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TRAPPING AND RECOMBINATION DYNAMICS IN
THIN-FILM CADMIUM SULPHIDE

by

Horst Arndt

B.A.Sc. University of British Columbia 1963
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A thesis submitted to the Faculty of
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Thin-Film Cadmium Sulphide"

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ABSTRACT

This thesis examines cadmium sulphide thin-films with the objective of determining the location of trapping and recombination centres native to these vacuum evaporated films and evaluating the effect of the defects on the photoresponse characteristics. This information is then used to explain some of the stability and aging characteristics observed for cadmium sulphide thin-film transistors.

By using the variation of conductivity with temperature, defect levels are found to exist at 0.029, 0.06, 0.14, 0.24 and 0.36 eV below the conduction band. These are in close agreement with defects native to single crystal cadmium sulphide. The speed of the photo-decay increases with increasing light intensity. This implies the existence of a deep level, about 1 eV above the valence band, which contributes prominently to the recombination mechanism in cadmium sulphide. The dynamics of the photoresponse are modelled with a non-linear set of rate equations which include both the trapping and recombination mechanisms. The solution is found to be in good agreement with the experimentally observed results.

This understanding of the trapping and recombination mechanisms is then used to explain some short term drift phenomena in cadmium sulphide thin-film transistors. In particular, if the bulk Fermi level is above the active traps, no deterioration of the T.F.T. characteristics is observed. If the carrier density is low enough to allow the Fermi level to be amid or below the trapping levels, appreciable aging occurs.

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LIST OF SYMBOLS

a	interelectrode spacing
a_i	electron capture coefficient for the i^{th} transition
A	operational amplifier gain
A_H^i	Hall coefficient of the i^{th} element
$\bar{A}_H$	average Hall coefficient
b	electrode
b_j	thermal emission coefficient for electrons of the j^{th} transition
B	magnetic flux density
d	distance between lattice collision sites
D_n, D_p	electron and hole diffusion constants
E	energy
$\bar{E}$	electric field intensity
E_F	Fermi level
E_{fn}	quasi-Fermi level for electrons
E_{fp}	quasi-Fermi level for holes
E_C	conduction band edge energy
E_V	valence band edge energy
E_{tpi}	energy of the i^{th} donor-type defect level
E_{tni}	energy of the i^{th} acceptor-type defect level
E_g	band gap energy
f_t	fraction of electrons occupying a level
g_L	generation rate of hole electron pairs due to light
g_m	thin-film transistor transconductance

G_o	conductance
h	Planck's constant
i, i_1, i_2, i_x, i_y	electric current
I_{SD}	source-drain current
j_x, j_y	current density
J_n	electron current density
J_p	hole current density
k	Boltzmann constant
l_1, l_2	lengths referring to polycrystalline mobility model
m	rate of change of free electron density with trapped electron density
m_o	rest mass of electrons
m_e^*	effective mass of electrons
m_h^*	effective mass of holes
M_C, M_V	effective number of equivalent minima in conduction and valence band
n	free electron density
n_t	trapped electron density
n_1, n_2	electron densities in crystallites and barriers in the polycrystalline mobility model
n_o	equilibrium free carrier density
n_s	slow part of the photogenerated electron density
n_{st}	steady state electron concentration
n_i	intrinsic free electron density
N_A	acceptor doping density
N_D	donor doping density
N_{ti}	density of donor i^{th} type defects

N_C	effective density of states in conduction band
N_V	effective density of states in valence band
N_l	number of crystallites in the conduction path
p	free hole density
p_t	trapped hole density
P_t	acceptor type defect level
q	charge
R	resistance
R_i	rate of electron current in the i^{th} transition
R_g	thermal generation rate
S_{ni}	electron capture cross-section of the i^{th} transition
t	semiconductor thickness
t	real time
T	temperature
U_n, U_p	electron and hole recombination rates
v_{th}	thermal velocity
$\langle v \rangle$	average thermal velocity
V	voltage applied to sample
V_C	critical voltage
V_e	voltage applied across a barrier
V_D	drain voltage
V_G	gate voltage
α	exponent of photogenerated electron concentration dependence on generation rate
β	exponent of electron lifetime dependence on generation rate

μ	mobility
μ_n	electron mobility
μ_p	hole mobility
μ_H	Hall mobility
ν	frequency of thermal lattice vibration
λ	wavelength
ρ	resistivity
σ	conductivity
ϕ	barrier potential
τ	time between lattice collisions
τ_n	lifetime of electrons in conduction band
τ_p	lifetime of holes in valence band
τ_i	initial decay constant of photocurrent decay
τ_t	time an electron remains on a trap
ξ	normalized free electron density
ξ_t	normalized trapped electron density

Chapter I

INTRODUCTION

This work investigates the behaviour of trapping and recombination mechanisms in thin-film cadmium sulphide. The work was initiated by the need to provide insight into the nature of stability problems associated with thin-film transistors. The investigation was carried out in conjunction with Bell-Northern Research who were developing piezoelectric cadmium sulphide active devices for application in tactile transducer arrays.

A significant feature of the II-VI compounds is their ability to respond to a variety of external stimuli. Two of the most important and most extensively studied are their photoconductive¹ and piezoelectric effects.^{2,3} The former has led to their application in photocells¹ and with the use of microcircuit technology to optical matrices^{4,5} which are useful as optical scanners. The piezoelectric property has been used to develop pressure sensitive transducers⁶⁻¹⁶, and tactile transducer arrays are a possible future application. When coupled with their semiconducting nature, these materials can be employed in hybrid circuits where they can have an active or a passive role.⁴ When used in a thin-film transistor (T.F.T.) configuration,¹⁷⁻¹⁹ these transducers contain the necessary interface to the electronic systems that process their outputs. Thin-film transistors have also been used with ferroelectric ceramic substrates²¹⁻²² to produce switchable memory elements. In this application also, thin-film microcircuit technology allows the deposition of high density matrices.

The principles of thin-film transistor design have been documented in some detail²³ and will not be repeated in this thesis. It suffices to say that the conductivity of the semiconducting material is an important parameter in the transistor's operation. It is desirable to have a low conductivity when the gate voltage is zero, with the object of increasing the conductivity in the surface layer with the application of a gate bias. This mode of operation is usually referred to as the enhancement mode of operation, and can be achieved with a material with high mobility and low carrier density or one with a low mobility and high carrier density. Keeping in mind a possible pressure transducer application, we would wish to use the material with the highest possible piezoelectric constant. If direct pressure is to be used to influence the T.F.T. characteristics, the d_{33} coefficient is of prime importance, while in a flexural mode, d_{31} is the important parameter. Of the two II-VI semiconducting compounds most often used in T.F.T. applications to date, namely CdS and CdSe, the former has the higher piezoelectric constants,² while the latter has a higher mobility. Since it is possible to alter T.F.T. sensitivity by manipulating the device geometry, the higher piezoelectric constant is the valid constraint which determines the choice of material for pressure transducer applications.

For light detection it is important to consider the wavelength of the light that is to be detected. For example, in order to detect blue-green light, near $5000 \text{ \AA}$, CdS gives the highest sensitivity. While in the red region, near $7000 \text{ \AA}$, CdSe is more suitable.²⁴ For a multiplicity of applications, CdS is a logical choice.

In the foregoing discussion it is evident that the thin-film transistor is the fundamental vehicle which allows the integrated utilization of the variety of properties that these materials exhibit. The major complication in successfully implementing these devices has been the stability of both the CdS and CdSe thin-film transistors.^{5,20,21,25,26} While the device operates satisfactorily immediately after fabrication, its performance is usually severely degraded with time. The reason for this behavior has been attributed to defect levels which act as slow trapping centres and

reduce the conductance by trapping charge carriers.

The exact location of these states is not clear. They have been shown to exist in the oxide, at the interface between the oxide and the semiconductor, and in the semiconductor itself. The effect of oxides on the surface conditions of a semiconductor have been well documented,^{27,28} and the motion of ions in the oxide is known to cause shifts in the turn-on potential of field-effect transistors. Experiments show, however, that the surface depletion due to ions or traps in a SiO_x -CdS interface can be reduced by using a thin layer of CaF_2 between the SiO_x and the semiconductor.²⁸ It has also been reported that the stability of T.F.T.'s has been markedly improved by the use of Al_2O_3 instead of SiO_x as the insulator.^{5,25,26}

It is clear that this interface between the semiconductor and the insulator is a region of severe mechanical stress. This is brought about by the fact that the growth of the insulators by vacuum deposition, sputtering, or anodization involves elevated temperature or bombardment of the surface with the atomic species that forms the oxide. This bombardment can cause physical damage of the semiconductor surface. Also, cooling from the elevated temperature will create mechanical stresses at the interface if the thermal expansion coefficients of the semiconductor and the oxide differ. This type of stress may cause dislocations in the semiconductor surface that display activation energies in the band gap of the semiconductor.

The third region of defect concentration is the semiconducting material. Much work dealing with the identification of defects in crystalline CdS has been reported (Chapter II). Relatively little, however, has been reported about the nature of defect levels in polycrystalline or thin-film CdS. The effect of the barrier on the mobility of the thin-films has been studied and it is generally thought that when the dimension of the crystallites is small compared to the length of the conductive path one can consider the film to be uniform with the effect of the barriers averaged over the entire conducting volume.²⁹ Trapping in the semiconductor is important. It is thought to affect not only the long term stability if slow traps are present but also the speed with which the surface

conductivity of a T.F.T. can be modulated.

The objectives of this thesis are the following:

1. To investigate the location of defect levels in polycrystalline thin-film cadmium sulphide and to establish to what extent they are consistent with those observed for cadmium sulphide crystals.
2. To determine, if any, the effect of the polycrystalline nature of the cadmium sulphide films on the mobility and conductivity.
3. To investigate the dynamics of the trapping and recombination mechanisms in untreated cadmium sulphide thin-film.
4. To interpret the stability characteristics of the thin-film cadmium sulphide transistor in the light of the information obtained from the above mentioned studies.

Chapter II summarizes the reported experiments which determine the location of defect levels in CdS. In Chapter III a simple model for the band gap structure is proposed and computations of carrier and trapped carrier concentrations, small signal lifetimes and recombination rates are performed. This chapter serves to lay a foundation for understanding the results of Chapters V and VI which involve steady state and dynamic analysis of the photoresponse. In Chapter IV we establish the mobility variation with light and temperature for samples of cadmium sulphide film. This is necessary information for interpreting the photoconductivity studies of Chapters V and VI. In Chapter VII we discuss the stability of a cadmium sulphide thin-film transistor using the results of Chapters V and VI. In Chapter VIII the results of the foregoing chapters are summarized. A bibliography of works referred to in the thesis follows this chapter of conclusions. Finally, three appendices deal with (i) the calculated results of steady-state conditions in cadmium sulphide type materials, (ii) some of the aspects of the evaporation and treatment of cadmium sulphide films and (iii) the experimental calibration of the light source used in the experiments to study the photoresponse of the thin-films.

Chapter II

REVIEW OF DEFECT LEVELS IN CdS

2.1 Intrinsic Cadmium Sulphide

The majority of reported experiments have been performed on single crystal CdS. To what extent these results can be applied to thin-film CdS is somewhat uncertain. In the following paragraphs the results of single crystal CdS investigations are summarized. The works reported here deal primarily with the factors that determine the type of conduction that one observes in CdS, and consequently focus on the location of donors, acceptors, traps and recombination centres in the band gap. The way that deep defects behave depends very much on the location of the quasi-Fermi level in the band gap. The donor and acceptor sites, which are by definition shallow centres, are usually thermally ionized.

A number of experimental techniques have been employed to study the details of the band gap structure. Among these are thermal current measurements, photo voltage decay, Hall effect, space charge limited currents and optical excitation experiments. The results of early investigations³⁰⁻³⁶ are summarized in Figure 2.1. The nature of defect levels near the conduction band in intrinsic CdS has more recently been reported in detail by a number of investigators and their findings are summarized in Table II.1.

Figure 2.1 Summary of band structure of CdS
(Compiled from References 30-36)

TABLE II.1

Summary of Trap Location Data

AUTHOR	LOCATION OF LEVELS BELOW E_c IN eV	METHOD
Nicholas & Woods ³⁷ (1964) crystal	0.05 0.14 0.25 0.41 0.63 0.82	Thermal currents
Brandhorst et. al. ³⁸ (1968) thin film	0.08 0.14 0.26 0.41	photo voltage decay const. as fcn. of T.
Büget & Wright ³⁹ (1965) crystal	0.16 0.24 0.45 0.45 0.63 0.82	Hall effect & SCL
Bube ⁴⁰ (1962) crystal	0.54 0.57 0.59 0.60	SCL
Trodden ⁴¹ (1967) crystal	0.46 0.51	SCL
Johnston Jr. ⁴² (1968) crystal	0.54	neutron irradiation effect on conductivity
Bube & McDonald ⁴³ (1960) crystal	0.20 0.25 0.40 0.46 0.55 0.35 0.46 0.54	Thermal currents, photo-Hall effect
Kulp ⁴⁴ (1965) crystal	0.14 0.25 0.35 0.46 0.57	optical
Skarman ⁴⁵ (1965) crystal	0.20 0.28 0.40 0.47 0.52 0.60 0.66	Thermal currents

Woods and Nicholas⁴⁶ describe the detailed behavior of the defect levels in order to establish their origin. The 0.05 eV centres were found in almost all the samples and their currents remained unaltered in size and shape regardless of the sequence of thermal or optical treatment the crystal experienced. The 0.25 and 0.63 centres were never found in the same crystal. The 0.25 centres was dominant in the Cd rich crystals while the 0.63 centre predominated in S rich crystals. The slow peaks associated with the 0.14 and 0.25 eV centres increased in size by an order of magnitude or more when crystals (as grown) were heated to 100°C for 30 minutes in the highest vacuum attainable (10^{-5} torr). On the other hand the concentration of centres at 0.14 eV, if large, could be reduced, but not eliminated, by irradiation at room temperature with an illumination intensity of 2000 ft. candles from a tungsten lamp. The 0.25 eV centre could be eliminated completely by similar illumination at room temperature. With these centres (unlike those at 0.14 eV), as their concentration was reduced, the double peak associated with the 0.41 and 0.83 centre appeared. This double peak could, however, be eliminated by heating the crystal to 100°C in vacuum. As the double peak disappears, the 0.25 eV centre reappeared. Their discussion concluded that the 0.05, 0.14 and 0.25 centres are common in Cd rich crystals (S vacancies). The 0.05 and 0.14 centres are associated with isolated S vacancies while the 0.25 eV centre is due to a complex S vacancy. An isolated Cd vacancy would have an effective negative charge and is unlikely to be detectable by conductivity glow measurements. On the other hand, associated Cd vacancies which comprise a colloidal sulfur complex would have a large cross section thus forming a centre which empties under fast retrapping conditions. The 0.63 eV centre has been observed exclusively in S rich crystals and may be such a complex. One assumes that heating at 100°C dissociates such a complex and it is only found at high temperature illumination. The 0.41 and 0.83 centres occur in Cd rich and S rich crystals and may be due to associated Cd and S vacancies in nearest neighbor sites. It is also suggested that the number of constituent vacancies of each type are unequal. The other authors in Table II.1 verify to a large

extent the findings of Nicholas and Woods. In a later experiment, Brailsford and Woods (1968)⁴⁷ attempt to gain more information on the nature of defects in undoped CdS crystals by means of electron spin resonance experiments. Their findings, while not conclusive, do support the notion that sulfur vacancies in CdS lead to shallow donors 0.03 eV below the conduction band.

We have discussed up to now only the existence of vacancies in CdS that result from non-stoichiometric deposition or growth of the crystal. We will say a few words about the reasons for S vacancies being donor-like and Cd vacancies acceptor-like (after Tickle²⁶) and then go on to doping of CdS with Group I, III, V and VII impurities.

In CdS the bonding between the Cd and S atoms is not purely covalent but partly ionic and partly covalent. Considering it to be purely ionic for the purpose of discussion we note that a Cd atom in the lattice loses its two electrons and a S atom gains two electrons. Thus the Cd and the S atoms may be regarded as donor and acceptor that compensate each other and do not give rise to holes and electrons. If there is a Cd vacancy two less electrons are available. This means that there are two S atoms lacking the eighth electron they would normally acquire from the Cd to complete their octet (or, less probably, one S atom lacking two valence electrons). Then two vacant states or holes exist and permit conduction in the valence band as the result of a Cd vacancy. Hence a Cd vacancy acts as an acceptor. A S vacancy, on the other hand acts as a donor. Since a S atom in the lattice normally gains two electrons from the Cd atoms, a missing S atom leaves two electrons available which may be thermally excited to the conduction band.

After the first electron is removed from its Cd atom, the resultant positive charge on the Cd atom makes the removal of a second valence electron more difficult. Hence two donor levels occur. However the ionization energy associated with the second level is much deeper than the first so that its effect is not as a donor but as a centre deeper in the band gap. Similarly two acceptor levels should occur as a result of a Cd vacancy. Due to the large

band gap (2.4 eV), the intrinsic carrier concentration is extremely small. Thus the vacancies are the principal source of carriers and dominate the conductivity of the intrinsic CdS.

2.2 Doped Cadmium Sulphide

Donor and acceptor levels may be introduced into CdS, the former with relative ease, the latter with more difficulty. Donor impurities consist of the Group II and Group VII elements while the acceptor are Group I and Group V elements. It was shown that Cl, Br and I act as donors by replacing the sulfur ion and are found at 0.03 eV below the conduction band. Also Al, Ga and In replace Cd to form donor levels at the same energy level. More recent works by H.H. Woodbury,^{48,49} Van Doorn⁵⁰ and Sharma⁵¹ examine the doping of CdS by means of diffusion of Group III and Group VII impurities into CdS single crystals at high temperatures. Cl and Br behave quite similarly as dopants in CdS. Both impurities can be easily introduced by diffusion with similar solubilities for given firing conditions with excess S pressure ($D \cong 3 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 800°C). Such crystals are largely compensated and show the red color and red fluorescence typical of the Cd vacancy-donor complex. Uncompensated doped crystals can be prepared by firing samples in CdCl_2 or CdBr_2 . Spectrographic analysis showed an approximate 1:1 correspondence between the electron carrier concentration and the chemical content.

The diffusivity of iodine in CdS is appreciably lower than that of the other halogens ($D \cong 5 \times 10^{-12} \text{ cm}^2/\text{sec}$ at 1000°C) possibly because the ionic radius of I is about $2.16 \text{ \AA}$ compared to 1.95, 1.81, and 1.36 for Br^- , Cl^- and F^- respectively. The substituted sulfur ion has a radius of $1.84 \text{ \AA}$. However once the I is incorporated the bulk conductivity is still relatively low, indicating a low electrical activity. The reason for this was due to the oxidizing reaction,

This is analogous to the reducing effect of O_2 on CdS except producing the opposite result. Fluorine behaves in a unique way in CdS. The F rapidly diffuses into CdS and Hall coefficient data on F doped CdS indicate that in addition to acting as a shallow donor it also readily forms a double acceptor complex. This double acceptor complex cannot be annealed out at lower temperatures and/or Cd pressures, as it can with the other Group VII dopants.

The diffusion of gallium into CdS produces about ten times higher electrical activity than Cl, Br or I. CdS can be doped by In which replaces the Cd ion similarly to Ga. Indium diffuses readily into CdS and electrical activity resulting from this type of doping indicates that degenerate conditions can be achieved. Moreover, by introducing a smaller amount of In into the firing, the In content can be controlled to any desired level. For lower In concentrations there appears to be no problem of In precipitation and there seems to be a 1:1 correspondence between chemical content and carrier concentration for donor impurity levels of about 10^{17} cm^{-3} . It is noted that the In doped crystals appear to be much more stable under repeated annealing when compared to the Cl and Br doped crystals. It was found that Sc, Y, and Tl failed to incorporate into the CdS.

The general conclusion is that doping CdS with donor-type impurities results in shallow donor levels at about 0.03 eV below the conduction band. Some additional information is provided by Brailsford and Woods,⁴⁷ who show from E.S.R. measurements on doped CdS that the donor-type impurities incorporate in the sequence:

$$\text{Cl (0.03 eV)} \approx \text{Ga} < \text{In} \approx \text{Tl} < \text{Al} \leq \text{B (0.1 eV)}$$

We note the fact that these authors report the successful doping with Tl while van Doorn⁵⁰ failed to incorporate Tl.

The incorporation of acceptor impurities and achievement of p-type conductivity proves to be a more difficult endeavor than the n-type doping of CdS. For CdS one would expect complete compensation of p-type conductivity by a combination of singly and doubly

ionized S vacancies. Substantial but not complete compensation of n-type conductivity is predicted⁵² due to compensation by singly ionized Cd vacancies. The picture of acceptor-type doping and the mechanism which causes the compensation of acceptor impurities is somewhat clouded by the lack of understanding of the compensation mechanism. We will summarize the experimental efforts to achieve p-type conduction in CdS.

The incorporation of Cu^{35,36,53} and Ag^{1,53} into CdS is a common procedure to achieve high sensitivity photo-conduction. Both of these impurities create defect levels at about 1 eV above the valence band. More recent investigations⁵⁴ explain in greater detail the behavior of copper and silver in CdS. Two kinds of resonance spectra due to copper impurities have been observed in CdS after excitation by light in characteristic bands at 1.5°K. The excitation spectra consist of rather broad bands centred at 2.29 eV and 2.17 eV below the conduction band. The former is attributed to interstitial Cu⁺ while the latter is thought to be due to substitutional Cu⁺. These are called Cu-A and Cu-B centres respectively. In either case, the excitation of Cu⁺ to Cu²⁺ by light results in the formation of a hole at about 1 eV above the valence band. Essentially then Cu in CdS creates a hole trap at 1 eV above the valence band. Similarly, the excitation spectrum for the resonance signal for silver in CdS consists of bands centered around 2.2 eV and 1.9 eV. Excitation by light from Ag⁺ to Ag²⁺ (light in the 2.2 eV band is dominant in this transition) causes photoconductivity and red luminescence occurring at 1.68 eV. This would indicate a hole trap level at about 0.7 eV above the valence band.

Other Group I elements act as acceptors in CdS. Li and Na for example have been found to incorporate into CdS by replacing the Cd⁺⁺ ion substitutionally. On the other hand K, Rb and Cs do not incorporate. It is interesting to note at this juncture that the ionic radii of both Li⁺ and Na⁺ are less than the ionic radius of Cd⁺⁺ while those of K⁺, Rb⁺ and Cs⁺ are greater. This seems to be a general rule of thumb which determines whether or not an

element is a possible acceptor in CdS.⁵²

Na and Li have been shown to be acceptors^{50,54} and Henry et. al.⁵⁵ attribute a shallow acceptor level at 0.165 eV to Na and Li. While this identification of Li and Na as shallow acceptors would indicate a possibility of doping the semiconductor p-type, these authors also note that the formation of such acceptors is accompanied by the simultaneous entry of Li or Na into interstitial sites to form compensating donors.

Group V elements should also act as acceptor-type impurities in CdS by replacement of the S^{2-} . Comparing the ionic radii of P^{3-} , As^{3-} , and Sb^{3-} (2.12 Å, 2.22 Å, 2.45 Å respectively) with that of S^{2-} (1.84 Å) we would deduce that a diffusion mechanism would be very slow and would be accompanied by much crystal lattice deformation. Recently, most attempts to incorporate Group V elements into CdS have been by means of ion implantation.

In 1968, Anderson and Mitchell⁵⁷ radiated 50 KeV phosphorus in beams from 0.5 $\mu A/cm^2$ to 5 $\mu A/cm^2$ ion density on CdS crystals. They found that 10^{15} ions/cm² dosages gave a maximum P concentration of $10^{20} cm^{-3}$ about 500 Å below the surface, with rapid decay 300 Å on either side. Ion implanted crystals were annealed for 10 minutes in a saturated CdS vapor. Type conversion was consistently observed after annealing at 450°C, while only marginal and inconsistent results were observed at a 415°C annealing temperature. A subsequent anneal at 500°C gave a decrease in p-type conductivity. They obtained a hole concentration of $1.6 \times 10^{13} cm^{-3}$. To show the conversion to p-type, a p-n junction diode was formed at the surface and a rectifying characteristic was demonstrated.

Chernow, Eldridge, Rose and Wahlin⁵⁸ reported high conductivity p-type CdS with Bi implantation. 25 kV ions of Bi²⁰⁹ with a beam current of 1 to 10 μA achieved an implantation density of 5×10^{13} to 10^{16} ions/cm³ to a depth of 2000 to 3000 Å in a room temperature crystal. The samples showed p-type Hall mobility without annealing the crystal ($\mu_h = 3 cm^2/V\text{-sec}$). Temperature dependent conductivity studies performed in the dark from 79°K to 375°K established the existence of a shallow level in the doped material with activation energy of 0.015 eV. These authors also

used the rectifying diode characteristic of a p-n diode at the surface as proof of type conversion. Tell and Gibson⁵⁹ repeated the experiment of Chernow et. al. and found no p-type conductivity because of compensation due to defects caused by structural damage. Their conclusion generally is that the ion implanted crystal should be annealed at a temperature high enough to reduce crystal damage or to make the ions electrically active while the temperature should be low enough to minimize self compensating effects. Hou and Morley⁶⁰ implanted phosphorous with energies from hundreds of keV's to 1 MeV to a mean depth of a fraction of a micron. Usually the implanted ions were electrically inactive and required annealing. Phosphorous implantation resulted in an activation energy of 0.13 eV with an associated energy at 0.75 to 0.8 eV which was generally enhanced by annealing. Tell et. al.⁶¹ implanted Na, Li and Xe in CdS with no evidence of type conversion. They nevertheless produced a luminescence due to shallow acceptors at about 0.17 eV associated with alkali impurities. The doping data presented above is summarized in Table II.2.

2.3 Surface States

The previous discussion has dealt exclusively with bulk states. In many device applications, surface states play an important role. These states arise at the surface because of the termination of the crystal lattice. Work on metal-semiconductor surface barriers⁶² led to the conclusion that CdS crystals have essentially no surface states, or if they do exist, that they are found near the band edges. This was substantiated by the fact that a metal-semiconductor potential barrier is a function of the difference in work functions of the two materials. Increasing the work function of the metal should increase the potential barrier. If surface states are present, the potential is pinned at the level of the surface states and should be independent of the metal work function. This was illustrated by Mead.⁶² The result is reproduced in Figure 2.2 to show the difference in potential barrier variation for CdS and CdSe. The conclusion that no significant surface states exist in CdS was also drawn from field-effect studies of oxygen adsorption on CdS surfaces.⁶³

TABLE II.2

Summary of Doping Data for CdS

A. Donors

Group III - replaced Cd^{++} ($0.97 \text{ \AA}^0$)

ion	Ionic radius	incorporated	method	energy level	n-type
B^{3+}	$0.20 \text{ \AA}^0$	yes	diffusion	0.10 eV	yes
Al^{3+}	0.50	yes	"	0.03	"
Ga^{3+}	0.62	yes	"	0.03	"
In^{3+}	0.81	yes	"	0.03	"
Tl^{3+}	0.95	No, yes	"	0.03	"
Sc	0.81	no	"	0.03	"
Y^{3+}	0.93	no	"		
La^{3+}	1.15				
Group VII - replaces $\text{S}^{=}$ ($1.84 \text{ \AA}^0$)					
F^{-}	$1.36 \text{ \AA}^0$	yes	diffusion	0.03	yes
Cl^{-}	1.81	yes	"	0.03	"
Br^{-}	1.95	yes	"	0.03	"
I^{-}	2.16	yes	"	0.03	"

TABLE II.2 (continued)

Summary of Doping Data for CdS

B. Acceptors

Group I - replaces Cd^{++} ($0.97 \text{ \AA}$)

ion	Ionic radius	Incorporated	method	energy level	p-type
Li^+	$0.60 \text{ \AA}$	yes	diffusion	< 1.3	no, compensated
Na^+	0.95	yes	ion impl'n	0.165	
K^+			diffusion	< 1.30	no, compensated
Rb^+	1.33	No	ion impl'n	0.165	
Cs^+	1.48	No	diffusion		
Cu^+	1.69	No	diffusion		
Ag^+	0.96	yes	diffusion	$0.6-1.0$	no, compensated
Au	1.26	yes	diffusion	$0.7-1.0$	no, compensated
1.37					
Group V - replaces $\text{S}^{=}$ ($1.84 \text{ \AA}$)					
N^{3-}	$1.71 \text{ \AA}$				
P^{3-}	2.12	yes	diffusion	0.13	
As^{3-}	2.22		ion impl'n	$0.13, 0.8$	yes
Sb^{3-}	2.45			$0.6 - 1.0$	
Bi^{3-}		yes	ion impl'n	0.015	yes

Figure 2.2 Potential barrier vs. electronegativity
For CdS and CdSe (After Mead, Ref. 62)

Aluminum with an electronegativity of 1.5 has been added to the graph to show that aluminum provides an ohmic contact on CdS. Gold, on the other hand, as evaporated on CdS produces a blocking contact with a barrier potential of 0.79 eV. With suitable heat treatment an ohmic contact can be achieved with gold electrodes. This is possibly due to diffusion of the gold into the semiconductor, thus producing some p-type doping and producing a tunneling contact. There is no evidence, however, that gold produces p-type CdS, but Au is in principle an acceptor-type impurity.

Chapter III

STEADY-STATE RECOMBINATION AND TRAPPING KINETICS IN CdS-TYPE MATERIALS

3.1 Possible Model for CdS Material

The discussion of Chapter II lays the basis for a typical model of the CdS band gap. Lack of stoichiometry introduces an acceptor level at about 1 eV above the valence band and a series of donor type centres which act as shallow donors and donor type centres up to 0.83 eV below the conduction band. It is possible however to localize a predominant centre at 0.25 eV with appropriate heat treatment. We shall use this centre as a typical one for further analysis. It seems that Bi can be ion-implanted in CdS to produce a shallow acceptor (0.015 eV). On the whole one can conclude that Figure 3.1 is a possible model of the band gap for which trapping and recombination kinetics can be investigated.

The populations of the defect levels N_t and P_t will be assumed controlled by electron capture and emission^{64,65} while the shallow donor and acceptor levels will be assumed to be thermally ionized.

Figure 3.1 Simple Model for the CdS band gap.

3.2 Rate Equations

The continuity equation⁶⁶ can be applied for any species of charge carrier in a unit volume of the semiconductor material, so that for free electrons

$$\frac{\partial n}{\partial t} = R_g - U_r + \frac{\nabla J_n}{q} + g_L \quad 1.$$

where $\frac{dn}{dt}$ is the time rate of change of free electrons/unit volume, and $\nabla J_n/q$ is the divergence of electron flux from the unit volume. R_g is the thermal generation rate from one band to the trapping level, or recombination centre, or from the level to the conduction or valence band. We neglect here transitions from one impurity band to the other and justify this by assuming that the density of states in the conduction band or valence band is much greater than the impurity level density. Another consideration which eliminates this type of transition from consideration is the fact that the defect centres are spatially separated in the material so that the carrier is first emitted to the conduction or valence band, where it is mobile. The term U_r represents the recombination term due to capture of electrons by capture centres. The last term in the expression, g_L , refers to generation of hole-electron pairs due to external influence such as radiation, in particular, visible light of an appropriate wavelength to cause band to band generation.

Figure 3.2 Electron transitions in the CdS band gap.

A two-trap system is shown in Figure 3.2. If n and p denote the free electron and hole population of the conduction and valence bands respectively, n_t and p_t the electron and hole concentration in the two defect levels, one can write the rate equations that describe the statistical behavior of the population densities. One further defines a_i as the product of capture cross-section and thermal velocity of the i^{th} electron transition and b_j as the coefficient associated with the thermal emission of an electron in the j^{th} transition. Then the rate equations for this system are:

$$\frac{\partial n}{\partial t} = -a_1 n p_t + b_3 (p_t - p) + b_5 n_t - a_7 n (N_t - n_t) + \frac{\nabla J}{q} n + g_L \quad 2.$$

$$\frac{\partial n}{\partial t} = -b_5 n_t - a_6 p n_t + b_8 (N_t - n_t) + a_7 n (N_t - n_t) \quad 3.$$

$$\frac{\partial p}{\partial t} = -a_1 n p_t - b_2 p_t + b_3 (p_t - p) + a_4 p (p_t - p) \quad 4.$$

$$\frac{\partial p}{\partial t} = b_2 p_t - a_4 p (p_t - p) - a_6 p n_t + b_8 (N_t - n_t) - \frac{\nabla J}{q} p + g_L \quad 5.$$

In the general case, if more than one trapping level of a certain type exists in the band gap, the particular terms will have to be summed over the number of defect levels.

The coefficients of the above equations are not independent. One can most easily investigate the relations between them in thermal equilibrium where the net flow through the trap in any direction must be equal to zero. All particle currents, J , are zero and this means that

$$a_1 n p_t = b_3 (p_t - p) \quad 6.$$

$$b_5 n_t = a_7 n (N_t - n_t) \quad 7.$$

$$b_2 p_t = a_4 p (P_t - p_t) \quad 8.$$

$$\text{and } a_6 p n_t = b_8 (N_t - n_t) \quad 9.$$

Invoking non-degenerate Fermi statistics⁶⁶ allows us to write

$$n = N_c e^{-(E_c - E_F)/kT} \quad 10.$$

$$p = N_v e^{-(E_F - E_v)/kT}$$

The hole concentration in the hole traps can be written as*

$$p_t = P_t \left[1 - \frac{1}{1 + e^{(E_{tp} - E_F)/kT}} \right] \quad 11.$$

Substituting equations 10 and 11 into 6 and 8 leads to the relations

$$\frac{b_3}{a_1} = N_c e^{-(E_c - E_{tp})/kT} \quad 12.$$

and

$$\frac{b_2}{a_4} = N_v e^{-(E_{tp} - E_v)/kT} \quad 13.$$

*The electron spin degeneracy factor has been assumed to equal one.

Similarly for the electron traps:

$$\frac{b_5}{a_7} = N_c e^{-(E_c - E_{tn})/kT} \quad 14.$$

and

$$\frac{b_8}{a_6} = N_v e^{-(E_{tn} - E_v)/kT} \quad 15.$$

From equations 12 and 13 it is evident that the ratio $b_2 b_3 / a_1 a_4$ is a constant for a given material, regardless of the trap's location or of the type of trap that it is. In fact

$$\frac{b_2 b_3}{a_1 a_4} = \frac{b_5 b_8}{a_6 a_7} = N_c N_v e^{-E_g/kT} \quad 16.$$

Eliminating p_t from equations 6 and 7 or n_t from 7 and 9 allows us to calculate the pn product. The result is

$$pn = \frac{b_2 b_3}{a_1 a_2} = \frac{b_5 b_8}{a_6 a_7} = n_i^2 \quad 17.$$

In the following treatment the capture cross-sections and thermal emission coefficients are assumed constant for equilibrium and non-equilibrium conditions and are considered to be a function only of the location of the defect levels.

3.3 The charge nature of the defects

Consider first of all a sulfur vacancy. This means that where a Cd^{++} would have exchanged two electrons with a sulfur atom, the sulfur atom is missing. This leaves a Cd^{++} ion and two electrons. One may assume, however, that the ionization potential for the second electron is much larger than the first so that one may deal primarily with Cd^+ and e^- . This electron is relatively free to move about the crystal and the occupation of the sulfur defect is determined statistically by the Fermi-Dirac probability. Depending on the position of the Fermi level, a fraction of the electrons will be free from the defect and will occupy the conduction band, leaving behind a net positive centre. The charge on the sulfur defect is then $+[N_t - n_t] = +N_t(1-f_t)$ where f_t is the Fermi statistic of the level being occupied, and n_t is the number of electrons in the defect level ($n_t = N_t f_t$).

Similar reasoning applies to any kind of deep donor impurity. For example elements from Group III which replace the Cadmium ion in the lattice would have a net positive charge and an extra electron after forming the double bond with $\text{S}^=$. The Group VII atoms replace $\text{S}^=$ and achieve a singly negative charge state. Cadmium, on the other hand, becomes Cd^{++} and has an electron left over. If this electron leaves the site of the II - VII complex, a net positive charge results. It is well known, however, that the Group III and VII elements are shallow donors, and are therefore thermally ionized. At room temperature these will be positive centres.

Acceptor type defects act in a similar manner. First of all, if we consider a cadmium vacancy, we are left with a neutral sulfur atom. Because sulfur has a high electronegativity, it has an affinity for electrons and its charge state will become S^- or $\text{S}^{=}$. Assuming that the first state is the more likely, we see that the sulfur site can be represented by a $[\text{S}^- + p_t]$ complex. That is, a negatively charged sulfur ion and a hole. When the site is populated with a hole the net charge is negative. So that the charge on the Cd defect state is $-[P_t - p_t]$.

A deep acceptor will behave in a similar manner. Group I elements which replace the Cd^{++} ion will create a negatively charged $\text{A}_I^+ \text{S}^-$ complex and Group V replacing the sulfur atom will cause a negatively charged $\text{Cd}^{++} \text{B}_V$ complex.

In all the preceding pages N represents the net impurity state (shallow and deep) concentration. For the computations that follow, we will replace N by its components, i.e. $N = N_L - P_t + N_D - N_A$.

Other parameters that need consideration are the density of states in the conduction and valence band. These are given by

$$N_c = 2M_c \left[\frac{2\pi m_e^* kT}{h^2} \right]^{3/2}$$

and

$$N_v = 2M_v \left[\frac{2\pi m_h^* kT}{h^2} \right]^{3/2}$$

The number of equivalent minima $M_c = 1$ and also $M_v = 1$. Furthermore, $m_e^*/m_o = 0.20$ and $m_h^*/m_o = 0.7$.⁶⁷ Using these we calculate $N_c = 2.33 \times 10^{18} \text{ cm}^{-3}$ and $N_v = 1.52 \times 10^{19} \text{ cm}^{-3}$.

3.4 STEADY STATE CONSIDERATIONS

3.4 1. Describing equations:

To study the surface and bulk behavior of a material with two or more trapping or recombination levels in the band gap, one requires in addition to the rate equations of the previous section, expressions for current and electric field or potential. The current is generally expressed for holes and electrons as the sum of diffusion and drift components, while the potential is related to the electron and hole concentrations by Poisson's equation. The complete set of equations that describes the system is

$$\frac{\partial n}{\partial t} = -a_1 n p_t + b_3 (p_t - p_t) + b_5 n_t - a_7 n (N_t - n_t) + \frac{\nabla \cdot \bar{J}}{q} n + g_L \quad 18.$$

$$\frac{\partial n_t}{\partial t} = -b_5 n_t - a_6 p n_t + b_8 (N_t - n_t) + a_7 n (N_t - n_t) \quad 19.$$

$$\frac{\partial p_t}{\partial t} = -a_1 n p_t - b_2 p_t + b_3 (p_t - p_t) + a_4 p (p_t - p_t) \quad 20.$$

$$\frac{\partial p}{\partial t} = b_2 p_t - a_4 p (p_t - p_t) - a_6 p n_t + b_8 (N_t - n_t) - \frac{\nabla \cdot \bar{J}}{q} p + g_L \quad 21.$$

$$\bar{J}_n = q D_n \nabla n + q \mu_n n \bar{E} \quad 22.$$

$$\bar{J}_p = -q D_p \nabla p + q \mu_p p \bar{E} \quad 23.$$

$$\nabla \cdot \bar{E} = \frac{q}{\epsilon_s} (p - n + p_t - n_t + N) \quad 24.$$

In these equations $\bar{E}$ is the electric field intensity and N is the net doping density $N_D - N_A$. In addition, the total current flowing in the material is expressed as

$$\bar{J} = \bar{J}_n + \bar{J}_p \quad 25.$$

Conservation of charge, however, requires that

$$\nabla \cdot \bar{J} = -\frac{\partial \rho}{\partial t} = -q \frac{\partial}{\partial t} (p + p_t - n - n_t + N) \quad 26.$$

which implies that one of the equations 18 to 21 is redundant. This fact will be considered in the solution of these equations in the subsequent sections.

3.4.2. Solution for the steady-state flat-band case

In this case $\partial/\partial t=0$ and $\partial/\partial x=0$ so that equations 18 to 24 reduce to

$$0 = -a_1 n_o p_{to} + b_3 (P_t - p_{to}) + b_5 n_{to} - a_7 n_o (N_t - n_{to}) + g_L \quad 27.$$

$$0 = -b_5 n_{to} - a_6 p_o n_{to} + b_8 (N_t - n_{to}) + a_7 n_o (N_t - n_{to}) \quad 28.$$

$$0 = -a_1 n_o p_{to} - b_2 p_{to} + b_3 (P_t - p_{to}) + a_4 (P_t - p_{to}) p_o \quad 29.$$

$$0 = p_o + p_{to} - n_o - n_{to} + N \quad 30.$$

We recognize that with $g_L = 0$ we have the equilibrium case, where the above expressions are very easily solved since

$$a_1 n_o p_{to} = b_3 (P_t - p_{to}) \quad 31.$$

$$b_5 n_{to} = a_7 n_o (N_t - n_{to}) \quad 32.$$

$$b_2 p_{to} = a_4 (P_t - p_{to}) p_o \quad 33.$$

$$p_o + p_{to} + N = n_o - n_{to} \quad 34.$$

Further reduction of these equations allows one to write

$$p_o n_o = \frac{b_2 b_3}{a_1 a_4} = \frac{b_5 b_8}{a_6 a_7} \quad 35.$$

$$n_{to} = \frac{a_7 N_t n_o}{a_7 n_o + b_5} = \frac{N_t n_o}{n_o + (b_5/a_7)} \quad 36.$$

$$p_{to} = \frac{b_3 p_t}{a_1 n_o + b_3} = \frac{p_t (b_3/a_1)}{n_o + (b_3/a_1)} \quad 37.$$

$$n_o + n_{to} = p_o + p_{to} + N. \quad 38.$$

One notes at this point that this set of equations allows the determination of the functional relation between n_o , p_o , n_{to} , p_{to} and N , the net doping density. Equation 38 can be written as a relation between n_o and N and the numbers can be easily computed for a given trapping scheme. We plot typical results for our assumed model in Figure 3.3.*

This approach is general and can be extended to any number of traps or recombination centres. At equilibrium, the rates into a level and out of a level in any direction must be zero, so that the trap population can be expressed as a function of n_o only. With the aid of the charge neutrality condition the functional relation between n_o and doping can be computed.

With incident uniform light on the material the problem becomes more complex. Now the pn product is no longer a constant and the trap population cannot be expressed simply as a function of n_o alone. While the neutrality condition still applies, the equations that have to be solved are:

* We note the similarity between this result and that commonly calculated for gold in silicon.

Figure 3.3 Net doping density vs. electron density at equilibrium (300°C) with N_t & P_t as parameters.

$$-a_1 n p_t + b_3 (P_t - p_t) + b_5 n_t - a_7 n (N_t - n_t) + g_L = 0 \quad 39.$$

$$-b_5 n_t - a_6 p n_t + b_8 (N_t - n_t) + a_7 n (N_t - n_t) = 0 \quad 40.$$

$$-a_1 n p_t - b_2 p_t + b_3 (P_t - p_t) + a_4 p (P_t - p_t) = 0 \quad 41.$$

$$p + p_t - n - n_t + N = 0 \quad 42.$$

It is possible to solve this set of non-linear simultaneous equations using a Newton-Raphson iteration technique. Some typical results are shown in Figure 3.4 and 3.5, while a more complete set of curves is included in Appendix A.

The curves of Figure 3.4 and 3.5 were plotted to determine the variation of electron concentration as a function of doping and light. The limit for low level injection is clearly indicated in Figure 3.5 as the point where the electron density becomes a function of light intensity. We further note that the electron density increases as a half power function of g_L ($n \propto g_L^{1/2}$) while the centres are not completely full and that $n \propto g_L$ once the centres are filled. We note that this transition is abrupt. Any power dependence on g_L other than 1/2 or unity for this particular model would be valid for not more than one half a decade of g_L .

From the calculated data it is possible to describe the motion of the quasi-Fermi levels with increasing light intensity. If we denote by E_f the Fermi level with no light, by E_{fn} the electron quasi-Fermi level measured positive below E_c and by E_{fp} the hole quasi-Fermi level measured positive above E_v , one can define

Figure 3.4 Concentrations as a function of generation due to light when $N_D > P_t$ or N_t .

Figure 3.5 Concentrations as a function of generation due to light when $N_D < P_t$ and N_t .

$$E_{fn} = \frac{kT}{q} \ln \left(\frac{N_c}{n} \right)$$

and

$$E_{fp} = \frac{kT}{q} \ln \left(\frac{N_v}{p} \right)$$

The variation of the quasi-Fermi levels is plotted in Figure 3.6 for a variety of doping conditions and $N_t = P_t = 10^{16}$.

We note that the quasi-Fermi level for electrons changes little until significant generation rates are achieved, while the hole quasi-Fermi level changes significantly even with small generation rates. This means that while low level injection for electrons is valid, the holes are experiencing a high level injection, and it will be difficult to apply a linear theory to this problem except under extremely specialized conditions.

3.5 Generation and Recombination Rates and Lifetimes

We have noted before that in a material where a number of traps or recombination centres exist in the band gap the lifetime of holes and electrons cannot in general be expressed simply. In this section we will study the generation and recombination mechanisms as functions of the generation due to light.

3.5.1 Capture and Emission Rates as a Function of g_L

Realizing that increased g_L increases the separation of the quasi-Fermi levels, one would deduce that the nature of the defect centres would also change. The levels that act as traps in equilibrium will become recombination centres as the quasi-Fermi levels pass through the defect levels and vice versa.

The flat band rates are computed as a function of the generation rate, g_L . We define

$$R_1 = a_1 n_o p_{to}$$

$$R_2 = b_2 p_{to}$$

$$R_3 = b_3 (P_t - p_{to})$$

$$R_4 = a_4 p (P_t - p_{to})$$

$$R_5 = b_5 n_{to}$$

$$R_6 = a_6 p_o n_{to}$$

$$R_7 = a_7 n (N_t - n_{to})$$

$$R_8 = b_8 (N_t - n_{to})$$

Figure 3.7 shows the rates through the defect levels for typical conditions of doping and defect concentration.

Let us postulate a small perturbation of electrons in the material and derive the resulting recombination rate

$$\Delta U_n = \left\{ P_t \left[\frac{a_1 a_4 p_o}{a_1 n_o + a_4 p_o + b_2 + b_3} \right] + N_t \left[\frac{a_6 a_7 p_o}{a_7 n_o + a_6 p_o + b_5 + b_8} \right] \right\} \Delta n$$

For holes we have

$$\Delta U_p = \left\{ \Delta U_n \cdot \frac{n_o}{p_o} \right\} \frac{\Delta p}{\Delta n}$$

These expressions allow the calculation of the small signal lifetimes of electrons and holes under steady state conditions, where

$$\tau_p = \left[\frac{P_t a_1 a_4 n_o}{a_1 n_o + a_4 p_o + b_2 + b_3} + \frac{N_t a_6 a_7 n_o}{a_6 p_o + a_7 n_o + b_5 + b_8} \right]^{-1}$$

and

$$\tau_n = \tau_p \left[\frac{n_o}{p_o} \right]$$

Figure 3.6 Motion of quasi-Fermi levels as a function of generation rate due to light.

Figure 3.7 Transition rates through the defect levels as a function of generation due to light.

The numerical values of τ_n and τ_p are calculated and shown in Figure 3.8.

A number of observations can be made from the graph. With low light (or low g_L) the conditions for equilibrium exist. That is the net rates up and down through the traps are zero. For example $R_1 = R_3$ and $R_2 = R_4$, etc. With increasing g_L both R_1 and R_4 increase and finally become equal. The behavior of the P_t defect has changed from that of a trap to that of a recombination centre. One would conclude that the demarcation level for this trap is then at an energy level that corresponds to the position of the quasi-Fermi level for holes with $g_L \cong 10^{-1}$ (since $a_1 = a_4$). Because of its proximity to the conduction band edge, the N_t defects require a greater change in the hole concentration before the capture of electrons from N_t by holes in the valence band becomes significant. This trap becomes a recombination centre for $g_L \cong 10^{17}$ or approximately where $E_{fn} = E_{nt}$. We also note that R_6 increases with a slope of unity until high level injection occurs, beyond which point R_6 increases at a larger slope (≤ 2).

3.5.2 Large Signal Hole and Electron Lifetimes

In the steady-state the net rates out of and into the conduction band can be written in terms of n and p ,

$$- \left[\frac{a_1 a_4 np - b_2 b_3}{a_1 n + a_4 p + b_2 + b_3} \right] P_t - \left[\frac{a_6 a_7 np - b_5 b_8}{a_7 n + a_6 p + b_5 + b_8} \right] N_t + g_L = 0$$

The first expression represents the traffic through the deep-lying centre and the second term is the net rate through the shallow centre. The total steady-state recombination rate for electrons in the conduction band and holes in the valence band is

$$U = P_t \left[\frac{a_1 a_4 np - b_2 b_3}{a_1 n + a_4 p + b_2 + b_3} \right] + N_t \left[\frac{a_6 a_7 np - b_5 b_8}{a_7 n + a_6 p + b_5 + b_8} \right]$$

Figure 3.8 Small signal decay time constants

Let us consider the case where high level injection is valid and n_o and p_o are equally large. Also $\Delta n = \Delta p$. In that case we can rewrite ΔU_n in the following way

$$\Delta U_n = \left[\frac{P_t a_1 a_4 n_o}{a_1 n_o + a_4 n_o + b_2 + b_3} + \frac{N_t a_6 a_7 n_o}{a_6 n_o + a_7 n_o + b_5 + b_8} \right] \Delta n$$

Hence τ_n is by definition

$$\tau_n = \frac{1}{\left[\frac{P_t a_1 a_4 n_o}{a_1 n_o + a_4 n_o + b_2 + b_3} + \frac{N_t a_6 a_7 n_o}{a_6 n_o + a_7 n_o + b_5 + b_8} \right]}$$

If $a_1 \simeq a_4$ and $a_7 \simeq a_6$, τ_n reduces to

$$\tau_n = \frac{1}{\left[\frac{P_t a_4^2 n_o}{2a_4 n_o + b_2 + b_3} + \frac{N_t a_7^2 n_o}{2a_7 n_o + b_5 + b_8} \right]}$$

Furthermore if $a_4 n_o \gg (b_2 + b_3)$ and $a_7 n_o \gg (b_5 + b_8)$ we have

$$\tau_n = \frac{1}{2(a_1 P_t + a_7 N_t)}$$

Hence for high level injection the decay time for photoexcited electrons is determined by the capture rate of electrons by the acceptor level which is at this stage half full of holes and the capture rate of holes by the donor level which is half full of electrons. The decay constant is therefore independent of electron and hole densities and is a constant independent of light.

With a constant decay constant of high light intensities we should experience decay of current to the same level before the effect of emission of traps becomes important. That is when the quasi-Fermi level passes through the trap level, or more precisely the demarcation level associated with that level, the time constant should change and trapping effects should also contribute to change

the rate of current decay. This change in decay rate should reflect the location of the demarcation level for the donor-type defect level. The slower portion of the decay is characterized by recombination through the acceptor-type defect and electron emission from the donor-type centre.

Chapter IV

MOBILITY MEASUREMENTS/ IN CdS THIN-FILM

4.0 Introduction

The mobility of single crystal cadmium sulphide has been studied and measured in detail. Bube and MacDonald⁴³ discuss a number of possible cases where the change in the quasi-Fermi levels due to optical excitation of the crystals changes the occupation of the defect levels. This alters the charge on these centres and hence the scattering mechanism is modified resulting in a change in the mobility. For example, positively charged centres, such as ionized donors, which are above the Fermi level in the dark, lose their charge as the Fermi level increases due to photo-excitation, and their coulombic scattering would subsequently decrease. On the other hand a neutral centre lying above the Fermi level in the dark would gain negative charge upon photo-excitation and the scattering would be strongly increased. It is clear that the first case would lead to an increase in mobility while the second to a decrease. Composite cases, i.e. those consisting of levels lying below and above the dark Fermi level, should exhibit stepwise changes in mobility depending on the location of the levels in the forbidden gap. Two centres could exhibit a mobility variation that first increased and then decreased or vice versa.

Rose⁶⁸ discusses the effect of trapping on the mobility of crystals. Drift mobility is defined as the average distance travelled in the direction of an applied electric field between lattice collisions d , divided by the time between lattice collisions τ . In the presence of trapping centres the possibility exists that the centre traps an electron at a rate $1/\tau_t = S_n v_{th} (N_t - n_t)$. Here S_n is the capture cross-section for electrons, v_{th} is their thermal

velocity, N_t is the density of trapping centres, and n_t is the number of electrons in the traps. The trap can hold an electron for a time and then release it. Let us postulate t lattice sites between every trap (one-dimensional) so that the distance travelled between trapping centres is then td , and the time between trapping centres is $t\tau$. If the electron is captured by the trap, it spends a time τ_e without motion so that the mobility in the presence of trapping is defined by

$$\mu = \frac{td}{t\tau + \tau_e}$$

If $\tau_e \gg t\tau$, $\mu = td/\tau_e$. Since $t = \tau_t/\tau$, the expression for mobility becomes

$$\mu = \frac{d}{\tau} \frac{\tau_t}{\tau_e} = \mu_o \left[\frac{v e^{-E_t/kT}}{S_n v_{th} (N_t - n_t)} \right]$$

where $\mu_o = d/\tau$ is the mobility of the material without trapping. In terms of the constants that were defined in Chapter II

$$\mu = \mu_o \left[\frac{b_5}{a_7 (N_t - n_t)} \right] = \mu_o \left[\frac{n_1}{N_t - n_t} \right] = \mu_o \left[\frac{n + n_1}{N_t} \right] \quad 1.$$

The mobility in polycrystalline materials has also been studied. Volger⁶⁹ discusses the conductivity and Hall potential in an inhomogeneous material. The model consists of a succession of high conductivity islands in a low conductivity background. This can arise physically due to irregularities in stoichiometry and intercrystalline barriers or grain boundaries. This material is represented by a one dimensional model shown in Figure 4.1.

The model postulates that $\rho_2 \gg \rho_1$ and that the average resistance of the sample is approximately equal to $\bar{R} \approx R_1 + R_2$. This means that $\bar{\rho}(\ell_1 + \ell_2) = \rho_1 \ell_1 + \rho_2 \ell_2$ or that

$$\bar{\rho} = \rho_1 + \rho_2 \left[\frac{\ell_2}{\ell_1} \right] \quad \text{if } \ell_1 > \ell_2$$

Figure 4.1 Model for polycrystalline film

For $\rho_2 \frac{\ell_2}{\ell_1} \gg \rho_1$, we have $i_1/i_2 = \ell_1/\ell_2$. A Hall voltage exists across each grain and a Hall voltage $BA_H^1 \ell_1 i_1$ exists across the boundary, where A_H^1 is the suitable Hall coefficient. The effective observed Hall voltage is

$$\bar{A}_H (i_1 + i_2) (\ell_1 + \ell_2) B = A_H^1 \ell_1 i_1 B + A_H^2 \ell_2 i_2 B$$

if $i_1 \gg i_2$

$$\bar{A}_H = A_H^1 + A_H^2 \left(\frac{\ell_2}{\ell_1} \right)^2 \simeq A_H^1$$

One sees that the effective Hall coefficient is that of the crystallites. This is to be expected because the Hall voltage is caused by an accumulation of charge and not by a flow in the direction of the Hall field. On the other hand $\bar{\rho}$ can be much greater than ρ_1 , so that the observed mobility $\bar{\mu} = \bar{A}_H / \bar{\rho}$ will be reduced from the purely crystalline value.

It is also possible to use this model to explain the temperature dependence of electron-mobility in CdS polycrystalline films.²⁹ Here the current is assumed to flow through the regions of low resistivity. The distance ℓ_2 is represented by a barrier potential ϕ due to differing carrier densities in the two regions. The current density is then given by

$$J = \frac{1}{2} e n_1 \langle v \rangle e^{-\phi/kT} \left[e^{qV_d/kT} - 1 \right]$$

The mobility is

$$\bar{\mu} = \frac{\bar{\sigma}}{n_1 q} = \frac{e \langle v \rangle e^{-\phi/kT}}{4n_1 kT} \quad 2.$$

where N_1 is the number of barriers per unit length and $\langle v \rangle$ is the average thermal velocity. The barrier height ϕ can be expressed as a function of the electron densities in the two regions

$$\phi = kT \ln \left[\frac{n_1}{n_2} \right] \quad 3.$$

The effect of illumination on the polycrystalline material is now to increase both n_1 and n_2 at low light intensities. When the illumination is strong n_2 tends to equal n_1 and ϕ goes to zero and thus causing no further increase in mobility.

It is possible that every process mentioned above may play a role in determining the behavior of the mobility in polycrystalline materials. The combination of these effects may produce a variety of results. If they aid each other, the net effect may be a large change in mobility and if they oppose each other, the net effect may be a mobility that is relatively insensitive to illumination.

The electron mobility for CdS single crystals has been quoted¹ to be equal to 200 cm²/volt-sec. The hole mobility is believed to be small and has not been measured directly. An indirect measurement was performed by Onuki and Hase⁷⁰ by irradiating single crystals of CdS with light of varying wavelength. The mobility of the sample increased with increasing wavelength and these results were interpreted on the basis of two carrier mobility. If the generation rates for holes and electrons were assumed equal, it was possible to deduce a hole mobility of 38 cm²/volt-sec. These results were consistent with the drift mobility of holes extrapolated from the high temperature values of Spear and Mort.⁷¹ Bube and MacDonald⁴³ have done photo-Hall measurement on single crystals of CdS and used the results to derive trapping parameters

for the material.

Considering these theories, one can expect difficulty in predicting the exact behavior of mobility in thin-film polycrystalline materials. Not only does trapping play the same important role as in single crystals but modulation of the intercrystalline barrier height could also affect the mobility. It is also possible that under particular types of excitation the trapping effects in the crystallites may be far exceeded by those in the intercrystalline boundaries. Indeed the results of Waxman et. al.²⁹ show the general trend of increasing mobility with decreasing barrier potential. The barrier potential is decreased by applying a gate voltage to a T.F.T. structure, but it is found that the increase of mobility is valid for low surface potentials only. At high potentials surface scattering predominates and mobility is again decreased. These measurements yielded electron mobilities from 10 to 60 cm²/volt-second. Dresner and Shallcross⁷² studied the effect of post-deposition treatment of CdS films and found large variations of mobility from 1 to 300 cm²/volt-second. This large change was attributed primarily to the diffusion of Cu into the CdS films. While it is suspected that this action causes drastic changes in the crystallinity of the films the exact nature of the diffusion and its effects on the material properties is not understood. The behavior of mobility in sintered layers of CdS is also studied by Bube et. al.⁷³ and it is found to decrease monotonically with increasing quasi-Fermi level for electrons (measured from conduction band) caused by photoexcitation. This supports the theory of decreasing intercrystalline potential barrier with increasing illumination. Neugebauer¹² studied the temperature dependence of the field-effect conductance in thin polycrystalline CdS films and reported that the mobility increases with the induced charge carrier density at low carrier densities, but becomes independent of it at high densities. This is interpreted to be due to a depletion layer at the grain boundary.

In all of the previously quoted measurements on polycrystalline films, the mobility was found to vary over a considerable range, usually from 5 to 30 cm²/volt-second. The variation in the observed results can be a function of the various parameters that affect the mobility of the material.

Since these are functions of the deposition technique, different experiments should get a variety of values for mobilities. It seems then that it is necessary to characterize the deposited material before any experiments are made. Since photoresponse measurements are carried out in Chapter V of this thesis it was deemed necessary to measure the change of mobility as a function of light intensity and wavelength.

4.1 Three-Electrode Technique

The technique used to measure the Hall mobility was developed by Dobrovol'skii and Strisenko⁷⁴ and Mortensen et al.⁷⁵ This is a three-point method and measures the Hall current instead of the usual Hall potential that results from a four-probe technique. The experimental apparatus used is similar to that employed by Schadt and Williams.⁷⁶ An advantage of this method over the four-point probe technique is that the electrodes used for a T.F.T. can be used if the source, for example, is divided. This allows the determination of material mobilities under T.F.T. geometries, thus including the effect of oxides and contacts.

The three-point method is based on the difference in current that arrives at two halves of an electrode when a magnetic field is applied orthogonal to the sample surface. The general geometry is outlined in Figure 4.2.

With no magnetic field $i_1 + i_2 = i_x$, and if the material is uniform and the second electrode is equally split, $i_1 = i_2$. With the application of a magnetic field B , a transverse current i_y results and the difference in i_1 and i_2 can be measured. Generally the areas of the sections of the split electrode will

Figure 4.2 Hall mobility circuit

not be exactly equal. R_1 and R_2 can be adjusted to equalize the inputs to the operational amplifier. Application of B causes $j_y = \mu B j_x$ if the transverse electric field is completely shorted by the electrodes. This is valid for small a/b ratios. If t is the thickness of the CdS sample

$$i_y = atj_y$$

$$\text{and } i_x = btj_x$$

Then it is easy to deduce that

$$\frac{i_y}{\mu B i_x} = \frac{a}{b}$$

One notes that the output from the operational amplifier is

$$e_o = (R_1 + R_2) A i_y$$

which together with the above expression yields

$$\mu = \frac{e_o}{i_x AB (R_1 + R_2) (a/b)}$$

As was mentioned before, this is valid for small a/b ratios only. For large a/b one uses the function of a/b theoretically derived by Mortensen et al. In section 4.3 this expression is experimentally verified.

4.2 Sample Preparation

The samples were CdS thin-films evaporated on glass substrates (for a discussion of thin-film evaporation techniques see Appendix B). The substrate temperature, rates, and thickness for the various samples are tabulated in Table IV.1.

Table IV.1

Experimental Samples

Sample Number	T _{substrate}	Rate	Thickness	a/b
335	200° C	27A°/sec	3000A°	0.75
332	200°	"	"	1.25
326	200°	"	"	0.25
283	200°	"	"	0.75
OS1.50	230°	97A°/sec	10,000A°	1.50

Aluminum electrodes were deposited on the CdS film to give the overall geometry shown in Figure 4.2

4.3 Experimental Verification of the Three-Electrode Theory

The experiment proceeded in the following manner. Starting with the sample of the smallest a/b ratio, μ was measured and the theoretical correction was used. After reducing the dimension b on the sample by scoring through the aluminum electrodes with a diamond scriber, mobility was measured again and a new correction was calculated to give the previous value of mobility. This is done for a number of samples and the results are compared to the theoretical prediction of Mortensen et al. in Figure 4.3.

Figure 4.3 Comparison of the experimental geometrical factor with the theoretical prediction of Mortensen et al.

4.4 Mobility measurements as a function of light intensity and Wavelength

Having established the technique and having verified the interpretation of the results, one can now continue to measure the variation of mobility with light intensity and wavelength. The apparatus shown in Figure 4.4 was used. The electrical connections were made to the sample as depicted in Figure 4.2. The details of the operational amplifier are given in Figure 4.5. The light was calibrated using an EGG SGD444 photodiode in conjunction with an operational amplifier output circuit. This is shown in Figure 4.6.

The photodiode dark current is compensated by passing a current through the $1M\Omega$ resistor to the summing node of the operational amplifier. This is done by adjusting V_1 until e_o is zero. Light shining on the diode then produces an output that is proportional to the light intensity. In Figure 4.6, A represents the active part and G the guard ring of the photodiode. V_2 serves to bias the diodes. During the measurements, this voltage was set at -40 V. Calibration of the source was carried out using a series of neutral density filters (see Appendix C for details).

The mobility was measured at various wavelengths and relative light intensities. These results are plotted in Figure 4.7. One notes that for wavelengths consistent with energies greater than the band gap, relatively small changes in mobility are observed with increasing light intensity. At $E \simeq E_g$ a larger change of mobility is observed while for $E < E_g$ the mobility changes with increasing intensity, but not as much as at $E \simeq E_g$. If these results are replotted for a constant electron density, thus taking into account the change in absorption coefficient of the material, one observes that for $\lambda > 5200\text{\AA}$ the change in mobility is significant (Figure 4.8). The change in mobility at constant intensity is also plotted in Figure 4.8.

Figure 4.4 Experimental illumination scheme

Figure 4.5 Details of the differential amplifier

Figure 4.6 Details of the calibration photodetector

Figure 4.7 Mobility variation with illumination

Figure 4.8 Measured Hall mobility as a function of wavelength.

4.5 Temperature dependence of Mobility

A number of scattering mechanisms contribute to the mobility of semiconducting materials. There are impurity, acoustic mode, optical mode, and piezoelectric scattering. These contribute $T^{3/2}$, $T^{-3/2}$, $e^{\phi/T}$, and $T^{1/2}$ types of temperature variations. These are quite valid for single crystal CdS and a typical experimental result for single crystal mobility variation with temperature is shown in Figure 4.9.

The temperature dependence most often observed for polycrystalline CdS films is of the type described in equation 2. It is an exponential dependence characterized by an activation energy usually associated with barrier potential that is postulated to exist at the intercrystalline boundaries. The results of some authors are summarized in Figure 4.10.

Figure 4.9 Variation of Hall mobility for CdS single crystals with temperature, showing the contributions of piezoelectric μ_{HP} and optical mode μ_{HO} scattering (after ref. 77)

Figure 4.10 Mobility variation with temperature for polycrystalline CdS thin-films

4.6 Conclusions

From Figure 4.7 it is evident that for the materials used in these measurements the mobility is a very weak function of light intensity. This fact suggests that for the light intensities used in these experiments, the ratio of n_1/n_2 remained constant. The increase in free carriers in the crystallites was accompanied by an increase of free carriers in the barriers thus keeping the potential barrier constant. The results of Figure 4.10, however, confirms the general temperature dependence suggested by equation 2. These results allow the interpretation of the photoconductivity measurements of Chapter V by assuming the mobility to be an independent function of illumination, thus attributing the change in conductivity at a given temperature solely to photoexcited carriers.

Chapter V

THE INFLUENCE OF HIGH FIELDS, TEMPERATURE AND ILLUMINATION ON THE CONDUCTIVITY OF CdS THIN-FILM

5.1 Experimental Apparatus

In order to study the conductivity of the CdS thin film, the semiconductor was deposited on a glass substrate and aluminum electrodes were deposited according to the geometry outlined in Appendix B.4. The circuit shown schematically allowed the study of the conductivity at various fields, temperature and illuminations. The basic circuit is much the same as that previously used in the mobility measurements, except that here the sample is placed in a cryostat, which allows both evacuation and cooling of the sample. The cooling was effected by using liquid nitrogen in the cryostat and a range of temperatures from room temperature to 125° K was easily attainable. Execution of several temperature cycles in succession was speeded up by rapidly evaporating the liquid nitrogen in the cryostat with a stream of dry air.

Light was supplied from the calibrated light source previously discussed in Chapter IV. The light was applied and removed from the sample by means of a mechanical shutter. The shutter's opening and closing speeds of 1 ms. were sufficiently fast to be used in the photoresponse measurements of the next chapter. A $5200 \text{ \AA}^{\circ}$ optical filter was used in conjunction with the source to ensure primarily band to band excitation.

5.2 Relative Photoresponse

To ensure that the photoresponse is indeed a maximum at $5200 \text{ \AA}^{\circ}$, the photoresponse was measured over a range of wavelengths.

The apparatus used was essentially that shown in Figure 5.1 with the exception that the optical filter was replaced by a Jarrell Ash monochrometer. The relative photoresponse of the sample as a function of exciting wavelengths is shown in Figure 5.2. The maximum photoresponse is indeed found to be at $5200 \text{ \AA}^0$ or at an energy of 2.38 eV, the band gap energy. All the following experiments are performed with illumination at $5200 \text{ \AA}^0$.

5.3 Current-Voltage Relationships

In order to establish the range of ohmic behavior in the CdS thin-film, the sample was stressed with an electric field and the current was measured. The results of Figure 5.3 show that the ohmic law holds for voltages less than 160 volts ($E = 8.4 \times 10^3 \text{ V/cm}$), while at higher potentials the current varies as a $3/2$ power of the applied voltage. The measurement was repeated for three sets of electrodes on the same evaporated film and the results were found to be consistent.

The field-dependent mobility measured by Miyaki and Onuki⁸⁰ for single crystals of CdS is a decreasing function of the field strength for fields greater than 1.3×10^3 volts/cm. This type of behavior is thought to arise from electron-phonon interaction due to the piezoelectric property of CdS. This type of mobility dependence is clearly not the case here, as the results of Figure 5.3 suggest a field dependent mobility of the type

$$\mu = \mu_0 \left(1 + \frac{V}{V_c}\right)^{\frac{1}{2}}$$

where V_c is a critical voltage. In this case it appears to be 160 volts.

Matare⁸¹ has studied the effect of potentials applied to grain boundaries and has found that the number of charges in the grain boundary states q is given by the relation

$$q = \frac{q_0}{2} \left\{ 1 + \left[1 + \frac{eV}{N_1 \phi} \right]^{\frac{1}{2}} \right\}$$

Figure 5.1 Apparatus for measuring the photoresponse

Figure 5.2 Spectral response of CdS film

Figure 5.3 V-I relation for CdS thin-film

where q_0 is the grain boundary charge at equilibrium, ϕ is the potential barrier height and V_e is the potential applied across the grain boundary. The potential barrier for a polycrystalline material was defined in Chapter IV as

$$\phi = kT \ln \left[\frac{n_1}{n_2} \right]$$

The free carrier density n_2 in the grain boundary is related to the charge in the boundary by a constant, so that, $n_2 = \gamma q$. The mobility (equation 2, Ch IV) can now be written as

$$\mu = \frac{e \langle v \rangle \gamma q_0 \left[1 + (1 + eV_e / \phi)^{1/2} \right]}{8N_1 kT n_1}$$

$$= \frac{\mu_0}{2} \left[1 + \left(1 + \frac{eV}{N_1 \phi} \right)^{1/2} \right]$$

1.

Here V is the potential applied to the sample and N_1 is the number of potential barriers in the total conduction path. This result shows no voltage dependence at low applied potentials, but a $\frac{1}{2}$ power dependence of mobility is evident when the applied potential per barrier exceeds the equilibrium potential barrier. To correlate this expression with the data of Figure 5.3 one must consider first the significance of V_e . Assuming that the applied potential V is dropped primarily over the potential barriers, one can compute V_e from the total applied voltage by dividing it by the number of crystallites in the conducting path. From electron microscopy studies of the evaporated CdS films (Appendix B) it is established that the average crystallite size is approximately $1000 \text{ \AA}$. The conduction path length for the sample of Figure 5.2 is 0.019 cm . This indicates the presence of 1.9×10^3 barrier potentials in the conduction path. It was noted in Chapter IV

that the barrier potential was determined from the mobility variation with temperature to be 0.08 eV. The onset of the 3/2 power law for current in Figure 5.2 appears at 160 volts. This yields a critical value of V_e of $(160)/(1.9 \times 10^3) = 0.084$ volts which is in close agreement with the barrier potential determined on the basis of mobility variation with temperature (see Figure 4.10).

On the basis of this argument the V-I relationship would be given by

$$I = \frac{n_o e \mu t}{2(a/b)} \left[1 + \left(1 + \frac{eV}{N_1 \phi} \right)^{1/2} \right] V = G_o \left[1 + \left(1 + \frac{eV}{N_1 \phi} \right)^{1/2} \right] V \quad 2.$$

This curve is computed with the value of G_o determined at 10 volts, with $\phi = 0.084$ volts and $N_1 = 1.9 \times 10^3$. It is plotted in Figure 5.3 for comparison with the experimental results.

5.4 Temperature Dependence of Conductivity

To explore the behavior of the semiconducting film as a function of temperature and to ascertain the existence and location of defect levels in the band gap, the conductivity of the thin-film sample was studied under dark conditions and at 50 volts. The results of this experiment are shown in Figure 5.4 where the conductivity is shown to decrease over several decades while the temperature of the sample was decreased from 350° K to 130° K. Several activation energies are evident in this curve. In analyzing the data, the conductivity is written as

$$\sigma = ne\mu$$

The mobility μ is represented by the expression discussed in Chapter IV,

$$\mu = \mu_o e^{-\phi/kT}$$

Figure 5.4 Dark conductivity as a function of temperature

The variation of conductivity reflects the variation of both the mobility and free electron concentration with temperature. For the dark condition, the shallow donors are assumed to be ionized and the following expression is assumed to hold:

$$n + \sum_i n_{ti} = N_D \quad 3.$$

As the experiment is performed slowly so that thermal equilibrium is valid at all times, the trapped electron densities can be expressed accordingly as

$$\sum_i n_{ti} = \sum_i \frac{n N_{ti}}{n + n_i} \quad 4.$$

Generally, levels below the Fermi level will be full of electrons while those above will be nearly empty. The occupation of the various defect levels will change as the Fermi level passes through them. It is a valid assumption to let $n_i \gg n$, where n_i represents the value of the electron concentration when the Fermi level is at the i^{th} defect level. Equation 3 can then be written as

$$n = \frac{N_D}{1 + \sum_i \frac{N_{ti}}{N_c} \exp [(E_c - E_{ti})/kT]} \quad 5.$$

The effect of temperature becomes evident as the exponential term in the denominator becomes increased in turn and each defect level becomes significant in turn. The expression for conductivity then becomes

$$\sigma = \frac{N_D e \mu_o \exp [-\phi/kT]}{1 + \sum_i \frac{N_{ti}}{N_c} \exp [(E_c - E_{ti})/kT]} \quad 6.$$

In interpreting the results of Figure 5.4, $\phi = 0.084$ eV is used and assumed to be constant for the range of temperature encountered in this data. The data of Figure 5.4 and equation 6 then yield the defect level energies of 0.36, 0.24, 0.14, 0.06 and 0.029 eV below the conduction band edge.*

5.5 Conductivity as a Function of Light

For an illuminated sample a different temperature variation is observed. While the conductivity decreases monotonically for a sample under dark conditions, the application of light results in an initial decrease in conductivity to a minimum value, followed by an increase in conductivity according to a $T^{-3/2}$ law. This latter behavior is usually associated with the lattice scattering contribution to mobility and is observed at low temperatures. The mobility was found to be independent of illumination at room temperature and the conductivity was assumed to be controlled by the grain boundary potential contribution. For illuminated samples of CdS thin-film it is necessary to consider a more complicated temperature variation than indicated in equation 6. On the other hand, the free electron density is now controlled by the light generated carriers so that $n = g_L \tau_n \gg N_D$. The conductivity variation must be expressed as

$$\sigma = e g_L \tau_n \mu$$

The results of Figure 5.5 must be interpreted to include the proper mobility and electron lifetime variation.

It is interesting to note the results of Miksig et. al.¹⁸ at this point. Their measured variation of transconductance of a CdS T.F.T. with temperature is shown in Figure 5.6. The transconductance is found to be a function of temperature according to a number of characteristic energies. The series of curves is generated by changing the gate potential thus modifying the surface potential and the location of the traps in relation

*The accuracy of these results is estimated to be $\pm 10\%$.

Figure 5.5 Conductivity as a function of temperature and light. The relative light intensities corresponding to the values of I_s are given in Figure C.2

Figure 5.6 Unit 5; Temperature dependence of transconductance (ref. 10)

to the quasi-Fermi level in the surface. The obvious similarity to the results of Figure 5.5 strengthens the conclusion that we are observing effects in the semiconductor. In fact the thin-film thickness of Unit 5 in Figure 5.6 is $4000 \text{ \AA}$. The film studies in our experiment was $2000 \text{ \AA}$ thick. As we observe similar temperature behavior with very similar effective trapping energies, we can make a significant conclusion. Since both experiments use optically polished glass substrates, the only difference is that our samples are not covered with an oxide. Hence we can conclude that the oxide contributes relatively little to the trapping character of the film structure. In fact, the nature of the traps is due completely to the thin-film material.

5.6 Photosensitivity of CdS Thin-Film

Figure 5.7 shows the dependence of photocurrent on the relative light intensity for a number of different temperatures. The power law usually employed to describe photocurrent as a function of light intensity was neither the linear nor the half-power law often predicted for photoconducting materials¹, and indeed by the calculations in Chapter III. Instead, the photosensitivity varied from a dependence of $g_L^{0.22}$ at 333° K, to $g_L^{0.33}$ at 273° K, to $g_L^{0.75}$ at 131° K.

A number of theories have been proposed to explain the sublinear behavior of photocurrents. One is the proposal that recombination takes place by means of impact⁸² or Auger^{83,66} processes where the energy released in the recombination process is transferred to a third carrier. Then

$$\frac{d(\Delta n)}{dt} = g_L - k(\Delta n)^3$$

and the steady-state concentration is

$$\Delta n_{st} = (g_L/k)^{1/3}$$

To be sure of this effect one must be able to detect the resultant "hot" carrier.

Moss⁸⁴ considers the problem where radiation is strongly absorbed on the surface of a semiconductor and where, in addition, strong surface recombination exists. In this case this author derives a $g_L^{1/3}$ dependence at high intensities. This result is valid for materials thicker than several diffusion lengths, so that a condition of $n = 0$ at sufficient depth can be assumed.

Tabak and Warter⁸⁵ also discuss the relation between sublinear photocurrents and surface recombination in CdS crystals. They assume that recombination in the bulk is monomolecular, with no important hole or electron traps in the bulk. Reducing the problem to one dimension with photocurrent flowing parallel to the illuminated plane, they show that at low light levels only the monomolecular bulk recombination is important and the photoresponse is a linear function of intensity. At intermediate light levels

Figure 5.7 Photocurrent variation with temperature

the bimolecular surface recombination dominates and the response drops off towards a square-root dependence of the photocurrent on the light intensity. At high light levels the surface becomes a sink for hole-electron pairs. The kinetics of the sink are unimportant. What matters is that the surface recombination clamps the concentration of the carriers at the surface to a level much lower than the peak concentration in the bulk. The photocurrent is again a linear function of the light intensity but with a sensitivity much lower than that at low light levels. This model, like Moss's model, assumes strong surface absorption of light and a thick enough crystal so that the injected carriers die away to zero deep in the bulk.

In our experiments we satisfy neither of these conditions. First the samples of CdS films are thin enough to transmit sufficient light so that when irradiated at the band gap energy ($\lambda \simeq 5200 \text{ \AA}^0$) the sample is almost uniformly illuminated throughout its thickness. A typical absorption, reflection, and transmission spectrum of our sample is given in Figure 5.8. Secondly, our samples are thin so that the assumption of a bulk at equilibrium is not valid. In addition we have a significant density of hole and electron traps or recombination centres. Our material is also polycrystalline so that significant recombination and trapping may take place at the intercrystalline barriers. The crystallite size is of the order of $1000 \text{ \AA}^0$. With an interelectrode spacing of $190 \mu\text{m}$ we have in the neighborhood of 2×10^3 intercrystalline barriers in the conduction path. We can calculate a typical ambipolar diffusion length for this material from $L = ((2kT/e)\mu_p \tau_p)^{1/2}$. With $\mu_p = 10 \text{ cm}^2/\text{v-sec}$ and $\tau_p = 10^{-6}$ seconds, $L = 7 \mu\text{m}$. If the intercrystallite regions are regions of high trap density, the diffusion profiles should be flat in the crystallites so that we may consider the voltage effect of the crystallite and barriers together, modelling the material as a uniform semiconductor, with negligible diffusion currents.

Figure 5.8 Typical absorption, transmission and reflection spectrum for a CdS thin-film of 2000 Å thickness.

Rose⁸⁶ suggests that sublinear photoresponses can arise if there exists an exponential trap distribution of the type

$$N_t(E) = A \exp \left[-(E_c - E_t)/kT_1 \right]$$

where T_1 is a formal parameter which is adjusted to make the trap density vary more or less rapidly with energy. As the Fermi level is raised through this distribution, trapping centres are converted to recombination centres. As the number of recombination states increases, the lifetime decreases, so that n increases at some sub-linear function of g_L . The functional relation derived by Rose is

$$n = \left[\frac{g_L N_c T/T_1}{kT_1 A v S_n} \right]^{T_1/(T+T_1)}$$

and since $T_1 \gg T$ the exponent lies between 0.5 and 1.0.

On the basis of the uncertainty of the location of the deep level one can postulate an exponential deep defect level distribution through which the quasi-Fermi level for holes moves as the light intensity is increased. If the distribution is described as

$$P_t = B \exp [-(E-E_v)/kT_2]$$

the hole density in these levels is given approximately by

$$\begin{aligned} p_t &= kT_2 B \exp [-(E_{fp}-E_v)/kT_2] \\ &= \frac{kT_2 B p^{T/T_2}}{N_v^{T/T_2}} \end{aligned}$$

Substituting this into the expression for the steady-state electron density we have

$$n = g_L \tau_n = \frac{g_L N_v^{T/T_2}}{a_1 kT_2 B p^{T/T_2}}$$

If τ_p is constant $p = g_L \tau_p$ and

$$n = \frac{N_v^{T/T_2} g_L^{(1-T/T_2)}}{a_1 kT_2 B \tau_p^{T/T_2}} \propto g_L^\alpha$$

where α denotes the exponent $(T_2 - T)/T_2$. A comparison of this result with the experimental slopes measured in Figure 5.7 is shown in Figure 5.9.

This result indicates that in addition to the shallow levels that exist in the CdS material a distribution of deep levels may exist. When it is approximated by an exponential distribution one can predict a photosensitivity variation with temperature, which is in good agreement with the observed experimental results.

Figure 5.9 Comparison of theory and experimental results for $\alpha = \frac{T_2 - T}{T_2}$ and $1-\beta$; where $n \propto g_L^\alpha$, and $\tau_n \propto g_L^{-\beta}$ define α and β
(from section 6.1)

The limiting case for high and low temperature may be simply worked out even in the case of a single discrete deep trapping level. Considering the configurations in Figure 5.10, it is evident that when the quasi-Fermi level for holes moves through the deep level its hole population changes. While it is partially full of holes at high temperatures it is completely filled at low temperatures. The quasi-Fermi levels shown in Figure 5.10

Figure 5.10 Schematic location of quasi-Fermi level for holes at different temperatures.

represent their location when high level injection of electrons is valid. In Figure 5.10(a) motion of the E_{fp} due to increased light intensity changes the population of defect level P_t significantly, while in Figure 5.10(b) the defect level P_t is essentially full of holes. Hence $\tau_n = (a_1 p_t)^{-1}$ is a stronger function of light in the high temperature case than in the low temperature one.

In Chapter III, the trapped hole concentration was referred to as

$$p_t = \frac{P_t(b_3 + a_4 p)}{a_1 n + a_4 p + b_2 + b_3}$$

where

$$b_2 = a_4 N_v \exp[-(E_{tp} - E_v)/kT]$$

and
$$b_3 = a_1 N_c \exp[-(E_c - E_{tp})/kT]$$

Both b_2 and b_3 will be small at low temperatures so that

$$p_t = \frac{a_4 p P_t}{a_1 n + a_4 p}$$

With E_{fp} close to the valence band, $p \approx n$ and p_t is nearly constant. Therefore

$$n = g_L \tau_n = \frac{g_L}{a_1 p_t} = \frac{g_L (a_1 + a_4)}{a_4 p_t}$$

This is a linear function of g_L and represents the low temperature limit of the photoresponse.

At high temperatures the deep defect level interacts strongly with the valence band so that its population is determined by the expression

$$p_t = \frac{a_4 p_t}{a_4 p + b_2} \simeq \frac{a_4 p_t}{b_2}.$$

With $p = g_L \tau_p$ and τ_p constant because the recombination time for holes is governed by $(P_t - p_t)$, one concludes that

$$n = g_L \tau_n = \frac{g_L b_2}{a_1 g_L} = \text{constant}$$

This represents the high temperature limit of photoconductivity.

Stockman⁸⁷ has dealt in some detail with the dependence of photocurrents on the excitation strength and concludes that a large number of power relations between electron density and generation rate is possible. In fact, in the case where acceptor-like traps are unoccupied with electrons and donor type recombination centres are likewise empty, while acceptor type recombination centres are essentially filled with electrons, the electron concentration is indeed an independent function of generation rate. This can be visualized physically by saying that the quasi-Fermi level for the holes when moving downward with increasing light intensity moves through a defect level, discharging this level, and thus increasing the number of recombination centres. Hence τ_n is a strong function of g_L causing $n = g_L \tau_n$ to be a weak function of g_L .

Chapter VI

DYNAMICS OF THE PHOTORESPONSE

6.0 Introduction

The dynamics of the photoconductor response have been studied in some detail to explain the trapping and recombination mechanisms in silicon,^{88,89} CdS crystals³⁶ and CdS thin-films.^{90,91} All these works deal with the evaluation of the depth and density of shallow and deep centres native to, or implanted in the material. Theoretical expressions for the decay of photocurrents have been proposed.⁹²⁻⁹⁴ Most of them deal with linearized models, where a constant minority or majority carrier lifetime is assumed, to make the problem tractable. In addition it is usually assumed that the traps are either not full or completely full so that certain simplifying assumptions can be made about their population density. In this chapter the problem of photoconductive decay will be considered where the lifetime for electrons, the current carrying species in CdS, is not assumed constant, and where the population of the levels is allowed to vary without restriction.

In the preceding chapter it was established that the CdS thin-film contains a number of defect levels in the band gap near the conduction band. Some of the parameters associated with these defects will be determined from photoconductive decay and photoconductive rise experiments. A sample of thin-film CdS, 2000 Å^o thick, provided with aluminum electrodes, by means of which contact is made to the semiconductor, is illuminated with 5200 Å^o light. A mechanical shutter is used to interrupt the beam of light incident on the sample. The rise and decay curves can be

observed by measuring the current flow through a 5000 ohm resistor in series with the sample. The circuit used is that of Figure 5.1. The power supply V is used to supply a dark current of $1\ \mu\text{A}$. The speed of the shutter was measured by means of photomultiplier tube. It was found to open or close in 1 millisecond. This speed was found to be sufficient as the fastest rise and decay times measured were in the neighborhood of 10 milliseconds. A typical set of photoresponse curves is given in Figure 6.1. These were obtained by illumination with successively increasing light intensities. It is immediately obvious that the rise and decay are not symmetrical. In fact, while the rise of photocurrent looks nearly exponential, the decay appears to have an initially fast part followed by a long slowly decaying tail. It also appears that a steady state is not quite reached during more than 3 seconds of illumination. On the other hand, the decay to the initial dark current value took several minutes for low levels of illumination and up to an hour for high levels of illumination.

Figure 6.1 Typical photoresponse curves; horizontal scale = 0.5 sec/cm, vertical scale = $1\ \mu\text{A/cm}$, $V_{\text{DC}} = 50\ \text{volts}$.

We will attempt to explain some of the details of the photoresponse using a simplified version of the model first suggested in Figure 3.1. We assume that recombination of electrons occurs only through the deep centre while the shallow centre acts as a trap. In spite of the fact that we have shown that several defect levels exist near the conduction band in the CdS thin-film we find that we can adequately model the dynamics of the photoresponse using the simplified model shown in Figure 6.2

Figure 6.2 Simplified model for calculation of the dynamics of the photoresponse

6.1 Time Constant of the Photodecay

Considering the transition rates in Figure 6.2, it is evident that in the steady state the trapping level is in equilibrium with the conduction band. This equilibrium is not disturbed until the free electron concentration in the conduction band is reduced. When this occurs, the emission rate from the trap exceeds the capture rate of electrons from the conduction band and the recombination of electrons through the deep level competes with a net emission of carriers from the trap. When the generation of carriers due to light is interrupted, the photocurrent decay proceeds initially according to the life time for the free

electrons and at a later time, proceeds with a net time constant which results from the competing mechanisms of recombination current and thermal emission for the trap. We can experimentally determine the initial rate of decay of photocurrent. This result is shown in Figure 6.3. We also show the calculated values for derived from the data of Figure 5.5. We note the reasonable agreement at high temperatures. The assumed mobility variation with temperature is also shown in Figure 6.3. Comparing these results with those of Figures 5.7 and 5.10, leads to the conclusion that the assumed model for mobility is quite valid. Denoting the conductivity dependence on g_L by $\sigma \propto g_L^\alpha$ and the lifetime dependence $\tau_n \propto g_L^{-\beta}$, leads to the conclusion that $\alpha + \beta = 1$ (for μ independent of g_L). At 125° K , $\alpha + \beta = 1.16$; at 200° K , $\alpha + \beta = 1.04$, and at 333° K , $\alpha + \beta = 1.03$.

6.2 Analysis of the Photoconductive Decay

If we refer to the steady state calculations made in Chapter III, in particular the results shown in Figure 3.4 and 3.5, we note that, depending on the initial steady state conditions, two different types of decay are possible. If the density of the trapping and recombination centres are low compared to the equilibrium electron density, these levels will be filled completely in the steady state case and the time constants for decay will be constant throughout most of the decay. In fact τ_n will be given by $(a_1 P_t)^{-1}$ and the decay will proceed according to a simple exponential law

$$n = (n_{st} - n_o) e^{-a_1 P_t t} + n_o \quad 1.$$

where the n_o and n_{st} are the equilibrium and steady state electron densities, respectively.

Figure 6.3 Initial time constant measurement compared to τ_n calculated from conductivity

A different and more complicated type of decay may occur when the trap and recombination level densities exceed the equilibrium density and possibly the steady state density of charge carriers. Referring, for example, to Figure 3.5 we note that decay from an initial steady state electron concentration in the neighborhood of 10^{15} cm^{-3} would also cause p_t to decrease, causing an increase in the time constant for electrons. In addition, recombination of electrons would cause the emission rate of electrons from the trapping level to exceed the capture rate. The net effect is an emptying of the trap into the conduction band which further decreases the rate of free carrier decay from the conduction band. We will model this phenomenon in the following paragraphs.

The model of Figure 6.2 suggests that the equations which describe the decay process are

$$\frac{dn}{dt} = -a_1 n p_t - a_7 n (N_t - n_t) + b_5 n_t \quad 2.$$

$$\frac{dn_t}{dt} = -b_5 n_t + a_7 n (N_t - n_t) \quad 3.$$

If we assume we have high level injection so that $n \gg n_0$, etc., we can neglect the equilibrium values and allow the above quantities to be the off-equilibrium values. From Figure 3.5 we see that p is usually very small so that the charge neutrality for high level excitation is given

$$p_t = n + n_t \quad 4.$$

We can now rewrite equations 2 and 3 as

$$\frac{dn}{dt} = -a_1 n (n + n_t) + b_5 n_t - a_7 n (N_t - n_t) \quad 5.$$

$$\frac{dn_t}{dt} = -b_5 n_t + a_7 n (N_t - n_t) \quad 6.$$

When written in this form we cannot define any sort of a time constant for the decay.

In the case where the trap is slow ($n > n_t \approx \text{constant}$), the decay can be represented by

$$\frac{dn}{dt} = -a_1 n^2 \quad 7.$$

The solution is

$$n = \frac{n_{st}}{a_1 n_{st} t + 1} \quad 8.$$

where n_{st} is the initial steady state electron concentration.

When significant re-emission of electrons occurs from the trap to the conduction band we would expect the decay to proceed at a slower rate, because while the electrons recombine through the deep centre, emission of electrons from the trap replenishes the conduction band concentration. And as $(a_1 p_t)^{-1}$ becomes large, the trap tends towards equilibrium with the conduction band, reducing the net emission of electrons to the conduction band.

This behavior is described by the non-linear equations 5 and 6. These can be solved using a graphical technique, similar to the phase plane method, so often applied in control system analysis. If we eliminate the variable time from equations 5 and 6, we get

$$\frac{dn}{dn_t} = \frac{-a_1 n(n + n_t)}{-b_5 n_t + a_7 n(N_t - n_t)} - 1 \quad 9.$$

We normalize the variables n and n_t in terms of the material parameters. We call

$$\begin{aligned} \xi &= n/n_1 \\ \xi_t &= n_t/n_1 \\ \alpha &= a_1/a_7 \\ \beta &= N_t/n_1 \end{aligned} \quad 10.$$

$$\begin{aligned}
 n_1 &= b_5/a_7 \\
 T &= b_5 t \\
 m &= dn/dn_t
 \end{aligned}
 \tag{10}$$

Equation 9 then becomes

$$\xi_t = \frac{\alpha \xi^2 + (m+1)\beta \xi}{(m+1)(\xi+1) - \alpha \xi}
 \tag{11}$$

and

$$\frac{d\xi}{dT} = -\alpha \xi^2 - \beta \xi + \xi \xi_t (1-\alpha) + \xi_t
 \tag{12}$$

The method of solution is as follows:

1) Equation 11 is used to compute a family of curves (isoclines) which show the relation between ξ and ξ_t during the decay.

2) Equation 12 is then used to compute the time dependence of ξ and ξ_t .

The parameters α and β play an important role. Large α means that the capture constant for the deep centre is much larger than that of the shallow trap so that the electron concentration will decay significantly before the trap and conduction band interact strongly. For small α the trap interacts strongly with the conduction band. The parameter β represents the trap concentration. A large β will give an initially faster decay rate because with β large, the steady state trapped electron density is also large, and consequently the initial decay is large.

Figure 6.4 shows a typical set of isoclines calculated for $\alpha=1$ and $\beta=10$. The graph gives the relationship between ξ and ξ_t during the decay. In Figure 6.5 we show the decay of with respect to a normalized time ($T = b_5 t$) for $\beta=10$ and

$\alpha = 0.1, 1.0$ and 10 . If we interpret the constants properly, we see that with T the same for all the curves, b_5 is constant and hence $a_7 n_1$ is also constant. Since we wish to compare the decay for the same initial value of $n(0)$, we keep a_7 and n_1 constant so that the figure illustrates the decay of electrons for different values of a_1 , the capture coefficient of the deep trap (recombination centre). Increasing α indicates increasing capture coefficients, hence a decreasing effective lifetime for the carrier. Figure 6.5 shows clearly the role of emission rate of electrons from the traps into the conduction band. Keeping the trapping parameters constant and increasing the capture constant for the recombination centre leads to a faster initial decay. Because n_t is initially in equilibrium with the conduction band, this balance is not changed until n is reduced and the recapture of electrons by the traps is reduced. In Figure 6.5 the time scale is normalized to that for $\alpha = 1$ to show more clearly the deviation from an exponential decay on a comparative basis. Since b_5 and n_{t0} are kept constant, the trap will emit electrons at the same rate in each of the illustrated cases. Since $\frac{dn}{dt} = -a_1 n n_t + \frac{dn_t}{dt}$, $\frac{dn}{dt}$ is significant when a_1 is small or α is small. Hence the effect of emission from the traps in increased degree for α going from 10 to 0.1 is clearly evident.

Figure 6.6 shows the corresponding decay of the trapped electron density with time. Here again the normalization of T has been carried out as in Figure 6.5 for reasons of comparison. It is noted that for a given T an appreciably larger amount of trapped electrons have been released for small α than for larger α , thus raising the concentration of free electrons in the conduction band. Figure 6.7 shows the effect of increased trap density on the initial decay rate of free electrons. Since $\tau_i \approx 1/a_1 n_{t0}$ one observes an increased initial

Figure 6.4 Typical isocline plot.

Figure 6.5 ξ as a function of T with curves normalized by b_5 for $\alpha = 1.0$ ($T = b_5 t$).

Figure 6.6 ξ_t as a function of T with curves normalized to b_5 for $\alpha = 1.0$

Figure 6.7 Increase in initial speed of response with increased β , $\alpha = 1$.

Figure 6.8 ξ as a function of T for different initial values of ξ ; $\alpha=1.0$, $\beta=10$.

rate for $\beta = 10$, ($\beta = N_t/n_1$) all other parameters being kept constant. Figure 6.8 shows the decay of a family of curves which would result from illumination with different intensities of light. This general shape is observed experimentally later in this chapter. This description of the photocurrent decay is qualitatively correct. Comparing the curves of Figure 6.8 with those of Figure 6.9 shows that the initial rapid decay is followed by a relatively longer decay as predicted from the non-linear type of decay.

Figure 6.9 Decay of photocurrent for different initial illuminations: vertical scale - 1 V/cm.
horizontal scale - 10 ms/cm.

In Figure 6.10 the experimental results of Figure 6.9 and the calculated values of the decay curves using the parameters $\alpha = 0.5$ and $\beta = 100$ are compared. In order to make the appropriate time conversion a value of $b_5 = 2.5$ is required. These results allow the calculation of some values that characterize the material. Attributing the major amount of trapping to the deeper centres at $E_t = 0.238$ eV lead to $n_1 = 3.88 \times 10^{14} \text{ cm}^{-3}$, which permits the calculation of a_7 and, assuming that $v_{th} = 10^7$ cm/sec, also S_{n7} the electron capture cross-section of the major trapping centre to be equal to $6.45 \times 10^{-22} \text{ cm}^2$. The capture cross-section for electrons by the recombination centre is then given by $S_{n1} = 0.55n_7 = 3.22 \times 10^{-22} \text{ cm}^2$. From the value of β one can calculate that $N_t = 3.88 \times 10^{16} \text{ cm}^{-3}$, from which the number of trapped holes, $p_t = n + n_t = n + nN_t/(n + n_1) = 3.0 \times 10^{16}$ is derived. The corresponding electron lifetime is computed to be

$$\tau_n = \frac{1}{S_{n1} v_{th} p_t} = 1.12 \times 10^{-2} \text{ seconds.}$$

The above values were computed for a high illumination value ($I_s = 5.0$ Amps.) when $n_{st} = 1.15 \times 10^{15} \text{ cm}^{-3}$. From the measurements of τ_i at room temperature $\tau_i \approx 10^{-2}$ seconds at this level of illumination. This shows a reasonable consistency in our interpretation of the dynamics of the photoconductive decay phenomenon.

6.3 Analysis of Photoconductive Rise

The rise of photoconductivity for a material represented by the model of Figure 6.2 is discussed in some detail by Ryvkin.⁸² This author deals primarily with two distinct types of trapping. The first is called α -type trapping and the second β -type trapping. In the former, equilibrium between the trapping level

Figure 6.10 Comparison of theory and experimental results for the decay of photogenerated carriers.

and the conduction band is established in a time θ which is much shorter than the lifetime τ_n . In the latter case $\tau_n \ll \theta$ and the major part of the photoconductive rise appears to occur in a time equal to τ_n , followed by a relatively small increase of considerable duration. The criteria for distinguishing between these two types of phenomena are

$$1. \text{ for } \alpha\text{-trapping } \frac{\Delta n_s}{\Delta n_{st}} \ll 1$$

$$2. \text{ for } \beta\text{-trapping } \frac{\Delta n_s}{\Delta n_{st}} \approx 1$$

Here Δn_s denotes the slow part of the rise. In Figure 6.11 a typical rise curve for the photogenerated current is shown. One notes that neither condition 1 nor 2 are satisfied.

Figure 6.11 Photoconductive rise of current.
 $V_{DC} = 50$ volts. Horizontal scale = 50 ms./cm.

In section 6.2 the decay of photocarriers was modeled by means of a non-linear decay through a single characteristic level. This is valid if one considers the fact that the decay of electrons is affected through the deep defect level which acts as a recombination centre. The shallow traps emit electrons to the conduction band at a rate that depends on the free electron concentration, which is in turn governed by τ_n .

The photoconductive rise, however, is more strongly affected by the filling of the individual trapping levels. Once τ_n is established by the trapping of holes in the deep level, the photocurrent will rise according to e^{-t/τ_n} until the first trap starts to fill and so on up through the trapping levels. We can illustrate this by the following set of equations.

$$\frac{dn}{dt} = -\frac{n}{\tau_n} - a_7 N_t n + a_7 n_1 n_t + g_L \quad 13.$$

$$\frac{dn_t}{dt} = a_7 n N_t - a_7 n_1 n_t \quad 14.$$

These equations are linear because we initially assume that $n_t \ll N_t$. By means of a Laplace transform we can derive

$$\frac{n(s)}{g_L \tau_n} = \frac{(a_7 n_1 / \tau_n)(1 + s/a_7 n_1)}{s \{s^2 + (1/\tau_n + a_7 n_1 + a_7 N_t)s + a_7 n_1 / \tau_n\}} \quad 15.$$

In the time domain the solution has the form

$$\frac{n(t)}{g_L \tau_n} = 1 - Ae^{-t/\tau_1} - Be^{-t/\tau_2} \quad 16.$$

Using the values computed from the decay curves one can calculate a result which predicts the long-time behavior quite well. The initial change in photocurrent is however not well described (Figure 6.12). It is evident that a fast shallow trap comes into play, reducing the number of free electrons by means of trapping. One can investigate the effect of two trapping levels in the following way. The equations can be written and are linear if one again assumes that the traps are not completely full so that $n_{t_i} \ll N_{t_i}$. We have then the following transfer function.

Figure 6.12 Comparison of experiment and single trap theory

$$\frac{n(s)}{g_L \tau_n} = \frac{(1/\tau_n)(s + a_{71}n_1)(s + a_{72}n_2)}{s \left\{ s^3 + s^2(a_{72}n_2 + a_{71}n_1 + \frac{1}{\tau_n} + a_{71}N_{t1} + a_{72}N_{t2}) \right.} \quad 17.$$

$$\left. + s(a_{71}a_{72}n_1n_2 + a_{71}a_{72}(N_{t1}n_2 + N_{t2}n_1)) + \frac{a_{72}n_2 + a_{71}n_1}{\tau_n} \right\} + \frac{a_{71}n_1 a_{72}n_2}{\tau_n} \}$$

This can be factored to give solutions in the time domain, of the form

$$n(t) = g_L \tau_n \left\{ 1 - Ae^{-t/\tau_1} - Be^{-t/\tau_2} - Ce^{-t/\tau_3} \right\} \quad 18.$$

A best fit to the experimental curves is computed and compared with the experimental results of Figure 6.1. It is evident that equation 18 properly describes the rise of photocurrent. In these calculations the measured value of τ_n plotted previously (Figure 6.3) was used for the appropriate intensity of illumination. It is interesting to note that as the illumination intensity is decreased and τ_n increases, the effect of the slow traps becomes more dominant in the photocurrent curve.

Figure 6.13 Comparison of experiment and best fit theoretical curves for a two trap model

Upon examination of equation 15 in some more detail for the case of high illumination where $\tau_n^{-1} \gg a_7 n_1 + a_7 N_c$, one notes that the two time constants are τ_n and $(a_7 n_1)^{-1}$. The long-time decay is governed by $\tau_t = (a_7 n_1)^{-1}$ and should be a function of temperature. In Figure 6.14 the photoresponse curves for high illumination intensity at 127° K, 295° K and 343° K are plotted. Since $n_1 = N_c \exp[(E_t - E_c)/kT]$,

$$\tau_t = \frac{1}{a_7 n_1} = \frac{\exp[(E_c - E_t)/kT]}{a_7 N_c}$$

which is a decreasing function of temperature. By comparing the value of τ_t at 127° K and at 293° K one can compute the depth

Figure 6.14 Photocurrent rise with temperature at high illumination.

of the trapping level which contributes to the slow increase in photocurrent. We find that $E_t - E_t \approx 0.03$ eV, a shallow level. This suggests that the shallow levels are relatively slow and hence play an important part in the final stages of the photo-response. On the other hand, for the decay of photocurrent the long slow decaying tail was determined by a deep trap. One can conclude that the slow behavior of the relaxation process is determined primarily by the active level nearest to the steady-state or equilibrium level.

6.4 Conclusion

It has been shown that a multitude of trapping levels exist in cadmium sulphide thin-films. Discrete levels were found near the conduction band at depths of 0.029, 0.06, 0.14, 0.24, and 0.36 eV below the conduction band. A distribution of deep levels is indicated by the steady state photoresponse dependence on temperature. The indication of the steady-state measurements suggested that the shallow levels play a primary role in trapping while the deep centre distribution controls the free electron lifetime. Illumination of the sample populates the deep levels with holes which then act as recombination centres.

The dynamic processes of photoconductivity are influenced strongly by the two sets of levels. The decay of the photo-response can be adequately modelled by assuming that these levels and distributions of defects can be represented by a single level which plays the predominant roles in the recombination and trapping mechanisms. The important result of the decay kinetics is that this process is a non-linear one. It proceeds at an initially fast rate, characterized by the small signal lifetime consistent with that level of illumination. Because the number of holes in the valence band is small, recombination occurs in the deep level after an electron is captured. This reduction in the hole population of the deep level consequently increases τ_n so that the decay proceeds at a slow rate. Because

of the sharp reduction in the free electron concentration, the capture rate of electrons from the conduction band by the trap is now exceeded by the thermal emission rate. This unbalance causes the trap to emit electrons to the conduction band thus providing a competing mechanism to the decay process. The rate of decay is thus further decreased and proceeds at a net rate of decay which is the difference between the recombination through the deep level and the replenishing of conduction band electrons from the trap. A type of quasi-equilibrium is then established which allows the decay to proceed at a relatively slow rate. This explains the initial fast part and the subsequent slow decay of photoconductivity in our samples.

The rise of photoconductivity can be modelled by a set of linear equations because we assume that the photogenerated holes are rapidly captured by the deep level. The process can then be modelled by a τ_n , which is constant for a given illumination intensity. It is found that a good fit can be made to the rise of photocurrent by using two trapping levels, one shallow and a somewhat deeper one.

While we can describe the dynamics of the photoresponse in terms of the electron lifetime and trapping parameters, the overall photoresponse time is much greater than the lifetime for electrons. For our sample, a steady-state is established in times of the order of seconds while the photo-decay to equilibrium took minutes. For the levels of illumination used in these experiments the total photoresponse time took from 2 minutes to approximately 30 minutes. This was the time required to obtain a reproducible dark current with repeated periods of illumination. Subjecting the sample to extended dark periods, for example 24 hours, causes a further slow decrease of the dark current.

The results described above are for thin-films deposited in vacuum for use in T.F.T. applications. No attempt was made to enhance the photosensitivity or to modify their properties in any way other than those inherent in the vacuum deposition process.

In the next chapter a CdS T.F.T. is studied and its stability effects will be studied and interpreted with the aid of the ideas pertaining to the photoconductive phenomena in the thin-films.

Chapter VII

T.F.T. STABILITY

7.0 Introduction

The previous experiments show that the decay rate of the photoexcitation in CdS thin-films is a very strong function of the population of the defect levels, particularly the population of the deep centre. If this centre is heavily populated, as it is under conditions of strong injection, the initial decay from the steady-state to equilibrium will proceed rapidly. However, as the electrons recombine with the holes in this level, the rate of decay continuously reduces. One can conclude from this model, that while the decrease of p_t in the deep centre contributes to the increase in τ , the re-emission of electrons from the shallow trap to the conduction band causes an additional decrease in the apparent decay rate. From the concentration vs. g_L curves (Figure 3.4 and 3.5) one concludes that at low level injection levels, where n and n_t , the majority carrier concentrations, are not significantly affected, p and p_t are strong functions of g_L . This means that the recombination lifetime is changed by weakly illuminating the sample. Therefore changes in ambient light illumination will have a significant effect on the time constant, and hence also the frequency behavior of the CdS sample. The effect of high temperature on the apparent lifetime of carriers seems to be very small (Figure 6.3) but it does have an effect on the long term relaxation of the free carrier concentration (Figure 6.14).

The chemisorption^{63,95-98} of gases in the CdS thin-film will also cause changes in the behavior of the film. For example

O^- is absorbed at 0.9 eV below the conduction band edge.⁹⁵ In the semiconducting films this centre is well below the Fermi level and would act as a recombination centre. Any additional centre will decrease the electron time constant for the material because the number of centres for recombination is increased.⁹⁶ By annealing CdS crystals at 100° C in an oxygen ambient, the photoconductive decay constant is reduced. It is possible to remove deep levels of this type in high vacuum.⁹⁹

While the long decay to equilibrium at low levels of injection can be properly explained by the long time constant due to the low hole population of recombination centres, it does not adequately predict the long term drift of the characteristics often observed in CdS T.F.T.'s. It has been shown that oxygen absorption does play a significant role in creating recombination centres in thin-film CdS. Since T.F.T.'s employ oxides as insulating layers, it is possible that exchanges of O^- ions between the oxide and CdS takes place on a long term basis. Due to slow diffusion and small absorption cross-section⁶³ this exchange would necessarily become apparent as a surface effect, and hence be of significance in a T.F.T.

Some of the drift characteristics displayed by CdS T.F.T.'s can however be explained using the ideas about trapping developed in the previous chapters. In this chapter these aspects of T.F.T. stability will be studied.

7.1 CdS T.F.T. Fabrication

Thin-film transistors were fabricated using vacuum evaporation techniques. The devices were produced on a polished glass slide substrate. The CdS thin-film was heat treated at 350° C for 3 hours after deposition which resulted in an increased mobility ($40 \text{ cm}^2/\text{volt-second}$). The oxide used was electron beam evaporated Al_2O_3 and the aspect ratio of the T.F.T. structure was 35. The details of the fabrication are given in Appendix B. The

results of sample 547 No. 3 and No. 4 will be discussed in the following sections and the properties of the CdS thin-film which were covered in detail in the previous chapters will be used to explain some of the peculiar drift characteristics of the thin-film transistors.

7.2 T.F.T. Characteristics

In Figures 7.1 and 7.2 the T.F.T. characteristics of our sample under room lighting and strongly illuminated conditions respectively are shown. One notes the decrease in turn on voltage from 6 volts to 2 volts and the increase in maximum drain current from 6.9 to 9.5 ma when the sample is illuminated. The first change is explained by the customary reduction in surface depletion with the application of light and the second is a consequence of the optically excited carrier contributing to the number of free carriers available for conduction.

7.3 Drift of the T.F.T. Characteristics

The drift characteristics of the T.F.T.'s can be explained in terms of the trap distribution discussed in the previous chapters. Considering the sample 547 No. 3 in some detail one finds that these different drifts occur depending on the particular illumination conditions. The initial characteristics of a T.F.T. under conditions of strong illumination is shown in Figure 7.3(a) and the final characteristic at $t = 1080$ minutes is shown in Figure 7.3(b). The drain current has increased from 1.94 ma to 2.20 ma in this period of continuous operation. This trend of increasing current is opposite to the trend of decreased performance usually observed in thin-film T.F.T.'s.

vert. 1mA/div.
 hor. 5v./div.
 steps 2v.
 $g_m = 500\mu\Omega^{-1}/\text{div.}$

Figure 7.1 T.F.T. 547 No. 4; illumination at room ambient

vert. 1mA/div.
 hor. 5v./div.
 steps 2v.
 $g_m = 500\mu\Omega^{-1}/\text{div.}$

Figure 7.2 T.F.T. 547 No. 4; strong illumination

vert. $200\mu\text{A./div.}$
 hor. 2v./div.
 steps 1v.
 $g_m = 200\mu\Omega^{-1}/\text{div.}$

(a) $t = 0$

vert. $500\mu\text{A./div.}$
 hor. 2v./div.
 steps 1v.
 $g_m = 500\mu\Omega^{-1}/\text{div.}$

(b) $t = 1080$ minutes

Figure 7.3 Aging characteristics of T.F.T. 547 No. 3 under conditions of strong illumination

At illumination consistent with room ambients, a decrease in source-drain current with time, from 1.9 ma at $t = 0$, to 1.66 ma at $t = 360\text{ min.}$ occurs. If the transistor is tested under dark conditions, first of all a decreased initial current and a subsequent faster decrease of current with time takes place. This is illustrated in Figures 7.4.

vert. $200\mu\text{A.}/\text{div.}$
 hor. $2\text{v.}/\text{div.}$
 steps 1v.
 $g_m = 200\mu\Omega^{-1}/\text{div.}$

(a) $t = 0$

vert. $100\mu\text{A.}/\text{div.}$
 hor. $2\text{v.}/\text{div.}$
 steps 1v.
 $g_m = 100\mu\Omega^{-1}/\text{div.}$

(b) $t = 60$ minutes

vert. $50\mu\text{A.}/\text{div.}$
 hor. $2\text{v.}/\text{div.}$
 steps 1v.
 $g_m = 50\mu\Omega^{-1}/\text{div.}$

(c) $t = 2500$ minutes

Figure 7.4 Aging characteristic of T.F.T. 547 No. 3 under dark conditions

Figure 7.5 Summary of T.F.T. aging results

These results are summarized in Figure 7.5 where the various decay phenomena are shown together for comparison.

An interesting result is obtained on illumination of the T.F.T. with the same amount of light used in Figure 7.3(a), after reaching the 0.46 ma current level at $t = 2500$ minutes (Figure 7.4(c)). The T.F.T. operation was restored to the condition of Figure 7.3(a) by this treatment. This is shown in Figure 7.6.

Figure 7.6 Restoration of T.F.T. characteristics after aging in the dark (Figure 7.4(c)) to the illuminated condition of Figure 7.3(a)

7.4 The Role of Traps in T.F.T. Stability

The above results were all taken under continuous operating conditions. It was also noted that the T.F.T. characteristic tended to return to its original dark condition if the operation of the device was interrupted by removing the applied potentials from the electrodes. In one half hour of non-operation, the characteristic had returned to the 300 minute point of Figure 7.5 (dark conditions).

All these results indicate a trapping phenomenon consistent with that already studied for the CdS thin-film material, and can be explained with the use of the trapping model. We must however distinguish between the motion of the Fermi level through the trapping levels due to band bending by virtue of the applied gate potential and the motion of the quasi-Fermi levels for electrons and holes due to illumination. It is clear that as the bands are bent at the film surface the traps are swept through the Fermi level changing the proportion of traps above and below it, thus changing the number of electrons captured by the traps. As discussed in Chapter IV, the long term trapping proceeds at a very slow rate.

Figure 7.7 shows a schematic representation of the band structure under saturated operating conditions at low and high drain voltage and the highest gate voltage used in the measurements (9 volts). At low drain voltage levels, with the sample illuminated, the Fermi level for electrons would appear as shown in Figure 7.7. Assuming that the light generated carriers cause the Fermi level to move above the highest trap level, the trap would be effectively filled and little additional trapping will occur. This is shown by the constant I_{SD} vs. time curve in Figure 7.5 when the device is operated at low drain voltage. Under this condition the electron Fermi level changes little from a linear connection between the two metal Fermi levels, Figure 7.7(a). At high drain voltage, the device saturates because the resistive drop along the channel creates a potential which effectively creates a depletion region in the channel. This is represented by having the electron Fermi level more nearer the intrinsic level at some length along the channel. This however results in a region of high field in the channel and hence field-aided emission of electrons from the shallower traps may occur. This would explain the apparent slow rise in drain current with time at high drain voltages.

Lower levels of illumination would cause the Fermi level for electrons to appear in the midst of the trapping states so that increasingly large numbers of traps are available for slow trapping of electrons. As the Fermi level distance from the conduction band increases, deeper traps are subjected to the high field regions because the shallow ones are less populated and less field emission of carriers occurs.

This results in the increased amount of trapping observed in the results of Figure 7.5.

The return to the illuminated condition of Figure 7.3(a), after aging of the sample for more than 2500 minutes, supports the theory that the main contributing mechanism to the decay of drain current is the slow trapping. One is essentially observing the complete

Figure 7.7 Typical band bending to illustrate increased trapping with increased V_D

filling of these traps with the light-generated carriers and hence the raising of the electron Fermi level to the condition of Figure 7.7(b). Similarly, the fact that the device regains some of its surface conductivity upon removal of the applied potentials, thus allowing the traps to discharge when the surface tends to depletion, also supports this conclusion. The surface is initially depleted because a turn-on voltage of about 6 volts is required in the dark condition.

It is extremely unlikely that the drift characteristics are due to motion of ionic impurities in the Al_2O_3 . Previous examination of the C-V characteristics with this oxide showed no appreciable hysteresis.⁷⁹

7.5 Conclusions

Some conclusions can be drawn from these arguments. First, the obvious solution to the drift problem is to reduce the density of the defect levels so that trapping can be minimized. It is obvious however that this is a very difficult proposition and all evidence for single crystal and thin-film studies show the occurrence of these in some large numbers. It may be advantageous however to reduce the number of shallow traps, i.e. those found at about 0.1 to 0.15 eV below the conduction band edge. These seem to figure most prominently in the trapping and field-stimulated emission of carriers. Hence the desired result would be to bury the trap deep in the band gap by means of a suitable heat treatment, possibly one suggested by Nicholas and Woods. If the defects were found much below the Fermi level they would be completely filled and would play no role in trapping. The Fermi level on the other hand could be raised to appear above all the significant traps at all times by suitable doping of the semiconductor with a donor type impurity. Table II of Chapter I suggests that most of the Group III and Group VII elements can be incorporated by diffusion to produce shallow donors. This of course creates a problem because efficient diffusion usually requires elevated temperatures much in excess of the 200° C commonly used in the vapor deposition of CdS thin-film. Most of the attempts to incorporate impurities in CdS by diffusion are reported to take place at 800° C.⁵¹ It is however necessary to perform these diffusions at excess sulphur or Cd pressures because the sublimation of CdS begins at 980° C at atmospheric pressures.¹⁰⁰ The melting point of CdS is raised by increasing pressure from 1475° C at 10.5 atmospheres to 1750° C at 100 atmospheres.

A more suitable and a far more convenient method of doping the film would be to coevaporate the dopant at the required partial pressure during the deposition of the film.

Chapter VIII

CONCLUSIONS

8.1 Defect levels

From the variation of conductivity with temperature several defect levels were found. These were located at energies of 0.36, 0.24, 0.14, 0.06 and 0.029 eV below the conduction band. These are in close agreement with those detected by Brandhorst et al.³⁰ for thin-films of polycrystalline CdS and generally are in good agreement with those that are usually found in CdS crystals. While no direct evidence of the deep centre is evident from the dark conductivity variation, some conclusions can be drawn about the nature of this defect from the behavior of the photosensitivity with temperature. The unusual temperature variation indicates a distribution of deep levels which may be the result of a number of deep impurities inherent in the evaporation process or due to the polycrystallinity of the thin-film. The presence of the crystallite boundaries may cause a dispersion of the defect level resulting in a broad band of deep centres.

The dynamics of the photoresponse in the samples considered in this thesis are unsymmetric. That is, the turn-on and turn-off stages of the photoresponse are not controlled by the same mechanism. The assumption that the lifetime for electrons is governed by the population of holes in the deep centre or centres, has been validated and the role of this concept in describing the photoresponse curves has been shown. The non-linear nature of the photodecay curves has been identified and attributed to the fact that free electrons recombine with holes in the deep defects. As that mechanism proceeds, the lifetime for electrons in the conduction band is increased. At the same time the decay of free electrons

is balanced by emission of electrons from the shallow traps which are trying to establish a steady-state with the conduction band. These competing effects result in a very slow decay of photocurrent towards its dark state. The rise of photocurrent is a linear phenomenon because the trapped hole concentration is rapidly established thus providing a constant τ_n . The dynamics of the process are adequately modelled using two trapping levels which increase the total photoresponse time.

While the initial phases of both the photocurrent rise and decay are governed by the lifetime for electrons, the final phase of both rise and decay are dominated by slow trapping mechanisms. The speed of the photoresponse, that is the time required to reach a steady-state value, is therefore governed by the density of trapping states near the conduction band, and in particular by the trapping level found closest to the final position of the Fermi level. This leads to the conclusion that the slow part of the photoresponse is governed by shallower traps than the slow part of the decay of photocurrent.

The ideal two trap model postulated in Chapter III is useful to establish an understanding of the results that occur in photoconduction, but such a model is too complicated to manipulate easily when one is dealing with the dynamics of the photoresponse. The concept of discrete levels was useful in analyzing the phenomena, because no exact information of the deep levels is required except the fact that these generally act as recombination centres. In that case one needs to consider only the total number of effective recombination centres in the analysis.

8.2 Grain Boundaries

The effect of grain boundaries on the behavior of the CdS thin-film was found to be not particularly important. It was most strongly evident in the mobility variation with temperature. Here it led to an exponential temperature dependence derived from a concept of a potential barrier existing at the grain boundary. The

effect of carrier injection into the grain boundaries was also observed in the high field conductivity measurement for the thin-films. This resulted in a voltage dependent mobility variation once the applied potential for grain boundary equalled the potential barrier height. When the thin-film was illuminated, the mobility variation with temperatures was modified and seemed to obey the exponential law only to a critical temperature around 200° K. This indicates that as the temperature is reduced the potential barrier is also reduced until ϕ/kT becomes a constant and the commonly observed $T^{-3/2}$ mobility variation at low temperatures governs the mobility variation.

8.3 T.F.T. Drift Characteristics

The long term drift characteristics of a CdS thin-film T.F.T. were investigated. The amount of deterioration of the source-drain current was measured as a function of time. It was found that with increasing light intensity the amount of observed current deterioration was reduced. In fact, at high light levels, the source-drain current actually increased slightly with time. This was attributed to high field emission because it appeared only at high drain voltages. At a low drain voltage, the T.F.T. current remained constant with time. At room illumination the T.F.T. experienced a current decrease of 15% in about 6 hours. In the dark, the current decreased by 50% in the first 6 hours and had dropped by 70% after 40 hours. The interesting phenomenon displayed by this T.F.T. is that upon illumination of the device, while in this deteriorated state, the device characteristics were restored to their original state before aging began. This indicated that the decrease in current is due primarily to the trapping of electrons by slow traps inherent in the CdS thin-film material. Impurity ion migration in the oxide was considered not to play a role at all because the aging due to such a phenomenon could not be eliminated by the

shining of light on the sample.

Two recommendations can be made for the production of T.F.T.'s. In order to eliminate the detrimental influence of the traps in the semiconductor and any that exist at the semiconductor-oxide interface, it is advisable that the bulk equilibrium concentration be high enough so that the Fermi level is above most of these levels. If this is achieved, particularly if the device is operating in the accumulation mode, the traps will always be filled and relatively small amounts of trapping should occur. A second point which is related to the speed of response of the T.F.T. is that the deep traps which act as recombination centres should be enhanced or reduced depending on the speed requirement of the device. If a short recombination time is required, as in high frequency applications, one should prefer a high density of deep states, while the opposite is true if long recombination times are necessary. One could achieve this result by co-evaporating a suitable impurity in the material during the fabrication of the semiconducting thin-film.

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APPENDIX A

Detailed Results of Steady-State Calculations

The following graphs illustrate in more detail the dependence of the electron, hole, trapped electron and trapped hole concentrations on generation due to light for a number of different doping and trap density conditions.

Figure A.1

Figure A.2

Figure A.3

Figure A.4

Figure A.5

Figure A.6

Figure A.7

APPENDIX B

Preparation of CdS Thin-Films

B.1 Survey of Vacuum Evaporation Techniques

A number of techniques are available by which one can deposit thin-films of CdS on suitable substrates.¹⁰¹ Direct evaporation of CdS from a powdered CdS source is probably the most common technique to be tried first. The problem that it poses, though, is that the vapor pressure of sulphur is orders of magnitude higher than that of cadmium at the same temperature.¹⁰² (Figure B.1) Thus the sulphur is depleted from the source more quickly, leaving a Cd-rich source behind. Since the sulphur molecule has a higher thermal velocity than the cadmium after evaporation, it is more mobile in the gaseous form and will be lost to the container walls more quickly than the cadmium. The result of this type of evaporation is very often a Cd-rich thin-film which exhibits high conductivity ($\approx 0.1 \Omega\text{-cm}$). One generally evaporates pure CdS powder from a quartz crucible heated to between 500° and 1000° C onto a heated substrate (180° to 250° C) in a vacuum of about 10^{-5} torr.

Low resistivity films are useful in depletion-type field effect transistors but not in the enhancement type where a large bulk resistivity is required to reduce the leakage current. While low resistivity films can be obtained by deposition of a poor stoichiometric film, this method allows very little control of the film properties. The stoichiometry of the evaporated films may be improved by co-evaporating Cd and S or CdS and S. From Figure B.1 one sees that the partial pressures of Cd and S are orders of magnitudes apart at a given temperature. In order to achieve stoichiometry one should have the same vapor pressure of each component present in the reaction chamber. This means heating

the Cd source to a much higher temperature than the S.

A second method to achieve better stoichiometry is to evaporate CdS in an excess sulphur atmosphere. Sulfur by itself will deposit only at temperatures below 50°C while Cd will deposit by itself only above 200°C . At temperatures between 50 to 200°C neither Cd or S will deposit unless both elements are present to form CdS on the substrate. Hexagonal CdS is deposited for substrate temperatures between 180 and 200°C while for $T < 180^{\circ}\text{C}$ both cubic and hexagonal phases are usually present.

To obtain thin-films showing good adhesion characteristics, the material to be evaporated must be pure.¹⁰³ Commercially available precipitated CdS, ZnS or ZnSe, for instance, contain up to 10 ppm of heavy metals and between 0.1 and 0.5% of chloride and sulfate. Firing reduces the non-metallic impurities to between 100 and 500 ppm. The evaporation of this type of source is at first accompanied by sputtering and outgassing and does not give reproducible films. The films usually appear cloudy and tend to peel off the substrate. Cloudiness is often observed in films deposited from impure materials and can be attributed to the formation of oxides. Thus cloudy regions in CdS films are easily attacked by acetic acid, whereas clear CdS film remains unaffected (CdO dissolves in acetic acid and CdS does not). Peeling is most probably caused by chloride contamination. Chlorine in the starting material forms cadmium chloride during heating. The chloride has a low boiling point and is therefore deposited first, forming a layer between the CdS thin-film and the substrate. Since the chloride is hygroscopic, it will induce peeling when exposed to the atmosphere.

Although lumps of CdS crystals can be used as evaporants, sublimed crystal platelets form the best source material for preparing films since they have the desired purity and are of a convenient size. If these are not readily available, it is possible to obtain good films, which adhere well, by melting the CdS crystal in a crucible and allowing it to degass for some time.

Figure B.1 Vapor pressure of S and Cd as a function of temperature (ref. 102).

Deposition can then be controlled using a shutter that shields the substrate from the source.

The effect of substrate temperature is very marked and influences many of the properties of the deposited layers. This is illustrated by the fact that considerable color variation can be obtained by evaporating on substrates of different temperatures. Typically, CdS appears black when evaporated on a cold substrate, whereas yellow films are obtained when substrate temperatures are maintained greater than 150°C . With increased substrate temperature an increased crystallinity and crystallite size is also observed. Cold substrates (35°C) will yield crystal sizes of $0.05\ \mu\text{m}$ while at 170°C , $0.1\ \mu\text{m}$ crystallites are common. While all these variables are of interest the electrical resistivity of the evaporated films is of paramount importance and is a good indicator of the degree of stoichiometry obtained. In Figure B.2 the results of some investigations reported in the literature are summarized. While many other factors such as source temperature, evaporation rate and ambient pressure influence the final properties of the film, a general trend is evident and the film resistivity is an increasing function of substrate temperature.

B.2 Survey of Post-Deposition Treatment

A most useful way of controlling the electric properties of CdS thin-films is by means of post-evaporation heat treatment.^{18,72,101} The conductivity of the film is a strong function of its stoichiometry and this may be altered by subjecting the film to heat under specified atmospheric conditions. CdS material generally exhibits n-type conductivity due to a sulphur deficiency. Thus crystals heated in cadmium vapor at a pressure of 0.1 atmosphere have a conductivity of the order of $0.5\ (\text{ohm-cm})^{-1}$, but after heating at a pressure of 3.7 atmospheres the conductivity is of the order of $10\ (\text{ohm-cm})^{-1}$. CdS films heated in sulphur vapor become insulating with an electrical resistivity of about $10^8\ \text{ohm-cm}$.

Figure B.2 Summary of Vapor Deposition Data

Figure B.2 Summary of Vapor Deposition Data

Heat treatment in other atmospheres results in doping of the film and has been alluded to in Chapter II.

B.3 CdS Thin-Films used in this Work

Cadmium Sulphide films evaporated from a CdS source onto glass substrates at substrate temperatures of 180 to 230° C were deposited to thicknesses of 1000 Å to 3000 Å. These were studied by J.W. Robinson and A.S. Brown of Bell-Northern Research in Ottawa using electron microscopy. It was found that the films were polycrystalline with the CdS grains approximately 1000 Å in size. The hexagonal form of cadmium sulphide predominated. The CdS films were all slightly preferred in orientation with a tendency for the [103] and [004] growth directions to be perpendicular to the substrate surface. Over the range of substrate temperatures and film thicknesses used, neither temperature nor thickness influenced the grain size or the crystallographic structure of the cadmium sulphide films.

B.4 Photoconductor Sample Geometry

The electrodes used in Chapter V to study the photoconductive properties of the CdS thin-film were vacuum-evaporated in the geometry shown in Figure B.3 on thin-film CdS of 2000 Å thickness.

B.5 CdS T.F.T. Fabrication⁷⁹

The T.F.T. structures studied in Chapter VII were deposited from an ultra pure CdS source onto Pyrex brand substrates of 7059 Corning Glass, at a typical evaporation pressure of 4 to 5×10^{-6} mm Hg. The evaporation steps were the following:

Figure B.3 Electrode geometry for photoresponse measurements.

1. Deposition of Aluminum source and drain
2. Deposition of 0.5 μm of CdS thin-film at a rate of 16 $\text{\AA}/\text{second}$ with a substrate temperature of 200 $^{\circ}$ C.
3. Baking of CdS film in an argon atmosphere at 500 $^{\circ}$ C.
4. Electron beam deposition of Al_2O_3 at 11kV and 110 mA.
5. Deposition of an aluminum gate electrode.
6. Heating of finished structure in a nitrogen atmosphere at 300 $^{\circ}$ C for one hour.

APPENDIX C

Calibration of the Light Source

The results of the light calibration are summarized here. The light source consisted of a DWY - 650 watt tungsten halogen lamp powered by a Sorensen DCR 300 - 5A power supply. The detector consisted of an EGG SGD 444 photodiode described in the text of Chapter III. The optical filters were Optics Technology Inc. Spectracoat monopass filters. Neutral density filters of 0.5, 1.0, 2.0, and 3.0 nominal optical density were used to determine the linearity of the light detector (Figure C.1). Monopass filters were then used to calibrate the source to translate the power supply current into relative intensity of illumination at various wavelengths. (Figure C.2).

The spectral response of the detector is given in Figure C.3.

The optical density is related to the incident (I_i) and transmitted light (I_t) by means of the relation

$$\text{optical density} = \log_{10} \left[\frac{I_i}{I_t} \right]$$

Figure C.1 Photocell Linearity

Figure C.2 Relative Light Intensity vs. Lamp Current

Figure C.3 Spectral Response of EGG SGD 444 Photocell