was made using a CdS crystal of about 0.5 cm$^2$ in area. This crystal was dipped in a copper chloride solution at about 85$^\circ$ C for about 30 minutes. It was done so that one side of the crystal was coated by a layer of Cu$_2$S (Bube and Fahrenbruch 1973). The contacts were made by the use of silver paint on the face which had Cu$_2$S, and indium on the opposite side. The crystal was placed in the sample chamber and the V-I characteristic was observed. This is shown in Fig. 3.2 for illumination with a 100W lamp, placed at about 6" from the crystal. This is the passive V-I characteristic of the device as it is like a resistor in the circuit. The V-I characteristic is in excellent agreement with that reported in literature (Bogus and Mattes 1972). The crystal is used as a battery in a circuit with a resistor and the current in the circuit is measured for various values of resistance in the circuit. The voltage across the cell drops as the current drawn from it is increased and these data are shown in Fig. 3.3. The open circuit voltage was 0.29 V and the short circuit current was 0.9 mA. The characteristic shows that the
Fig. 3.2 The Passive V-I Characteristics for the Cu₂S-CdS Photovoltaic Cell
Fig. 3.3 The Dynamic V-I Characteristic for the Cu$_2$S-CdS Photovoltaic Cell
device is not a resistor, but is more like a battery. The power delivered by the photocell was calculated and plotted for different voltages in Fig. 3.4. The values of V and I at the peak power output, $V_M$ and $I_M$, are 0.17 V and 0.75 mA respectively. The peak power output is 0.013 mW.

Finally, the photoresponse of the photovoltaic cell (short circuit photocurrent) was obtained and is shown in Fig. 3.5. The peak is at about 517 nm and is different from that of CdS. Also at the longer wavelengths, the photoresponse does not fall off as rapidly as it did for CdS. Degradation has been observed in the cell and this can be reduced by evaporating a thin transparent layer of copper on the Cu$_2$S layer of the cell (Hovel 1975).
Fig. 3.4 The Power Versus Voltage Characteristic for the Cu$_2$S-CdS Photovoltaic Cell
Fig. 3.5 The Photoresponse Spectrum of the Cu$_2$S-CdS Photovoltaic Cell by the A. C. Method
IV. MICROCOMPUTER INTERFACING

The data presented in the photoconductivity experiment were taken on the x-y recorder with the monochromator scanning continuously. Both the incident light intensity and the photocurrent were noted from these graphs and entered into the computer manually for the analysis that is described in the previous chapters. An attempt has been made to automate the above procedure using a microcomputer to control the motion of the monochromator, to take data and store it in the memory, and to normalize the photocurrent to yield the photoresponse directly. The computer chosen is the M6800 D2 microcomputer with 512 bytes of memory and one peripheral interface adapter (PIA) for interfacing. The PIA has 16 input/output lines designated as PA0-PA7 and PB0-PB7.

The North American Phillips' SAA1027-CMOS stepper motor integrated circuit driver is used to interface the stepper motor on the monochromator to the computer. The frequency of the clock determines the speed of the motion and the direction bit can be chosen 1 or 0 for forward or backward motion. The two transistors in these inputs are to convert the 5 V logic level of the computer to the 12 V logic level of the driver. The driver generates the four phase signals necessary for the stepper motor. The clock and direction lines are connected to the PB0 and PB1 output lines of the computer. The circuit diagram is shown in Fig. 4.1. Thirty-six pulses are needed to move 1 nm. The maximum speed on the stepper motor yields 600 nm/min on the monochromator. A speed of 336 nm/min was chosen for the program.
Fig. 4.1 The Circuit Diagram for Interfacing the Stepper Motor of the Monochromator to the Microcomputer
The Teledyne 8703-8 bit monolithic CMOS A/D converter is used to interface the analog current, corresponding to either the light intensity or the photocurrent, to the computer. The 'initiate conversion' signal is from the computer (PB2) to start conversion. The 'Busy' signal is to the computer (PB7) to indicate when the conversion is complete. The enable control switches the outputs to a high impedance or off state when held high and this is connected to the PB3 output from the computer. This is held low during the time of reading the data into the computer. The eight output lines from the converter are connected to PA0-PA7 inputs of the computer. The circuit diagram is shown in Fig. 4.2.

The following program is written to move the monochromator and take the analog data from the experiment. It uses the locations 100H-1B7H for the program, 10H-1AH for the variables, and 20H-FFH for data. The location 'size' determines the size of the step and can be chosen from 1 to 99 nm. The locations 'stepsh' and 'steps1' determine the number of steps and can be chosen from 1 to 9999. Both the above pieces of information are given in decimal and the program which operates in hexadecimal automatically adjusts them. The location 'Directn' determines the direction of motion. The program steps the monochromator through the chosen size, waits for 1 sec for the data to settle, takes the data through the A/D converter, and stores the data in consecutive memory locations. The above process is repeated until it has gone through the desired number of steps or 224 (20H to FFH), whichever is smaller. This guarantees that the data do not overflow into the program. The program is run with the
Fig. 4.2 The Circuit Diagram for Interfacing an Analog to Digital Converter to the Microcomputer
current from the photomultiplier tube (incident light intensity) as the input through the chosen wavelength region. A copy of the program is given in the following pages.

The program can be modified so that it takes the data from the crystal, divides the data with the incident light intensity and stores the result (photoresponse) in the memory. After the execution of both the programs is completed, the data stored in the memory is plotted on an x-y recorder by interfacing a D/A converter to the computer.
NAM PHEXP2 PHOTOCO NDUTIVITY EXPERIMENT

0010 1 SIZE RMB 1 STEP SIZE IN NM (DECIMAL)
0011 1 STEPSH RMB 1 #OF STEPS IN
0012 1 STEPSL RMB 1 DECIMAL
0013 1 DIRCTN RMB 1 DIRECTION. 0-FWD, ELSE BWD
0014 1 TSIZE RMB 1
0015 1 TSTEPH RMB 1
0016 1 TSTEPL RMB 1
0017 1 WIDTH RMB 1 MONOCHROMATOR SPEED
0018 1 PULSES RMB 1 #OF PULSES FOR 1 NM
0019 1 TEMP RMB 1
001A 2 DATAB RMB 2

*PIA INITIALISATION. PAO-PA7 AND PB7 ARE INPUTS

0100 7F 0005 BEGIN CLR CRA PB0-PB6 ARE OUTPUTS
0103 CE 0004 LDX #4 PB0-MONOCHROMATOR MOTION
0106 FF 0004 STX DDRA PB1-DIRECTION
0109 7F 0007 CLR CRB PB2-INITIATE CONVERSION FOR A
010C CE 7F04 LDX #$7F04 PB3-ENABLE FOR A/D
010F FF 0006 STX DDRB PB7-BUSY FROM A/D
0112 CE 0020 LDX #$20 BEGINNING OF DATA TABLE
0115 DF 1A STX DATAB
0117 86 FF LDA A #$FF GIVES 336 NM /MIN
0119 97 17 STA A WIDTH
011B 86 48 LDA A #$48 2*36 FOR 1 NM
011D 97 18 STA A PULSES
011F 86 99 LDA A #$99 99'S COMPLIMENT OF STEPS
0121 90 11 SUB A STEPSH
0123 97 15 STA A TSTEPH
0125 86 99 LDA A #$99
0127 90 12 SUB A STEPSL
0129 97 16 STA A TSTEPL
012B 8D 41 BSR TEST ADD1 TO GET 100'S COMPLIMENT
012D 96 13 LDA A DIRCTN
012F 26 04 BNE BWD
0131 86 08 LDA A #$8 ENABLE=1,FWD,IC=M0N0=0
0133 20 02 BRA SKP
0135 86 0A BWD LDA A #$A ENABLE=1,BWD,IC=M0N0=0
0137 B7 8006 SKP STA A DRB
013A CE 8004 NXSTP LDX #DRA LOAD X WITH ADDR OF PIA
013D D6 10  LDA B  SIZE
013F 86 99  LDA A  #$99
0141 10  SBA
0142 88 01  ADD A  #1  MAKE 100'S COMPLIMENT OF SIZE
0144 19  DAA
0145 97 14  STA A  TSIZE
0147 8D 10  NEXTNM  BSR  MOV
0149 96 14  LDA A  TSIZE  DECREASE SIZE BY 1
014B 88 01  ADD A  #1
014D 19  DAA
014E 97 14  STA A  TSIZE
0150 26 F5  BNE  NEXTNM  CHECK FOR END OF STEP
0152 8D 29  BSR  GETDAT  BRANCH TO GET DATA FROM A/D
0154 8D 18  BSR  TEST  CHECK FOR END OF SCAN
0156 26 E2  BNE  NEXSTP
0158 3F  SWI  END OF ROUTINE
0159 96 18  MOV  LDA A  PULSES
015B 97 19  STA A  TEMP
015D A6 02  MOV1  LDA A  2,X
015F 88 01  EOR A  #1  COMPLIMENT PBO
0161 A7 02  STA A  2,X
0163 D6 17  LDA B  WIDTH
0165 5A  LOOP1  DEC B
0166 26 FD  BNE  LOOP1
0168 7A 0019  DEC  TEMP
016B 26 F0  BNE  MOV1
016D 39  RTS
016E 96 16  TEST  LDA A  TSTEP1
0170 8B 01  ADD A  #1
0172 19  DAA
0173 97 16  STA A  TSTEP1
0175 96 15  LDA A  TSTEPH  DEC STEPS BY 1
0177 89 00  ADC A  #0
0179 19  DAA
017A 97 15  STA A  TSTEPH
017C 39  RTS
017D CE 0000  GETDAT  LDX  #0
0180 09  LOOP  DEX
0181 26 FD  BNE  LOOP  1 SEC DELAY LOOP
0183 CE B004  LDX  #DRA
0186 A6 02  LDA A  2,X
0188 8A 04  ORA A  #4
018A A7 02  STA A  2,X  MAKE INITIATE CONV=1
018C 86 0A  LDA A  #$A
018E 4A  LOOP2  DEC A
018F 26 FD  BNE  LOOP2  100 MICROSEC DELAY

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MOTOROLA M68SAM CROSS-ASSEMBLER  PAGE 3

0191 A6 02  LDA A 2,X
0193 84 7B  AND A #$7B  MAKE INITIATE CONV=0
0195 A7 02  STA A 2,X
0197 A6 02  CKBUSY  LDA A 2,X
0199 48  ASL A  CHECK FOR BUSY=0
019A 25 FB  BCS CKBUSY
019C A6 02  LDA A 2,X
019E 84 77  AND A #$77  MAKE ENABLE LOW
01A0 A7 02  STA A 2,X
01A2 E6 00  LDA B 0,X  READ DATA
01A4 A6 02  LDA A 2,X
01A6 8A 08  ORA A #8  MAKE ENABLE HIGH
01A8 A7 02  STA A 2,X
01AA DE 1A  LDX DATAB  LOAD X WITH DATA BASE ADDR
01AC E7 00  STA B 0,X  STORE DATA
01AE 08  INX
01AF DF 1A  STX DATAB
01B1 8C 00FF  CPX #$FF
01B4 26 01  BNE RTN
01B6 3F  SWI  END THE ROUTINE
01B7 39  RTN RTS

8005 CRA EQU $8005
8004 DRA EQU $8004
8004 DDRA EQU $8004
8007 CRB EQU $8007
8006 DDRB EQU $8006
8006 DRB EQU $8006
END

SYMBOL TABLE

SIZE 0010  STEPSH 0011  STEPSL 0012  DIRCTN 0013  TSIZE 0014
TSTEPH 0015  TSTEPL 0016  WIDTH 0017  PULSES 0018  TEMP 0019
DATAB 001A  BEGIN 0100  BWD 0135  SKP 0137  NEXSTP 013A
NEXTNM 0147  MOV 0159  MOV1 015D  LOOP1 0165  TEST 016E
GETDAT 017D  LOOP 0180  LOOP2 018E  CKBUSY 0197  RTN 01B7
CRA 8005  DRA 8004  DDRA 8004  CRB 8007  DDRB 8006
DRB 8006
V. CONCLUSIONS

The normalized photoresponse spectra of all the II-VI compounds studied in the project are shown in the Fig. 5.1. The cadmium sulphide is the most sensitive among the four compounds studied and ZnS is the least sensitive one. The study of photoconductivity spectra yields information about the energy band structure of the solid near the band gap. The energy band gaps obtained from the spectra are 2.35 eV for CdS, 1.6 eV for CdSe, 2.7 eV for ZnSe and 3.6 eV for ZnS and are in excellent agreement with the values reported in the literature (Ray 1969). These values are for the room temperature energy band gaps as the spectra were taken at the room temperature. The two weak peaks seen in the CdS spectrum at 2.38 eV and 2.43 eV correspond to the first and second exciton formation (bound electron-hole pair) and this is the first time that these are seen at room temperature. At lower temperatures like 77° K and 4° K, the photoresponse spectrum shows a rich structure corresponding to a number of excitonic levels (Park 1968).

The normalized photoresponse spectra of the CdS photoconductor and the Cu$_2$S-CdS photovoltaic cell are shown in the Fig. 5.2. The peak in the photovoltaic cell is shifted to lower wavelengths compared to the photoconductor. The solar cell behavior can conveniently be examined through three main parameters: the open circuit voltage $V_{0C}$, the short circuit current $I_{SC}$ and the fill factor FF. The fill
Fig. 5.1 The Normalized Photoresponse Spectra of the II-VI Compounds by the A.C. Method.
Fig. 5.2 The Comparison of the Photoresponse Spectra of the CdS Single Crystal and the Cu$_2$S-CdS Photovoltaic Cell
factor is defined as the ratio of maximum power output \(\frac{V_{M1}}{V_{M1}}\) to the product of \(V_{OC}\) and \(I_{SC}\). The open circuit voltage obtained for the photovoltaic cell was 0.29 V. This is equal to the difference in Fermi energies of Cu and CdS, as expected. The fill factor is found to be 0.49. The efficiency of the cell is defined to be the ratio of maximum electrical power output to the incident light power. The approximate value of the efficiency for the cell is calculated to be 10\%. The calculation is only approximate since the incident light power is only approximately known.

The experiment can be extended further to study the photoconductivity at low temperatures to get valuable information about the energy band structure near the band gap of the material. A number of potential photoconductors can be studied for their application in solar cells. Different photovoltaic cell configurations can be investigated by high vacuum and evaporation techniques to achieve higher efficiency and less degradation of performance of the cell. The microcomputer instrumentation part of the project is only an attempt in that direction. The program can be made flexible by writing it in a higher level language like FORTRAN or BASIC which uses a number of assembly language subroutines. This simplifies the analysis part tremendously and the data files can be managed more conveniently. By fully automating the experiment, the pulsed response, response time, . . . etc. can be studied in greater detail.
REFERENCES


