

AD/A-005 019

STUDY OF FIELD ASSISTED PHOTOCATHODES
WITH DOUBLE HETEROJUNCTION STRUCTURE

A. G. Milnes, et al

Carnegie-Mellon University

Prepared for:

Advanced Research Projects Agency

February 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

STUDY OF FIELD ASSISTED PHOTOCATHODES WITH
DOUBLE HETEROJUNCTION STRUCTURE

Fourth Semiannual Technical Report

A. G. Milnes D. L. Feucht P. K. Govil

412-621-2600

February, 1974

Carnegie-Mellon University
Electrical Engineering Department
Pittsburgh, Pennsylvania 15213

Sponsored By

ADVANCED RESEARCH PROJECTS AGENCY

ARPA ORDER NO. 2182

PROGRAM CODE NO. 2D10

CONTRACT NO. DAAK02-72-C-0206

Effective Date of Contract: 1 February 1972

Contract Expiration Date: 30 June 1974

Amount of Contract: \$90,244.00

This research was supported by the Advanced Research Project of the Department of Defense and was monitored by the Night Vision Laboratory under Contract DAAK02-72-C-0206.

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U.S. Government.

Distribution of this document is unlimited.

ABSTRACT

The photocathode concept under study is that of a pGe-vZnSe - p⁺GaAs (Cs-0) structure. Photons of energy greater than 0.7 eV (wavelength < 1.7 μ m) create thermal electrons in the Ge conduction band and these are then to be transferred through the lightly doped fully-depleted ZnSe layer (about 2 μ m thick) into the p⁺GaAs layer (about 1 μ m thick) and emitted at the negative electron affinity surface.

Effort has been concentrated on the Ge-ZnSe interface but the quality of the growths has been only marginally satisfactory and unreproducible. One problem is that of etching of the Ge by the HCl gas in the close-spaced transport system used for depositing the ZnSe layer. Many of the specimens grown exhibit an electrical switching action which is presumably trap induced and makes the junction unsuitable for electron transfer studies.

The electrooptical properties of some non-switching junctions have been examined and the transport of photo induced electrons from the Ge into the ZnSe measured as a function of photon energy, intensity, bias light (to change the trap population) and temperature. Transfer efficiencies of only a few percent are typical in the best junctions made so far.

TABLE OF CONTENTS

	<u>Page</u>
1. Introduction	1
2. Analysis and Design Calculations	1
3. Fabrication	1
4. Measurement of the Electron Transport Across p Ge/vZnSe Interfaces.	6
5. Conclusions	20
6. Presentations	20
7. Personnel Engaged on the Project	20
8. Energy Conservation Measures.	21

LIST OF ILLUSTRATIONS

- Fig. 1. Modified lower Si-block to ensure more uniform seed heating.
- Fig. 2. Set up for temperature calibration measurements.
- Fig. 3. Schematic diagram of the system for photo-response measurement of a $\nu\text{ZnSe}/\text{p-Ge}$ heterodiode in presence of biasing light, and at reduced temperature.
- Fig. 4. Variation of gain with bias light wavelength and intensity.
- Fig. 5. Variation of gain with bias light intensity for two photo energies.
- Fig. 6. Two diode system used to determine the area modulation effect in the presence of the biasing light of various wavelengths and intensities.
- Fig. 7. Ratio of diode photocurrent when the diodes are connected in parallel to the sum of the individual diode photocurrents $(I_{D_1} + I_{D_2}) / I_{D_1} + I_{D_2}$ as a function of bias light energy for various bias light intensities.
- Fig. 8. Variation of photocurrent (or gain) with infrared radiation intensity for various bias light intensities, having a wavelength of $0.49 \mu\text{m}$. PCS-6 S-11 is a Ge/ZnSe diode where the Ge is p type 0.3 ohm-cm and the ZnSe is a grown layer approximately $4 \mu\text{m} \times 0.2 \text{ cm} \times 0.2 \text{ cm}$ and the ZnSe side is provided with an indium contact of $.025 \text{ cm}$ diameter and the illumination is provided on this side.
- Fig. 9. Variation of photocurrent (or gain) with infrared radiation intensity for various bias light wavelengths keeping in intensity of the bias light constant.
- Fig. 10. Variation of gain with bias light wavelength for various bias light intensities at room temperature.
- Fig. 11. Variation of gain with bias light wavelength for various bias light intensities below room temperature.
- Fig. 12. C-V plots for $\nu\text{ZnSe}/\text{p-Ge}$ heterodiode at various temperatures in dark. Hysteresis is evident in all these plots.
- Fig. 13. C-V plots in the presence and absence of room light below room temperature.

1. Introduction

The work on the research grant is concerned with the general concept of double heterojunction field assisted photocathodes. In order to accomplish this study the following three areas of investigation have been defined:

- a) Design analysis to determine the required structure and the quantum yield for double heterojunction field assisted cathodes.
- b) Development of the materials and device fabrication techniques for the Ge/ZnSe/GaAs structure.
- c) Measurement of the electron transport properties in Ge/ZnSe/GaAs structures.

2. Analysis and Design Calculations

No new analysis and design calculations were made during the period covered by this report except for calculations associated with electron transport and efficiency studies.

3. Fabrication

During the period covered by this semiannual report most of the effort was concentrated on improvement of our close-spaced HCl epitaxy system for growing ZnSe on Ge, investigating the growth of the ZnSe layer, and improving the quality of the surface preparation of the Ge substrate material.

3.1 Several modifications were made in the growth system to eliminate potential sources of contamination. A cold trap was inserted in the vent portion of the HCl-H₂ supply system to prevent back diffusion from an oil bubbler. This might have been a factor in causing some flow meters to stick and may have caused surface contamination on the seed. Static

electricity was also found to cause some sticking of the flow meters floats. The rubbing of the sapphire float against the wall of the flow meter resulted in static charges on the inner wall of the flow meters which caused sticking. The problem was partially solved by discharging the float at intervals by allowing it to touch an earthed wire inserted in the base of the flow meter.

The HCl supply was replaced, a new regulator obtained, and the monel feed tube replaced with pyrex to eliminate corrosion contaminants from this source. The H₂ purifier was also repaired.

Other minor modifications were done in the growth system to reduce the system contamination. The exhaust end acid bubbler was replaced with an oil bubbler containing a low vapour pressure silicone diffusion pump oil (from Dow-Corning). During a thorough clean-up of the growth system a little vacuum pump oil contamination was found near the vacuum line connection to the growth system. This could have contributed contamination to the substrate and affected growth morphology. The vacuum pump has since been replaced by a cryogenic sorption pump, in which no oil is used.

Another modification involved the lower Si-block that carried the Ge substrate in a rectangular notch. A new Si-block was prepared with a groove running across the top surface, Fig. 1, instead of a notch. Since the surface of the groove can be polished well, it has removed the problem of uneven contact between the seed and the somewhat ridged surface of the notch. In the past this has resulted in temperature gradients across the seed surface which have been detrimental to the quality of the epitaxial growth.

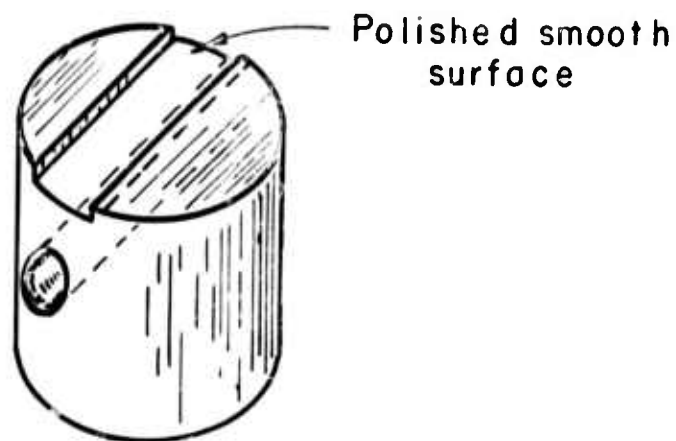


Fig. 1 Modified lower Si-block to ensure more uniform seed heating

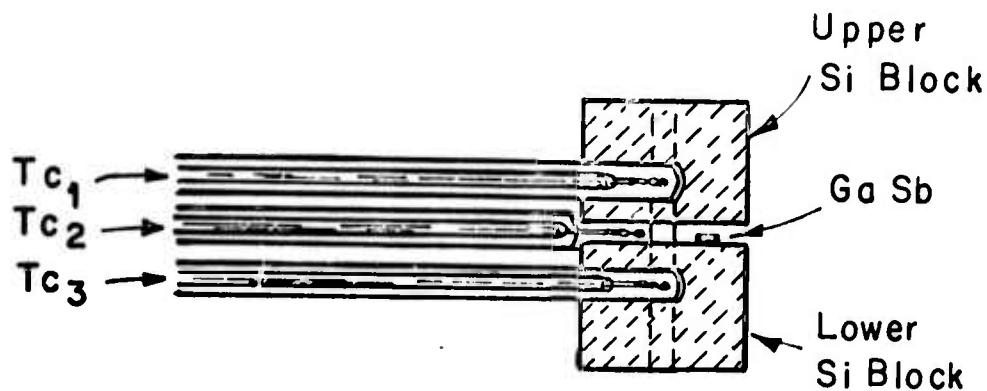


Fig. 2 Set up for temperature calibration measurements

GaSb melting point:

Tc_1	720°C
Tc_2	720°C
Tc_3	715°C
M.P. (actual)	703-712°C

Temperature correction:

Actual T is 8 to 17°C lower than block temp.
at 700-750°C.

- 3.2 All flowmeters in the system have been recalibrated. The actual gaseous flow rates have been found to differ from the previously calculated rates by as much as a factor of 2. This error makes the HCl concentration in the previous runs less than the expected percentages.
- 3.3 Temperature corrections were determined for the temperature of the top surface of the lower Si-block by two different techniques. In one a GaSb crystal was placed at the top surface of the Si-block and its apparent melting point temperature was observed and compared with the established melting point. In the second technique a calibrated thermocouple (Fig. 2) was placed on the top surface of the Si-block and temperatures measured at the top of the lower Si-block. For a wide range of temperatures this correction was found to be between 1° - 15°C . Therefore the original temperatures indicated on the system controllers for previous growth runs were adequately close to the truth and we can be even more precise now.
- 3.4 Several growths were done with the improved system. These have shown some improvement and in some growths a growth morphology similar to PCS-6 has been obtained. PCS-6 is the growth which has given us the encouraging photo-response. Similar electrical characteristics have not been observed, however. It appears that surface preparation of the Ge seeds is of critical importance.
- 3.5 The effects of different surface preparation on the growth morphology was investigated by growing ZnSe simultaneously on two germanium substrates having different final etching techniques. The best growths obtained have been on germanium substrates which have had a final etch of NaOCl. The final etchants tried to date listed in the order of the quality of the growths obtained are NaOCl: White Etch: CP4: HF: No

Etch. When an Anger spectrometer system becomes available, we will evaluate substrate cleanliness obtained by these different processes.

If any of these etches are used to remove extensive material the resultant surface is deteriorated, hence it is not clear that all work damage is removed. Therefore various new schemes were tried to prepare Ge seeds free of scratches and etch pits. None has so far given the final perfection desired of the Ge Seed. Various techniques tried include

- a) HCl vapor phase etching of (100) Ge seeds in flowing HCl-H₂ atmospheres
- b) Hand lapping with colloidal silica
- c) Hand lapping with a 3 μ m, 1 μ m and 0.3 μ m aluminum oxide grits followed by hand lapping with .05 μ m grit slurried with 5% NaOCl solution. This is a chemical and mechanical polishing step. However we still find scratches on seeds or faint haze on the (100) surfaces.

A recent note by D.B. Holt (J. Appl. Phys. 45, p. 966 (1974)) comments on difficulties in obtaining repeatable epitaxial growth of ZnSe on (111) Ge. Presumably his problems, like ours, are connected with or made worse by difficulties of achieving adequate substrate finish and system cleanliness.

3.6 Recent growth runs have shown uniformity of the grown layers and freedom from "stains". However the substrate has often shown signs of slight etching of the seed under the ZnSe. When this is observed the ZnSe perfection is not good and the diode characteristics of the junction either show undesired switching action or have rather high leakage currents.

3.7 It was suspected that the quality of the solvents used in the substrate preparation might be a cause of irregular and non-reproducible surfaces. The use of redistilled acetone reduces the presence of haze often seen on prepared substrates. Therefore the purity of these solvents was checked using the gas chromatography. The result indicated that most the solvents in use are reasonably pure and should not cause any problem in growth of ZnSe on Ge.

4. Measurement of Electron Transport Across pGe/vZnSe Interfaces

It was noted in the previous semi-annual report that there was a marked increase in quantum efficiency in the presence of bias light (room light). This improved quantum efficiency was quite encouraging and suggested that a detailed investigation was needed to determine the mechanism which was responsible for the increase. It was not clear from the early measurements whether the bias light was filling traps or whether it was reducing the ZnSe resistivity so the effective junction area (area of collection) was increased.

It was decided to make photoresponse measurements in the presence of the bias light of various wavelengths and intensity. A cooling chamber employing a two-stage thermoelectric cooler was built to permit experiments at lower temperatures. Fig. 3 shows the schematic diagram of the system for photoresponse measurements of a vZnSe/p-Ge heterodiode in the presence of biasing light and at reduced temperatures.

A set of experiments was conducted at room temperature to determine the effect of bias light wavelength (or energy) on the gain while keeping the intensity of the source constant. Gain is defined as follows:

$$\text{Gain} = \frac{\text{Photocurrent due to infrared radiation in presence of biasing light}}{\text{Photocurrent due to infrared radiation in absence of biasing light}}$$

As the energy of the bias light was increased above 2eV significant improvement in the gain was noticed. For bias light of energy greater than 2eV the gain increased as the intensity of the bias light was increased. Below a bias light of energy 2eV the increase in gain with intensity was very small. Fig. 4 and Fig. 5 show these results.

It was considered that since the ZnSe contact did not cover more than a small part of the layer some of the effect of the bias light might involve a change of the ZnSe resistance and so change the area over which the photo-induced current is collected. To determine the extent of the area modulation effect upon the gain increases, a two-diode system experiment was conceived which is shown in Fig. 6. Photoresponse measurements on the diodes were taken separately and with both connected in parallel. The results plotted in Fig. 7 for various light intensities show that bias light of high intensity and high energy produces an area modulation collection effect of 30%. Hence the area effect cannot be responsible for all the increase in gain observed (up to a factor of 20) with the bias light. In conclusion, we have shown that the area collection modulation can be part of the effect but is not the dominant part.

Further bias light experiments were done at reduced temperatures to fully characterize the effects and determine the extent of its usefulness in a photocathode device. The effect of the IR radiation intensity was investigated on the gain. The photocurrent increases linearly as a function of IR

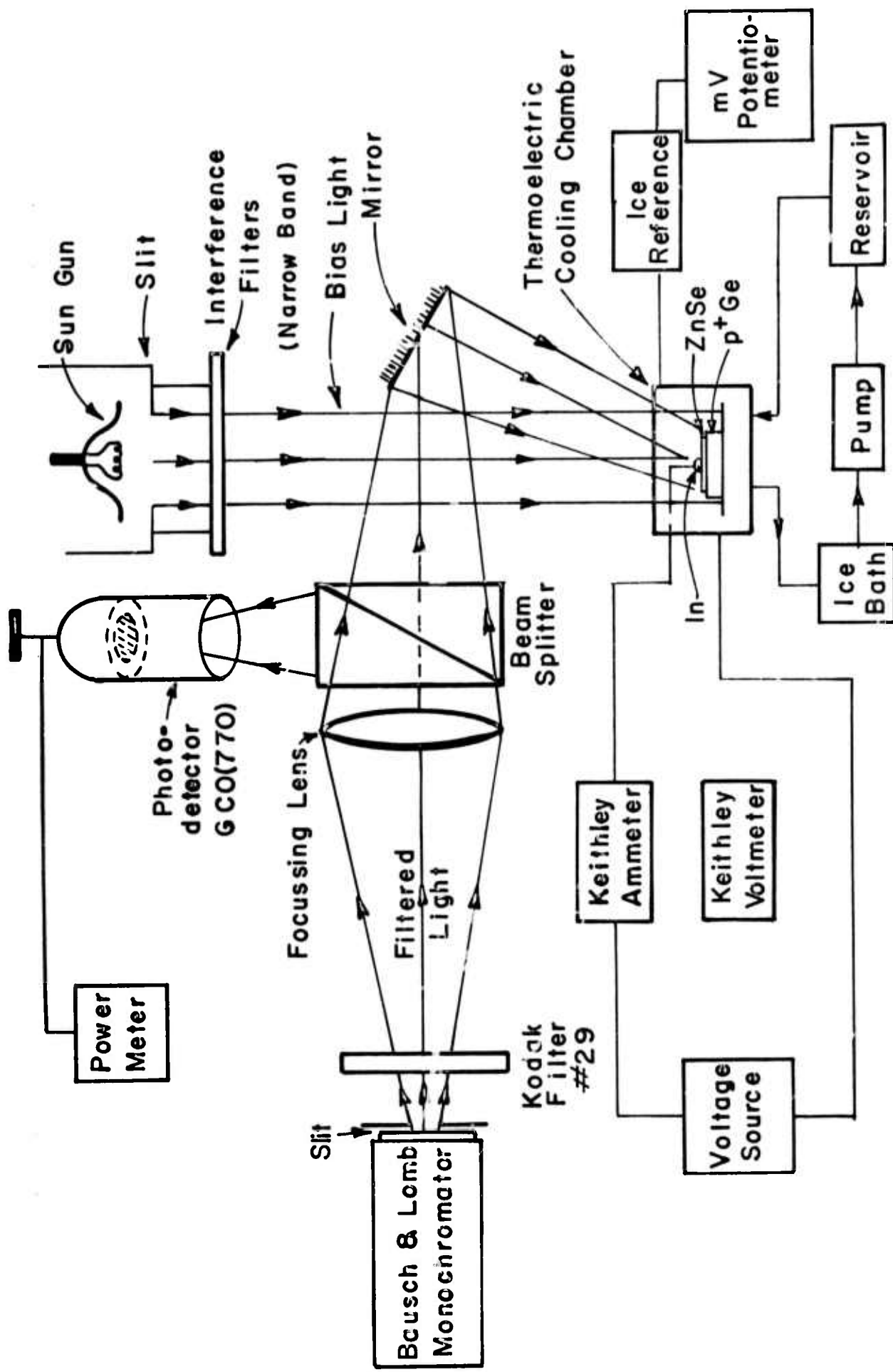
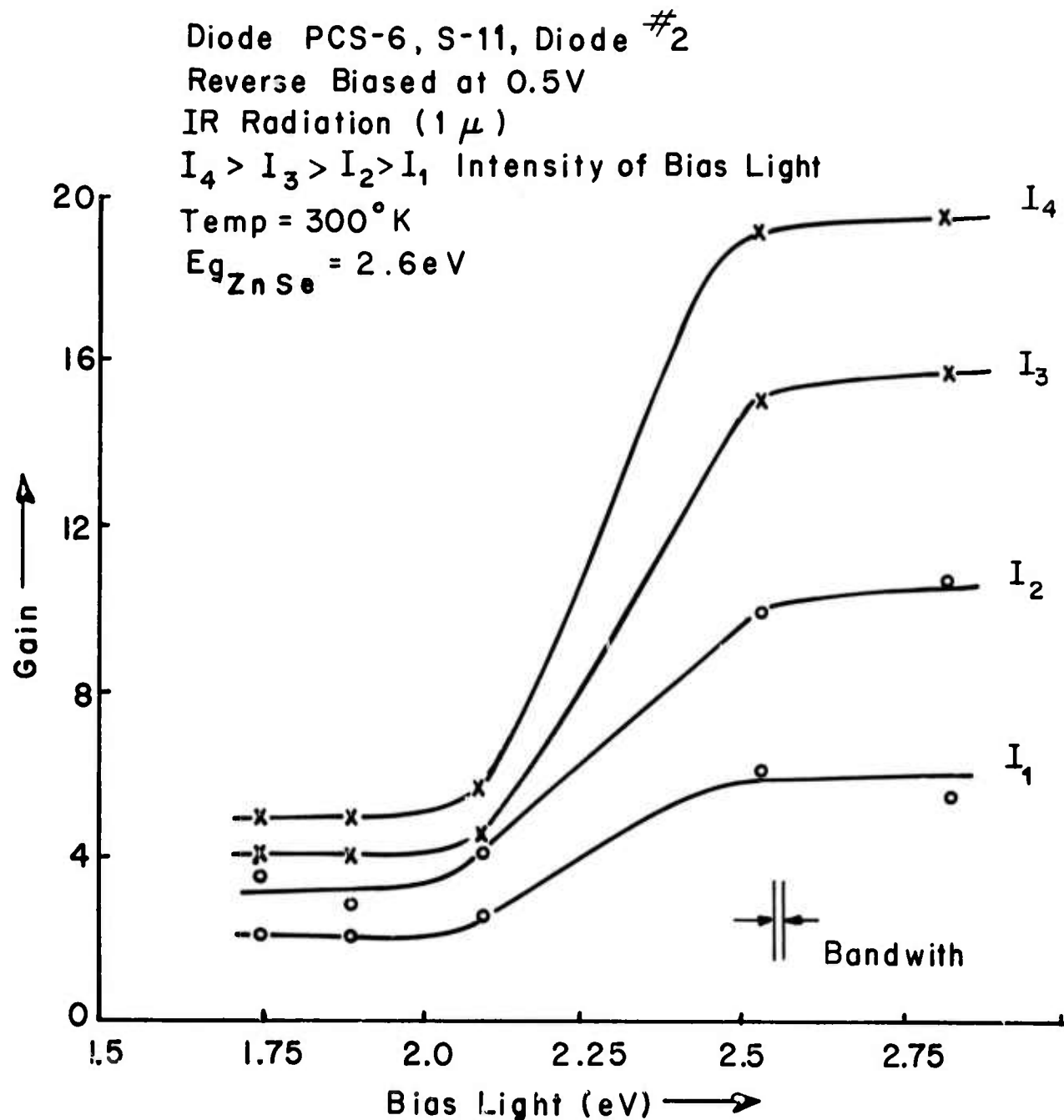
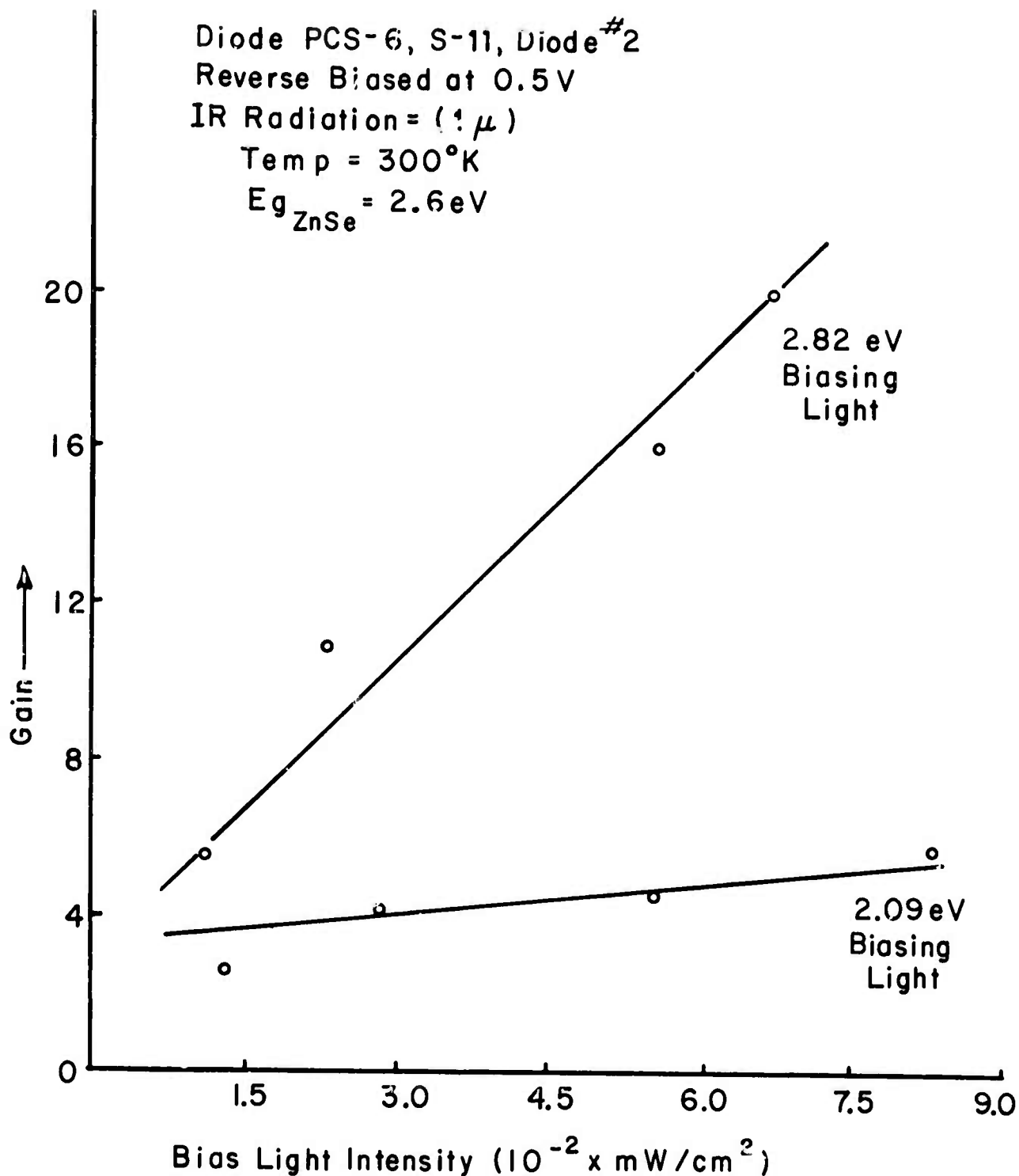


Fig.3 Schematic diagram of the system for photo-response measurement of a ZnSe/p-Ge heterodiode in presence of biasing light, and at reduced temperature



$$\text{Gain} = \frac{\text{Photocurrent Due To IR Radiation In Presence Of Biasing Light}}{\text{Photocurrent Due To IR Radiation In Absence Of Biasing Light}}$$

Fig. 4 Variation of gain with bias light wavelength and intensity



$$\text{Gain} = \frac{\text{Photocurrent Due To IR Radiation In Presence Of Biasing Light}}{\text{Photocurrent Due To IR Radiation In Absence Of Biasing Light}}$$

Fig. 5 Variation of gain with bias light intensity for two photon energies

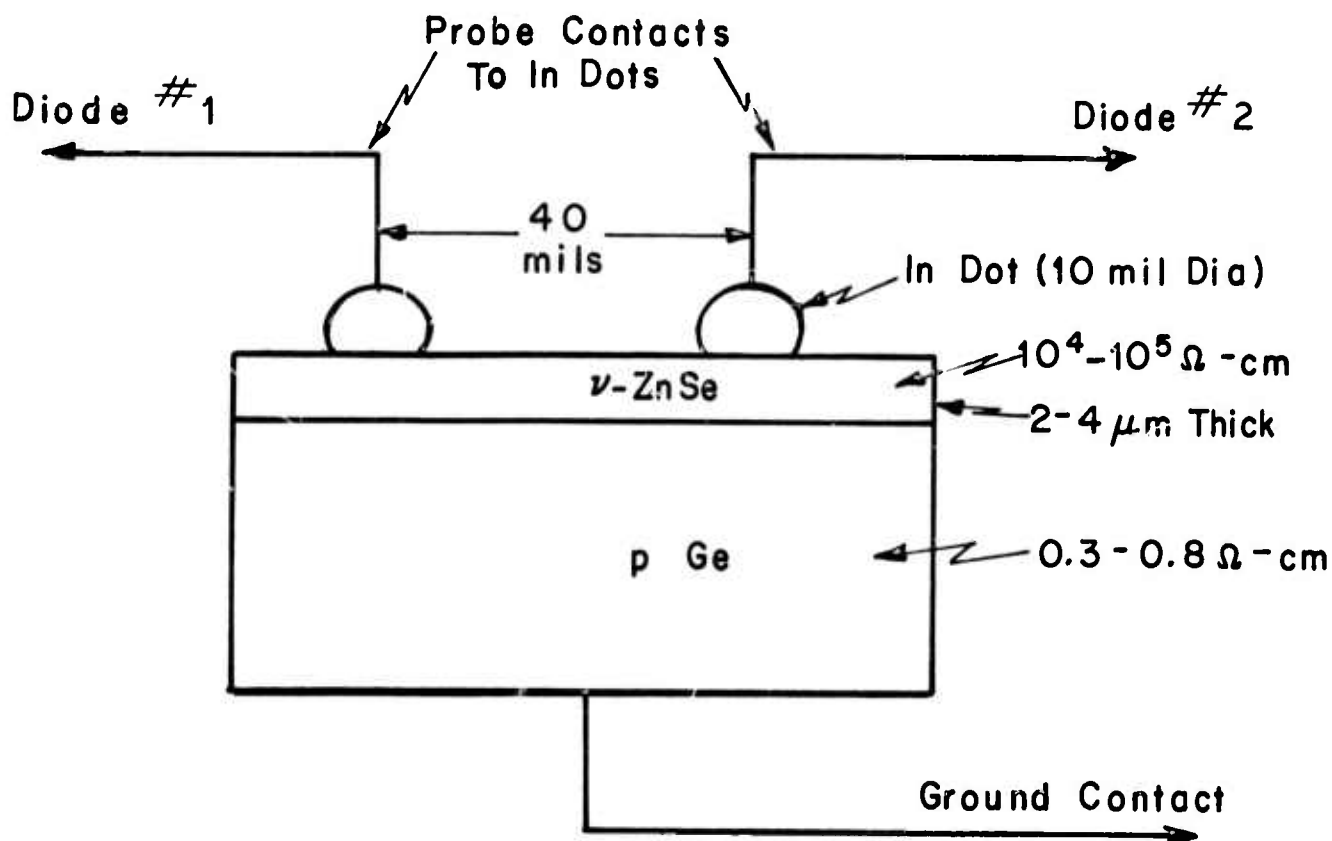


Fig. 6 Two diode system used to determine the area modulation effect in the presence of the biasing light of various wavelengths and intensities

Diode PCS-6, S-11, Diode #1 & #2

Reverse Biased at 0.5 V

IR Radiation (1μ)

$I_4 > I_3 > I_2 > I_1$ Intensity of Bias Light

Temp = 300°K

$E_{g_{ZnSe}} = 2.6\text{ eV}$

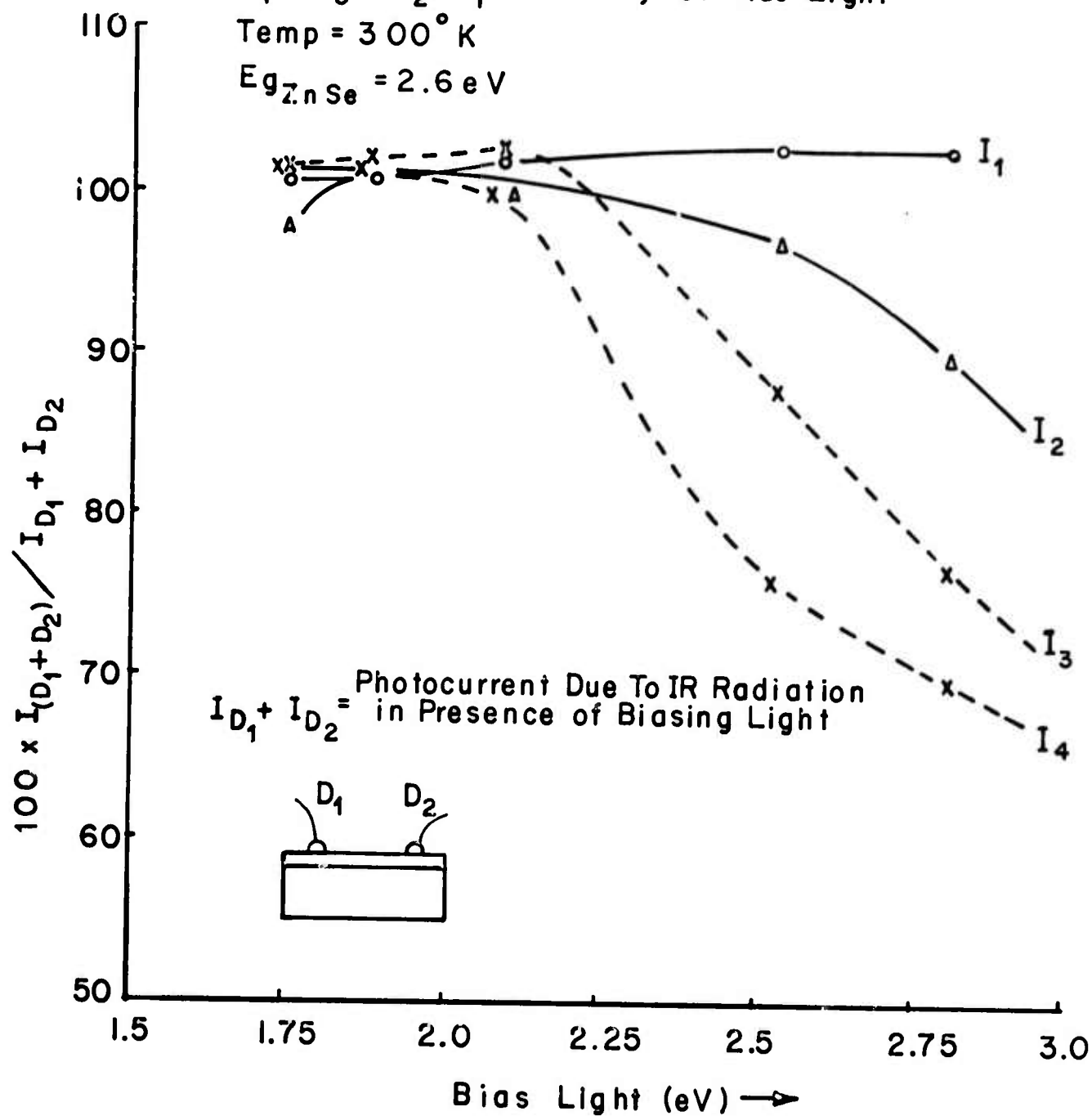


Fig. 7 Ratio of diode photocurrent when the diodes are connected in parallel to the sum of the individual diode photocurrents ($I_{(n_1 + n_2)} / I_{D_1} + I_{D_2}$) as a function of bias light energy for various bias light intensities

radiation intensity which is the expected result. Fig. 8 and Fig. 9 show plots of photocurrent vs. IR radiation intensity for different bias light intensities. The photocurrent plotted is in the presence of the biasing light. Photocurrent in the absence of the biasing light is a constant value. Therefore variation of gain as a function of the IR radiation intensity is the same as that of the photocurrent in the presence of the biasing light. Fig. 10 and Fig. 11 show gain vs. bias light intensity for two different temperatures (293°K and 273°K). There is an increase in quantum efficiency as the temperature is lowered, but the improvement is not sufficient to be exciting, and typical quantum efficiencies are only a few percent.

Some transient effects of the bias light reported previously indicate trapping phenomena are involved in the transport of electrons across the Ge/ZnSe interface. It was decided therefore to attempt to characterize the device in terms of the active trap levels and their densities.

As one approach to this characterization, capacitance (at 1 MHz) versus voltage measurements have been made with and without light at room temperature and below, see Fig. 12 and Fig. 13. The nature of the capacitance variation with voltage and with temperature is somewhat similar to effects seen in MOS type structures due to interface and bulk traps. It should be possible to model and extract information from such studies, and we are looking into this although our major effort is devoted to improving the grown layers.

Some transient capacitance vs. time measurements and transient current vs. time measurements have also been attempted to characterize the trap levels and their densities. But some instrumentation problems have affected the results. If these can be solved, transient capacitance studies have

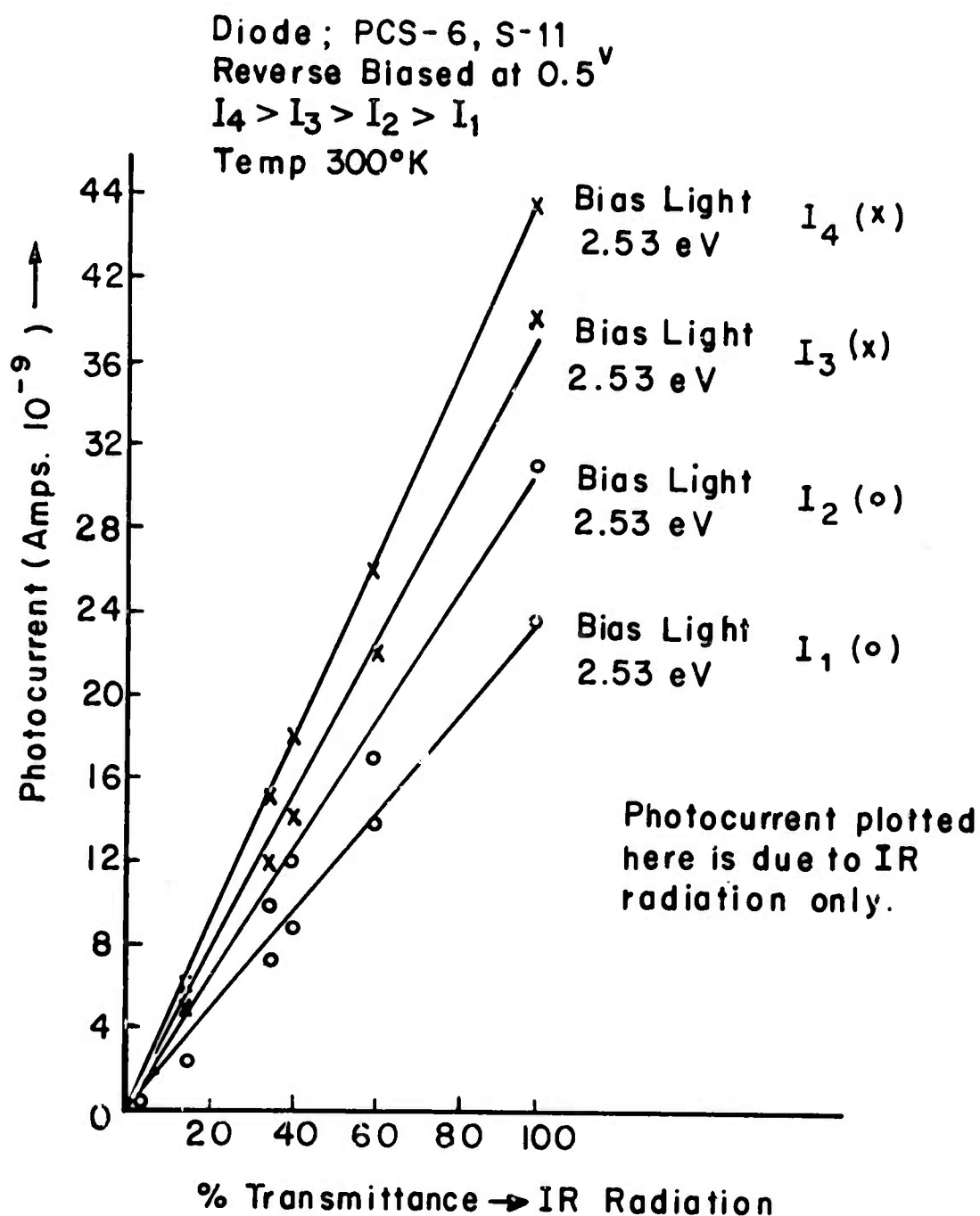


Fig. 8 Variation of photocurrent (or gain) with infrared radiation intensity for various bias light intensities, having a wavelength of 0.49 μm . PCS-6 S-11 is a Ge/ZnSe diode where the Ge is p type 0.3 ohm-cm and the ZnSe is a grown layer approximately $4\mu\text{m} \times 0.2\text{ cm} \times 0.2\text{ cm}$ and the ZnSe side is provided with an indium contact of .025 cm diameter and the illumination is provided on this side.

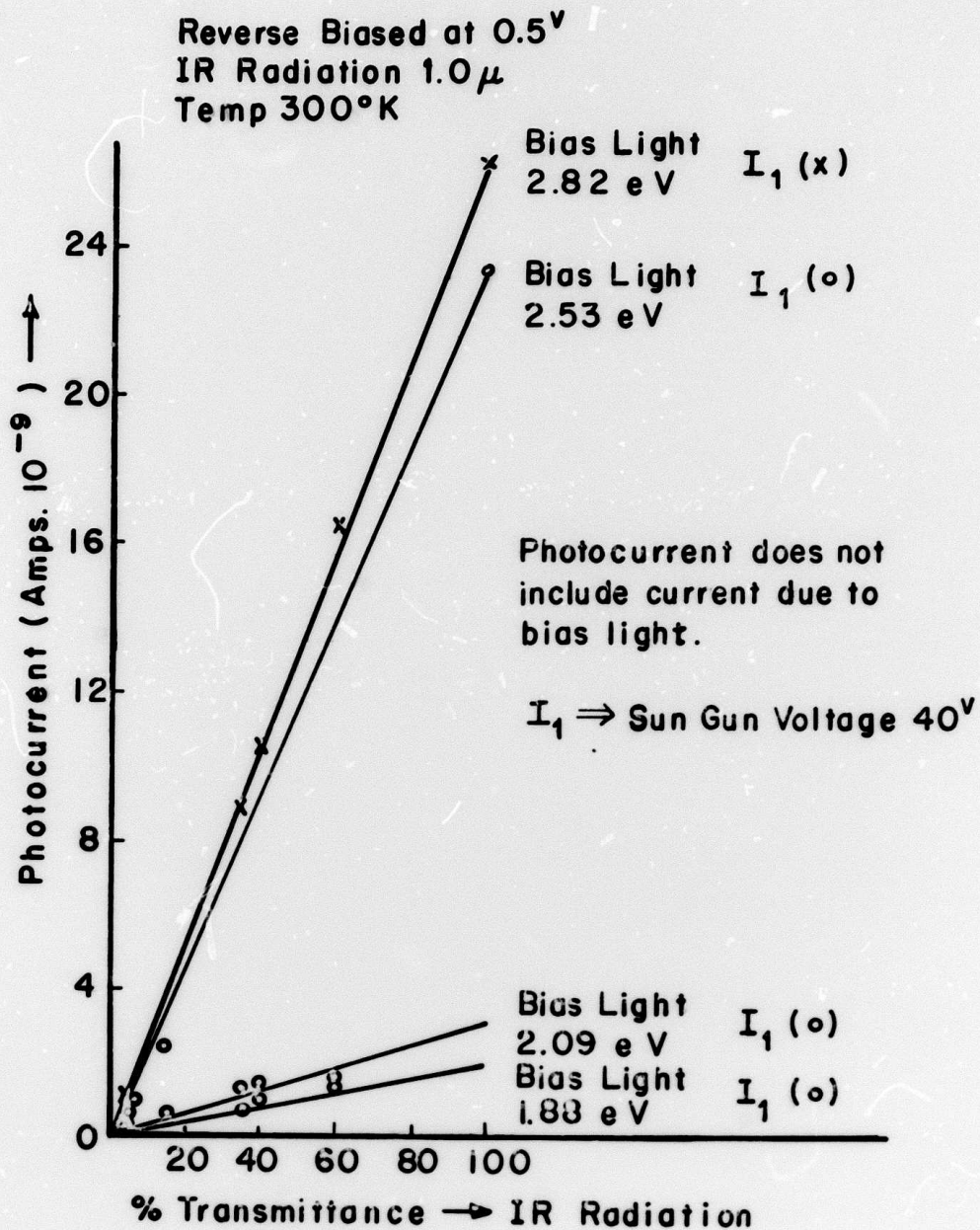


Fig. 9 Variation of photocurrent (or gain) with infrared radiation intensity for various bias light wavelengths keeping the intensity of the bias light constant.

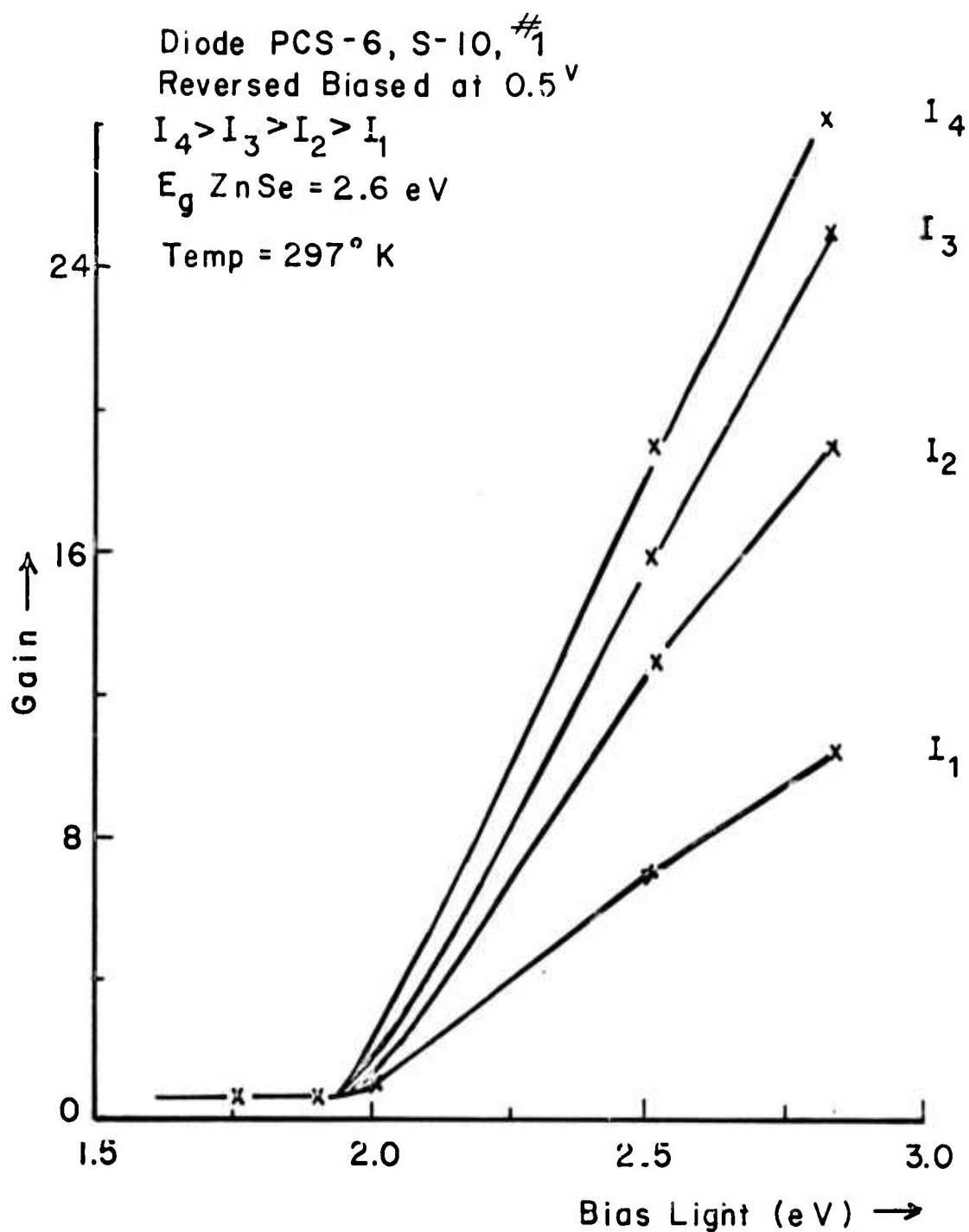


Fig. 10 Variation of gain with bias light wavelength for various bias light intensities at room temperature.

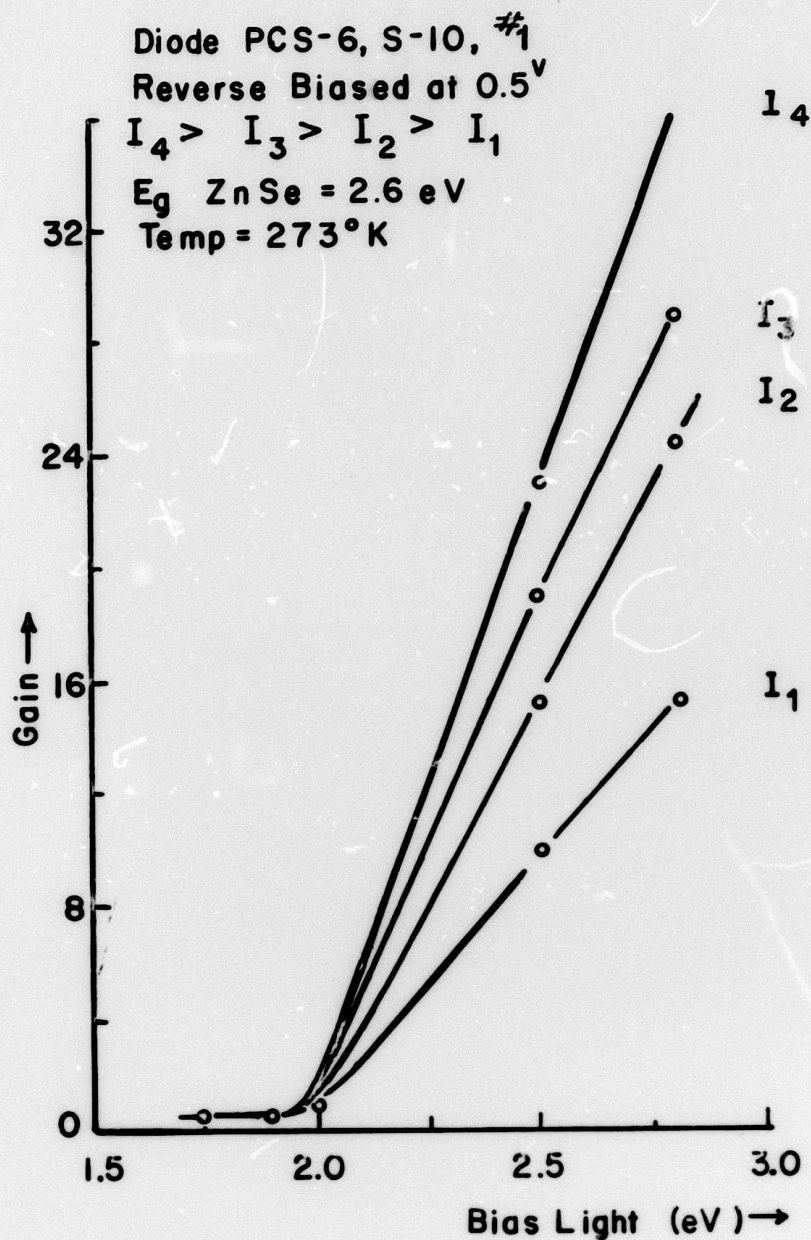


Fig. 11 Variation of gain with bias light wavelength for various bias light intensities below room temperature.

Diode PCS-6, S-12, #2
Frequency 1 MHz

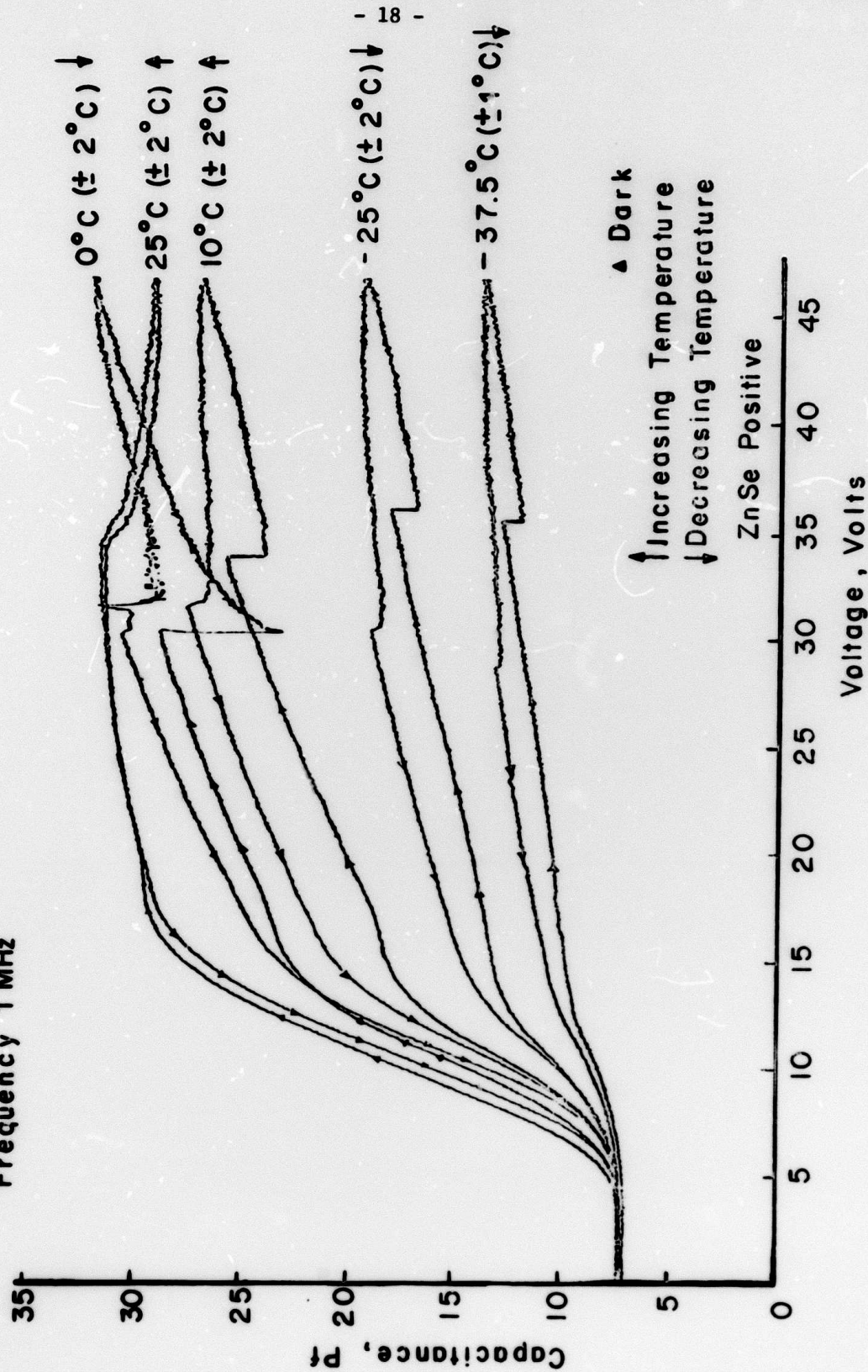


Fig. 12 C-V plots for vZnSe/P-Ge heterodiode at various temperatures in dark. Hysteresis is evident in all these plots.

Diode PCS-6, S-11M, #2
Temp (-25°C)

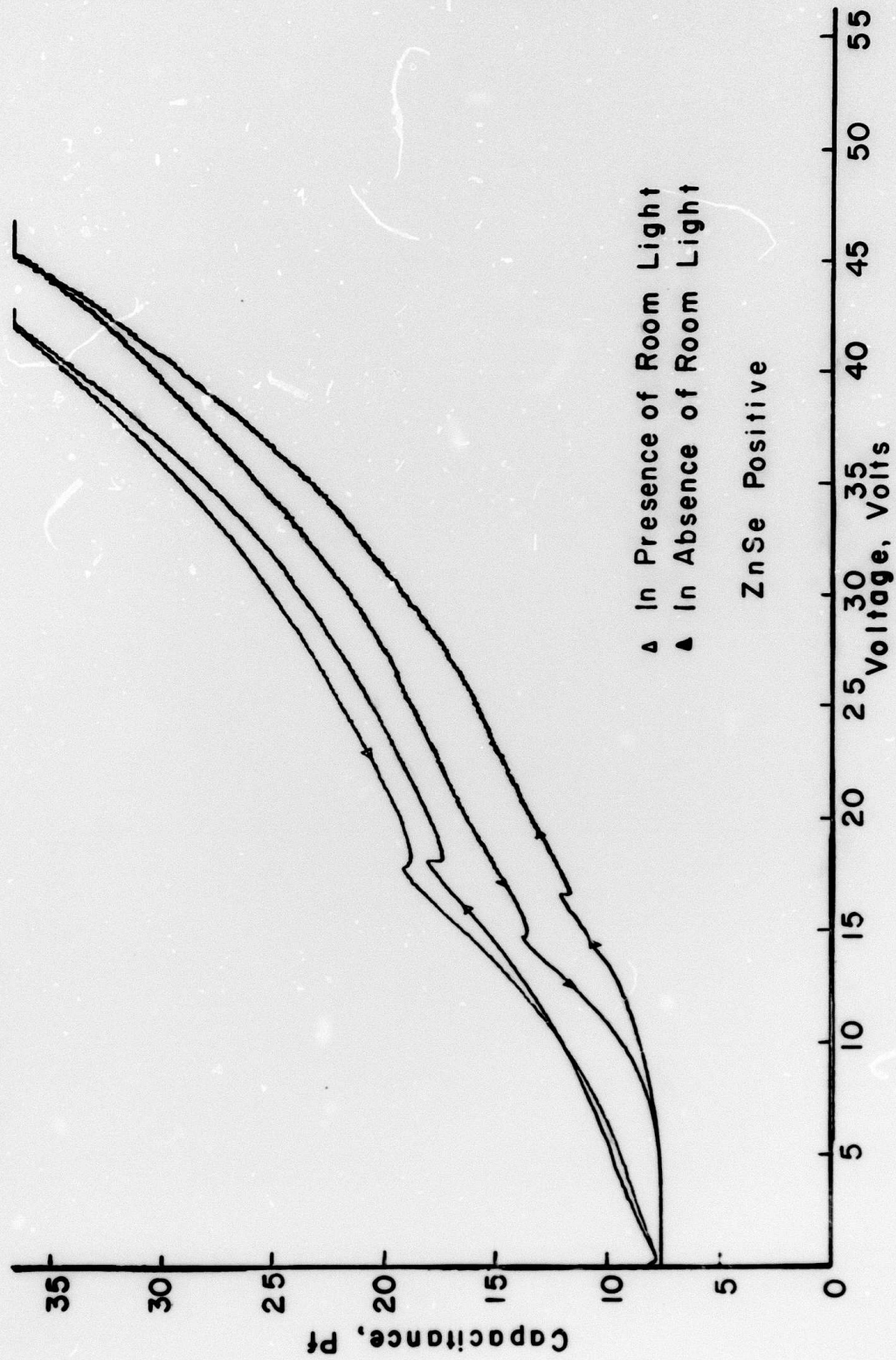


Fig. 13 C-V plots in the presence and absence of room light below room temperature.

the potential of providing further information about trap conditions.

5. Conclusions

The growth of ZnSe on Ge using the close-spaced HCl transport process is still not reproducible. The cause may be either substrate preparation problems and system cleanliness or undesirable HCl etching of the Ge substrate before the ZnSe layer fully develops. Most of the growths made exhibit switching action associated with trapping actions either at the interface or in the ZnSe.

The vZnSe/pGe structures that have non-switching characteristics have been studied to examine the transfer of electrons (induced in the Ge by 1 μ m infrared light) across the interface into the ZnSe. The efficiencies of transfer are low (a few percent) and it is apparent that many undesired trapping effects are taking place.

More perfect growths may perhaps reduce these trapping actions to an acceptable level and raise the electron transfer efficiency and this is being worked towards.

6. Presentations

No papers were published during the report period.

Mr. P. K. Govil reported at the semi-annual ARPA Program Review on November 27, 1973 in Arlington, Virginia.

7. Personnel Engaged on the Project

The personnel employed on the project during the six month period were Prof. D.L. Feucht and A.G. Milnes (Principal investigators, part time); Mr. P.K. Govil (research engineer and Ph.D. student, full time) and Mr. Dan Niebauer (growth technician, full time).

8. Energy Conservation Measures

The University has instituted energy conservation measures that include lowering of lighting and temperatures in laboratories, offices and classrooms.

In the use of the experimental equipment for this contract, the engineer and technician involved have been taking all sensible energy conservation measures.