

TRAPPING LEVELS AND ELECTRICAL
CONDUCTIVITY IN CdS PLATELETS

by

IAN MERKER, BSc(Eng), ACGI

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ABSTRACT

Factors affecting electrical conductivity in thin platelets of cadmium sulphide grown by the vapour phase transport method have been studied using the analysis of thermally stimulated current results. Indium electrodes evaporated onto the two large faces of the crystal were generally used, though some experiments involved more complex electrode configurations or employed silver contacts.

Oxygen desorption from the surface was found to enhance the TSC spectrum between 120K and about 200K and was attributed to the release of carriers from intrinsic surface traps of depth 0.2 - 0.4 eV. This value is consistent with that calculated for surface traps formed by the termination of the CdS lattice.

A large TSC peak with a maximum above 300K was observed on most crystals and found to be dependent on the nature of the bias applied to the specimen during cooling. A model involving the slow migration of cadmium vacancies is used to explain the creation of a trap responsible for the peak. The model is consistent with the contact forming process for indium electrodes, involving the diffusion of indium through surface contamination and into the bulk via cadmium vacancies at the positive electrode. The results indicate that a slow change takes place at the anode, and that the bias dependent peak may be attributed to a region very near to the electrode rather than in the bulk.

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PRINCIPAL SYMBOLS

A	area
a	density of absorbed photons
B	Poole-Frenkel trap lowering constant
b	volume
β	heating rate
D	diffusion coefficient
d	lattice distance or thickness
E_c, E_v	energy of conduction and valence band edges
E_t, E_R	energy of traps and recombination centres
E_F, E_{F_0}	Fermi level energy and equilibrium Fermi level energy
E_{F_n}, E_{F_p}	quasi Fermi energy for free electrons and holes
$E_{F_n}^t, E_{F_p}^t$	quasi Fermi energy for trapped electrons and holes
e	electronic charge
ϵ_0	permittivity of free space
ϵ	dielectric constant
$\mathcal{E}$	electric field strength
$\mathcal{E}_c, \mathcal{E}_i$	electric field strength at cathode and across the insulator
f_t, f_R	probability of occupation of trapping and recombination level
G	gain factor
HTP	high temperature peak
h	hole
I	electric current
i_{ph}, i_{TSC}	instantaneous photocurrent and TSC
J	electric current density
K	degrees Kelvin
k	Boltzman's constant
$\ln$	natural logarithm
$\log$	logarithm, base ten

m_o	mass of electron
N_c, N_v	density of states in conduction and valence band
N_t, N_R	density of traps and recombination centres
n_o, p_o	equilibrium density of free electrons and holes
n, p	density of free electrons and holes
P_E, P_T, P_R	probability of escape, trapping and recombination
Q_{ss}	surface charge concentration
S_T, S_R	trap or recombination centre cross section
T	absolute temperature
T^*	temperature at which a peak attains maximum current
TSC, TSD	thermally stimulated current, desorption
t	time
t_n, t_p	electron and hole transit times
τ	carrier lifetime
τ_n, τ_p	electron and hole lifetimes
u	atomic displacement in the c direction
μ_e, μ_h	electron and hole mobilities
μm	micrometer
V	voltage
V_{Cd}, V_S	cadmium and sulphur vacancies
v	thermal velocity
ν	frequency factor
Z	impedence
ϕ	barrier height
ψ	work function
χ	electron affinity
Δ_n	excess carrier concentration
Δ_o	total potential across barrier
Δ_s	contribution to barrier potential from surface charge

CHAPTER I

INTRODUCTION

1.1. II - VI Compounds

II - VI compounds in their widest sense include materials formed by the elements of group II and group VI of the periodic table. Such a definition encompasses the oxides, sulphides, selenides and tellurides of beryllium, magnesium, zinc, cadmium and mercury. In terms of practical efforts, research has been directed towards comparatively few of these; the sulphides, selenides and tellurides of cadmium, zinc and mercury. These materials have been, and are continuing to be, the subject of much intensive investigation.

In spite of the vast literature, many of the properties of II - VI compounds are, as yet, poorly understood. Topics such as the exact nature of the band structure, the mechanism of deep and shallow centres, the transport properties and the properties of surfaces require more work to develop a clearer understanding.

In recent years, advances made in the growth of ultra high purity single crystals has given particular emphasis to measurements of the electrical properties of II - VI compounds, whereas previous work concentrated more on the study of photoconductivity in CdS, and photoluminescence from deep centres in ZnS.

One would expect that the bonding in II - VI compounds would have a character intermediate between the covalency of group IV semiconductors and the ionic solids of group I - VII compounds. Indeed, the bonds are

iono-covalent exhibiting, according to Suchet (1965), about a 75% ionic character. This ionicity corresponds to a formula $\text{II}^{1.5+} \text{VI}^{1.5-}$. However, calculations of this type are necessarily inaccurate because they depend upon some estimation of the effective charge and in the following work, the compound will be treated in the main as if it were ionic.

II - VI compounds generally exist in one of two basic crystallographic forms; zinc blende (sphalerite) and wurtzite. Sphalerite is related to the close packed face centred cubic structure, with a bias of two atoms per lattice point, whereas wurtzite is derived from the close packed hexagonal lattice with a bias of two atoms on each lattice point.

The lattice positions for atoms of the same species in a sphalerite structure are shown in figure 1.1(a) and for those having a wurtzite structure in figure 1.1(b). The atomic positions in the unit cell are indicated by shaded circles. Inclusion of the second species into the lattice in both cases gives rise to tetrahedral bonding with the four nearest neighbouring atoms (all of the other chemical species). Figures 1.1(c) and 1.1(d) show the position of the second species with respect to the four nearest neighbours translated directly from figures 1.1(a) and 1.1(b) respectively. The lattice structure for group II atoms is identical to that of the group VI atoms in both cases; the displacement for sphalerite being along the body diagonal by one quarter of its length, and for the wurtzite being a displacement by $00u$, where $u = \frac{3}{8}$ for the figures shown. The co-ordinates of each species in the unit cell of the two structures are given below

	<u>1st. Species</u>	<u>Other Species</u>
Sphalerite	$000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0$	$\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}$
Wurtzite	$000; \frac{1}{3}\frac{2}{3}\frac{1}{2}$	$00u; \frac{1}{3}\frac{2}{3}(u + \frac{1}{2})$

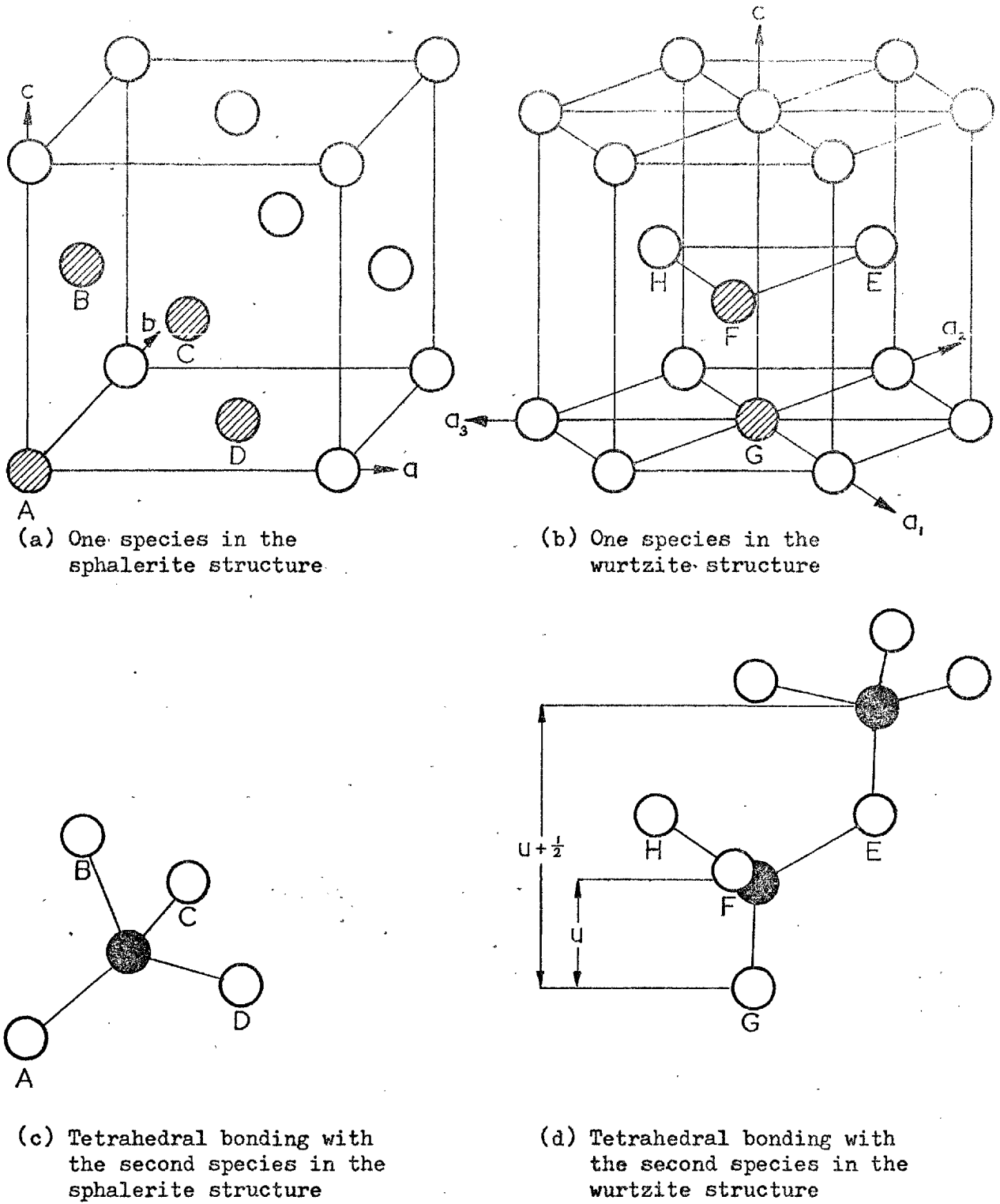


FIGURE 1.1

SPHALERITE AND WURTZITE STRUCTURES

Growth of II - VI compounds from the vapour phase requires the simultaneous presence of both constituent elements in the gaseous form. Dynamic methods involve continuous use of a carrier gas to transport vapour along the growth tube. Frerichs (1947) used hydrogen to transport vapour of the metallic element which was mixed with hydrogen sulphide or selenide. At high temperatures, decomposition of the hydride leads to combination of sulphur or selenium with the metal giving rise to the growth of single crystals on the furnace wall.

Fochs and Lunn (1963) modified the method by using an inert gas to transport the vapour of the compound to a cooler region of the growth tube, giving rise to single crystal platelets, needles or ribbons on the tube walls. The method has been particularly applied to CdS and is considered in more detail in section 4.1. Growth of single crystals at lower temperatures has been reported using iodine as a transport gas, however traces of iodine influence properties of the resulting crystals. Boule crystals grown from the melt or by vapour phase transport in a closed tube are extensively used, particularly for the preparation of specimens for industrial work. Numerous methods reporting the growth of single crystals have been published, and excellent summaries are available, for example Aven and Pren~~er~~ (1967).

With regard to the principle energy bands of II - VI compounds, it appears that for both sphalerite and wurtzite lattices the band gap in the majority, if not all compounds, is direct with the extrema of the conduction and valence bands at $\underline{k} = 0$ in k space. This has been verified experimentally by observations of direct exciton production. The conduction band of most II - VI compounds is generally thought to be singular and parabolic in shape, but due to the effects of spin orbit splitting (which can give rise to lifting of the degeneracy of the levels) the nature of the valence bands ¹⁵ ~~are~~ more complex. The band structure of CdS is typical

of II - VI compounds of the wurtzite form, and is shown in figure 1.2. The non symmetry of the uppermost valence band results from the strong mass anisotropy with crystallographic direction.

1.2. Cadmium Sulphide

Literature on CdS dates back to the end of the last century when Lorenz (1891) first produced synthetic crystals. Comparative ease of growth and exceptional photoconductive qualities have ensured continued interest in CdS, particularly following development of the growth of high purity single crystals.

Values of resistivity varying by over twelve orders of magnitude; from 10^{12} Ωcm down to 10^{-1} Ωcm have been measured for CdS. The variation depends on sample purity and/or deviation from stoichiometry. CdS crystals as grown always exhibit n type conductivity.

With a direct band gap material like CdS, preparation of p type samples would be highly desirable for applications such as lasers and photovoltaic cells. Several attempts have been made to prepare p type CdS (Woods and Champion, 1959, Aven and Woodbury, 1962 and Bube et al, 1962) by heavily doping with copper (1 - 2%). Woods and Champion concluded from X-ray and thermoelectric power measurements that impurity band conduction was most likely, though more recent reports (Sturner and Bleil, 1964) suggest the conductivity mechanism is most probably along filaments of cuprous sulphide, which is known to be a p type semiconductor. Observation of filaments by optical microscopy leads to the rejection of an impurity band conduction theory. The concentration of copper atoms exceeded the measured value of hole concentration by over three orders of magnitude, suggesting that

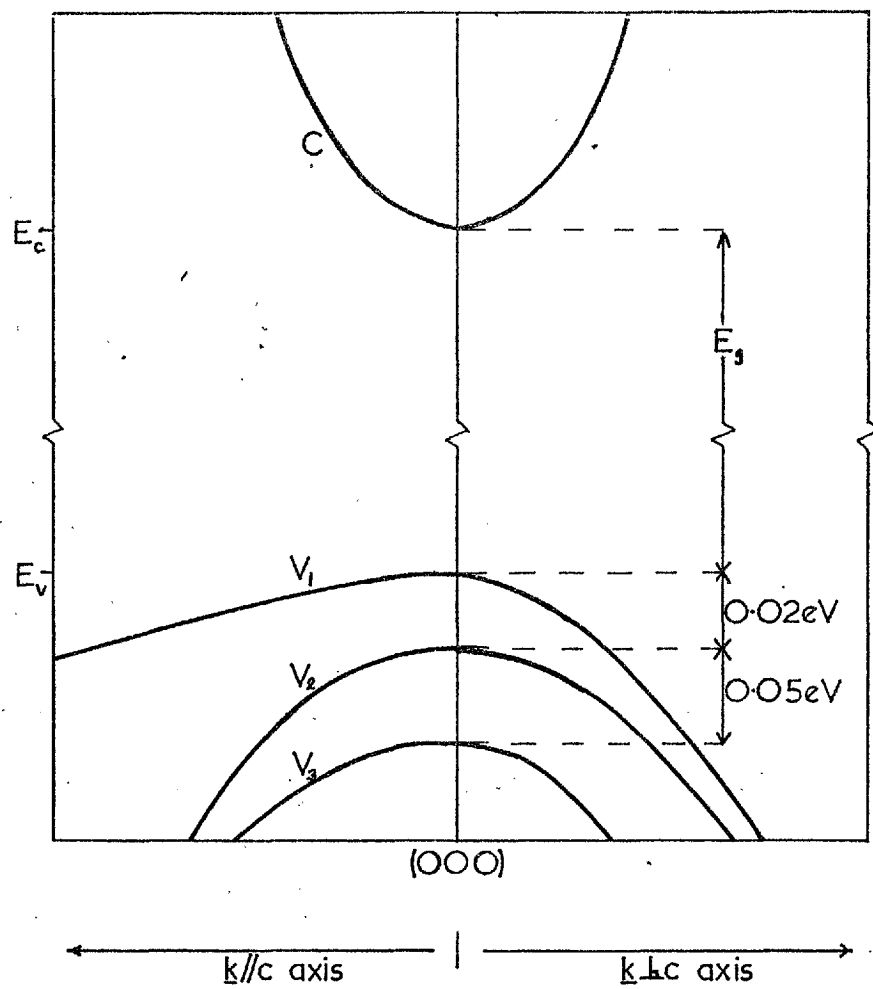


FIGURE 1.2

THE BAND STRUCTURE OF CdS AFTER
BLAKEMORE (1969)

compensation or copper precipitation occurs.

Several independent estimates of the band gap indicate a value of 2.4eV at room temperature. Variation with temperature, taking into account volume changes is given by Piper et al (1958) in the form

$$E_G(T) = E_{G_0} - 5.2 \times 10^{-4}T \quad \text{.....(1.1)}$$

The study of transport phenomena in II - VI compounds (CdS in particular) has progressed in a haphazard manner due possibly to the pressure to market commercial devices. In addition to the more usual carrier scattering processes, namely acoustic mode phonon and impurity scattering, two other mechanisms are of importance in CdS. The first is polar optical mode scattering, resulting from the polar interaction between charged carriers and optical phonons, and the second is piezoelectric scattering, resulting from polarisation fields caused by mechanical stress, usually in the form of acoustic lattice vibrations. Such fields modify the transport properties of carriers particularly at lower temperatures.

As technological advances produce methods of increasing purity, higher values of carrier mobility are being quoted. The measurements of Piper and Halsted (1961) on the temperature dependence of electron mobility confirm that optical and piezoelectric scattering mechanisms are the most probably process in CdS.. These gave values of electron mobility ranging from about $200 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 300K to about $4000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 77K. Estimates of hole mobility vary considerably. Spear and Mort (1963) obtained consistent values of $15 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ by measuring drift mobility using a modified Haynes - Shockley photoinjection method, whereas Onuki and Hase (1965), measuring the AC photo Hall mobility in CdS under DC illumination as a function of wavelength calculated Hall mobility to be $38 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

For the effective mass of carriers in CdS, a generally accepted value for electrons is $0.2 m_0$ and was obtained from Hall mobility work by Piper and Halsted (1961) and analysis of exciton spectra by Hopfield and Thomas (1961). Estimates of the effective mass of holes are scarce and less consistent. Hopfield and Thomas (1961) indicate that $m_h \sim 0.7 m_0$, whereas Sawamoto (1963) suggested an average hole mass of $0.81 m_0$.

In the previous section, the partially covalent nature of II - VI compounds has been discussed. An estimate of 74% ionicity is given by Suchet (1965), and a value of between 70% and 100% was calculated from Fourier analysis of X-ray diffraction structure factors by Weber (1961), though the accuracy of such an estimate is low due to the difficulty in assessing electron distributions at large distances from the nucleus. A detailed survey of chemical bonding in different forms of CdS structure is given by Fass (1969). Further ideas relating to the $11\bar{2}0$ surface of CdS are discussed in section 3.2.

1.3. Applications of CdS

CdS is extensively employed in photoconducting cells to detect radiation in a spectral region extending from visual to gamma radiation, and, under special conditions involving a two stage excitation process, to detect infra red radiation. The disadvantage of a relatively slow response time (particularly for shorter wavelengths) compared with materials like silicon is compensated by the advantage of exhibiting extremely high photosensitivity and being able to handle power levels of several watts. CdS is widely used on the domestic market for applications including automatic headlamp dippers for cars, automatic garage doors, burglar alarms and measurement of illumination intensity for photographic light meters. Exceedingly small detector probes implanted into the body have been useful

in medical research as a means of continually monitoring radioactivity levels emitted from body organs. It is the long term, possibly photochemical changes which occur in CdS that limit its overall reliability as a photodetecting material.

CdS has featured prominently in the development of ultrasonic amplifiers and transducers. Amplification of ultrasonic waves was first observed by Hutson et al (1961) and occurs when the drift velocity of optically excited electrons, under the influence of a large applied electric field, exceeds the velocity of sound in the crystal. Losses in the amplifier are minimised by highly polishing the crystal surfaces and using a thin layer of indium to bond the transducer (usually quartz) to the crystal surface. An integrated CdS amplifier consisting of an initial conducting layer formed by cadmium diffusion followed by application of a transducing layer created by copper diffusion has been reported Churbachi et al (1964). A gain of 35 dB at 54MHz was obtained. Golinnaya et al (1959) observed current oscillations in CdS at high fields associated with the piezoelectric properties. As the device current increases, carrier interaction with the piezoelectric fields eventually causes current saturation, and the energy of the applied field is converted into ultrasonic energy. The motion of high field domains which travel through the crystal have been studied by Fass (1969) using thin CdS platelets, and more recently observed by Das and Steckl (1970) in samples having optically polished parallel surfaces.

Single crystal platelets and thin films of CdS have been used successfully to fabricate space charge limited devices. Both diodes and triodes have been constructed and operations at sub millimetre frequencies are possible. Input impedances of between $10^{12}\Omega$ and $10^{15}\Omega$ have been obtained using insulated gate CdS triodes. Economic production of thin

film CdS transistors is however unlikely, due mainly to hysteresis effects and non reproducible electrical properties from sample to sample.

Green electroluminescence from CdS suggests that the material could be used to produce lasers in this region of the spectrum. Unfortunately, the complex defect nature producing states throughout the band gap of CdS makes it difficult to obtain population inversion, and hence laser action. However, CdS lasers have been produced by Hurwitz (1966) using cadmium rich samples and cathode ray excitation. These emit at 4900Å (in the blue) and have a power output of 350 watts operating at 110K with an overall efficiency of 26.5%.

Silicon and CdS were the original materials used for solar cells over ten years ago. Recent research has been directed towards thin films CdS and CdTe devices where a large surface area and the low cost of fabrication more than compensate for the reduced efficiency compared with bulk single crystal photovoltaic devices. A review of the use of CdS for solar cells has been published by Shirland (1966). Efficiencies up to 6% for a 50cm^2 area have been obtained by Hill and Keramidas (1966) using the p - n junction formed by evaporating CdS onto p type Cu_2S .

The comparative ease of crystal growth and device fabrication coupled with high photosensitivity have resulted in CdS being used in many device applications, for example, image intensification and even electrophotography. The poor long term reliability of the devices is mainly responsible for the limited use of CdS devices. Reasons for this unreliability must be sought as much in the nature of surface effects and the mechanisms governing electrical contacts to crystals as with the anomalous bulk phenomena.

1.4. An Outline of the Present Study

The complex bulk nature of CdS single crystals has, in the past, promoted extensive research into understanding the mechanisms responsible for electrical carrier trapping within the forbidden energy gap. Trapped carriers do not participate in current flow, but instead form a space charge which causes band bending and influences transport processes. A vast literature relating to work on trapping models has accumulated and numerous surveys are available, for example, Nicholas and Woods (1964). In section 2.4. a summary of the present understanding of trapping phenomena is given, but the exact nature of bulk trapping in CdS remains a matter of some conjecture.

The method of thermally stimulated conductivity, as discussed in chapter 2, has been extensively employed to investigate CdS traps, and provides the basis for most results in the present work. Single crystal platelets grown by the vapour phase transport technique, measuring typically several millimetres square by thirty microns thick have been used throughout the study. They provide a means of fabricating simple devices which have been used to investigate (a) the contribution due to surface effects, (b) phenomena due to the metal-crystal interface at the contacts and (c) the redistribution of crystal defects near the electrical contacts. Two and three electrode configurations have been used employing, in the main, indium electrodes, however some results for silver contacts are included.

The work is mainly concerned with thermally stimulated currents between 77K and 400K using a constant heating rate of about half a degree per second. In the low temperature region (77K to 120K), peaks attributed to traps generally seen in bulk crystals were exhibited by these platelets.

The effect of oxygen was also studied and seen to contribute to peaks observed in the mid-temperature region; these were characterised to surface traps. The high temperature region (above 300K) however was related to traps formed in a layer adjacent to the electrical contact and explained using a theory involving trap creation by the formation of complex cadmium vacancies.

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CHAPTER II

A REVIEW OF CARRIER TRAPPING IN CdS

2.1. Carrier Trapping

2.1.1. Conceptual Basis

Structural defects and impurities in a semi-insulator give rise to carrier traps, the existence of which is thermodynamically inevitable in all practical materials. Electrical carrier recombination processes may be analysed by considering the trapping of electrons or holes by localised energy levels lying deep within the forbidden energy gap.

Differentiation between donor and acceptor levels and electron and hole traps is simple. A trap lying energetically above the equilibrium fermi level is neutral when empty, whereas a donor or acceptor centre is charged when ionised. The creation of traps by donor and acceptor centres is possible by agglomeration of equal numbers of oppositely charged centres. The distribution of photochemically created traps in CdS has been calculated by Tscholl (1968), though the exact nature of defects responsible for such centres is open to conjecture.

A detailed understanding of conduction mechanisms in semi-insulators requires some quantitative knowledge about trapping centres in the material. In addition to the trap depth, it is necessary to know the capture probability of a centre in order to assess the density of traps and to establish the kinetics of the trapping processes. The capture probability depends on the capture cross section of the centre and is determined by the potential variation in the neighbourhood of the centre.

For N recombination sites per unit volume, the lifetime of a charge carrier, τ is given by

$$\tau = (vSN)^{-1} \dots\dots\dots(2.1)$$

where v is the thermal velocity of the carrier, $(\frac{2kT}{m})^{\frac{1}{2}}$ and S is the capture cross section. A simple representation of potential distribution for specific centres is given in figure 2.1(a).

It must be remembered that centres can act as either electron or hole traps and it is the state of charge of the centre that determines its capture cross section, and hence its propensity to capture charge carriers.

Recombination processes in materials were first investigated by Shockley and Read (1952) by considering the statistics of occupation of trap levels. The four basic processes involving electron-hole recombination through trapping centres are as shown in figure 2.1(b).

2.1.2. Methods of Analysis

The following measurements can be used to supply trapping data:

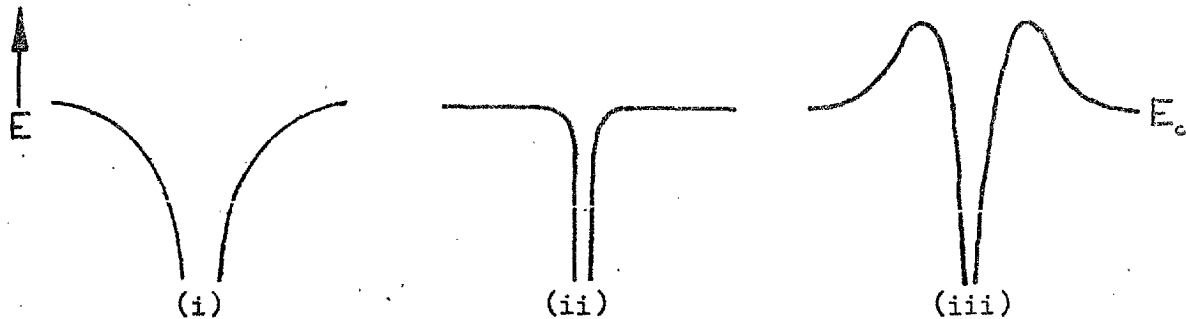
(i) Growth and decay characteristics

Application or removal of radiation generally involves a non-equilibrium situation during which trap kinetics dominate the conduction mechanism. Careful evaluation of the area under decay curves measured under given conditions may be used to evaluate the trapping parameters.

(ii) Photoconductivity measurements made during the change in behaviour of a centre

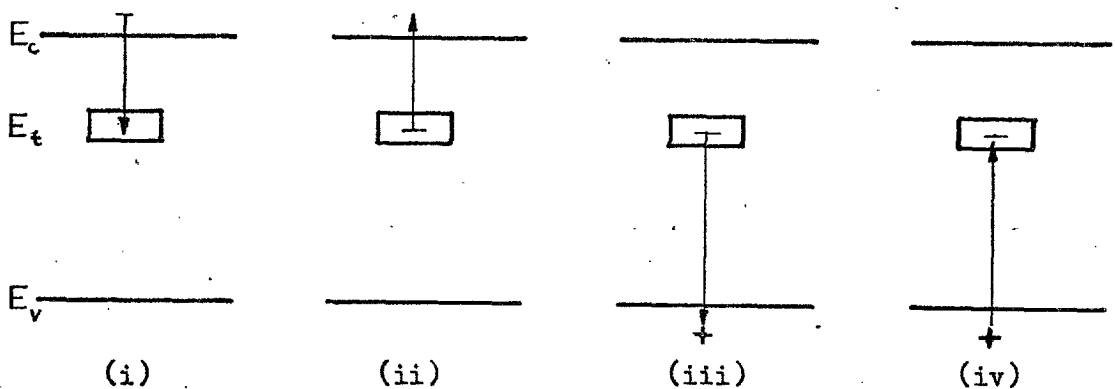
A change in light intensity or temperature is often sufficient to raise or lower the electron fermi level in a material which may change

FIGURE 2.1



(a) Schematic representation of potential distributions about (i) coulombic attracting (ii) neutral and (iii) coulombic repelling centres

$$S_{(i)} \gg S_{(ii)} \gg S_{(iii)}$$



(b) The four fundamental processes involved in recombination through traps;
 (i) the capture of a conduction electron by an empty trap,
 (ii) the emission of an electron from the trap to the conduction band,
 (iii) the capture of a hole from the valence band by a trap containing an electron,
 (iv) the promotion of a valence electron into an initially empty trap.

electron trapping levels into recombination levels, and vice versa. From the change in photocurrent, calculation of fermi level position then indicates the depth of the centres contributing to this current.

(iii) I - V characteristics

The variation of space charge limited current for carriers injected into the solid from an ohmic contact, measured as a function of applied electric field may be used to assess trapping parameters. The onset of the trap filled limit can yield the density and energetic location of traps, together with a crude estimate of cross section (see, for example, Lampert, 1964).

(iv) Photodielectric effect

An increase in magnitude of dielectric constant in the presence of radiation has been shown to occur in some materials, and this is potentially a useful method for investigating trapped carriers located in orbitals around trapping centres. The effect is reported predominantly in powder structures, indeed Garlick (1955) found very little photodielectric change in single crystals of CdS and ZnS, and concluded that the effect was peculiar to powders, and attributable to space charge formation at grain boundaries. A comprehensive discussion is given by Bube (1960).

(v) Photogenerated noise

Trapping transitions in photoconducting semi-insulators cause fluctuations in the number of photogenerated current carriers which can be observed as electric current noise. Brophy and Robinson (1960) show that trap depths and trapping transition probabilities may be determined from the noise current against frequency spectrum under strong monochromatic irradiation conditions.

(vi) Thermally and optically stimulated trap emptying

If traps are filled by excitation at low temperatures, they may be emptied by rapidly increasing the temperature (usually at a constant rate). The resulting curve of conductivity against temperature is used to determine

trap depth, estimate capture cross section and trap density, and indicates the kinetic process associated with a trap.

Filled traps may be emptied also by the absorption of optical energy rather than thermal energy. Trap depths may be determined from the stimulation spectrum of either photoconductivity or luminescence.

The thermally stimulated conductivity (TSC) measurement is undoubtedly the best single method for obtaining the maximum amount of trapping data. Its advantages include:

- (i) Experimental simplicity.
- (ii) Each discrete trap is represented by a singular current peak.
- (iii) A simple method for estimating trap depths.
- (iv) The method can be varied considerably, e.g. additional illumination at high temperatures and/or variation of heating rate.
- (v) The shape of the TSC curve can, in certain cases, indicate the dominant kinetic process.
- (vi) Several methods for evaluating trapping parameters from a TSC curve provide a self checking mechanism for data.

2.2. TSC Theory

2.2.1. Introduction to Non Equilibrium Conditions

Before embarking on formal analysis of theory relating to the thermal stimulation of carriers out of trapping centres, it is important to consider the conceptual basis of the method.

Under equilibrium conditions at room temperature, the thermal energy, kT is about 0.025eV. In the present system however, TSC peaks appearing at about room temperature correspond to trap depths over 0.5eV. It is this ability to release trapped electrons from depths corresponding to twenty times their thermal energy (kT) that establishes TSC as a very useful tool for carrier trapping analysis.

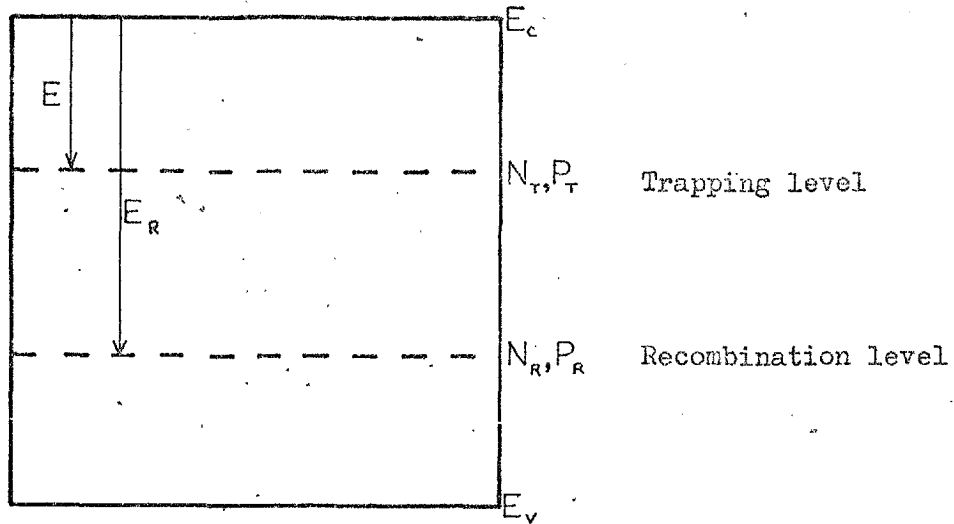
Thermal equilibrium conditions are not maintained during TSC heating. This provides the essential difference between the energy attributed to a TSC peak at a particular temperature, and the corresponding value of kT . By rapidly increasing the temperature of a semi-insulator, non equilibrium conditions are maintained, and the resulting current, namely the rate of flow of carriers $\frac{dn}{dt}$ is then related directly to the temperature in $\frac{dn}{dT}$. The system can thus be visualised as a form of thermal "acceleration" of carriers out of their traps, due to the rapid heating.

The concept of the quasi fermi level provides an alternative means of analysis to explain the non equilibrium conditions involved with TSC, and is outlined in section 2.2.3.

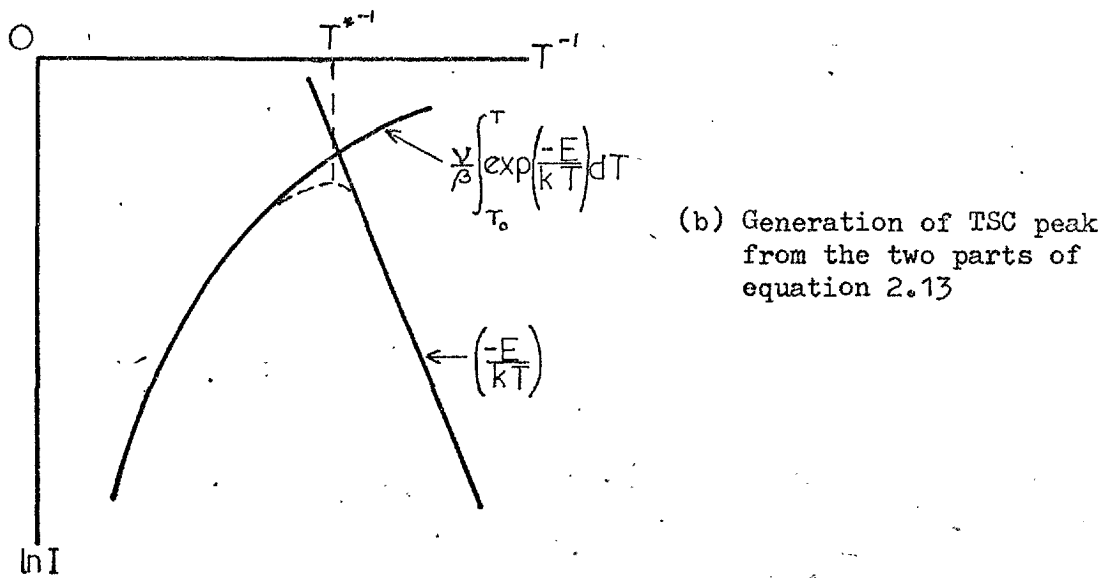
2.2.2. Basic theory

At least two different methods have been used in the past to interpret TSC results. Here we shall show by means of a simple model that both are valid and indeed are essentially identical. Figure 2.2(a) shows the most elementary system (for electrons) involving one discrete trapping level, and one carrier recombination level.

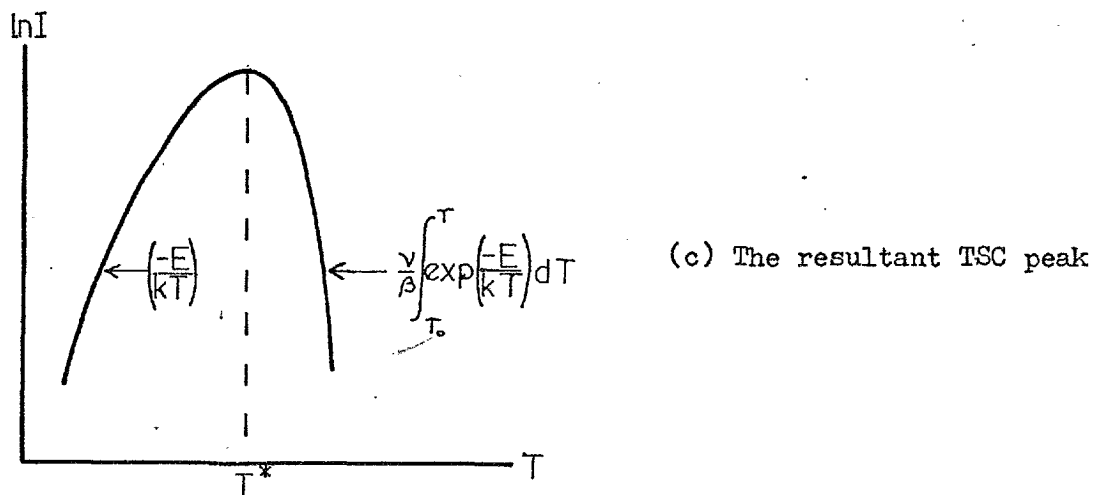
The rate of capture (or escape) of carriers depends on the density of



(a) Simple energy diagram for TSC theory



(b) Generation of TSC peak from the two parts of equation 2.13



(c) The resultant TSC peak

FIGURE 2.2

carriers in the conduction band (or traps), the density of traps (or states in the conduction band) and the probability of capture (or escape) of the carrier from the centre.

The rate of release of electrons from a trap into the conduction band is

$$N_t f_t N_c P_E \dots\dots\dots(2.2a)$$

The rate of capture of conduction band electrons by the trapping level is

$$n N_t (1 - f_t) P_c \dots\dots\dots(2.2b)$$

And the rate of removal by recombination of conduction band electrons is

$$n N_R (1 - f_R) P_R \dots\dots\dots(2.2c)$$

Where n is the density of free electrons in the conduction band, N_t and N_R are densities of trapping and recombination centres, N_c the effective density of states located at the bottom of the conduction band, f_t and f_R the occupation probability of the respective centres, and P_E , P_t and P_R the probabilities of escape, trapping and recombination of carriers.

From equations 2.2(a), (b) and (c), the rate of change of concentration of electrons in the conduction band at any time is

$$\frac{dn}{dt} = N_t f_t N_c P_E - n N_t (1 - f_t) P_c - n N_R (1 - f_R) P_R \dots\dots\dots(2.3)$$

and the rate of change of concentration of trapped electrons at any time is

$$\frac{dn_t}{dt} = - N_t f_t N_c P_E + n N_t (1 - f_t) P_t \dots\dots\dots(2.4)$$

where n_t is the density of trapped electrons.

Combining equations 2.3 and 2.4 for a steady state

$$\frac{dn}{dt} = - \frac{dn_t}{dt} - n N_R (1 - f_R) P_R \dots\dots\dots(2.5)$$

The probability of recombination, P_R , depends only on the thermal velocity v , and the capture cross section S_T such that

$$P_R = v S_T$$

Equation 2.5 then becomes

$$\frac{dn}{dt} = - \frac{dn_t}{dt} - n N_R (1 - f_R) v S_T$$

Remembering that $N_R(1 - f_R)$ represents the total density of available recombination centres, and using equation 2.1, equation 2.5 becomes

$$\frac{dn}{dt} = - \frac{dn_t}{dt} - \frac{n}{\tau} \dots\dots\dots(2.6)$$

Equation 2.6 is frequently used as a starting point for TSC analysis, and can be intuitively deduced from figure 2.2(a).

Analysis usually proceeds by dividing the possible TSC kinetics into three categories:

- (i) Monomolecular recombination (no retrapping)
- (ii) Bimolecular recombination (an equal probability of retrapping or recombination)
- (iii) Fast retrapping (equilibrium between trapped and conduction band electrons)

For the purpose of the present study, only monomolecular recombination is considered in detail as the complex and often intractable equations evolved by (ii) and (iii) are developed from comparatively simple extensions to the theory outlined, as well as documented in the literature (see, for example, Nicholas and Woods, 1964).

The effect of negligible retrapping eliminates the term $n N_t (1 - f_t) P_t$ in equations 2.3 and 2.4, and means that the number of free electrons, n , in the conduction band results only from the thermal release of carriers from traps (see equation 2.8 below).

It is generally assumed that the effective lifetime is sufficiently small to neglect the $\frac{dn}{dt}$ term in equations 2.3, 2.4 and 2.6 (i.e. $\frac{n}{\tau} \gg \frac{dn}{dt}$). From equation 2.5

$$-\frac{dn_t}{dt} - n N_R (1 - f_R) P_R = \frac{dn}{dt} = 0 \quad \dots\dots\dots(2.7)$$

Substituting for P_R and using $n = N_c \exp(-\frac{\Delta E}{kT})$ where E is the trap depth below the bottom of the conduction band

$$\frac{dn_t}{dt} = - N_c \exp(-\frac{\Delta E}{kT}) N_R (1 - f_R) S_T v \quad \dots\dots\dots(2.8)$$

The term $N_R (1 - f_R)$ represents the total density of available centres for recombination which, due to charge neutrality, must equal the total trapped carrier density, n_t , so equation 2.8 becomes

$$\frac{dn_t}{dt} = - N_c S_T v n_t \exp(-\frac{\Delta E}{kT})$$

or

$$\frac{dn_t}{dt} = - n_t v \exp(-\frac{\Delta E}{kT}) \quad \dots\dots\dots(2.9)$$

where

$$\gamma = N_c S_t v,$$

the frequency factor discussed in section 2.2.4.

For TSC measurements, a constant rate of heating, β is used

$$T = T_0 + \beta t$$

and differentiating

$$dT = \beta dt \quad \dots\dots\dots(2.10)$$

Rearranging equation 2.9 and substituting equation 2.10

$$\frac{dn_t}{n_t} = -\left(\frac{\gamma}{\beta}\right) \exp\left(-\frac{\Delta E}{kT}\right) dT \quad \dots\dots\dots(2.11)$$

Integrating

$$\int_{n_0}^n \frac{dn_t}{n_t} = -\frac{\gamma}{\beta} \int_{T_0}^T \exp\left(-\frac{\Delta E}{kT}\right) dT$$

where n_0 and T_0 are initial trap density and starting temperature respectively.

$$\ln\left(\frac{n_t}{n_0}\right) = -\frac{\gamma}{\beta} \int_{T_0}^T \exp\left(-\frac{\Delta E}{kT}\right) dT$$

$$n_t = n_0 \exp \left[\left(\frac{\gamma}{\beta}\right) \int_{T_0}^T - \exp\left(-\frac{\Delta E}{kT}\right) dT \right] \quad \dots\dots(2.12)$$

Equation 2.12 gives the number of electrons in the conduction band (due to TSC) at any time and the instantaneous current $I \propto \frac{dn_t}{dt}$ may be calculated.

$$I \propto \frac{dn}{dt} = n_0 \gamma \exp\left(-\frac{AE}{kT}\right) \exp\left[\left(\frac{\gamma}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{AE}{kT}\right) dT\right] \dots\dots(2.13)$$

Equation 2.13 describes the simplest form of TSC curve, and was first developed for luminescence spectra by Randal and Wilkins (1945).

Figure 2.2(b) is a schematic diagram of $\ln I$ against T^{-1} for equation 2.13 to show development of the resulting TSC curve, shown in figure 2.2(c).

Further development of equation 2.13 correlates the temperature of the TSC peak maximum, T^* with the trap activation energy, E . Writing equation 2.13 as

$$\ln I = \text{const} - \frac{AE}{kT} - \left(\frac{\gamma}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{AE}{kT}\right) dT$$

differentiation with respect to temperature and equating to zero gives

$$\frac{d}{dT}(\ln I) = \frac{E}{kT^{*2}} - \left(\frac{\gamma}{\beta}\right) \exp\left(-\frac{E}{kT^*}\right) = 0$$

Yielding

$$E = kT^* \ln\left(\frac{\gamma kT^{*2}}{E\beta}\right) \dots\dots\dots(2.14)$$

2.2.3. Quasi Fermi levels

The concept of a fermi level applies strictly to conditions of thermal equilibrium. Under these circumstances the local electron and hole densities n_0 and p_0 are specified by non degenerate statistics:

$$n_o = N_c \exp \frac{(E_{F_o} - E_c)}{kT} \dots\dots\dots(2.15a)$$

and

$$p_o = N_v \exp \frac{(E_v - E_{F_o})}{kT} \dots\dots\dots(2.15b)$$

Where E_{F_o} is the equilibrium fermi level and other parameters have their usual meaning.

For situations involving carrier densities in excess of those in thermal equilibrium, Shockley (1950) introduced the concept of "quasi fermi levels" as an aid to analysis of processes in semiconductors. Under the influence of, for example, irradiation or thermal transients, the electron population is in quasi equilibrium with itself, all carriers adopting their lowest possible energy level. The hole population behaves similarly. Electron concentrations need not, of course, be in equilibrium with hole concentrations under such circumstances.

Considering initially the case for electrons only, with Δn being the excess carrier concentration:

$$n = n_o + \Delta n \dots\dots\dots(2.16a)$$

$$\therefore n = (1 + \frac{\Delta n}{n_o}) N_c \exp \frac{(E_{F_o} - E_c)}{kT} \dots\dots\dots(2.16b)$$

Suppose equation 2.16(b) may be replaced by

$$n = N_c \exp \frac{(E_{F_n} - E_c)}{kT} \dots\dots\dots(2.17)$$

where E_{F_n} is the quasi fermi level for electrons. Equating equations 2.16(b) and 2.17, and assuming a large excess current, i.e. $\Delta n \gg n_o$

$$\left(\frac{n}{n_0} \right) N_c \exp \frac{(E_{F_0} - E_c)}{kT} = N_c \exp \frac{(E_{F_n} - E_c)}{kT}$$

Yielding

$$E_{F_n} = E_{F_0} + kT \ln \left(\frac{n}{n_0} \right) \dots\dots\dots(2.18)$$

or from equation 2.17

$$E_{F_n} = E_c - kT \ln \left(\frac{N_c}{n} \right) \dots\dots\dots(2.19a)$$

similarly for holes

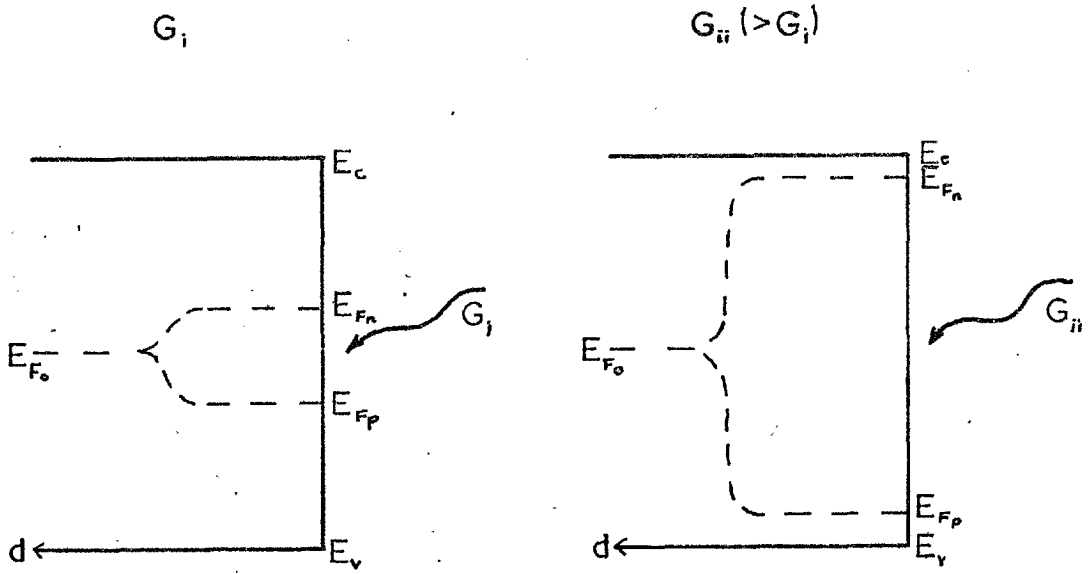
$$E_{F_p} = E_v + kT \ln \left(\frac{N_v}{p} \right) \dots\dots\dots(2.19b)$$

From equations 2.19(a) and 2.19(b) it is clear that by increasing the excess carrier concentrations, the quasi fermi levels are driven nearer to the band edges. In figure 2.3(a), the energy band diagrams are shown as a function of distance into the bulk for photoexcited carriers under different illumination intensities. The statistical probability of occupancy of a state is shown graphically in figure 2.3(b).

Under conditions of non equilibrium steady state, Simmons and Taylor (1971a) have shown that the distribution of trapped electrons can be represented in the form of a modulated Fermi-Dirac form about an energy $E_{F_n}^t$ (or $E_{F_p}^t$) which acts as a quasi fermi level for trapped electrons (or holes). The trapping densities before and after illumination are shown in figure 2.4 for two temperatures $T_1 > T_2$ (the distributions for T_1 being exaggerated). For conditions of uniform illumination in which the free excess carrier density is far less than the trapped carrier density, the number of trapped electrons above E_{F_0} is identical to the number of

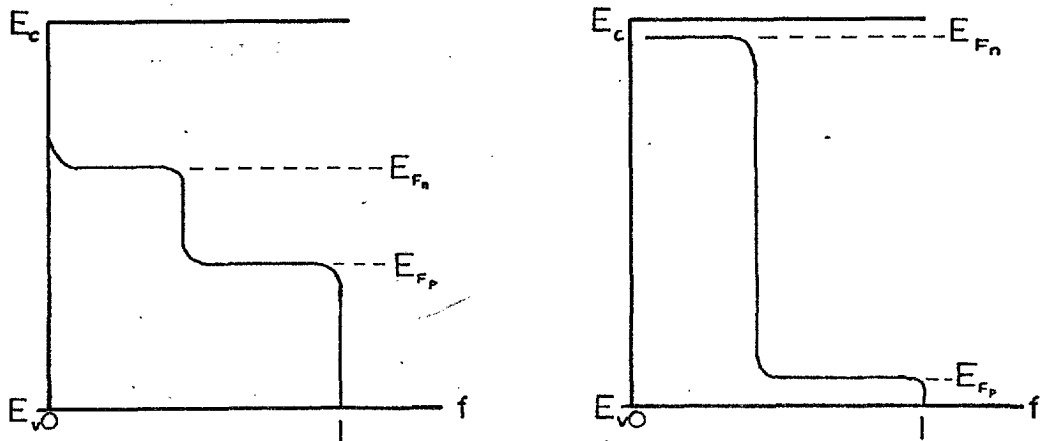
FIGURE 2.3

(a) Energy diagram (into bulk)



E_{F_0} is the equilibrium fermi level

(b) Occupation function (in excitation region)



trapped holes below E_{F_0} , and is indicated by equal shaded areas on each curve in figure 2.4(b). It will be noted that the effect of increased illumination or decreased temperature shifts the quasi fermi level for trapped carriers nearer to their respective band edges.

The quasi fermi level for trapped carriers is of utmost importance in TSC. Initial intense irradiation at 77K forces each quasi fermi level close to its respective band edge. If the temperature is sufficiently low so that there is insufficient thermal energy to release carriers, the position of the quasi fermi level for trapped electrons will remain essentially unchanged after the removal of the irradiation. Subsequent rapid heating will produce a non equilibrium state in which the quasi fermi levels start to move towards the equilibrium fermi level, E_{F_0} . As the quasi fermi level passes through a trapping level, carriers will be released and produce a TSC peak. Equation 2.14 shows that the trap depth is proportional to TSC temperature (and therefore to TSC time), so with a linear heating rate, the quasi fermi levels must move at a constant rate away from their respective band edges.

2.2.4. The frequency factor

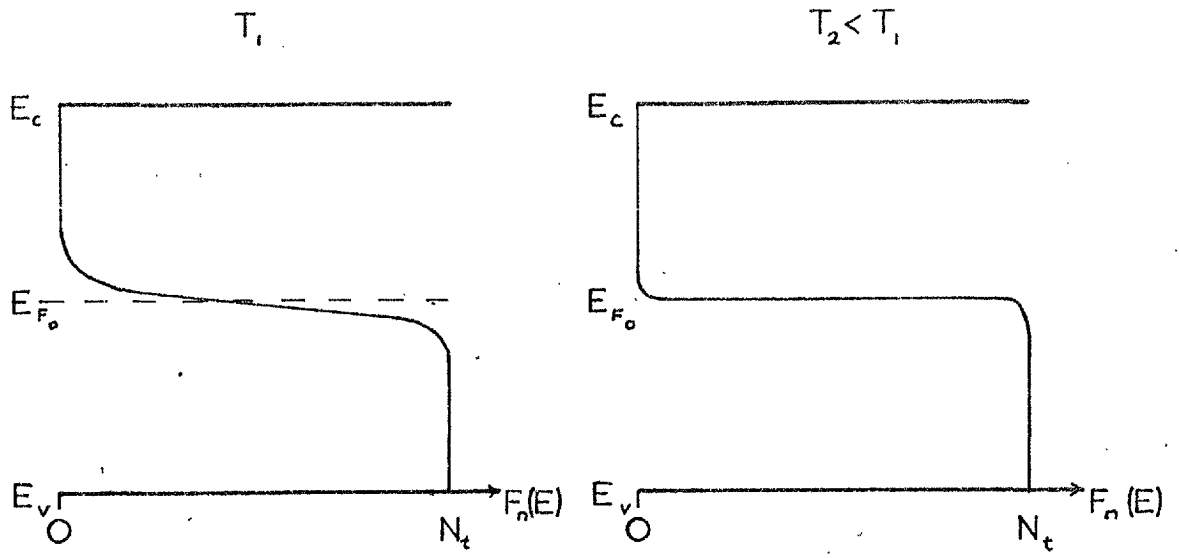
The frequency factor (or 'attempt to escape frequency'), ν , occurring in equation 2.9 is used to provide a link between the Maxwellian distribution for thermal energies, E and the escape probability per unit time, P , expressed as follows:

$$P = \nu \exp\left(-\frac{E}{kT}\right) \dots\dots\dots(2.20)$$

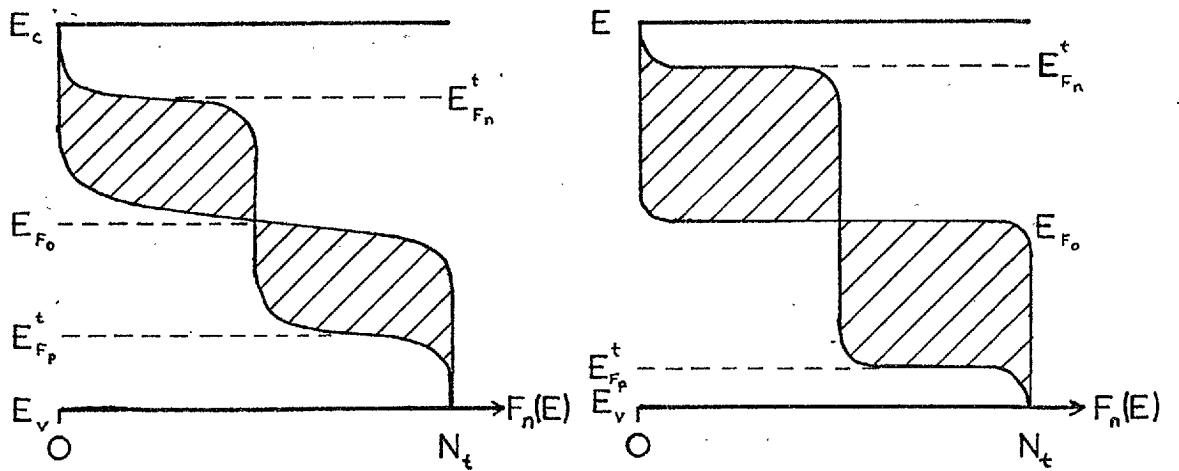
where

$$\nu = N_c \nu S_T$$

for simple energy band surfaces. ν has the dimensions t^{-1} .



(a) Filling diagram of a solid before illumination at T_1 and at T_2



(b) Filling diagram of a solid after illumination at T_1 and at T_2

FIGURE 2.4

If the trap is regarded as a potential box, ν expresses the product of the frequency with which an electron strikes the sides of the box and of the reflection coefficient. It is therefore reasonable to suppose the order of ν to be somewhat less than that of the lattice vibrational frequency of the crystal, $\frac{kT}{h} \sim 10^{12} \text{ sec}^{-1}$.

A survey of estimated magnitudes of ν for TSC measurements on CdS is given in table 2.1, and a value of $\nu = 3 \times 10^{11} \text{ sec}^{-1}$ is used henceforth.

REFERENCE	FREQUENCY FACTOR
Mark (1965)	$\nu \sim 10^{11} \text{ sec}^{-1}$
Bube et al (1966)	$\nu \sim 3 \times 10^{11} \text{ sec}^{-1}$
Tscholl (1968)	$\nu = \exp\left(\frac{E}{0.035\text{eV}}\right) \sim 3 \times 10^{11} \text{ sec}^{-1}$ (for traps at depth 0.9eV)
Brophy and Robinson (1960)	$\nu \sim 5 \times 10^{10} \text{ sec}^{-1}$

Table 2.1. A Survey of Frequency Factors for CdS

2.2.5. Photoconductivity gain

Photocurrents exist in one of two forms; primary photocurrent, created as a direct result of photon energy absorption, and secondary photocurrent, resulting from the passage of a primary photocurrent. In II - VI compounds particularly, the lifetime of carriers produces by one photon may greatly exceed the carrier transit time between electrodes. To

maintain charge neutrality (assuming ohmic contacts) electrons are then injected into the conduction band many times throughout their effective lifetime. The photoconductivity gain factor, G is defined as

$$G = \left(\frac{\tau}{t}\right) \dots\dots\dots(2.21)$$

where τ is the carrier lifetime and t the transit time. For primary photocurrent, where the excited carrier may recombine before reaching an electrode, the gain is smaller than unity, but for secondary photocurrent, values in excess of 10^4 can exist. The gain factor may also be expressed as:

$$G = \left(\frac{i_{ph}}{eab}\right) \dots\dots\dots(2.22)$$

where i_{ph} is the photocurrent produced by a , the density of absorbed photons and b , the volume of the specimen. Due to the difficulty in estimating the absorbed photon density, evaluation of G is difficult.

Release of electrons from traps during TSC measurements will similarly produce currents dependent on the gain factor, and it is generally assumed that the photoconductivity gain factor may be used in TSC experiments. For a particular TSC peak, the trap density, N_t is given by

$$N_t = (Geb)^{-1} \int_{TSC} i_{TSC} dt = a \int_{TSC} (i_{TSC}/i_{ph}) dt \dots\dots\dots(2.23)$$

where i_{TSC} is the thermally stimulated current (which must be integrated over a certain peak). As the carrier lifetime varies with excitation density and while the photocurrent is decaying, only an approximate value of N_t is possible. Value of G as low as 5.5 have been reported by Levine and Mark (1966) for TSC analysis, whereas Ballentyne (1971) found

values of G as high as 10^6 for photoconductivity experiments.

Evaluation of trap densities from TSC curves is therefore difficult and requires absorption measurements on each sample and for each temperature range. In view of the large number of samples tested, the complexity of additional measurements and the uncertainty in the final results, analysis of trap densities has not been considered further herein.

2.2.6. Estimation of trap depth

For fixed values of initial filling and energy depth, the TSC maximum moves to higher temperatures as β increases and as ν decreases. In figure 2.5, a comparison of trap depth for TSC peak temperature is given using the following references:

(i) From equation 2.14, a linear dependence corresponding to $E \sim 29kT$ is obtained for $\nu = 3 \times 10^{11} \text{ sec}^{-1}$ and $\beta = 0.56 \text{ K sec}^{-1}$. This compares favourably with the generally accepted value between $22kT$ and $30kT$ given, for example, by Randall and Wilkins (1945) and Bube et al (1966) for CdS.

(ii) Detailed analysis of TSC based on Shockley-Read statistics has been developed by Simmons and Taylor (1971b), yielding the relationship between temperature of the maximum and trap depth of:

$$E = T^* \left[1.92 \times 10^{-4} \left(\frac{\nu}{\beta} \right) + 0.32 \times 10^{-3} \right] - 0.0155 \text{ eV} \quad \dots (2.24)$$

where E is the trap depth and T^* the temperature of the TSC maximum. From figure 2.5, the graphical representation of equation 2.25 shows similarity to (i) above, and corresponds to $E \sim 31kT$.

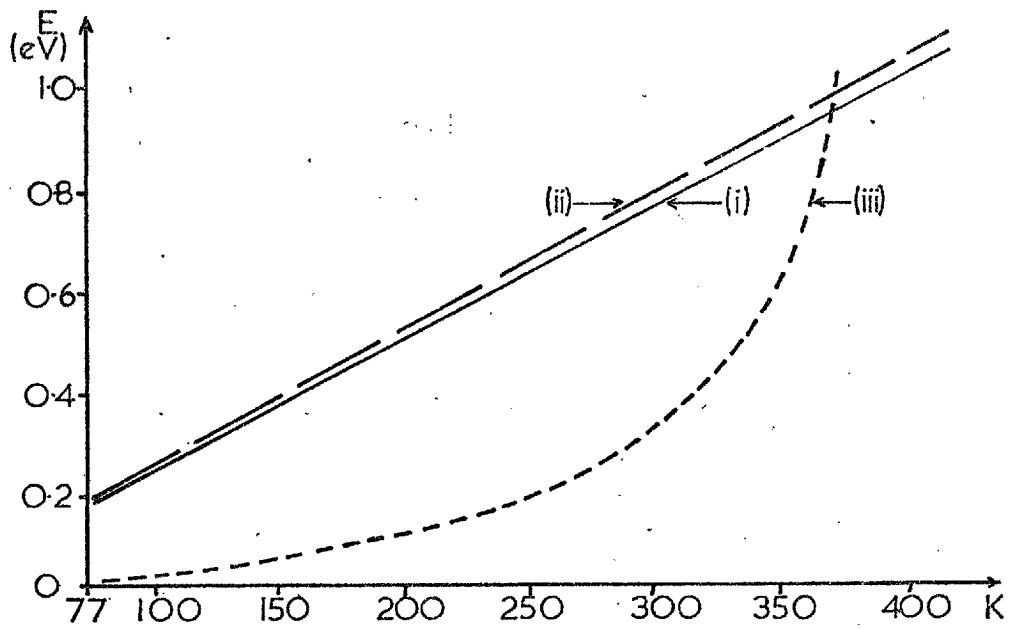


FIGURE 2.5

EVALUATION OF TRAP DEPTH FROM TEMPERATURE
OF TSC MAXIMA

(iii) In section 2.4 the work of Tscholl (1968) is discussed.

From a survey of the capture cross sections of traps in CdS, an empirical formula was developed relating the frequency factor, ν , with the trap depth, E , measured in eV

$$\nu = \nu_0 \exp\left(\frac{E}{0.035}\right) \dots\dots\dots(2.25)$$

The resulting non linear relationship between T^* and E is shown in figure 2.5 using the value of $\nu_0 = 1$.

An independent and reliable assessment of trap depth is also given by the slope of $\ln I$ versus T^{-1} for the initial rise of a TSC peak, as shown in figure 2.2(b).

2.3. Extensions To The Simple Approach

2.3.1. Trap kinetics

Recombination of an electron thermally excited from a trap into the conduction band may be via recombination centres or by retrapping one or more times. Equations to describe TSC curves have been obtained for three conditions:

(i) Electrons spend a time τ in the conduction band before recombining. This is the case of monomolecular kinetics (no retrapping) and is considered in section 2.2.

(ii) The electron has an equal chance of being retrapped or recombining. The condition is described by bimolecular kinetics.

(iii) Electrons are retrapped several times before returning to the valence band. This case also involves bimolecular kinetics, but is generally termed fast retrapping to avoid confusion.

Many methods have been proposed for solving such equations, but as these solutions depend upon different approximations, large discrepancies are found between the results so obtained. From published work on TSC analysis, Nicholas and Woods (1964) have surveyed important contributions relating to trapping kinetics, and only a brief outline is included in this section. The relevant equations are listed in table 2.2.

Garlick and Gibson (1948) were first to consider the bimolecular case showing the shape of the TSC curve depended on the extent of initial trap filling, n_{t_0} . For fast retrapping, where conduction band electrons are essentially in equilibrium with trapped electrons at the TSC peak temperature, Haering and Adams (1960) and Bube et al (1966) obtained expressions to describe the TSC curve. It is not possible to assess the capture cross section of a trap obeying fast retrapping kinetics, however Boer et al (1958) showed that an estimate of recombination capture cross section was possible at the TSC peak temperature.

The theoretical shapes of TSC curves resulting from retrapping kinetics are plotted by Garlick (1949) for several trap depths and initial occupancy conditions. The effect of retrapping is twofold:

- (i) The TSC peak temperature depends on the extent of initial trap filling.
- (ii) Reduction in magnitude and increase in width of the TSC peak invalidates the initial rise method for evaluation of trap depth (as described in section 2.2.6).

REFERENCE	EQUATION	CONDITIONS
Garlick and Gibson (1948)	$\sigma = \frac{n_{t_0}^2 \tau \mu e \nu \exp\left(\frac{-E}{kT}\right)}{N_t \left[1 + \frac{n_{t_0}}{N_t} \frac{\nu}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT \right]^2}$	BIMOLECULAR KINETICS (n_{t_0} is the density of traps initially filled)
Herring and Adams (1960)	$\sigma = \frac{N_c e \mu}{N_t} n_{t_0} \exp\left(\frac{-E}{kT}\right) - \frac{e}{N_t \beta \tau} \int_{T_0}^T N_c \exp\left(\frac{-E}{kT}\right) dT$	FAST RETRAPPING
Eube et al (1966)	$E = kT^* \ln \frac{N_c}{n_c^*} - \frac{\eta}{1-\eta}$	EXTREMELY FAST RETRAPPING (η is the fraction of traps occupied at T^* when the density of free electrons is n_c^*)
Boer et al (1958)	$S_{R^v} = \frac{E}{kT^*} \cdot \frac{\beta}{n_c^* T^*}$	An estimate of recombination cross section during fast retrapping conditions

TABLE 2.2. TSC EQUATIONS FOR BIMOLECULAR AND FAST RETRAPPING KINETICS

2.3.2. Other TSC methods

Various attempts have been made to minimise the shortcomings in the basic TSC measurements, such as lack of peak resolution and the assumption that mobility and carrier lifetime are temperature independent. In this section we shall give a general outline of these processes and the reasons for these modifications.

The method of thermally stimulated capacitor discharge was introduced by Zhdan et al (1968). One electrode of a simple parallel plate capacitor consisted of a thin film of CdS to which ohmic contacts were attached. The capacitor was cooled from a high temperature under equilibrium conditions with a field applied. At sufficiently low temperature, the capacitor was short circuited, and after partially discharging, contained only charge from trapped carriers. Subsequent heating of the semiconductor released trapped electrons giving rise to current peaks in the external circuit. The motion of these carriers to the metal electrode, acting as a recombination channel was independent of carrier mobility. In a later publication, Zhdan et al (1970) show that an additional parallel capacitor can be used to enhance resolution of current peaks.

The influence of an electric field on trap filling has been considered by many workers, and can be used as an alternative to optical irradiation. Bordovskii and Izvozhikov (1970) combine SCIC and TSC methods to obtain field filling rather than field ionisation of traps. Deep traps can be filled without cooling the specimen, so the method is advantageous for systems in which excessive cooling promotes contact failure. It is also suggested that trap parameters could be deduced from thermal depolarisation of the quasiphotoelectret state, formed during the flow of SCIC. It appears however that Semak et al (1967) used essentially the same method by combining

both electric field effect and optical irradiation methods for trap filling. A sample was illuminated at low temperature while an electric field was applied. Carriers excited by light were separated by the field and captured by levels, giving rise to an internal electric field, i.e. a photoelectret state. Removal of the field and subsequent heating gave a TSC spectrum shown to be dependent on the square (not the first power as for normal TSC) of carrier density in the conduction band. Narrower and therefore better resolved peaks were produced.

The provision of energy from thermal stimulation produced by a rapid increase in heating is universally applicable to systems requiring energy in excess of kT but less than one or two electron volts. Trapping parameters for ionic conductivity in alkali halides were considered in an analogous way to TSC by Bucci and Fieschi (1964). Polarisation of the crystal during cooling followed by measurement of the relaxation current whilst heating, a process called "ionic thermoconductivity" showed current peaks similar to TSC peaks from which ionic trapping parameters can be deduced. A similar method has been used by Servini and Jonscher (1969) to detect deep ionic traps in thin films of SiO_2 .

Thermal stimulation by rapid heating has been used by Schubert and Boer (1971) to desorb oxygen from the surface of CdS platelets. From the dependence of oxygen partial pressure (measured by a mass spectrometer) with temperature, oxygen chemisorption energies were estimated for peaks in the spectrum.

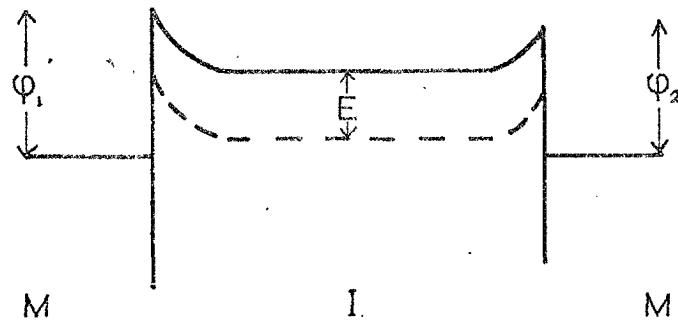
A T^2 heating rate, often thought advantageous for TSC analysis, was shown to be of little use by Manchanda and Mathur (1971). The temperature dependence of the free electron concentration eliminated TSC peaks under charge neutrality conditions.

Several attempts have been made to improve analysis of TSC curves. Haine and Carley-Read (1968) derived expressions describing the slope, position of maximum and area under a TSC curve, and proposed the constant temperature method of TSC. If heating is quickly stopped during the initial rise of a TSC peak, the subsequent decay curve can be analysed to provide data independent of relative rates of retrapping and recombination. Both methods involve complex equations and require well formed TSC peaks. Though they used CdS as an example, such analyses would not be generally applicable to the complex TSC spectra usually found for CdS. Wright and Allen (1966) investigated conditions of optical stimulation and trap emptying processes, extending their method to explain the appearance and disappearance of specific peaks, and Cowell and Woods (1967) reported a method for accurate trap analysis using curve fitting techniques. Though each method has advantages under particular conditions for specific TSC results, it appears that no definite improvement has been made to the general TSC theory, implying that TSC analyses of this kind must be used only with extreme care.

2.3.3. Dielectric relaxation

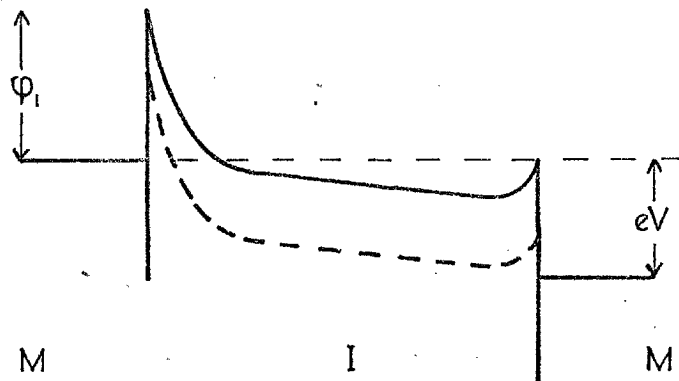
Simmons and Taylor (1971b) have recently reported interesting thermal electric characteristics resulting from dielectric relaxation in Metal-Insulator-Metal systems having blocking contacts. In figure 2.6(a) the energy band diagram of the unbiased system is shown (metal-semi-insulator interfaces are considered in section 3.3). Application of a voltage V causes an immediate change in the band diagram shown in figure 2.6(b) which relaxes to a (quasi) steady state situation, figure 2.6(c).

Consider now the effect of a bias V_1 applied at a high temperature,

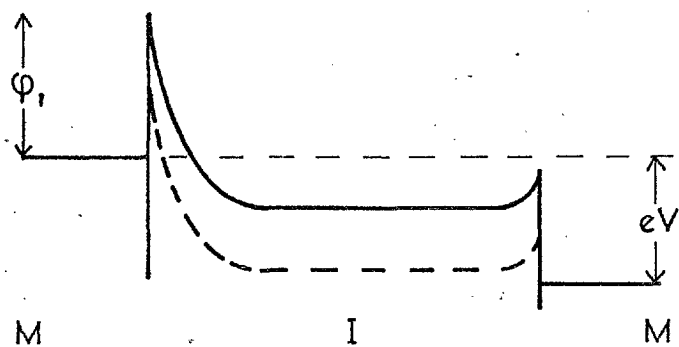


(a) M-I-M structure zero bias

ϕ_1 and ϕ_2 are heights of contact barriers due to blocking contacts



(b) Immediately after application of voltage V



(c) (quasi) Steady state condition V applied

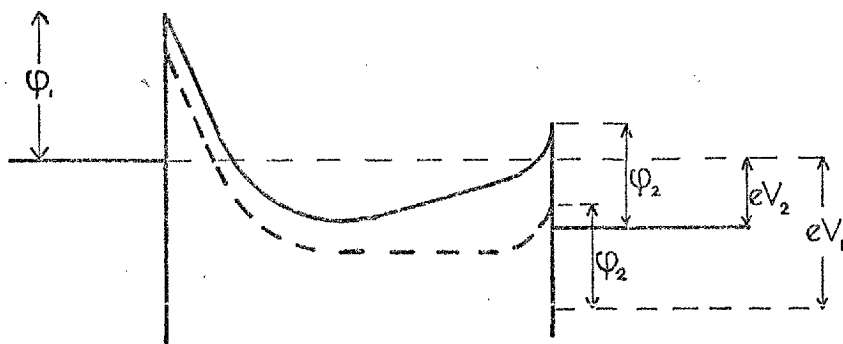
FIGURE 2.6

figure 2.7(a). The system is in steady state and will be maintained as such during slow cooling to say 77K. Here, by reducing the bias from V_1 to V_2 and heating up rapidly, two relaxation processes will be promoted. Initially, the conduction will be controlled by a non steady state bulk limited process, and relaxation to a quasi steady state results, as shown in figure 2.7(b). At higher temperatures, a steady state condition develops involving charge transfer from one electrode depletion region to the other (i.e. a redistribution of space charge brought about by the initial bias, V_1). Figure 2.7(c) shows the final steady state condition for V_2 .

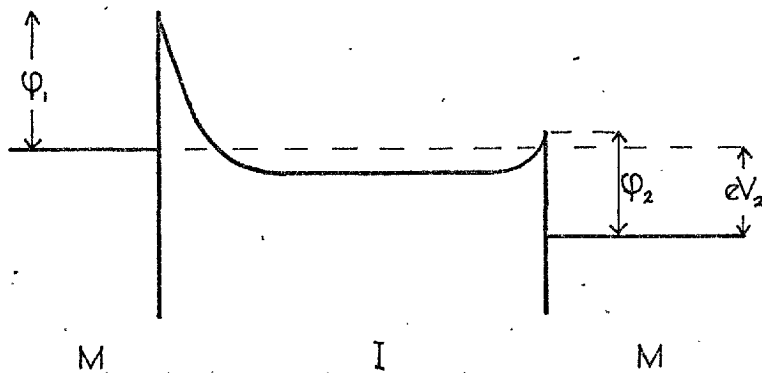
Although relaxation processes in thin film systems are of little immediate relevance to the present work, the results pertaining to contact region relaxation are of considerable importance for high temperature peak analysis.

Blocking contacts prevent the injection of carriers into the system at all but high temperatures. Current will however flow in the external circuit as charge is transferred from one side of the insulator to the other. Current peaks in the low and mid temperature regions result only if traps are initially filled, but the higher temperature peaks due to electrode depletion regions will occur if bias during cooling differs from the heating bias.

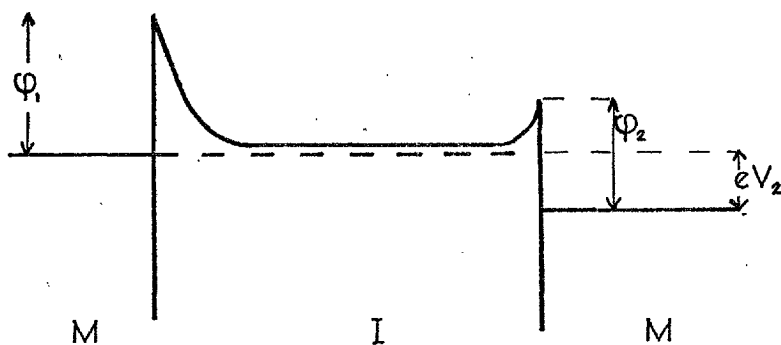
It is also interesting to note that under certain circumstances (e.g. cooling with a larger voltage than that used during subsequent heating) the relaxation current flow is in the opposite direction to that expected for the bias applied. Figure 2.8 shows the TSC spectrum for a simple system consisting of one trap, depth E , having blocking contacts and plotted as $\ln J$ versus T^{-1} .



(a) Steady state condition for V_1 , applied (dashed) and immediately following reduction from V_1 to V_2 in M-I-M system



(b) Relaxation to quasi steady state for V_2



(c) Relaxation to final steady state for V_2

FIGURE 2.7

In figure 2.8 the effective Poole-Frenkel trap lowering factor ($B\mathcal{E}^{1/2}$) has been included. $\mathcal{E}_c$ is the field at the relevant cathode and $\mathcal{E}_i$ the field across the insulator ϕ_1 is the height of the lower contact barrier and $B = e^{3/2} (\epsilon \epsilon_0 \pi)^{-1/2}$.

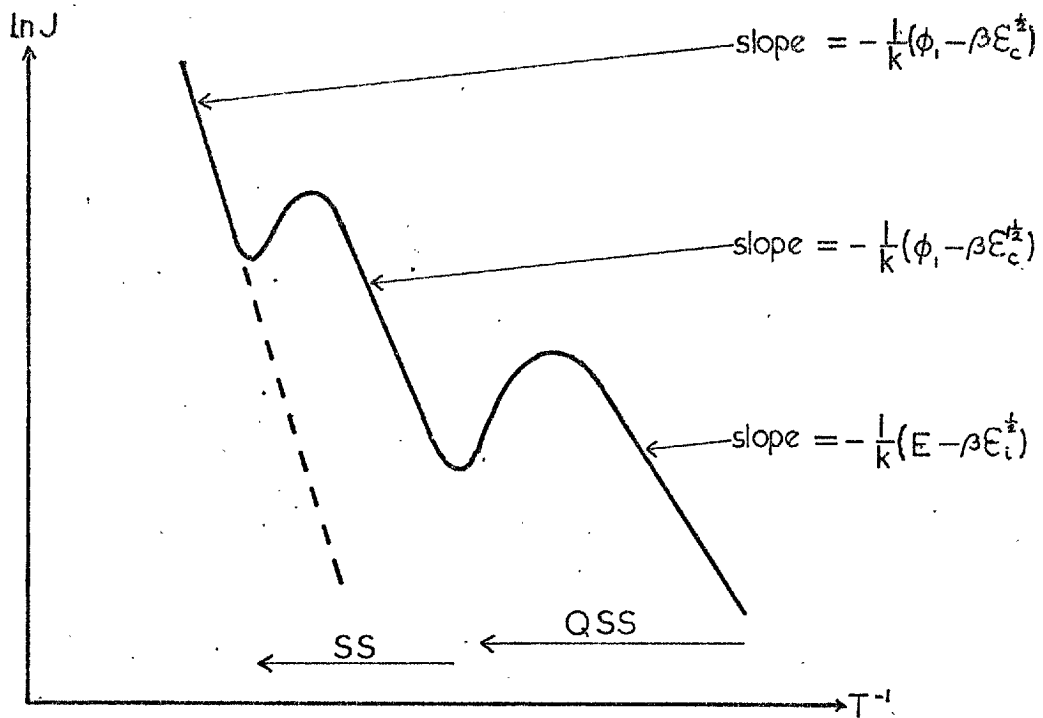
To summarise, the high temperature peak will not appear if the same bias is used for both cooling and TSC heating. For thicker crystals, optical stimulation would be necessary to observe the bulk (low temperature) TSC peaks, and the effect of a bulk electric field, $\mathcal{E}_i$ could be neglected. Blocking contacts onto any dielectric (thin film or thin crystal) should therefore produce an "electrode dependent" TSC peak under correct biasing conditions.

2.4. Evaluation of TSC Data For CdS

2.4.1. Introduction

The transformation from theoretical TSC curves to actual results obtained from CdS crystals is difficult and it is not surprising therefore that many of the published results are contradictory, particularly as TSC curves are frequently not reproducible from one run to the next even on the same specimen. Qualitative rather than quantitative results are obtained from TSC curves for CdS. Detailed analyses using more sophisticated techniques do not generally improve the situation.

A survey of traps created by impurities or specific post growth treatments ~~are~~ omitted because the platelets used in the present work were tested in "as grown" conditions. Theories relating stoichiometric variations with intrinsic bulk traps will be considered only to the extent



QSS = Relaxation to quasi steady state
 SS = Relaxation to steady state

FIGURE 2.8

GRAPH OF $\ln J$ vs T^{-1} FOR DIELECTRIC RELAXATION
 AFTER SIMMONS AND TAYLOR (1971)

of direct relevance to the bulk phenomena observed in platelets, and discussions will be directed towards formation and annihilation of high temperature TSC peaks.

2.4.2. Bulk trapping

Many attempts have been made to review bulk trapping in CdS crystals. Ditfield and Voigt (1963) studied eleven ways of analysing TSC data without particular success, however Nicholas and Woods (1964) found definite correlations in their study of nine TSC methods. The existence or not of discrete or continuous distributions of traps has not been conclusively established. Bube et al (1966) and Tscholl (1968) favour the latter, whilst Nicholas and Woods (1964) together with the majority of other workers at present prefer the concept of discrete traps.

Discrete trapping levels in CdS are characterised by either trap depth, E or the temperature T^* at which the TSC maximum occurs. No simple relationship exists between T^* and E because of the different kinetic emptying mechanisms. The data shown in table 2.3 gives estimated depths of major traps in CdS and the approximate temperature range in which their corresponding maxima occur, following the survey of Nicholas and Woods (1964),

E (eV)	T^* (K)
0.05	90 - 150
0.14	135 - 190
0.25	170 - 295
0.41	270 - 300
0.63	320 - 350
0.83	~ 290

Table 2.3.

No single TSC run exhibits all traps. The first peak, occurring at about 90 - 100 K is usually observed, and is characteristic of bulk trapping in CdS. The detection of the next three traps in table 2.3 varies from sample to sample, and generally depends on specimen stoichiometry. Traps at 0.63 eV and 0.83 eV never occur together on the same TSC run, and the controversy regarding models to explain both creation and annihilation of these traps is critically reviewed in the following five sections.

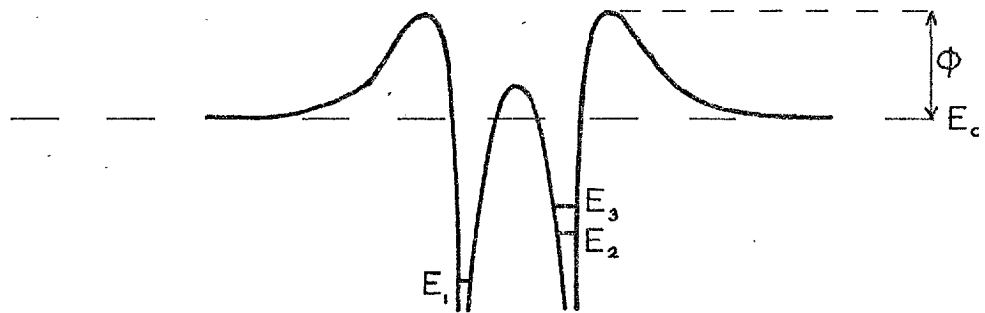
2.4.3. The Nicholas and Woods model

Continuing from the initial work by Woods and Wright (1958) on identifying traps due to chlorine, gallium and copper impurities in CdS, Nicholas and Woods (1964) proposed the following model for undoped CdS. The three traps with the lowest energy (see table 2.3) all have very small cross sections ($\sim 10^{-20} \text{ cm}^2$) and are attributable to sulphur vacancies. Cadmium vacancies were thought responsible for the traps at 0.83 eV and 0.63 eV, and in a later publication, Woods and Nicholas (1964) reported photochemical creation of the 0.41 eV and 0.83 eV traps (which always occur together) by irradiating the crystal with the temperature maintained between 220 K and 300 K. The 0.83 eV trap exhibited a very large cross section ($\sim 10^{-14} \text{ cm}^2$) but emptied monomolecularly due to dissociation of the trap following electron emission. The 0.63 eV trap was created only at high temperatures ($\sim 350 \text{ K}$) during irradiation, and exhibited fast retrapping kinetics during emptying with an estimated recombination cross section of 10^{-16} to 10^{-18} cm^2 . Association of cadmium vacancies which give rise to a "colloidal" sulphur complex having a large capture cross section could form such a trap, and would dissociate when heated to higher ($\sim 350 \text{ K}$) temperatures. Association of charged cadmium and sulphur vacancies were suggested for the 0.83 eV trap following

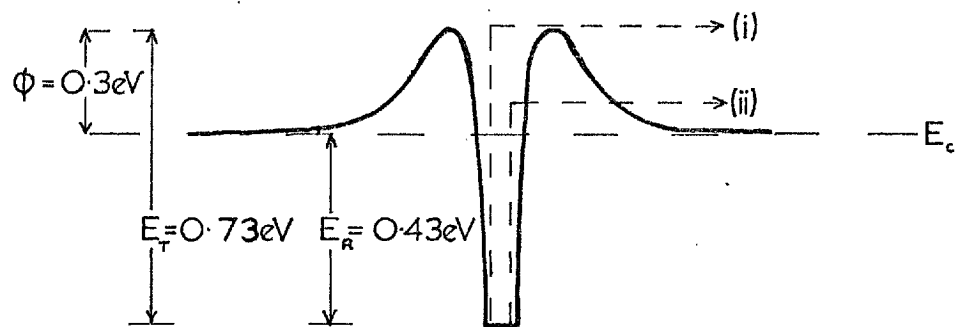
the work of Van Gool and Diemer (1962). Apple and Williams (1959) showed that dipolar association of such pairs of defects can lead to sets of energy levels which permit radiative recombination. The theory of donor and acceptor pair agglomeration was extended by Tscholl (1968) for CdS, and is summarised in section 2.4.6.

2.4.4. The Trofimenko model

Trofimenko et al (1964) investigated the effect of temperature, the duration of white light irradiation and the illumination procedure prior to a TSC run on crystals of CdS treated with sulphur vapour. The redistribution of traps producing peaks at 263 K, 301 K and 338 K (corresponding to Nicholas and Woods traps at 0.41 eV, 0.83 eV and 0.63 eV respectively) ~~was~~ ^{was} explained by assuming the three trapping levels were very close in space (neighbouring lattice sites) and surrounded by a common coulombic repulsion barrier, as shown in figure 2.9(a). The barrier exists when all three trapping levels are empty, and increases as an electron becomes trapped. The energy levels, E_1 , E_2 and E_3 correspond to the TSC peaks at 338 K, 301 K and 263 K respectively. At low temperatures (< 190 K) it is assumed that S_1 is far smaller than S_2 and S_3 , the corresponding capture cross sections of the trap, whilst at higher temperatures the inequality changes sign. Illumination at low temperatures fills E_2 and E_3 , whilst illumination at higher temperatures fills E_1 preferentially. The magnitude of the barrier ϕ is determined by the state of charge within the trap, and when calculated from the dependence of TSC peak magnitude with illumination temperature appears to be 0.7 eV to 1 eV. The concept of hold capture by the centre without hold-electron recombination is necessary to reduce the barrier height, ϕ to a practical value.



(a) The model of Trofimenko et al



(b) Double acceptor trap of Bube

- Process (i) excitation over the barrier (higher temperature)
 (ii) tunnelling through the barrier (low temperature)

FIGURE 2.9

2.4.5. The double acceptor model of Bube

On the basis of a quasi continuous trap distribution, Bube et al (1966) calculated the density of traps in CdS over the trapping spectrum between 0.1 eV and 0.7 eV using an analysis based on quasi fermi levels. A discrete trap of depth 0.75 eV with a cross section of $\sim 10^{-14} \text{ cm}^2$ was responsible for a peak at 289 K, produced by continuous illumination whilst cooling. The illumination dependence and emptying kinetics of the latter were explained using a similar model to Trofimenko et al (1964) but involving a non photochemical approach.

A trap E_R of depth 0.43 eV surrounded by a potential barrier ϕ , of height 0.3 eV is shown in figure 2.9(b). At low temperatures, Bube postulated electron release by excitation to the conduction band, followed by tunnelling through the barrier (process (ii) in figure 2.9(b)), whereas at higher temperatures, excitation is over the barrier (process (i)), requiring a total activation energy, E_T of 0.73 eV. Through the emission cross section was $\sim 10^{-14} \text{ cm}^2$ for the 289 K peak, the magnitude of the capture cross section of the centre, a parameter that reduces exponentially with decreasing temperature, was $< 10^{-20} \text{ cm}^2$ at low temperature, and the trap was not filled for excitation below 210 K. The 289 K peak corresponded to the 0.83 eV trap of Nicholas and Woods (1964), having comparable depth, cross section and trapping kinetics. Bube made no mention of the 0.63 eV trap. In a later paper (Im et al, (1970)), following the work of Tscholl (1968), Bube finally accepted the existence of photochemical effects in CdS, and postulated an illumination dependence on trap filling involving both temperature and wavelength of the excitation.

2.4.6. The photochemical model of Tscholl

An excellent summary of photochemical interpretations of phenomena in CdS crystals has been given by Tscholl (1968). The TSC spectrum rather than isolated traps is considered, and the proposed model is based on one kind of trap formed by the interaction of donor and acceptor defect pairs. Trapping depths and capture cross sections are modified by the separation of the pairs; long distance separations corresponding to shallow traps and shorter distance pairs to deeper traps. The acceptor is assumed to be the trap, and the close proximity of a positively charged donor effectively increases the trapping depth. Photoinduced phenomena are attributed to illumination promoting a change in distribution of pair distances at temperatures above 240 K. Analysis is based on the individual constituents retaining their effective charge and energy level within the band gap. Tscholl used isovalent impurity atoms (nickel) to increase defect densities but maintain charge neutrality in the dark to verify the model.

It is possible that Tscholl's photochemical hypothesis could be linked with Bube's double acceptor model via a two stage internal transition. Transferring an electron from one defect to the other before release involves an effective tunnelling mechanism and may be compared with Bube's tunnelling model for low temperatures. Direct escape of the trapped electron from the pair to the conduction band would then be analogous to Bube's explanation of higher temperature excitation over the barrier.

In view of Bube's recent publication (Im et al, (1970)) favouring photochemical creation of trapping centres, it should now be possible to substantially develop the present models used for bulk trapping phenomena in CdS crystals.

2.4.7. Cowell and Woods' interpretation of deep traps in CdS

Following their successful work on the evaluation of TSC peaks using successive approximations and curve fitting techniques, Cowell and Woods (1969) developed further the model proposed by Nicholas and Woods (1964) to explain the behaviour of deep traps in CdS. The 0.63 eV and 0.84 eV traps were attributed to charged cadmium vacancies. The former trap results from an association of two cadmium vacancies that dissociate under illumination above 270 K to form two 0.84 eV traps. The 0.84 eV centre is also surrounded by a potential barrier 0.35 eV high that does not allow it to be filled below 200 K. Cowell and Woods suggested that the potential barrier could be due to a cadmium vacancy having already one electron associated with it, and the 0.84 eV trap arises from its ability to trap a second electron, released by a photochemical reaction. The 0.63 eV trapping centre is created from the association of two cadmium vacancies formed by baking in the dark.

Cowell and Woods were first to attribute the deeper trapping levels to particular associated defects, and in the discussion of results, recent work on cadmium vacancies in CdS is shown to substantiate their model.

2.4.8. Summary

The wealth of literature reporting trapping phenomena in CdS is reduced for present requirements to three important traps; the generally observed low temperature TSC peak at ~ 90 K, characteristic of bulk trapping, and the 0.83 eV and 0.63 eV centres exhibiting TSC peaks at about 290 K and between 320 K and 350 K respectively. Photochemical creation of the 0.83 eV trap is now widely accepted, and general agreement exists for both the conditions necessary for formation and annihilation of

the centre. Fast retrapping kinetics apply to the 0.63 eV trap, causing a spread in both temperature of the TSC maximum and shape of the TSC peak, depending on initial filling conditions, as outlined in section 2.3.1. Recent models suggest that agglomerations of cadmium vacancies yield the complex defect responsible for the deep traps.

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CHAPTER III

SURFACE EFFECTS INFLUENCING ELECTRICAL CONDUCTION IN CdS

3.1. The Role of the Surface

The properties of crystals in the form of thin platelets are considerably influenced by surface effects. In this chapter, surface effects contributing to electrical conduction are considered. The nature of the surface itself, i.e. the termination of a crystal lattice, gives rise to "dangling" bonds which cause surface traps, enabling a high density of holes and electrons to be trapped simultaneously on the surface.

Two major factors which influence the surface are considered in some detail, (i) the behavior of oxygen molecules on II - VI surfaces and (ii) the effect of a metal contact used to form an electrode. The second concept is developed in the last section which reviews specifically indium contacts to CdS.

3.2. Carrier Trapping on the Surface of CdS

3.2.1. Intrinsic surface states

Detailed studies of intrinsic surface states have been reported for metallic and covalent crystals, but surprisingly few consider ionic crystals. Levine and Mark (1966) developed a comprehensive theory for estimating the surface parameters of ionic crystals and applied it to numerous halides, oxides and sulphides. The model used is based on simple electrostatics, and surface ions are considered equivalent to bulk ions

except for their reduced Madelung constant. Here, emphasis will be placed on results relating to the $11\bar{2}0$ surface of CdS crystals.

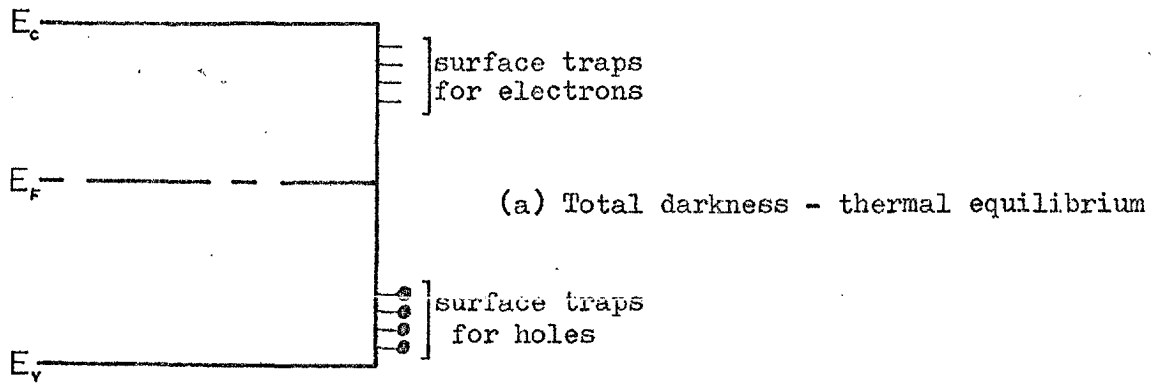
Modification of their purely ionic model is necessary to account for the ionic-covalent nature of the bonds in CdS. Calculations can be made in the same way but using values of reduced effective ionic charge which allow for the degree of covalency. These yield trap depths within the range 0.2 to 0.4 eV.

Optical filling of the surface traps depends critically on the minority carrier lifetime. During optical irradiation the electron concentration in the conduction band of n type CdS exceeds the hole concentration in the valence band by several orders of magnitude because of the inequality in carrier lifetimes, $\tau_n \gg \tau_p$. If the hole transit time, t_p exceeds τ_p , holes will never reach the surface, and the accumulation of electrons will be limited only by electric field strength in the potential barrier at the surface which results from bulk compensation of the surface trapped electrons. Figures 3.1(a) and 3.1(b) show respectively the energy band structures for darkness and just after illumination commences. An increase in optical irradiation intensity decreases t_p , and hole capture by the surface begins when $t_p \lesssim \tau_p$, as shown in figure 3.1(c). In figure 3.1(d) the photocurrent and response time measured by Levine and Mark are shown for CdS platelets as a function of the intensity of illumination. A sharp rise in response time is exhibited (corresponding to 10^{-6} A photocurrent) due to the sudden penetration of holes to the surface which begin to compensate the trapped surface electrons. With only electrons trapped on the surface, trap filling is limited to 10^{-4} of the total number of available traps (10^{14} cm^{-2}) whereas compensating surface holes and electrons enable almost all traps to be filled. From results using adsorption of various gases, an experimental estimate of surface trap

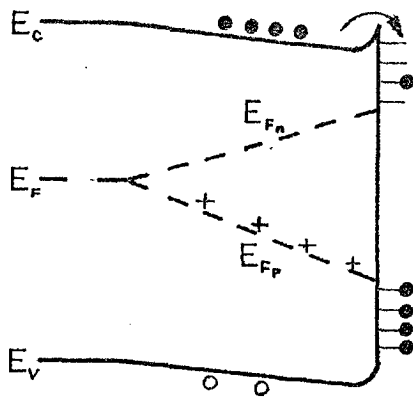
FIGURE 3.1

THE ENERGY BAND STRUCTURE FOR A CdS SURFACE
AND CORRESPONDING ILLUMINATION CHARACTERISTICS

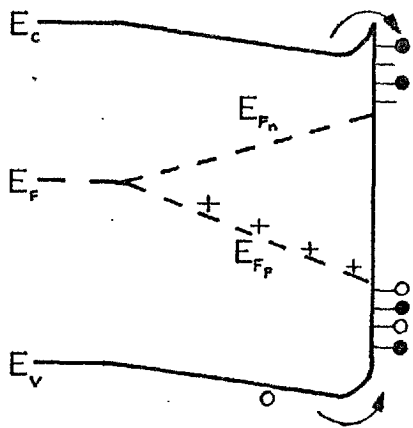
(after Levine and Mark, 1966)



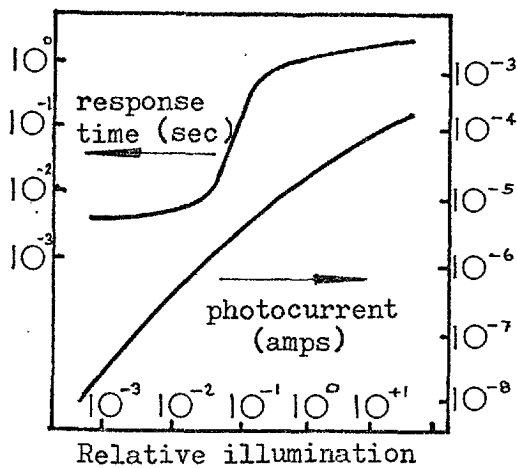
(a) Total darkness - thermal equilibrium



(b) Just after illumination



(c) Steady state condition under illumination when $t_p < \tau_p$



(d) Response time and photocurrent vs illumination

depth of between 0.2 and 0.7 eV was obtained.

Reed and Scott (1965) proposed the existence of surface states above the Fermi level that behaved as electron traps in oxygen free conditions. Measurements of the field effect mobility on the surface of photosensitive CdS by Shirshov et al (1969) suggested surface traps lying within the energy interval 0.1 to 0.3 eV below the conduction band and an investigation by Bugatti (1969) on the absorption edge of CdS indicated surface trap depths of about 0.3 eV with an estimated density of 10^{13} cm^{-2} . These results appear reasonably consistent with the model of Levine and Mark.

3.2.2. Exciton creation

Coulombic attraction between a photogenerated hole and electron in close physical proximity can produce an exciton. The bound configuration can be visualised as the two carriers revolving about their common centre of mass with quantitized angular momentum. Until scattering processes dissociate the complex into a hole-electron pair, the effectively neutral exciton can either migrate through the lattice or be associated with a charged or neutral donor or acceptor, or a donor-acceptor pair. In either case, the exciton carries with it a quantity of energy.

The existence of excitons was first demonstrated using CdS. Absorption lines of complex fine structure that are observed on the absorption edge were attributed to excitons. An experiment has been reported by Balkanski (1957) in which two electrodes were placed at one end of a crystal, and the crystal was irradiated in a narrow region at the other end. A field independent current flow between the electrodes indicates that energy is transported (several millimetres) along the crystal

without the transport of individual charges. A diffusion constant of $100 \text{ cm}^2 \text{ sec}^{-1}$ with a lifetime of 10^{-3} sec and diffusion length of 0.3 cm were deduced for the exciton. The activation energy for dissociation of excitons in CdS was calculated by Seitz (1949) to be $< 0.17 \text{ eV}$ whilst Diemer and Hoogenstraaten (1957) found it to be 0.1 eV.

Creation of an exciton complex during optical irradiation followed by migration to the surface (during a lifetime of 10^{-3} sec) could be important in the present work. Dissociation of the exciton at the surface would produce a high surface carrier density and intrinsic surface traps would rapidly fill. There are two objections to this idea:

(a) The energy of the irradiation (Xenon tube) is far in excess of the CdS energy band gap, and exciton creation is most likely when irradiation energies very close to the intrinsic band gap are used.

(b) An exciton model cannot be used to explain the sudden rise in response time observed by Levine and Mark.

During the course of surface TSC investigations the emptying kinetics of surface trapping states are important whereas the exact nature of optical filling is of little consequence. Even if excitons were responsible for surface trap filling, no simple method exists for confirming this by TSC measurements. The binding energies of excitons ($\sim 0.1 \text{ eV}$) are too low to account for the surface phenomena reported in section 5.5.3. and indeed the likelihood of excitons being themselves trapped on the surface for a period of several minutes (between irradiation and TSC heating) is very small. The role of excitons in the present study of CdS platelets is probably minimal and it will be ignored.

3.3. The Effect of Oxygen

3.3.1. Introduction

The mechanisms governing the effects of oxygen, on electronegative gas, on the surface of CdS single crystals still remain a subject of conjecture inspite of the considerable attention paid to them in recent years. In this section, a brief resume of the proposed models will be presented.

3.3.2. Mechanisms for oxygen adsorption and desorption

Annihilation of TSC peaks attributed to sulphur vacancies following oxygen admission led Woods (1958) to conclude that oxygen molecules were adsorbed onto sulphur vacancy sites. This simple adsorption model was later rejected by Mark (1965) on the basis of chemisorption and desorption measurements. The energy levels due to oxygen ions are located 0.9 eV below the conduction band. In the dark, these deep lying electron traps are full and are compensated by ionised shallow bulk donors. A depletion barrier is created which extends $\sim 10 \mu\text{m}$ into the platelet. In thin platelets ($< 20\mu\text{m}$ thick) the entire band structure of the crystal is raised, making it more insulating. In the absence of oxygen, surface band bending is minimal, but after oxygen uptake, a barrier of height 0.37 eV resulted, as shown later in figure 3.2(d). The rate limiting step during photoinduced absorption or desorption is the transfer of charge from the bulk to the surface across the depletion layer.

In oxygen free conditions, Mark postulates a very high density of trapped carriers located on the surface and situated in energetic troughs, separated by energy maxima. This theory has been substantiated by Levine and Mark (1966) as described in section 3.2. Recombination of carriers

trapped on the surface is promoted by exposure to oxygen. The energy band structure proposed by Mark is shown in the discussion, section 3.3.3. (figure 3.2).

The basic model of Mark has been extended by Weber (1970). He suggested that oxygen is first physically adsorbed as molecules, then captured by active surface centres (defects, vacancies etc.) before being chemisorbed as charged molecules, O_2^- . Photodesorption of the molecules initially involves hole capture by the oxygen followed by a thermally activated step to free the oxygen from the active surface centre. It is interesting that the maximum value of the activation energy measured by Weber for photodesorption (0.34 eV) is very near the depletion barrier height (0.37 eV) calculated by Mark, so a rate limiting step requiring an electron to surmount the depletion barrier may be involved.

Further evidence that oxygen occupies a sulphur vacancy was reported by Novikov and Cherednicherko (1970). An emission line characteristic of an exciton plus sulphur vacancy defect was quenched after oxygen admission, but reappeared following electron bombardment in vacuum to remove the oxygen.

In contradiction to the above models, Schubert and Boer (1971) published some results indicating the desorption of oxygen as an atomic species rather than as a molecule. Thermally stimulated desorption (TSD) of oxygen from the surface of CdS platelets was measured using a partial pressure analyser. The TSD spectrum resembled a TSC peak, and indicated an activation energy of 0.9 eV in agreement with the results of Mark. Species of monatomic oxygen were observed with negligible participation of oxygen molecules. The species of oxygen taking part in adsorption and chemisorption was not discussed, and the study was mainly concerned with

oxygen desorption and the electronic sensitization of the Cd rich near-surface region ($< 10^{-5}$ cm thick) of CdS platelets. It was shown that 3×10^{15} atoms cm^{-2} could be accommodated on the surface of CdS, and an increase in both photo and dark current up to 10^6 times resulted from successive oxygen desorption. The random walk time of photoexcited minority carriers determined both oxygen desorption and the recombination of holes and electrons on the surface in the presence of oxygen. Centres with large capture cross sections ($\sim 10^{-14}$ cm^2) in the bulk were attributed to defect agglomerates, most probably in the form of Cd vacancies.

The role played by oxygen in the metal contact evaporation process has been considered recently by several authors, and this will be briefly discussed in section 3.4.

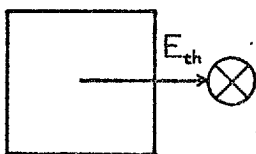
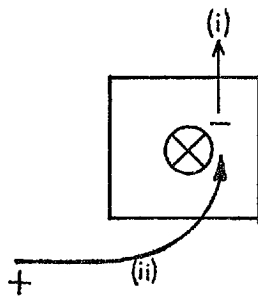
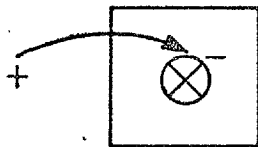
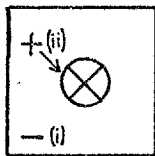
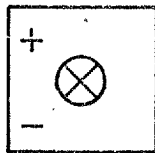
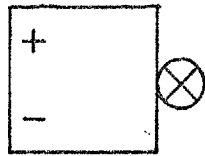
3.3.3. Discussion

It is apparent from section 3.3.2. that considerable agreement has been reached regarding the mechanisms involved for the adsorption and desorption of oxygen on CdS surfaces. Oxygen would appear to give rise to an energetic level 0.9 eV below the conduction band and, within certain limits, the way in which chemisorption proceeds is well understood. It is, therefore, surprising to find the discrepancy involved as to the nature of oxygen species which is absorbed. The hypothesis of Weber renders Schubert and Boer's mass spectrometer work more convincing, but further studies are necessary to be certain about the nature of oxygen participating in adsorption and chemisorption. For the present study it is not important whether oxygen exists as O or O_2^- on the surface of CdS.

The chemisorption mechanisms are summarised in figure 3.2. The

FIGURE 3.2

Schematic representation of centre



E band diagram

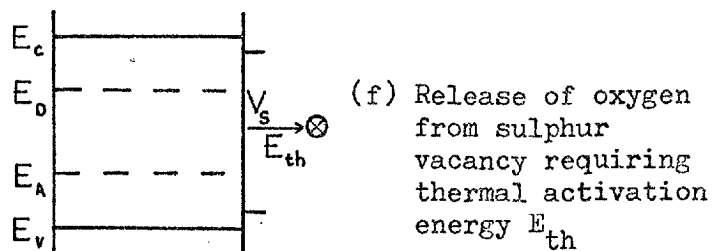
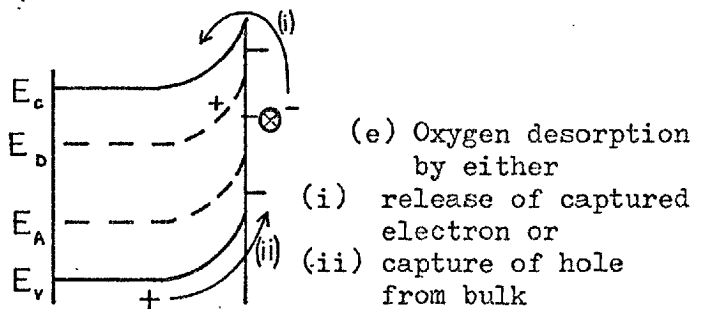
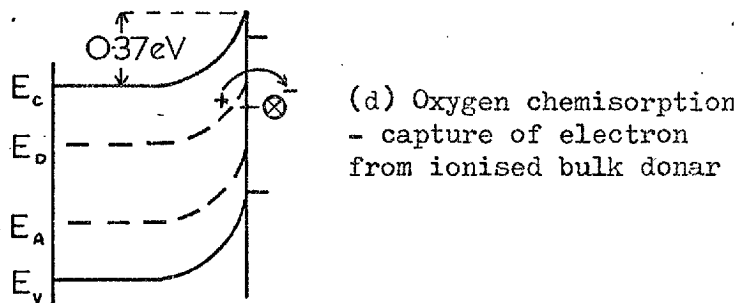
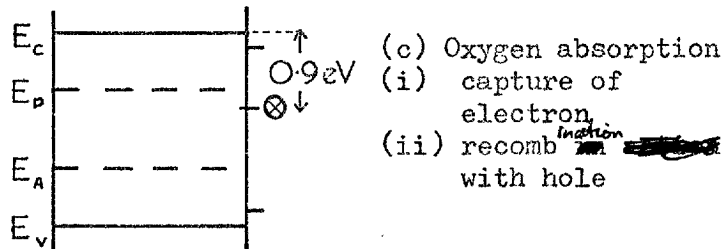
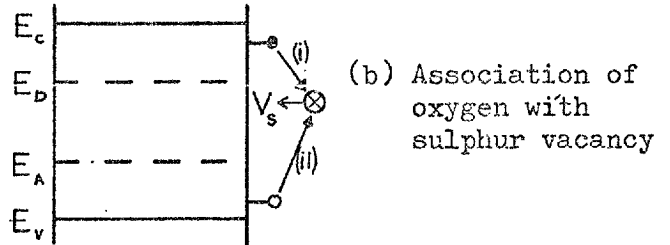
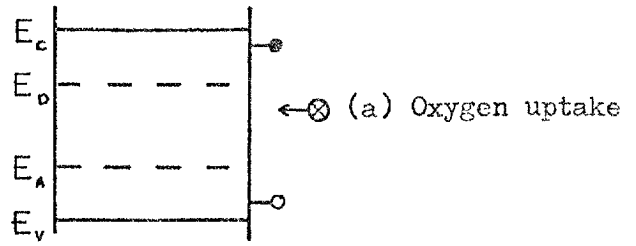


diagram is a schematic representation of an active surface centre which in physical terms could be a sulphur vacancy, and the corresponding energy band diagrams. Plus and minus signs represent holes and electrons respectively, trapped on the surface. The symbol  has been used to represent oxygen (atom or molecule) because of the uncertainty of participating species. Referring to figure 3.2., on oxygen uptake, (a), the oxygen impinges upon the centre and subsequently forms an association with it, (b). Recombination of the electron and hole trapped on the surface results, (c), followed by capture of an electron from an ionised bulk donor, (d), i.e. chemisorption.

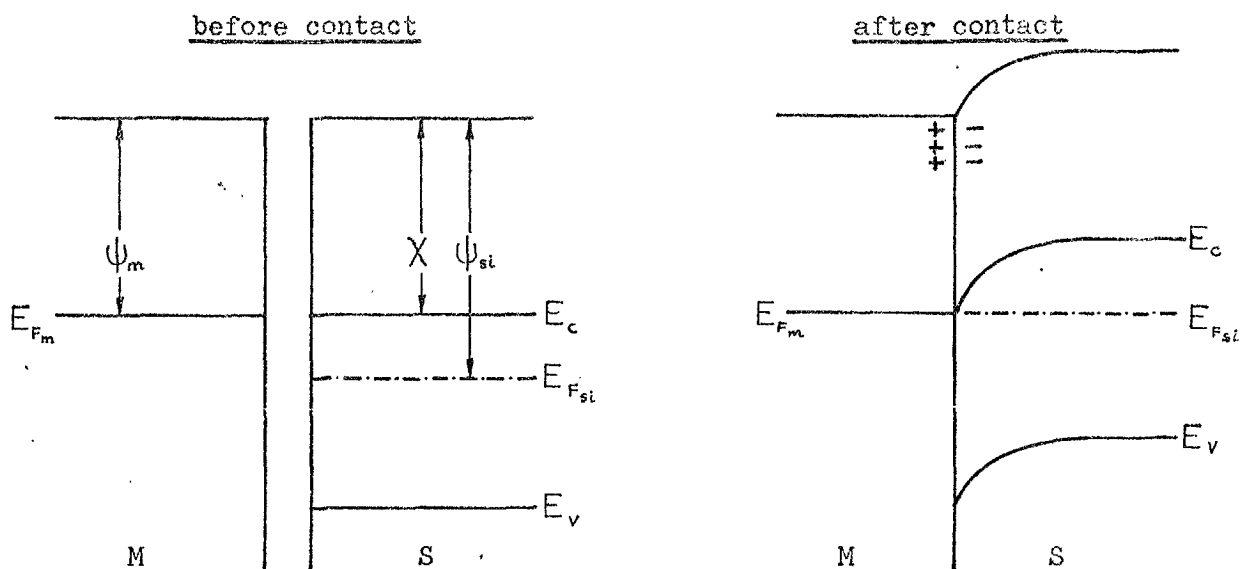
Desorption can proceed by one of two ways, (e); release of the captured electron to the conduction band or by capture of a bulk (possibly photogenerated) hole. Following the work of Weber (1970), a thermal activation energy, E_{th} , is required to finally release the oxygen from the surface, (f).

3.4. Electrical Contacts to Semi-Insulators

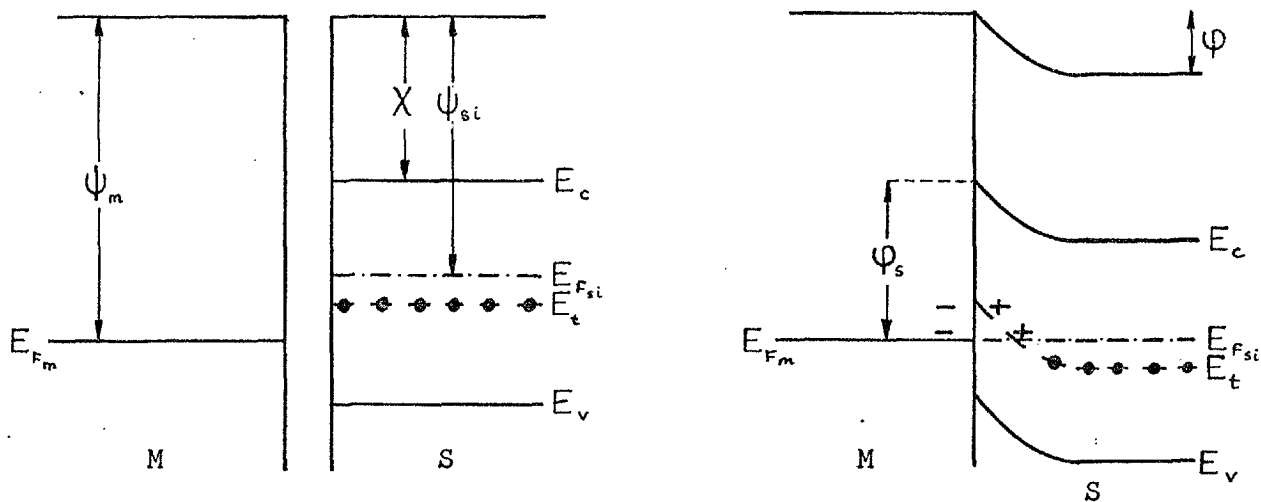
3.4.1. Basic considerations

When a metal is brought into intimate contact with an extrinsic semi-insulator, the system will energetically balance by means of a charge flow between the metal and the semi-insulator. In the absence of deep surface states, the relationship between the conduction and valence bands in the semi-insulator and the metal fermi level is determined by the relative work functions of the materials. In figure 3.3 the energy diagrams before and after contact are shown for various work function conditions. If the semi-insulator work function exceeds that of the metal

FIGURE 3.3 METAL SEMIINSULATOR CONTACTS



(a) Ohmic contact



(b) Blocking contact

Symbols used: ψ work function
 χ electron affinity
 ϕ barrier height

(figure 3.3(a)) electrons flow from the metal into the semi-insulator, forming a space charge region and bending down the conduction and valence bands to ensure alignment of fermi levels at the interface. The degree of band bending is calculated by solving Poisson's equation in the semi-insulator. When the bending is sufficient for the conduction band edge to coincide with, or go below the metal fermi level the contact is termed ohmic. Similarly, a blocking contact is formed when the work function of the metal exceeds that of the semi-insulator, as shown in figure 3.3(b), exhibiting the well known Schottky barrier.

It would appear that the barrier height, ϕ_s for a given semi-insulator should depend only on the work function of the metal electrode. This relation is observed for many contacts, but not for all systems. The existence of surface states can explain this comparative independence of barrier height from the value of the metal work function.

3.4.2. The effect of surface states

Termination of the crystal lattice gives rise to unavoidable energetic states at the surface of a semi-insulator. It is the position of such states within the energy gap that determines the role that surface states will play following application of a metal contact to a semi-insulator. When a balance results from charge flow between the metal and surface states of a semi-insulator, the role of the bulk semi-insulator is unimportant, and the band bending is less dependent on the difference between work functions.

With reference to the classic paper on surface states by Shockley (1939), Mead (1966) was able to deduce the energetic position of surface states

and assess their influence on the formation of surface barriers. Figure 3.4(a) shows the essential features of the Shockley model for splitting of atomic energy levels as the wave functions of atoms overlap, together with the energy of surface states as a function of lattice spacing. At small separations the wave functions overlap and surface states are situated near the mid gap position. Intrinsic surface states on the CdS lattice, assumed to be essentially ionic with little overlap, are located near the band edges, as described in section 3.2. and shown in figure 3.4(b). It is interesting to note that in materials with a high density of surface states, the majority of states are located two thirds of the way down the energy gap, as shown in figure 3.4(c).

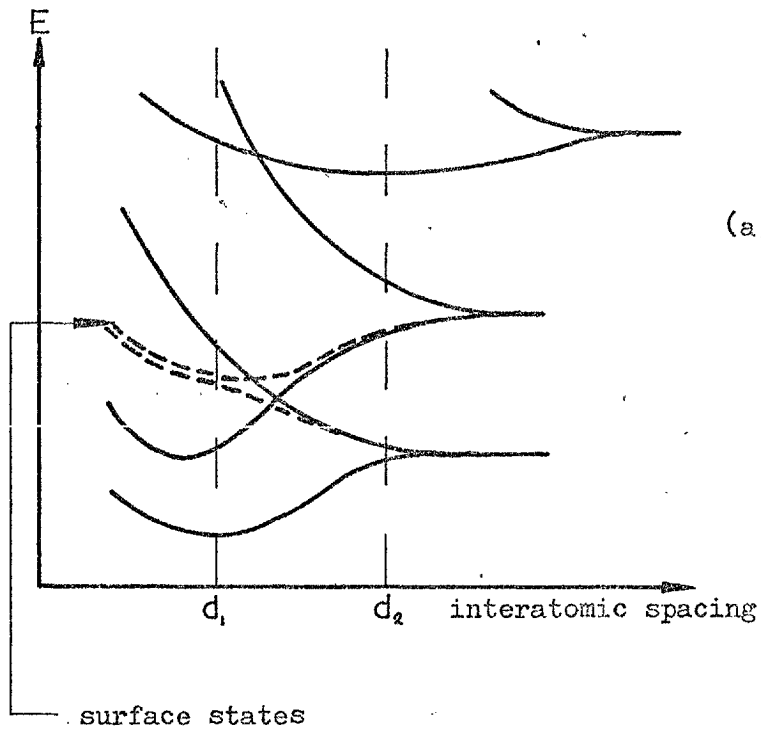
An elegant experiment reported by Mead (1965) unequivocally demonstrated the behaviour of surface states. CdS and CdSe have totally different surface properties; CdSe has a high density of surface states, whereas CdS is effectively free from mid energy gap surface states. By measuring the barrier heights produced by four different metals using photoresponse techniques on samples of Cd(S - Se) mixed crystals, it was found that ϕ_B varied directly with the metal work functions for 100% CdS. As the proportion of Se increased, so ϕ_B became less dependent on the metal and stabilised to a constant value towards 100% CdSe. This experiment demonstrated the influence of surface states on the relationship between work function and barrier height.

3.4.3. An interfacial layer

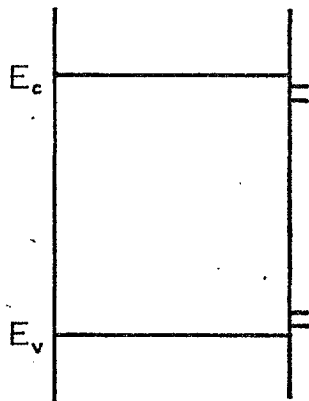
By considering the thermodynamics of the following reactions at the crystal growth temperature, the likelihood of formation of oxide, sulphate or sulphur vacancies on the surface may be assessed.

FIGURE 3.4

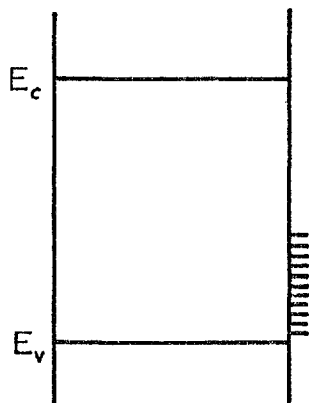
SURFACE STATES



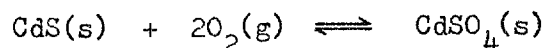
(a) Energy bands as a function of interatomic spacing, after Shockley (1939)



(b) Intrinsic surface states near band edges



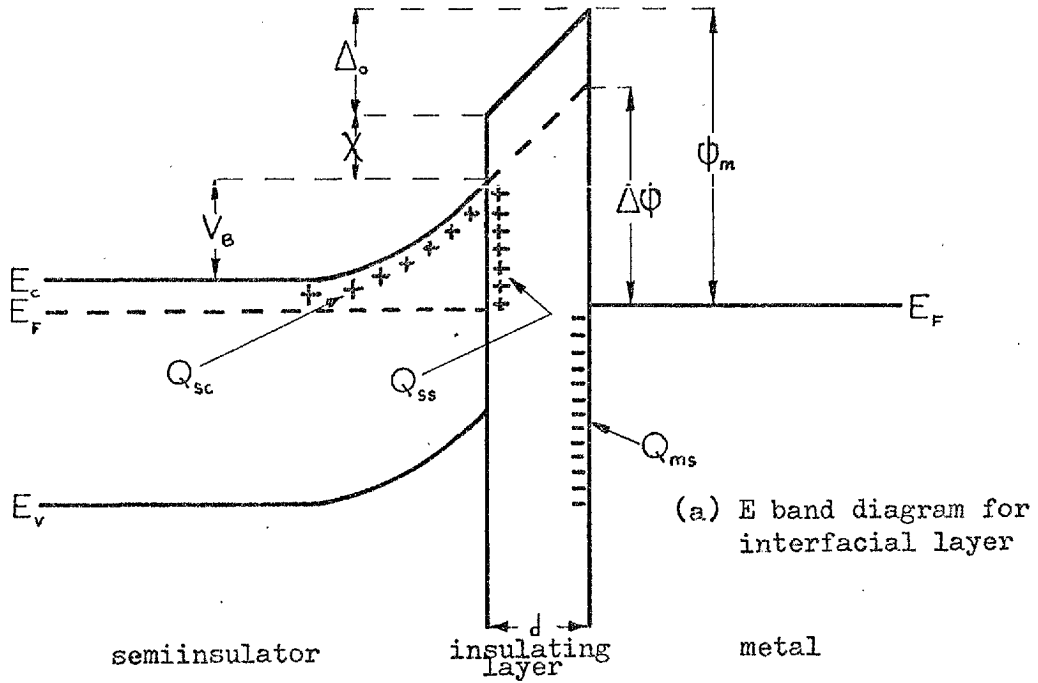
(c) Location of states for a material having a high density of surface states



Release of sulphur and the corresponding formation of cadmium oxide is the least probable reaction. Creation of sulphur vacancies and cadmium sulphate are both likely to occur, however the probability of vacancy creation increases at higher temperatures, whereas the probability of cadmium sulphate formation decreases with increasing temperature. It is therefore reasonable to assume that both sulphur vacancies and some cadmium sulphate will be present on the surface of CdS platelets after growth.

The existence of an insulating interfacial layer on the surface of a semiconductor can considerably modify the electrical properties measured by conventional methods. Weber (1969) has reported that the surface of CdS platelets can be contaminated by the formation of CdSO_4 , and Williams (1962) suggested that a layer of CdO of thickness exceeding 10Å could exist on the surface of CdS crystals. Goodman (1963) considered the influence of an insulating interfacial material on the measurement of metal-semiconductor barrier heights with particular reference to a CdO layer on CdS etched surfaces. Assuming the continuation of a space charge region into the insulating layer, as shown in figure 3.5(a). Goodman evaluated the potentials due to the insulating layer for an assumed initial barrier height, V_0 of 1 volt, and a surface charge Q_{ss} of 10^{11} cm^{-2} (the latter being a reasonable estimate in the light of more recent studies, as discussed in section 3.2.). The table shown in figure 3.5(b) indicates the additional barrier height (Δ) due to the CdO layer of thickness d .

FIGURE 3.5
(after Goodman, 1963)



d (cm)	$(\Delta_o - \Delta_s)$ eV	Δ_s ($Q_{ss} = 10^{11} \text{ cm}^{-2}$)	Δ_s ($Q_{ss} = 10^{12} \text{ cm}^{-2}$)
10^{-7}	5.5×10^{-3}	1.6×10^{-3}	16×10^{-3}
10^{-6}	55×10^{-3}	16×10^{-3}	160×10^{-3}

(b) Table of surface barrier heights due to interfacial layer, d

Δ_o is the total potential across the CdO barrier and Δ_s the contribution to Δ_o from surface charge Q_{ss} only. The formation of thick oxide layers on the surface of CdS vapour phase grown platelets is less likely compared with the etched surfaces used by Williams (1962), so one may assume the smaller value of layer thickness. Recent publications (Weber 1969) regarding the formation of $CdSO_4$ rather than CdO on platelet surfaces indicate the need for recalculation of Δ_o . Goodman however assumed similar values of dielectric constant for CdS and CdO, so if one assumes $\epsilon_{CdS} \sim \epsilon_{CdSO_4}$, the additional barrier heights for $CdSO_4$ would not be very different from those tabulated in figure 3.5(b).

A discussion of how a metal electrode is expected to modify the surface of a semiconductor has been published by Heine (1965) but refers mainly to materials having a high density of mid band gap surface states, and is therefore of little relevance to CdS.

Okazaki et al (1970) found the potential barrier due to oxygen on the surface of CdS did not change when a gold electrode was deposited on it, from which they deduced that surface state charges on a free surface remain unchanged after being brought into contact with gold. On the other hand, Karpovich and Kalinin (1970), in their study of surface doping of CdSe thin films, postulated a neutralisation of the chemisorbed oxygen by impinging metal ions, and a corresponding change in work function of the crystal caused by impurities forming a layer at the surface.

In the next section, it will be seen that indium can diffuse through the surface layer, and the apparent contradiction about the effect of evaporated metal on an oxygen covered semi-insulator surface is not applicable.

3.5. Indium Contacts

3.5.1. The work function of indium

Inspite of the considerable use made of indium and gallium for semiconductor contact materials, there is a paucity of data on their work functions. From the periodicity of data presented in his survey of elemental work functions, Michaelson (1950) estimated a value of 4.0 eV for indium. Smith (1955), discussing ohmic contacts to CdS, arrived at a value of work function for indium between 3 and 4 eV. Consideration of the relationship between work function of the elements and their ionisation potential yields a value of $\psi \sim 3$ eV for indium. A work function for indium not exceeding 4 eV is implied from measurement of the surface barrier height by Aven and Mead (1965).

3.5.2. Penetration of indium into CdS

By measuring the concentration of species below the crystal surface, O'Tuama and Richter (1970) were able to show that indium diffused preferentially into cadmium vacancies. This process was deemed to be important in a study of contacts on ZnS by Blount et al (1966). Ohmic contacts were produced by indium electrodes evaporated onto ZnS single crystals inspite of the apparent mismatch of work functions. As the temperature increased, indium ions penetrated the exhaustion region near the ZnS surface, and then the indium diffuses through zinc vacancies. The subsequent formation of a donor region near the electrode provided a substantial improvement in contact quality, but at higher annealing temperatures, the thermal creation of zinc vacancies produced a deterioration in the quality of the contact.

3.5.3. Ohmic contacts to CdS

Indium electrodes are mainly used to provide ohmic contacts to CdS. Firstly, the electron affinity of CdS is 4.2 eV (Bugatti, 1968), and with the work function of indium lying approximately between 3 and 4 eV, the basic requirement for an abrupt ohmic contact may well be satisfied. Secondly, however, the penetration of indium into the CdS lattice via cadmium vacancies may create a graded metal - highly n type - n type structure giving rise to a good ohmic contact in the manner discussed above with respect to ZnS.

Indeed, the fact that ohmic indium contacts have usually to be formed by passing a large current for a small time rather supports the second hypothesis. The diffusion of indium will be facilitated by the Joule heating at the contact.

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CHAPTER IV

EXPERIMENTAL WORK

4.1. Crystal Growth

4.1.1. A review of growth techniques

Synthetically grown single crystals of cadmium sulphide were first prepared before the turn of the century by Lorenz (1891) as part of a study of synthetic materials. In 1912, Allen and Crenshaw reported CdS single crystal growth from a solution, but it was not until 1947 that Frerichs prepared thin ribbon crystals by a vapour phase transport technique. Cadmium vapour, carried by hydrogen gas reacted with a stream of hydrogen sulphide to form single crystals of CdS. Improvements to the Frerichs technique were made by Kroger in 1954 by using CdS as an initial charge to give more control over evaporation rates. Better crystals were prepared by Fochs and Lunn (1963) using a two element furnace (with argon transport) to control the position of nucleation. The dynamic (gas flow) system gives rapid crystal growth and enables the removal, via the carrier gas, of impurities that are evolved during charge evaporation.

The method of Fochs and Lunn has been adopted for platelet growth in the present work, and is reported in detail by Fass (1969). The following section is a brief outline of the crystal growth technique.

4.1.2. Experimental details

The furnace consisted of a Kanthal Al wire element wound around an

open ended alumina tube. The desired temperature profile was achieved by a graded main winding in conjunction with an independent end winding. The stable temperature profile, as shown in figure 4.1. was maintained by an Ether 991 anticipatory controller.

A non symmetrical U shaped silica tube, shown in figure 4.2. was used for crystal growth. For convenience, a flat glass disc was attached to the outlet end of the B-34 socket to allow observation of crystal growth during a run. The shape of the growth tube allowed rapid removal from the furnace after a run, without disrupting the argon flow.

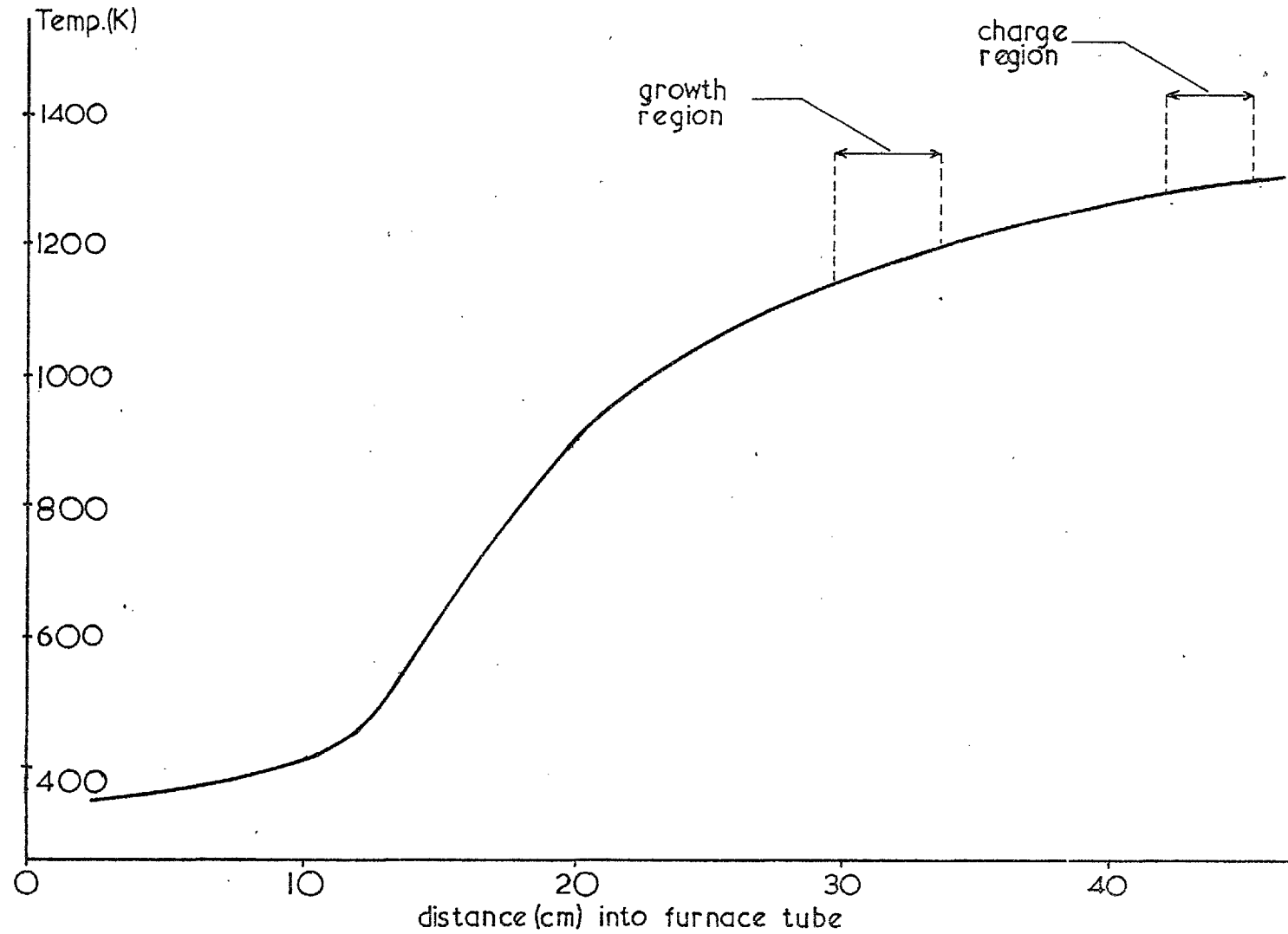
Preparation of the growth tube was of utmost importance. Following the removal of superficial deposits of CdS from any previous runs using aqua regia, the tube was thoroughly washed with deionised water, and etch polished with a solution containing 5% hydrofluoric acid; 35% nitric acid; 60% deionised water. After further washing with deionised water, the tube was dried and flamed to white heat with an oxyhydrogen torch. Volatile impurities were removed from the silica surface and local melting of the tube formed a smooth surface, reducing the density of nucleation sites on the walls.

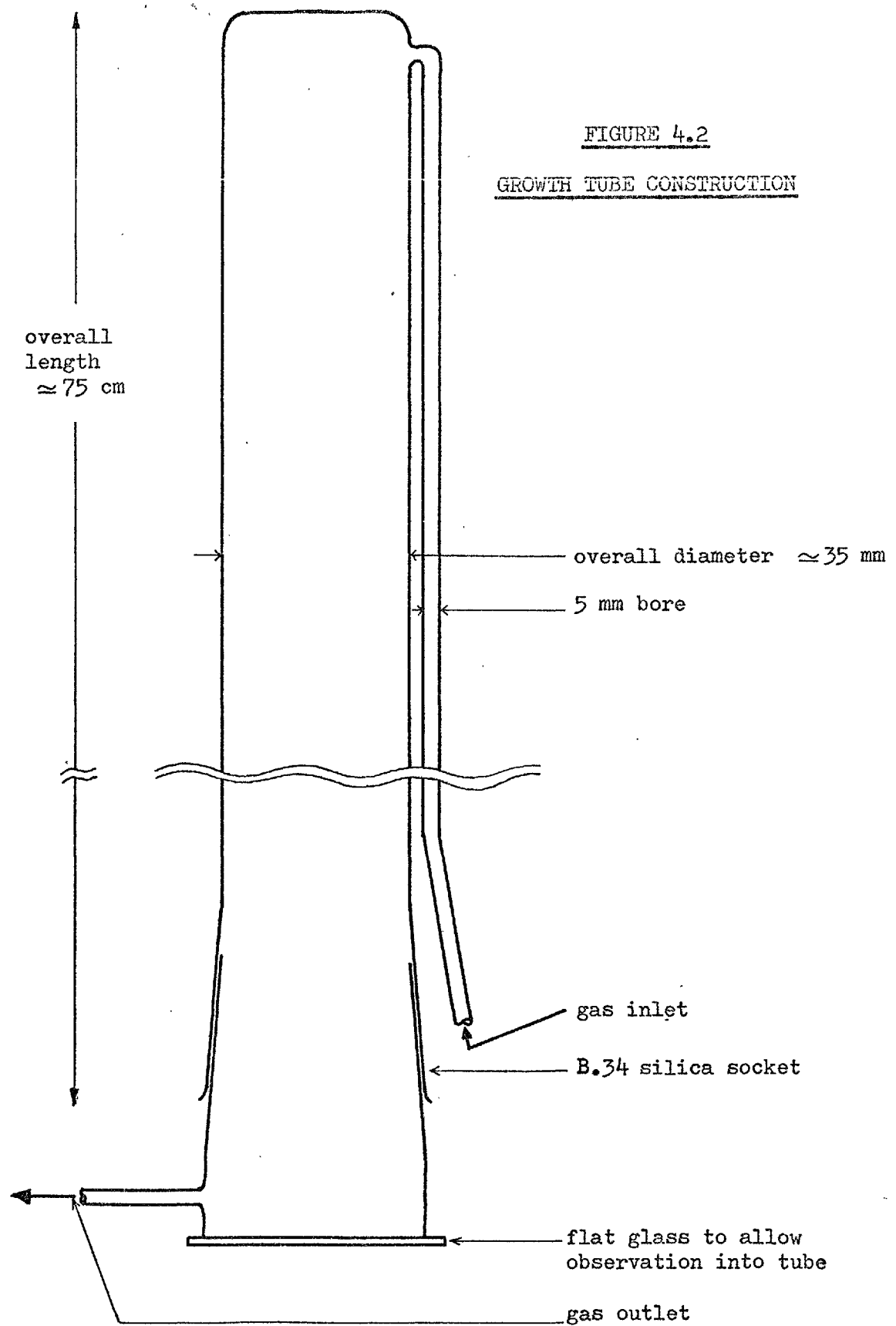
Following flaming, the tube was quickly positioned in the furnace and allowed several hours (with argon flowing) to reach thermal equilibrium before charge was transferred to the hot zone. Polycrystalline lumps of CdS (5N purity) were used as charge. Sintering (in argon at 1180K) appeared to produce slightly inferior crystal yields. As runs varied greatly in perfection of crystals, this fact is of little significance.

The charge, placed near the outlet socket was transferred to the hot region by rotating the furnace into the vertical position for several

FIGURE 4.1

TEMPERATURE PROFILE IN FURNACE





seconds allowing the charge to fall to the bottom of the growth tube. During growth an argon flow rate of about 250 ml. per minute was used. After several minutes the charge commenced to evaporate, and platelet crystals started to grow in a cooler region, as shown in figure 4.1. Typical runs lasted one and a half hours, and platelets generally grew on tube walls between 1130 K and 1200 K (at a gradient of 14 K cm^{-1}) as shown in figure 4.1.

Some thirty seven runs were made, all of which yielded at least several good crystals. Platelet thickness could be controlled using the technique of Fass (1969) who obtained thinner crystals by terminating the run after a short time (about thirty to forty five minutes). Thicker crystals were produced by reducing the flow rate to as low as 100 ml. per minute as suggested (for ZnS platelets) by Cusdin (1970).

The majority of platelets were of the order 4 mm square by 30 μm thick, however crystals as thin as 5 μm and as thick as 200 μm were also grown. The fortuitous growth in one particular run of several rod shaped crystals (typically 1 mm square by 8 mm long) along with the platelets provided specimens for investigation of bulk effects in crystals grown from a common charge.

4.1.3. Thickness measurement.

Several methods for measuring platelet thickness were investigated:

(i) A thin film interferometer was tried, but with platelets, the closeness of the interference lines made fringe counting very difficult. It was not possible to see whether an end ridge (see figure 4.3.)

was present at the crystal edge.

(ii) An interference wedge, using two optically flat glass plates (8 cm long) showed wider spaced fringes but again would not distinguish an end ridge. Large errors could be produced by dust particles between the glass plates and the thin end of the wedge.

(iii) Calculation of thickness from weight, density and surface area produced inaccurate values for wedge shaped crystals or platelets with end ridges, and involved intricate dimensional measurements.

(iv) Inspection of a crystal edge under an Olympus metallurgical microscope, equipped with a micrometer eyepiece produced the best results. Crystal thicknesses were assessed approximately before device fabrication and then accurately (to within $\pm 2 \mu\text{m}$) after mounting, when all edges could be easily inspected. Over half the crystals used had parallel faces and were free from end ridges. Figure 4.3. shows the cross section of a typical poor crystal. Electrodes were deposited on the parallel portion of such crystals.

Crystals used for the present study were divided into four categories:

- (i) Crystal platelets $\sim 30 \mu\text{m}$ thick (used for the majority of devices).
- (ii) Thin platelets, approximately $< 10 \mu\text{m}$ thick.
- (iii) Thick platelets, over $\sim 80 \mu\text{m}$ thickness.
- (iv) Rod crystals, obtained during platelet growth $\sim 1 \text{ mm}$ square by 8 mm long.

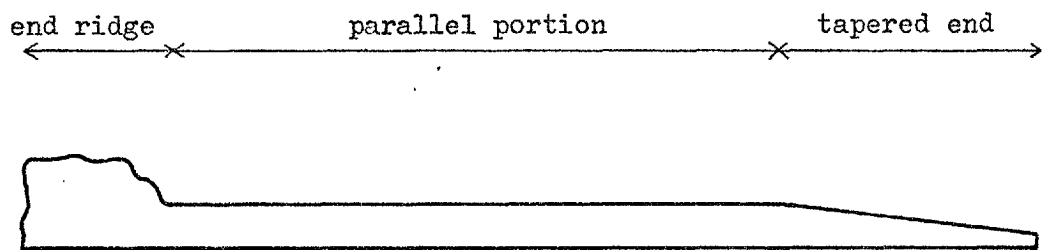


FIGURE 4.3

TYPICAL CROSS SECTION OF PLATELET WITH END RIDGE

(not to scale)

4.2. Device Fabrication

4.2.1. Electrode configurations

Electrode configurations became more complex as the work progressed.

Three basic electrode patterns were used:

(i) Two electrode devices In the initial stages of the work, a simple circular electrode on each large face of a platelet was used. Effects due to illumination between contacts was studied using interdigital electrodes, as shown in figure 4.4(a).

(ii) Three electrode devices A study of surface mechanisms required two contacts having the figure 4.4(a) configuration on the same surface, but for comparison of these with previous devices, a third electrode was placed on the other face, as shown in figure 4.4(b).

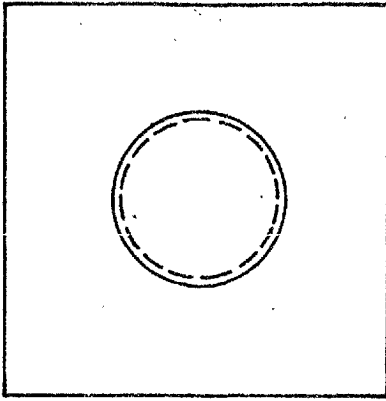
(iii) Guard ring electrodes Experiments designed to distinguish between bulk and surface conduction were performed using the guard ring electrode configuration in which the electrode on the upper surface was replaced by a ring electrode and a concentric inner electrode, as shown in figure 4.4(c).

4.2.2. Mask preparation

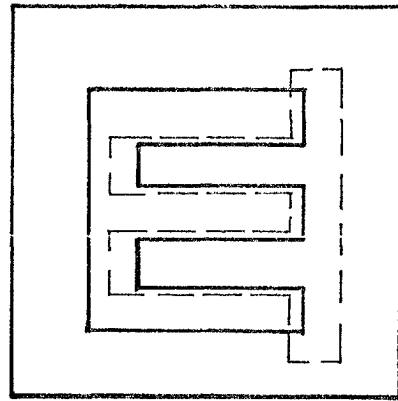
For the simple circular electrodes, masks made by drilling a hole in thin aluminium plate proved satisfactory. The interdigital electrodes were made using masks prepared by the photoetching technique.

In a recent publication Oliver (1970) suggests a method for producing continuous guard rings. A tapered hollow cylinder suspended by soldering to a mesh of thin silver wire was accurately located in a larger hole cut

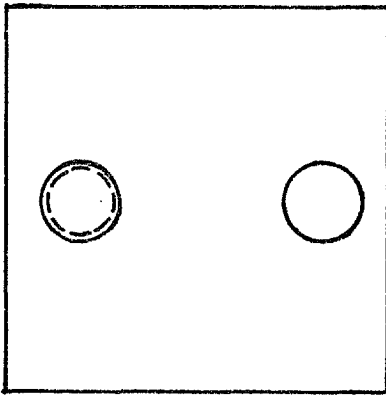
FIGURE 4.4
ELECTRODE CONFIGURATIONS



(a) Two electrode device



(b) Three electrode device



(c) Guard ring electrodes

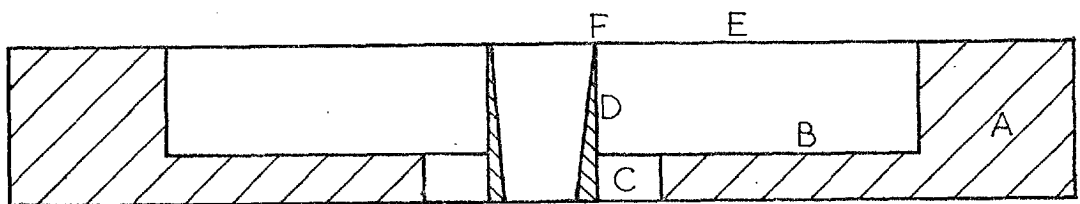
(dotted lines represent electrodes on the under surface)

in a thin metal plate. Figure 4.5 depicts the essential features of the mask. Oliver's mask has the obvious advantage of producing a continuous ring, but the system has two drawbacks; extreme difficulty to manufacture and the inability to keep the tapered cone in contact with the crystal during upward evaporations (i.e. source below the mask).

For the present work, a simple system involving a two stage process was used which seemed to produce satisfactory results. The end of a length of 0.25 mm diameter silver wire was bent into a 1.5 mm diameter circle and pressed between two glass slides until slight flattening was observed. This step ensured overall flatness of the ring. Figure 4.6(a) shows a diagram and cross section of the ring. A shallow channel was cut radially outwards from a 2.5 mm diameter hole drilled in a thin aluminium plate, as shown in figure 4.6(b). The ring was positioned in the groove and secured by DAG915 silver conducting paint, as shown in figure 4.6(c). Excess dag was removed from the mask (after hardening for several hours).by scraping with a glass slide to ensure that the top surface of the mask was flat. The evaporated ring produced by the mask was not continuous and required a spot of silver dag to complete the circle.

4.2.3. Evaporation

Contacts of high purity (5N) indium or silver were evaporated from a molybdenum boat at 2×10^{-5} torr pressure in an Edwards 12E vacuum plant. Typical electrode thicknesses measured by a Talysurf machine were of the order 0.1 μm .



A Body of mask

C Hole

E Supporting wire mesh

B Undercut portion around hole

D Tapered hollow cylinder

F Solder joints

FIGURE 4.5

THE GUARD RING MASK PROPOSED BY OLIVER (1970)

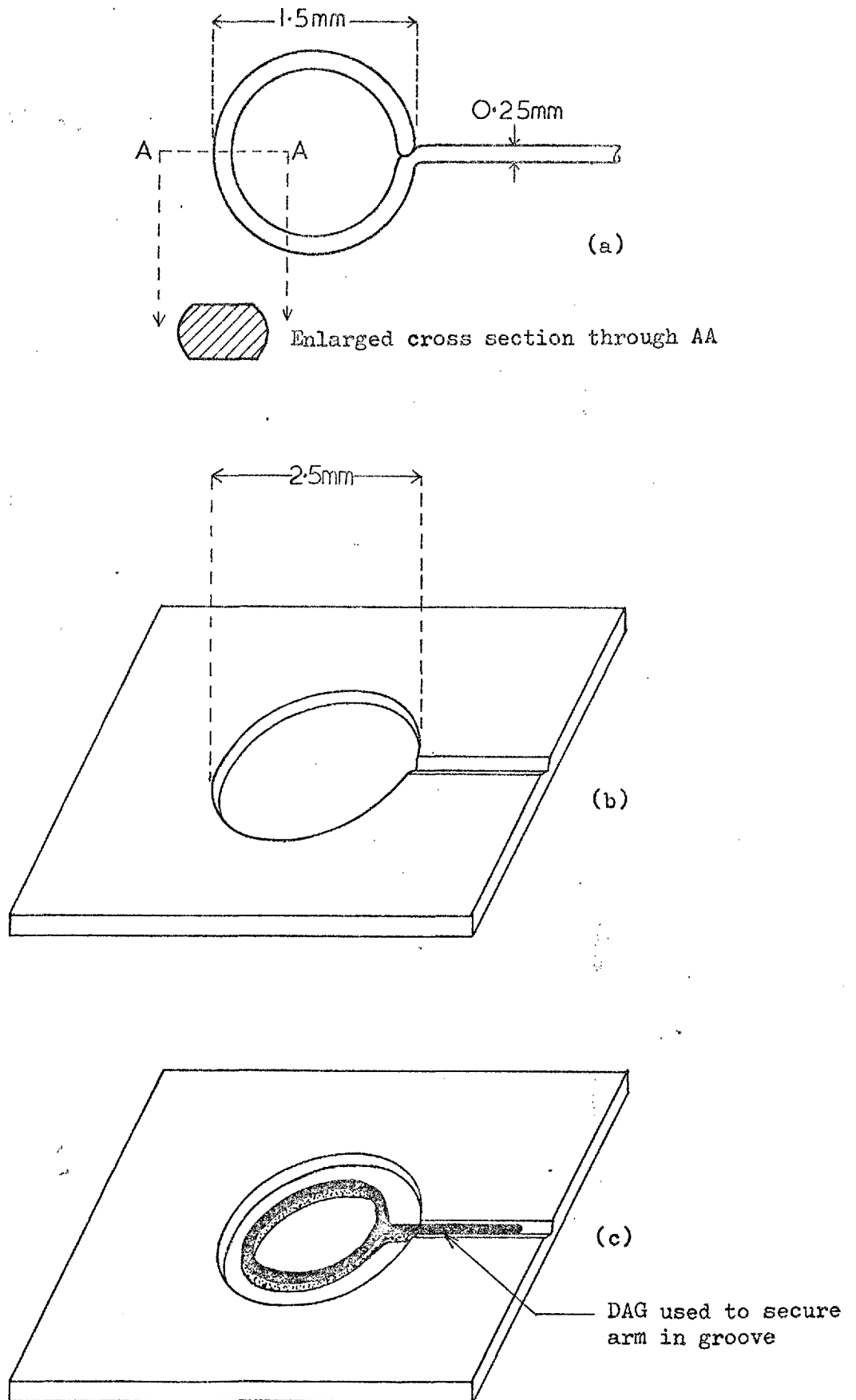


FIGURE 4.6

GUARD RING MASK PREPARATION

4.2.4. Surface treatment

Although the majority of crystals tested were not deliberately treated before evaporation, several samples were washed in deionised water, acetone or alcohol before contact evaporation. The effect of ion bombardment (for 30 seconds) prior to evaporation was investigated for both direct bombardment (using the mask as a discharge electrode) and indirect bombardment (an argon ion discharge in the vicinity of the crystal). Neither washing nor bombardment appeared to affect noticeably measurements compared with those on non treated crystals.

4.2.5. Mounting

Rapid thermal cycling from 77 K to 400 K caused deterioration of connections to the evaporated metal contacts. A significant portion of the practical work involved development of the mounting techniques necessary for such conditions, ensuring accurate monitoring of the crystal temperature.

Crystals were mounted on a 7 mm diameter glass filled metal transistor header having three 0.5 mm diameter lead through wires. The centre wire was cut off flush with the top surface and used for temperature monitoring (see section 4.2.6).

Connection to the evaporated metal electrodes by ultrasonic bonding proved totally unsuccessful. Although 0.025 mm diameter aluminium wire could be bonded to indium or silver, the minimal strength and extremely brittle nature of the thin platelets would not allow an adequate welding tip pressure.

Satisfactory electrical connections were made to the contacts using 0.04 mm or 0.05 mm diameter pure gold wire fixed to the evaporated contact with DAG915 colloidal silver conducting paint. Thin wire was necessary to minimise thermal stresses between the contact and header connections, and gold was chosen for its physical softness and high electrical conductivity.

The following procedure, whose steps were somewhat critical, was adopted (a ten times magnification binocular microscope being used throughout the mounting process):

(i) The end of a length of gold wire was bent into a flat ring shape, approximately 0.2 mm diameter.

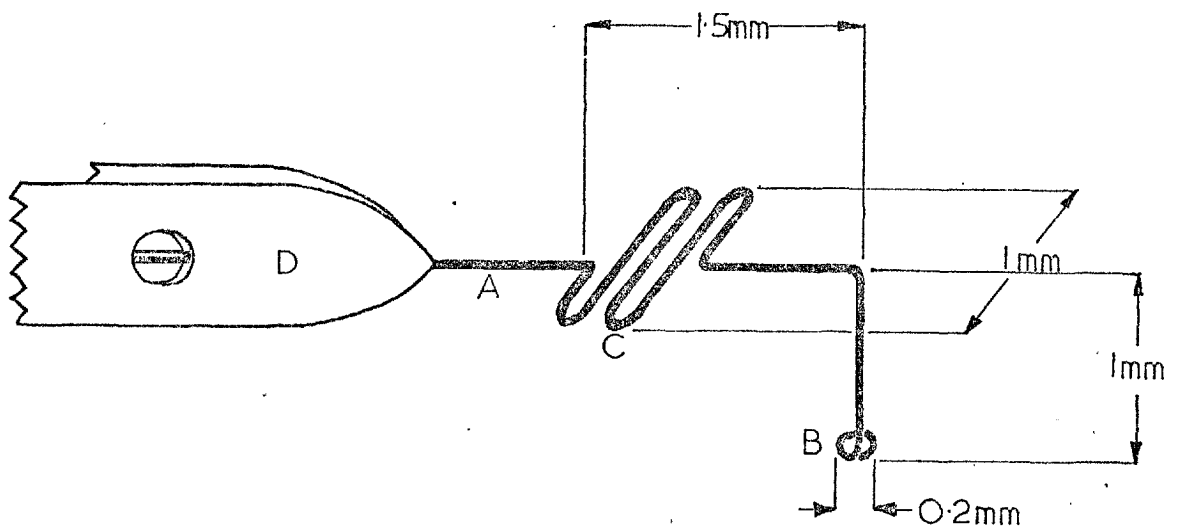
(ii) The wire was bent into the shape shown in figure 4.7, and mounted in a micromanipulator. To further reduce thermal stress between contact and header during rapid thermal cycling, several additional bends in the middle of the wire were included.

(iii) The crystal was placed directly beneath the end ring of the wire and aligned such that the ring could quickly be moved vertically downwards onto the centre electrode.

(iv) Silver dag was repeatedly applied to the ring, each time building up a larger diameter bead at the end of the gold wire. The process required considerable speed in order to keep the dag wet.

(v) With the diameter of the bead approximately 0.4 mm, the wire was rapidly lowered onto the crystal until the wet bead touched the evaporated contact, whereupon the dag flowed outwards, wetting a larger area of contact.

(vi) The connection was allowed to harden for several minutes before the crystal, still mounted in the micromanipulator was aligned with a transistor header (mounted on a suitable clamp). Two conditions were required:



- A 0.04 mm to 0.05 mm diameter gold wire
- B End ring
- C Several bends in wire to minimise thermal stress
- D Micromanipulator

FIGURE 4.7

CONFIGURATION OF CONNECTING WIRE

- (a) The lower electrode was put in the centre of the header top.
- (b) The other end of the gold wire was arranged to be touching (or very near to) the header pin, as shown in figure 4.8(a).

(vii) With the crystal raised above the header, a very small bead of wet dag was placed in the middle of the header top, and the crystal rapidly lowered, forcing the dag between header top and lower electrode.

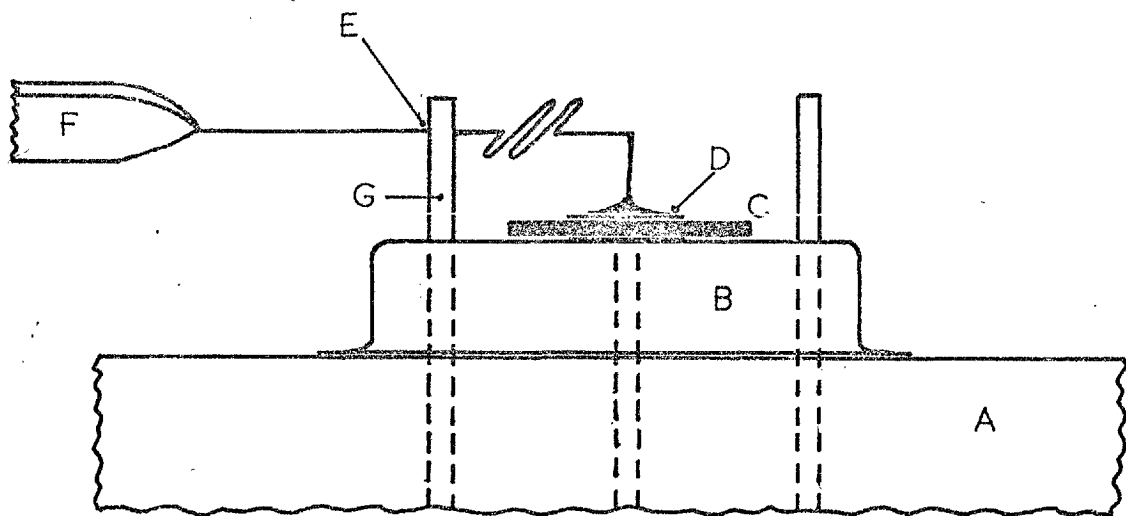
(viii) Silver dag was immediately used to fix the gold wire to the header pin, the gold wire being quickly unclamped from the micromanipulator. This was an important part of the mounting process. Rigid clamping tended to restrict the slight movement of the wire during hardening of the 'Dag', causing a small stress in the wire often resulting in failure of the connection after several thermal cycles.

(ix) After allowing to harden for an hour or more, excess wire was trimmed off and silver dag used to connect the remaining pin to the header. Figure 4.8(b) shows a section through a typical device.

A similar method was employed for mounting three electrode crystals. The reduced area of the lower contact (particularly in guard ring devices) necessitated a different mounting process. To ensure connections to the evaporated contact only, and to minimise the risk of 'dag' running onto the surrounding crystal surface, the lower electrode was connected to the header top by a short (2 mm to 3mm) length of gold wire. The method outlined in (iii) to (v) above was used initially to connect the straight gold wire to the lower electrode.

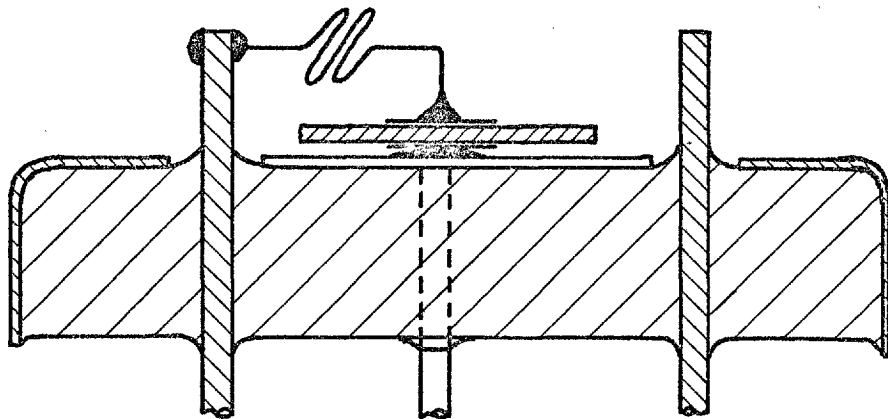
Connection to the upper electrodes utilised the same wire configuration (figure 4.7) connecting each electrode to its corresponding header pin, as shown in figure 4.9. Residual stresses in the gold wire were again

FIGURE 4.8

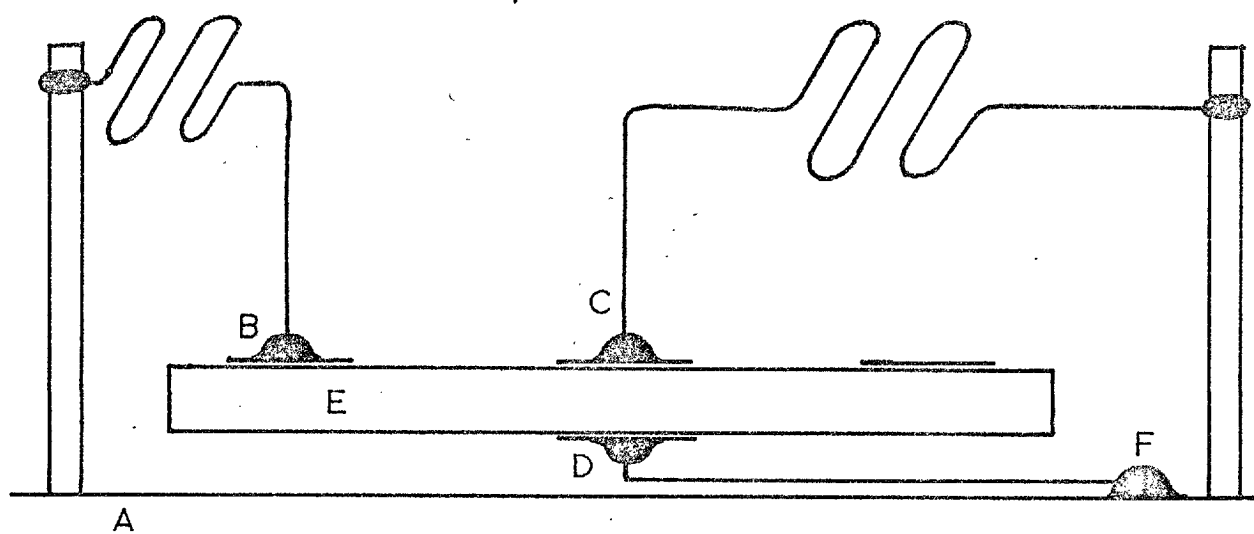


(a) Device construction

- A Header Clamp
- B Header
- C Crystal
- D Upper and lower electrodes
- E Wire touching lead through
- F Micromanipulator
- G Lead through



(b) Section through typical device



- A Header
- B Guard ring connection
- C Centre connection
- D Lower electrode connection
- E Crystal
- F Base connection

FIGURE 4.9

A GUARD RING DEVICE

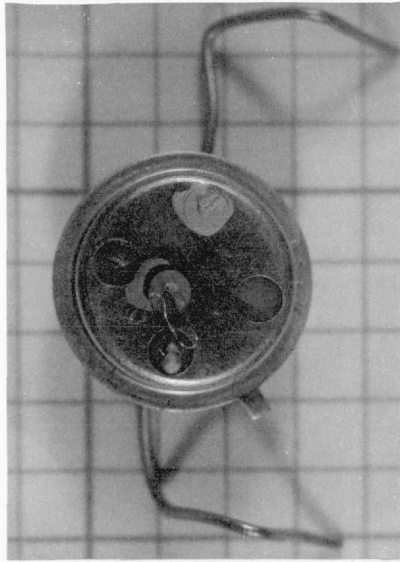
minimised by unclamping the wire as soon as possible after the application of the 'dag'. The various forms of completed device are shown in figure 4.10.

4.2.6. Temperature monitoring

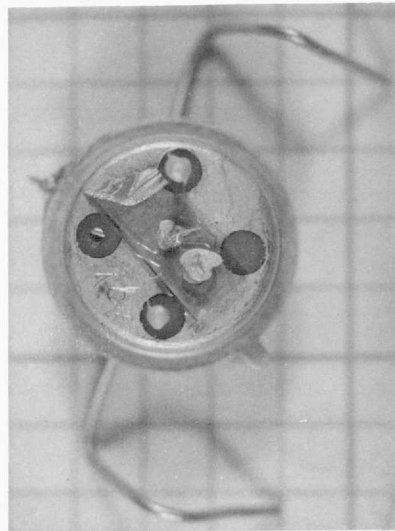
A number of methods for measuring the crystal temperature were tried but the best results were obtained by soldering a chromel-alumel thermocouple onto the centre lead of the transistor header, which had previously been cut flush with the top surface of the header. The lower end of the lead protruded several millimetres below the bottom of the header allowing the thermocouple to be soldered in place.

Monitoring a rapid temperature increase ($\sim 0.5 \text{ K sec}^{-1}$) required good thermal conduction between the crystal and a thermocouple in the header. The temperature during heating was checked initially by soldering indium-gallium electrodes on to a crystal, having determined independently the melting point of the contact material. Melting of the electrodes was indicated by a small flat region on the dark current curve (the crystal temperature briefly remained constant as the electrode material melted, but the thermocouple output continued to rise). Occasionally a sudden increase in current resulted as the melting electrode flowed onto the crystal to form an improved electrical contact. Temperatures indicated were within $\pm 3 \text{ K}$ of the melting point. A further check was made by recording the dark current for rapid heating and cooling. The difference in curves was again $\pm 3 \text{ K}$.

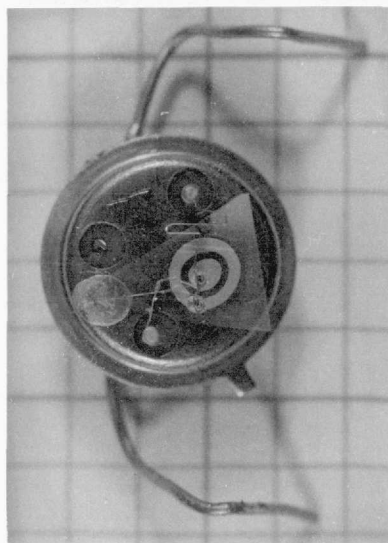
It was interesting to observe that only a small ($< \pm 2 \text{ K}$) additional error was introduced in guard ring experiments by connecting the lower



(a) A simple two electrode system.



(b) A three electrode system.



(c) A guard ring device.

electrode to the header base by a short length of gold wire. Thermal conduction between the header and crystal was due to helium gas, rather than conduction through the 'dag' and wire.

4.3. Experimental Apparatus and Its Evaluation

4.3.1. Basic apparatus

Figure 4.11 is a block diagram of the complete system. The cryostat was evacuated using a Speedivac EO2 vapour diffusion system capable of pumping to pressures below 10^{-5} torr. Facilities for admitting controlled quantities of helium or oxygen were included. Radiation from a Mazda xenon tube, type XE/D 250W AC (ref. no. 98-0351), was transmitted to the crystal via a one centimetre diameter silica light pipe.

Figure 4.12 shows schematically the system devised for TSC measurements. The specimen holder, heating apparatus and electrical measuring system are described separately.

4.3.2. Specimen holder

The design of the specimen holder depended on two conflicting factors; the need for a large metal mass to minimise temperature fluctuations, compared with the need for a small mass to obtain rapid heating rates. In the system used, the body of the brass holder measured 2.5 cm diameter by 4 cm long. Figures 4.13(a) and 4.13(b) are photographs of the complete unit inside the cryostat, and the device holder (with cover removed) respectively. A detailed drawing of the system is shown in figure 4.14. The

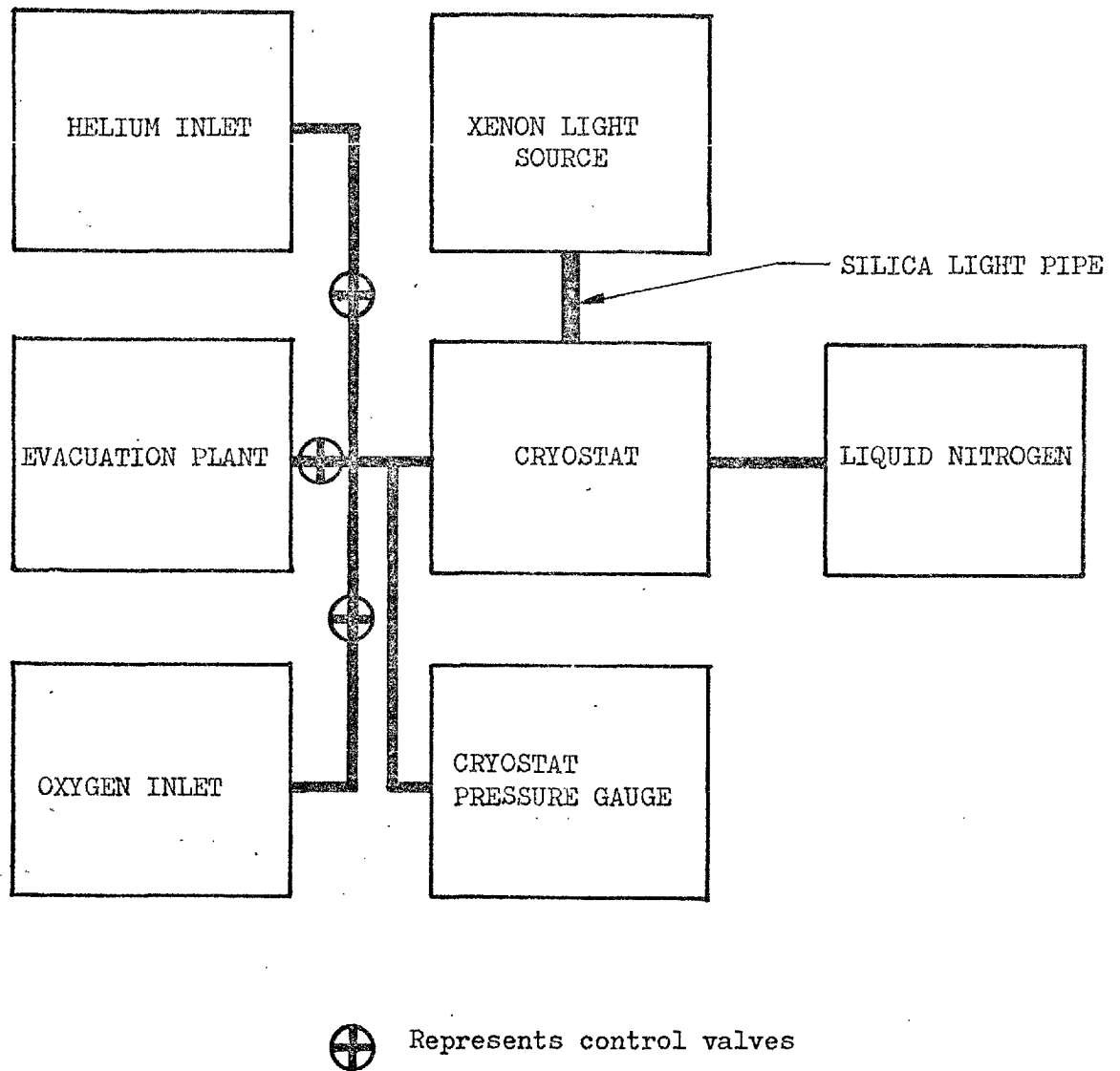


FIGURE 4.11

SCHEMATIC DIAGRAM OF CRYOSTAT SYSTEM

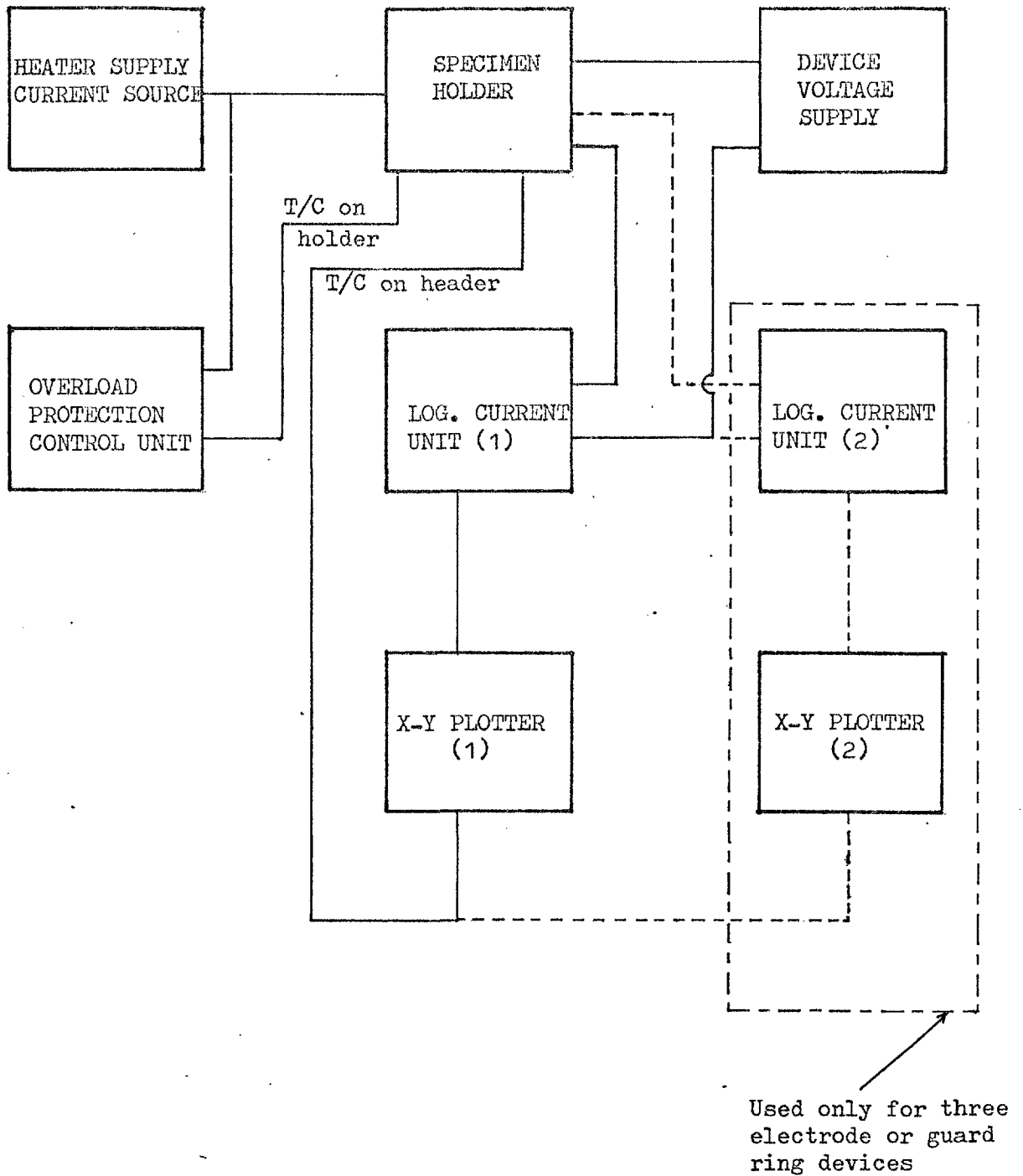
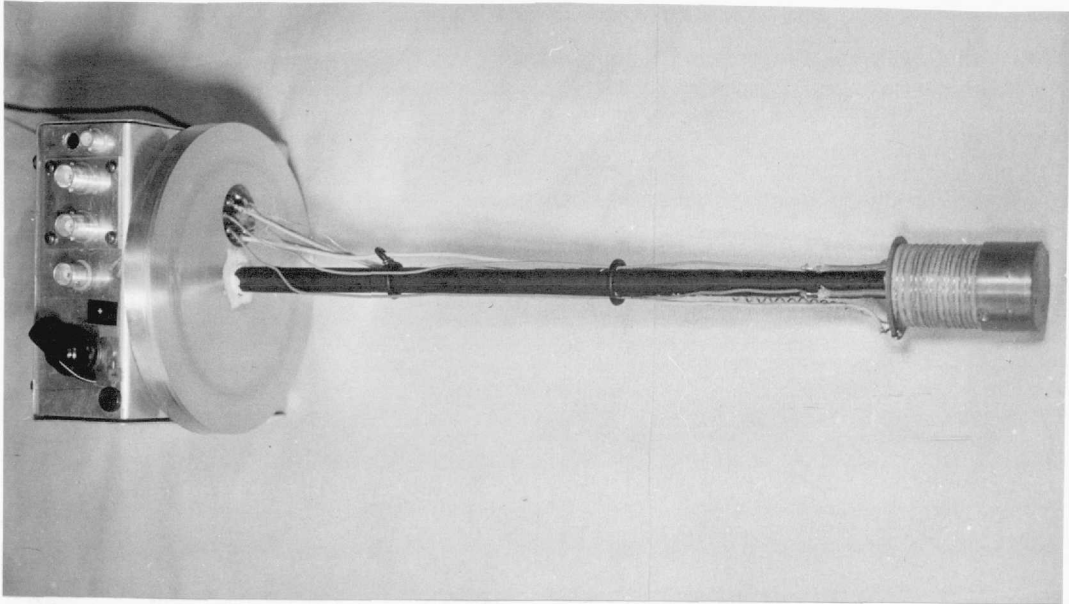
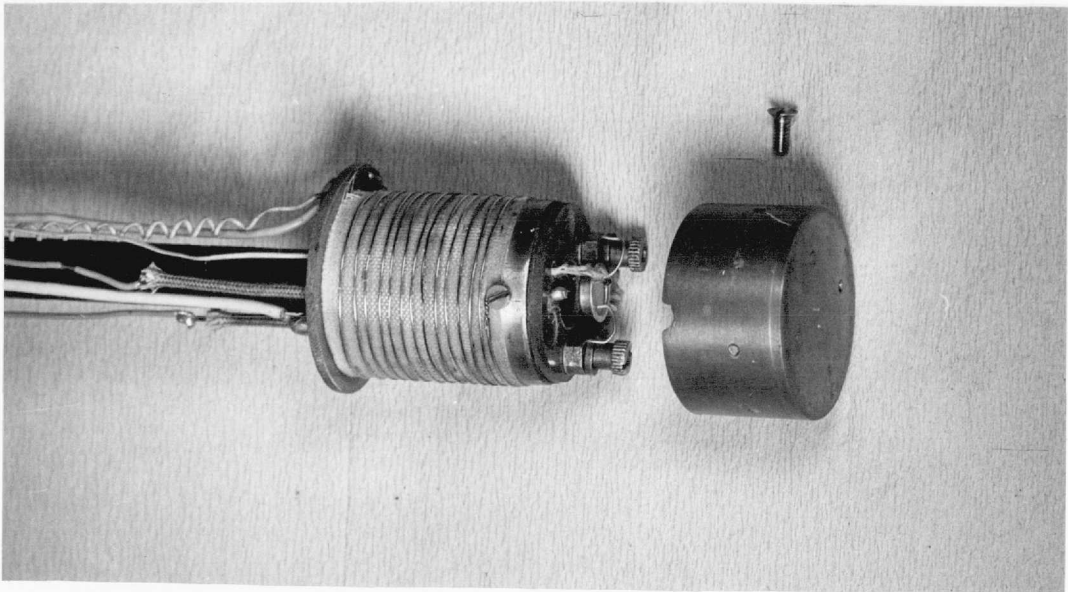


FIGURE 4.12

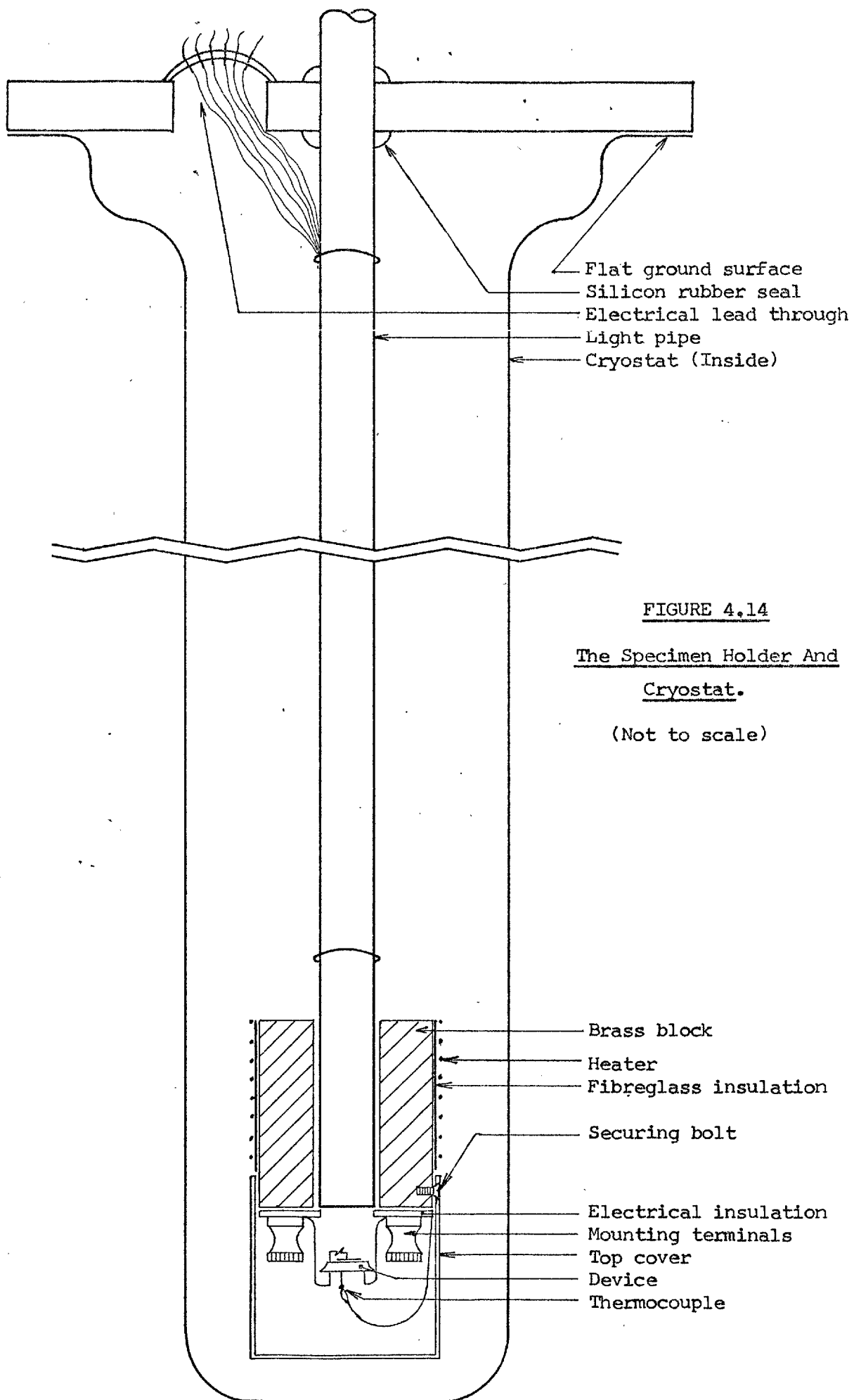
SCHEMATIC DIAGRAM OF SPECIMEN APPARATUS



(a) The complete measuring system.



(b) The device holder (with cover removed).



specimen was enclosed by a tight fitting brass cover which in turn was secured to the brass block by a small bolt. Thin fibreglass sheet insulation was used for the ni-chrome heater. Two discs of paxolin 1 mm thick were used to insulate electrically the specimen which was clamped directly onto the two mounting terminals.

4.3.3. Electrical measuring apparatus

As the current varied over eight decades, for some TSC runs, a current measuring circuit was designed to record the logarithm of current flow. The reverse bias characteristics of a simple diode are given, as a first approximation, as $I \propto \exp V$. By monitoring the potential across a reverse biased diode, a voltage proportional to the logarithm of the diode current is given directly. In the present study, the base emitter junction of a 2N930 transistor was used. Tscholl (1968) reported that these transistors functioned logarithmically over ten decades; from below 10^{-12} A to almost 10^{-2} A. The diode characteristics and measuring circuit are shown in figure 4.15. The circuit was not sensitive to changes in ambient temperature, the maximum change in diode voltage being only a few percent.

The straight line of figure 4.15 is represented by the equation

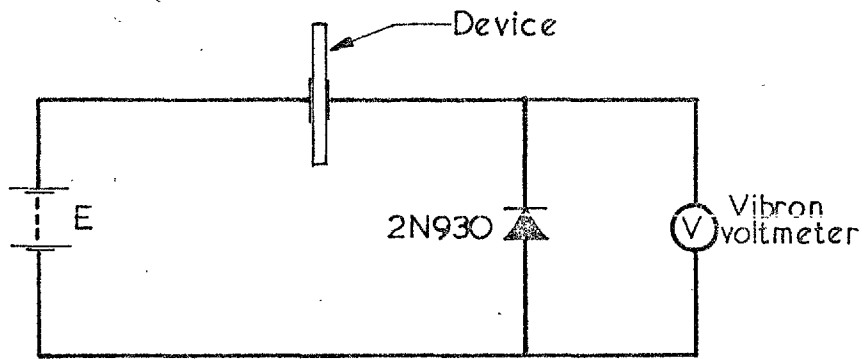
$$V = 0.84 + 0.06 \log I \quad \dots\dots\dots(4.1)$$

or
$$V = 0.84 + 0.026 \ln I \quad \dots\dots\dots(4.2)$$

From which the impedance Z_o of the diode is deduced

$$Z_o = \frac{dV}{dI} = 0.026 I^{-1} \quad \dots\dots\dots(4.3)$$

where V and I are diode voltage and current respectively.



Current measuring circuit

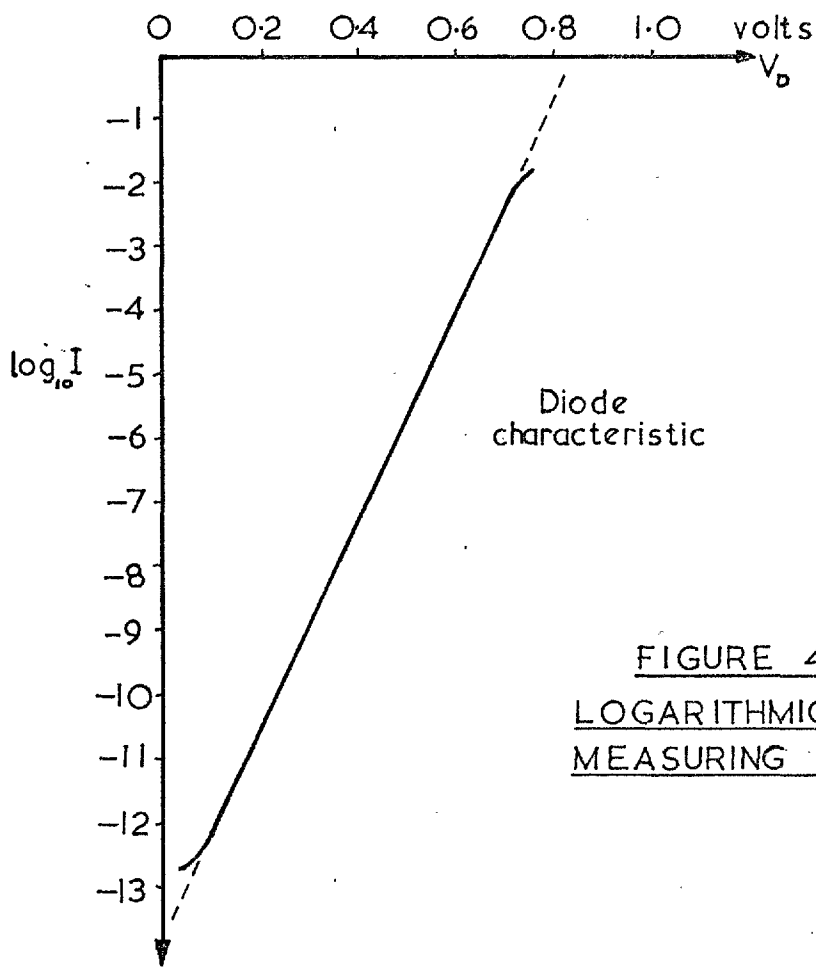


FIGURE 4.15
LOGARITHMIC CURRENT
MEASURING SYSTEM

Compared with a perfect (zero impedance) ammeter a measuring error of under 3% for 1 V across the crystal, or under 0.3% for 10 V across the crystal was introduced by the log. ammeter. The diode voltage was measured using a Vibron model 33 B electrometer (input impedance $> 10^{15} \Omega$).

In view of the contribution to TSC due to surface conductivity (which will be considered in section 6.3) it was necessary to include in the system facilities for simultaneously measuring two logarithmic currents from a device with three electrodes, one electrode being common to both currents. The circuit used is shown in figure 4.16. The potential of the centre electrode and guard ring electrode was always positive with respect to the lower face (common) electrode. The circuit necessitated a negative collecting voltage E with respect to earth and allowed thermally stimulated currents from each of the two upper electrodes to be measured simultaneously with respect to the common lower electrode.

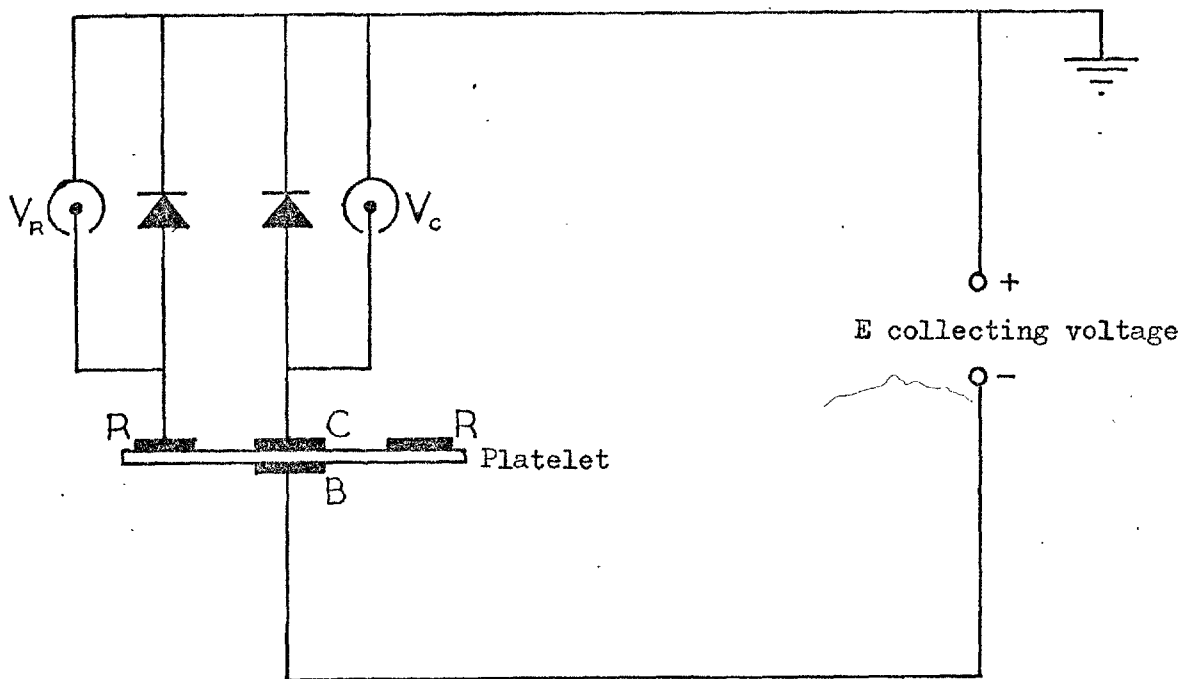
4.3.4. Heating rate

Analysis of TSC spectra is greatly simplified by adopting a linear heating rate. By carefully adjusting the heater current provided by Wareham model C190 10A current controlled power supply, a linear warming rate of 0.56 K sec^{-1} was obtained between 77 K and 430 K. The high thermal capacity of the device holder prevented transient temperature fluctuations as the current was adjusted).

4.3.5. Overheating protection

Accidental overheating of the delicate device holder was prevented

Electrodes: C Centre dot
R Guard ring
B Lower surface electrode



Vibron input for V_R and V_C was negative (w.r.t. earth)
Output from supply E was negative (w.r.t. earth)

FIGURE 4.16

CIRCUIT FOR GUARD RING AND THREE ELECTRODE DEVICES

using a simple control unit monitoring the signal from a separate thermocouple mounted on the holder. If the temperature of the holder exceeded a specific value (predetermined by adjustment of the controller) the heater current was automatically disconnected. The system was extended to provide continuous high temperature control within a limited range by cutting out the heater current at a high temperature and switching back on at a somewhat lower temperature (typically 20 K lower than the cut out temperature). A complete circuit of the control unit is shown in figure 4.17.

References for Chapter 4

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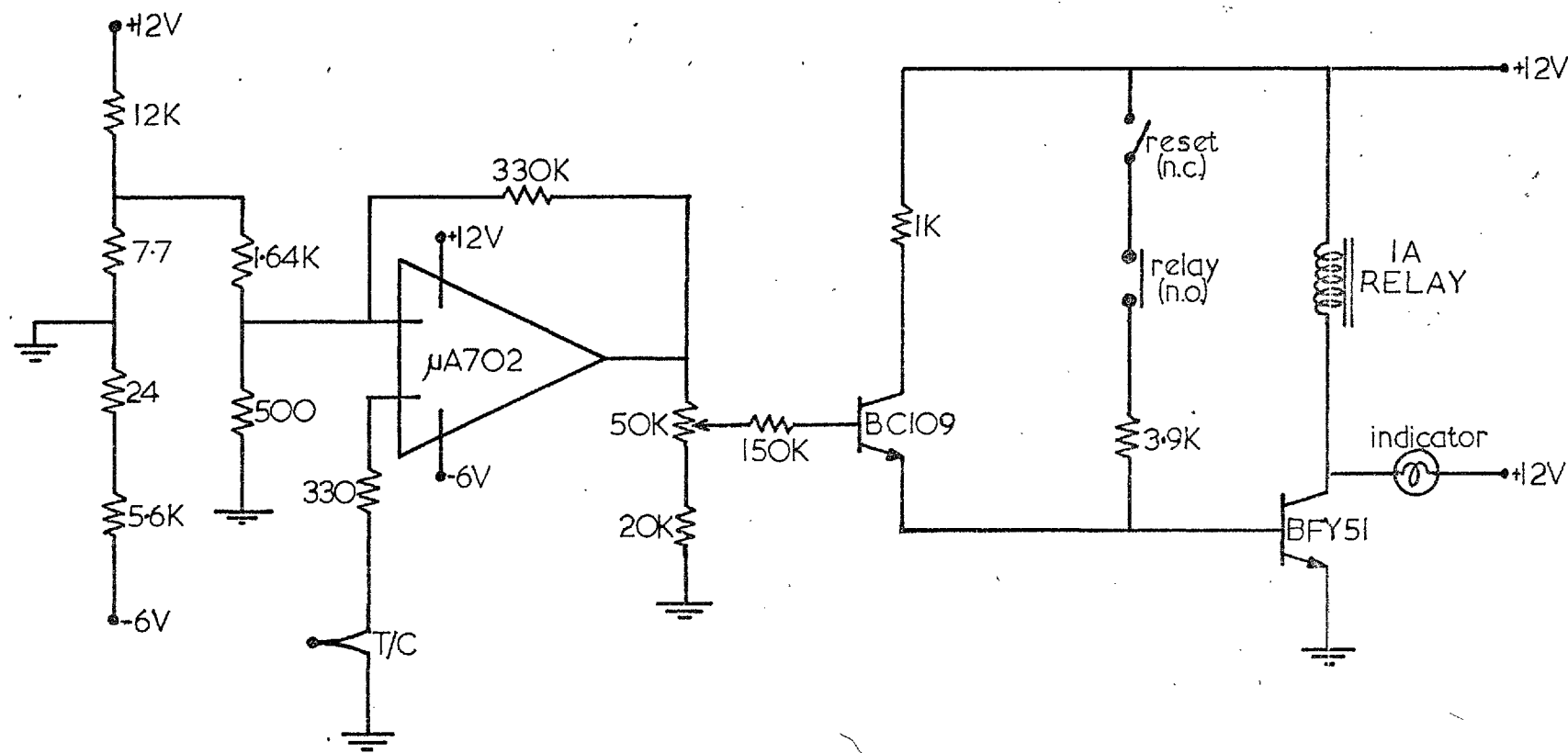


FIGURE 4.17
OVERHEATING PROTECTION
CIRCUIT

CHAPTER V

RESULTS

5.1. Introduction

In section 2.2 the experimental method and elementary theory of TSC was outlined. The following standard procedure was adopted in each experiment:

(i) For each run, the mode of connection to the electrodes together with the magnitude and polarity of the collecting bias were noted.

(ii) An independent plot of log. current against time from the moment of application of the constant bias voltage was made for each TSC run.

(iii) Irradiation from the xenon light source at 77 K filled all the traps within a very short time (certainly less than one second). Normally a period of one minute of irradiation, followed by one minute in total darkness before heating, was adopted to ensure maximum trap filling and constant initial conditions for each run. In section 2.4.3. it was shown that irradiation above 240 K during cooling changed the spectrum of traps, possibly by photochemical reactions. These resulted in the development of TSC peaks above room temperature. In the present work, peaks with maxima occurring at temperatures above 300 K which did not arise from photochemical effects were of importance. To be able to differentiate between these two types of traps, it was essential to maintain the crystal in total darkness at all times except during irradiation at 77 K, and it may be assumed that this technique has been used for all results unless otherwise stated.

(iv) The termination temperature of each run was recorded. 400 K (corresponding to at least 1.1 eV energy depth) was generally sufficient to ensure the emptying of all known traps in CdS. However, because of diffusion of contact material into the crystal appeared to be possible at higher temperatures, some runs were terminated at or below room temperature.

(v) To eliminate any slow build up of gaseous impurity within the sealed cryostat, it was re-evacuated and refilled with helium gas when the devices were tested continually over a long period (several days). No measurable changes due to such re-evacuations were ever observed.

The sequence of operations for each TSC run was:

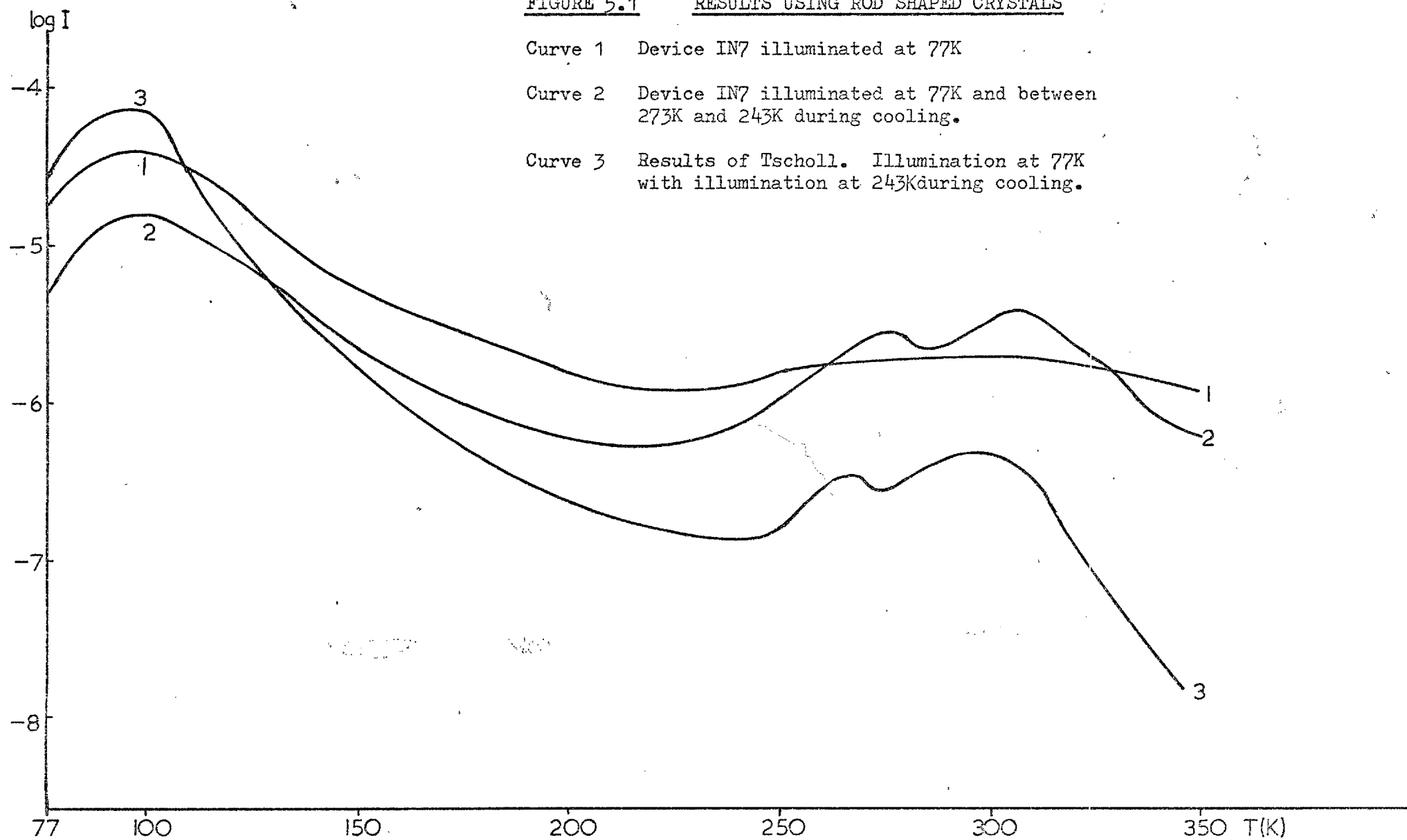
- (i) Cooling to 77 K with no bias applied (unless otherwise stated.
- (ii) Optical irradiation for one minute using a Xenon light source.
- (iii) One minute in total darkness (to allow for photocarrier decay).
- (iv) Application of a bias voltage.
- (v) Heating at a constant rate (0.56 K s^{-1}) recording current against temperature.
- (vi) Termination at a predetermined temperature by removal of heating current and bias voltage.
- (vii) Cooling to 77 K and repetition.

5.2. Bulk Characteristics From Rod Shaped Crystals

Curve 1 of figure 5.1. shows the TSC spectra obtained for a rod shaped crystal having soldered indium contacts. For comparison, the development of photochemically created bulk traps was shown by irradiating the crystal (with a Xenon source) from 273 K to 233 K during cooling as well as at 77 K (figure 5.1, curve 2). It is interesting to compare curve 2 with curve 3 the results of Tscholl (1968) using a similar crystal subjected to illumination at 233 K as well as at 77 K. The two curves show traps at similar temperatures and since Tscholl showed his results to be due to photochemical effects, it is clear that avoidance of illumination during cooling prevents the development of peaks due to this effect.

FIGURE 5.1 RESULTS USING ROD SHAPED CRYSTALS

- Curve 1 Device IN7 illuminated at 77K
Curve 2 Device IN7 illuminated at 77K and between
 273K and 243K during cooling.
Curve 3 Results of Tscholl. Illumination at 77K
 with illumination at 243K during cooling.



5.3. Two Electrode Devices

5.3.1. The TSC spectrum for CdS platelets

No measurements on a single device gave a TSC spectrum which produced all the peaks observed in CdS platelets. Careful discrimination between factors such as contact formation, appearance of the characteristic peak at 100 K, development of peaks above 300 K or the shape of the intermediate (150 K to 250 K) region was necessary before the effect of a particular parameter (e.g. bias potential and polarity or ambient atmosphere) could be linked with specific features of the TSC spectrum. A typical result is shown in figure 5.2. Results for simple two electrode devices are presented in the rest of this section.

5.3.2. Initial results

The first results obtained from two electrode devices showed no similarity to the bulk characteristics of rod shaped crystals under the same conditions. After the initial run, all subsequent results for a particular crystal resembled each other, but differed considerably from the first run. It was also noticed that successive runs exhibited a small increase in magnitude of TSC compared to the previous run, as shown in figure 5.3. Curve 1 shows the initial spectrum and curves 2 to 8 the subsequent runs.

An interesting result was obtained after the removal of the specimen from the cryostat for inspection at the end of run 8. When it was re-inserted into the cryostat, curve 9 was obtained which exhibited similar characteristics to curve 1. All subsequent runs (not shown) were similar to curves 2 to 8.

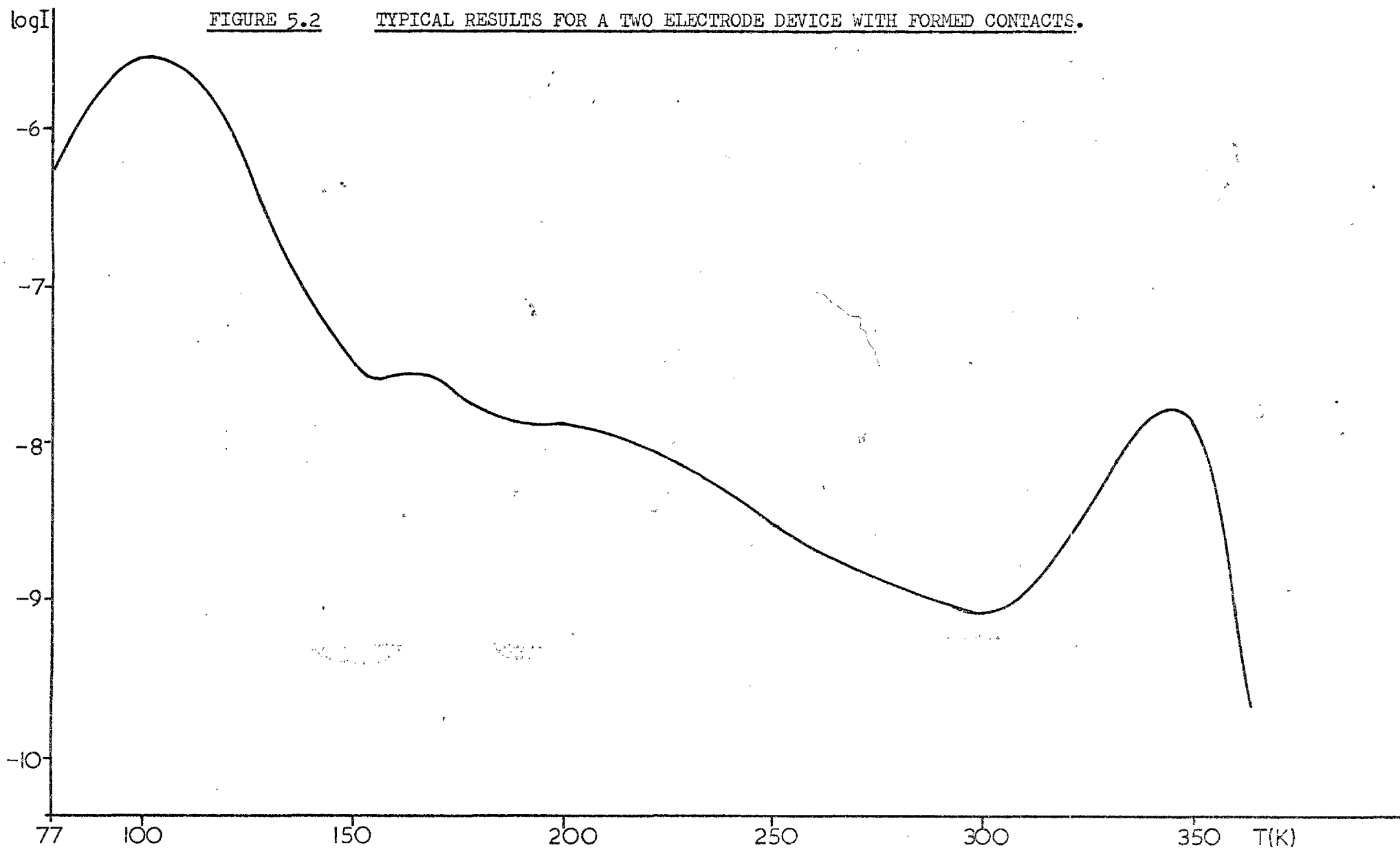
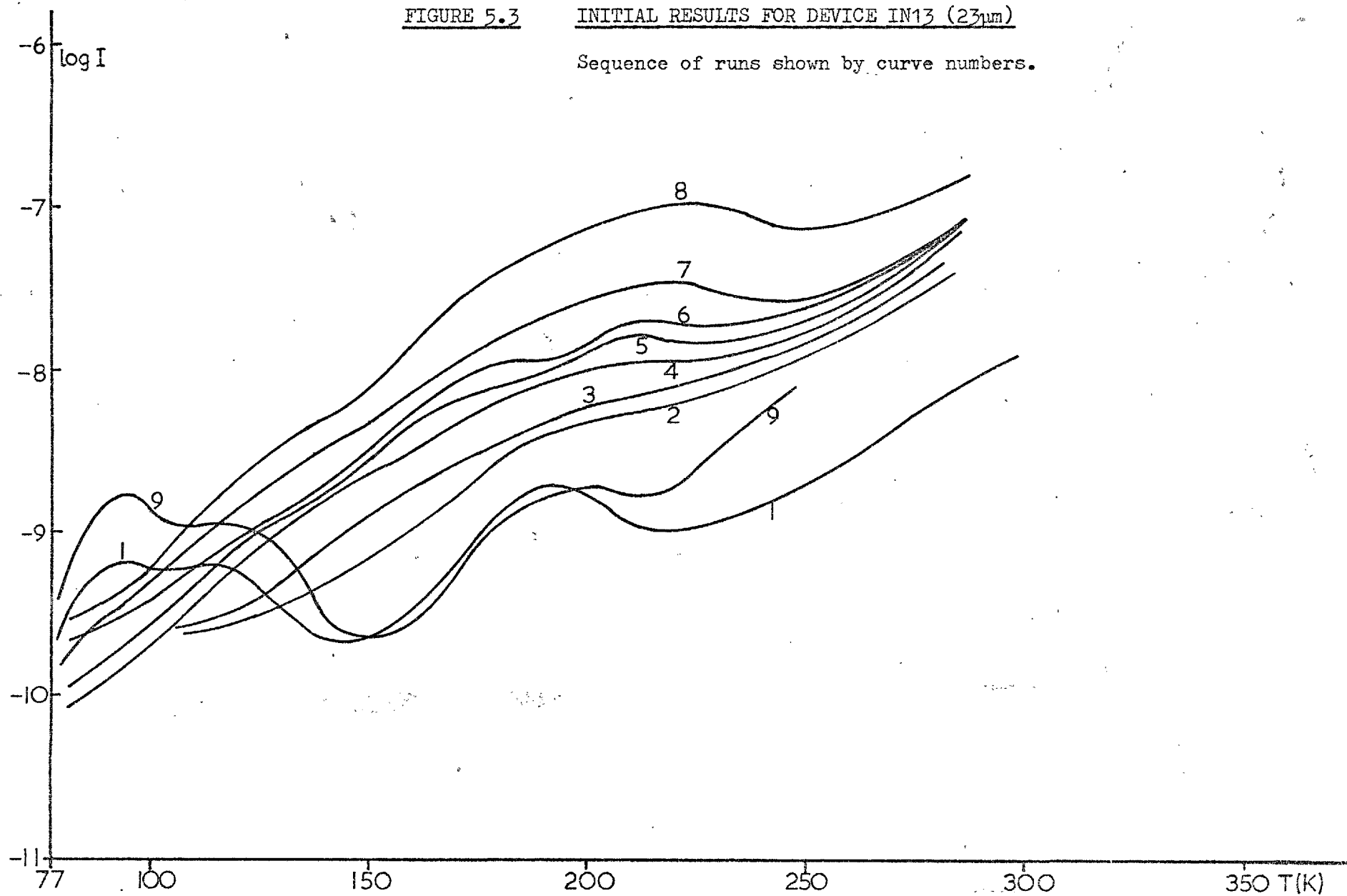


FIGURE 5.3

INITIAL RESULTS FOR DEVICE IN13 (23 μ m)

Sequence of runs shown by curve numbers.



The TSC spectra shown in figure 5.3. were typical of the first devices used. It was suspected that surface conduction played an important role in the gradual increase in magnitude of the TSC spectra, so a series of guard ring experiments was undertaken. Results are given in section 5.5.

5.3.3. Peaks above 300 K

The first runs on a virgin crystal rarely exhibited peak maxima above 300 K, but the majority of devices tested developed such peaks after a number of runs. Several aspects of the high temperature peaks (HTP) became apparent at an early stage:

(i) Formation of an HTP occurred after numerous TSC runs had been performed.

(ii) The HTP did not require previous optical irradiation of the specimen at low temperature.

(iii) The HTP was completely quenched if a bias was applied to the crystal during cooling and maintained with unchanged polarity and magnitude during the TSC heating run.

(iv) The HTP magnitude could be enhanced by cooling the specimen with a bias applied having opposite polarity to that used during TSC heating.

The remainder of the TSC spectrum was essentially unaltered by the cooling bias (the appearance of peaks at 100 K will be discussed later). Figure 5.4., curve 1 shows these TSC spectra for device IN19 obtained by varying the bias conditions during cooling. These were no bias, reverse bias and same polarity bias (compared with the collector potential during heating) for curves 1, 2 and 3 respectively.

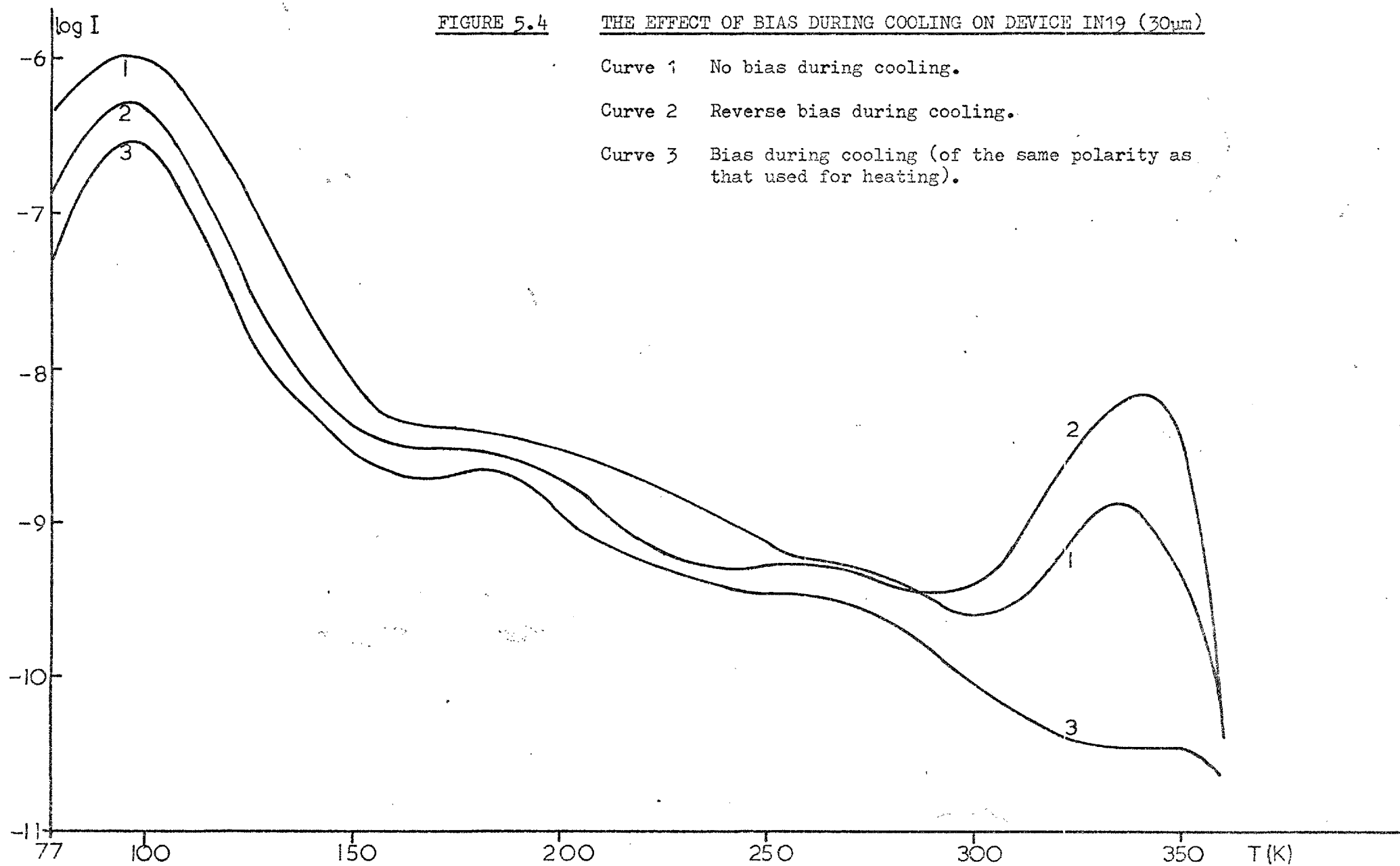
FIGURE 5.4

THE EFFECT OF BIAS DURING COOLING ON DEVICE IN19 (30 μ m)

Curve 1 No bias during cooling.

Curve 2 Reverse bias during cooling.

Curve 3 Bias during cooling (of the same polarity as that used for heating).



Below 300 K one effect of cooling the specimen applying the same bias as that used for warming was to produce a small decrease in current magnitude of the TSC spectrum up to about 280 K. However, the peak at 340 K decreased in size by one and a half orders of magnitude. In other results (to be described later) a reduction of current by up to six orders of magnitude was obtained on similar application of bias during cooling.

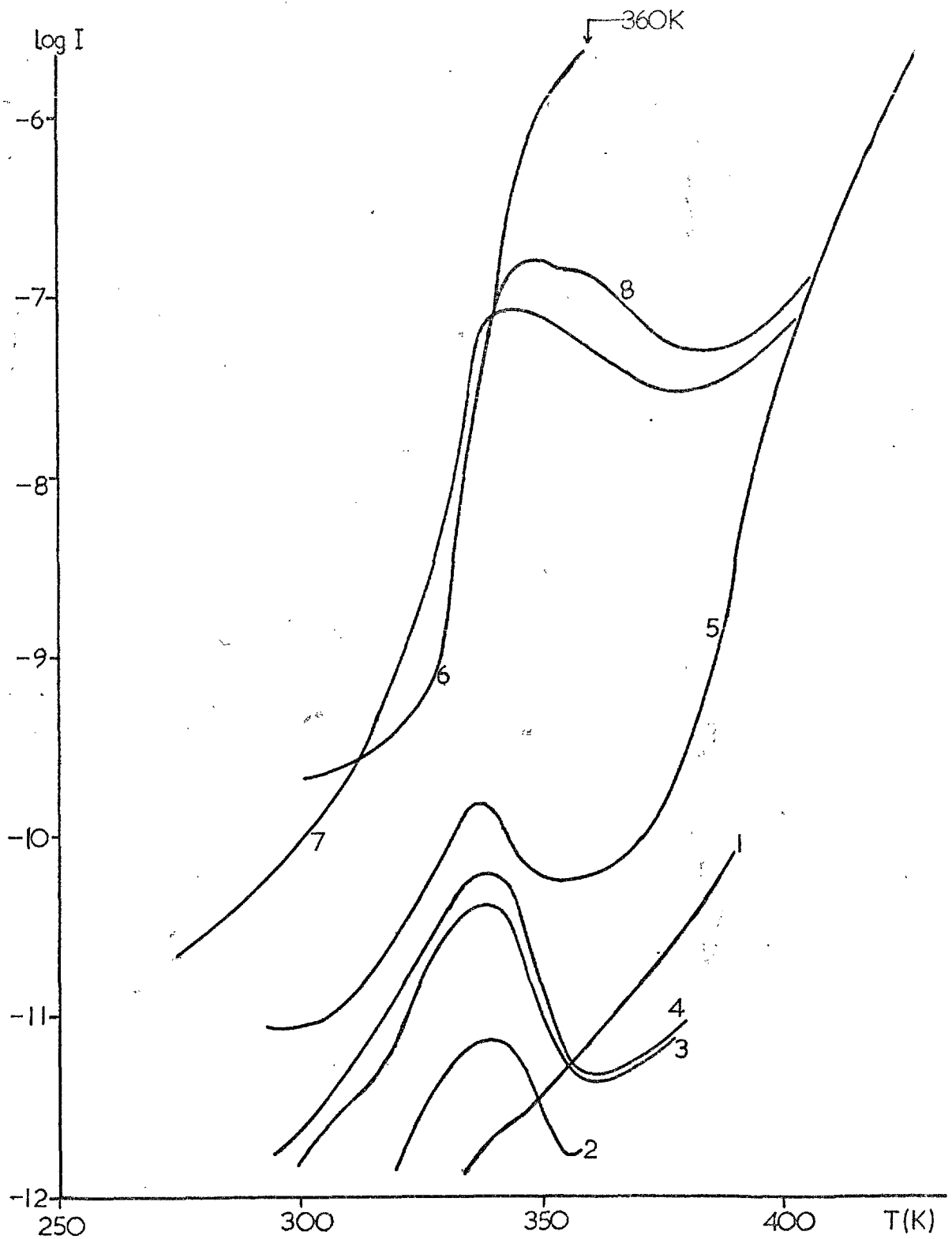
5.3.4. Formation of the HTP

Figure 5.5 shows the results for device IN26 as the HTP developed. Since earlier results had shown that irradiation at low temperature was not necessary to the development of this peak, these experiments were confined to thermal cycling between 200 K and a maximum temperature of 400 K, with and without applied bias.

The slowly increasing magnitude of the peak at 340 K is seen in curves 1 to 5, using a collecting bias of 15 V during heating (and no bias during cooling). The high temperature limit for run 5 was increased, resulting in a "run away" of current, limited only by a protective resistor. The specimen was cooled without bias, and a further run (curve 6) was made. At 340 K, the peak current was found to have increased by four orders of magnitude, and the run was terminated at 360 K.

Two subsequent runs using only 5V bias during heating are shown in figure 5.5, curves 7 and 8. No apparent damage was caused by the comparatively high currents of runs 5 and 6. Development of the HTP appeared dependent on the temperature at which the TSC heating was terminated, and the magnitude of collecting bias during heating.

FIGURE 5.5 THE DEVELOPMENT OF A PEAK AT
340K FOR DEVICE IN26 (25 μ m)



5.3.5. Polarity dependence of HTP formation

To investigate the role of collector bias polarity, a virgin specimen (device IN24) was subjected to numerous TSC runs with the same polarity* of collecting bias (starting with fifteen runs at + 10 V to 'form' the device then fourteen runs at + 2V). Curve 1 of figure 5.6 shows the resultant reproducible curve for + 2V collecting bias. Curves 2, 3 and 4 (in that sequence) were obtained when a - 2 V collecting bias was used (the first time a negative polarity had been used on device IN24). The effect of using a higher collecting bias during a TSC run is shown in curve 5 for - 7 V. Reverting back to - 2 V collecting bias, curves 6 and 7 were obtained. Finally, in the absence of illumination, curve 8, showing a peak at 370 K was produced.

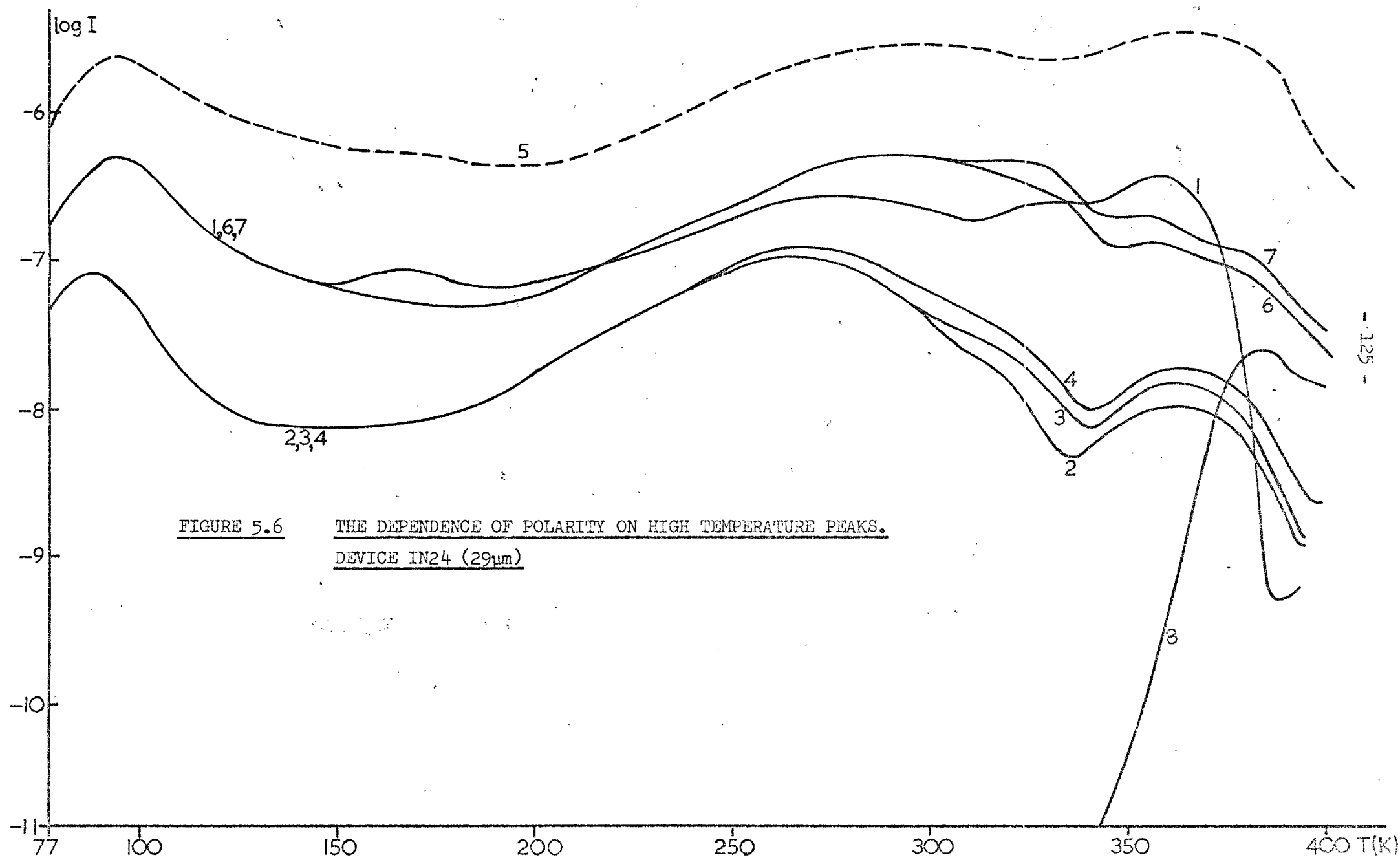
The results for this device can be summarised as follows:-

(i) Using only positive polarity collecting biases, a stable TSC spectrum is obtained for a given bias voltage (+ 2 V) as in curve 1 of figure 5.6.

(ii) Reversal of the bias to - 2 V substantially reduces the magnitude of the TSC curve, especially for the HTPs.

(iii) Increasing the negative bias to - 7 V for one run produces increased TSC magnitude for subsequent runs at - 2V. An increase of over half an order of magnitude was observed below 300 K, and by over one order of magnitude above 300 K. Therefore, one could assume that below 300 K, TSC curves for collecting biases of + 2V and - 2 V are almost identical.

* To avoid unnecessary confusion, the polarity of the collecting bias is referred to the top electrode, so positive polarity means top electrode positive.

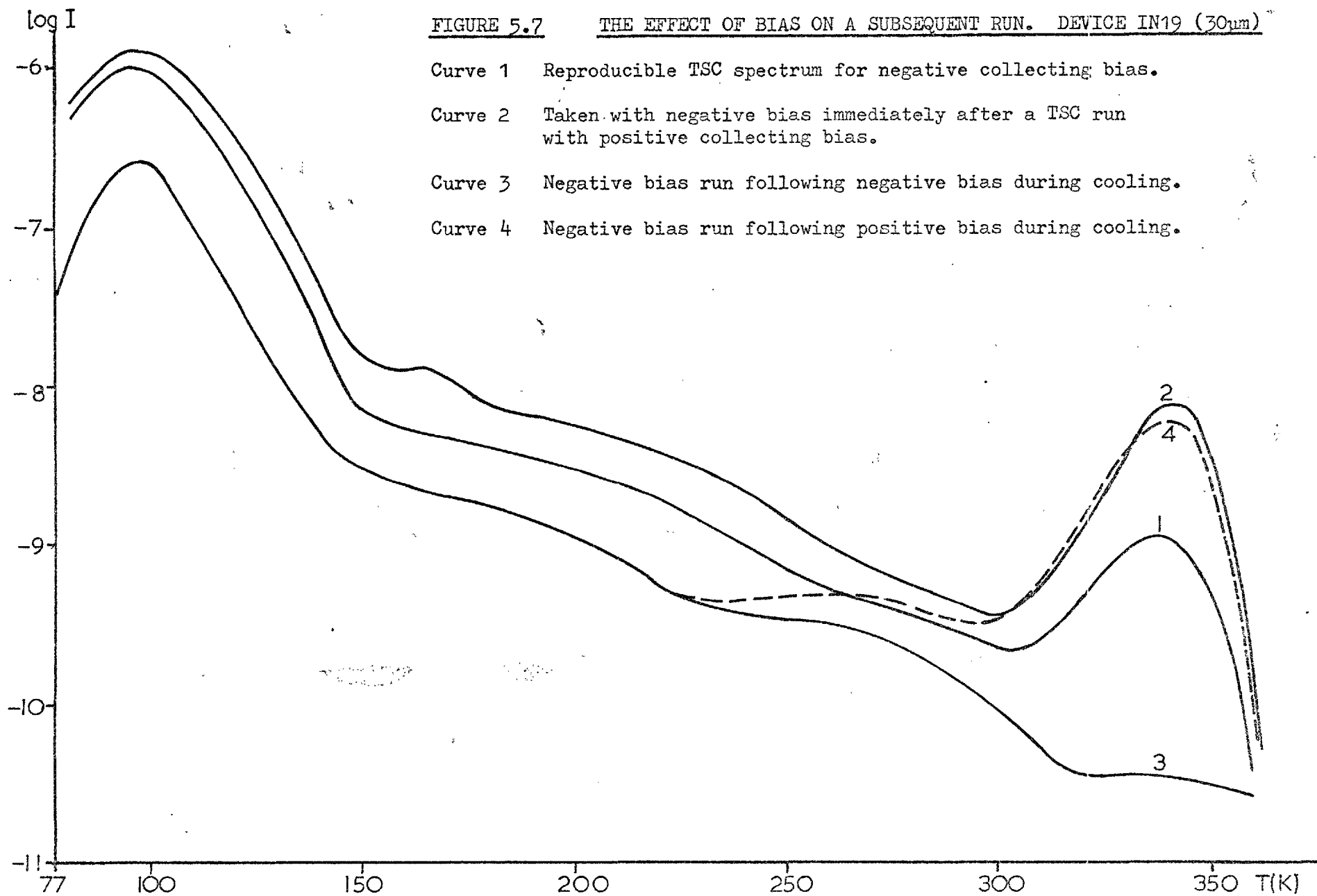


(iv) In the case of no low temperature irradiation, a peak appears at 370 K.

Bias polarity and the temperature to which previous runs were taken to appear to be important factors in development of HTPs. The repeated cycling of a specimen from 77 K to high temperatures may be expected to affect both electrodes similarly. However, the polarity of the bias would determine the type of charge received at each electrode. The fact that after the application of large biasses, both + 2V and - 2 V curves gave similar TSC curves after the first run suggests some sort of forming process takes place, possibly of similar nature to the well known method of forming contacts using high fields. This process would appear, from these results, to require both thermal cycling and the application of large bias voltages.

5.3.6. Polarity effect on following runs

In view of the results of section 5.3.5. indicating a change in magnitude of TSC currents over the entire spectrum depending upon the initial polarity of the applied fields, the effect of the direction of bias during cooling and of polarity of the previous runs were investigated. Figure 5.7 shows the results obtained for device IN19 (all with a negative polarity collecting bias). Here curve 1 exhibits a normal TSC spectrum whilst curve 2 was obtained with the same negative bias immediately after a run with positive polarity applied to the crystal. Below 300 K the magnitude of the spectrum was approximately twice that of curve 1, and for the HTP almost one order of magnitude larger. The effect of bias during cooling is shown in curves 3 and 4 (dotted) for negative and positive polarities respectively. Negative bias during cooling produced a decrease in magnitude of about three



times compared to curve 1, and completely quenched the 340 K peak. Positive bias during cooling produced a very similar HTP to that of curve 2. The results were repeated many times and are completely reproducible.

5.3.7. Appearance of the peak at 100 K

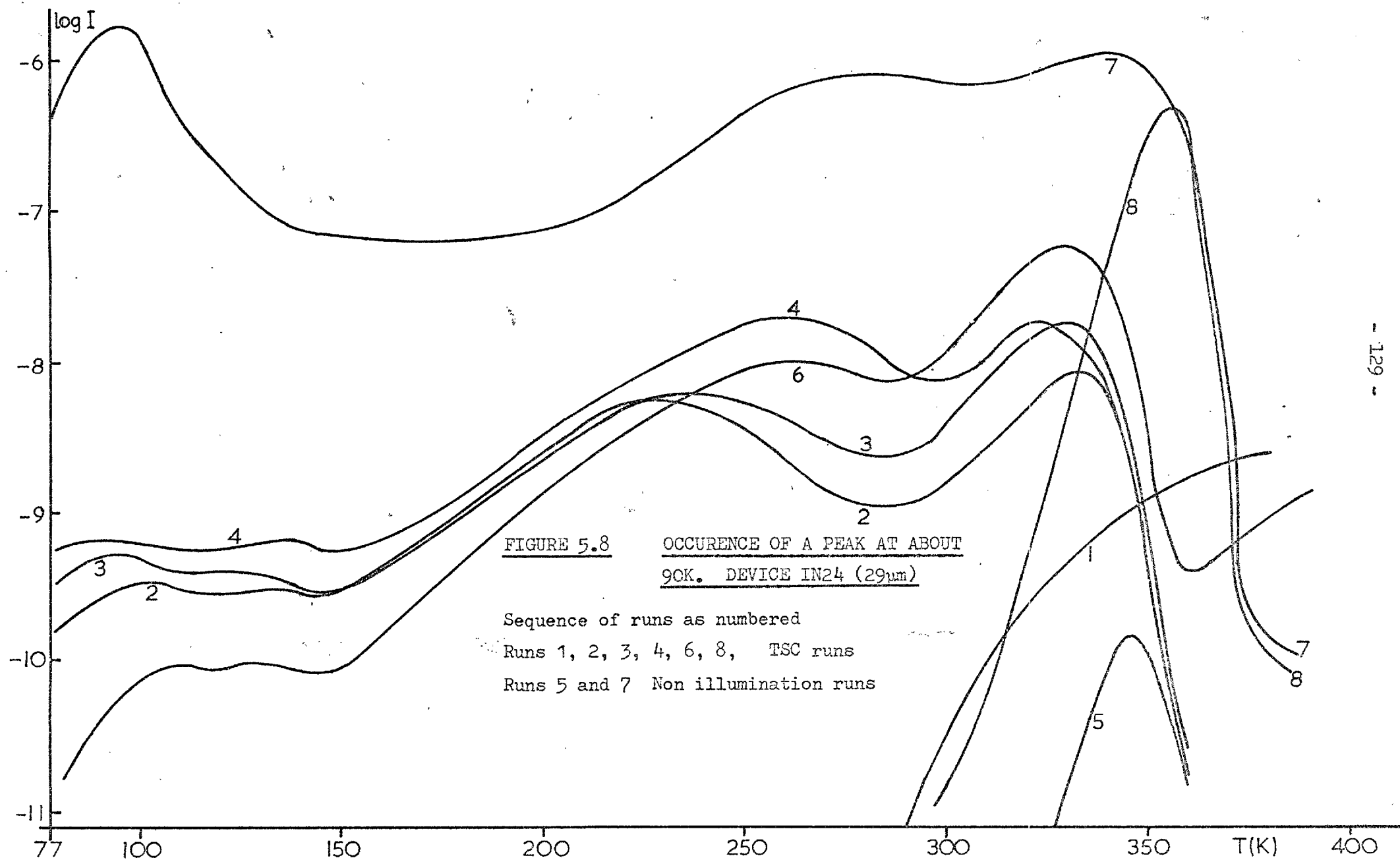
The appearance of a peak at 100 K often occurred suddenly. In several runs, a definite link was found to exist between HTP development and the occurrence of this peak. Figure 5.8. shows such a transformation. Initial runs (curves 1 to 6 inclusive) show the formation of an HTP (~ 350 K) exhibiting only a very small peak if not irradiated at 77 K (curve 5). Curve 7 showed a sudden transformation to a characteristic reminiscent of the bulk specimen and curve 8 is the resultant HTP produced in the absence of low temperature irradiation.

Thin crystals ($< 10 \mu\text{m}$) rarely exhibited TSC peaks at 100 K. Further insight into this process follows results obtained on guard ring devices in section 5.5.2.

5.3.8. Silver contacts

Evaporated silver electrodes were initially noisy, but changed to good, possibly ohmic contacts after several runs. Characteristics were similar to those with indium contacts. The decay of HTPs after attaining their maximum appeared to occur more rapidly than with indium electrodes.

Device AG20 exhibited what appeared to be two HTPs; at 340 K and 370 K. Optical irradiation at low temperature was not required for formation of

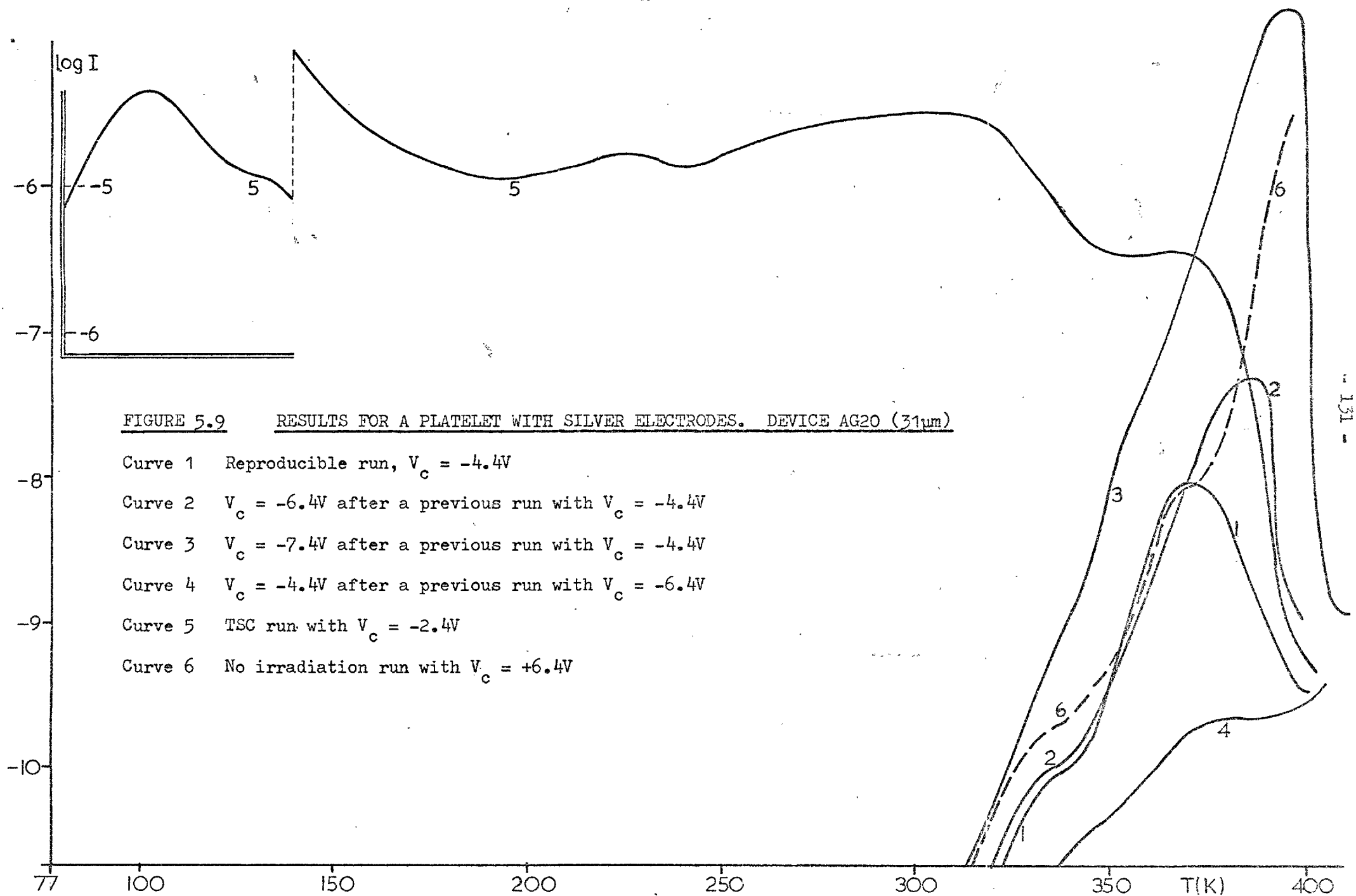


these peaks. Curve 1 of figure 5.9 shows the reproducible TSC spectrum obtained for - 4.4 V collecting bias. Curves 2 and 3 show respectively the results taken for - 6.4 V and - 7.4 V collecting biases, each run following a previous run at - 4.4 V. An increase in both the temperature of the maximum and the magnitude of the peak resulted from an increase in collecting bias. Correspondingly for a decrease in collecting bias magnitude compared to the previous run, a reduction in peak height was observed. Curve 4 shows the result for a - 4.4 V collecting bias taken immediately after a run with - 6.4 V.

The effect of reversing collecting polarity of the bias produced the same two peaks (340 K and 370 K) followed by a very sharp rise in current, as shown in curve 6. The run was terminated at 400 K with the current still rising. Subsequent runs were however unaffected by the large increase in current, indicating no measurable damage to the crystal.

It must be remembered that the HTP results were all taken in the absence of irradiation at lower temperatures. Curve 5 shows a normal TSC run with a collecting bias of - 2.4 V. Two points were of interest, firstly the magnitude of the peak at 370 K was increased inspite of the lower collecting bias, and secondly the relative magnitude of the HTP region compared with the rest of the spectrum was smaller compared with other devices. The possibilities of the HTPs being independent of bulk CdS effects must be considered.

A resume of the HTPs recorded for CdS platelets with silver contacts, together with conditions necessary for observation is presented in table 5.1.



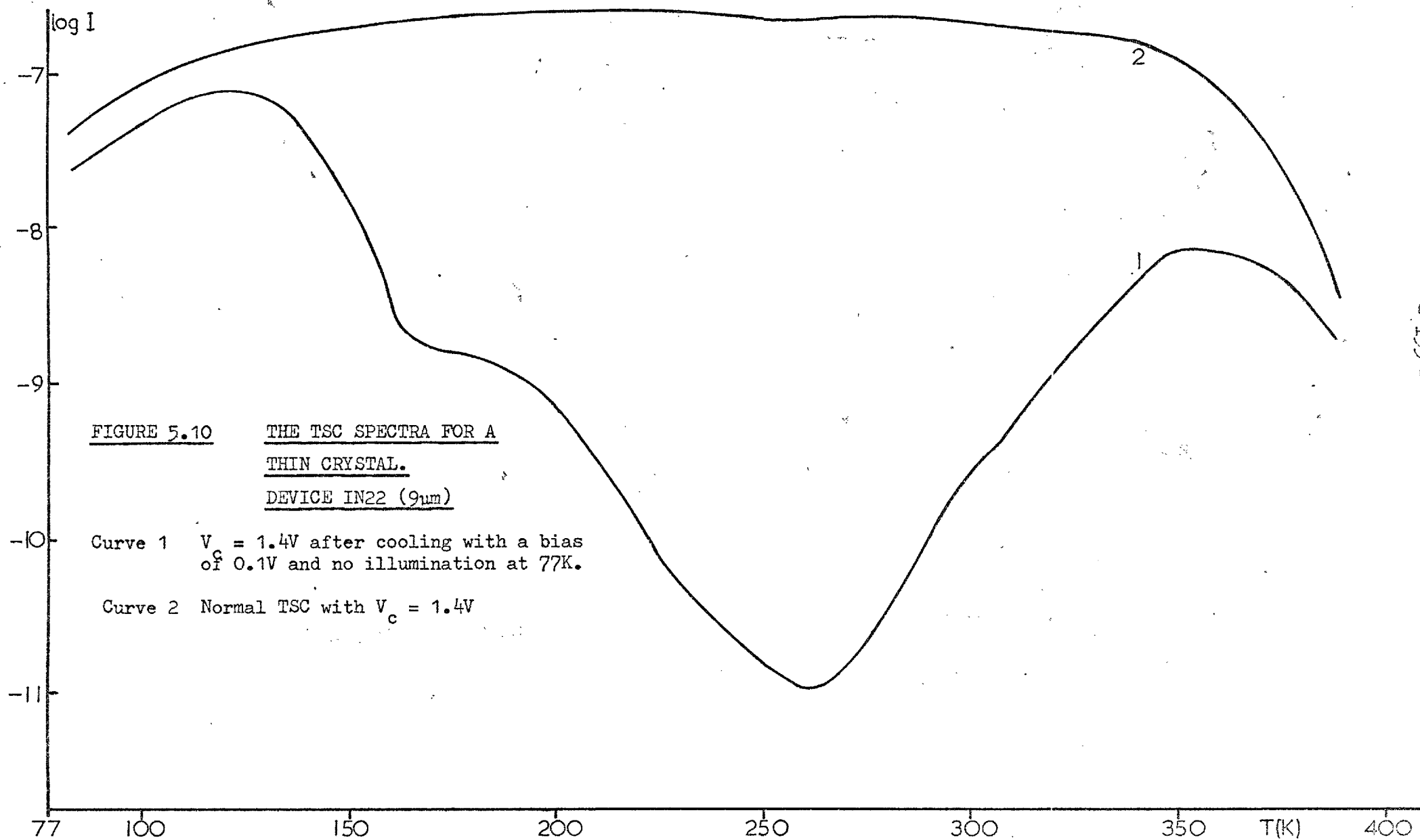
T PEAK	I PEAK	CONDITIONS NECESSARY
395 K	$> 10^{-5}$ A	Large -ve bias after zero or +ve bias during cooling
370 K	$< 5 \times 10^{-8}$ A	Observed if the previous run exhibited on HTP
340 K	$\sim 2 \times 10^{-10}$ A	Generally observed for all collecting biases

TABLE 5.1. HTPs For Devices With Silver Electrodes.

5.3.9. Thin crystals

Crystals having a thickness not exceeding $10 \mu\text{m}$ were selected for use in high field investigations. Rapid development of HTPs (~ 360 K) with magnitude in excess of 10^{-5} A occurred in thin crystals. The collecting voltages necessary to produce HTPs ^{were} ~~was~~ lower than with normal ($30 \mu\text{m}$) crystals. This implied an electric field dependence for peak formation. Here, a 2 V bias was sufficient to produce an HTP for a $6 \mu\text{m}$ thick platelet.

Figure 5.10 shows the TSC spectrum produced by cooling a $9 \mu\text{m}$ thick crystal with a small bias applied, and heating with a collecting bias of opposite polarity, but without irradiation at 77 K. The result was therefore due to the effect of electric field only. Using the same collecting bias curve 2 shows the TSC spectrum produced by illumination at 77 K in the absence of bias during cooling.



5.3.10. Summary

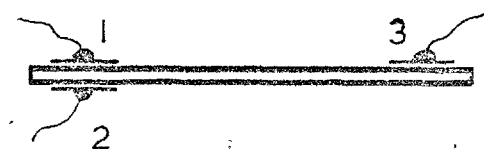
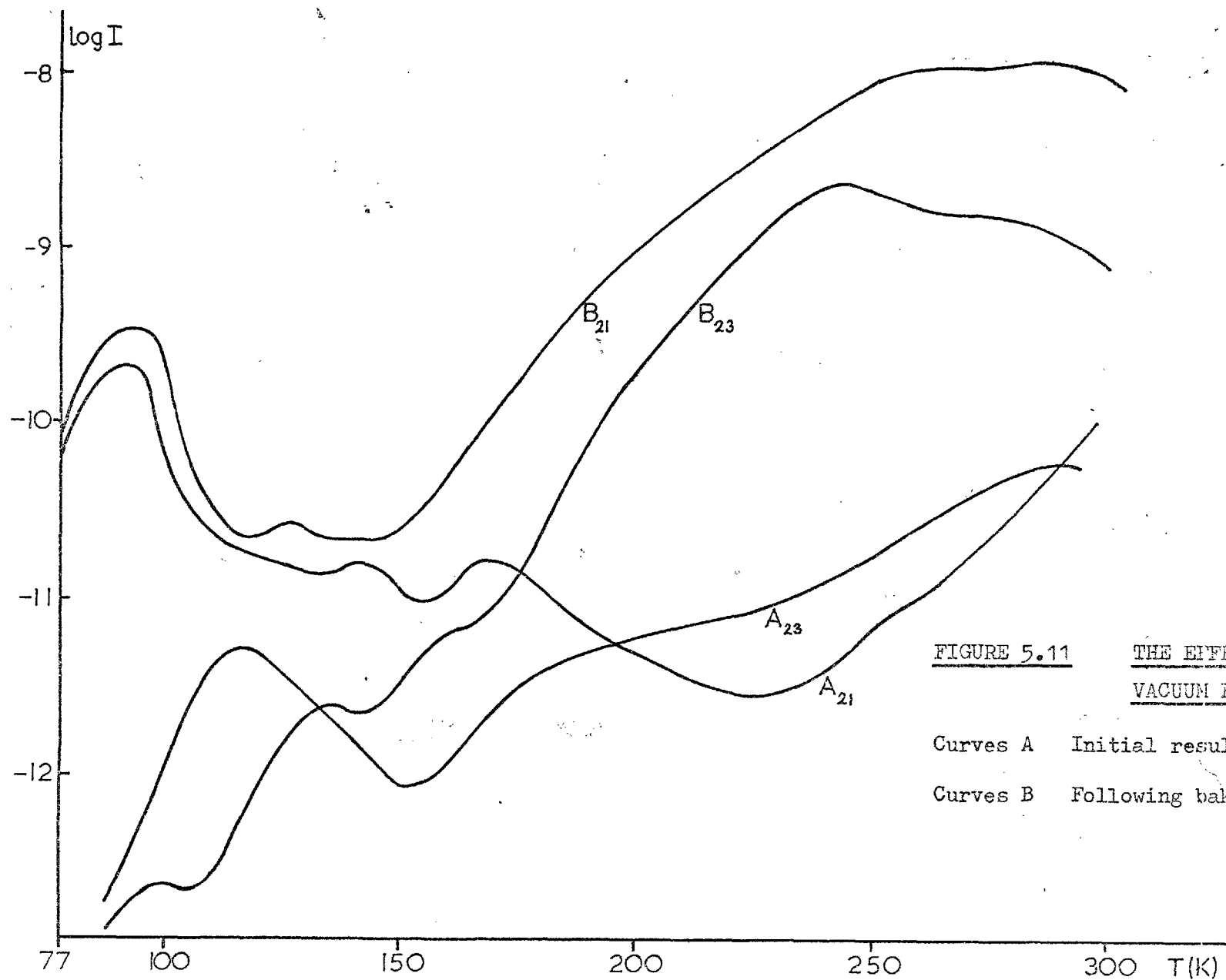
The results obtained using crystals of different thickness with two simple, opposite face electrodes indicate the effect of bias potential on the TSC spectra. In section 5.3.7 it was reported that the peak at 100 K was rarely observed in thin crystals. The effect of oxygen adsorption and desorption complicated results by modifying surface current contribution, and the appearance of bias dependent peaks above 300 K, possibly coupled with the peak at 100 K possibly implied contact effects.

In order to obtain more information to gain insight into these complex results recorded for two electrode devices, surface currents were investigated using a guard ring electrode configuration and contact effects using three electrode specimens.

5.4. Three Electrode Devices

5.4.1. Initial observations

Simultaneous TSC results from a three electrode specimen, device IN46 were recorded for several runs, each cycle being taken to 300 K. Figure 5.11 shows the electrode configuration and initial results recorded for opposite face (curve A_{12}) and same face (curve A_{13}) electrodes respectively (electrode 1 was common). The results (shown as curves B_{21} and B_{23} of figure 5.11) were recorded after evacuating the cryostat whilst maintaining the specimen temperature at 400 K for several minutes following the previous TSC run. A substantial increase in magnitude of the curve above 150 K resulted for both electrode connections. TSC spectra reverted to curves A_{21} and A_{23} following air admission into the cryostat during cooling.



ELECTRODE CONFIGURATIONS
FOR DEVICE IN46.

FIGURE 5.11

THE EFFECT OF BAKING AT 400K IN
VACUUM FOR DEVICE IN46 (72 μ m).

Curves A Initial results.

Curves B Following baking in vacuum at 400K.

These observations suggest that the non-reproducibility of earlier results (figure 5.3. for example) may have been due to ambient atmospheric effects on the surface. They also indicated that the TSC spectrum above 150 K could be related to surface behaviour. It was therefore decided to use the guard ring electrodes as a means of investigating surface effects separately.

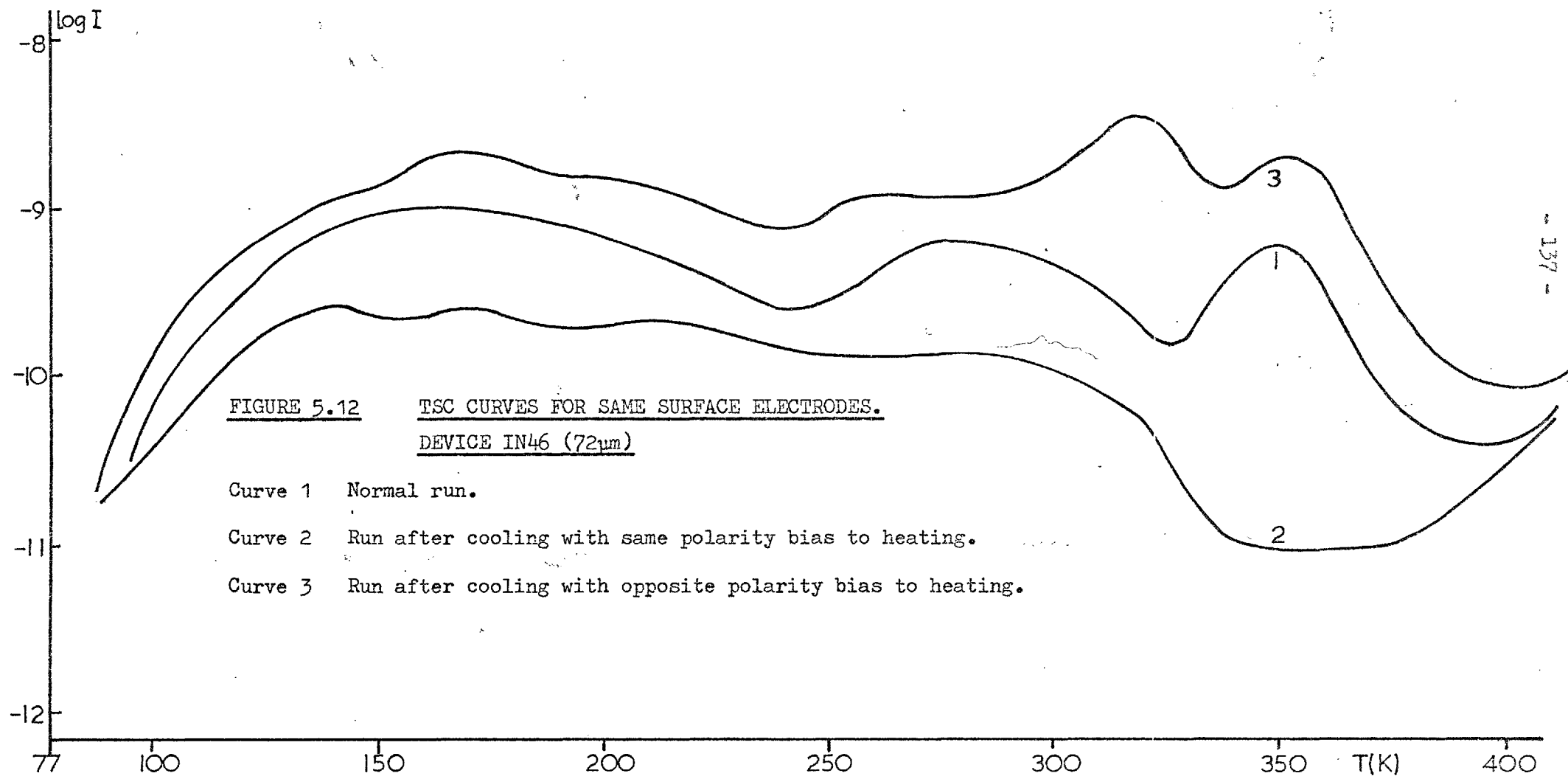
5.4.2. Properties of HTPs from "same surface" electrodes

Figure 5.12 curve 1 shows the TSC spectrum recorded for a device with electrodes on the same crystallographic face. The effects of the same and opposite polarity bias during cooling are shown in curves 2 and 3 respectively. The similarity between HTPs in figure 5.12 and corresponding results from simple two electrode devices (figure 5.4) suggest that this peak is not associated with surface effects. This interpretation is further supported by the fact that this peak was unaffected by the admission of oxygen.

5.4.3. Association of HTPs with a particular electrode

In light of the results reported in 5.4.2. further runs were recorded for a three electrode device using a different common electrode for each run. Figure 5.13 shows the electrode configuration for the results shown in figure 5.14.

The HTP is seen to be dependent on the particular electrode which is positive rather than path length or surface effects. Few TSC runs were performed with positive voltage on electrode 2, so the corresponding HTP



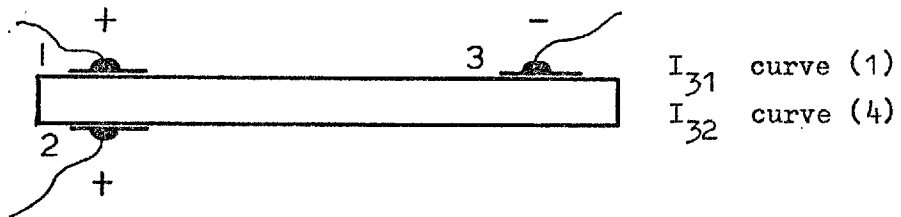
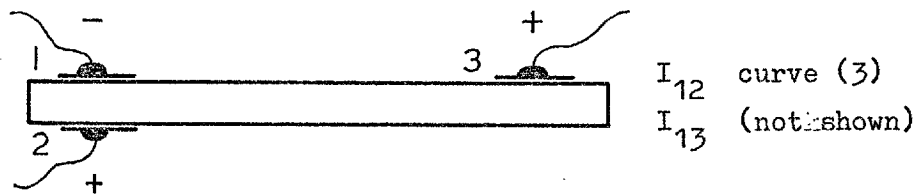
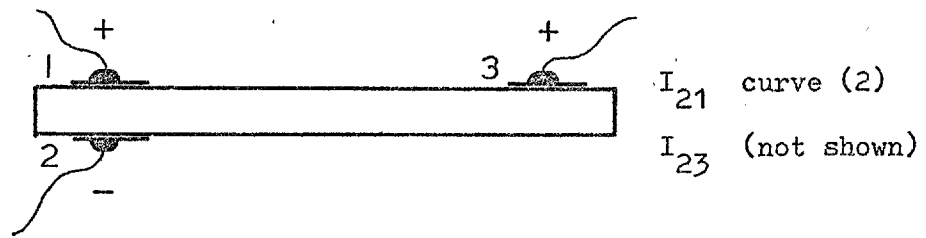
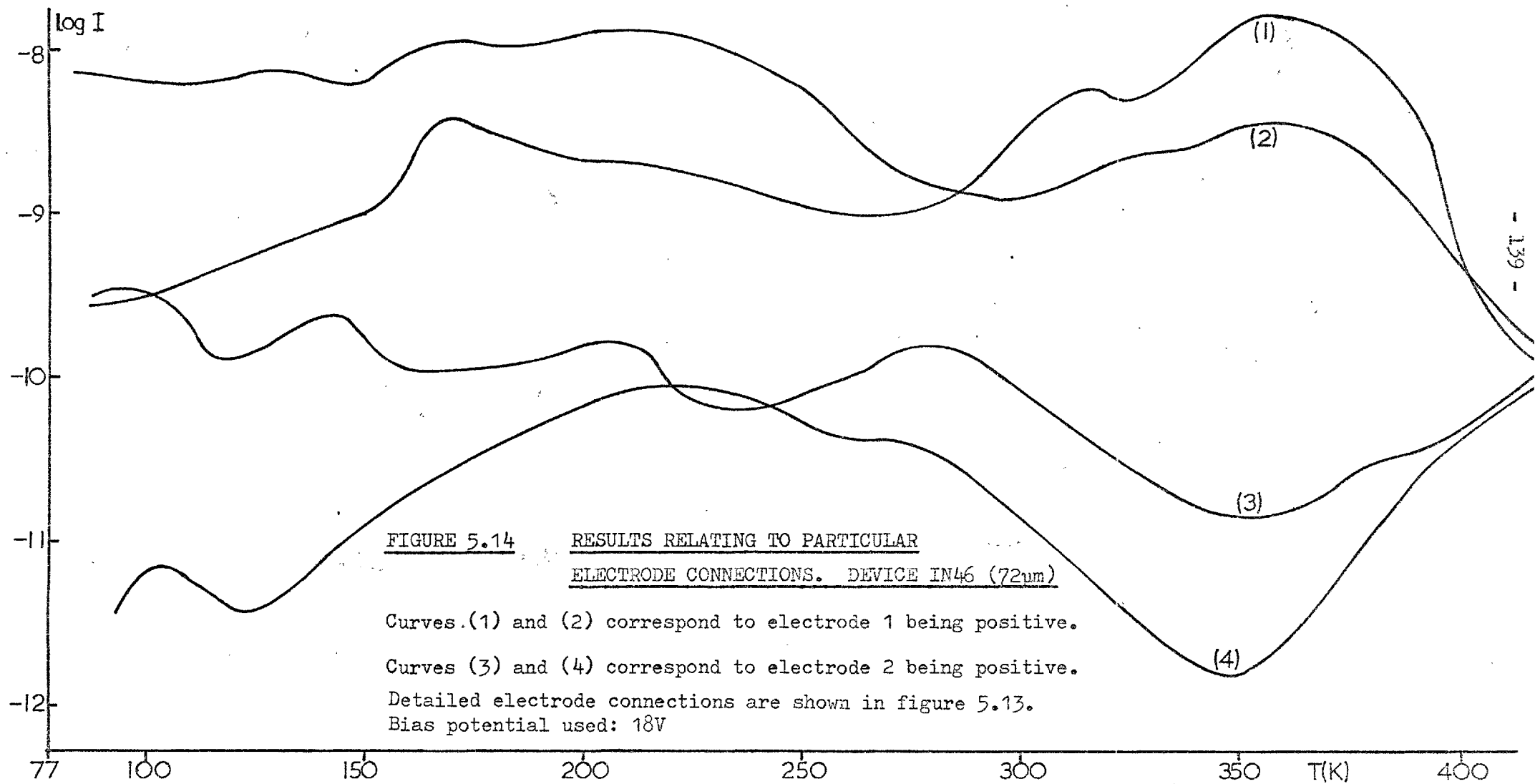


FIGURE 5.13

ELECTRODE CONNECTIONS FOR THE
RESULTS SHOWN IN FIGURE 5.14



development was small (see figure 5.14). Similar dependences were exhibited for all three electrode devices tested, namely a particular HTP could be attributed to the action of a certain electrode.

Results for electrode 3 having positive polarity with respect to electrodes 1 or 2 exhibited similar properties in the high temperature region, but were omitted from figure 5.14 to avoid confusion. It would in any case be unwise to attach too much importance to similarities between such results as both bulk and surface path lengths between electrode 3 and either 1 or 2 were comparable.

5.5. Guard Ring Electrodes

5.5.1. Observations of bulk characteristics

The results from a guard ring electrode structure on a very thick (160 μm) crystal presented conclusive evidence of bulk trapping in CdS platelets. The TSC results for both centre and guard ring electrodes are shown in figure 5.15 curves 1_c and 1_{GR} respectively. Qualitatively similar curves were produced. To change the distribution of bulk traps in the platelet, the crystal was subjected to irradiation (by Xenon illumination) during cooling from 300 K to 77 K. Curves 2_c and 2_{GR} show the corresponding TSC results obtained. Here again, the similarity of both top electrode current spectra can only be due to bulk trapping, since the guard ring and centre electrodes have no potential difference between them.

5.5.2. Decay of current due to collecting bias field

The guard ring electrode configuration provided a direct means of

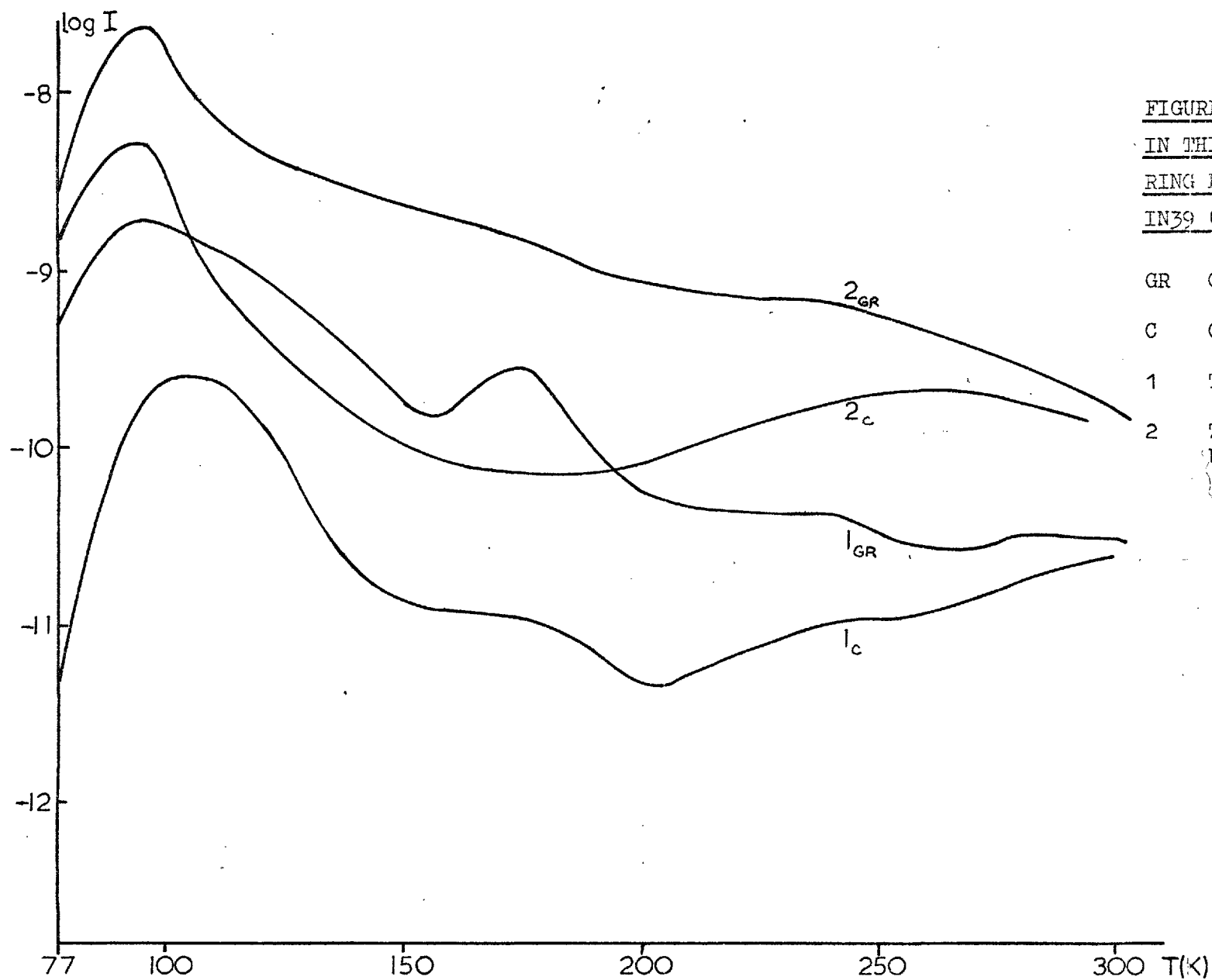


FIGURE 5.15 BULK CHARACTERISTICS
IN THICK PLATELETS USING A GUARD
RING ELECTRODE SYSTEM. DEVICE
IN39 (160 μ m)

- GR Guard ring current
- C Centre electrode current
- 1 TSC curve
- 2 TSC curve after irradiating
between 300K and 77K

assessing the mechanism causing decay of current following irradiation at 77 K. The rapid decay of photoexcited carriers following removal of the irradiation was generally comparable to the response time of the mechanical X - Y plotter (~ 0.3 s). A secondary decay was often noticed however, particularly for two electrode devices. This decrease appeared to be associated with crystal thickness (faster decay for thinner crystals). To differentiate between thermal emptying and electric field emptying of traps, the decay of currents through the guard ring and centre dot electrodes was recorded under two different conditions:

- (i) When the collecting bias was applied to the device directly after irradiation at 77 K.
- (ii) When the collecting bias was applied after a period of several minutes in the dark after irradiation at 77 K.

The results for both conditions were identical, and are shown in figure 5.16(a). Allowing several minutes to elapse before connecting the bias would have permitted thermal emptying to take place. By applying the same voltages between the bottom electrode and both the guard ring and centre electrodes, only appreciable decay was observed for the latter. Here the decay could be attributed to emptying the traps with the electric field.

5.5.3. Surface conductivity

With the circuit connected as shown in figure 5.16(b), in which the two ammeters were of equal impedances, there would be no electric field across the surface between the centre and guard ring electrodes. Therefore the current flowing to the centre electrode contained no surface contribution and was bulk current only.

The measurements were extended to include surface currents by ^{shorting} ~~starting~~ the ammeter A_{GR} which had the effect of producing a small potential

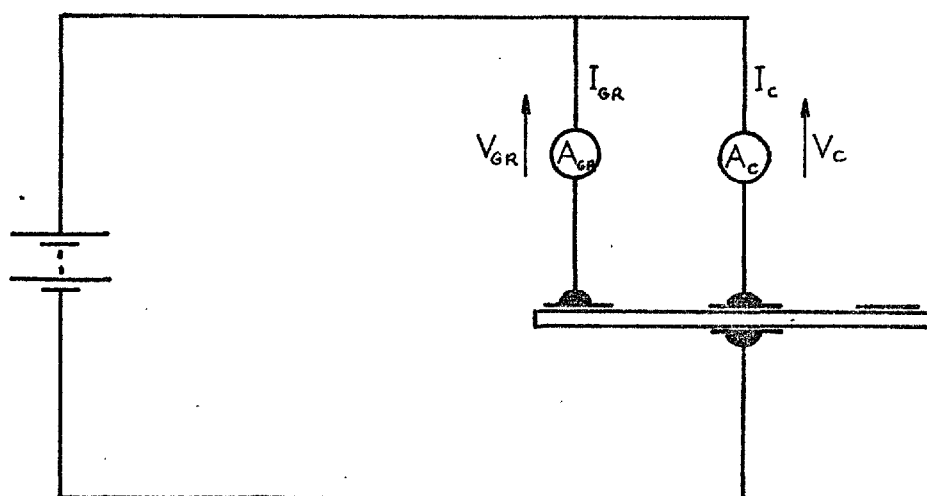
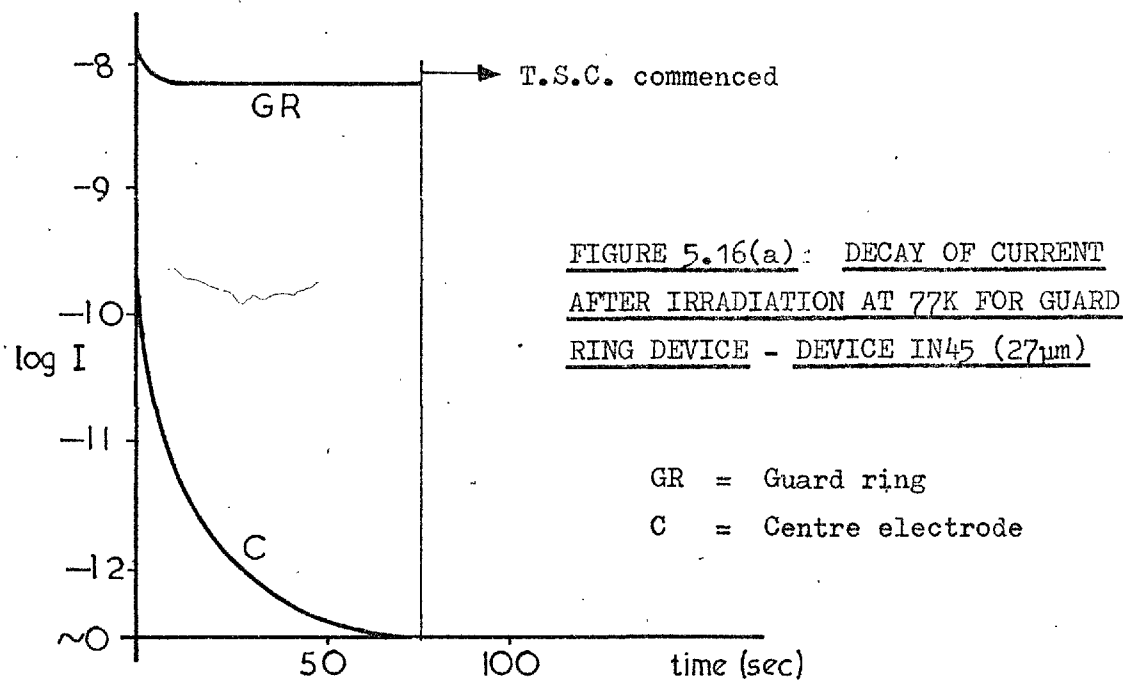


FIGURE 5.16(b) CONNECTION OF GUARD RING CIRCUIT

difference between the centre and guard ring. A current was recorded giving a decrease of reading of ammeter A_c . For comparison only the guard ring ammeter was disconnected completely, and the surface contribution between centre and guard ring was recorded as an increasing reading of ammeter A_c . Device IN45 exhibited widely differing, but reproducible results for currents to guard ring and centre electrodes, as seen in figure 5.17, curves 1_{GR} and 1_c . Also the effect of shorting the guard ring ammeter is shown in curve 2_c , and that of disconnecting the guard ring electrode in curve 3_c . Detailed interpretation of these results is given in section 6.3.

5.6. I - V Measurements

After the reproducible TSC results were obtained from device IN19, the room temperature current-voltage characteristics were also measured for both directions of current, and are shown in figure 5.18(a), curves A and B. The similarity of these characteristics for the two directions indicate the device is symmetrical, and the results are consistent with those taken under similar conditions by other workers, for example Bube (1962), Lampert (1954) and Marlow and Woods (1963).

When the voltage was slowly reduced after reaching a maximum of 40 V, the current correspondingly decreased and eventually reversed in direction when the applied voltage fell below about 1 V, as shown in figure 5.18(a), curve 3. A current just in excess of 10^{-12} A initially flowed when the device was short circuited. This effect has also been observed by Gershun and Timan (1968) and can be attributed to the relaxation of a dipolar layer in the contact region. The results are discussed further in section 6.4 during the development of a model to explain the TSC curves.

FIGURE 5.17

SURFACE CONDUCTIVITY EXPERIMENTS

USING GUARD RING ELECTRODES.

DEVICE IN45 (27 μ m)

Curves 1_{GR} and 1_C ; currents for a normal TSC run.

Curve 2_C ; centre electrode current for guard ring "ammeter" shorted.

Curve 3_C ; centre electrode current for guard ring disconnected.

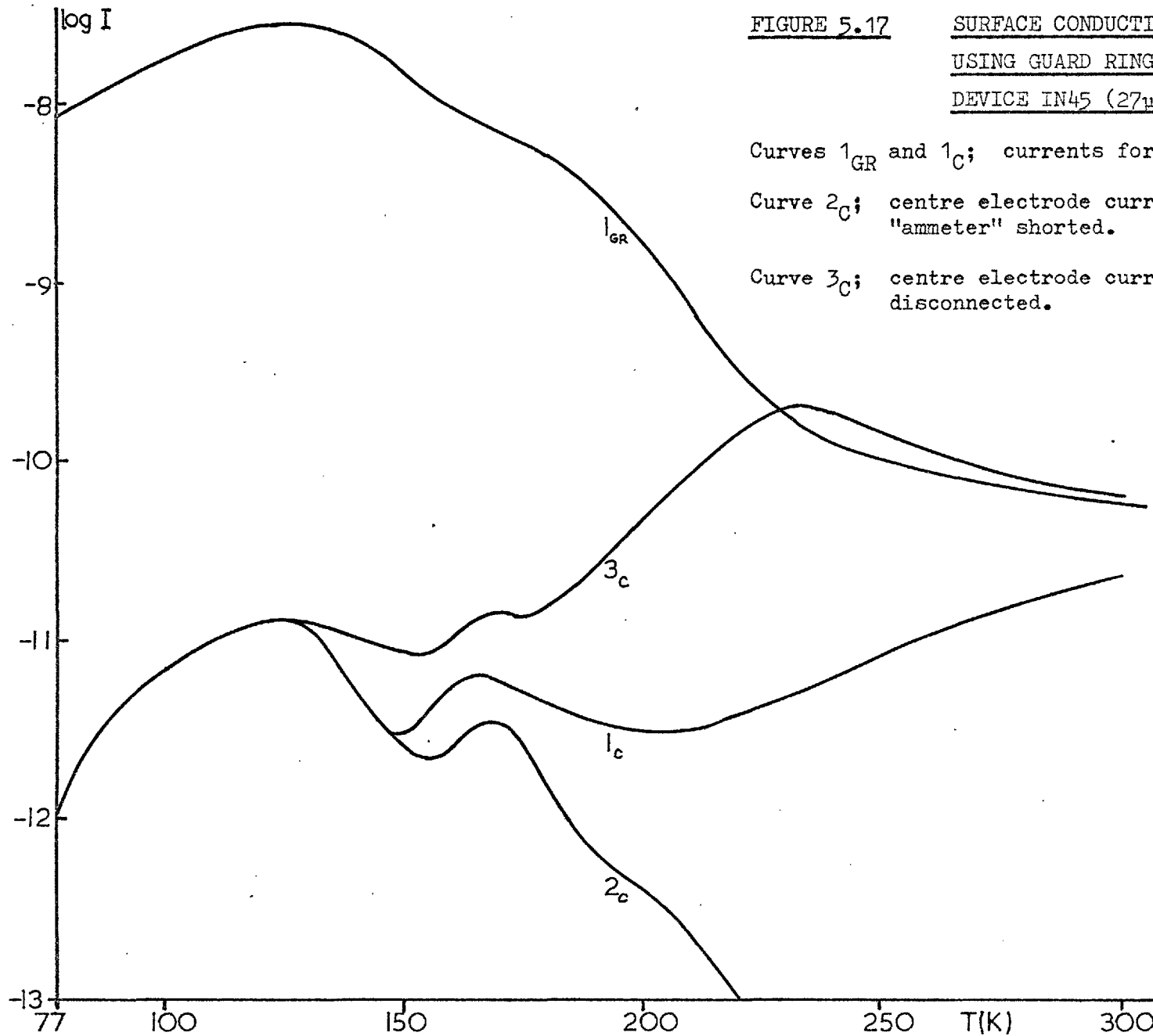


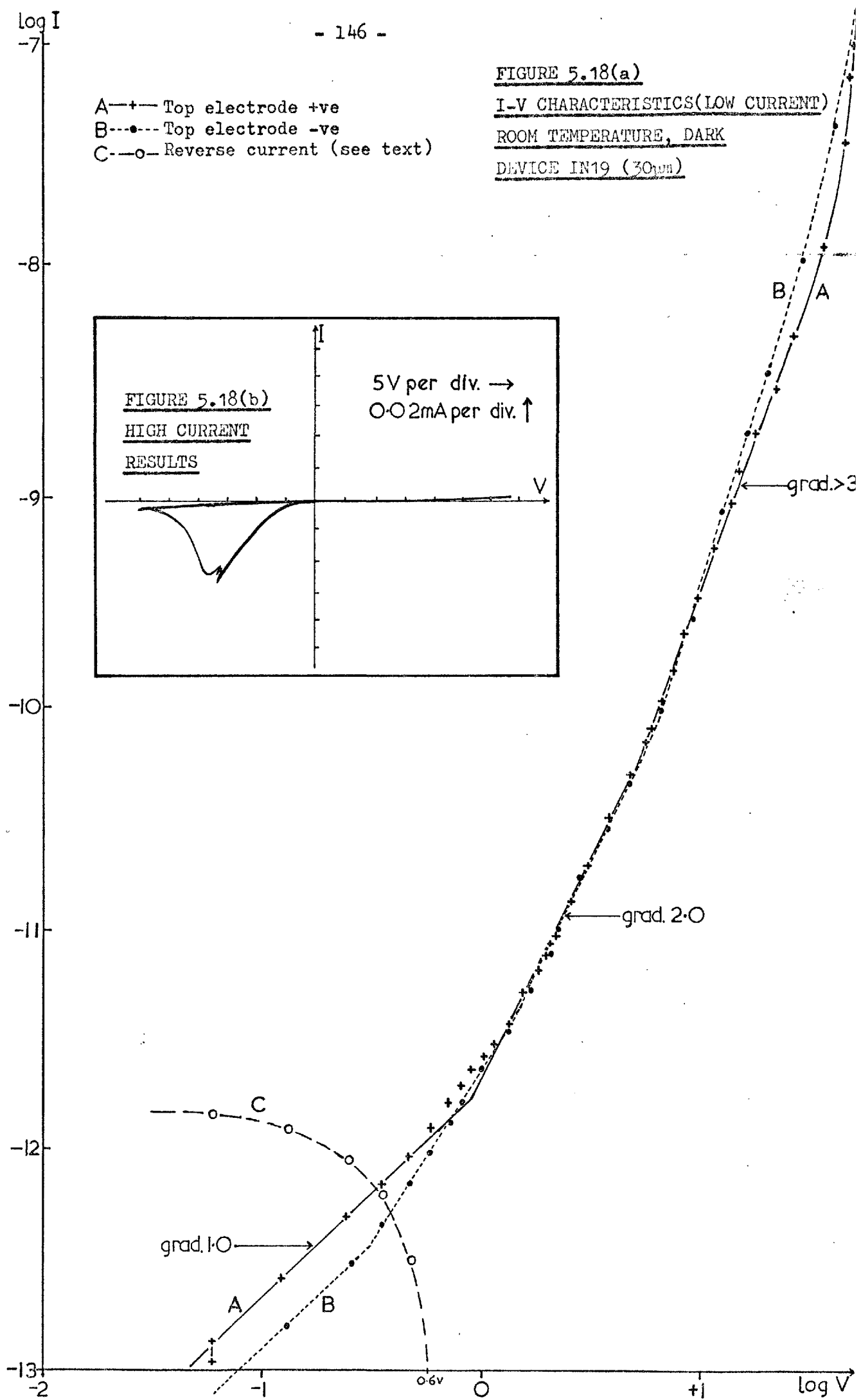
FIGURE 5.18(a)

I-V CHARACTERISTICS (LOW CURRENT)

ROOM TEMPERATURE, DARK

DEVICE IN19 (30 μ m)

- A—+— Top electrode +ve
B---•--- Top electrode -ve
C---o--- Reverse current (see text)



Considering curve A of figure 5.18(a), the initial portion below about 1 V appears to be approximately $V \propto I$, which could suggest ohmic conduction, followed by a square law region, possibly indicating space charge limited conduction. For higher voltages (> 10 V), the current increases very steeply with voltage. These results are difficult to interpret and the gradients involved are, in any case, unreliable because their range corresponds to less than two orders of magnitude of current. Curves A and B could also be approximately fitted to an exponential curve, through plotting in the form of $\log I$ vs V , $\log I$ vs $V^{\frac{1}{2}}$ or $\log(I/V)$ vs V or $V^{\frac{1}{2}}$ show straight line dependences over a limited range; again less than two orders of magnitude of current.

A room temperature linear plot of $I - V$ characteristics for high fields was obtained using a Tetrónix transistor tester for a device that had previously been tested using only one bias polarity. Results shown in figure 5.18(b) show that negative resistance occurs at about 10^{-4} A. This indicates a double injection phenomenon, and is discussed further in section 6.4.

With the exception of specific measurements on very thin crystals, collecting voltages used for TSC experiments produced fields of the order 10^3 V cm⁻¹ or less (assuming the voltage to be uniformly distributed across the crystal). This is too low to invoke Poole-Frenkel or other high field mechanisms, and little error will be involved on TSC plots by operating with collecting voltages of this magnitude.

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CHAPTER VI

DISCUSSION

6.1. Contacts to CdS

6.1.1. Assessment of indium electrodes

Let us discount for a moment the electrical properties of indium - CdS interfaces, and investigate the nature of the physical contact formed. The results indicate the need for several initial runs before good ohmic contacts are formed. Furthermore, it appears that contact formation occurs preferentially at the anode, although the effect of thermal cycling undoubtedly assists the forming process.

Inspection and selection of crystals after growth was carried out at room temperature and pressure, hence adsorption of oxygen onto the crystal is inevitable, and the formation of a sulphate layer or oxygen occupying sulphur vacancies is possible (as discussed in section 3.4.3). Indium contacts evaporated at room temperature onto this layer cannot initially penetrate the surface region, and such electrodes act as poor contacts. The influence of an electric field at relatively high temperatures (> 300 K) assists diffusion of In^{3+} ions into the crystal surface, initially penetrating the interfacial layer, and then diffusing into the CdS lattice.

The mechanisms governing indium electrode diffusion via cadmium vacancies into the CdS lattice were described in section 3.5.2. The model used for the present high temperature results (discussed in more detail in section 6.4) involves the formation of a high concentration of cadmium vacancies near the anode which explains the observed characteristics

of the devices.. Indium ions will "see" a comparatively high density of cadmium vacancies into which they can diffuse under the influence of an electric field.

Confirmation that indium ^{diffusion} occurs during the forming process was provided by the results of a microprobe analysis. After the crystal had been subjected to numerous TSC runs, a total concentration of 0.07% by weight of indium was found in the CdS surface after removal of the electrode.

The existence of an insulating interfacial layer on CdS platelets has been considered in section 3.4.3. Formation of a layer of CdSO_4 has been postulated by Weber (1969) but present guard ring results (sections 5.5 and 6.3) indicate intrinsic surface trapping on CdS, and are unlikely to be compatible with a surface coverage of CdSO_4 . Adsorption of oxygen from the air during storage or inspection under irradiation from the microscope illumination is probably the cause of the interfacial layer. In section 3.3, mechanisms for oxygen adsorption and desorption are discussed, and it is the space charge region resulting from oxygen surface adsorption, as proposed by Mark (1965) that acts as the insulating barrier. Okazaki et al (1970) have shown that the height of the barrier due to oxygen adsorption remains essentially unchanged after indium evaporation, resulting in a blocking contact. Under such circumstances, the forming process is simply the field assisted diffusion of ionised indium into the contact - near region (via cadmium vacancies) to compensate the existing space charge region, thus reducing the effect of oxygen.

Bombardment by argon ions prior to evaporation produced surprisingly little improvement to contact quality. Removal of oxygen and replacement by argon, or impurities in the argon gas may have been responsible, but in any case these results indicate that the contact forming process involves the

field assisted diffusion of ionised indium via vacant cadmium sites.

Contact quality was assessed as follows. Initial TSC runs exhibited noisy, non reproducible results, particularly for the characteristic low temperature peak (see section 6.2) as shown in figure 5.9. After several runs, a sudden change in the characteristic usually appeared giving a steady TSC spectrum, which was reproducible for all subsequent runs taken under similar conditions. It is, therefore, proposed that the step from poor contacts to ohmic contact formation had occurred when good, reproducible TSC curves were observed, especially the appearance of the peak at 90 K. It will be seen later that the observation of the high temperature peak is also consistent with this model for the contact region.

Penetration depths are difficult to assess. O'Tuama and Richter (1970) estimated less than $1\text{ }\mu\text{m}$ after the diffusion of indium at 800 K for 60 minutes using a measured diffusion coefficient of the order $10^{-14}\text{ cm}^2\text{ sec}^{-1}$. In the present work, temperatures not exceeding 400 K for several minutes were used. Assuming that indium diffuses substitutionally into cadmium sites, both thermal and field assisted diffusion at 400 K would be negligible. Diffusion via the increasing density of cadmium vacancies (see section 6.4) near the anode is, therefore, proposed as the dominant mechanism. Insufficient data relating to the diffusion coefficient of indium under such circumstances prevents quantitative calculation.

Returning finally to the electrical properties, estimates of the difference in work functions between indium and CdS were shown in section 3.5 to lead to ohmic contacts. The effect of indium diffusion then leads to an intermediate, highly n type layer, also conducive to good contacts.

6.1.2. Silver electrodes

It is a little difficult to understand why silver produces ohmic contacts as holes cannot carry current in CdS. The magnitude of barrier heights measured for silver electrodes on CdS varies considerably; Spitzer and Mead (1963) reported values of between 0.4 and 0.58 eV, whereas Goodman (1964) estimated 0.37 ± 0.03 eV, giving the work function of silver as 4.31 eV. Realising the better correlation between barrier height and metal electronegativity than with metal work functions, Spitzer and Mead (1963) suggest a possible role played by the partial covalent nature of the CdS - metal bond in determining the value of barrier height.

Observations of ohmic contacts using silver are not however unique. Using current pulse techniques, Sinhoven and Boyd (1958) report ohmic contacts between CdS and numerous metals including silver. Such contacts are only formed when the polarity of the pulse, produced by a 0.1 μ F capacitor charged to 300 V and applied to the silver electrode, is positive with respect to an ohmic contact on the opposite face of the crystal. In the present work, the same polarity dependence is necessary to form silver contacts. Sinhoven and Boyd postulate tunnelling from a highly conducting region just under the surface through a very thin surface exhaustion region to the metal electrode. Application of a current pulse of positive polarity substantially increases tunnelling and destroys the atomic structure in the vicinity of the silver electrode, giving rise to an ohmic contact. Penetration of the exhaustion region (possibly the same as the surface layers discussed in section 3.4.3) by silver diffusion, and the corresponding creation of an ohmic contact for electrons allows interpretation of the present results in an identical manner to that used for indium contacts.

The appearance of additional high temperature peaks (see figure 5.9

and table 5.1) using silver electrodes is, at present, not understood. Kroger et al (1954) have shown that silver in CdS can give rise to acceptor levels between 0.4 eV and 0.7 eV above the valence band, not too dissimilar, energetically, from singly charged cadmium vacancies. It may be possible that the presence of such centres near the contacts, together with cadmium vacancies, can give rise to a complex similar in form to that discussed in section 6.4., but having a slightly different trap depth. Field assisted diffusion of charged defects during cooling could then be responsible for the creation of additional centres, explaining the conditions for observation of the various peaks, as listed in table 5.1.

6.1.3. Summary of the contact forming process

(i) Indium slowly penetrates the insulating layer (possibly the oxygen depletion region) by means of field assisted diffusion above 300 K via cadmium vacancies at the anode.

(ii) Simultaneously, negatively charged cadmium vacancies migrate towards the anode.

(iii) Contact formation results when the indium has penetrated the interfacial region and enters the bulk as donor impurities.

(iv) Ohmic contacts can be formed with silver electrodes when the polarity of the bias applied to the electrode is positive with respect to the crystal, and penetration of silver destroys the blocking nature of an exhaustion layer near the surface.

(v) The appearance of additional peaks near to the usual high temperature peak could be due to the association of cadmium vacancies with silver impurities.

6.2. The Low Temperature Region

6.2.1. Bulk characteristics

A peak in the TSC having a maximum at about 90 K was observed in most CdS platelets tested, provided contacts to the crystal were ohmic and that the crystal thickness exceeded about 10 μm . It has been previously observed in TSC measurements on CdS single crystals grown by a variety of methods (see, for example, the references listed in chapter 2).

That the 90 K peak is due to bulk phenomena can be demonstrated by three independent types of measurement:

(i) The use of rod crystals The growth of rod shaped crystals simultaneously with platelets provided an independent means of investigating bulk trapping effects. In section 5.2 results obtained exhibit a prominent TSC peak at 90 K. Charges in bulk trapping induced by irradiation above 250 K were similar to those reported by Tscholl (1968) under similar conditions, as outlined in figure 5.2. These indicate that the bulk behaviour of CdS used in the present study is consistent with other bulk measurements on CdS attributed to the photochemical creation of traps during a period of irradiation during cooling (see section 2.4.6.).

(ii) The use of guard ring electrodes The TSC results obtained simultaneously using centre and guard ring electrodes (with the lower surface electrode common) on a thick (160 μm) platelet are explained in section 5.5.1. The results shown in figure 5.15, curves 1_c and 1_{GR} are qualitatively similar, and are typical of bulk results (e.g. figure 5.1.). To confirm that these were bulk characteristics, the bulk trapping distribution was changed by irradiating the crystal during cooling from 300 K to 77 K. In the subsequent run, curves 2_c and 2_{GR} were qualitatively similar to each other (indicating they were a measure of the same trapping

level) but were, however, different from curves l_c and l_{GR} because of the changes induced in the bulk trapping levels. The 90 K peak, common to all bulk results is characteristic of bulk trapping in CdS.

(iii) Appearance of the low temperature peak In section 6.1. the formation of contacts results in the sudden appearance of a TSC spectrum, in particular, the peak at 90 K. With ohmic contacts, bulk trapping mechanisms would be expected to be dominant. This supposition is supported by the fact that quenching of surface traps using oxygen had no effect on the 90 K peak.

As the peak maximum occurred very near to the minimum temperature of the system, analysis of the 90 K TSC peak was difficult. Indeed Cowell and Woods (1967) concluded that detailed analysis of their low temperature peak was impossible by both initial rise and curve fitting techniques. Evaluation of the temperature at which the maximum occurred was also difficult due to the width of the peak and the reduced sensitivity of the thermocouple at low temperatures.

6.2.2. Electric field effects

Even after the formation of ohmic contacts on very thin ($\sim 6 \mu m$) platelets, the 90 K peak was rarely observed. Two reasons may be put forward for this:

(i) A depletion layer extending from the surface through the entire platelet could prevent the filling of the shallow traps.

(ii) The magnitude of the TSC collecting bias could be sufficient to empty the traps at 77 K.

It is unlikely that a barrier and corresponding depletion region could

exist with well formed ohmic contacts, and removal of oxygen from the surface eliminated the possibility of a depletion region due to oxygen chemisorption (see section 3.3). If the collecting bias was applied after irradiating a thin crystal at 77 K, a rapid decrease in current was observed. The guard ring experiments discussed in section 5.5.7, figure 5.16, showed conclusively that the electric field strength (10^4 V cm^{-1}) was responsible for annihilation of the 90 K peak. The reduction in magnitude of the trap depth due to an electric field, $\mathcal{E}$, was calculated using the Poole-Frenkel factor:

$$\text{Trap lowering, } \Delta E = B \mathcal{E}^{\frac{1}{2}} \quad \dots\dots\dots(6.1a)$$

where

$$B = \left[\frac{e^3}{(\epsilon \epsilon_0 \pi)} \right]^{\frac{1}{2}} \quad \dots\dots\dots(6.1b)$$

ϵ_0 is the permittivity of free space and ϵ the dielectric constant.

For $\mathcal{E} = 10^4 \text{ V cm}^{-1}$ and $\epsilon = 10$

$$\Delta E \sim 0.025 \text{ eV}$$

In section 2.4 it has been shown that estimates of trap depth for the characteristic peak at 90 K range from about 0.05 eV to 0.2 eV. The approximate trap depth relating to a peak at 90 K taken from figure 2.5 is 0.05 eV for Tscholl's theory and about 0.21 eV for the basic TSC theory, indicating considerable discrepancy in the evaluation of trap depths, for such peaks. In both cases, an effective trap lowering of 0.025 eV would undoubtedly promote thermal emptying of the trap at 77 K with a 10^4 V cm^{-1} field applied.

Consider, with the aid of figure 2.5, a trap of depth 0.21 eV

(corresponding to the 90 K peak) being reduced by 0.025 eV in depth to 0.185 eV. As a first approximation, using $E \propto T^*$ (equation 2.14), the temperature at which the peak due to a trap at 0.185 eV occurs is given by

$$\frac{T^*}{0.185} = \frac{90}{0.21} \dots\dots\dots(6.2)$$

giving $T^* = 79 \text{ K}$

This is so near to the minimum temperature of the cryostat that thermal emptying at 77 K undoubtedly occurs. For the case of Tscholl's theory, which indicated a depth of 0.05 eV for a 90 K peak, reduction by 0.025 eV would result in total trap emptying at 77 K. For fields approaching 10^4 V cm^{-1} , Bube (1962) suggested that impact ionisation of shallow traps could become dominant.

6.2.3. Summary

It has been confirmed that the TSC peak attaining a maximum at 90 K is characteristic of CdS, and is attributed to bulk trapping. The present results are consistent with those of Tscholl (1968) based on a photochemical model for trap creation involving donor - acceptor pair agglomeration, as outlined in section 2.4.6. A cryostat capable of operating down to liquid helium temperatures would be necessary for a quantitative evaluation of data for the 90 K peak. By simultaneously comparing the field between the lower and centre electrodes (directly across the platelet) and the lower and ring electrodes (separated by several mm of CdS) of a guard ring device, trap emptying due to an electric field was confirmed. For fields above 10^4 V cm^{-1} the Poole - Frenkel trap lowering factor could account for decay of the characteristic 90 K peak at 77 K.

6.3. Surface Effects

6.3.1. The role of the surface in TSC measurements

Changes brought about on the surface of CdS crystals due to the effect of oxygen have been discussed in section 3.3. A quantitative investigation of surface phenomena in CdS platelets was not possible using the results obtained in this work, but a qualitative discussion of the role of the surface structure in determining the electrical surface conduction of CdS is possible.

The results are divided into two sections; those relating to the effect of oxygen on TSC measurements and the interpretation of guard ring electrode results to give quantitative information about intrinsic surface trapping phenomena.

6.3.2. The effect of adsorbed oxygen

In the early stages of TSC measurements, the magnitude of the mid temperature TSC region was seen to steadily increase with each run, as shown in figure 5.3. Reversal of the effect following exposure to oxygen led to a more detailed investigation using three terminal devices as described in section 5.4.

The contribution made by carriers released by surface traps is seen in figure 5.11, curves B_{21} and B_{23} . Baking the device of 400 K in a vacuum promoted oxygen desorption, enabling intrinsic surface traps to participate in TSC. This observation is consistent with the results outlined in section 3.3. The enhanced magnitude of the TSC for the mid temperature

region was quenched by oxygen adsorption, as shown in curves A_{23} and A_{21} of figure 5.11.

The gradual increase in magnitude of the TSC curves in figure 5.3 can be explained by thermally assisted desorption. As more oxygen is desorbed during the higher temperature interval of TSC heating for each successive run, the current observed during the following run will include a larger contribution from uncompensated surface traps able to capture photogenerated carriers. Indeed Schubert and Boer (1971) have shown by mass spectrometer analysis that a thermally stimulated oxygen desorption peak occurs at 405 K. This is in keeping with the present work in which the effect of a gradual release of oxygen is seen during repeated runs to less than 400 K, but thermal cycling to temperatures in excess of 400 K results in a significant increase in magnitude of the mid temperature region. For most crystals, TSC results for that region appeared to reach a saturation after numerous runs to above 400 K, indicating that the maximum surface contribution corresponded to maximum oxygen desorption.

Photoassisted desorption was difficult to investigate. Irradiation with intense illumination at high (> 300 K) temperatures may promote photochemical changes (see section 2.4) as well as surface desorption rendered all experiments of this nature inconclusive.

Reproducible changes due to adsorption and desorption of oxygen are seen here for the first time on a TSC curve, indicating enhanced surface conduction and enabling, in the following section, estimates to be made of the energy of surface trapping levels. A guard ring electrode was necessary to obtain surface data and to enable quantitative calculations from thermally stimulated surface conductivity in the absence of adsorbed oxygen.

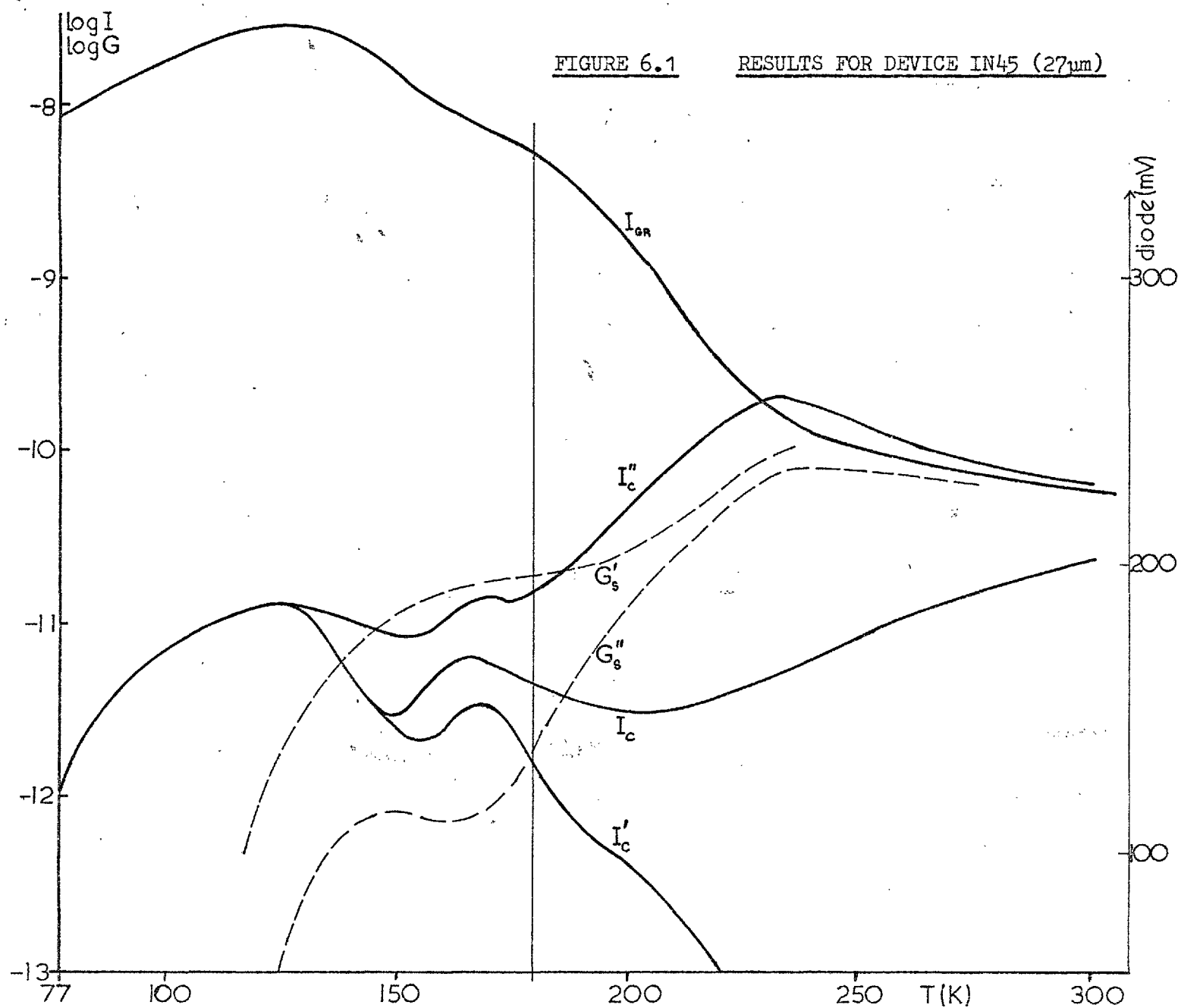
6.3.3. Surface conductivity

The qualitative ideas relating to the termination of an ionic crystal lattice are used to explain surface phenomena in CdS, and have been outlined in section 3.2.1.

Guard ring electrode experiments have enabled the separation of surface contribution from bulk conduction data. In section 5.7, results are shown for TSC data from both guard ring and centre electrodes under normal conditions. The TSC results for the centre electrode changed considerably when the guard ring electrode was shorted directly to the collecting voltage supply. Confirmation of a change is also obtained if the experiment is repeated leaving the guard ring disconnected. The results are shown again in figure 6.1.

A current contribution due to the release of surface trapped carriers will result when the potentials of the centre and guard ring electrodes are dissimilar. Figure 6.2(a) shows the circuit of the guard ring device measuring system.

When the ammeters are identical, and of very low impedance compared with the device, the potentials at C and GR are equal. However, if the guard ring electrode is shorted directly to the positive rail, as shown in figure 6.2(b), the non zero impedance of the centre electrode ammeter will promote a small potential across the surface. The voltage across the 'ammeter' is known (from the scale shown in figure 6.1) and the surface current is simply the difference between curve I_c and curve I_c' on figure 6.1. From section 5.6 it is shown that for potentials below about 1 volt, the $I - V$ characteristics are probably ohmic, so an assessment of surface conductance may be made. For example, at 180 K (see figure 6.1)



Curves I_{GR} and I_C ; normal guard ring and centre electrode characteristics.

Curves I'_C and I''_C show TSC curves for centre electrode with guard ring shorted to positive and open circuited respectively.

Curves G'_S and G''_S show estimated dependences on surface TSC (conductances).

Collecting bias; 7V

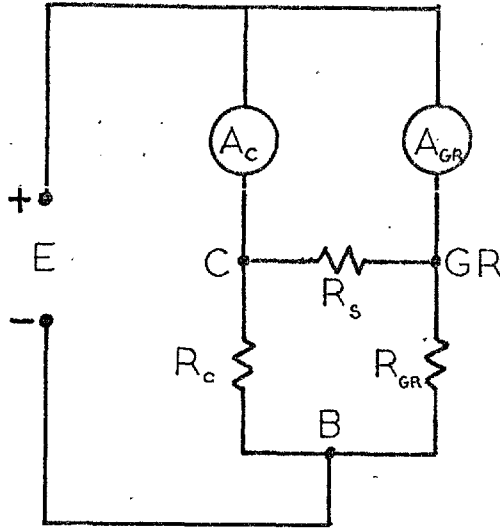
FIGURE 6.2

The electrical path between electrodes is graphically represented by a resistor:

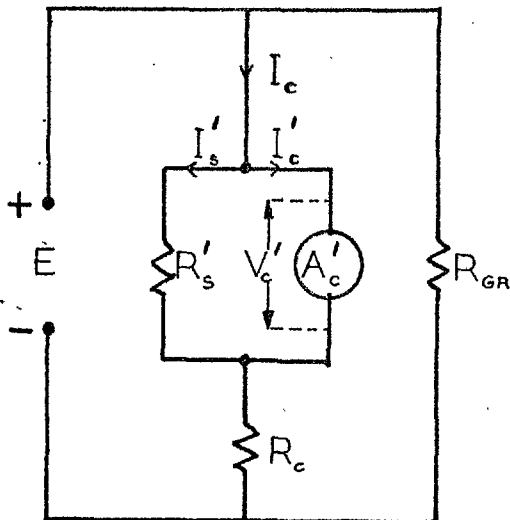
between GR and centre electrode: R_S

between GR and bottom electrode: R_{GR}

between centre and bottom electrode: R_C

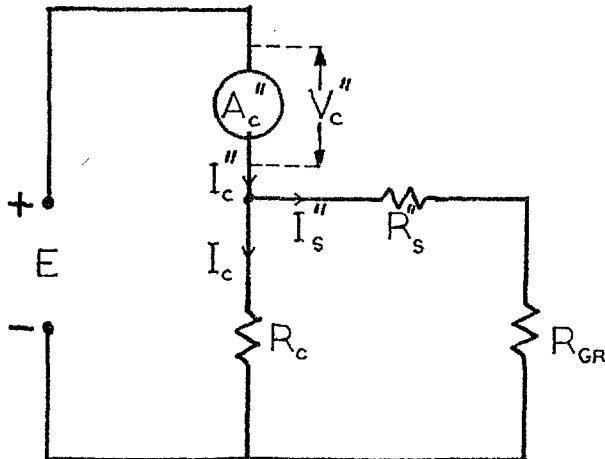


(a) Basic circuit for guard ring



(b) Guard ring shorted directly to positive

$$I'_S = I_C - I'_C$$



(c) Guard ring open circuited

$$I''_S = I''_C - I_C$$

$$I_c' = 1.6 \times 10^{-12} \text{ A}$$

$$I_c = 5.2 \times 10^{-12} \text{ A}$$

$$\therefore I_s' = 3.6 \times 10^{-12} \text{ A}$$

$$\text{and } V_c' = V_s = 0.132 \text{ V}$$

$$\text{so } G_s' = 2.7 \times 10^{-11} \text{ mho}$$

The method may be extended to give quantitative data from the open circuited guard ring results, the circuit of which is shown in figure 6.2(c)

$$I_s'' = I_c'' - I_c \quad \dots\dots\dots(6.3)$$

and assuming $E \gg V_c''$,

$$E = I_s''(R_s'' + R_{GR}) \quad \dots\dots\dots(6.4)$$

$$\text{Using } E = I_{GR} R_{GR} \quad \dots\dots\dots(6.5)$$

the value of R_{GR} may be calculated using data from curve I_{GR} . Then

$$E = (I_c'' - I_c)(R_s'' + \frac{E}{I_{GR}}) \quad \dots\dots\dots(6.6)$$

$$R_s'' = E \left[\frac{1}{(I_c'' - I_c)} - \frac{1}{I_{GR}} \right] \quad \dots\dots\dots(6.7)$$

$$G_s'' = \frac{1}{E} \left[\frac{1}{(I_c'' - I_c)} - \frac{1}{I_{GR}} \right]^{-1} \quad \dots\dots\dots(6.8)$$

Taking again, as an example, the values at 180 K

$$I_c'' = 1.9 \times 10^{-11} \text{ A}$$

$$I_c = 5.2 \times 10^{-12} \text{ A}$$

$$I_{GR} = 5.4 \times 10^{-9} \text{ A}$$

Then
$$G_s'' = \frac{1}{7} \left[\frac{10^{11}}{1.4} - \frac{10^9}{5.4} \right]^{-1} \text{ mho}$$

$$G_s'' = 2 \times 10^{-12} \text{ mho}$$

Curves G_s' and G_s'' show variation of the surface contribution of TSC with temperature. It must be stressed however, that the magnitudes of conductance calculated include large errors resulting from subtraction of two close values taken from logarithmic plots.

General trends indicate a substantial rise in surface contribution above 120 K, in keeping with the measured surface conductances seen from development of the mid temperature region (figures 5.3 and 5.11). Discrepancies between 130 K and 180 K are probably due to the errors outlined above. By leaving the guard ring electrode disconnected, the resulting TSC is effectively that of a simple two electrode device. The floating potential of the guard ring will, however, introduce larger errors than in the previous experiment in which the guard ring was connected directly to the collecting bias.

Using the simple dependence between trap depth and TSC peak temperature as shown in figure 2.5(i), and realising that a small error is involved when considering a continuum of traps rather than discrete levels, an estimate of trap depths from surface contributions gave between 0.25 eV and 0.55 eV.

These values correspond to the surface trapping depths calculated for CdS by Levine and Mark (1966) of about 0.2 eV to 0.4 eV based on the termination of an ionic lattice, as outlined in section 3.2.1. The present work therefore appears to support the model of ionic surfaces on CdS hitherto only considered theoretically.

6.4. The High Temperature Region

6.4.1. Assessment of possible mechanisms

The properties of the TSC peak reported by Simmons (1971) due to dielectric relaxation are similar to those of the high temperature peaks observed in the present work, and initially Simmons work appeared to offer a complete explanation for the anomalous high temperature results. Elimination of the peak by cooling with the same bias applied as that used for subsequent TSC heating was predicted by Simmons (section 2.3.3), and was observed in the present results (section 5.3.6). The position of the peak on the TSC spectrum also occurred in the predicted position. Two factors, however, are difficult to explain by this mechanism: (i) the magnitude of the TSC peak was several orders higher than that of Simmons (ii) for the dielectric relaxation model to apply, blocking contacts are essential. Results of the present work are in favour of ohmic contacts (section 3.5) and the dielectric relaxation model must be tentatively excluded.

The formation of an ohmic contact involves electron injection into the semi-insulator, and implies a corresponding blocking contact for holes. An extension to Simmons theory is thus possible in this case, namely the main contribution to the high temperature peak being a hole current. The condition of blocking contacts is then satisfied, and the flow of holes across the crystal during dielectric relaxation could be responsible for the high temperature peak. It is, however, difficult to visualise how the flow of holes could lead to a current peak in a system which is n type and highly compensated. A hole current would undoubtedly result in considerable recombination of the released holes with the electrons in the hole traps or in the conduction band. That holes could be responsible for current peaks in a material that has never been known to be p type without

deliberate doping is therefore improbable.

In the next section, it will be seen that an electric field can cause the anode to become blocking to electrons. If the blocking nature remains after removal of the bias polarity and after several TSC runs, the conditions necessary for Simmons relaxation theory to apply, namely a blocking cathode, would be fulfilled. The concept is unlikely for two reasons; firstly, a deterioration of the high temperature peak (as the contact reverts to an ohmic nature) was not observed, and secondly, the magnitude of the peak was greater than that predicted for Simmons model, as outlined above.

Driver and Wright (1963) used a diode fabricated from a CdS platelet with one ohmic (indium) contact and one blocking (gold) contact. With a forward bias of 30 V applied during cooling to fill the traps, and a reverse bias of 30 V during TSC heating, a peak at 180 K of magnitude 2×10^{-12} A was seen. The peak could still be observed after cooling without bias, through its magnitude diminished to 1×10^{-12} A. This was attributed to trap emptying from the depletion layer brought about by the blocking contact, and bears remarkable similarity to Simmons new theory of dielectric relaxation (see section 2.3.3). A rapid increase in current above 250 K was attributed to the reverse current of the diode. Had they continued heating, a high temperature peak similar to those reported herein should have been produced. Under similar circumstances during the present study, several samples exhibited a small increase in TSC at about 180 K, but was too wide for a TSC peak. Non reproducibility from sample to sample and the very small magnitude (10^{-12} to 10^{-13} A) prevented further investigation.

To explain the high temperature results, a new concept appears to be necessary. An obvious choice would be the transport of defects through the lattice, most probably in the form of vacancies. This process could

lead to two possible effects:

- (i) the defects could carry sufficient charge to produce the high temperature peak, which would then be due to ionic migration.
- (ii) defect association could produce centres capable of trapping the charge responsible for high temperature peaks.

The magnitude of the high temperature peak seems to exclude the first possibility, and in the following sections, the evidence supporting the idea of trap creation due to vacancy associations will be discussed.

6.4.2. The role of vacancies in CdS

In a series of publications by Gershun and Timan (1966 - 1968), nonlinearities and hysteresis effects in I - V characteristics for CdS platelets with indium contacts have been explained by a redistribution of charge promoted by the diffusion of vacancies through the lattice. Their model is based on results from experiments which measured I - V curves, the time dependences of current with electric field strength, luminescence at the anode and the appearance of a back e.m.f. in the system.

They postulate the occurrence of an ionic process at the anode, involving the migration of charged cadmium vacancies at room temperature, a mechanism already shown to be possible by Woodbury (1964) from his study of diffusion of cadmium in CdS. The concept of vacancy migration is not new. An electrolytic process producing excess cadmium and sulphur under opposite electrodes was postulated by Woods (1957). Above 470 K, sulphur could reach the surface and evaporate, but below 470 K, cadmium migrates towards the cathode, and excess sulphur remains at the anode, promoting a noisy, blocking contact.

Under the influence of an applied field, the accumulation of cadmium vacancies near the anode results in a space charge layer in the anode region tending to make it blocking to electrons, but capable of injecting holes. The activation energy of the cadmium vacancy diffusion process was calculated to be between 0.6 and 0.8 eV, and the width of the anodic region to be 0.1 μm . Much of Gershun and Timan's work was concerned with voltage dependent effects for indium electrodes placed on opposite faces of the platelet. A critical voltage, V_0 (~ 10 V) was observed such that for voltages less than V_0 , the I - V characteristics were apparently ohmic and the current magnitude for a constant voltage decayed with time. For voltages exceeding V_0 , non linearities in the I - V curve appeared. An initial decrease in current (for a period of some minutes) was followed by an increase in current magnitude to a saturation level. This effect was attributed to the onset of double injection, the initial decay period allowing sufficient time for vacancies to diffuse to the anode. Application of much larger fields promoted green luminescence in the vicinity of the anode after a short period of time, provided the current had reached $\sim 10^{-4}$ A. In section 5.6 it is seen that the appearance of a negative resistance regime at one electrode (in I - V measurements taken between 10^{-5} and 10^{-4} A) confirmed that double injection occurred in devices used in the present study, at about the same current as that reported by Gershun and Timan.

The application of a field across the system polarised the platelet, and redistributed a quantity of charge in the anode region. The magnitude of the charge was essentially independent of applied voltage, and increasing the bias increased the rate of charge accumulation. Gershun and Timan calculated the amount of charge to be 2×10^{-9} coulombs. The polarisation brought with it a reverse e.m.f. in the system that was observed as hysteresis in I - V plots, and was dependent on the applied voltage and

time. Identical results were obtained in the present work, as described in section 5.6 where, after removal of the bias, a small current ($\sim 10^{-11}$ A) flowed for several minutes. For voltages greater than V_0 , vacancy migration to the anode and the corresponding formation of a space charge region promoted larger electric fields in the vicinity of the anode. The vacancy density near the anode is calculated to be at least 10^{17} cm^{-3} .

In conclusion, the work reported by Gershun and Timan has been confirmed in detail during the present study, and their model of cadmium vacancy migration appears to be responsible for the high temperature results.

A satisfactory explanation of the association of vacancies to form two bulk traps in CdS was given by Cowell and Woods (1969). A fast retrapping centre located 0.62 eV below the conduction band is created at high temperatures (baking at 400 K in darkness) by the association of two cadmium vacancies. Photochemical reactions above 270 K are responsible for dissociating the centre into two single negatively charged cadmium vacancies which individually trap a second electron, possibly with the aid of an additional sulphur vacancy. The 0.84 eV trap dissociates when the electron is released, and because of its photochemical nature is of little relevance to the high temperature peak discussions. It is the 0.62 eV bulk trap, giving rise to TSC peaks within the range 320 K to 350 K (depending on initial filling characteristics etc.) that is the basis of the postulated model for the high temperature TSC peaks.

In a paper by Kroger et al (1954) the energetic state of vacancies in CdS was considered, and the trap due to an electron associated with a single cadmium vacancy was located about two thirds of the way down the energy gap from the conduction band. Kroger concluded the position of the trap due to a second electron captured by a cadmium vacancy is just above the bottom

of the conduction band. The model proposed by Cowell and Woods (1969) for the 0.84 eV trap must, therefore, depend on the creation of a more complex centre involving two negatively charged cadmium vacancies which effectively trap one electron rather than a cadmium vacancy localising two electrons. Indeed in an earlier paper, Woods and Nicholas (1964) postulated that the association of both sulphur and cadmium vacancies gave rise to the 0.84 eV trap. The creation of the 0.62 eV trap is also difficult to explain. Association of two similar defects must involve the stable formation of a centre effectively bound by at least one trapped electron, and it is reasonable to assume a splitting of the electron energies to differentiate the pair centre from two isolated defects in close proximity. Tscholl (1968), in his development of the donor-acceptor pair concept for photochemical trap creation, calculates trap energies resulting from an isolated trap modified by a charged defect at a nearby lattice site. His hypothesis follows work concerning the association of oppositely charged point defects by Van Gool and Diemer (1962) and bears similarity to the dipolar association of pair defects that create energy levels within the band gap, as suggested by Apple and Williams (1959). Tscholl's hypothesis involves for the first time a distance dependence for trap depth. A positively charged defect close to the trap encourages the trapped electron to remain in the trap, thus effectively increasing the trap depth. The close proximity of a negatively charged defect however repels the trapped electron, tending to reduce the trap depth. Tscholl (1968) has discussed the model whereby centres are produced by intrinsic vacancies and impurity atoms. For this, he concludes that creation of a pair complex involves a small shift in energetic position of the two isolated defect energy levels, though both retain their effective individual charges after agglomeration.

To produce a quantitative picture of the trapping levels due to complex defects is beyond the scope of the present work. However, a qualitative

picture can be presented. The model to explain the high temperature peaks is postulated to be due to an energy level created as a result of the association of two charged cadmium vacancies forming a complex centre.

6.4.3. The proposed model

It may be helpful, before embarking on the development of a new model, to list the essential features of the high temperature results from sections 5.3 and 5.4 that must be explained by such a model.

- (i) An electrode forming process occurs.
- (ii) The anode characteristics change.
- (iii) A high temperature peak is attributable to a specific electrode.
- (iv) The peak is observed after the sample is allowed to cool with no bias applied.
- (v) The peak is quenched when the bias used during heating is the same as that used during cooling.
- (vi) The peak magnitude is enhanced by cooling with a reverse bias.
- (vii) A 'run away' current is often observed when plotting a high temperature peak using a large collecting bias.
- (viii) The peak has a rapid rise and decay.
- (ix) The peak generally occurs only for a collecting bias exceeding 9V.
- (x) The peak is independent of the nature of the contact (once formed).
- (xi) The peak is independent of the gaseous ambient, especially of oxygen.

We shall assume the combination of two singly charged cadmium vacancies and assume that in this situation the electron energy level due to the single vacancy splits into an upper and a lower level. There is no specific reason for this contention, but it will be seen later that an adequate explanation

of the high temperature results is provided by such a model.

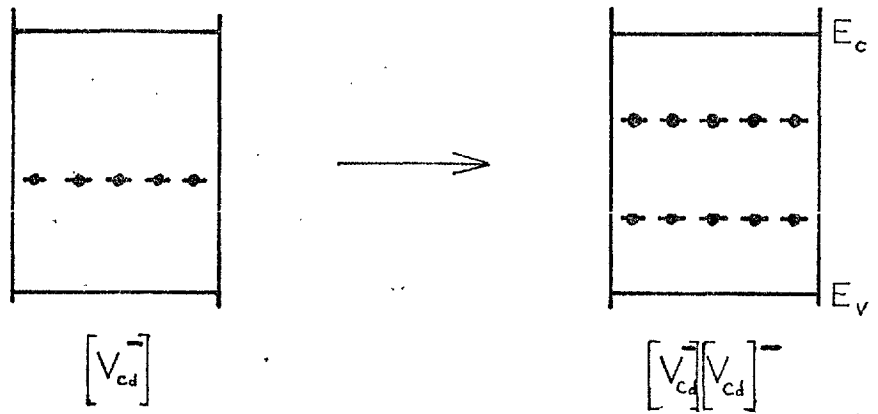
Migration of the cadmium vacancies towards the anode increases their density in the anode region and increases their probability of associating to form trapping centres. Using the symbol $[V_{Cd}]$ for the cadmium vacancy, the singly charged vacancy will be represented as $[V_{Cd}^-]$, i.e. an electron within the centre. To avoid confusion, the centre resulting from the association of two cadmium vacancies is represented by $[V_{Cd}^-][V_{Cd}]^-$ indicating that one electron is effectively less bound than the other, as shown in figure 6.3(a).

To explain trap creation and annihilation under the influence of a bias, several possibilities may be considered:

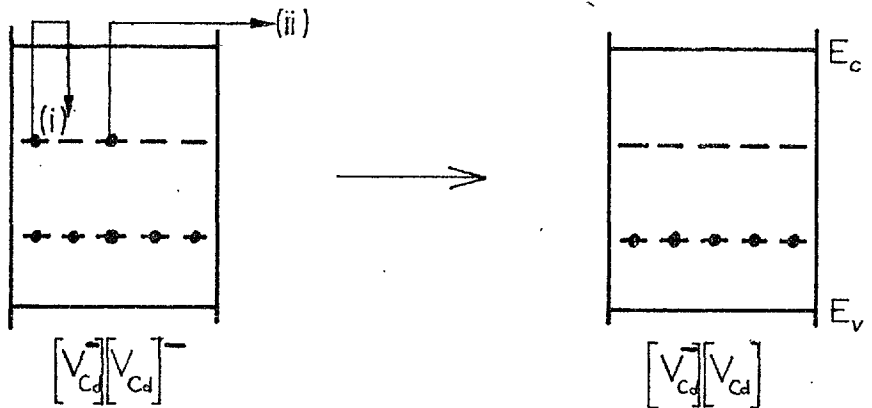
- (i) In the vicinity of the anode, the centre $[V_{Cd}^-][V_{Cd}]$ will still exist after the trapped electron is released, as shown in figure 6.3(b).
- (ii) The centre will dissociate after its trapped carrier is released into, possibly, its two constituent vacancies, as shown in figure 6.3(c).
- (iii) Hole injection from the anode will maintain the trap in an empty state during cooling and subsequent warming with unchanged bias.
- (iv) The centre may be an agglomeration of a larger number of defects (e.g. four cadmium vacancies) but such a postulate does not clarify the model further.

Gershun and Timan (1968b) reported that the vacancy diffusion process was extremely slow (the order of minutes). This observation implies that a rapid association of defects into traps followed by rapid diffusion and migration back into the bulk after dissociation from each TSC run is less likely to occur than a slow continual build up of traps near the anode, the state of occupancy of which is controlled by the applied bias.

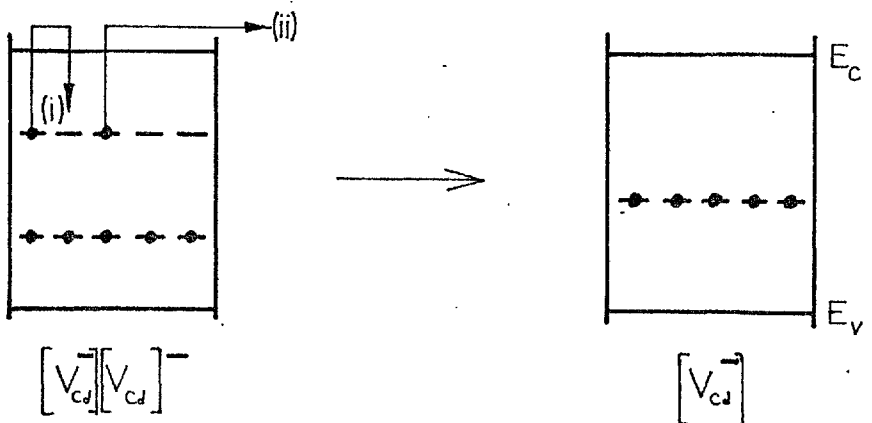
FIGURE 6.3



(a) Formation of a divacancy complex



(b) Emptying of the divacancy complex (after initial retrapping)



(c) Dissociation of the divacancy complex (after initial retrapping)

Process: (i) Retrapping
(ii) Final release of electron

Further support for the latter is offered by Swalin (1962) who reports that divacancies rather than single vacancies are more probable at lower temperatures in II - VI compounds.

If, after TSC heating, the collecting bias is not disconnected, the specimen will be maintained in a polarised state, and trap filling will not occur. Removal of the bias during cooling from about 350 K will allow conduction band electrons to be trapped in the fast retrapping centres, and, indeed, reversal of the bias would inject electrons into the traps. The important difference between the present model for platelets and the more conventional bulk trapping theory is the electric field strength and its possible effect on carrier transit time, and hence gain. By invoking a thin sub electrode layer ($\sim 10^{-5}$ cm thick) in a system having an electric field of 10^3 V cm $^{-1}$ (possibly larger across the sub electrode region), different trapping kinetics are likely to prevail.

Using a tentative model such as the one proposed above inevitably involves a certain degree of uncertainty, particularly where vacancy associations are concerned. The model does not lead to an obvious solution to the observation of a 'run away' current (section 5.3) when the bias voltage is excessive. Under non equilibrium conditions with high fields, an electronic breakdown across the entire crystal could lead to a high run away current (often $> 10^{-5}$ A). Several of the thinner crystals exhibited very large high temperature peaks (section 5.3.9) consisting of what appeared to be a run away current that eventually slowed down and finally decreased in magnitude. This observation appears to support the theory that a high field alters trapping kinetics and the resultant TSC curves in a way that cannot easily be analysed. Again, in contradiction to these results, it was shown in section 2.3.1. that fast retrapping kinetics should indicate a lower, not a higher effective activation

energy from the initial rise of the TSC peak.

Whilst it is clear that in conditions of equilibrium a bias of 10 V across a platelet at room temperature will promote only a very small current (see figure 5.18), the non equilibrium conditions produced by a TSC run, with a corresponding release of trapped charge, will significantly alter the electrical conduction across the platelet. In conventional TSC experiments, the bias applied during heating simply acts as a collecting potential for carriers that reach the electrode. In the present system, the applied bias produces a field of the order 10^3 V cm^{-1} . It is difficult to assess the effect that the release of excess carriers from within the semi-insulator will have on the resulting TSC. It is possible that this charge will produce a similar effect on the resultant current to that caused by increasing the applied voltage by a small amount. Operating in the range where current varies steeply with voltage, it is suggested that excess charge will produce a disproportionate increase in current, as seen in both the initial rapid increase of the high temperature peaks and the run away current. As the traps empty, excess charge in the crystal is reduced, and correspondingly a rapid decrease in current is seen after the TSC has reached a maximum.

That the rapidly increasing portion of the I - V curve is attributed to total trap filling has been questioned by Marlor and Woods (1963) who postulated that trap emptying could occur at higher fields. In a later paper, Marlor and Woods (1965) showed that by passing very large currents through platelets (10^{-3} to 10^{-2} A), the 0.41 eV and 0.61 eV traps could be filled. This was demonstrated by subjecting the device to a TSC run with a very low collecting bias (~ 0.1 V), but the results were complicated by a contact voltage of the same order of magnitude as the bias. In spite of considerable analysis of the contact voltage, Marlor

and Woods were not able to demonstrate, unequivocally that space charge limited currents would fill traps in CdS platelets. From the present work, it is considered unlikely that the 9 V collecting bias would be responsible for the filling of deep traps. This was indicated by the very low TSC currents ($< 10^{-12}$ A) that flowed in the low and mid temperature regions after cooling without bias in the dark, refraining from irradiation at 77 K, and heating with a 9 V bias.

A necessary condition for the migration of vacancies and formation of the layer beneath the anode was a bias in excess of a critical voltage, V_o , found by Gershun and Timan (1968a) to be between 8 and 12V. In the present study, peaks generally occurred for collecting biases in excess of 9 V. In all but the exceedingly thin platelets, a bias of about 4 V or below never appeared to produce high temperature peaks.

The present model depends on the movement of intrinsic defects after the formation of good contacts and should be independent of electrode material as observed. The exact way in which silver, with a work function in excess of that for CdS, forms an ohmic contact remains difficult to explain. Contact formation by current pulse techniques has been reported by Sinhoven and Boyd (1958) who showed that many large work function metals (including silver) made ohmic contacts to CdS, though the exact nature of such contacts was not discussed.

By introducing a model invoking the formation of traps in a layer below the electrode, the changes induced by surface contamination, for example, oxygen adsorption, should be minimal. Indeed, the high temperature results generally appeared to be independent to an oxygen ambient.

The eleven points listed at the beginning of this section can be

explained by the use of the proposed model. The nature of contacts has been discussed extensively in section 3.5 and 6.1, and the migration of charged cadmium vacancies can account for changes in anode characteristics and the appearance of bias dependent, high temperature peaks. Tentative explanations have been put forward to account for the rapid increase in current (e.g. figure 5.5) but it is clear that a more detailed study is needed to correlate the effects of higher fields on TSC measurements, particularly for the evaluation of trap densities where a non-linear field across the crystal could considerably affect the magnitude of the gain factor.

6.4.4. Summary

It is surprising to note that trap formation giving rise to a bias dependent peak of considerable magnitude has not been seen before in other TSC experiments. The exact nature of the process controlling trap creation and emptying kinetics is still uncertain. The model provides a basis on which the formation of traps, particularly those due to electrode effects, may be developed, and is shown to be consistent with the present study. Further work is necessary to be conclusive, especially relating to the format of the centre after the release of its trapped electron. To avoid unnecessary complications, the effect of other traps or defects within the CdS lattice has been neglected. The role played by such defects could be important at higher electric fields.

6.5. Conclusions and Future Work

A number of factors that influence electrical conduction in thin CdS platelets have been investigated using the results of TSC measurements.

The results are mainly concerned with the nature of two well known TSC peaks in CdS, one having a maximum at 90 K attributed to bulk trapping, and one occurring above 300 K created from the association of cadmium vacancies. The appearance of the 90 K peak was used to indicate the onset of contact formation.

A model involving the slow, field assisted migration of cadmium vacancies towards the anode is invoked, and is consistent with both the mechanism of contact forming and the creation of traps near to the anode. In order to produce good contacts onto the platelets (as grown), indium ions diffuse through the surface contamination then into the crystal via the cadmium vacancies near to, and at, the surface. Ohmic contacts were also produced by silver electrodes after the bias had been applied a number of times. TSC peaks that are dependent on the direction and magnitude of the bias applied during the TSC cycle were observed in the range 300 K to 400 K and are thought to arise from the creation of traps by the association of cadmium vacancies in the region near to the anode. Polarisation of the specimen during cooling determines whether the TSC peak is enhanced or disappears during a subsequent run.

The contribution to electrical conductivity made by the crystal surface appears to be highly dependent on the chemisorption of oxygen. The surface resistivity was increased if oxygen was present, however after several TSC runs, oxygen was apparently desorbed and the effect of intrinsic surface traps increased the TSC between 120 K and about 200 K. The corresponding values of trap depth were consistent with those calculated using a model based on the electrostatic surface properties of CdS (in this case, assuming ionic bonding). Further work with a cryostat capable of attaining higher temperatures and a harder vacuum would provide facilities for controlled oxygen desorption experiments from

which a detailed TSC analysis might obtain more quantitative surface trapping data. At the other end of the temperature range, a cryostat designed for use down to helium temperatures could be used to study in more detail the characteristic peak at 90 K.

A theoretical study could be undertaken to assess the effect of collecting voltage on TSC results and to correlate trap depths found on the one hand by I - V measurements and, on the other by TSC. Marlor and Woods (1965) have approached this subject filling the traps by passing high currents, and Simmons (1971) is at present involved in producing a generalised model linking I - V and TSC theory.

Additional information could be obtained by deliberately introducing impurities into the surface before contact evaporation. Controlled experiments to vary the stoichiometry of the platelet could test the present theory, study changes at the anode and investigate the appearance of several closely spaced peaks associated with silver electrodes. The nature of trapping centres may be confirmed by luminescence experiments on non stoichiometric surfaces.

The model has been used to explain the results and is consistent within the limitations of the experiment. The project has provided conclusive evidence for changes in electrical properties, which are important when considering device fabrication, consistency and reliability.

References for Chapter 6

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