OXYGEN ADSORPTION ON
CADMIUM SULPHIDE FILMS

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CONTENTS

REFERENCES

SUMMARY

The thesis begins with a brief summary of some of the theory relating to semiconductors and in particular, to semiconductor surfaces, which is relevant to the experimental work, followed by a brief review of a few of the recent theories and experimental results pertaining to cadmium sulphide. Then the methods of measuring the amount of gas adsorbed on cadmium sulphide films are discussed and the reasons for using the quartz crystal oscillator are given. A brief comparison of the properties of cadmium sulphide crystals and films is then made.

In chapter 2 the vacuum system, the quartz crystal oscillator, and the evaporation equipment are discussed to show the factors influencing the design of the vacuum system and why certain experimental procedures were used. A discussion of the kinetics of formation of cadmium sulphide films concludes the chapter.

Chapter 3 is concerned with the spurious changes in frequency which occurred. All the possible causes of the spurious frequency changes are reviewed and it is concluded that a photodielectric effect is being observed. The quartz crystal is then evaluated as a method of studying the photodielectric effect. This is followed by a comparison of the band gap photoconductivity spectrum with the results obtained previously by Law-

rance (1964). Then with the spurious frequency changes eliminated experiments in which adsorbed gas effects could be considered likely to occur have been performed and where possible the actual amount of oxygen involved in the experiment has been measured. These experiments are described in chapters 4 and 5.

Chapter 4 is concerned with the adsorption of oxygen on the surface of cadmium sulphide films under dark conditions. The adsorption kinetics have been shown to fit the Langmuir curve for simple adsorption and the sticking coefficient of oxygen on cadmium sulphide films has been calculated as a function of surface coverage.

The role of light in the adsorption and desorption of oxygen from cadmium sulphide films is investigated by mass spectrometry and with the quartz crystal oscillator in chapter 5. No evidence that either photo-adsorption or photo-desorption occurs has been found.

In chapter 6 the results presented in chapters 4 and 5 are discussed in relation to the theories presented in chapter 1 and the conclusion reached that the quartz crystal oscillator is not very suitable for the study of the adsorption of gases on cadmium sulphide as the amounts of gas involved are too small to be measured. A brief discussion of possible future experiments then brings the thesis to a close.

DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of the author's knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

(R. D. GOODWIN)

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Chapter 1

INTRODUCTION

1.1.1 Introduction

Cadmium sulphide is a member of the group 2A-6B semiconductors which consist of the oxides, sulphides, selenides and tellurides of zinc, cadmium, mercury and lead. Its bonding is partially ionic and its optical band gap is 2.43eV. at room temperature. As cadmium sulphide has been the subject of a large number of research papers no attempt will be made to summarize all its properties. Instead the theory and a few of the more general results relevant to the rest of this thesis will be discussed. The experimental results obtained by other authors will be referred to where appropriate.

1.1.2 Bulk and Surface Effects

The properties of semiconductors can be divided into two categories, bulk effects, and surface effects. Such a classification must be treated with caution however as the region of origin of some effects is unknown, e.g. the slow states in cadmium sulphide can be explained by a photochemical bulk reaction (Nicholas and Woods 1964, Tscholl 1968) or by a surface effect (Mark 1966). The centres which are responsible for charge trapping are known as "states". As cadmium sulphide crystals and films are n type semiconductors we are mainly interested in the trapping of electrons. Thus in the following discussions all states referred to will be electron traps unless specifically mentioned as hole traps. The states present at the surface will now be discussed.

1.1.3 Surface States

From a theoretical viewpoint surface states are classified into two distinct types:-

(a) intrinsic surface states

These exist solely because the surface interrupts a periodic lattice and will be present even on an uncontaminated surface. From theoretical considerations of the properties of cadmium sulphide Mark and Levine (1966) predict intrinsic acceptor surface states with a density of 10^{15}/sq.cm. Many et. al. (1969) using field effect measurements have shown that there is no significant (i.e , experimentally measurable) density of surface states on cadmium sulphide crystals, where the minimum number of surface states detectable experimentally is less than 10^{10}/sq.cm..

(b) extrinsic surface states

Extrinsic surface states are due to any sort of impurity present at the surface such as adsorbed atoms, oxides, or mechanical damage to the surface. On a "real" surface (by "real" we mean a surface such as encountered under experimental conditions) we expect to find both types of surface states present, but in the case of cadmium sulphide only extrinsic states have been detected.

Experimentally surface states are divided into two different classes, "fast" and "slow" surface states. The terms "fast" and "slow" relate to the relative speeds with which the states capture from, or lose carriers to, the underlying bulk. The fast states react in microseconds or less, the slow states in milliseconds up to hours. Both types exist in cadmium sulphide.

The fast states are believed to be situated at the interface between the crystal and the surface oxide layer. The results presented in this thesis, and the deductions of Mark (1965), indicate that if an oxide layer exists in the case of cadmium sulphide then it is less than 0.01 monolayers thick. The fast states are not dependent on the surrounding gases and their origin is unknown. Their density in cadmium sulphide is of the order of $3x10^{11}$ /sq.cm. (Many et. al. 1969).

The slow surface states are believed to be located at the surface of the oxide layer and to arise from adsorbed gas atoms. Their density is at least 10^{13} /sq.cm. (Many et. al.) but little is known about their cross-sections and other characteristics.

The bulk properties of semiconductors also exhibit fast and slow states.

1.1.4 Surface Barriers

For a perfect crystal lattice the conduction band and valence band will be flat even where they meet the surface, figure 1.1(a). If states exist at the surface which can trap charge carriers (e.g., electrons) figure 1.1(b), then there is a build up of trapped electrons at the surface leaving uncompensated positive centres in the bulk of the material. Thus when electrons approach the surface they are moving against an electric field and their potential energy must increase. A potential barrier to electrons is formed at the surface and this is represented diagramatically by band bending, figure 1.1(c).

The position of the surface states relative to the fermi level changes according to the amount of band bending occurring at the surface. States below the fermi level contain trapped electrons while those above are empty. The amount of band bending is dependent upon the amount of gas adsorbed at the surface. Thus the occupancy of surface states is determined by the prevailing surface conditions.

When the potential barrier arises from the ionization of impurities present at the surface (e.g., adsorbed gas) it is known as a Schottky barrier. The width of the Schottky barrier in cadmium sulphide is believed to be of the order of 20 - 30 nanometres.

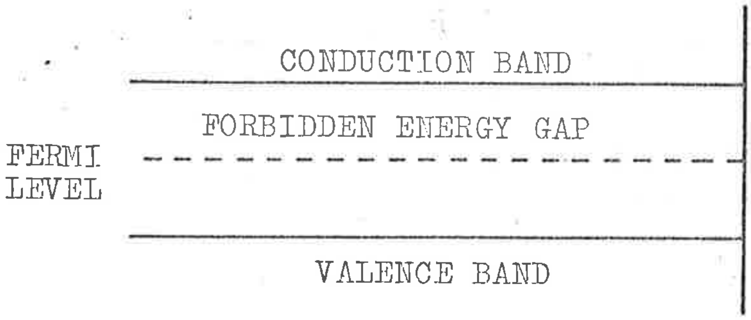


FIGURE 1(a)

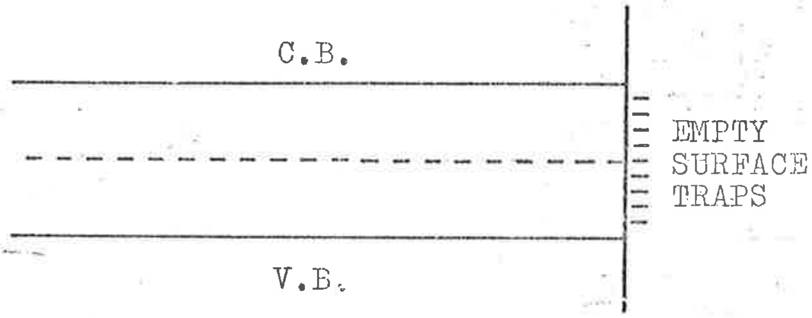


FIGURE 1(b)

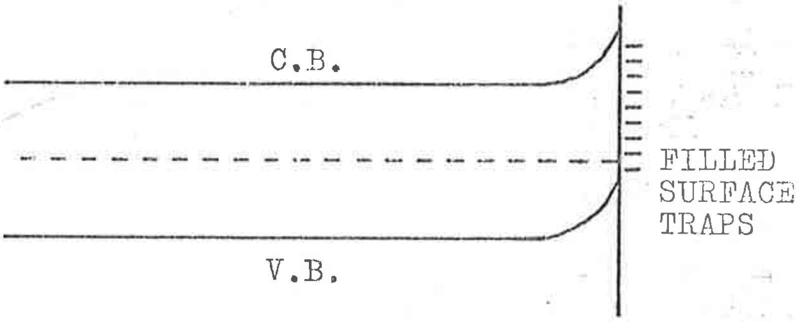


FIGURE 1(c)

FIGURE 1.1

1.1.5 Adsorption

Two forms of adsorption may occur at the surface of a semiconductor;

(a) Physical adsorption occurs due to forces of physical attraction (van der Waals forces) between the surface atoms and the gas molecules. The surface coverage is rarely more than two or three monolayers (Langmuir 1961).

(b) Chemisorption occurs when there is a transfer of electrons between the adsorbent and the adsorbate. The bonding energies are generally higher than in the case of physical adsorption and the amount of gas chemisorbed is limited to a layer one molecule thick. Physical adsorption always precedes chemisorption.

1.1.6 The Elovich Equation

Chemisorption is accompanied by the formation of a Schottky barrier at the surface. Thus the electrons involved must be transfered to or from the bulk (depending on whether the adsorbed gas species is an electron donor or an electron acceptor) through a potential barrier. The rate of chemisorption is characterized by an equation of the form

$$\frac{dN_s}{dt} = a \exp(-bN_s)$$

where N_s is the surface density or adsorbed atoms, t is the time, a is a pressure and temperature dependent constant, and b is a pressure dependent constant. This is known as the Elovich Equation and was originally used by Elovich (1939) to describe the adsorption of hydrogen and ethylene on nickel. Medved (1961) used it to describe the adsorption of oxygen on the group 2A - 6B compound, zinc oxide. Mark (1965) used Medved's theory to explain chemisorption on cadmium sulphide crystals.

As the Elovich Equation can be derived from quite general considerations involving the transfer of electrons from the bulk to the surface across a potential barrier it is difficult to draw any conclusions about the processes occuring at the surface from it. Its occurrence simply demonstrates that a potential barrier exists between the surface and the bulk.

1.2.1 Surface Chemical Reactions

The actual chemical reactions occurring at the surface of cadmium sulphide have been the subject of several papers (Haas et. al. 1965, Bootsma 1968, and Schubert and Boer 1971). The methods used can be divided into two categories, direct methods where the actual amount of gas involved is measured, and indirect methods where a parameter such as conductivity, which depends on surface conditions, is studied and the number of atoms involved at the surface is deduced.

Gas volumetric measurements, in which the amount of gas involved is measured by recording changes in pressure, have been made by Haas et. al. and Bootsma. Bootsma presents evidence that three different reactions occur depending on the temperature of the cadmium sulphide:

(1) At room temperature adsorbed oxygen occupies sulphur lattice vacancies causing a decrease in the conductivity.

(2) At higher temperatures the reaction

$$2CdS_s + 3O_2 \longrightarrow 2CdO_s + 2SO_2\uparrow$$

occurs. The subscript s indicates the atom which occupies a sulphur lattice site. This reaction also results in a decrease in the conductivity.

(3) At temperatures above 500°C the reaction

$$S_s + O_2 \longrightarrow SO_2\uparrow$$

creating sulphur lattice vacancies and hence an increase in the conductivity occurs.

The gases desorbed from cadmium sulphide crystals by heating under ultrahigh vacuum conditions have been studied by Schubert and Boer (1971) using mass spectrometry. Monatomic oxygen was the principal product with water vapour having a comparable desorption rate near 420° K. No sulphur dioxide formation was found.

Weber (1969) found that washing cadmium sulphide crystals in distilled water increased the conductivity of the distilled water after the first washing, but subsequent washings in fresh distilled water did not change the conductivity of the distilled water. This he attributed to cadmium sulphate being present on the surface. Other experimental results will be considered in chapter 4 where relevant.

1.2.2 <u>Field Effect Measurements</u>

A.C. and D.C. field effect measurements constitute one of the indirect methods of studying surface reactions. D.C. field effects allow the study of the slow surface states which are believed to be introduced by gas molecules adsorbed at the surface (Many et. al. 1969, and Sawamoto 1965). Weber (1969) disagrees with this source of origin of the slow states.

In field effect measurements an electric field, applied perpendicular to the surface of the crystal, is used to vary the height of the potential barrier at the surface. When the barrier height is raised so that the fermi level lies more than 0.91eV. below the conduction band the chemisorbed oxygen on the surface must pass to a state of physical adsorption. Lowering the barrier height results in chemisorption. By recording the resulting changes in surface conductance the electron trapping kinetics can be studied.

The results of Many et. al. indicate that there are no intrinsic surface states in cadmium sulphide crystals contrary to the theoretical predictions of Mark and Levine (1966). Many associates the slow surface states with adsorbed oxygen molecules; the unoccupied states with physically adsorbed molecules and the occupied states with chemisorbed molecules. The amount of gas involved has not been measured directly but instead is deduced from the density of trapped charge. During the chemisorption process the conduction band electrons are believed to interact with a fixed number of physically adsorbed atoms whose number is determined by the partial pressure of the gas concerned i.e., as each atom is chemisorbed it is immediately replaced by another physically adsorbed atom. However no attempt to verify this has been made.

Weber (1969) has also investigated the slow surface states using D.C. field effects. His interpretation of the nature of the effect and the position in the crystal of the slow surface states differs from that of Many.

Weber considers that the slow surface states are not due to adsorbed gas molecules because:

(a) Treatment of the surface (i.e., removing cadmium sulphate from the surface by washing in distilled water) does not alter the density of the surface states.

(b) The desorption times for chemisorbed oxygen measured by other authors (e.g., Mark 1965 used the relaxation in the conductivity associated with chemisorption) are far greater than the relaxation times measured using D.C. field effects.

(c) The kinetics of photoresponse, which Weber assumes to be a bulk effect, are the same as those observed for slow field effects. Hence the same slow trapping centres must be responsible for both processes

There is insufficient information in the paper by Weber for a comparison to be made between his D.C. field effect results and those of Many. et. al.. Many associates the observed slow states with oxygen because oxygen is known to drastically alter the electronic structure of the surface.

Further evidence that the centres studied by field effects and by photo-induced effects are the same is provided by a comparison of the trapping levels and cross-sections obtained by Sawamoto (1965) using field effects and Nicholas and Woods (1964) using thermally stimulated currents. These are shown in table 1. The two sets of results agree fairly well even though field effects are generally believed to measure surface states and thermally stimulated currents bulk states.

Oxygen adsorption on cadmium sulphide has also

SAWAMOTO		NICHOLAS and WOODS	
$E_c - E_t$ (ev.)	S_n ($cm.^2$)	$E_c - E_t$ (ev.)	S_n ($cm.^2$)
0.043	7×10^{-21}	0.05	10^{-24}
0.08	1×10^{-23}	0.14	10^{-23}
0.3	6.9×10^{-19}	0.25	10^{-24}
0.43	2.3×10^{-18}	0.41	10^{-20}
0.6	4.6×10^{-16}	0.63	10^{-18}
0.82	2.5×10^{-13}	0.83	10^{-14}

S_n = TRAPPING CROSS-SECTION

$E_c - E_t$ = CONDUCTION BAND ENERGY

\- TRAPPING LEVEL ENERGY

TABLE 1

been studied by measuring the effect of oxygen on the surface photovoltage (Haas 1965, Williams 1962), photoconductivity and dark conductivity (Mark 1964, Faeth 1967). In each case no attempt has been made to measure the amount of gas actually present on the surface.

1.3.1 Photo-adsorption and Photo-desorption

The role of light in the adsorption and desorption of gases from the surface of cadmium sulphide has been the subject of many papers. However no conclusive evidence of the occurrence of either effect has been presented. The occurrence of both effects is generally inferred from the nature of the photo-conductivity curves obtained.

Photo-adsorption occurs on the surface of a semiconductor when the electrons needed for chemical bonding are provided by photons creating electron hole pairs. Photo-desorption occurs when an incident photon breaks a chemical bond.

Schubert and Boer (1971) find that photodesorption from cadmium sulphide crystals cannot be detected by mass spectrometry. If light of sufficiently high intensity is used desorption can be achieved, but it is due to the resulting heating of the crystal. They explain the observed accelerated changes in electrical properties when a crystal is illuminated under vacuum conditions without recourse to photo-desorption. The explanation is as follows.

The incident light creates electron-hole pairs in the near surface region. The photogenerated holes diffuse towards the surface due to the influence of the Schottky barrier where they combine with electrons released by desorbed oxygen molecules. The photogenerated electrons diffuse away from the surface. The resultant effect of the illumination is to facilitate the redistribution of the electrons to their new equilibrium positions in the near surface region and the rate of change of the electrical properties is increased.

1.3.2 Light Induced Slow Phenomena in Cadmium Sulphide

Two light induced slow phenomena are present in cadmium sulphide;

(1) There is a slow decrease in the conductivity at constant illumination. It has been established by Boer (1954) that it is due to a slow decrease in the number of free electrons in the bulk.

(2) There are slow light induced changes in the spectra of thermally stimulated currents (conductivity glow curves).

The two phenomena are believed to be closely related.

The interpretation of the two phenomena is generally divided into two parts; the interpretation of the photoinductance, and the interpretation of the slowness. It is agreed by all authors that the photoinduction is the recharging of the crystal lattice defects. There are however, three common interpretations of the slowness.

(a) The slowness is due to the mechanism by which the homogeneous bulk of the crystal is charged. The trapping centre is considered to be a defect surrounded by a coulomb repulsive barrier. For electrons to be freed from the trap they must be excited over the potential barrier. This model was used by Bube (1957) and Bube et. al. (1966) but has subsequently been rejected by Bube (1970).

(b) The slowness is due to photochemical sorption. Mark (1964, 1965 and 1966) has proposed and developed a model for the chemisorption of gases on the surface of cadmium sulphide. The slow light induced effects are explained by photo-adsorption or photodesorption which changes the density of surface traps. Electrons diffuse from the bulk to the surface where they are trapped by adsorbed gas molecules. The slowness is due to the presence of the potential barrier region across which the electrons must diffuse to reach the surface traps.

(c) The slow states are created by photochemical bulk reactions and the slowness is due to the difficulty of diffusion of the associated crystal defects. The measured rate of diffusion of defects in cadmium sulphide at room temperature is too low, Boer et. al. (1964), and has not as yet been conclusively reconciled with the theory. Tscholl (1968) has overcome the problem by proposing that only defects initially within 10 nanometres of each other are involved in each centre. This theory, proposed by Nicholas and Woods (1964) to account for the results they obtained using conductivity glow curves, is however currently the most popular (Bube et. al. 1970, Tscholl 1968).

The photochemical model for the slow states involves the concept of the agglomeration of defects to form a particular trap under the influence of photoexcitation. The subsequent thermal emptying of this trap is associated with the dispersal of the defects and hence with the destruction of the trap.

There is no conclusive evidence as to the nature of the traps. Photochemical effects are, however, well known for the ionic alkali halides (electronegativity data shows that cadmium sulphide is 22% ionic (Pauling 1945)) and this knowledge has been applied to the results obtained with cadmium sulphide.

Nicholas and Woods propose that the states are agglomerates of sulphur vacancies with the possibility of cadmium vacancies being involved in some cases as crystals with an excess of sulphur show a different trapping spectrum to those with an excess of cadmium.

Tscholl proposes a model in which all the thermally stimulated conductivity peaks are associated with a single type donor-acceptor pair, the apparently different activation energies arising from the possible variations in the distance between the members of the pair. The donor-acceptor pairs are believed to involve an impurity which he identifies as being nickel.

1.3.3 Discussion

Some aspects of the literature considered in the preceding sections will now be considered briefly. Doubt as to the possibility of photochemical effects being able to explain the slow states has been expressed by Bube (1966) and although he has subsequently supported the theory (1970) the objections raised in the first paper have not been refuted. Furthermore evidence has been presented by Weber (1969) showing that the slow states measured using D.C. field effects obey the same kinetics as the photo-induced slow states thus questioning the role played by the illumination in the slowness of the states.

The role of oxygen in many experiments is not understood. Tscholl finds that conductivity glow curves are only reproducible if oxygen is present in the ambient inert gas, yet the slow states are explained as bulk states and no attempt is made to explain the role of the oxygen. Similarly Nicholas and Woods find that the conductivity glow spectrum is ambient dependent but they cannot conclusively explain the effect.

The mechanism by which oxygen causes changes in the photoconductivity and dark conductivity of cadmium sulphide is not known. Many (1969) reports that oxygen introduces trapping levels at the surface, whereas Mark (1966) shows from theoretical considerations that oxygen removes trapping levels.

The amount of oxygen which can be chemisorbed on the surface of cadmium sulphide is also questioned. Many (1969) and Schubert et. al. (1971) find monolayer coverages (10^{15} atoms per sq. cm.) while Farnsworth and Campbell (1968) and Mark (1965) find coverages of less than 0.001 monolayers (10^{12} atoms/sq. cm.). All of the above results were obtained with cadmium sulphide crystals.

1.3.4 Summary

In the preceding sections it has been shown that a distinction between surface and bulk effects cannot in many cases be easily made. In particular it is obvious that the role of gas molecules adsorbed on the surface in determining many of the properties is not understood yet no attempt has been made to measure the amount of gas present on the surface during the actual experiments.

This thesis is concerned with the measurement of the amounts of gas involved in some experiments with cadmium sulphide in an attempt to shed further light on the theories discussed in the preceding sections.

The experimental work presented includes;

(a) measurements of the amount of oxygen present on the surface for dark conditions as a function of the pressure and the dark conductivity of the sample to determine the number of oxygen atoms necessary to cause a given change in the number of charge carriers present. Hence the role of oxygen may be determined as many more oxygen atoms will be involved if the atoms are acting as trapping centres than if they are acting as recombination centres.

(b) a study of the rate of adsorption of oxygen under band gap illumination conditions to determine if photo-adsorption or photo-desorption occurs.

(c) measurement of the amount of oxygen present as a function of the wavelength of the illumination to which the cadmium sulphide film is exposed to determine whether any of the trapping levels reported in cadmium sulphide are due to adsorbed oxygen.

1.4.1 Measurement of the Amount of Adsorbed Gas

The discussion of the properties of cadmium sulphide in the preceding sections shows the need to be able to measure small amounts of gas present on a surface. There are several possible methods, ellipsometry (Archer 1962), LEED (low energy electron diffraction) (Campbell and Farnsworth 1968), vacuum microbalances ("Vacuum Microbalance Techniques" vols. 1-8), and the quartz crystal oscillator (Sauerbrey 1959).

Ellipsometry and LEED measure the thickness of the adsorbed gas film whereas the other two methods measure the actual amount of gas involved. Of the four methods the quartz crystal oscillator was chosen because it is robust, fairly easily operated and not very difficult to construct. A mass sensitivity of 4×10^{-10} gm./cm.^{2} is readily obtainable and with refinements can be extended to 10^{-12} gms./cm.^{2}. From the table given in chapter 2, section 2.2. it can be seen that less than a monolayer of all gases except hydrogen can be detected with the oscillator used. The quartz crystal oscillator also allows a continuous monitoring of the gases present on the surface. The other three methods are all more difficult to operate and do not give a worthwile improvement in sensitivity.

1.5.1 Cadmium Sulphide Crystals and Films

Most of the published experimental results on the surface properties of cadmium sulphide have been obtained using single crystals. The measurement of the amount of gas present during experiments with a quartz crystal oscillator necessitates the use of films. Thus it is necessary to consider the similarities and differences of crystals and films.

A film may be considered to consist of many crystallites interconnected by conducting necks. This idea is supported by two pieces of experimental evidence.

(a) the surface and bulk electron mobilities of cadmium sulphide crystals are almost equal (Many et. al. 1969). Hence the mobility is virtually independent of crystal size.

(b) the electron mobilities of crystals and films are similar (Lawrance 1964). If the films do consist of many small crystallites then (a) explains why films have electron mobilities comparable with those of crystals.

As a consequence of consisting of many interconnected crystallites films have a much greater surface to volume ratio than crystals of a comparable size, and surface effects will be more pronounced.

The chief differences between crystals and films arise from the greater departure from stoichometric proportions, and the incorporation of impurities, in films during formation. Thus films have a greater defect density. In comparisons of results for crystals and films the above factors must be considered.

CHAPTER 2

APPARATUS

2.1.1 Introduction

Some of the trapping centres found in cadmium sulphide have cross-sections of the order of 10^{-20} to 10^{-22}cm.^{2}. The cross-section of a neutral lattice site is approximately 10^{-15}cm.^{2} implying that the centres with smaller cross-sections may be surrounded by a repulsive potential barrier. It has been suggested by several authors (e.g. Mark 1964 Lawrance 1964) that these trapping centres may be situated at the surface of the cadmium sulphide crystal or film with the Schottky barrier providing the repulsive potential. The importance of the surface has been shown by the marked effect the ambient gas has on the conductivity of cadmium sulphide crystals and films (Mark 1964, 1965, Bube 1966, Faeth 1967) yet most experiments have been performed in vacuum systems with a base pressure of 10^{-6} torr. or higher.

At 10^{-6} torr. and room temperature there are $4\text{x}10^{14}$ collisions with a surface per sq. cm. per second. Hence gases with a reasonably high sticking probability will rapidly contaminate the surface. A paper by Hughes and Carter (1967) indicates that a rapid contamination of the surface of cadmium sulphide films occurs at 10^{-6} torr. This is contrary to expectation as Campbell and

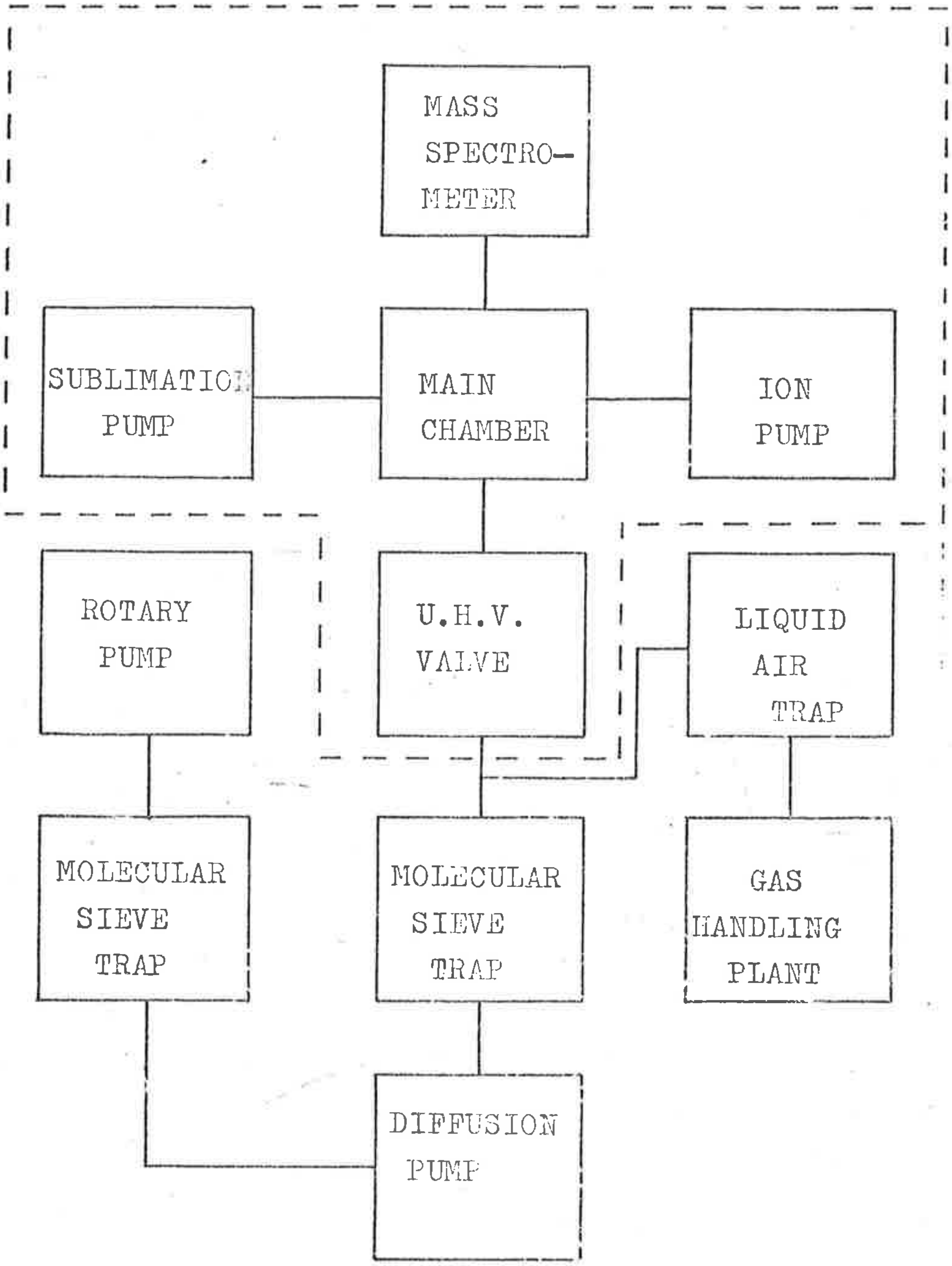
Farnsworth (1968) found that the sticking coefficient of oxygen on cadmium sulphide crystals is less than 10^{-13} which would mean that less than 40 atoms are adsorbed per second.

The preparation of cadmium sulphide films with consistent properties has always been a problem. Hughes and Carter (1967) have shown that films with consistent properties can be prepared by evaporating under ultrahigh vacuum conditions. (Their criterion for consistent properties being that films of the same thickness have the same dark current and photosensitivity). Thus an ultrahigh vacuum system is needed for the study of cadmium sulphide films. The vacuum system designed by the author and constructed in the Physics Dept. Workshop is described in the following sections.

2.1.2 <u>The Vacuum System</u>

A schematic sketch of the vacuum system is shown in figure 2.1, and a general view of the system in figure 2.2. The vacuum system was designed to meet the following requirements:-

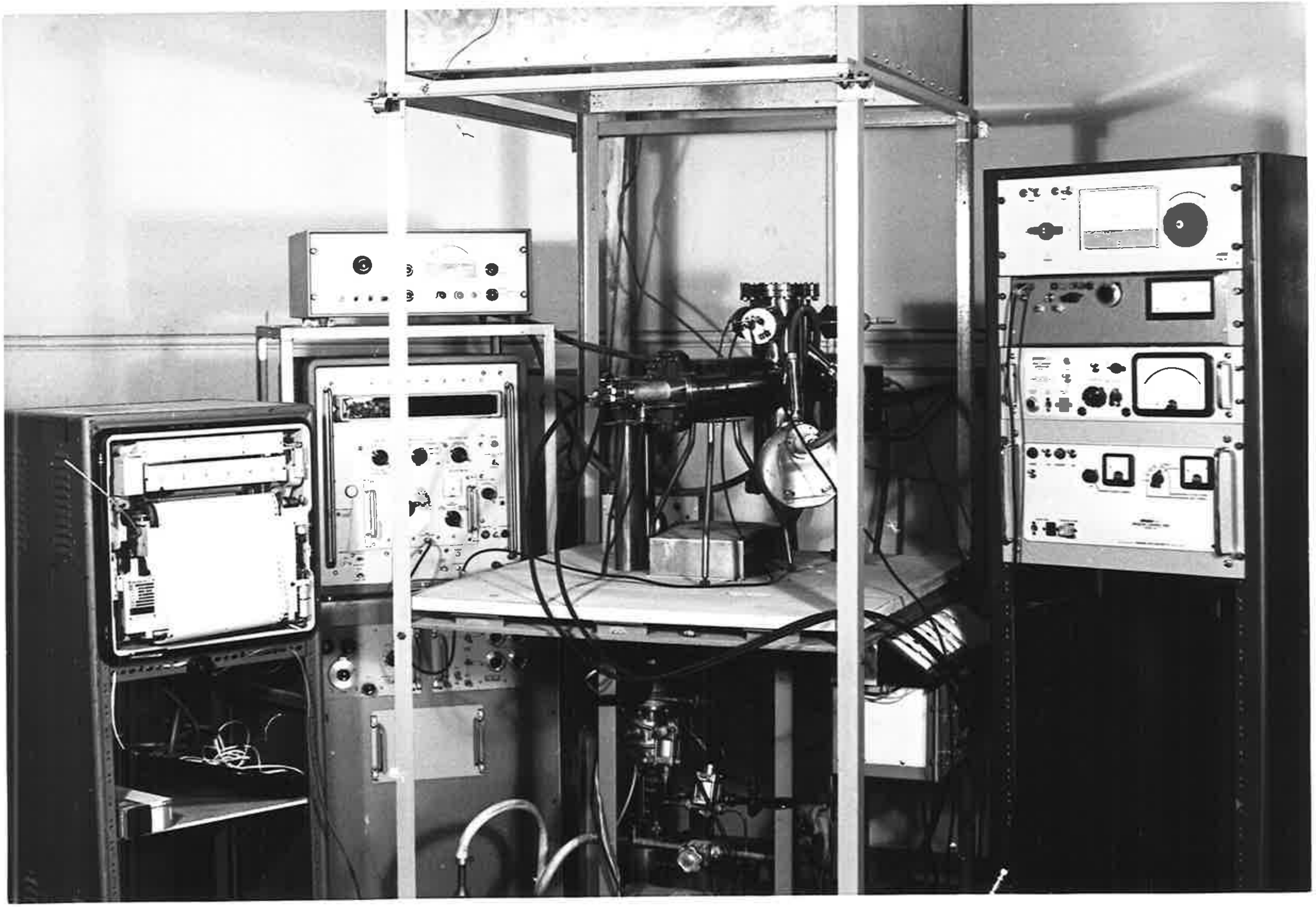
(a) The ultrahigh vacuum section must be bakeable and have as high a pumping speed as possible. The high pumping speed is needed during evaporations when any gaseous products formed must be pumped away as quickly as possible to prevent their incorporation into the film.



THE VACUUM SYSTEM

FIGURE 2.1

FIGURE 2.2



(b) A gas handling plant capable of admitting pure gases at any desired pressure is needed.

(c) Provision for mounting a mass spectrometer to monitor the gases present in the vacuum system during an evaporation.

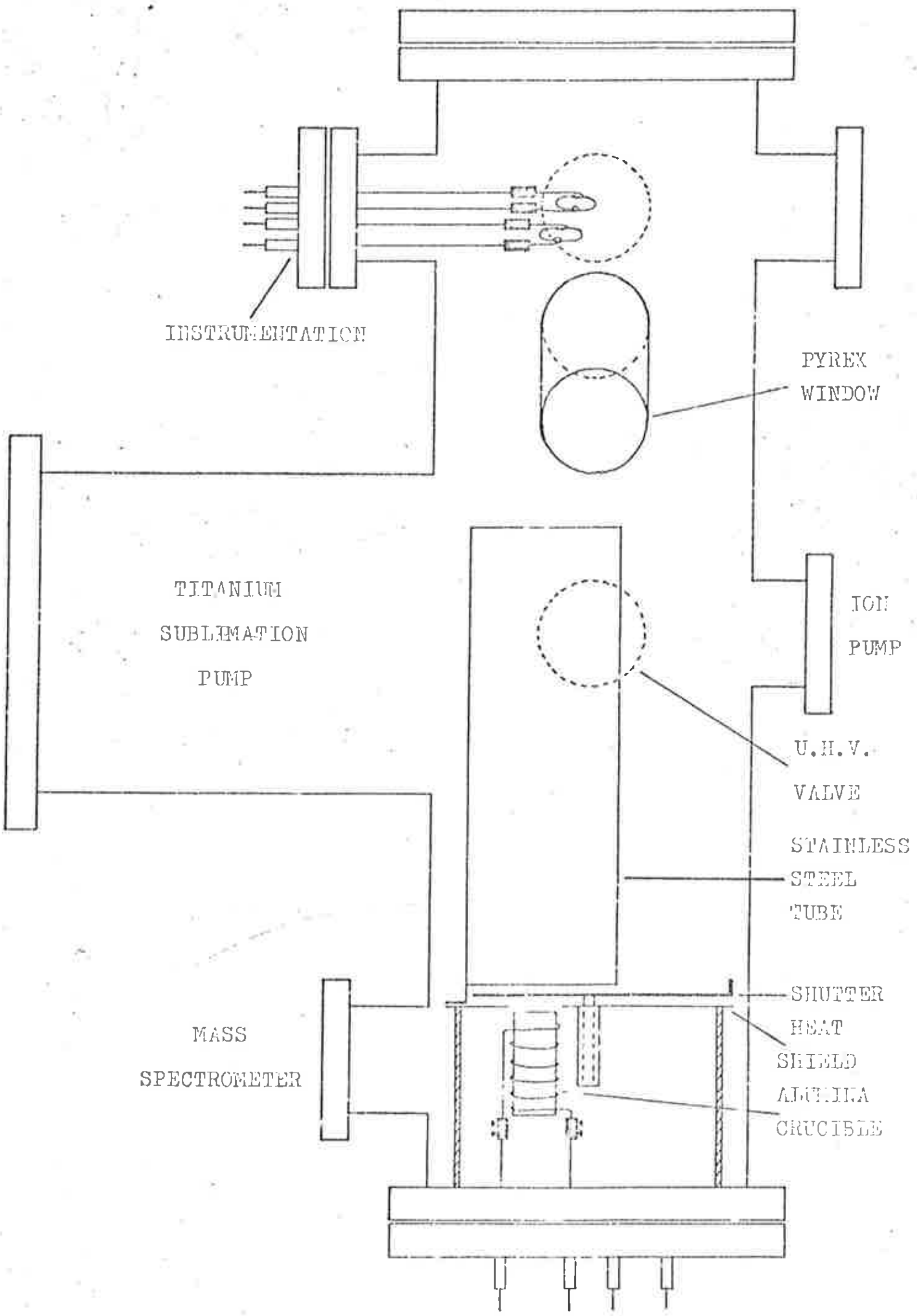
(d) A quartz or pyrex window situated so that the cadmium sulphide films can be illuminated in situ.

(e) Provision for mounting electrical feedthroughs in such a way that a variety of experiments can be performed.

These requirements were incorporated in the vacuum system used. The design, construction and initial performance evaluation of the vacuum system and associated equipment occupied the first two and a half years of the four years devoted to the study of gas adsorption on cadmium sulphide.

2.1.3. Ultrahigh Vacuum Chamber

The ultrahigh vacuum chamber is basically a stainless steel tee section with arms of 5" diameter (figure 2.3). Ports of 1½" diameter have been placed in the required positions. The horizontal arm of the tee contains an A.E.I. TS4 titanium sublimation pump with an unbaffled pumping speed of 1,000 litres/sec. This pump provides the high pumping speed required during evaporations. System pressure during experiments was maintained



THE U.H.V. CHAMBER

FIGURE 2.3

by an 11 litre/sec. ion pump mounted directly opposite the titanium sublimator. To prevent ions from the ion pump entering the main chamber a stainless steel screen was placed across the mouth of the ion pump. This reduced the number of ions present in the main chamber to an undetectable level; i.e. no change in the current flow between two isolated feed-throughs (isolation resistance 10^{11}ohms) with a 45 volt battery connected across them, could be detected when the ion pump was switched on.

The vertical section of the tee has 5" ports top and bottom. The evaporation equipment and associated feed-throughs were mounted on the bottom flange. The top flange was left blank with the intention of converting it for use in thermally stimulated conductivity measurements at a later date.

The three 1½" ports at the top were used for instrumentation and a secondary light source. A pyrex window on the port angled at 45° to the vertical section enabled illumination of the samples in situ. The A.E.I. minimass spectrometer was attached to the lowest 1½" port. A Granville Phillips ultrahigh vacuum valve served the dual purpose of being the roughing valve for the main chamber and the variable leak for admitting gases to the vacuum system at any desired pressure.

The whole of the ultrahigh vacuum system could be enclosed in an oven lowered by a pulley system enabling bakeout to 200°C with a roughing pressure of 10^{-6} torr. Figure (2.4) shows the bakeable section of the vacuum system and the monochromator. Bakeout time was typically 48 hours. The dotted line in figure 2.1 indicates the bakeable portion of the vacuum system.

2.1.4 Roughing System

The roughing system consists of a 2" oil diffusion pump filled with silicone 705 fluid backed by a single stage rotary pump. Molecular sieve traps isolate the rotary pump from the diffusion pump and the diffusion pump from the main chamber. The roughing system was used to evacuate the gas handling plant as well as the main chamber.

2.1.5 Gas Handling System

The gas handling plant is of stainless steel construction with gold wire seals. Teflon seals are used in the valves. A specially constructed double valve with a small known volume between the two seals was used to admit small amounts of gas. To admit gas at a constant pressure below 10^{-5}torr. the ion pump was left on and the ultrahigh vacuum valve was used as a variable leak. In this way any pressure below 10^{-5}torr. could be easily obtained. A liquid air trap was used to dry the gases.

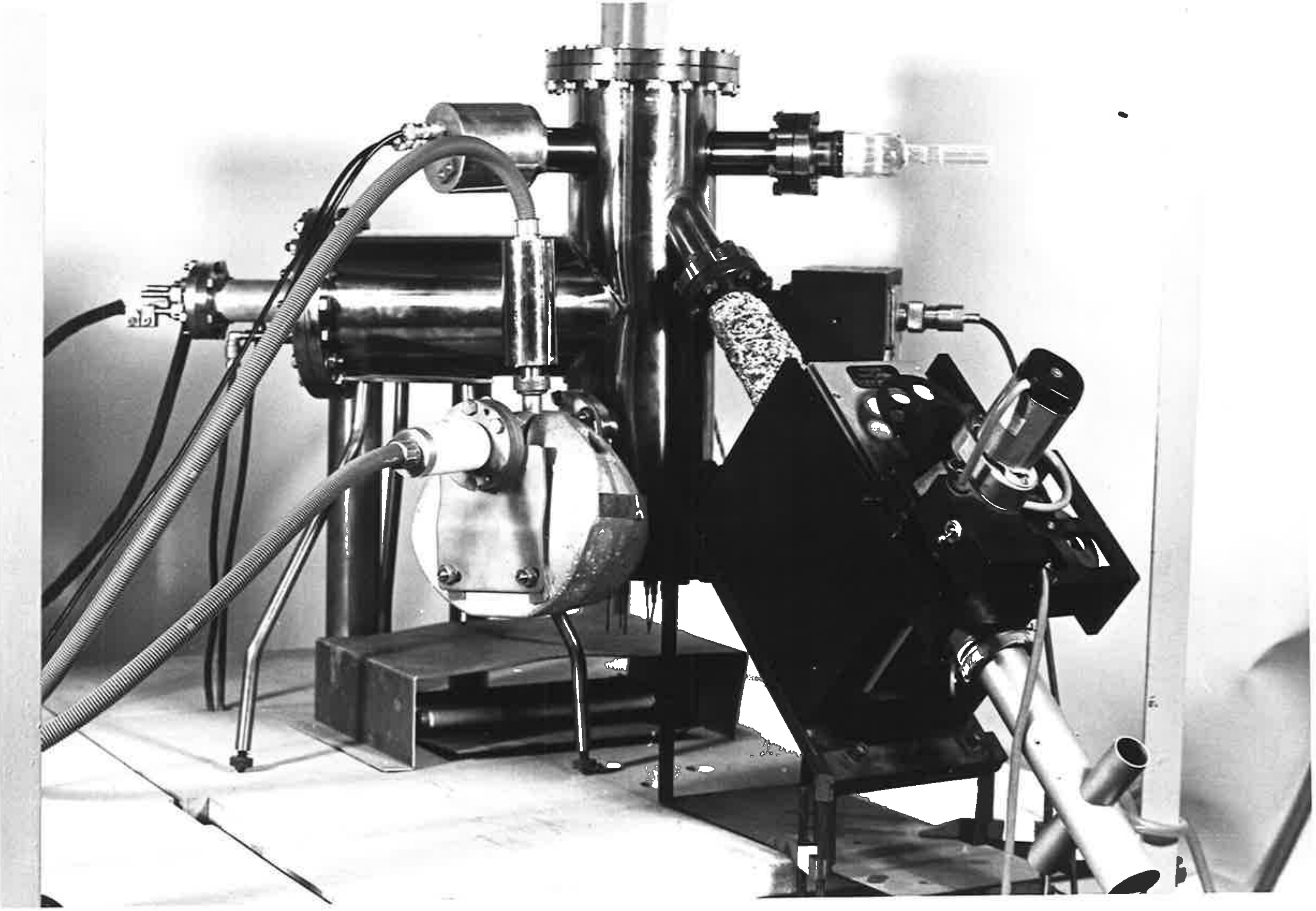


FIGURE 2.4

2.1.6 Cleaning

The ultrahigh vacuum system was ultrasonically cleaned in teepol, vapour degreased using trichlorethylene, then washed in distilled water and dried in a dust free cupboard before assembly. Cleaning by this method enabled pressures of 10^{-8}torr. to be reached without bakeout provided that there was no cadmium sulphide present in the system. The vapour degreasing bath, the ultrasonic bath and the dust free cupboard were designed and constructed by the author and another research student.

2.1.7 Illumination System and its Calibration

The source of illumination was a 12 volt, 55 watt, vertical filament quartz iodide globe mounted in a tube with two quartz lenses such that the emitted light is focussed on the entrance slit of the monochromator. This gives maximum efficiency for coupling light from the filament into the monochromator.

The monochromator used was a Bausch and Lomb high intensity monochromator with three interchangeable gratings spanning the wavelength range from 3,200 nanometres to 200 nanometres. The gratings and the filters used in association to remove the higher orders were as follows;

(1) 3,200 to 1,400 nanometres with a Jena UG6 filter.

(2) 1,600 to 700 nanometres with Kodak Wratten 87C and 25 filters.

(3) 700 to 200 nanometres with a Kodak Wratten 2C filter.

Two sets of slits, the A and C slits, with entrance widths of 5.36mm. and 1.34mm. and exit widths of 3.00mm. and 0.75mm. respectively were used. These two sets of slits are referred to as either the A slits or the C slits in the text.

The monochromator was attached to the vacuum system by using a stand, which clamped to the asbestos base plate, to hold it at 45^{0} to the horizontal with the exit slit close to the ultrahigh vacuum system window. Aluminium foil was used to make a light tight joint between the monochromator and the vacuum system. A shutter attached to the monochromator after the exit slit enabled the gratings to be changed without illuminating the cadmium sulphide film. The light emerging from the exit slit dispersed sufficiently in the distance between the exit slit and the quartz crystals for even illumination of both cadmium sulphide films to occur. Two quartz crystals, mounted in the holder shown in figure 2.6, have been used, one for frequency measurements and the other for conductivity measurements.

The monochromator could be used either manually, with the wavelengths being selected point by point, or automatically by scanning through the wavelength range of the grating using a motor drive unit coupled to the shaft of the grating housing. Different gearing ratios enabled the wavelength scanning time to be altered.

Knowledge of the number of photons incident on the cadmium sulphide films at each wavelength was required to determine whether the incident flux was sufficiently intense to cause significant heating of the quartz crystals and hence cause changes in frequency. This is discussed in section 2.2.4.

The intensity of the complete illumination system (comprising light source, monochromator, filters and pyrex window) was measured over the wavelength range 3,200 to 400 nanometres using a thermopile of known sensitivity as the detector. The variation in illumination intensity with wavelength with the A slits on the monochromator is shown in figure 2.5. The experimental arrangement used for the calibration was identical with that used in actual experimentation except that the thermopile replaced the quartz crystals. The output voltage was amplified by a D.C. microvoltmeter and then displayed on a chart recorder during the scan of each wavelength range. When the C slits were used the intensity was reduced by a factor of 16.

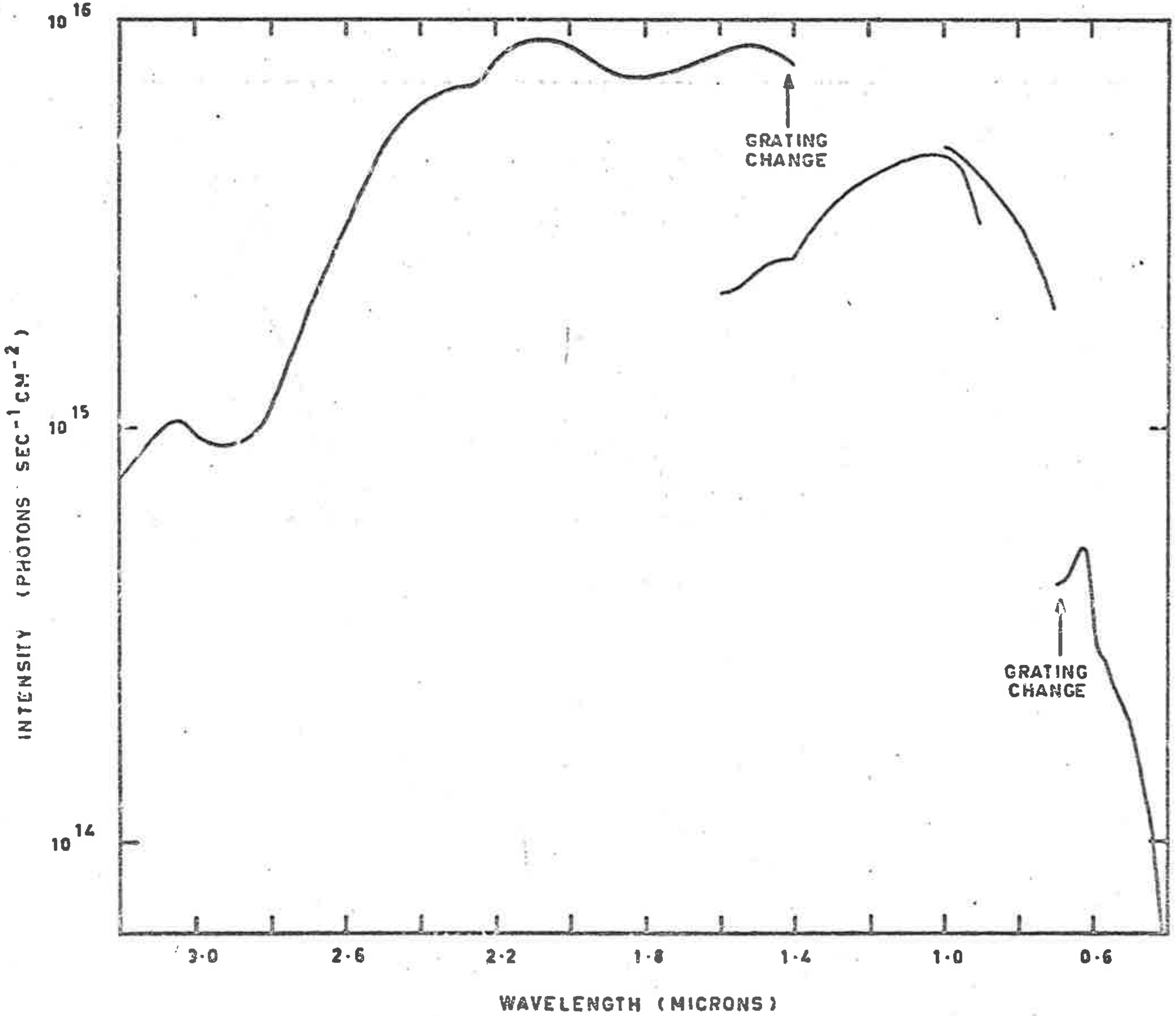


FIG. 2·5 INTENSITY SPECTRUM OF PRIMARY ILLUMINATION.

2.1.8 Apparatus Limitations

The configuration used for the ultrahigh vacuum chamber presented problems when photodesorption measurements were performed. These arose because both the titanium sublimator and the ion pump caused secondary illumination of the sample. Optical baffles could have been used to eliminate this but, without extensive modifications to the chamber, they would have caused a considerable reduction in the pumping speed of the system which was even more undesirable.

From the conductivity curves of several cadmium sulphide films it was found that the ion pump did not cause a detectable change in conductivity when switched on at pressures below 10^{-5} torr. The titanium sublimator heating coils illuminated the chamber at all pressures. Hence when dark conditions were required only the ion pump was used and then only at pressures below 10^{-5}torr.

2.2 Quartz Crystal Oscillator

2.2.1 Introduction

While it has been long known that the loading of the surface of a quartz crystal causes a change in frequency, the use of quartz crystals as mass measuring devices has only been recent. In the following experimental work the quartz crystal served a dual role;

(1) It allowed the film thickness and evaporation rate to be monitored continuously during the actual evaporation of the film.

(2) It enabled the measurement of the amount of gas adsorbed or desorbed from the surface of the film whilst varying the environmental conditions.

Because the oscillator consituted an important part of the measuring system its mode of operation and the possible sources of error will be considered in detail at this stage.

2.2.2 The Oscillator

The experimental arrangement of the oscillator circuit and the monitor crystal on an 8 pin feed-throgh is shown in figure 2.6. The quartz crystal was held in place by the tungsten springs which allow electrical contact with the gold electrodes. With bakeout temperatures not exceeding 200°C the problem of migration of gold electrodes and the subsequent loss of electrical contact was avoided (Macdonald 1966).

The frequency measurements were made using a Hewlett Packard 524C counter. The 10 second count position enabled the frequency to be measured to one tenth of a hertz. The short term stability of the counter is ±3 parts in 10^8 which is sufficient to meet experimental requirements.

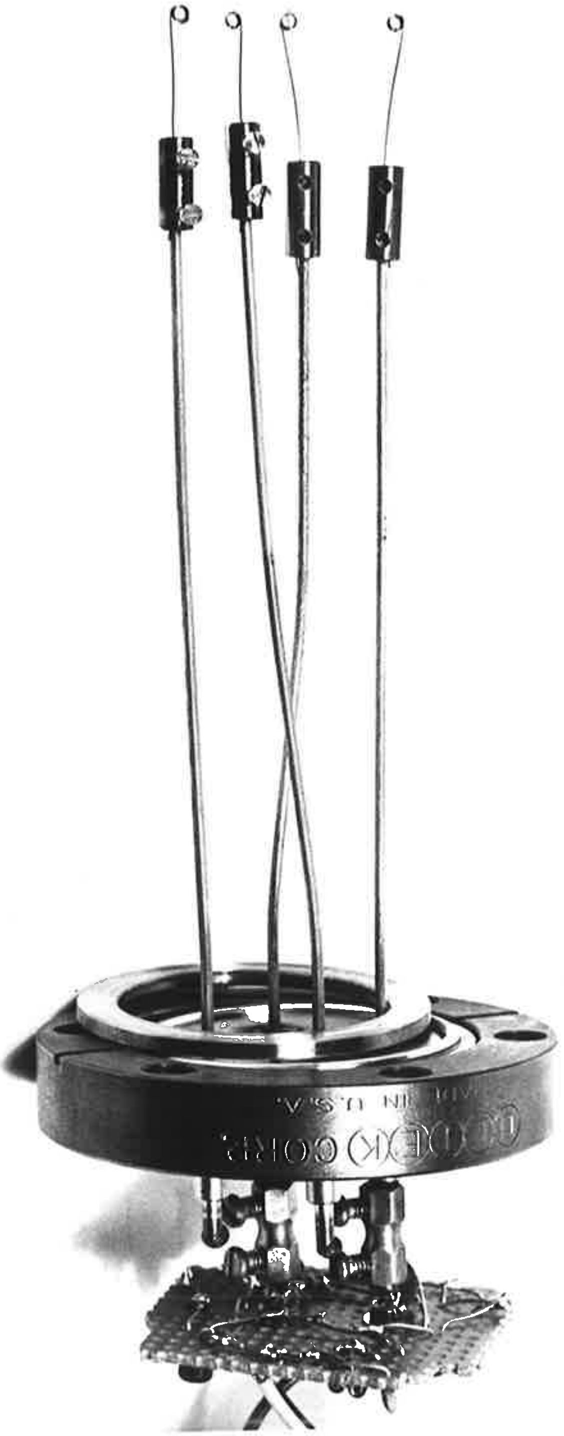


FIGURE 2.6

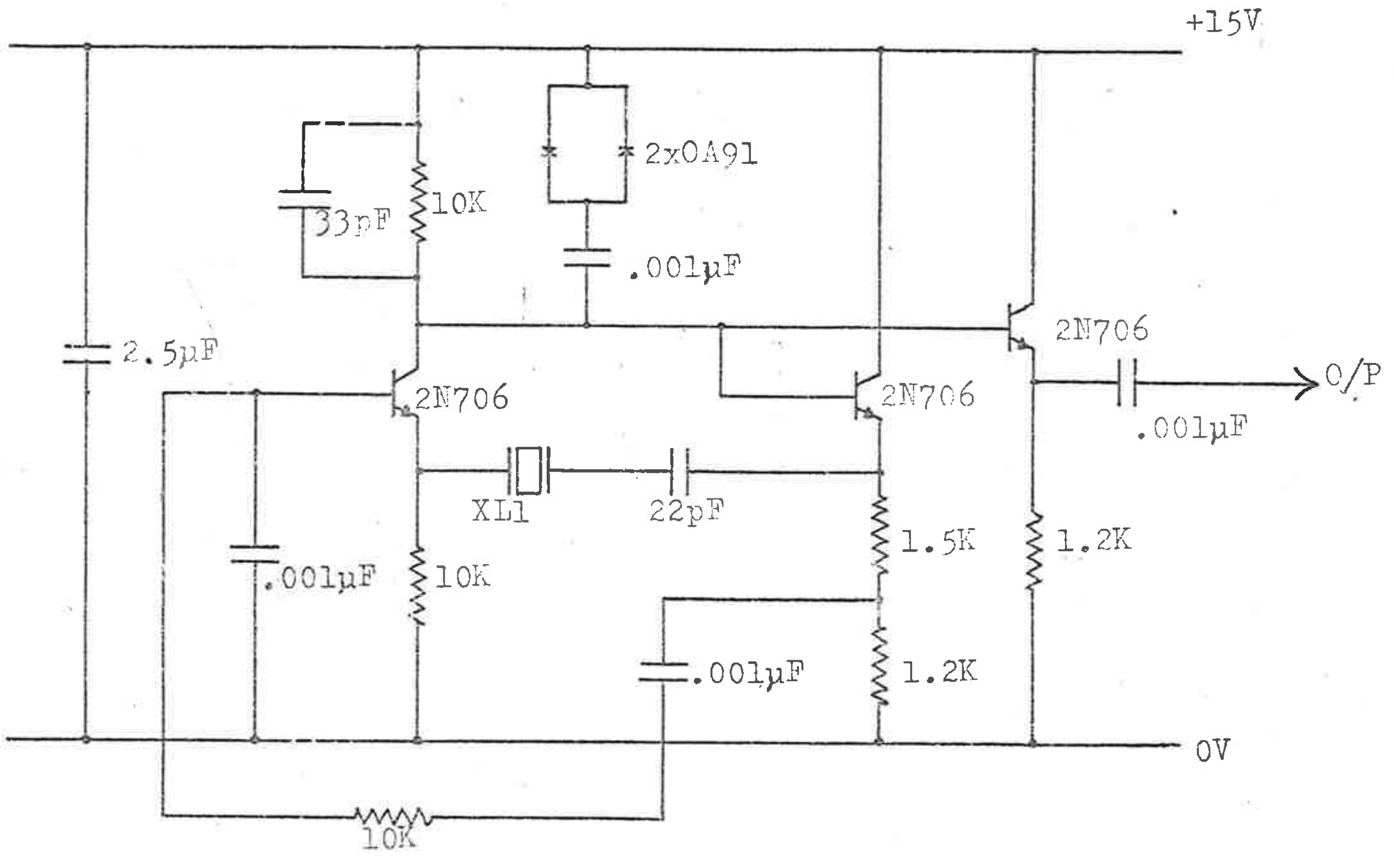
The oscillator circuit used is shown in figure 2.7. The circuit was wired on printed circuit board with two 10 B.A metal threads providing electrical connection to the feed-throughs and hence the quartz crystal, via brass connectors. This enabled the printed circuit board to be attached rigidly to the vacuum system eliminating the possibility of capacitance changes between the leads which would cause fluctuating frequency readings. Figure 2.6. does not show the printed circuit board oscillator used. Earthing the oscillator circuit to the ultrahigh vacuum chamber and enclosing the whole of the circuit in an aluminium container, prevented stray "pick up" and improved the stability of the circuit.

2.2.3 Choice of Crystal Frequency

AT cut quartz crystals were used as their properties have been investigated under ultrahigh vacuum conditions by Stockbridge and Warner (1962) and Stockbridge (1966) and shown to be suitable for mass measurement experiments. Also AT cut crystals with a minimum temperature coefficient at room temperature are readily available commercially.

The choice of crystal frequency used is determined by three factors;

(1) The mass sensitivity required, which is given by



QUARTZ CRYSTAL OSCILLATOR CIRCUIT

FIGURE 2.7

$$\frac{\Delta F}{F} = \frac{\Delta M}{M}$$

where ΔF is the change in frequency, F is the crystal frequency, M is the mass of quartz underlying the film, and ΔM is the change in mass.

Table 2.1 gives the minimum number of molecules of various gases on the surface of a cadmium sulphide film detectable by a 5 megahertz and a 10.7 megahertz quartz crystal. There are 10^{15} lattice sites per sq. cm. on the surface of a cadmium sulphide crystal (Many et. al. 1969), hence we can also compute the frequency change expected for a monolayer of adsorbed gas. These are also given in table 2.1. For a film surface the frequency change per monolayer will be higher as we must take into account the roughness factor of the surface.

(2) The ease of handling.

The frequency of a quartz crystal is inversely proportional to its thickness. A 10.7 megahertz crystal is 0.16 mm. thick whereas a 5 megahertz crystal is 0.32 mm. thick making the handling of the latter considerably easier.

(3) The Q factor.

The higher the frequency the lower the Q factor of the resonator. Stockbridge and Warner (1962) have shown that a 5 megahertz crystal gives the best compromise. In the following experiments both 5 and 10.7 megahertz crystals were used, the 10.7 megahertz crystals only when

CRYSTAL FREQUENCY	10.7mhz	5.0mhz.
THICKNESS	0.166mm.	0.32mm.
MASS SENSITIVITY	4.3×10^{-10} gm/cm^2.	1.7×10^{-9} gm/cm^2.

GAS	MIN. NO. OF ATOMS DETECTABLE BY EACH QUARTZ CRYSTAL	
	5.0mhz.	10.7mhz.
O_2	3.2×10^{13}	8.1×10^{12}
N_2	3.7×10^{13}	9.2×10^{12}

GAS	FREQUENCY CHANGE PER MONOLAYER (hertz)	
	5.0mhz.	10.7mhz.
O_2	3.1	12.5
N_2	2.7	10.8

CALIBRATION OF THE QUARTZ CRYSTAL

TABLE 2.1

extra sensitivity was required.

2.2.4 Sources of Error

The sources of error investigated by Stockbridge and Warner will be considered briefly and the precautions taken discussed. The crystal frequency stability is sensitive to;-

(1) temperature fluctuations

For an AT cut crystal the temperature coefficient of frequency is less than one part in 10^8 over an interval of $\pm 5^\circ$C at room temperature, if the angle of the AT cut is close to the zero coefficient value at room temperature (Stockbridge and Warner 1962). All crystals used were checked for changes in frequency with temperature. The crystal blanks used showed a drift in frequency with time due to temperature changes. This for the average crystal was about 0.2 hertz per degree Centigrade and hence experiments of long time duration could not be performed. The cause of the temperature drift in frequency was due to the heating and cooling of the quartz crystal and oscillator circuit. As temperature changes during the actual experiments were less than 1°C errors from this source were negligible.

(2) vibrational amplitude and exciting voltage

The vibrational amplitude of the quartz crystal must be kept as small and as constant as possible. This is achieved by using an oscillator circuit with amplitude control. The stability of the oscillator power supply was checked for short and long term drifts with a digital voltmeter.

(3) hydrostatic pressure effects

Changes in frequency due to hydrostatic pressure only occur at pressures above 10^{-1}torr. Crystals used in this range were checked for the pressure at which detectable changes in frequency occurred before use.

(4) temperature shocks

While frequency changes for a slow variation in temperature are negligible, sudden changes in temperature can cause the crystal frequency to fluctuate appreciably and hence must be avoided. The possibility of temperature shocks occurring when the crystal is illuminated was investigated. Light from the monochromator yielded a negative result but white light caused large fluctuations in frequency. Hence the need to use a neutral density filter to reduce the intensity of the white light source to an acceptable value. Sudden changes in pressure above 10^{-1}torr. also caused the frequency to vary as though the crystal had been temperature shocked.

2.2.5 Stress Relaxation

After bakeout quartz crystals show a prolonged drift in frequency with time. This is believed to be due to stress relaxation occurring between the electrodes and the underlying quartz (Stockbridge and Warner 1962). Evaporations were performed one day after bakeout by which time changes in frequency due to this effect were small. The crystal frequency always increased slowly for two to three hours after an evaporation. This drift was attributed to stress relaxation between either the gold electrode and the evaporated film or the gold electrode and the quartz as heating of the quartz crystal occurred during the evaporation.

2.2.6 Possible Sources of Error due to the Cadmium Sulphide Film

Quartz crystal plates can be used as high Q factor feedback devices in oscillator circuits because alternating electric fields cause the quartz to vibrate in a natural mode. As cadmium sulphide in its crystalline form is piezoelectric, and in view of some of the results obtained it is necessary to consider what effects could possibly occur when a cadmium sulphide layer is deposited on a quartz crystal.

The quartz plates oscillate in a thickness shear mode with the surfaces of the crystal as the antinodes. The evaporated layer acts as a damping force on the oscillations and must not store potential energy. This is true if the evaporated film is less than 1% of a wavelength thick i.e., less than 2% of the crystal thickness.

Thus the maximum allowed thickness for a film deposited on a 10.7 megahertz crystal is 1.6×10^5 nanometers. All of the films studied were two orders of magnitude thinner than this.

The piezoelectric nature of the cadmium sulphide films is unlikely to affect the quartz crystal frequency as films evaporated at room temperature are poorly orientated (Johnson 1964, Shallcross 1967) and hence will have no nett piezoelectric properties. Johnson considers the cadmium sulphide films to consist of many randomly orientated crystallites whose size depends on the degree of orientation. Such films should not affect the modes of vibration of the crystal. Thus a cadmium sulphide layer should move with the surface layer of the quartz without affecting its actual vibration.

The two most likely sources of error are;

(1) changes in the dielectric constant on illumination resulting in changes in the capacitance between the electrodes of the quartz crystal,

(2) polarization of the cadmium sulphide film by uneven illumination which could cause changes in the magnitude of the exciting voltage

The first effect could be eliminated by the use of a mask to confine the evaporation to the central area of an electrode. However as the light source was, by necessity, situated at 45° to the evaporating source a mask would cause uneven illumination of the evaporated film (figure 2.8). The mask was situated approximately 2mm. in front of the quartz crystal and could not be removed without allowing the vacuum system to air. If the film was unevenly illuminated a polarization voltage would have been set up as the majority carriers (electrons) diffuse to the regions of lower illumination intensity faster than the minority carriers as their mobility is higher. This is the Dember effect.

For the preliminary experiments the mask was dispensed with, resulting in the frequency changes discussed in chapter 3. For the subsequent work a mask was used as uneven illumination was found to have no effect on the crystal frequency.

An extra turn on one of the tungsten springs which hold the quartz crystal in place, provided the point of attachment of the mask.

2.3 Evaporations

2.3.1 Introduction

A study of the literature on the evaporation and properties of cadmium sulphide films shows a wide variation in the properties of the films even though spectroscopically pure samples were used. Individual workers (Lawrance 1964, Hughes and Carter 1967, Wedland 1962) have found the

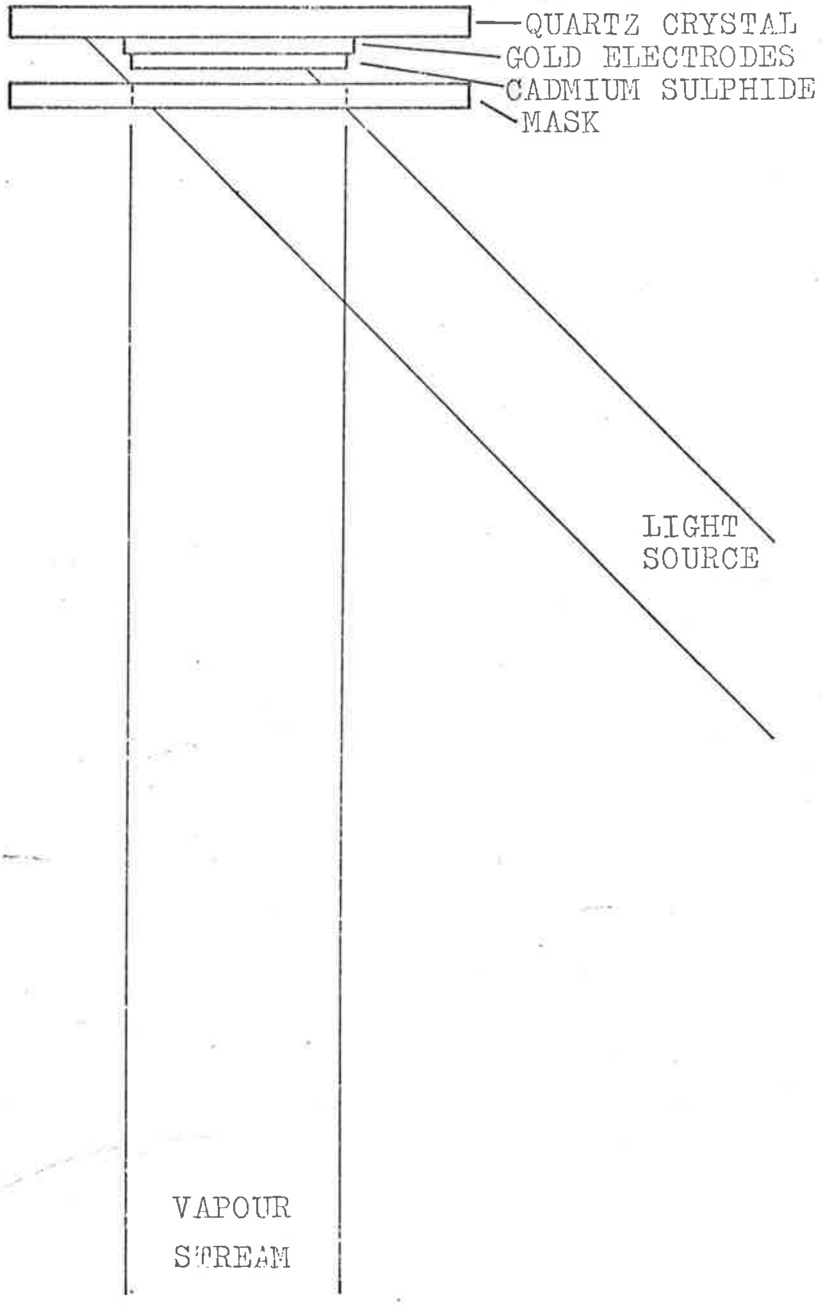

QUARTZ CRYSTAL
GOLD ELECTRODES
CADMIUM SULPHIDE
MASK
LIGHT SOURCE
VAPOUR STREAM

FIGURE 2.8

reproduction of film properties difficult even when using the same sample of cadmium sulphide and the same evaporation technique for each film. As these evaporations were performed at 10^{-5}torr. it is possible that the residual gases in the vacuum system caused the wide range in properties. Hughes and Carter found that they could obtain films with reasonably consistent properties by preparing them under ultrahigh vacuum conditions. Thus it would appear that the gases present in the vacuum system do constitute the main source of contamination.

Other sources of contamination have been listed by Lawrance, and Hughes and Carter, and will be considered where relevant.

2.3.2 Evaporation Source

The evaporating source is shown in figure 2.9 The alumina crucible was supported by the molybdenum heating coil which in turn was supported by the electrical feedthroughs. The heat shield was of stainless steel construction and supported the shutter which was operated externally by a magnet. The stainless steel tube above the source prevented excessive deposition of cadmium sulphide on the side walls of the chamber. The evaporator could be easily cleaned between evaporations whereas cleaning the main chamber involved a considerable amount of dismantling and reassembling. Removal of the cadmium

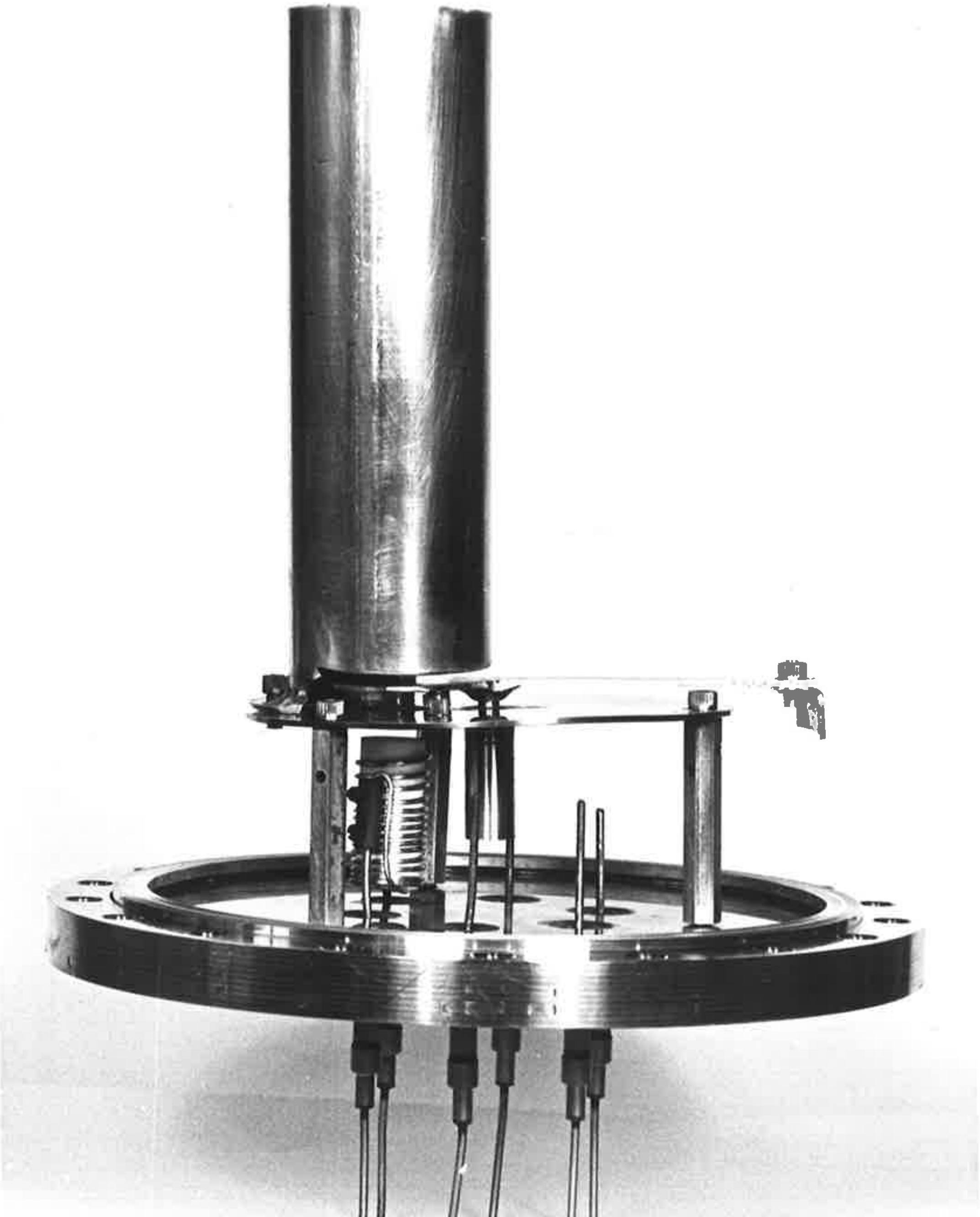


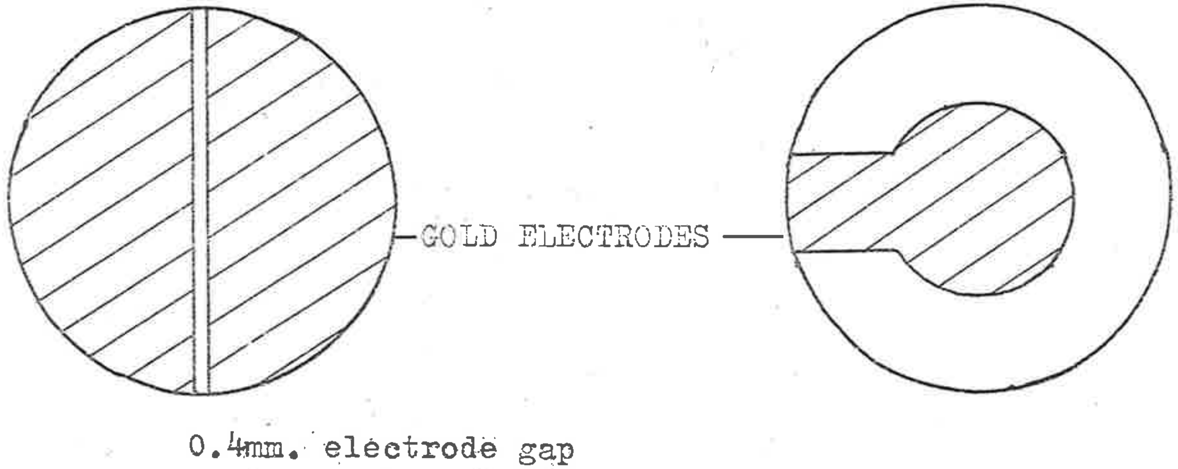
FIGURE 2.9

sulphide was necessary as deposits of it caused considerable outgassing thus lengthening the pump down time of the system. The evaporating source was ultrasonically cleaned, vapour degreased, washed in distilled water and then dried in a dust free cupboard before use.

2.3.3 Substrates

The two substrates, one for current measurement and the other for mass measurement, were both 5 or 10.7 megahertz quartz crystal blanks with the appropriate gold electrodes evaporated onto them. The electrodes were evaporated in a conventional vacuum system. Figure 2.10 shows both quartz crystals as prepared for an evaporation of cadmium sulphide. The crystal on the left was used for conductivity measurement and the one on the right for changes in mass.

The electrode gap for current measurement was achieved by placing a 0.4mm. diameter wire over the quartz blank. By evaporating the gold from a fairly diffuse source (a molybdenum basket) and keeping the film as thin as possible consistent with a continuous film it was hoped that the transition from gold electrode to quartz substrate could be made as smooth as possible. Thus when the cadmium sulphide film was evaporated over the gold the discontinuities in the film due to the electrode edge should have been minimized.



CURRENT MEASUREMENT CRYSTAL

MASS MEASUREMENT CRYSTAL

FIGURE 2.10

No evaluation of this junction as opposed to the "sharp edge" junction has been made. After each evaporation the voltage-current characteristics of the film were checked before the experiments discussed in chapters 3, 4 and 5 were performed.

Before the deposition of the electrodes the substrates were ultrasonically cleaned, vapour degreased in trichlorethylene, washed in running distilled water and then dried using lint free cloth. This process was repeated before the substrates were used in the ultrahigh vacuum system.

2.3.4 Evaporation Technique

During the actual evaporation several factors can affect the conductivity of the resultant film (Lawrance 1964, Hughes and Carter 1967):

(1) the gases present in the vacuum system

These were monitored using the mass spectrometer to ensure that the conditions for each evaporation were similar.

(2) the thickness of the film

Hughes and Carter found that the conductivity and photosensitivity of their films decreased with increasing film thickness. This they attributed to the temperature of the substrate increasing with time during the evaporation due to radiation heating by the evaporator.

(3) the evaporation rate.

The conductivity of cadmium sulphide films depends on the rate of deposition (Berger et. al. 1968). Lawrance (1964) reports that cadmium sulphide films must be deposited as quickly as possible as otherwise thermal dissociation of the cadmium sulphide with the subsequent deposition of only cadmium may occur. All of the films studied were deposited at approximately the same rate as determined from the rate of change of frequency with time.

(4) impurities present in the cadmium sulphide sample.

These were kept to a minimum by using spectroscopically pure powder and thoroughly cleaning the evaporator each time before use. The heating coil was kept at -80 volts with respect to the rest of the vacuum system to prevent the emission of ions from the heater which could contaminate the film. Lawrance found that a molybdenum heater and an alumina crucible emitted quantities of K^+ ions unless a potential was applied to the heater. This was also true of the evaporator used in the ultrahigh vacuum system.

(5) non uniform composition of the vapour.

It is known (Lawrance 1964, Shallcross 1966) that excess sulphur is present in the vapour at the beginning of an evaporation and that excess cadmium is present nearing the end of the evaporation. This problem is minimized by using a shutter to avoid deposition at the beginning and at the end of an evaporation. Even when this precaution is taken the composition of the vapour stream varies with time. Also the rates of re-evaporation of sulphur and cadmium from the substrate surface differ resulting in further departure from stoichiometry.

The films were evaporated at 10^{-6} torr. with the ion pump and the titanium sublimator operating after a 48 hour bakeout at 200°C. Outgassing of the cadmium sulphide powder was achieved by running the evaporator at a temperature just below the evaporating point until an increase in the temperature did not cause undue outgassing. A continuous chart recording of the gases present during the evaporation was made using the minimass mass spectrometer. The shutter was closed when a film of the desired thickness was obtained. The conductivity of the evaporated film, and the crystal frequency, took several hours to stabilize sufficiently for experiments. Hence the preliminary work involved in preparing each cadmium sulphide film occupied 3 to 4 days.

2.3.5 Crystallinity of the films

The degree of crystallinity and the orientation of cadmium sulphide films depends upon (Shallcross 1966)

(a) the substrate temperature,

The degree of orientation and crystallinity of a film increases with increasing substrate temperature. As the films were evaporated onto room temperature substrates we would expect them to be poorly orientated and show very little crystallinity. Hence they should not be piezoelectric.

(b) film thickness,

As cadmium sulphide grows preferentially in the direction of the C axis the degree of orientation increases with increasing film thickness. All of the films studied were very thin (less than 3000A^{o}). Hence again we would expect the degree of orientation to be small.

Although no electron microscope studies of the films were made, consideration of the above factors would indicate that the films obtained were poorly orientated and showed very little crystallinity.

2.3.6 Kinetics of Formation of the Films

The rate of deposition of the cadmium sulphide films can be monitored by recording the frequency at suitable time intervals. As no automatic recording system was available the time between successive frequency readings was adjusted to allow sufficient time for manual recording. For these measurements an Elron counter with a variable display time was used.

Typical results have been plotted in figure 2.11.

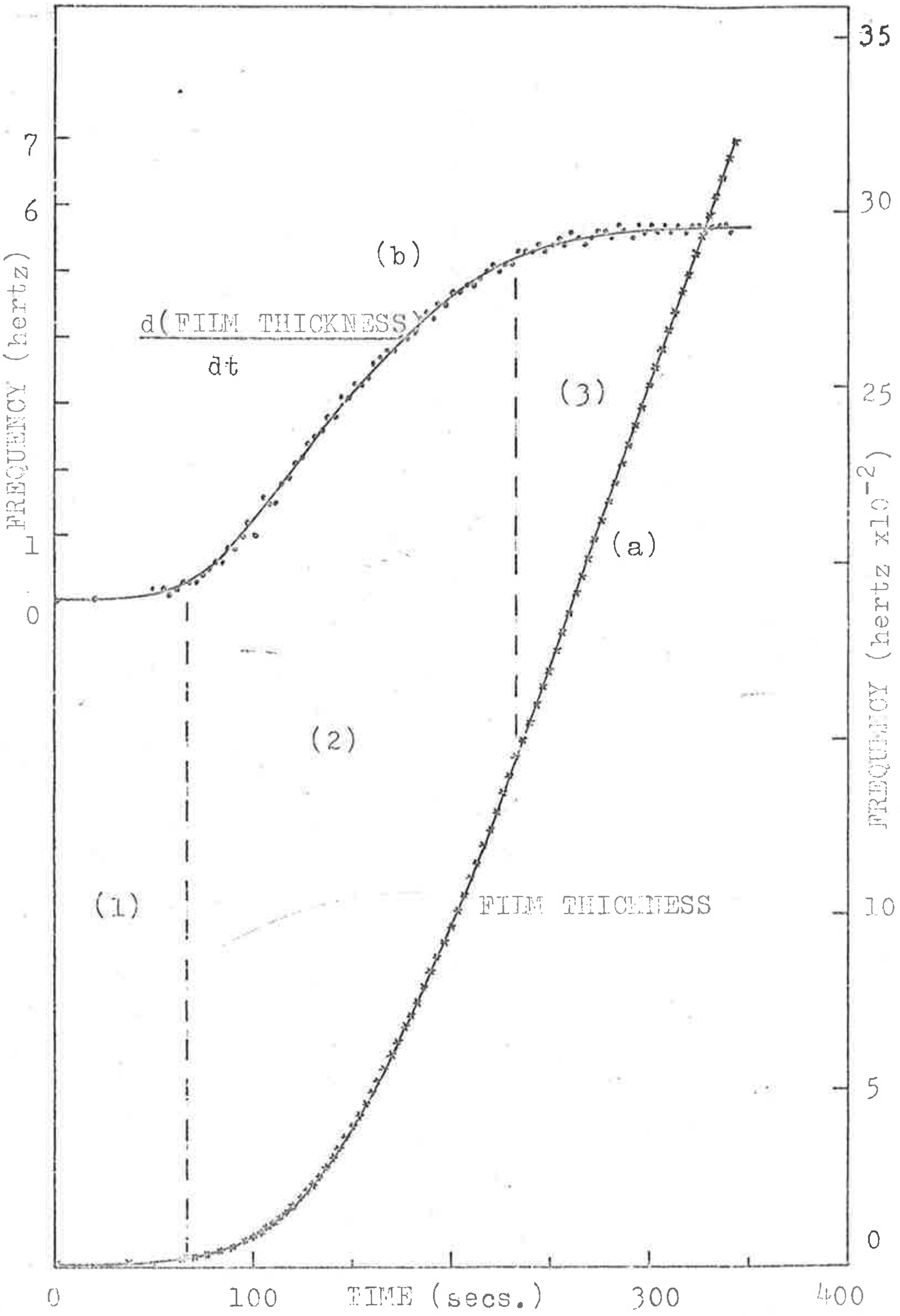

7
6
1
0
FREQUENCY (hertz)
35
30
25
10
5
0
FREQUENCY (hertz x10^{-2})
(b)
d(FILM THICKNESS)/dt
(3)
(a)
(2)
(1)
FILM THICKNESS
0
100
TIME (secs.)
300
400

FIGURE 2.11

Curve (a) is a plot of frequency against time and curve (b) shows the rate of change of frequency with time. Thus curve (a) yields the thickness of the film and curve (b) gives the rate of deposition of the cadmium sulphide. Both curves have three distinct regions indicated by (1), (2), and (3) on the graphs. These results agree with those reported by Johnson (1964) who deposited cadmium sulphide onto 10 megahertz quartz crystals.

The three regions are believed to correspond to the following processes;

Region 1

This is a period of no mass change even though cadmium sulphide vapour is incident on the surface of the quartz crystal. (The small changes in frequency observed during this period are due to radiation heating from the evaporating source.) During this time it is believed that nucleation sites are being formed on the surface of the crystal.

Region 2

This is a linear time dependence region (Johnson), i.e., from curve (b) we can see that the rate of change in the thickness of the film increases linearly with time . During this time the film grows laterally from the nucleation sites.

Region 3

The rate of deposition of cadmium sulphide is constant with time. It corresponds to the surface having a constant sticking coefficient, having been completely covered with cadmium sulphide.

The existence of region 1 indicates the necessity of giving both the monitor crystal and the conductivity measurement crystal the same pre-deposition treatment otherwise the thickness of both films may not be the same. Johnson (1964) has shown that the nucleation time depends on both the treatment of the surface and the substrate temperature. Errors in thickness may also arise because part of the conductivity measurement film is deposited on quartz in the electrode gap, and quartz may have a different nucleation time. To guard against this the resistance of the film was monitored during evaporations to ensure both films commenced deposition simultaneously. Films for which this did not occur were discarded.

The nature of the nucleation centres is not known. Johnson considers the possibility of them arising from (a) adsorbed gas molecules (b) impurities present in the cadmium sulphide vapour and (c) sites intrinsic to the surface of the substrate. He considers the third case is the most likely. This is supported by the results obtained in the ultrahigh vacuum system. On several occasions deposition occurred on both sets of gold electrodes but did not occur on the quartz between the gold electrodes of the conductivity measurement crystal. This could only have been caused by the absence of nucleation centres on the quartz as (a) is eliminated by bakeout and (b) obviously does not apply. The reason for the deposition not occurring on the quartz in some cases could not be determined.

From the above discussion it is clear that the use of two different substrates in the experiments is undesirable, but necessary, and that the measured film thickness may differ considerably from the conductivity film thickness if the above precautions are not taken.

The existence of region 3 enables an evaluation of the evaporator as a source of constant flux. A constant rate of deposition indicates that there is a constant flux incident on the surface of the quartz crystal. By using a quartz crystal already coated with cadmium sulphide (regions 1 and 2 no longer exist) the flux was found to be constant over a period of 5 minutes which is longer than the evaporation time of the films.

2.3.7 Voltage Current Characteristics of the films

To ensure that the photoconductivity measurements applied to the bulk of the cadmium sulphide film and not to just the gold-cadmium sulphide junctions the voltage-current characteristics of each film were determined to ensure that the electrodes were ohmic, or at least approximately ohmic at 1,100 volts/cm. the voltage used.

Smith (1955) found that gallium and indium made good ohmic contacts to cadmium sulphide crystals but as gallium melts just above room temperature and indium melts at 150°C neither of these two metals was suitable as it was necessary to bake the vacuum system at 200°C during the preliminary outgassing. Lawrance (1964) found that gold electrodes gave approximately ohmic contacts to cadmium sulphide films, and in consideration of the fact that it was suitable for use on the quartz crystal used for frequency measurements, gold was used as the electrode material.

The voltage-current characteristics of the films were determined by both dynamic and static methods. The dynamic measurements were made using a 0-100volts linear voltage sweeper and recording the corresponding changes in the conductivity with a Hewlett Packard 425A microvoltmeter and a chart recorder. Range changes on the microvoltmeter were avoided as they caused zero errors which could not be easily eliminated.

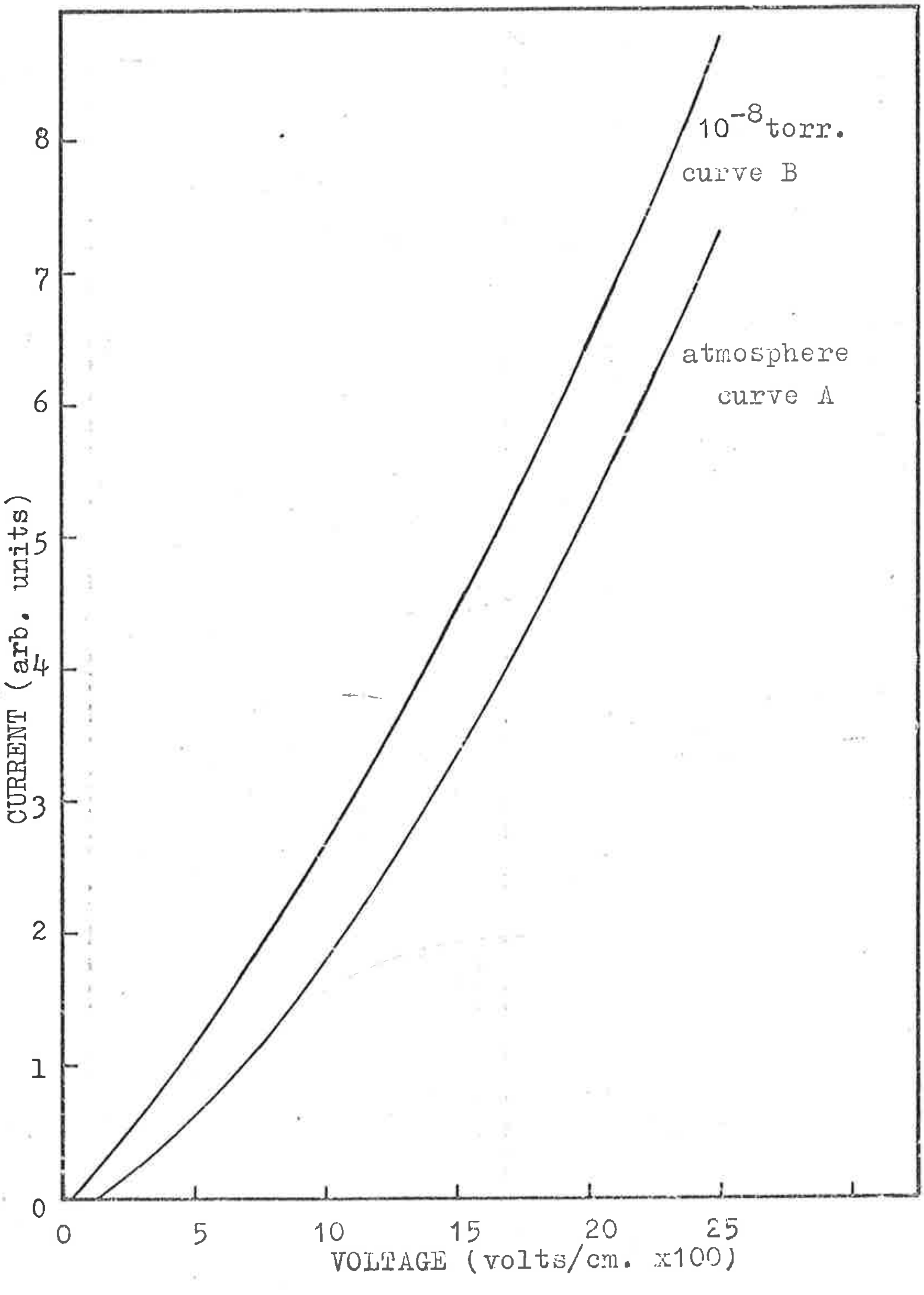
The static measurements were taken at one volt intervals with sufficient time for the current to reach its equilibrium value being allowed between each measurement. The current was measured by recording the voltage drop across a resistor in series with the cadmium sulphide film on a digital voltmeter. A second digital voltmeter was used to measure the voltage applied to the electrodes of the cadmium sulphide film.

The results obtained by both methods were similar and the typical voltage-current characteristics at air (curve A) and under ultrahigh vacuum (curve B) are shown in figure 2.12. The photoconductivity measurements were made in the region of 1,100 volts/cm. and hence in a region of approximately ohmic behaviour.

The voltage-current curves obtained under ultrahigh vacuum conditions did not show rectifying characteristics. The curves obtained at atmospheric pressure did show some rectifying characteristics the magnitude of which increased with decreasing film thickness. The results shown in figure 2.12 are for a very thin film, approximately 50 nanometres. The direction of the curent flow through the cadmium sulphide film did not affect the results.

Thus all the current measurements were made in the region of near ohmic conduction and thus bulk properties rather than near electrode region properties have been measured.

The dark current of the cadmium sulphide films studied was typically 1 mA. and the band gap photocurrent was 0.01 mA. with the C slits on the monochromator.



VOLTAGE-CURRENT CHARACTERISTICS

FIGURE 2.12

Chapter 3

SPURIOUS MASS CHANGES

3.1.1 Introduction

In this chapter the preliminary experimental results, which are concerned with spurious changes in mass, are presented in chronological order except where recourse to evidence obtained at a later date is necessary to support the arguments presented. In this way it is hoped that the reasons for performing the various experiments will become clearer.

Two samples of spectroscopically pure cadmium sulphide powder were used, the first one being that used by Lawrance (1964). A twofold purpose was served by starting with this sample:

(1) It enabled a check on the vacuum system and associated equipment to ascertain if everything was operating correctly, as the dark conductivity and photocurrent measurements should be similar to those obtained by Lawrance. Evaporation conditions similar to those used by Lawrance could be obtained by using the diffusion pump of the gas handling plant to evacuate the main chamber during the actual evaporation.

(2) Experiments performed by Lawrance could be repeated under ultrahigh vacuum conditions and the results compared in an attempt to elucidate the role of adsorbed gases in the various experiments.

The two samples of cadmium sulphide gave similar results; the results presented are typical of both samples.

3.1.2 Band gap photoconductivity:

Bandgap photoconductivity was chosen as the starting point of the investigations for two reasons:

(1) as cadmium sulphide is a semi-insulator it was considered unlikely that the adsorption or desorption of gases on the surface would occur under dark conditions due to the paucity of free electrons or holes near the surface (MARK 1965, BUBE 1966, FAETH 1967). By irradiating the sample with band gap illumination free electrons and holes were photo generated in the near surface region and thus an effect considered likely to give mass and hence frequency changes was being studied.

(2) Lawrance (1964) claimed to have obtained a new trapping spectrum near the bandgap edge by subtracting the photoconductivity curve obtained by a quasi continuous long wavelength to short wavelength scan of the band gap from the photoconductivity curve obtained by a quasi continuous short to long wavelength scan of the band gap.

His results were obtained by using a tungsten lamp, behind a tapered interference filter with a quoted bandwidth of 10 nanometres, to illuminate the cadmium sulphide films, and recording the photocurrent point by point from 700 to 400 nanometres. Lawrance's results agreed with those obtained previously for cadmium sulphide crystals by Reynolds et. al. (1955) in that the peak photoconductivity for the short to long wavelength photoconductivity curve was shifted to longer wavelengths when compared to the long to short wavelength photoconductivity maximum. Because of the trapping spectrum he obtained near the band gap edge Lawrance was able to propose electron trapping as the mechanism explaining the observed shift. As a Bausch and Lomb monochromator with a variable speed scan had become available it was hoped that a judicious choice of scan speed would enable quasi-equilibrium band gap curves, which revealed the trapping spectrum in more detail, to be obtained. The scan speed chosen must be slow enough to allow each trapping level to almost empty before the next level is reached but not too slow so that drifts in the recording instruments become significant. The results are discussed in section 3.3.1.

The first film was evaporated at 10^{-5}torr. using the diffusion pump to evacuate the chamber. The quartz crystal substrates were not masked as illumination problems were expected (section 2.2.6). The photocurrent was recorded continuously using a Hewlett Packard voltmeter-ampmeter and a Multelec Mk. 3 pen recorder. The frequency readings were recorded manually every 20 seconds.

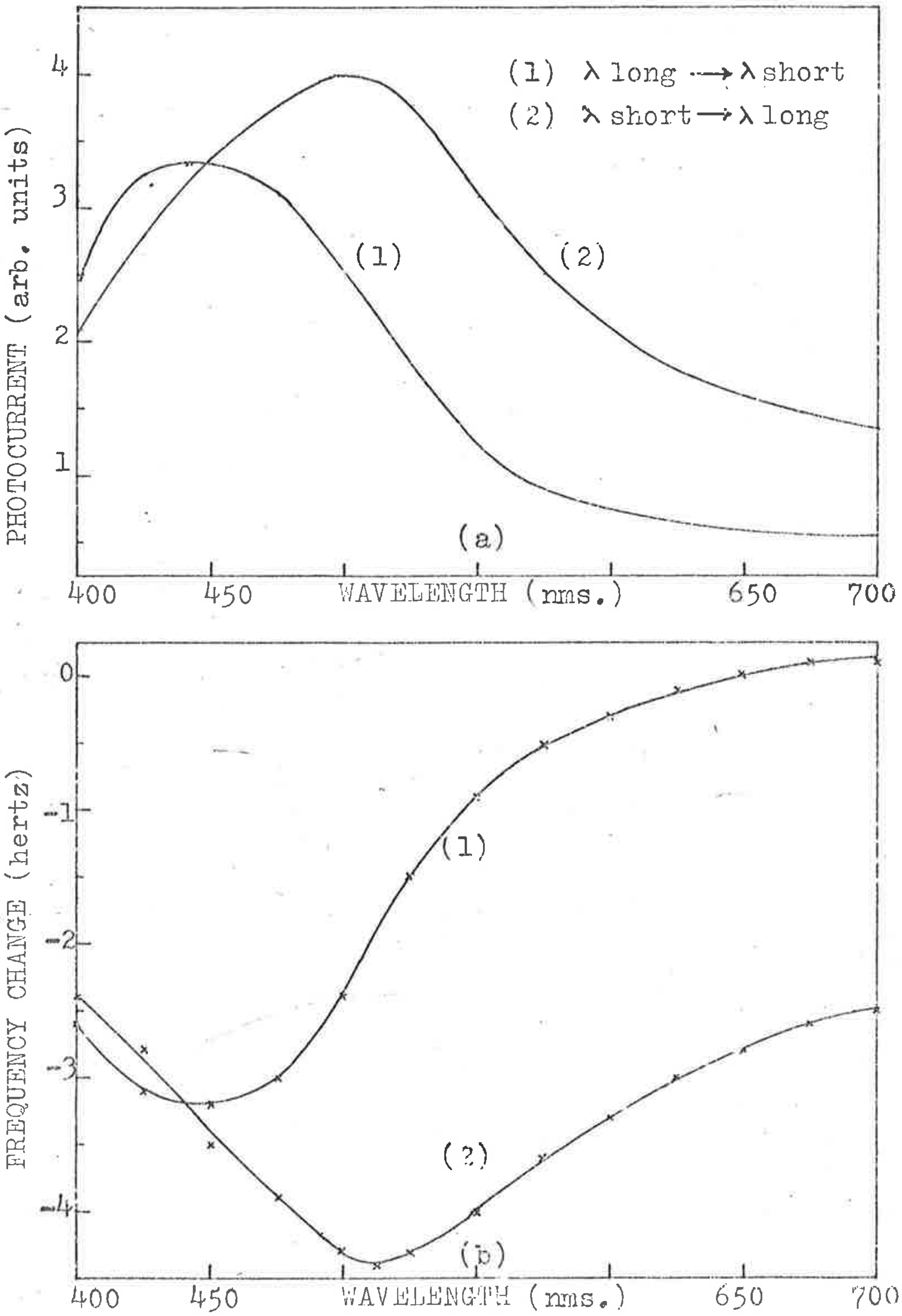
The results obtained are shown in Fig 3.1. The photocurrent curves, shown in Fig. 3.1(a), for the forward and reverse direction scans behaved as expected. The maxima of the two curves were displaced according to the scan direction and the band gap edge was near 2.5 eV as expected. Subtraction of the two curves failed to reveal any structure. This is discussed later in section 3.3.1.

The quartz crystal frequency curves (figure 3.1(b)) showed an apparent change in mass as the band gap was scanned. The frequency decreased, which is equivalent to an increase in the mass. On the basis of 10^{15} surface sites per sq. cm. for cadmium sulphide crystals (Many 1969) the frequency change corresponded to approximately a monolayer of gas. Due to surface roughness the frequency change corresponding to a monolayer of gas on a cadmium sulphide film would be expected to be greater than that for a cadmium sulphide crystal. However the results presented in section 4.1.3 suggest that there are 10^{15} surface sites per $cm.^2$ on the cadmium sulphide films.

A comparison of the two sets of curves showed that a close relationship existed between the photocurrent and frequency changes.

3.1.3 Sources of frequency changes

Because the preliminary experimental results



Wavelength Variation of Crystal Frequency and Photocurrent

FIGURE 3.1

showed an apparent increase in mass when band gap illumination was used, contrary to expectation when the theory of Mark (1965) was considered, it was suspected that the changes in frequency were being caused by an effect other than a mass change. It was therefore necessary to consider very carefully all possible sources of error as the quartz crystal oscillator results constitute the most important part of the thesis.

The equation of motion and the equivalent electrical circuit of the quartz crystal will now be considered to show all the possible sources of the observed frequency changes. The differential equation describing a damped harmonic motion in one dimension is:-

$$m \frac{d^2x}{dt^2} + r \frac{dx}{dt} + kx = 0 \text{ ---- } (1)$$

Where m is the mass, r is the damping constant and k is the shear stiffness constant.

Solving for the angular velocity w gives:-

$$w = \sqrt{\frac{k}{m} - \frac{r^2}{4m^2}} \text{ --- } (2)$$

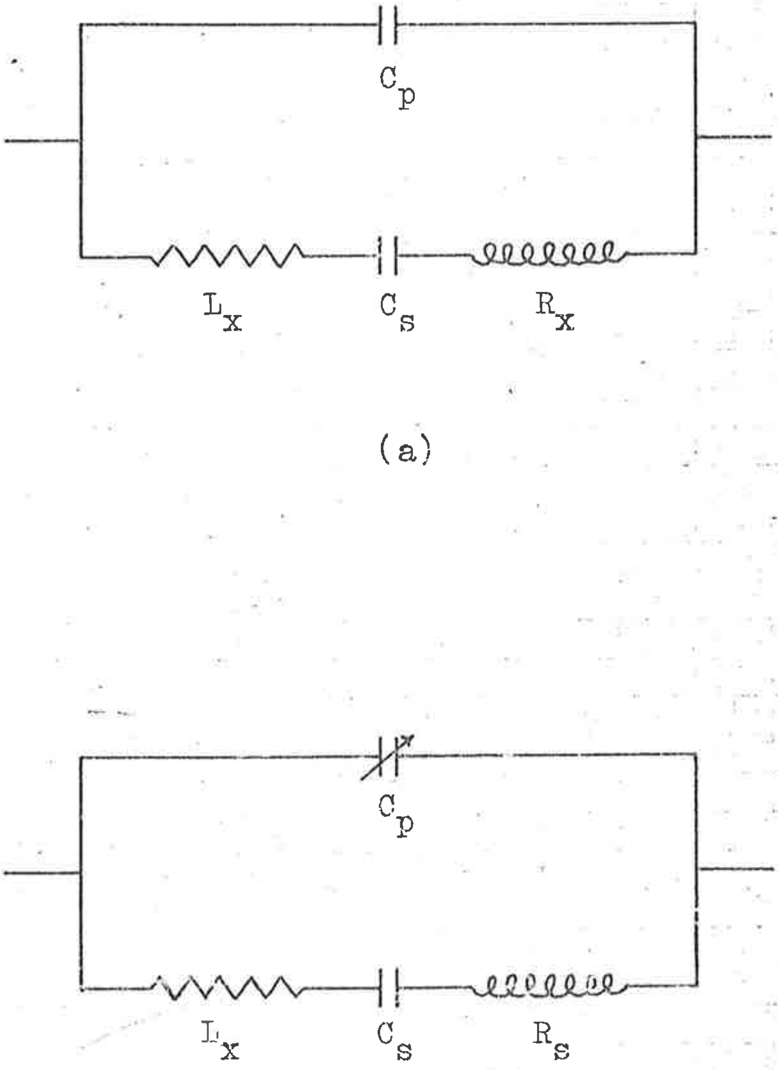
Hence changes in m, k and r can affect the frequency.

Changes in the mass, m, due to photo - adsorption or desorption are expected but do not necessarily occur.

The damping constant, r, is determined by the bonding between the quartz and the gold electrodes and by the internal damping which occurs due to the lattice planes sliding relative to each other. A slow relaxation of the bonding occurs with the magnitude of the effect decreasing with time. The process is known as "ageing" and results in a slow increase in the frequency of the quartz crystal. Illumination of the cadmium sulphide where it overlaps the gold electrodes could either reduce or increase the bonding between the cadmium sulphide and the quartz resulting in an increase or a decrease in the frequency respectively.

A decrease in the shear stiffness constant, k, will cause a decrease in the frequency. Ogawa et. al. (1971) have observed that bandgap illumination can cause a decrease in the piezoelectric constants of cadmium sulphide of up to 20% and Wilson (1966) up to 70%. Thus the possibility that the cadmium sulphide is mechanically coupling to the quartz and forming an active part of the resonator via its piezoelectric constants instead of just acting as a damping force and not storing potential energy as required, must be considered, although evidence has been presented in chapter 2.2.6 that the cadmium sulphide films studied should have no nett piezoelectric properties.

The ways in which the cadmium sulphide overlapping the electrodes can affect the frequency are seen more readily by considering the equivalent electrical circuit of the quartz crystal. The equivalent circuit is shown in figure 3.2(a) (Sauerbrey 1959).



(a)

(b)

Equivalent Circuit of the Quartz
Crystal Oscillator

FIGURE 3.2

for the series resonant circuit

$$W_s = \sqrt{\frac{1}{L_x C_s}} \qquad \text{--- (3)}$$

for the parallel resonance circuit

$$W_p = \sqrt{\frac{1}{L_x} \cdot \frac{C_s + C_p}{C_s C_p} - \frac{R_x^2}{L_x}} \qquad \text{--- (4)}$$

at resonance the damping is small

$$W_p = \sqrt{\frac{1}{L_x} \cdot \frac{C_s + C_p}{C_s C_p}}$$

$$\approx W_s \left(1 + \frac{C_s}{2C_p}\right) \qquad \text{--- (5)}$$

W_p is the measured resonant frequency.

The cadmium sulphide overlapping the electrodes can be considered to be acting as either a variable dielectric, because the illumination changes the dielectric constant of cadmium sulphide (Bube 1960), in the fringing field of the capacitor or as an extension of the area of one of the electrodes; i.e., the cadmium sulphide can be considered to increase the capacity between the electrodes by increasing the area of one of the plates by an amount dependent on the resistance of the cadmium sulphide. In either case C_p now becomes a variable capacitor (figure 3.2 (b)).

By substituting typical values in equation (5) the change in the capacitance necessary to cause a given change in the frequency can be calculated. The ratio

C_s/C_p is typically 0.001 (Sauerbrey 1959) and Wp is of the order of 10^6 hertz. Thus a 0.4% change in capacity will cause a 10 hertz change in the frequency. The maximum frequency change observed was 17 hertz with the average frequency change for a film being 3-4 hertz. Hence small changes in capacity can account for the observed results.

Thus there were two possible explanations of the observed frequency changes,

(a) it was a real mass change and could be accounted for by photo-adsorption of molecules from the residual gases.

(b) it was due to changes in the capacity between the electrodes of the oscillator crystal caused by either changes in the dielectric properties of the cadmium sulphide, or changes in the resistance of the cadmium sulphide which caused changes in the "effective" area of the electrodes. The possibility that both (a) and (b) are occurring simultaneously must also be considered.

If photo-adsorption of a specific gas species was occurring, the vacuum pressure (10^{-7}torr.) was sufficiently low for a measurable change in the partial pressure of the gas concerned to occur. At this stage no mass spectrometer was available necessitating other experiments to determine the cause of the frequency changes. When the mass spectrometer became available no changes in the composition of the residual gases present during a bandgap photoconductivity scan were detectable, thus providing a check on the conclusions reached in the following sections. The mass spectrometry results are discussed in chapter 4 where it is shown that the sensitivity of the mass spectrometer is sufficient to detect the changes in the ambient gases necessary to cause the observed changes in frequency.

3.1.4 The Nature of the Effect

To establish whether or not the frequency changes were due to capacitive effects a mask was used to confine the evaporated film to the centre of the gold electrode. Thus the capacitive effects can no longer occur.

The evaporation was performed with two quartz crystals, one masked and the other not masked as a check to ensure that the frequency changes occurred as in the previous evaporation. Bandgap illumination of the masked crystal did not cause a change in the frequency whereas illumination of the unmasked crystal did cause a change in the frequency.

To ensure that the failure to observe a frequency change was not due to the presence of the mask, the vacuum system was exposed to the atmosphere, the mask removed, and then the vacuum pressure returned to

10^{-7}torr. This check was necessary as there was only a 1mm. air space between the quartz crystal and the stainless steel mask which was electrically connected via the tungsten spring to the gold electrode directly beneath it and thus the mask may have been acting as part of the capacitor formed by the gold electrodes resulting in changes in the fringing fields. Again the unmasked crystal exhibited frequency changes under illumination while the crystal with the film confined to the central area of the electrode did not. Thus the frequency change was shown to be due to a change in capacity and not a change in mass.

It was decided to further investigate the nature of the effect and to evaluate the quartz crystal oscillator as a method of studying the observed changes in frequency which are shown (section 3.1.6) to be possibly due to photo-dielectric effects.

At this stage it will be assumed that we are observing a photo-dielectric effect rather than a resistive effect. The supporting experimental evidence follows later in this chapter in section 3.1.6.

It is possible that the results obtained could be explained in terms of changes in the barrier height at the junction between the cadmium sulphide film and the underlying gold electrode. However as the voltage-current characteristics indicated that the gold-cadmium sulphide junction was ohmic, and hence that a potential barrier may not exist at the junction, an explanation of the results in terms of changes in barrier height has not been presented.

3.1.5 Photodielectric Effects

Data obtained with cadmium sulphide powders, and in isolated cases with the crystalline form, show that when cadmium sulphide is used as a dielectric in a capacitor and is subjected to bandgap illumination its dielectric constant apparently increases by a factor of two or more.

There are three theories as to the nature of the apparent change in the dielectric constant;

(a) it is due to the photoconducting electrons produced by the band gap illumination.

Due to the heterogeneity of the cadmium sulphide film the photoconductivity effectively reduces the distance between the plates of the capacitor (this is for a capacitor composed of two plates with a cadmium sulphide film between them) and hence there is an apparent increase in the dielectric constant. (Bube 1960).

(b) it is a real change in the dielectric constant i.e., the illumination creates a large number of highly polarizable centres.

(c) the same as in (b) except that the cause is the formation of a space charge at the grain boundaries in the material.

As the photodielectric effect has been occasionally observed in crystals, which do not have grain boundaries, it is generally assumed that the third possibility does not apply (Bube 1960). This is not strictly true as crystals with grain boundaries have been observed in some cases. Also the observation of the effect in crystals may indicate that none of the above explanations are correct.

A study of the relationship between the frequency changes and the corresponding changes in photoconductivity for the films studied should make it possible to distinguish between effects (a) and (b) as for (b) a change in frequency does not necessarily correspond to a change in conductivity, e.g. if the illumination forms trapping centres with nett dipole moments (as is the case for the trapping centres proposed by Tscholl (1968) to account for the photo-induced slow phenomena in cadmium sulphide) then these centres will cause a change in the dielectric constant but will not necessarily contribute to the photoconductivity.

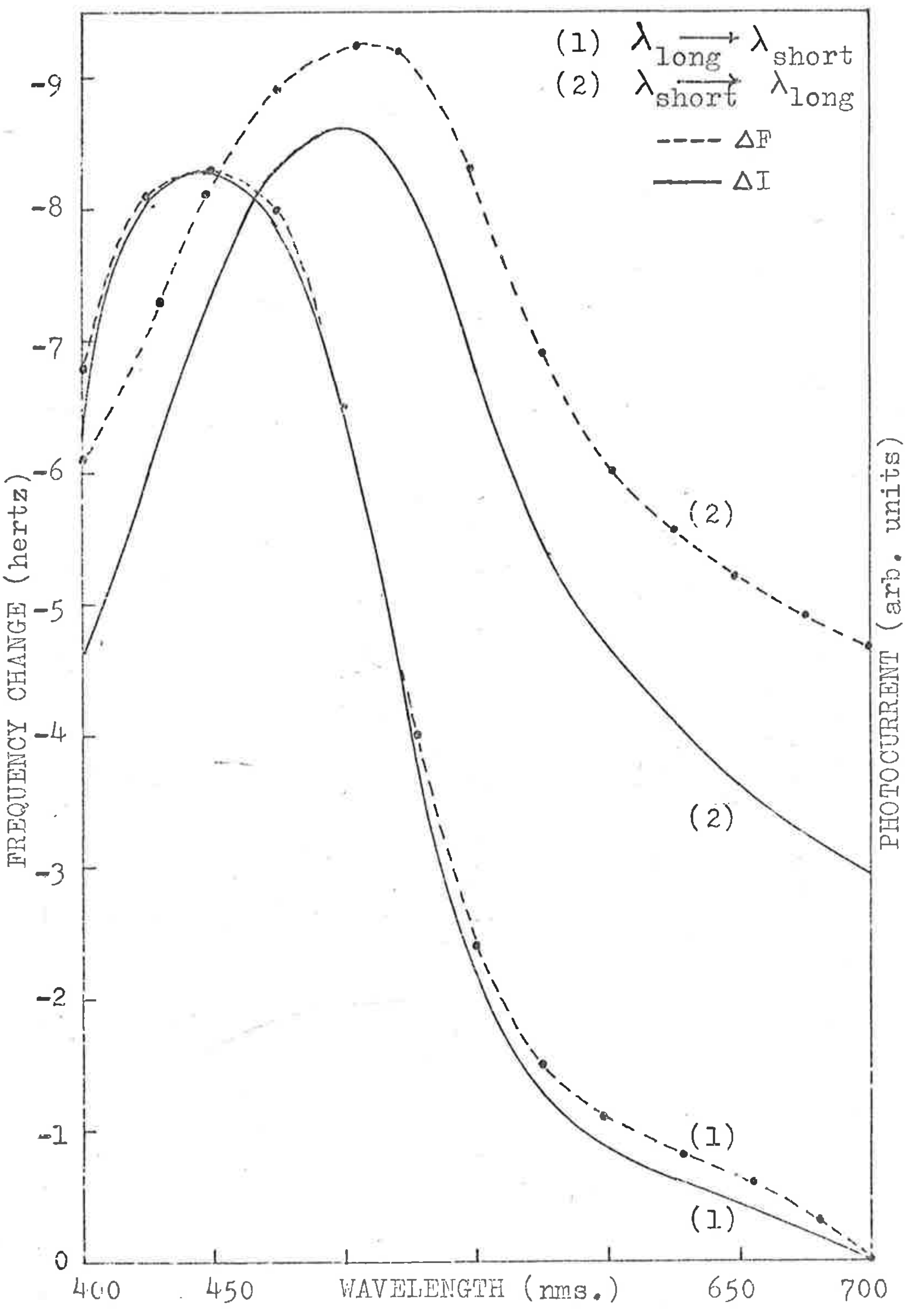
To determine the relationship between the kinetics of the frequency and photocurrent changes the following experiments were performed;

(a) The variation of the frequency and the photocurrent for a one hour scan of the band gap was measured. If the frequency change is directly dependent on the photocurrent (i.e., the free electron concentration) then it would be expected that the frequency curve and the photocurrent curve will superimpose when normalized. If however, one of the two curves shows a different wavelength dependence to the other then the change in frequency may not be due to just the photogenerated free electrons

(b) The variation of the frequency and the photocurrent with time when subjected to band gap illumination of a fixed wavelength starting from dark conditions at t = 0, and the subsequent variations when the illumination was switched off were measured. As in part (a) above the plotting of the normalized frequency and photocurrent curves will enable the relationship between the frequency change and the free electron concentration to be determined.

3.1.6 Band Gap Photoconductivity

The frequency and conductivity changes obtained for a one hour scan of the band gap using the A slits on the monochromator are shown in figure 3.3. The curves are plotted for a scan from long to short wavelengths starting from dark conductivity conditions.



Wavelength Variation of the Crystal
Frequency and Photocurrent (A slits 1hr. scan)

FIGURE 3.3

The scales for the current change and frequency change curves were chosen such that the maxima of both curves coincided in the case of the first scan. The reverse scan curves were plotted on the same scales. The curves have not been corrected for constant energy of illumination.

Several points of interest arise from the curves;

(a) The photoconductivity curves and the corresponding frequency change curves are almost identical in shape. Thus the processes causing both changes must be closely related.

(b) The short to long wavelength frequency curve is always displaced above the corresponding current change curve. The displacement is approximately 1.5 hertz at 700 nanometres and is too large to be accounted for by drifts in the crystal frequency. Thus the process causing the change in frequency is either decaying slower than the free electron concentration, or wavelengths longer than the bandgap wavelenth cause larger changes in the dielectric properties than in the free electron concentration, suggesting that dipoles are being formed. The second explanation is further supported by the fact that the frequency rises faster than conductivity at the commencement of a long to short wavelength scan when starting from dark conditions.

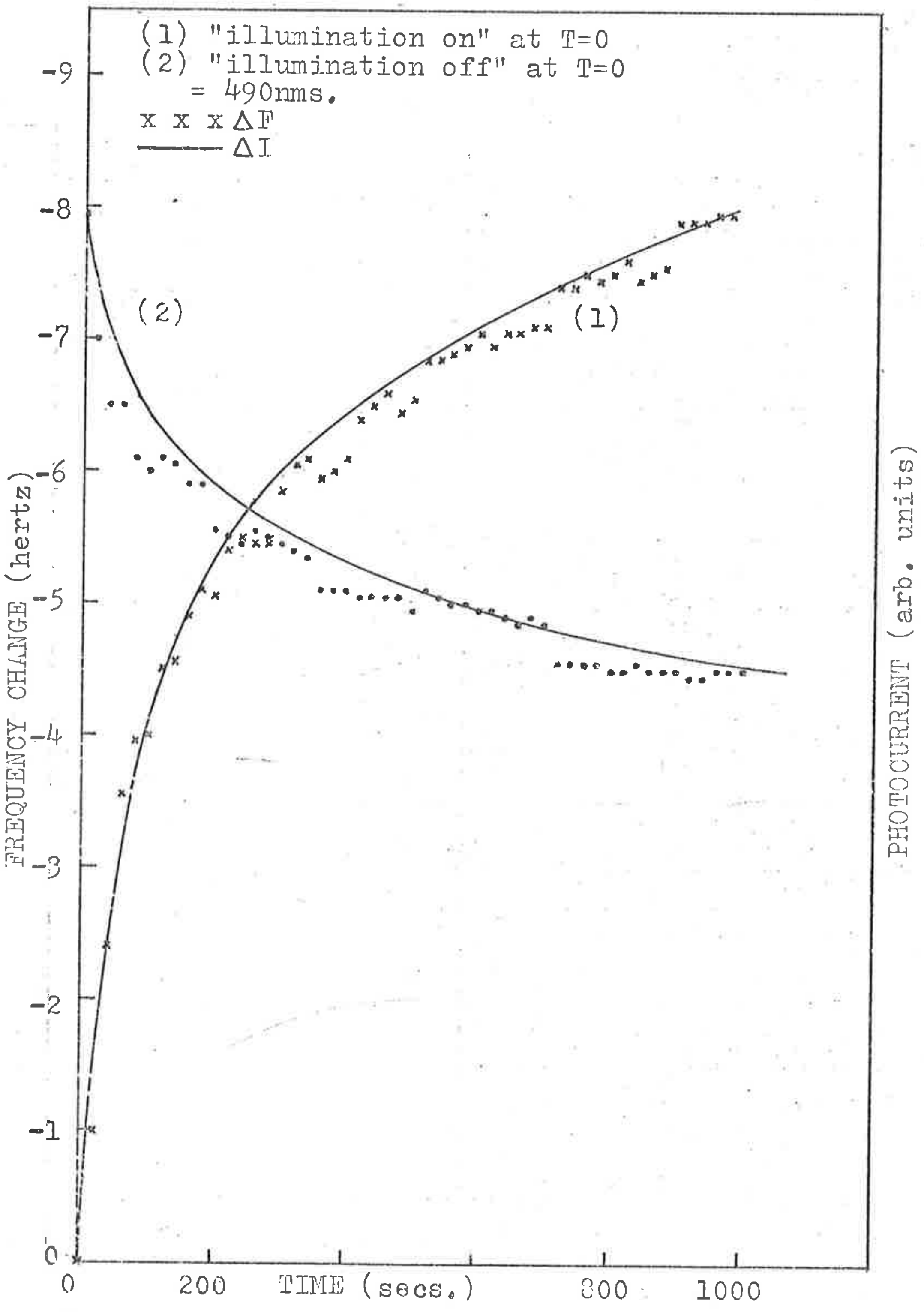
As the frequency and current curves do not superimpose (within the limits of experimental error) a dielectric effect involving the formation of dipoles rather than a purely resistive dielectric effect is being observed,

(c) Although not shown in figure 3.3 there was some evidence of structure on the frequency curves. This was investigated and is discussed in section 3.2.

Thus the band gap scan curves indicated that the large scale structure of both curves could have been due to conduction band electrons with the small differences between the curves possibly being accounted for by the formation of centres with dipole moments.

3.1.7 Photoconductivity versus time for constant band gap illumination

The normalized changes in frequency and conductivity with time when subjected to band gap illumination are shown in figure 3.4. The monochromator was used to provide the 490 nanometres illumination. For both "illumination on at t = 0" and "illumination off at t = 0" the frequency and current change curves are almost identical. The frequency change curves show some small scale structure which is too large to be accounted for by errors in measurement. Thus the structure must arise from processes occurring within the cadmium sulphide films.



Variation in Frequency and Photocurrent with time for Illumination at a Constant Wavelength

FIGURE 3.4

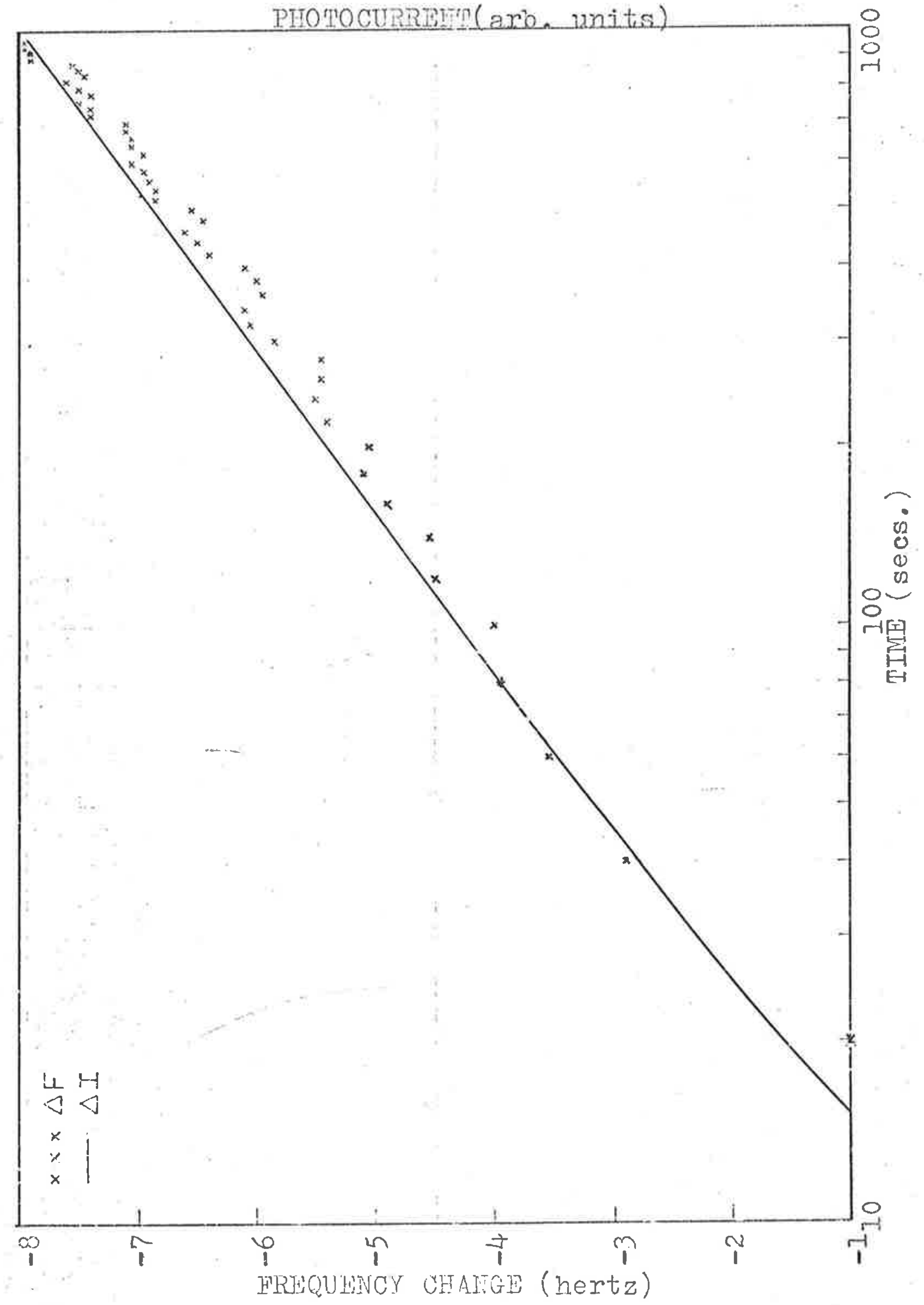
A plot of the current and frequency changes against the logarithm of time (figure 3.5) showed that both processes are approximately exponential. Hence the bandgap photoconductivity curves indicate that the one process may be responsible for both effects.

3.1.8 Band Gap Scan with the Cadmium Sulphide film Exposed to the atmosphere

The conductivity and frequency changes obtained for a band gap scan with the film exposed to the atmosphere, starting from equilibrium dark conductivity conditions are shown in figure 3.6. Again a close correlation between the normalized curves occurs. The ratio of maximum frequency change at air to maximum frequency change at 10^{-7}torr. was the same as the ratio of the conductivity change in each case. In the case of very thin films exposed to the atmosphere, when the dark conductivity decreased by two orders of magnitude there was no detectable change in frequency, indicating that the frequency change had also decreased by at least two orders of magnitude. Hence again it can be seen that the magnitude of the frequency change is closely correlated to the density of the free electrons.

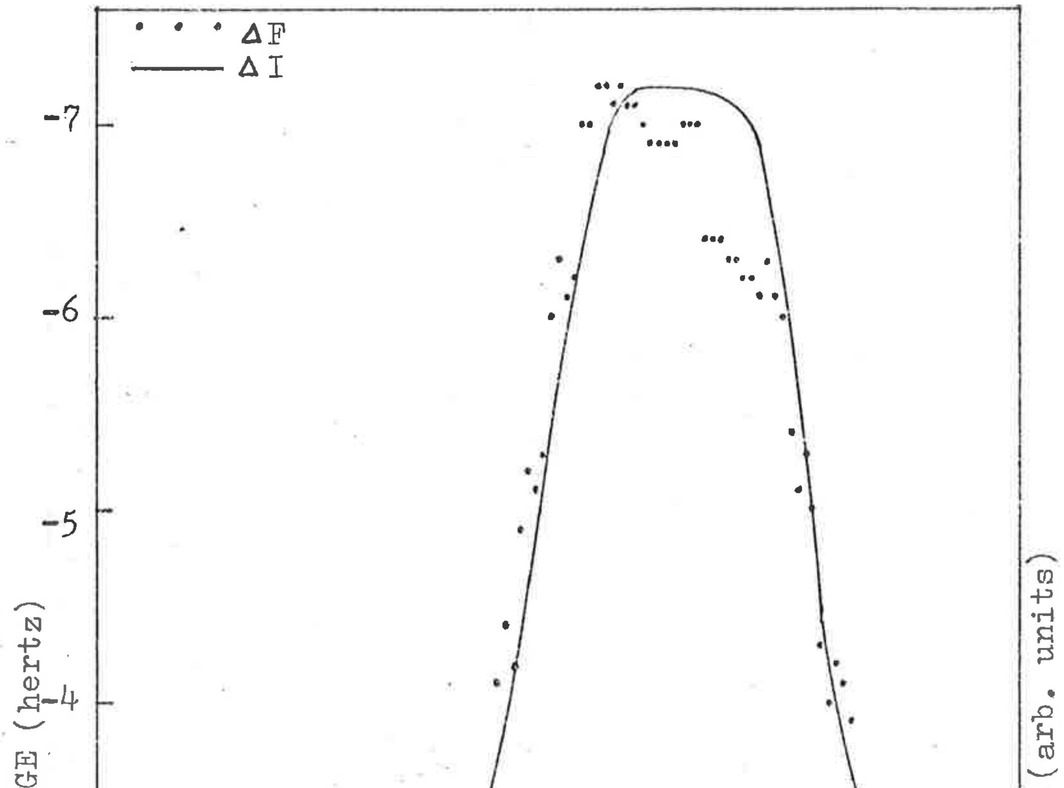
3.1.9 Infrared Photoconductivity

Photoconductivity in the infrared region, 3,200



Variation in Frequency and Photocurrent with the logarithm of time for illumination at a constant wavelength

FIGURE 3.5



Variation in Frequency and Photocurrent with wavelength (C slits on the monochromator)

FIGURE 3.6

to 800 nanometres, was studied under both ultrahigh vacuum conditions and with the cadmium sulphide exposed to air for two different situations;

(a) with the cadmium sulphide initially in dark conditions

(b) with the cadmium sulphide exposed to a weak source of secondary illumination.

By using extrinsic radiation which could only fill or empty trapping levels it was hoped that changes in the frequency without changes in the photocurrent could be produced. This would indicate that changes in the dielectric constant were occurring due to the formation of traps with dipole moments.

The results obtained under ultrahigh vacuum conditions showed no changes in the photoconductivity or the frequency. The results obtained with the cadmium sulphide exposed to the atmosphere differed only in that a small change in photoconductivity occurred at 0.83 ev. on the first infrared scan at atmospheric pressure. It did not appear on subsequent scans. This is discussed further in chapter 4. No change in frequency corresponding to this change in conductivity could be detected. Hence the reaction which occurs at 0.83 ev. apparently does not change the dielectric constant of the material.

3.1.10 Summary

The results presented indicate that a photodielectric effect is being observed with the main component probably due to conduction band electrons decreasing the effective distance between the electrodes as discussed in section (3.1.5). There is also some evidence that a change in the dielectric constant due to the formation of dipoles is occurring as well. This will be considered in the following section on the nature of the fine structure observed.

3.2 Nature of the Fine Structure in the frequency curves.

3.2.1 Introduction

It has been pointed out in the preceding sections of this chapter that the frequency change curves for band gap scans and for illumination at a fixed wavelength, show fine structure. Examples of this can be seen in figs. 3.4, and 3.6. In the following sections the nature of this fine structure is considered and a possible explanation is proposed and discussed.

3.2.2 Photoconductivity versus time at constant illumination

The results obtained are shown in fig. 3.4. As the fine structure was observed in both the frequency change curves for band gap scans (figure 3.6) and the frequency change curves for illumination at a constant wavelength, the correlation between the change in photocurrent and the order of each peak was checked. In figure 3.7 the photocurrent against peak number has been plotted for,

(1) "illumination on" curve A which is a good approximation to a straight line and,

(2) "illumination off" curve C which is also a good approximation to a straight line. The change in photocurrent against the order of the minima has also been plotted (curve B) for the case of "illumination off".

Thus the appearance of each peak in a frequency change curve corresponds to a change in the photocurrent by a constant amount. Comparing the slopes of A, B, and C, there is a close agreement between the spacing of the peaks for "illumination on" and the peaks and minima for "illumination off". Thus it would appear that there exists a series of energy levels which, when filled, result in the formation of a dipole. When emptied, the dipole is removed.

The process can be described qualitatively in terms of the band theory and surface states. In figure 3.8 the energy level diagrams of the band gap of cadmium sulphide for various conditions are shown. For a clean

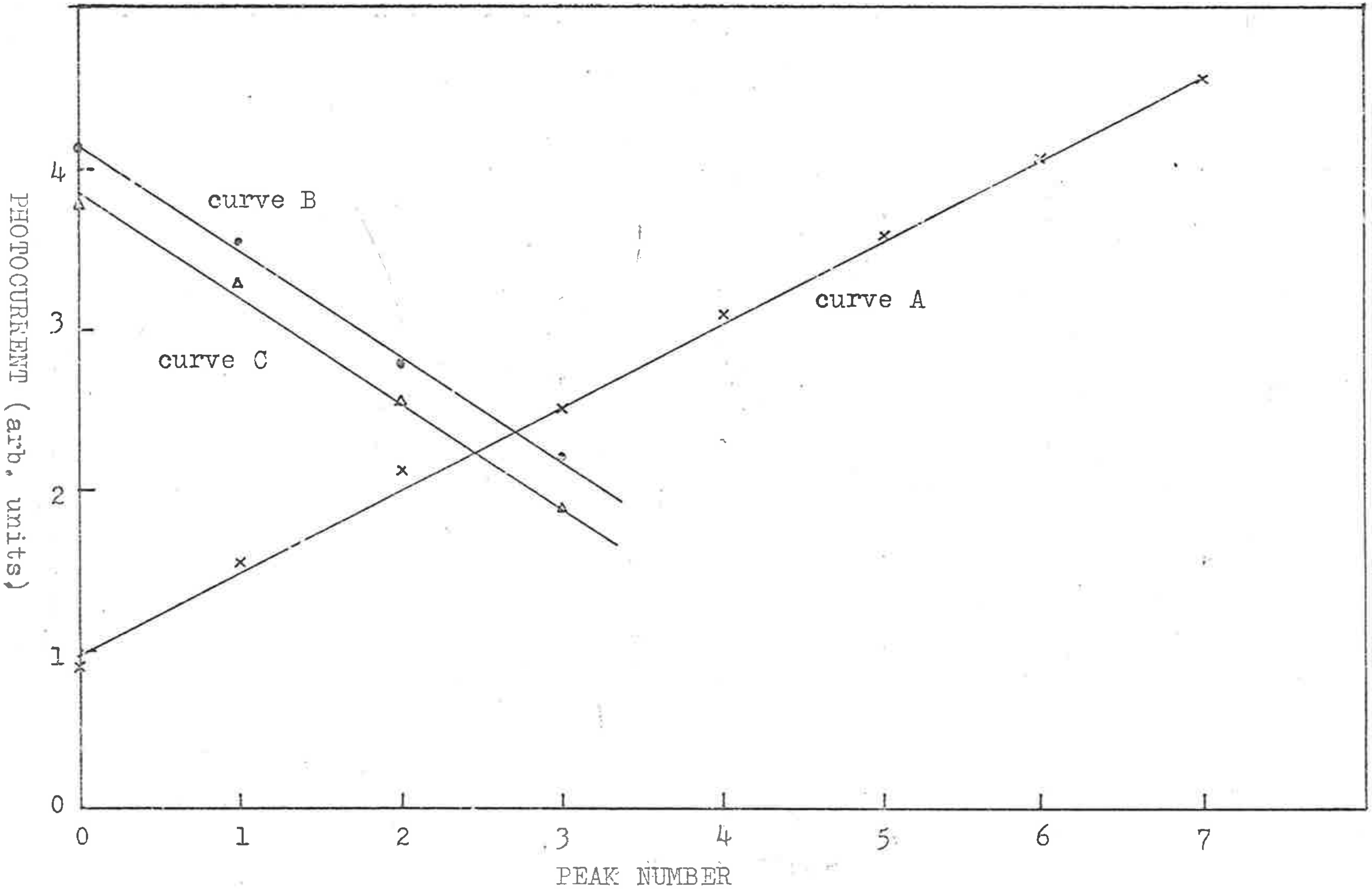
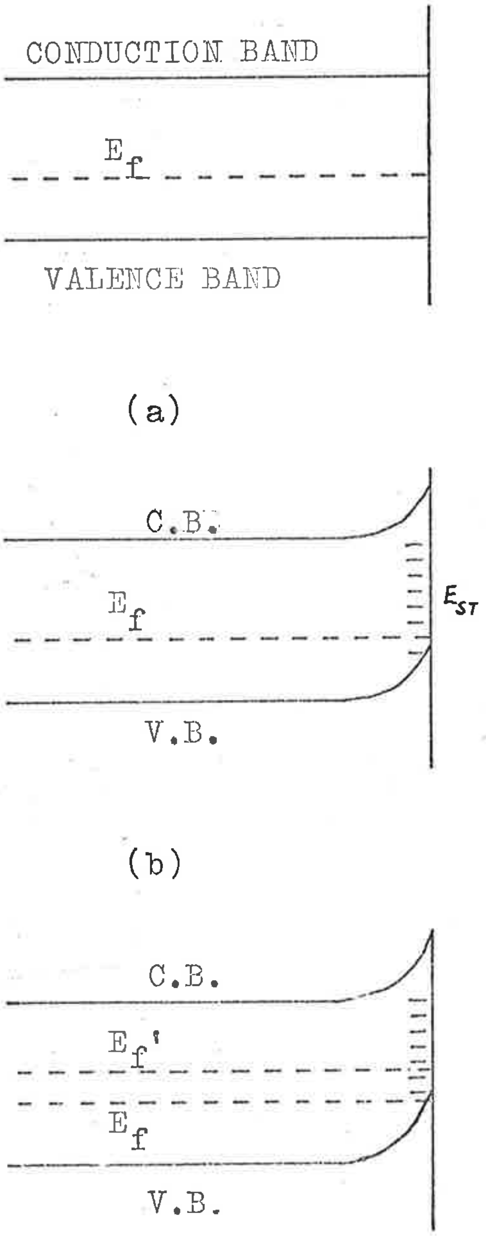

curve B
curve C
curve A
PHOTOCURRENT (arb. units)
0
1
2
3
4
0
1
2
3
4
5
6
7
PEAK NUMBER

FIGURE 3.7



(a)

(b)

(c)

FIGURE 3.8

surface and no surface states the energy bands are flat (figure 3.8 (a)). If there is a distribution of trapping levels at the surface (they may be intrinsic or extrinsic but cannot arise from adsorbed gas molecules as they are observed under ultrahigh vacuum conditions) the situation is as in figure 3.8(b). In this figure the surface states are represented by a series of discrete energy levels E_{ST}, which are assumed to be electron traps. E_F gives the position of the electron fermi level under dark conditions. The surface states below E_F will be occupied by electrons whereas those above will be empty. The electrons trapped at the surface constitute a negative charge which may be balanced by a positive charge in the bulk of the cadmium sulphide. The nett charge would be zero and a dipole would be formed. However this does not explain the changes which occur in the dielectric constant as equal and opposite dipoles will be formed at opposite surfaces and hence the nett change in the dipole moment will be zero. Also no band bending has been observed in cadmium sulphide crystals under high vacuum conditions (Mark 1965) hence an alternative explanation of the origin of the dipoles is needed. To account for the failure to observe band bending even though the theoretical predictions of Mark and Levine (1966) indicate a high density of trapping levels in the near surface region Mark (1965) has proposed that each trapped electron is compensated by an adjacent trapped hole. Hence each point of the lattice is effectively at zero potential and thus band bending does not occur. Each compensated electron hole pair will constitute a dipole and it is proposed that the fine structure observed is due to changes in the number of compensated electron hole pairs. This model will now be discussed in relation to the fine structure observed. In section 6.1.4 it will be shown that the concept of electron hole pairs also enables a possible explanation of the results of Many et al. (1969) which does not contradict the theoretical predictions of Mark and Levine (1966).

What happens in terms of electron trapping only, will now be considered. The explanation in terms of hole trapping will be analagous.

When the cadmium sulphide sample is illuminated the situation will be as in figure 3.8(c) if only electrons are involved. E_f' gives the position of the fermi level under the new equilibrium conditions resulting in the occupancy of more surface states by electrons. If the dynamics of the transition from situation (b) to situation (c) are considered then each time the fermi level reaches a new trapping level there is an increase in the number of electrons trapped at the surface. The processes involved in the filling of the hole traps are analogous. If each new electron trapping level and hole trapping level is reached almost simultaneously then there will be an additional dipole moment added as each new electron hole pair is formed and hence the observed fine structure. If the electron hole pairs possess rotational freedom then the dipole moments from opposite surfaces will be additive and hence there will be a change in the dielectric constant. The mathematical equations governing the above processes will now be considered to determine the nature of the energy spacing between the levels observed.

3.2.3. Rate of change of Fermi level with change in electron concentration

The position of the electron fermi level under equilibrium conditions is given by

$$n_c = N_c \exp\left(-\frac{E_F}{kT}\right) \text{------}(6)$$

where n_c is the density of electrons in the conduction band, N_c is the density of states in the conduction band, k is Boltzmann's constant and T is the temperature. Although the above formula is only true for equilibrium conditions for the following discussions it will be used as though also true for quasi equilibrium conditions i.e. conditions under which the fermi level is changing slowly with time.

Differentiating equation (b) with respect to E_f

$$\frac{\partial n_c}{\partial E_F} = -\frac{N_c}{kT} \exp\left(-\frac{E_F}{kT}\right) \text{------}(7)$$

substituting equation (6) in equation (7) and rearranging gives

$$\delta n_c = -\frac{n_c}{kT} \delta E_f \text{------}(8)$$

The change in electron density was small ($\delta n_c = \cdot 04$) as the films were not very photosensitive and the illumination intensity was low. kT is constant under the experimental conditions and hence δN_c is approximately proportional to δE_f.

For a one carrier semiconductor such as cadmium sulphide the conductivity σ is given by

$$\sigma = n_c e \mu_e \text{------}(9)$$

where e is the electronic charge and μ_e is the electron mobility.

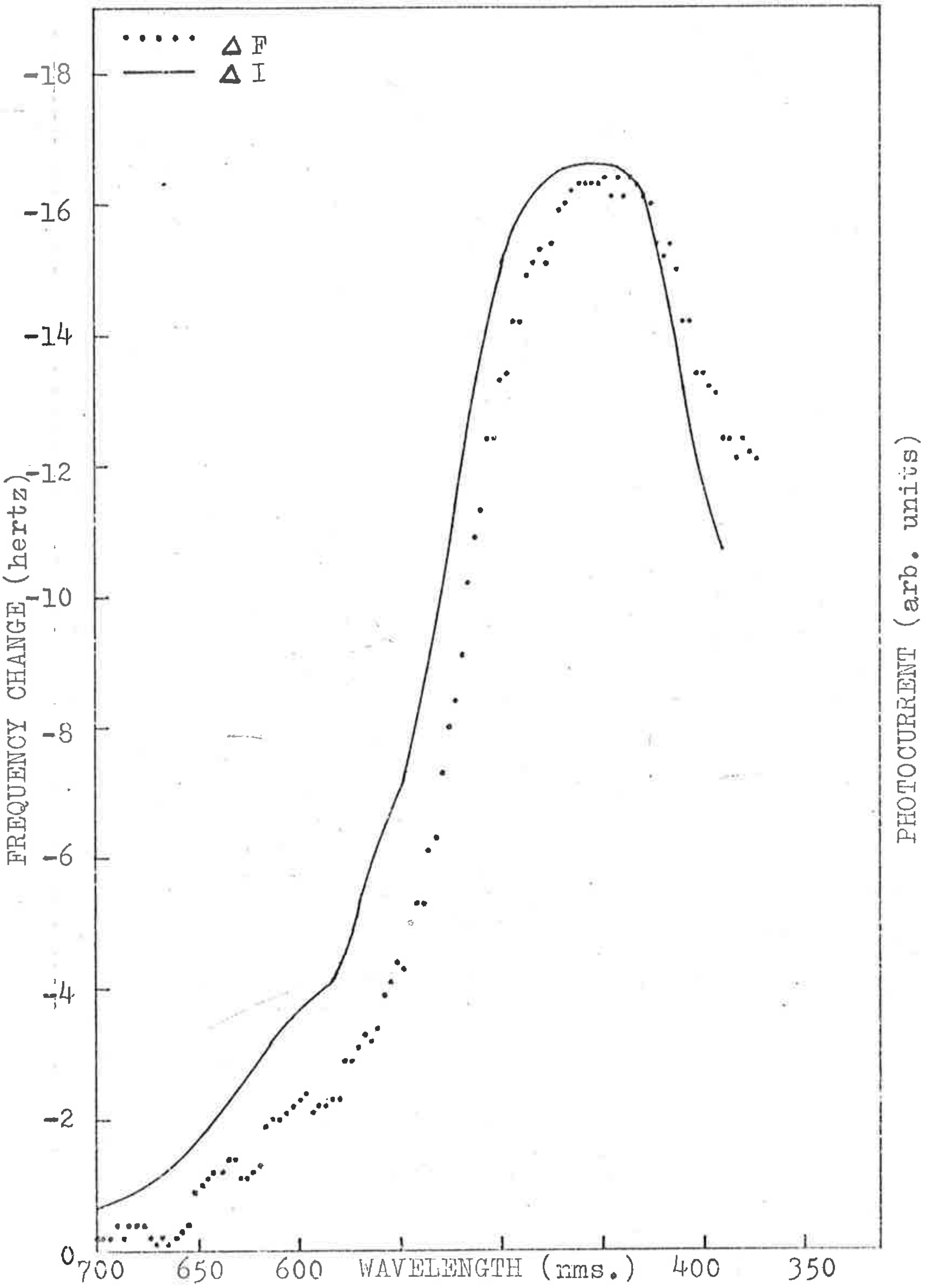
Hence from equations (8) and (9) $\delta\sigma$ is proportional to δE_F

Thus the change in the fermi level height is directly proportional to the change in photoconductivity for a small change in the electron concentration. Hence as the fine structure peaks occur at current change intervals of constant magnitude the energy spacing between successive trapping levels must be constant.

3.2.4. Variation of the Photoconductivity with Wavelength

Figure 3.9 shows typical changes in the frequency across the band gap using the C slits on the monochrometer for a one hour scan. Curve A is for a scan from short to long wavelengths and curve B for long to short wavelengths. The change in current has been plotted for the long to short wavelength scan only. A plot of current change against peak number again yields a straight line, within the limits of the accuracy to which the spacing between the peaks can be measured. Thus the results support those obtained using illumination at a constant wavelength.

The spacing of the peaks with respect to energy was also checked. Again there were apparently straight line relationships with the energy spacing depending on the position of the peaks on the band gap curves. The energy spacings were (.034, .045, .085 and .176 eV) for the curve shown but varied from film to film. That the position of the peaks for a particular film was not dependent on the wavelength of the illumination but instead on the number of electrons in the conduction band could be shown by varying the intensity of the illumination. This caused a change in the wavelength spacings of the peaks. Similarly the peak spacing changed when the photoconductivity was reduced by allowing oxygen into the system. Thus the improved resolution of the peaks obtained



ΔF
ΔI
-18
-16
-14
-12
-10
-8
-6
-4
-2
0
FREQUENCY CHANGE (hertz)
PHOTOCURRENT (arb. units)
700
650
600
WAVELENGTH (nms.)
400
350

FIGURE 3.9

by using the C slits on the monochromator was not due to narrowing the bandwidth. It was due to the decrease in intensity of illumination resulting in a decrease in the rate of change of the fermi level. Hence the results obtained with the band gap scans support the model presented .

3.2.5. Summary.

The results presented in this chapter suggest that the major component of the photodielectric effect is due to the conduction band electrons and hence it is only an "apparent" increase in dielectric constant that is observed. That a much smaller real change in dielectric constant also occurs due to the formation of electron - hole pairs and hence dipoles, is indicated by the occurrence of the fine structure.

The investigation of the photodielectric effect ends at this stage for two reasons;

(1) While frequency changes of up to 17 hertz were occasionally obtained the usual frequency change observed, 3-4 hertz, was not sufficient for a detailed study of the effect. The reason for the variation in the observed frequency changes from film to film could not be determined.

(2) The investigation of the effect of adsorbed gas on the properties of cadmium sulphide was considered

to be the more important aspect of the work. The adsorbed gas results are presented in chapters 4 and 5.

For these two reasons further aspects of the spurious mass changes were not investigated.

A comparison of the bandgap scan results with those obtained by Lawrance (1964) and Reynolds et al. (1955) in the next section brings this chapter to a close.

3.3.1. Band Gap Trapping Spectrum.

One of the reasons given at the beginning of this chapter for starting with a study of the band gap photoconductivity was that Lawrance (1964) claimed to have found a new trapping spectrum near the band gap edge which he did not investigate in detail. The spectrum was obtained by subtracting the long to short wavelength band gap photoconductivity curve from the short to long wavelength band gap curve. A shift in the wavelength of the photoconductivity maximum in the direction of the band gap scan relative to the wavelength of the equilibrium photoconductivity maximum was also reported; i.e. the short to long wavelength curve showed a shift in the photoconductivity maximum towards the longer wavelength, in agreement with Reynolds et al. (1955).

Reynolds et. al. believed that the shift was due to the actual mechanism by which photoconduction occurred. Lawrance interpreted the shift in terms of the trapping levels he obtained, and his interpretation was as follows.

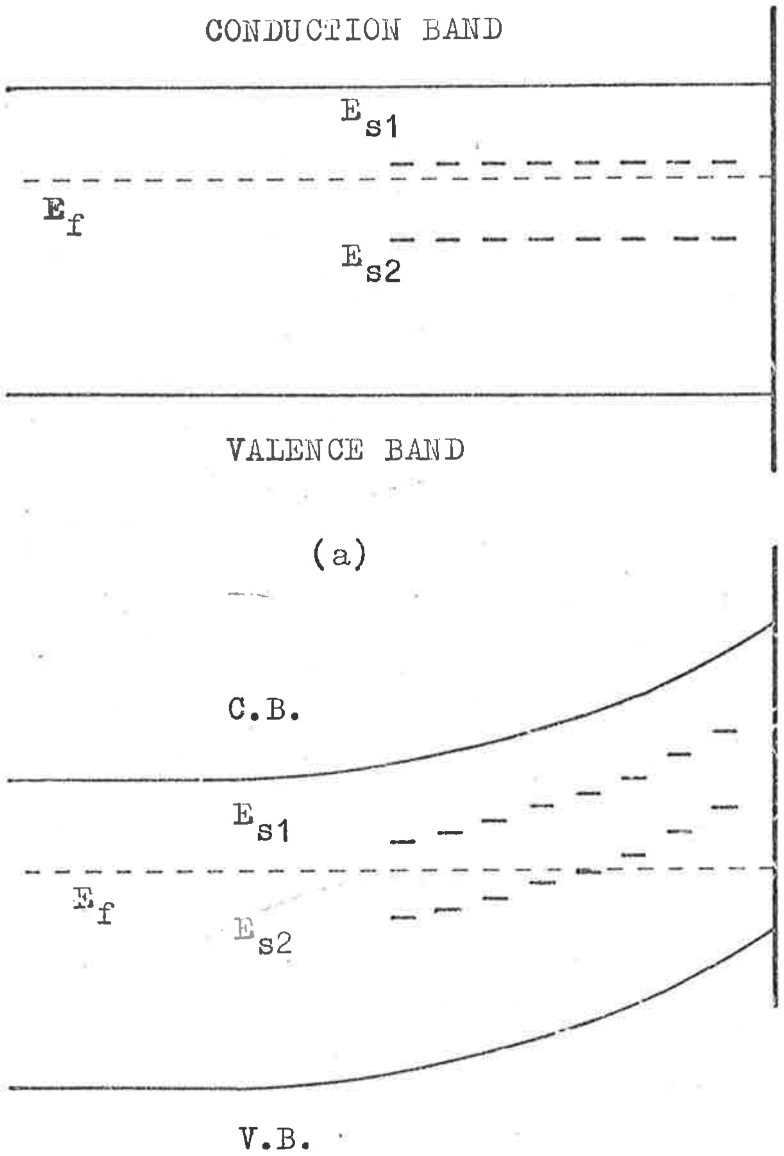
If we commence a wavelength scan of the band gap photoconductivity from 400 nanometres then from this point to 500 nanometres the excitation is intrinsic and electrons are excited from the valence band to the conduction band and hence into deep traps just above the valence band. When illumination is at a wavelength longer than the intrinsic wavelength the deep traps are re-emptied by optical excitation producing free electrons in the conduction band and hence the photoconductivity is larger than its value under equilibrium conditions. This process shifts the photoconductivity peak towards the infrared. For a band gap scan from long to short wavelengths the excitation of electrons from the valence band to the conduction band and hence to the deep traps, does not occur until the intrinsic excitation wavelengths are reached. The rate of growth of the photoconductivity is initially limited by the filling of the deep traps thus shifting the photoconductivity maximum towards shorter wavelengths.

3.3.2. Results.

The band gap was scanned in both directions at the two available scan speeds, 13 minutes and one hour, for several films of various thicknesses with several point by point plots being made as well without any evidence of a trapping spectrum being found. In each case the photoconductivity peak was shifted in the direction of the scan in agreement with the results of Lawrance and Reynolds et. al. The experiments were repeated at various vacuum pressures and at atmospheric pressure but in no case could a trapping spectrum be detected. Thus the results obtained do not support the results of Lawrance.

3.3.3. Discussion.

If trapping levels are responsible for the observed shifts in the photoconductivity maximum the apparent absence of trapping levels could be explained by proposing that the levels are situated in the surface barrier region and that the band bending occurring near the surface changes the discrete trapping spectrum into a continuum of levels, i.e. consider the trapping levels E_{s1} and E_{s2} in the near surface region shown in figure 3.10.(a). When band bending occurs at the surface the energy of these levels follows the curve of the conduction band, as they have constant energy when measured with respect to the conduction band edge, while the fermi level E_f remains flat, figure 3.10(b). Thus as the fermi level changes due to illumination it can be seen that the traps are either filling continuously or emptying continuously and hence the discrete distribution of energy levels will not be detected. This is a possible explan-



(a)

(b)

FIGURE 3.10

ation if as Weber (1969) proposes, the slow states in cadmium sulphide are situated in the near surface region, but why Lawrance obtained the trapping spectrum cannot be explained.

If, as proposed by Reynolds et. al. the shift in the photoconductivity maximum is due to an unknown mechanism by which photoconduction occurs then it would be expected that the photoconductivity maximum will shift by an amount proportional to the scan speed provided that the rate limiting process has a fixed time constant. There is, however, no measurable change in the shift of the photoconductivity peak with a change in scanning speed although the rather flat maximum of the photoconductivity curves for the films makes an accurate determination of the position of the photoconductivity maximum difficult. Thus no definite conclusion can be drawn concerning the nature of the mechanism.

If the photo-induced slow states proposed by Nicholas and Woods to account for their conductivity glow curve results are responsible for the shifts in the photoconductivity maximum the interpretation would be more consistent with the present theory as to the cause of the slow effects in cadmium sulphide. As the trapping spectrum reported by Lawrance could not be obtained this section of the work was not pursued any further.

In concluding this chapter it must be pointed out that the results reported here indicate that it would be worthwhile to investigate further the dielectric properties of cadmium sulphide by the conventional method, i.e. with the cadmium sulphide crystal or film being the dielectric of a parallel plate capacitor and using the capacitor to control the resonant frequency of an electrical circuit. The photodielectric properties of cadmium sulphide were studied between 1930 and 1955 and the stability and accuracy of the measuring apparatus used has been greatly improved since then. One of the electrodes would need to be a conducting glass to enable easy illumination of the film. The resonator should be designed such that a small change in capacity causes a large change in frequency, in order to maximize the frequency change corresponding to a small change in the dielectric constant.

The experiments to be performed would include

(a) plotting the dielectric constant as a function of wavelength.

(b) studying the change in the dielectric constant when illumination of a fixed wavelength is switched on and when it is switched off.

Both of these experiments should be performed at various light intensities in an attempt to determine the conditions under which the fine structure is best resolved. From these experiments further insight as to the nature of the photodielectric effect should be provided.

CHAPTER 4

ADSORBED GAS EFFECTS

4.1.1. Introduction

In chapter 1 the main theories and some of the experimental evidence concerning the role of oxygen in the various properties of cadmium sulphide have been considered and the conclusion drawn that it would be worthwhile to investigate the amounts of oxygen present on the surface of cadmium sulphide under various environmental conditions. In this chapter the results obtained from the study of the adsorption of oxygen on cadmium sulphide films under dark conditions are recorded and discussed. The adsorption of oxygen in detectable amounts i.e., greater than 0.01 monolayers, is shown to occur only in the 10^{-2} to 10^{-1} torr. pressure range and the rate of adsorption of oxygen at constant pressure is shown to fit the Langmuir adsorption curve for simple adsorption. A discussion of the sticking coefficient of oxygen on cadmium sulphide as a function of surface coverage follows. The chapter is then concluded with a discussion of the adsorption of oxygen at atmospheric pressure.

4.1.2. Dark Conductivity Results

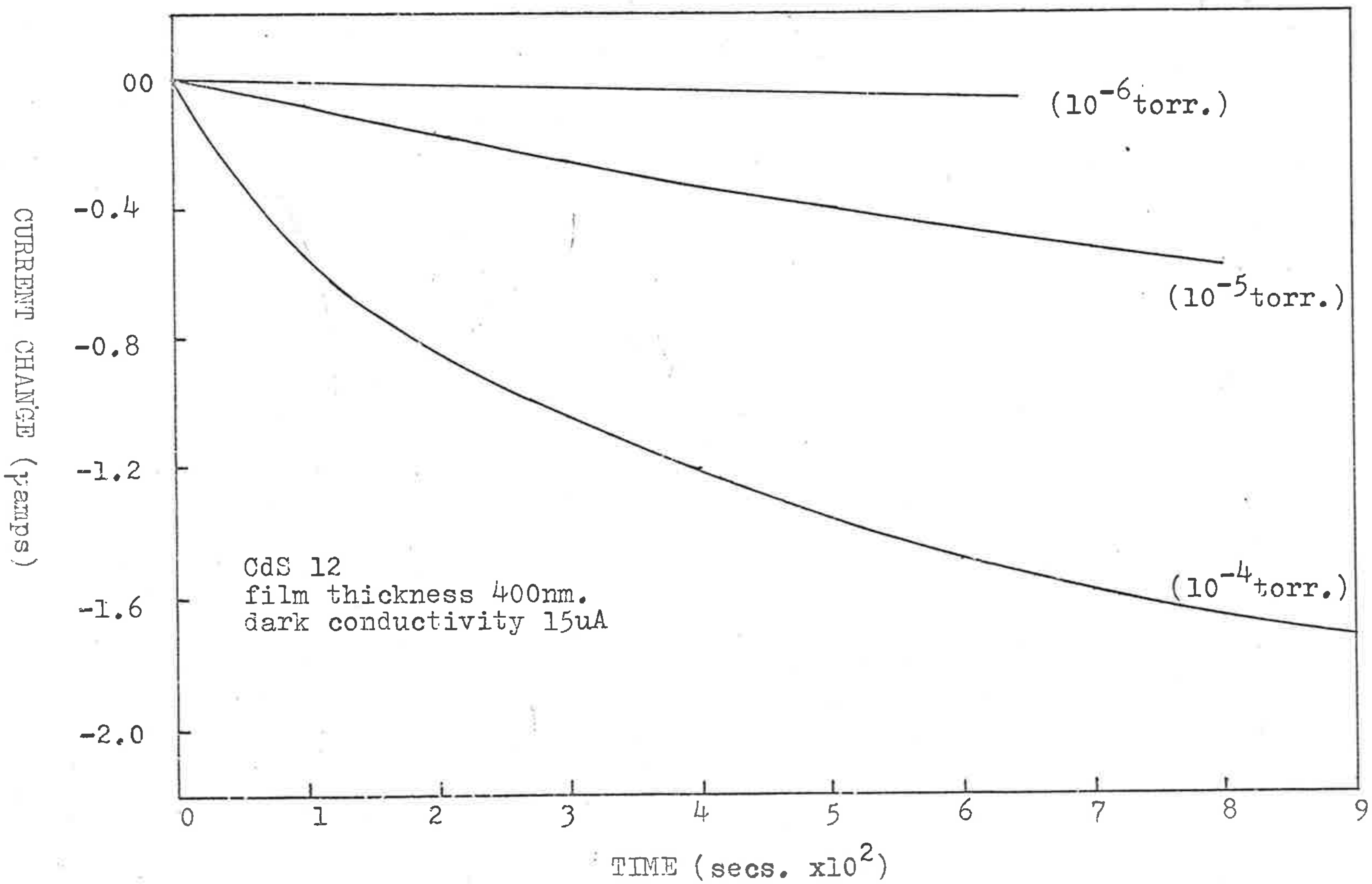
It was first decided to determine the vacuum pressure at which detectable changes in the dark conductivity of the cadmium sulphide films occurred as there is a difference of two orders of magnitude in the pressures at which adsorbed gas effects are detectable in cadmium sulphide crystals (10^{-4} torr. Mark 1965) and in cadmium sulphide films (10^{-6} torr. Hughes and Carter 1964). Their cadmium sulphide films were evaporated at 10^{-6} torr.

The measurements were made with the sample in equilibrium dark conditions. The changes in current were measured as changes in the voltage appearing across a 22K resistor connected in series with the cadmium sulphide film. Voltage backoff was used so that only the actual changes in voltage were recorded. The air used was dried by passing it through the liquid air trap in the gas handling plant.

The results are shown in figure 4.1 . As there were no detectable changes in the frequency it has not been plotted. Changes in the dark conductivity were detectable when dry air was leaked into the system at various pressures in the range 10^{-6} to 10^{-4} torr. It was subsequently shown that of the two main constituents of air, dry oxygen gave similar results while dry nitrogen had no effect on the dark current. This was as expected from the published results of other authors. The gas adsorption was in each case reversible i.e., restoring the vacuum chamber to ultrahigh vacuum condit-

FIGURE 4.1

Variation in the dark conductivity with time at various pressures



ions resulted in the dark conductivity returning to its original value. These results are in agreement with those obtained by Hughes and Carter (1964) for cadmium sulphide films. Thus the necessity of working under ultrahigh vacuum conditions to avoid contamination of the surface is clearly illustrated.

It is of interest to compare the results obtained for the cadmium sulphide films with those obtained for cadmium sulphide crystals by other authors in the following two respects;

(a) Adsorbed gas effects have been considered to be unimportant at 10^{-6} torr. in the case of crystals. Mark (1965) showed oxygen effects on the conductivity to begin at 10^{-4} torr. Many et. al. (1969) reported that there are no experimentally detectable (less than $2x10^{-11}/cm.^2$) surface states on cadmium sulphide crystals at 10^{-6} torr. The surface states they detected at higher pressures were attributed to adsorbed oxygen. Hence at 10^{-6} torr. it is considered that there are very few oxygen atoms present on the surface of cadmium sulphide crystals. As the quartz crystal frequency did not change during the above experiments the density of oxygen which caused the observed changes in the dark conductivity of the cadmium sulphide films is less than $8.1x10^{-12}$ atoms/$cm.^2$ i.e., less than 0.01 monolayers.

(b) Adsorption and desorption occurred on the cadmium sulphide films to a significant extent in the dark as in the results of Hughes and Carter (1964). Oxygen atoms incident on the surface of cadmium sulphide crystals under dark conditions have been shown to have a sticking probability of less than 10^{-13} (Campbell and Farnsworth 1968). The sticking probabilities obtained for the cadmium sulphide films studied were much higher (of the order of 10^{-5}) and are discussed in section 4.1.7. The very small sticking probability for oxygen on cadmium sulphide crystals under dark conditions is one of the reasons why photoadsorption has been proposed as the mechanism to account for the accelerated rate of decrease of the conductivity observed when a cadmium sulphide crystal is exposed to air whilst subjected to bandgap radiation. This is discussed further in section 4.2.2. The experimental results for the cadmium sulphide films indicate that adsorption and desorption occur to a significant extent in the dark which would indicate that only physical adsorption has occurred as 0.91ev. is required to desorb chemisorbed oxygen (Mark 1965). This is discussed further in section 4.1.3.

4.1.3 Pressure range in which the amount of oxygen adsorbed becomes detectable

As oxygen was found to be the constituent of air which caused the observed changes in the dark conductivity of the cadmium sulphide films, confirming the results of others, commercial grade oxygen from a gas cylinder was used in the following experiments. Any water vapour present in the oxygen was removed by the liquid air trap in the gas handling system.

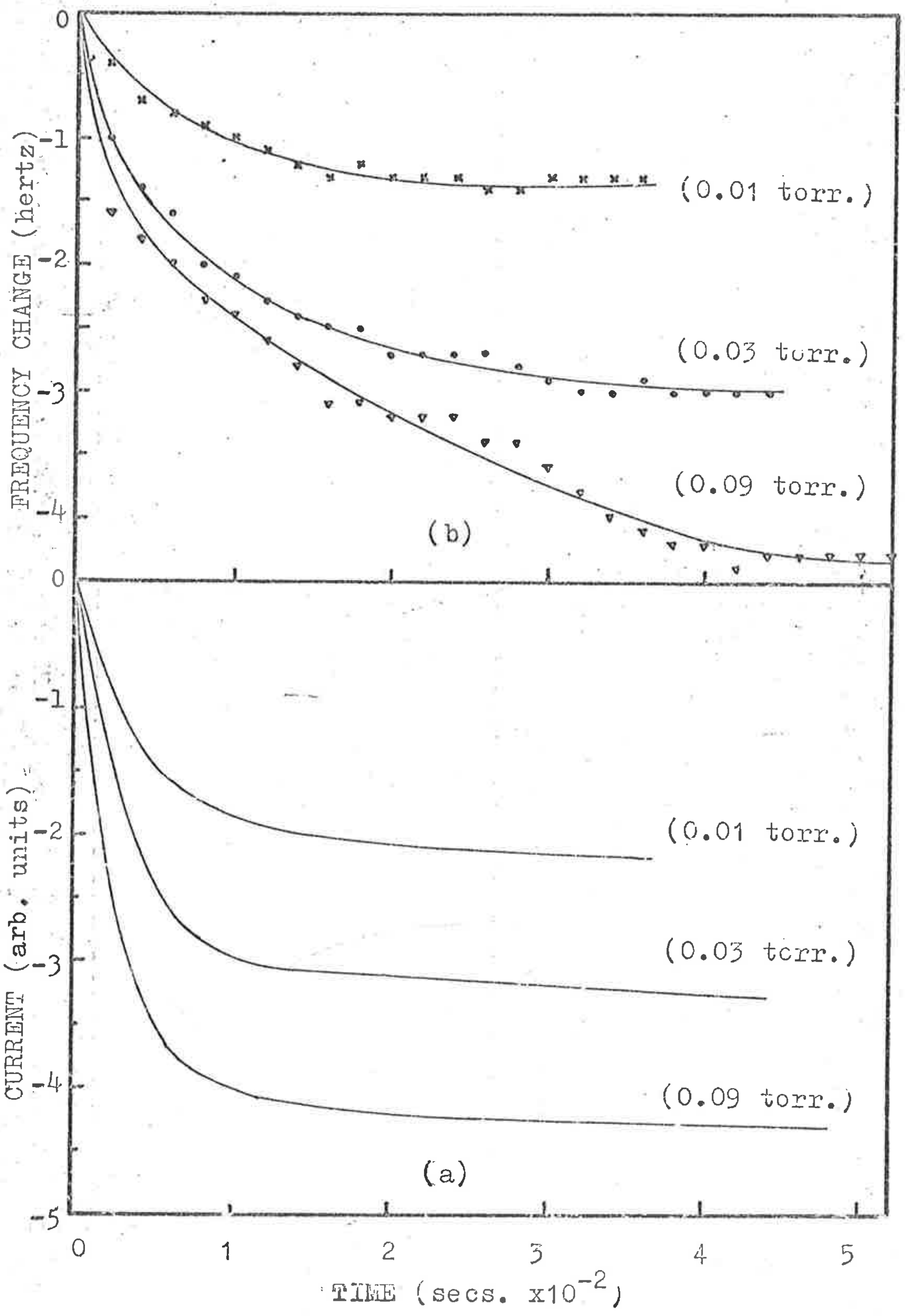
By using the ultrahigh vacuum valve as a variable leak the partial pressure of oxygen in the vacuum system was increased until the frequency of the quartz crystal changed by a measureable amount. This occurred in the 10^{-3} to 10^{-2}torr. pressure range. The highest pressure at which the quartz crystal oscillator gives meaningful readings is 10^{-1}torr. due to hydrostatic damping effects which were discussed in chapter 2, section 2.2.4. The change in frequency with pressure due to hydrostatic damping effects could be determined before depositing the cadmium sulphide film on the quartz crystal. However this would only be useful in determining the equilibrium amount of gas adsorbed at a given pressure as the quartz crystal is unstable for up to 30 minutes after the admission of gas at these pressures. Hence it cannot be used to determine the rates of adsorption of gases at pressures above 10^{-1}torr. As pressures in the vacuum system above 10^{-1}torr. could not be measured accurately without modifying the vacuum system, the results obtained in this pressure range were inconsistent and therefore have been omitted. Thus the adsorption of oxygen was only studied in the 10^{-2} to 10^{-1}torr. pressure range.

Experiments were performed to determine the amount of oxygen adsorbed and the corresponding change in dark conductivity at several pressures in this pressure range for each of a number of films. Typical results are shown in figure 4.2. The decreases in dark current at three different pressures are plotted in figure 4.2(a) and the corresponding decreases in frequency in figure 4.2(b). The curves have been terminated at a time when the frequency readings became constant to ±0.1 hertz. A comparison of the two sets of curves shows that the kinetics of adsorption of oxygen and the change in the dark conductivity are not the same.

The Elovich equation, which was discussed in section 1.1.6, has a solution of the form

$$N = c + d\log_{10}t$$

where N is the number of atoms adsorbed/sq. cm., c and d are constants and t is the time. As the adsorption of each atom removes an electron from the conduction band the change observed in the conductivity is a measure of the adsorption taking place at



FREQUENCY CHANGE (hertz)
0
-1
-2
-3
-4
(0.01 torr.)
(0.03 torr.)
(0.09 torr.)
(b)
CURRENT (arb. units)
0
-1
-2
-3
-4
-5
(0.01 torr.)
(0.03 torr.)
(0.09 torr.)
(a)
0
1
2
3
4
5
TIME (secs. x10^{-2})

FIGURE 4.2

the surface. Thus in the case of cadmium sulphide crystals e.g. Mark (1964, 1965), the change in the dark conductivity with time has been fitted to the Elovich equation to show that the rate limiting step in the chemisorption of oxygen is the diffusion of electrons across the potential barrier in the near surface region. Thus the two sets of curves have been plotted against the logarithm of time in figure 4.3.

The frequency change curves, figure 4.3(b), can be approximated by a straight line during the period of uptake of oxygen on the surface. Hence the uptake of oxygen is approximately an exponential process. It will be shown later, section 4.1.5, that the frequency changes also fit the Langmuir equation for simple adsorption at constant pressure. The measuring system is not sufficiently accurate to distinguish conclusively between exponential and Langmuir type processes.

The current decay curves, figure 4.3(a), do not show an exponential dependence on time and hence cannot be fitted to an Elovich equation. The departure of the current curves for the cadmium sulphide films from the exponential behaviour exhibited by crystals is to be expected due to the greater changes in conductivity observed in the case of cadmium sulphide films. The application of the Elovich equation requires that the change in conductivity be only a few percent of the

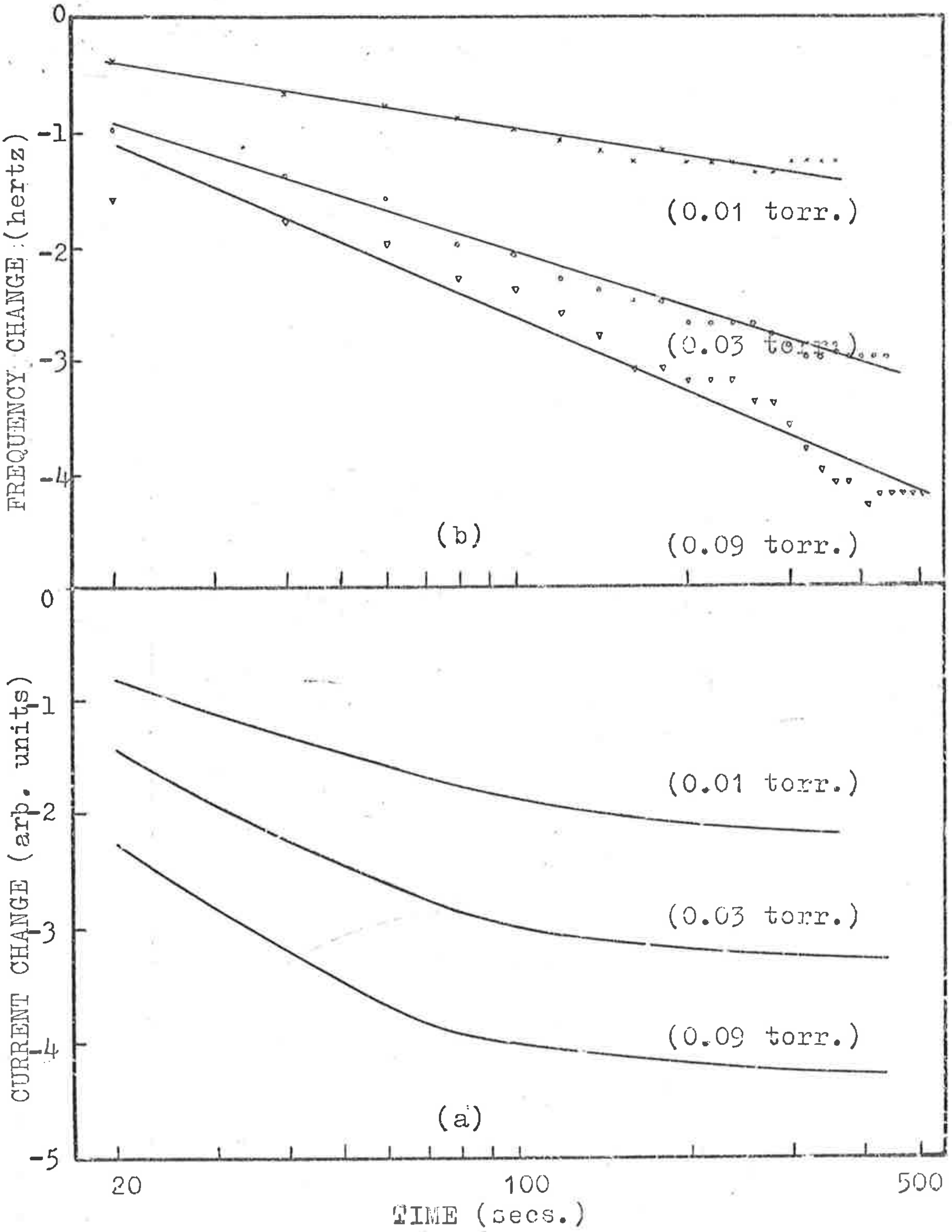

0
-1
-2
-3
-4
FREQUENCY CHANGE (hertz)
(0.01 torr.)
(0.03 torr.)
(b)
(0.09 torr.)
0
1
2
3
-4
-5
CURRENT CHANGE (arb. units)
(0.01 torr.)
(0.03 torr.)
(0.09 torr.)
(a)
20
100
500
TIME (secs.)

FIGURE 4.3

dark conductivity. This is not true of the films studied which showed changes in the dark conductivity of more than 50 percent when exposed to oxygen at pressures in the region of 10^{-1}torr.

An inspection of the logarithmic plots of current change in figure 4.3(a) indicates that the curves consist of two linear parts with the change in slope occurring at approximately 100 seconds after exposure to the oxygen. This suggests that the oxygen may cause the dark conductivity to decay by two different mechanisms. Several possible explanations of the two linear parts will now be considered briefly.

(a) The change in slope could correspond to the completion of the adsorption of the first monolayer on the surface. The frequency change corresponding to a surface coverage of one monolayer of oxygen is approximately 3.2 hertz. From figure 4.3 it can be seen that the change in the slope of the dark current curve does not correspond to a surface coverage of one monolayer and hence the change in slope of the dark current curve does not occur at the completion of the adsorption of one monolayer.

(b) The initial rapid decrease in the dark conductivity could be attributed to the adsorbed oxygen causing an increase in the surface barrier height. Campbell and Farnsworth (1968) from their studies of cadmium sulphide crystals believe that oxygen causes band bending of 0.2ev. at the surface. As the conducting necks between the crystallites of which the film is believed to be composed will be thin when compared to the distance the Schottky barrier extends into the interior of the crystallite the adsorption of oxygen will cause each conducting neck to become a potential barrier to the current flow. The second region could then be due to the exponential adsorption of oxygen which causes an increase in the number of recombination centres available and hence an increase in the rate of decay of the dark conductivity. The first region would not be expected to occur in the case of cadmium sulphide crystals as there is not a large number of crystallites for the oxygen to change the resistance between. This is in agreement with the results of Mark (1965) which are linear when the decay in the dark conductivity is plotted against the logarithm of time.

(c) A third possible explanation is that the oxygen is adsorbed on the surface of the cadmium sulphide film at two different types of lattice sites, the adsorption at the first type of lattice site corresponding to the first part of the current decay curve, and the subsequent adsorption at the second type of lattice site corresponding to the second part of the dark current decay curve. Campbell and Farnsworth (1968) have shown that the sticking coefficient of oxygen on the $(000\bar{1})$S surface of cadmium sulphide crystals when the surface is illuminated is between 10^{-10} and 10^{-9}. On the illuminated (0001)Cd surface the sticking coefficient is between 10^{-11} and 10^{-10}. The sensitivity of their apparatus was not sufficient to make a similar comparison for the two types of surface under dark conditions. If we assume that the two rates of adsorption occur on cadmium sulphide films under non illumination conditions, and that both surface types occur simultaneously, then the change in the slope of the dark current curves could be attributed to a cessation of adsorption at the $(000\bar{1})$S surface. However if this was the explanation of the observed change in the slope of the dark current decay curves it would be expected that the frequency change curves would show a change in slope at the same time as the dark current decay curves. As a change of slope was not evident in any of the results obtained this explanation is not valid. Hence explanation (b) is favoured although no really conclusive evidence can be presented.

As in the previous section both the dark conductivity and the crystal frequency were restored to their initial values, within the limits of experimental error, by re-evacuating the vacuum system providing further evidence that the desorption of oxygen from cadmium sulphide films is spontaneous under dark conditions. Thus the results obtained indicate that the oxygen is physically adsorbed on the surface of the cadmium sulphide films i.e., no chemisorption occurs.

The crystal frequency curve for the admittance of oxygen at 0.09torr. shows a departure from purely exponential behaviour. The curve could be considered to consist of two exponential parts with the first exponential part ending at 3.2 hertz. As this change in frequency is equivalent to a monolayer of oxygen the two exponential parts represent the adsorption of the first monolayer of oxygen and the partial adsorption of a second monolayer. Further investigation of the adsorption past the one monolayer stage was not possible as hydrostatic damping effects cause errors at pressures above 0.1torr.

4.1.4. Langmuir's Theory of Adsorption

In chapter 1 the distinction between chemisorption and physisorption has been drawn but the theory of physical adsorption as developed by Langmuir has not been discussed. In Langmuir's theory of adsorption, all the molecules incident on a surface condense and then re-evaporate. It is the rate of re-evaporation which determines the amount of gas present on the surface and hence the degree of surface coverage. The rate of re-evaporation is dependent on the temperature and the nature of the surface.

In the case of simple adsorption it is assumed that the adsorption process takes place on a plane surface which has only one kind of elementary space and that each elementary space can hold only one adsorbed gas molecule. The amount of gas present on the surface is given by an equation of the form

$$\theta = \frac{kP}{1 + kP} \qquad \text{----- 4 (1)}$$

where θ is the fractional surface coverage, P is the pressure, and k is a temperature dependent constant. This equation yields the Langmuir adsorption isotherms.

For gas adsorption at a constant pressure the rate at which equilibrium is reached is given by an equation of the form;

$$\frac{N_o}{N}\frac{d\theta^1}{dt} = a\mu - (v_1 + a\mu)\,\theta^1$$

where a is the rate of condensation of molecules striking the surface and is approximately equal to one, N is Avogadro's number, N_o is the number of elementary spaces per square centimetre of surface, μ is the number of gram molecules of gas striking each square centimetre per second, v_1 is the rate of re-evaporation from the surface and θ^1 is the instantaneous surface coverage. This equation can be integrated with respect to time to give;

$$t = \frac{N_o}{Nv_1(1 + \sigma_1\mu)} \ln \frac{\theta_1}{\theta_1 - \theta^1} \quad \text{--- } 4\ (2)$$

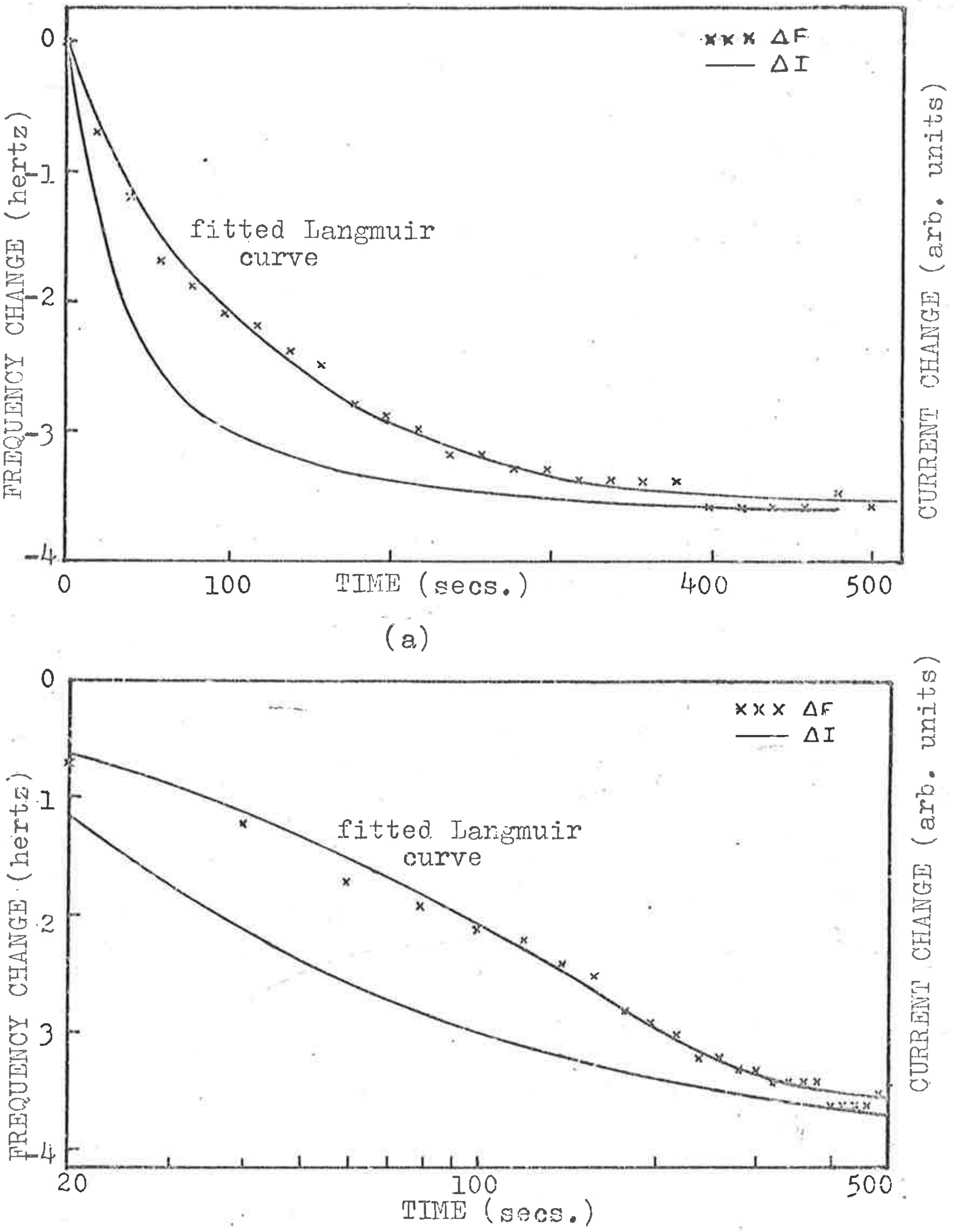
where θ_1 is the maximum fractional surface coverage

and
$$\sigma_1 = \frac{a}{v_1}$$

4.1.5 Langmuir's Equations and the rate of adsorption of oxygen

(a) At constant pressure

The pressure in the vacuum system which corresponded to the adsorption of a monolayer of oxygen on the surface of the cadmium sulphide film was determined by slowly increasing the pressure. This occurred at 0.04 torr. The system was re-evacuated to desorb all the oxygen and when equilibrium had been obtained the pressure was returned to 0.04 torr. The resulting changes in frequency and conductivity with time are shown in figure 4.4(a). To the frequency points the Langmuir adsorption curve for simple adsorption has been fitted using equation 4 (2). The same results plotted on a logarithmic time scale are shown in figure 4.4(b). The frequency points obtained fit the Langmuir curve within the limits of experimental error (approximately 0.1 hertz).



Langmuir's Equation fitted to the frequency changes

FIGURE 4.4

(b) Surface coverage and pressure

In figure 4.5(a) the equilibrium surface coverage has been plotted as a function of pressure for the set of results given in figure 4.2. An additional point for a different film (CdS 20) has also been plotted and is in close agreement with the rest of the results. The curve obtained is the characteristic shape of a Langmuir adsorption isotherm.

Hence for agreement with the initial assumptions of Langmuir the adsorption of oxygen on the surface of cadmium sulphide involves only one kind of lattice site and only one molecule is adsorbed per lattice site, i.e., oxygen is physically adsorbed in molecular form.

Many et. al. (1969) in explaining the nature of the slow states observed on the surface of cadmium sulphide crystals by field effects have assumed that the electrons are interacting with a fixed density of physically adsorbed oxygen atoms and that the density of these atoms is directly proportional to the pressure. The results obtained in the case of cadmium sulphide films indicate that the density of physically adsorbed atoms on the surface is not directly proportional to the pressure and hence indicates that the assumption of Many et. al. is not valid. The results of Many et. al. will be discussed further in section 6.1.4. as the results of section 4.1.6., the next section, also reveal a

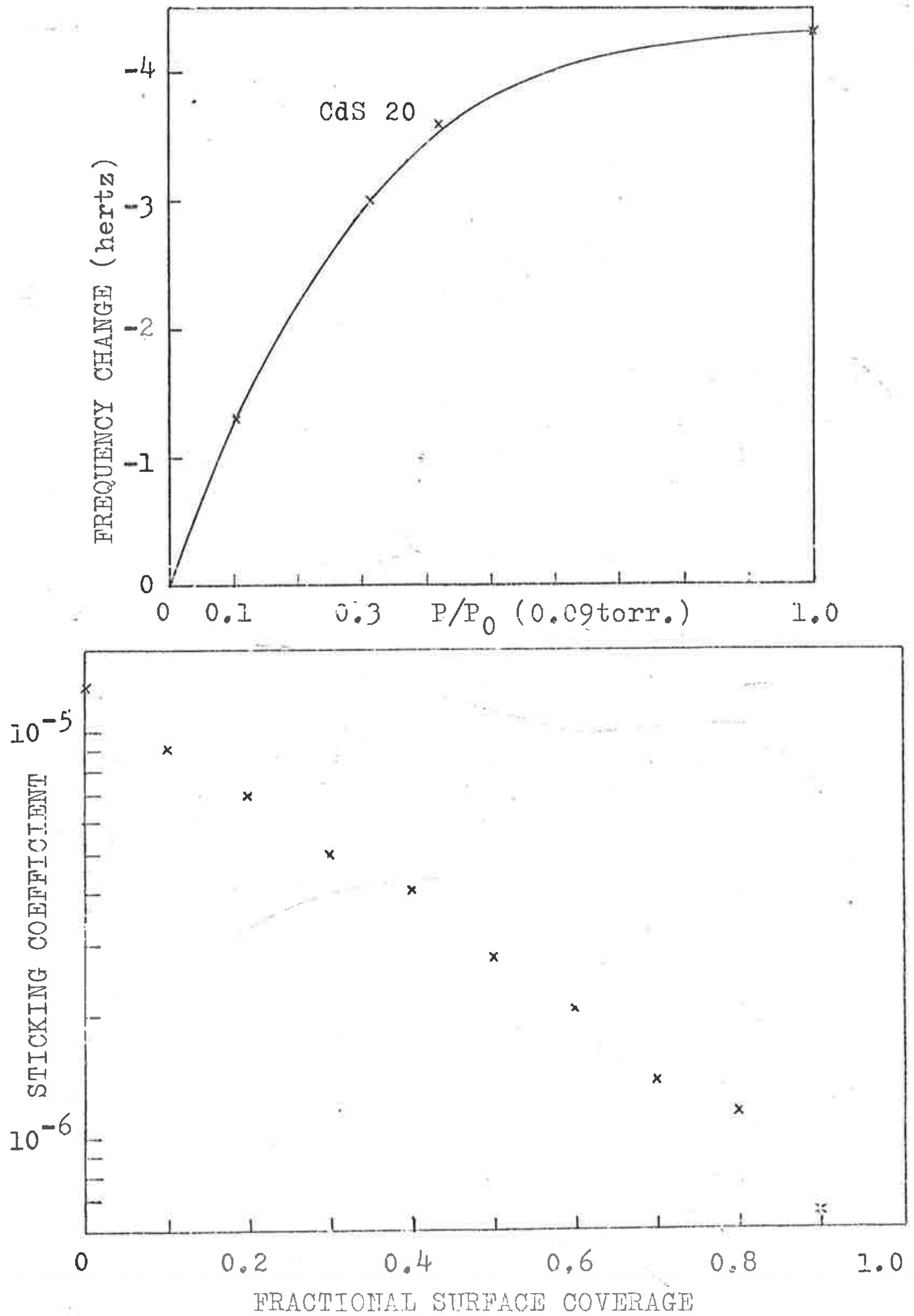

-4
-3
-2
-1
0
FREQUENCY CHANGE (hertz)
CdS 20
0
0.1
0.3
P/P$_0$ (0.09torr.)
1.0
10^{-5}
10^{-6}
STICKING COEFFICIENT
0
0.2
0.4
0.6
0.8
1.0
FRACTIONAL SURFACE COVERAGE

FIGURE 4.5

very significant departure in the behaviour of oxygen on the surface of cadmium sulphide from that predicted by Many et. al.

Future work would involve the determination of the temperature dependence of the adsorption and desorption of oxygen on the surface of the films. These experiments are not possible in the apparatus used. As these processes are both spontaneous at room temperature and under dark conditions the oxygen must be physically adsorbed and it would be of interest to determine the binding energy for physical adsorption as it is not known. The binding energy for chemisorbed oxygen as measured by thermally stimulated conductivity curves, is believed to be 0.91 eV.

The binding energy could be determined by measuring the amount of oxygen adsorbed at equilibrium as a function of temperature for a constant pressure. To improve the sensitivity it would be desirable to use a 15 megahertz quartz crystal, e.g., King (1971), mounted in a holder whose temperature can be held constant at a number of values, e.g., Baker (1967), Shiojiri et. al. (1969). The surface coverage is plotted against the logarithm of the inverse of the absolute temperature and the slope of the curve determines the binding energy.

4.1.6 Sticking Coefficients

The sticking coefficient of a gas on a surface is defined as the probability that an atom incident on the surface will remain on the surface. From the gradient of the curve plotted in figure 4.4(a) for the adsorption of oxygen to a coverage of one monolayer the sticking coefficient of oxygen on cadmium sulphide can be obtained for various fractional coverages. The sticking coefficient under dark conditions as a function of surface coverage is plotted in figure 4.5(b) and varies from 10^{-5} at zero surface coverage to 8×10^{-7} for a 90% surface coverage.

These values will be higher than the true values for a perfectly flat surface due to the surface roughness, but even so they are in error by less than one order of magnitude. These values are considerably higher than those obtained for cadmium sulphide crystals by Campbell and Farnsworth (1968) using L.E.E.D.. They found that the sticking coefficient under dark conditions was less than 10^{-13}. Thus a marked difference between the properties of crystals and films has been found.

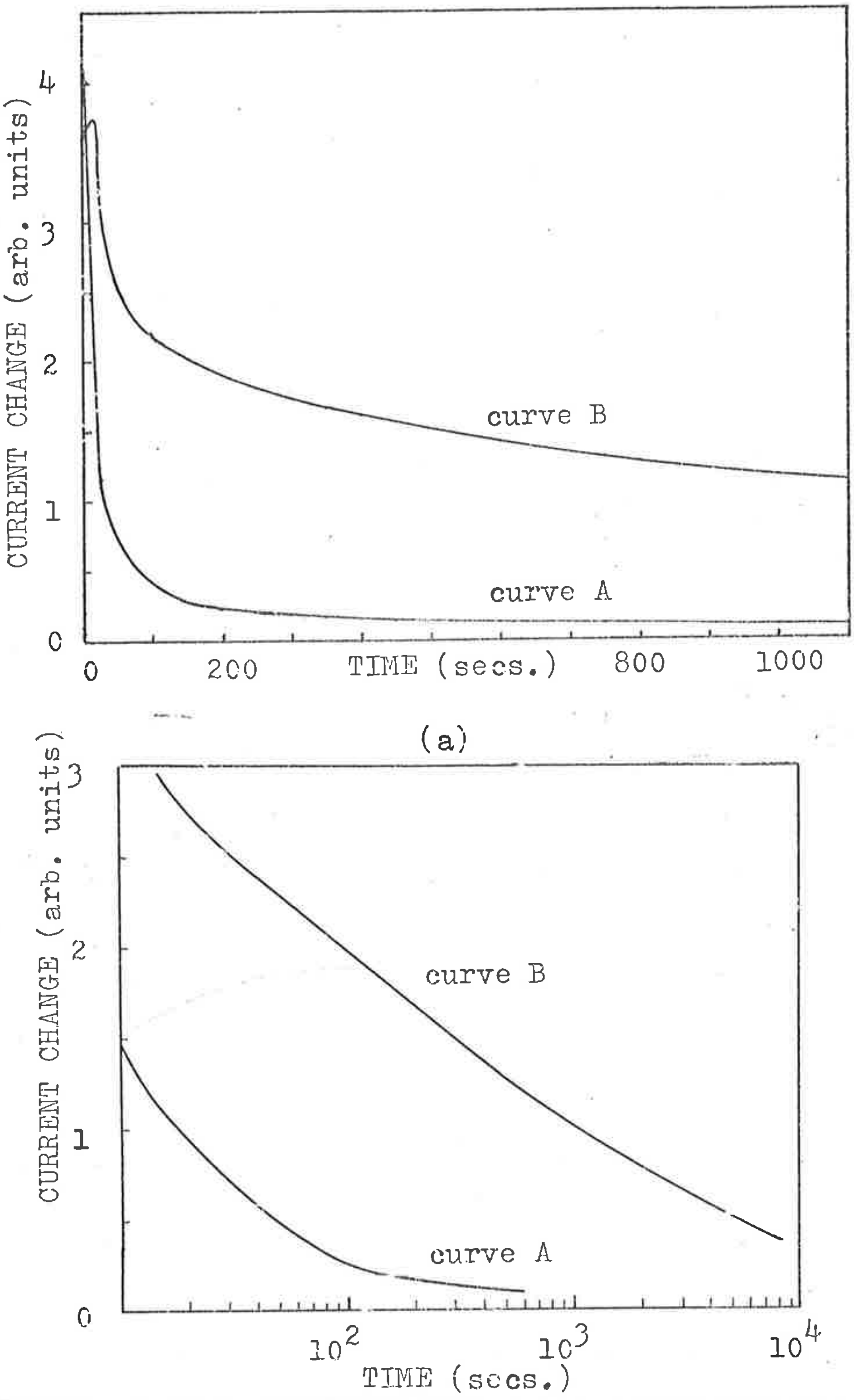
Many et. al. (1969) from their interpretation of their D.C. field effect results deduce that 10^{12} oxygen atoms / cm.^{2} are physically and then chemically adsorbed on the surface of their cadmium sulphide crystals during a D.C. field effect experiment at 10^{-5} torr.

As there are approximately 2 x 10^{15} oxygen atoms incident on the surface / cm.^{2} / sec at a pressure of 10^{-5} torr. the time taken to physically adsorb 10^{12} oxygen atoms can be calculated using the sticking coefficients calculated by (1) Campbell and Farnsworth (1968) for cadmium sulphide crystals which will be assumed to be 10^{-13} although it was less than this by an unknown amount, and (2) using the value of 10^{-5} obtained for cadmium sulphide films at zero surface coverage in this thesis. 10^{-13} gives the time taken for the experiment to be 5 x 10^9 secs (≑ 10,000 days) while 10^{-5} gives a time of 50 seconds which is more reasonable. Hence either the sticking coefficient of oxygen on cadmium sulphide crystals obtained by Campbell and Farnsworth (1968) is incorrect or in D.C. field effect experiments the oxygen atoms do not act as trapping centres as proposed by Many et. al. The role of oxygen will be considered further in section 6.1.4.

4.1.7 Oxygen adsorption at atmospheric pressure

Typical changes in the conductivity when the films were allowed to atmospheric pressure are shown in figure 4.6(a).

For convenience both curves have been plotted on arbitrary scales. Curve A is typical of a very thin film (100 nanometres thick) and shows a large change in the


CURRENT CHANGE (arb. units)
4
3
2
1
0
curve B
curve A
0
200
TIME (secs.)
800
1000
CURRENT CHANGE (arb. units)
3
2
1
0
curve B
curve A
10^2
10^3
10^4
TIME (secs.)

(a)

(b)

FIGURE 4.6

dark conductivity when exposed to the atmosphere. The dark conductivity when exposed to the atmosphere was one percent of its value under ultrahigh vacuum. Curve B is typical of the results obtained with thicker films. The curve shown is for a film 255 nanometres thick and the change in the dark conductivity when it is exposed to the atmosphere is much smaller (the dark current at atmosphere is 10 percent of its value under ultrahigh vacuum conditions). In figure 4.6(b) curves A and B are shown plotted on a logarithmic time scale. The frequency changes observed were meaningless as they were affected by hydrostatic damping and therefore have not been plotted.

From the two graphs of the curves it can be seen that the dark conductivity approaches its new equilibrium value when exposed to the atmosphere at a faster rate in the case of the thinner films. This is as would be expected because the conducting electrons are closer to the surface in thinner films and hence will be affected by changes in the surface properties at a faster rate than in the case of thicker films.

The plot of the decay of the dark current against the logarithm of time for the thicker film follows an Elovich type equation much more closely than in the case of a thin film. This is to be expected as the assumption of the Elovich equation, that the electrons are being drawn from the bulk across a potential barrier, is more closely approximated in the case of the thicker films, as the barrier is 20 to 30 nanometres wide. If even thicker films had been studied the trend in the shape of the curves in figure 4.6(b) suggests that results similar to those of Mark (1964), who used crystals, would have been obtained.

The reason for the initial rise in the dark conductivity in the case of the thicker film (curve B) is not known but its occurrence has been reported previously for crystals (Mark 1964).

The initial rise in the dark current occurred for the thicker films but not the thin films. Its occurrence is also dependent on the rate at which the vacuum system attains atmospheric pressure from ultrahigh vacuum conditions. When the vacuum pressure was raised rapidly to atmospheric pressure the peak occurred, but when the rate of rise to atmospheric pressure was much slower the peak did not occur.

When the films were restored to ultrahigh vacuum conditions, which takes several hours, it was found that the dark conductivity returned to a value lower than its initial value. The reason for this will at this stage be given as that oxygen molecules have diffused into the surface region of the crystallites of which the film is composed. As oxygen acts as either a trap or a recombination centre it will thus reduce the conductivity. This will be discussed further in section 6.2.3.

CHAPTER 5

PHOTOEFFECTS AND OXYGEN ADSORPTION

5.1.1. Introduction

In the previous chapter the adsorption and desorption of oxygen from the surface of cadmium sulphide films has been studied with the cadmium sulphide films under dark conditions. The experiments reported and discussed in this chapter have been performed with the cadmium sulphide films exposed to various wavelengths of illumination to determine if either photo-adsorption or photo-desorption occur. In every experiment in which the quartz crystal oscillator could be used unambiguously as a mass change measuring device, no evidence of either photoadsorption or photodesorption was obtained. This was a consistent result for all of the cadmium sulphide films studied, even when the 10.7 megahertz quartz crystals were used to improve the sensitivity with which mass changes could be measured.

As has been pointed out in chapter 1, the evidence presented by Mark (1964) that photo-adsorption occurs on the surface of cadmium sulphide crystals, was obtained by comparing the time taken for the sample to reach its new dark conductivity when exposed to the atmosphere under dark conditions with the time taken for the sample to reach its dark conductivity when it has been exposed to bandgap illumination for part of the time in which it is decaying to its dark conductivity at atmospheric pressure. Because the dark conductivity at atmospheric pressure was reached faster when the cadmium sulphide crystal had been illuminated, it was taken as evidence that photoadsorption had occurred. It was also pointed out that Schubert and Boer (1971) have explained the above result without recourse to photo-adsorption.

It was also shown in chapter 1 that the slow light induced phenomena observed in cadmium sulphide could be explained in terms of the photo-adsorption of gas molecules (Mark 1964, Lawrance 1964) or alternatively by other theories which do not involve gas adsorption (Tscholl 1968, Nicholas and Woods 1964). Hence the following experiments have been performed to determine the amounts of oxygen present on the surface of cadmium sulphide films under various illumination conditions.

5.1.2 Rate of decay to the dark conductivity when exposed to the atmosphere for illuminated and non-illuminated conditions

A comparison of the rate of decay to the dark conductivity when exposed to the atmosphere for dark conditions with the rate of decay to the dark conductivity for illuminated conditions was made first to determine if the cadmium sulphide films being studied gave results similar to those reported by other authors for cadmium sulphide crystals. In each experiment the film was exposed to the atmosphere under dark conditions and while the dark conductivity was decaying the film was illuminated, to determine whether or not the rate of decay increased.

The results have been plotted in figure 5.1. Figure 5.1(b) is typical of the results for the cadmium sulphide films studied and figure 5.1(a) is typical of the results for cadmium sulphide crystals (from Bube 1966). The frequency changes observed were not significant due to hydrostatic damping effects and have not been plotted. From figures 5.1(a) and (b) it can be seen that the behaviour of the films differed from the behaviour of crystals in that an enhanced rate of decay of the conductivity due to illumination was not observed i.e., the dark conductivity did not decay to its new equilibrium any faster when it was illuminated than when it was not illuminated. This was true for both band gap illumination and white light for a number of the films studied.

Hence the results obtained for the cadmium sulphide films indicate that the mechanism proposed by Schubert and Boer (1971) i.e., that the role of the light is to enhance the redistribution of the charge carriers in the crystals, explains the observed increase in the rate of decay of the conductivity in the

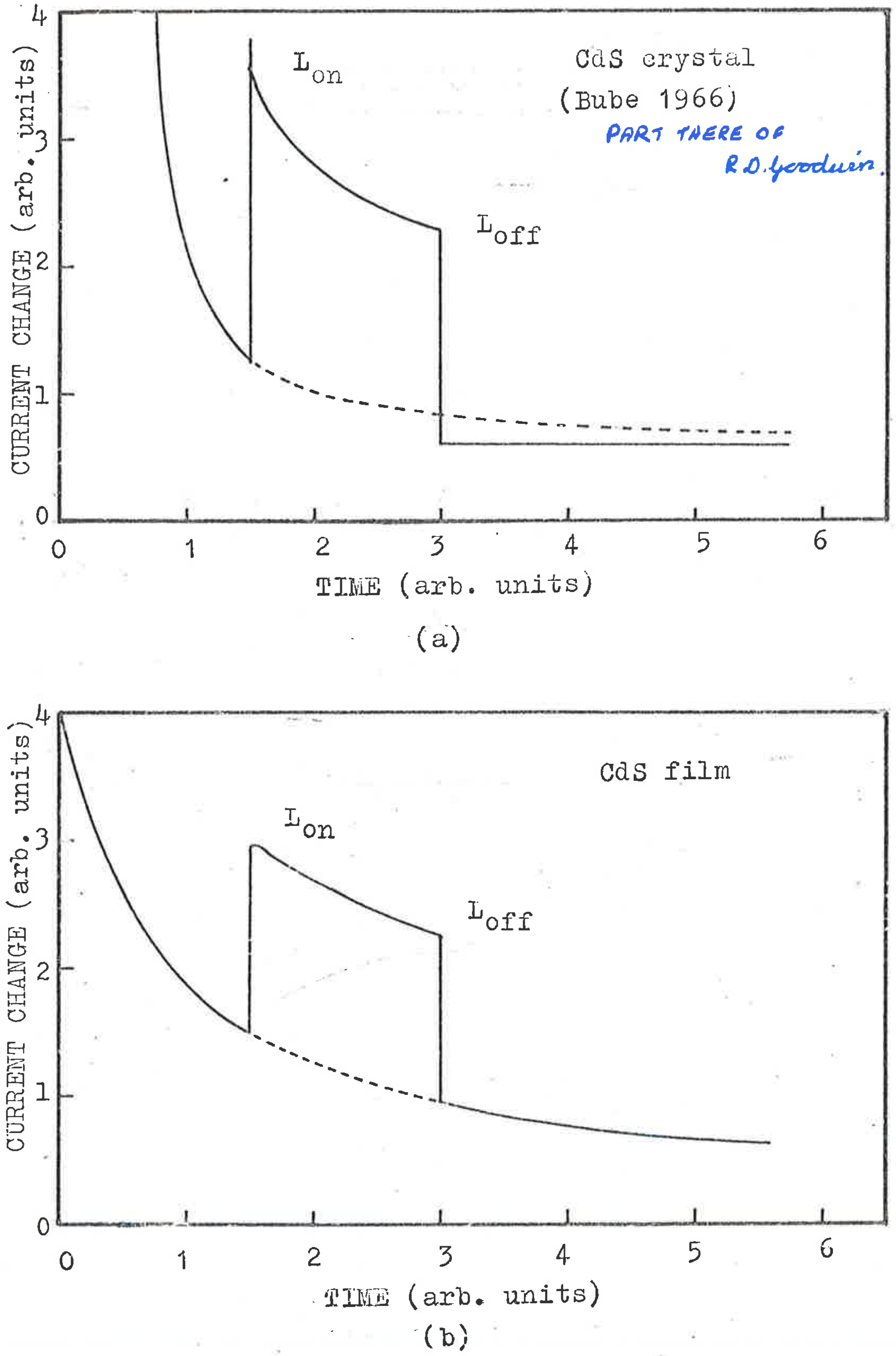


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FIGURE 5.1

case of cadmium sulphide crystals. For the thin cadmium sulphide films studied the average distance between the charge carriers and the surface is sufficiently small that the diffusion of the carriers to the surface is not the rate limiting factor in the decay of the dark conductivity at atmospheric pressure and hence illumination is not needed to enhance the rate of diffusion of the electrons to the surface .

5.1.3 Oxygen adsorption at pressures of 10^{-8} to 10^{-1} torr, and the effect of illumination

To determine whether or not illumination enhanced the rate of adsorption of gases onto the surface of the cadmium sulphide films the experiments discussed in section 4.1.3. were repeated with the sample subjected to either band gap illumination or to white light whose intensity had been reduced sufficiently that it did not affect the frequency of the quartz crystal by heating. The results obtained were identical to those obtained with the sample not illuminated i.e., the rate of uptake of oxygen did not change within the limits of experimental error, which was ± 0.4 hertz due to the difficulty in reproducing a given pressure. Thus the experiment suggests that either photo-adsorption does not occur to a marked extent in the case of cadmium sulphide films or that the amount of oxygen involved in photo-adsorption is less than 0.02% of a monolayer. This result does not agree with that of Campbell and Farnsworth (1968) who found that the sticking coefficient and hence rate of adsorption, of oxygen on cadmium sulphide crystals increased by at least one order of magnitude when the crystal surface was illuminated. If a change in sticking coefficient of one order of magnitude had occurred for the films studied, a marked increase in the rate of adsorption of oxygen and in the equilibrium surface coverage would have been observed.

As in the previous section the explanation of the difference in the rates of adsorption for cadmium sulphide crystals and films most likely lies in the fact that in the case of films there are many more conduction band electrons close to the surface and the rate of supply of electrons is not the factor limiting the rate of adsorption of oxygen. The resistivity of the films studied was approximately 100 ohm/cm. whereas the crystals studied by Campbell and Farnsworth were very high resistance, probably of the order of 10^{10} to 10^{11} ohm/cm. although no actual values are given.

5.1.4 Infrared Photoconductivity

In chapter 3 the experimental results pertaining to infrared photoconductivity have been discussed in relation to the spurious mass changes obtained. The experiments were repeated for the films for which the spurious mass changes had been eliminated. The infrared photoconductivity in the 3,200 to 700 nanometres wavelength range was studied at various vacuum pressures between 10^{-8}torr. and atmospheric pressure with the sample initially in either dark conductivity conditions or exposed to low intensity band gap illumination. The secondary illumination was used to provide more conduction band electrons which would raise the fermi level and consequently increase the occupancy of trapping levels within the forbidden energy gap. The possibility that the secondary illumination empties some trapping levels within the forbidden energy gap also exists. If the trapping levels had discrete energies there would be an increase in the photocurrent when the infrared wavelength was such that electrons could be excited from a trapping level into the conduction band.

The photocurrent was recorded by amplifying the change in voltage appearing across a 44 K ohm resistor connected in series with the cadmium sulphide film. The results obtained were similar to those presented in chapter 3. No changes in frequency were observed for any of the combinations of experimental conditions used. The photo-current showed a slow but fairly uniform increase with decreasing wavelength until near the band gap edge when the rate of change of photocurrent with wavelength increased sharply. Thus if the increasing photocurrent is due to trap emptying, then the energy distribution of the traps must be quasi-continuous, i.e., while it is expected that each trapping level has a discrete energy, the energy spacing of the trapping levels is less than the resolution of the monochromator in the wavelength range studied.

The first infrared wavelength scan of every film at atmospheric pressure showed a small increase in the photocurrent at approximately 0.83 eV. On subsequent scans this energy level did not appear. The energy level could be made to reappear by baking out the vacuum system and hence the cadmium sulphide film between 100° C and 200° C at 10^{-6} torr. for several hours. The peak would then disappear again after the first infrared wavelength scan at atmospheric pressure.

Nicholas and Woods (1964) studied a trapping level occurring at 0.83 ev. in cadmium sulphide crystals by the method of thermally stimulated conductivity. They proposed that the 0.83 ev. centre was a complex aggregate of point defects which dissociated when an electron was ejected thermally into the conduction band. Once the electron had been ejected the trapping level no longer existed. Thus the trapping level at 0.83 ev. studied by Nicholas and Woods shows similar behaviour to the 0.83 ev. level found in the cadmium sulphide films in that both are destroyed when the trapped electron is removed from them. The method of creation of the 0.83 ev. level in the cadmium sulphide crystals was however different to that used to create the level in the films.

Nicholas and Woods produced the 0.83 ev. centre by illuminating the cadmium sulphide crystals with light from a one kilowatt tungsten lamp while the crystal temperature was held between -50° C and +20° C. In section 5.2.1 it is pointed out that using a light source of such a power level will cause considerable heating in the near surface region of the cadmium sulphide crystal. Hence thermal desorption of oxygen possibly occurred but as the vacuum pressure at which the crystal was illuminated was not given no conclusions as to whether desorption occurred can be reached on the basis of the results of Schubert and Boer (1971) which are discussed in section 5.2.1. Nicholas and Woods also found that baking the cadmium sulphide crystals at 100° C removed all trace of the 0.83 ev. trap. Again the vacuum pressure is not given, nor is it indicated whether or not the crystals were illuminated, and thus again no definite comparison with the behaviour of the cadmium sulphide films studied can be made. It can only be said that if the same 0.83 ev. is being studied the method of producing the level in cadmium sulphide crystals is not the same as the method used to produce the level in the cadmium sulphide films studied.

The results obtained do however indicate that if the 0.83 ev. trap observed in the cadmium sulphide films was the trapping level observed in cadmium sulphide crystals then it is not a photochemical effect because it was produced in the cadmium sulphide films studied without illumination.

Because a bakeout at 10^{-6} torr was required to restore the 0.83 ev. level in the cadmium sulphide films the diffusion of defects is implied. These defects could be sulphur and cadmium lattice vacancies. If the results of Bootsma (1968) given in section 1.2.1, are considered the result of bakeout would be either the formation of sulphur dioxide with oxygen atoms being substituted at sulphur lattice sites or purely the desorption of sulphur dioxide from the surface. Both processes would cause a decrease in the weight of the cadmium sulphide film. The first process would result in a decrease in the conductivity as oxygen is more electronegative than sulphur and hence when in a sulphur lattice site will act as an electron trap. The second process would cause an increase in the conductivity as the crystal will be left with excess cadmium atoms which are electron donors.

Increases in both the frequency and dark conductivity were observed after each bakeout at 10^{-6} torr. but only the increase in the dark conductivity provided acceptable experimental evidence as the increase in frequency can equally as well be attributed to stress relaxation within the quartz and in the bonding between the gold electrodes and the quartz. In fact an increase in the frequency of each quartz crystal was observed after the bakeout prior to the evaporation of each cadmium sulphide film indicating that stress relaxation had occurred.

Hence although the changes observed in the dark conductivity indicate the formation of sulphur lattice vacancies no definite conclusions can be reached unless the system is modified so that the mass spectrometer can be used to analyze the gases present during bakeout and a large area cadmium sulphide film used to improve the sensitivity. If the 0.83 ev. trapping level observed is the same as the one studied by Nicholas and Woods then the method of production used, i.e., baking the films under dark conditions would indicate that it is not a photochemical effect.

5.2 Photoeffects and mass spectrometry

5.2.1 Introduction

The permanent increase in the dark current of cadmium sulphide crystals, previously exposed to air, which occurs after illumination under high vacuum conditions has been presented by various authors e.g. Mark (1965) as evidence that photodesorption occurs. Schubert and Boer (1971) have explained the observed increase in the dark current without recourse to photodesorption. They propose that the intensity of illumination used for such experiments causes considerable heating of the surface region and that thermal desorption rather than photo-desorption occurs. Experimentally Schubert and Boer found that 3×10^{15} oxygen atoms / cm.^{2} can be thermally desorbed from the surface of cadmium sulphide crystals and that the shift in the band gap edge observed when the cadmium sulphide crystals studied were illuminated corresponded to a temperature rise of 25° C.

Genequand (1971) supports the contention of Schubert and Boer by pointing out that most photodesorption experiments have been performed using light intensities such that the radiative power focussed on the sample was of the order of one watt. As most of the incident light energy is believed to be adsorbed in the near surface region (Bujatti 1961), the actual adsorption depth for cadmium crystals is not given by the author, and as semiconductors are poor thermal conductors, the illumination will cause large changes in temperature in the near surface region. Thus thermal desorption rather than photo-desorption will occur.

Experiments were conducted in an attempt to determine whether or not these same effects occurred in cadmium sulphide films. The effect of illumination of various wavelengths on the partial pressures of the gases present in the vacuum system was determined using either the monochromator whose radiative power was sufficiently small to avoid thermal desorption as the source of illumination, or a focussed 55 watt white light source whose radiative power was sufficient to cause thermal desorption as the source of illumination. That heating occurred in the case of the white light source was verified by the quartz crystal oscillator which showed a typical temperature shocked response when the white light source was turned on. (Frequency changes of up to 400 hertz were observed). For the light from the monochromator no changes in the frequency of the quartz crystal oscillator occurred implying that an insignificant amount of heating (less than a 1° C temperature change) occurred.

5.2.2 Mass Spectra and Band Gap Illumination

The cadmium sulphide film was first exposed to air at atmospheric pressure under either dark or bandgap illumination conditions (although previous experiments had suggested that photo-adsorption did not occur) until the conductivity reached steady state conditions. The system was then re-evacuated to a base pressure near 10^{-8} torr. using only the diffusion pump and the ion pump. The partial pressure of oxygen in the system was about 10^{-9} torr. The titanium sublimator could not be used as it would have illuminated the sample. The cadmium sulphide film was then subjected to band gap illumination from the monochromator using the A slits (2×10^{14} photons / sec.). By using back off on the voltage output of the mass spectrometer changes in the partial pressure of a gas species of the order of 10^{-11} torr. were detectable. For a monolayer of gas approximately 10^{15} molecules / sq. cm. will be desorbed. At 10^{-11} torr. there are 3×10^{5} molecules / c.cm. and the volume of the vacuum system is approximately 10 litres. The pumping speed of the ion pump (11 litres / sec.) must also be taken into consideration as this will decrease the magnitude of the pressure change observed. Hence a numerical change in the number of molecules in the vacuum system of the order of 10^{10} should be detectable.

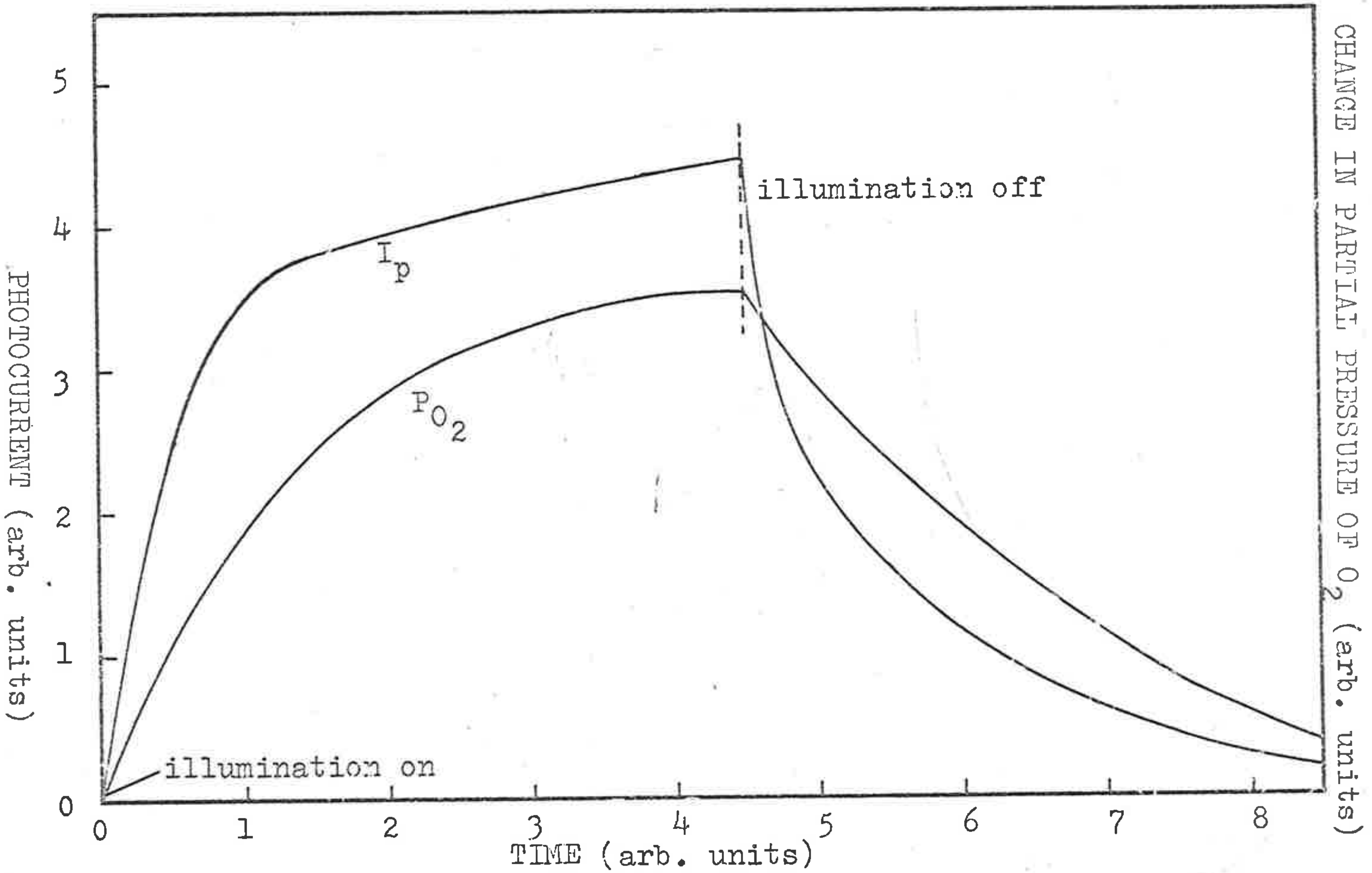
No change in the partial pressures of any of the gases present in the vacuum chamber could be detected when the films were exposed to the atmosphere under dark conditions prior to illumination or when the films were exposed to the atmosphere and band gap radiation prior to illumination. Thus the results obtained indicate that either photodesorption does not occur or that the number of molecules photodesorbed is much less than a monolayer. Hence the results obtained by mass spectrometry agreed with those obtained with the quartz crystal oscillator.

5.2.3 Illumination with white light

In section 4.3.1 it was pointed out that Schubert and Boer (1971) and Genequand (1971) considered that the effect of illuminating cadmium sulphide with white light was to cause thermal desorption due to heating effects rather than photo-desorption. The treatment of the cadmium sulphide prior to illumination was the same as in section 5.1.2 except that the monochromator was replaced by the white light source. The results obtained are shown in figure 5.2. The photocurrent and the partial pressure of oxygen in the vacuum system have both been plotted against time with t = 0 corresponding to the instant at which the illumination was switched on. The frequency changes have not been plotted as they were meaningless because the quartz crystal was in a temperature shocked state.

The effect of the white light was to increase the partial pressure of oxygen in vacuum system. Hence the white light must be causing desorption from the cadmium sulphide films. It must be remembered however that because the white light source cannot be focussed to

FIGURE 5.2


PHOTOCURRENT (arb. units)
CHANGE IN PARTIAL PRESSURE OF O_2 (arb. units)
TIME (arb. units)
0
1
2
3
4
5
6
7
8
I_p
P_{O_2}
illumination on
illumination off

illuminate only the surface of the cadmium sulphide films it can also cause desorption from the walls of the vacuum system. Desorption from the walls could not be prevented by baking the vacuum system as this would have also desorbed the cadmium sulphide film. Any gas desorbed from the walls is however most likely typical of the desorption from the cadmium sulphide film as the section of the vacuum system illuminated has cadmium sulphide deposited on it during the evaporation. Desorption from the cadmium sulphide deposited on the walls will increase the sensitivity as desorption is occurring from an increased surface area.

The dark conductivity, after illumination under ultrahigh vacuum conditions, has a higher value than prior to illumination. In section 4.1.8 it was pointed out that the dark conductivity under ultrahigh vacuum conditions decreased after the cadmium sulphide film had been exposed to the atmosphere. This was attributed, without any reason being given, section 4.1.7, to the diffusion of oxygen atoms into sulphur lattice vacancies. If this does occur then illumination with white light reverses the process. The diffusion of oxygen into lattice vacancies as the mechanism was selected because Schubert and Boer had found that 3×10^{15} oxygen atoms / cm.^{2} were desorbed, i.e., more than one monolayer of oxygen. The position in the lattice of the adsorbed cadmium sulphide will be discussed further in section 6.1.4

In the case of the cadmium sulphide films studied the gas desorbed was predominantly diatomic oxygen with some evidence of the desorption of water vapour as well. Why Schubert and Boer observed monatomic oxygen could possibly be attributed to the very close proximity of their mass spectrometer to the surface of the cadmium sulphide crystals. In the vacuum system used for the study of the cadmium sulphide films the mass spectrometer was either 15 cms. or 30 cms. from the cadmium sulphide films depending on which 1½" port was used for mounting. Hence monatomic oxygen, if desorbed, may have recombined to form diatomic oxygen.

When the experiments were repeated using white light of a sufficiently low intensity to avoid the temperature shocks which affect the quartz crystal there was no detectable desorption of oxygen. To avoid temperature shocks the temperature change must be less than 1°C (Stockbridge and Warner 1962). Thus the results obtained support the contention of Schubert and Boer (1971) that white light causes thermal desorption rather than photo-desorption from the surface of cadmium sulphide.

For further investigation of the desorption products it would be desirable to use a much larger area film in a small ultrahigh vacuum chamber in order to maximize the changes in partial pressures as the background noise on the mass spectrometer was comparable with the magnitude of the pressure changes observed. The illumination system would need to be arranged such that only illumination of the cadmium sulphide film occurred to avoid desorption from other parts of the vacuum system. Thermal desorption experiments using joule heating of the cadmium sulphide films could also be performed to check the results. It would be desirable to use joule heating of the cadmium sulphide films as this would minimize the heating of the other parts of the vacuum system.

CHAPTER 6

Summary of results and Conclusions

6.1.1 Introduction

In this chapter the results presented in the preceeding chapters are summarized and conclusions drawn with regard to the meaning of the results obtained. In particular the results are discussed in consideration of the theories presented in chapter 1 to show which of the theories the results support. The chapter is then concluded by briefly discussing experiments which could lead to a further understanding of the properties of cadmium sulphide.

6.1.2 Preparation and study of cadmium sulphide films

The results of Hughes and Carter indicated that cadmium sulphide films could be prepared with consistent properties provided that they were prepared under ultra-high vacuum conditions. The results obtained with the cadmium sulphide films studied in this thesis indicated that other factors, which could not be determined, were also affecting the properties of the films deposited. Hence films which were not of uniform thickness and were not yellow in colour were rejected. It was also found that the nature of the substrate affected the deposition of the films for reasons which could not be determined conclusively. The effect of the substrate on the deposition was attributed to different nucleation centres being present on the gold and quartz surfaces and was discussed in section 2.3.6.

The results obtained also indicate that the surface of a cadmium sulphide film is contaminated by adsorbed gases at pressures above 10^{-6} torr, and hence the properties of cadmium sulphide are affected by adsorbed gases in experiments performed in vacuum pressures higher than this value.

6.1.3 The suitability of the quartz crystal oscillator for the study of adsorption on cadmium sulphide films

From the experimental results presented in chapter 4 it can be seen that the quartz crystal oscillator in its present form is not suitable for the study of the effect of gases on the properties of cadmium sulphide as the amounts of gas involved are too small to be measured. An improvement in the sensitivity of one order of magnitude could be obtained by controlling the room temperature to ± 1°C. This would enable the amount of gas present on the surface in the 10^{-3}torr. to 10^{-4}torr region to be measured but whether the improvement in sensitivity is worthwhile is questionable as far as photo-effects are concerned as the experiments conducted in the 10^{-2} to 10^{-1}torr. range indicate that the increased amount of oxygen adsorbed, if any, by photo-effects is probably too small to be measured. An improvement in the sensitivity of the quartz crystal oscillator would however, enable a more accurate measurement of the rate of adsorption of oxygen under dark conditions and hence provide more insight into the nature of the adsorption mechanism.

One possible application of a more stable quartz crystal oscillator could be in the determination of the nature of the 0.83eV peak which was observed in the infrared photoconductivity curves. With improved stability the cadmium sulphide film could be weighed before and after the 0.83eV peak occurred. If a frequency change was observed it could give some idea as to the nature of the reaction which causes the 0.83eV peak. However a calculation of the approximate number of electrons involved, the assumptions made in the calculation being that an ambient gas atom is involved, that each atom releases one electron, and that the electron mobility is 1 cm.^{2}/volt-sec. ~~cm/sec/volt~~, indicates that the number of gas atoms involved is several orders of magnitude less than the minimum sensitivity of the crystal oscillator and hence it is doubtful if a change in frequency would be observed.

Possibly the best use of the quartz crystal oscillator that could be made is a study of the nature of the nucleation centres present on the substrates by determining the nucleation times, as in section 2.3.6 for different pre-evaporation surface treatments. The experimental arrangement to be used in such experiments is discussed briefly in section 6.1.7.

6.1.4 The role of oxygen in the conductivity and photoconductivity of cadmium sulphide films

It was pointed out in section 1.3.3 that the role of oxygen in the various processes occurring in cadmium sulphide is not definitely known and the conclusion was reached that it would be worthwhile to try to measure the amount of oxygen present on the surface of cadmium sulphide under various experimental conditions. The experiments performed have been described in chapters 4 and 5. The quartz crystal oscillator results indicated that more than one hundreth of a monolayer of oxygen was only adsorbed on the surface of cadmium sulphide films at pressures higher than 10^{-3}torr. As the oxygen was spontaneously desorbed on re-evacuation of the vacuum system the experimental results indicate that the oxygen was only physically adsorbed. The results obtained by mass spectrometry in chapter 5 indicate that when the films are exposed to oxygen at atmospheric pressure some oxygen can be subsequently removed by heating under ultrahigh vacuum pressures. It was proposed that this was oxygen that had diffused into the surface layers of the cadmium sulphide film. The effect of oxygen, whether adsorbed on the surface or diffused into the surface is to decrease the conductivity. The question to be resolved is whether the oxygen decreases the conductivity by acting as a trapping centre or by acting as a recombination centre.

The mechanism, proposed by Mark (1965), by which oxygen acts as a recombination centre is as follows. When an oxygen molecule is adsorbed on the surface it is first converted into a negative ion at the site of a trapped electron. The second step in the recombination process is the neutralization of the negative oxygen ion by a neighbouring trapped hole. Hence there is now one less trapped electron-hole pair and the neutral oxygen molecule. By this mechanism each adsorbed oxygen atom may cause many trapped electron-hole pairs to recombine. When oxygen adsorption occurs the surface density of trapped electron hole pairs is believed to decrease from $10^{14}/cm^2$. to $10^{11}/cm^2$. If oxygen atoms act as recombination centres such a decrease could occur without the adsorption of a detectable amount of oxygen. If, however, the electron-hole pair numbers are decreased to $10^{+11}/cm^2$. by the trapping of electrons at the surface by oxygen atoms, 10^{14} oxygen atoms/cm.^{2} must be trapped at the surface and hence a change in frequency should be detectable. Thus the results obtained with the cadmium sulphide films suggest that oxygen acts as a recombination centre rather than a trapping centre.

As there is some doubt as to the existence of the electron-hole pairs the number of oxygen molecules required to cause the observed decreases in the conductivity can also be calculated on the basis of the assumption that each oxygen atom removes one electron from the conduction band. If we assume the electron mobility is 1 ~~cm./volt/sec~~ cm^2/volt-sec. (Lawrance 1964) and take typical figures for the dark current and the change in the dark current, when the film is exposed to oxygen at 10^{-1}torr. and the film thickness then the number of oxygen molecules needed to cause the observed changes in dark current by electron trapping can be calculated. The number of electrons trapped at the surface is then of the order of 10^{11} to 10^{12}/sq.cm. i.e., an amount too small to be measured. Hence if charge trapping occurs under the conditions as specified by the above assumptions the amount of oxygen involved would be too small to be measured and hence whether the oxygen molecules are acting as trapping centres or recombination centres could not be determined conclusively on the basis of the quartz crystal oscillator results.

The theories of Mark (1965) and Many et. al. (1969) as to the role of adsorbed oxygen on the surface of cadmium sulphide crystals will now be discussed with reference to the results reported in this thesis to show that the theoretical predictions of Mark and Levine (1966) the results of Many et. al., and the results presented here are reconcilable if the adsorbed oxygen atoms act as recombination centres.

The theoretical prediction of a large density of trapped electrons at the surface of cadmium sulphide crystals by Mark and Levine and the failure to observe band bending at the surface of cadmium sulphide crystals led Mark to propose that equal numbers of electrons and holes are trapped in close proximity to each other at the surface to preserve charge neutrality throughout the crystals. This concept of electron-hole pairs was used in chapter 3 to explain the fine structure observed on the spurious mass change curves. That Many et. al. failed to observe any intrinsic surface states would be explained by all the trapping levels being occupied i.e., the electron traps lie below the fermi level when the CdS is under high vacuum conditions.

When the CdS film is exposed to an oxygen ambient the adsorbed oxygen atoms would act as recombination centres, empty some electron trapping levels and hence lower the fermi level. The emptied trapping levels would then be detected by D.C. field effects. Thus a few oxygen atoms would produce a much larger number of trapping levels and explain why the amount of adsorbed oxygen measured using the quartz crystal oscillator was less than that required by Many et. al. to explain their D.C. field effect results in terms of adsorbed oxygen acting as electron traps. Oxygen acting as a recombination centre will also remove the disagreement, discussed in section 4.1.6, between the sticking coefficient of oxygen on CdS crystals as measured by Campbell and Farnsworth (1968) and the sticking coefficient of oxygen of CdS crystals as deduced from the experimental results of Many et. al. The model of oxygen acting as a recombination centre is also compatible with the experimental evidence that the oxygen is only physically adsorbed on the surface.

Thus it can be seen that the model of oxygen acting as a recombination centre provides an unambiguous explanation of the results for cadmium sulphide crystals and films presented here.

6.1.5 Nature of the Slow States

In chapter 1 the three theories concerning the nature of the slow states in cadmium sulphide have been presented. The theory of particular interest was that of Mark (1965), that the slow-states were due to the photo-adsorption of oxygen at the surface. If this was the correct theory then the quartz crystal oscillator might enable the measurement of the amount of oxygen involved. It was also pointed out that the region of origin of the slow states is unknown. A comparison of the results of

Sawamoto (1965), who studied what are believed to be surface states, and the results of Nicholas and Woods (1964), who studied what are believed to be bulk effects, indicated that the same set of slow states was studied by both authors. This was discussed in section 1.2.2.

Sawamoto considered that the density of one of the slow states that he studied was greater than 10^{12}/cm.^{2} and hence if this state arose from adsorbed gas effects it might be detectable with the quartz crystal oscillator. The slow state had a cross-section of 10^{-13} cm^2, i.e., it was an attractive centre to electrons in the conduction band, and it had an energy level of 0.82 eV below the conduction band. Hence it has similar properties to the energy level at 0.9 eV below the conduction band which is believed to be formed by chemisorbed oxygen atoms.

The experiments discussed in chapter 4 showed no sign of the chemisorption of oxygen during illumination if, as explained previously, the amount of oxygen physically adsorbed on the surface is independent of the amount of oxygen chemically adsorbed on the surface. Hence either the density of the slow states is less than 10^{13}/cm.^{2} the minimum number detectable, or they do not arise from adsorbed gas effects. Thus while the results obtained do not conclusively prove that the slow states do not arise from adsorbed gas effects they do indicate that there is a considerable element of doubt in the explanation presented by Mark (1965).

6.1.6 Photoadsorption and Photodesorption

As discussed in section 5.1.3 none of the experimental results obtained showed evidence that either photo-adsorption or photodesorption occurred for cadmium sulphide films. The results obtained are typical of small crystallites, and the experimental evidence indicated that the films consist of many small crystallites e.g. the kinetics of evaporation of the cadmium sulphide films section 2.3.6 and the voltage current characteristics section 2.3.7. If it is assumed that the results are also typical of single crystals then the explanation given by Schubert and Boer (1971) to explain the results previously given by Mark (1965) evidence of photo-adsorption and photo-desorption, i.e., that the role of illumination is to accelerate the redistribution of the charge carriers and to cause thermal desorption, is supported by the evidence presented in this thesis.

6.1.7 Future Experiments

The results reported in this thesis indicate that the most useful application of the quartz crystal oscillator to the study of the properties of cadmium sulphide would be in determining the nature of the nucleation centres. The nucleation times for various pre-deposition treatments could be measured with one quartz oscillator which would be shielded from the evaporator by a shutter until the rate of evaporation of cadmium sulphide is constant. A second quartz crystal oscillator which had already been coated with cadmium sulphide and hence in region 3 of the evaporation kinetics, section 2.3.6, would be exposed continuously to the evaporator to determine when the evaporation rate had reached a constant value, and hence when to open the shutter. The evaporation rate must be the same for each experiment.

To obtain further information concerning the nature and the location of the slow states in either crystals or films of cadmium sulphide both the thermally stimulated conductivity and the D.C. field effects of each crystal or film should be studied to determine whether or not both experimental methods are studying the same set of trapping levels. The effect of adsorbed oxygen on the conductivity of cadmium sulphide films indicates that some of the measurements should be made under ultrahigh vacuum conditions. That further investigation of the properties of cadmium sulphide by the method of thermally stimulated currents is desirable is indicated by a recent paper by Zhdan and Messere (1971) who report anomalous narrow peaks in the thermally stimulated conductivity curves which are accompanied by large increases in the pressure in the vacuum system (i.e., 2 x 10^{-6} torr to

5 x 10^{-5} torr.). They attribute the pressure changes to the desorption of gas from the surface of the cadmium sulphide crystal and have estimated that a monolayer of gas is involved. With modifications to the ultrahigh vacuum system these results could be checked with the mass spectrometer enabling identification of the gas species involved. It is surprising however, when the magnitude of the observed pressure changes is considered, that the effect was not observed during studies of thermally stimulated currents by other authors. Unless further experimentation indicates that the density of the surface states present in cadmium sulphide films is greater than $10^{12}/cm^2$, which is near the limit of sensitivity for a quartz crystal oscillator, further study of the nature of the slow states with the quartz crystal oscillator would be fruitless.

REFERENCES

Archer R.T. J. Opt. Soc. of America, 1962, vol. 52, no. 9, P970

Baker M.A., Laurenson L. Vacuum, 1967, vol. 17, no. 12, P647

Boer K.W. Physica, 1954, vol. 20, P1103

Boer K.W., Boyn T., Goede O., Phys. Stat. Solidi, 1964, vol. 3, P1684

Bootsma G.A. Surface Science, 1968, vol. 9, P396

Bube R.H. "Photoconductivity of Solids" 1960

Bube R.H. J. Phys. Chem. 1957, vol. 1, P234

Bube R.H., Dussel G.A., Ho C.T., Miller L.D. J. Appl. Phys. 1966, vol. 37, no. 1, P21

Bube R.H., Im Ho B., Matthews H.E., J. Appl. Phys. 1970, vol. 41, no. 6, P2581

Bube R.H., Shear H., Hilton E.A., J. Electrochem. Soc. 1965, vol. 112, no. 10, P997

Bujatti M. J. of Appl. Phys. 1969, vol. 40, no. 1, P2965

Campbell B.D., Farnsworth H.E. Surface Science, 1968, vol. 10, P197

Elovich S.Yu. J. Phys. Chem. (U.S.S.R.) 1939, vol. 13, P1761

Faeth P.A. J. Electrochem. Soc., 1967, vol. 114, no. 5, P511

Haas K.J., Fox D.C., Katz M.J. J. Phys. Chem. Solids 1965, vol. 26, P1779

Hughes D.M., Carter G. Vacuum, 1967, vol. 17, no. 10, P555

Johnson J.E. Vacuum Microbalance Techniques, 1964, vol. 4, P81

King W.H. Vacuum Microbalance Techniques, 1971, vol. 8, P183

Langmuir I. "The Collected Works of Irving Langmuir vol. 9, 1961

Lawrance R. Ph.D. Thesis, University of Adelaide 1964

Macdonald R.J. Proc. of the Radio Research Board Symposium (Adelaide) 1966, P11

Mark P. J. Phys. Chem. Solids 1964, vol. 25, P911

Mark P. J. Phys. Chem. Solids 1965, vol. 26, P1767

Mark P. R.C.A. Review 1965, vol. 26, no. 4, P461

Mark P., Levine J. Phys. Rev. 1966, vol. 144, no. 2, P751

Many A., Shappir J., Shaked U. Surface Science 1969, vol. 14, P156

Many A., Shappir J., Surface Science 1969, vol. 14, P169
Medved D.B. J. Phys. Chem Solids 1961, vol. 20, P255

Nicholas K.H., Woods J. Brit. J. Appl. Phys. 1964,
vol. 15, P1361

Ogawa T., Oikawa H., Kojima A. Jap. J. Appl. Phys. 1971,
vol. 10, no. 5, P593

Pauling L., "Nature of the Chemical Bond" 1945

Reynolds D.C., Czyzak S.J., Allen R.C., Reynolds C.C.
J. Opt. Soc. Am. 1965, vol. 45, P136

Sauerbrey G. Z. Phys. 1959, vol. 155, P206
Sawamoto K. Jap. J. of Appl. Phys. 1965, vol. 4, no. 3,
P173
Schubert R., Boer K.W. J. Phys. Chem. Solids 1971,
vol. 32, P77
Shallcross F.V. R.C.A. Review 1967, vol. 28, no. 4, P569
Shiojiri M., Hasegawa Y., Murata Y., Matsumura S. Jap.
J. Appl. Phys. 1969, vol. 8, P783
Smith R.A. Phys. Rev. vol. 97, no. 6, P1531
Stockbridge C.D., Vacuum Microbalance Techniques 1966,
vol. 5, P147
Stockbridge C.D. Vac. Micro. Tech. 1966, vol. 5, P179
Stockbridge C.D., Warner A.W. Vac. Micro. Tech. 1962,
vol. 3, P55

Tscholl E. Phillips Research Reports Supplements 1968,
nos. 1-6, no. 6

Weber E.H. Phys. Stat. Solidi 1969, vol. 36, P175
Wedland P.H. J. Opt. Soc. Amer. 1962, vol. 52, P581
Williams R. J. Phys. Chem. Solids 1962, vol. 23, P1057
Wilson J. Appl. Phys., 1966, vol. 37, P1932

Zhdan A.G., Messerer M.A. Soviet Physics - Solid State
1971, vol. 13, no. 1, P