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PREPARATION AND STUDY OF ELECTRO-OPTICAL PROPERTIES OF OXIDE
FILMS OF AG, CU AND THEIR ALLOYS USING THE PHOTOVOLTAIC EFFECT

by

Efstathios TSELEPIS

Submitted to the School of Graduate studies
of the University of Ottawa in partial
fulfillement of the requirements for the
degree of Doctor of Philosophy in Physics.

Department of Physics
Faculty of Science
University of Ottawa

Ἀφιερώνω τὴν δουλειὰ αὐτὴ στοὺς Γονεῖς μου

ποὺ μοῦ συμπαραστάθηκαν με' κάθε τρόπο ὅλα τὰ

χρόνια τῶν σπουδῶν μου.

to my parents

ABSTRACT

The Photovoltaic effect produced by illumination of oxide semiconductor/metal barriers was used as a probe to study certain electro-optical properties of the only materials, Ag_2O , Cu_2O and their mixed oxides, that have the Cuprite crystalline structure. Ag_2O and the mixed Ag-Cu oxides were grown by anodic oxidation, while Cu_2O was grown thermally. The Schottky junction was formed between the oxide and the metal it was grown onto.

Ag_2O film thicknesses of over 10 μm were obtained for the first time. The photovoltaic spectra taken at 300 K give a bandgap of $E_g \approx 1.42 \pm 0.02$ eV, while Ag_2O exhibits p-type conductivity. Evaporated gold on Ag_2O is Ohmic while silver, aluminum and platinum are rectifying. The barrier height of Ag, Al and Pt with Ag_2O seemed to be the same, about 0.92 ± 0.04 eV.

The semiconducting oxide films grown on Ag-Cu alloys exhibited p-type conductivity too. It was found that the mixed oxides were unstable in the presence of other oxide phases and Cu. Photovoltaic spectra taken at room temperatures illustrate the energy gap variation of the grown oxides as a function of the Cu atomic percentage in the metallic alloy.

The photovoltaic spectra of the $\text{Cu}_2\text{O}/\text{Cu}$ junction were taken at low temperatures for two types of samples :

type I, thermally grown Cu_2O films on Cu, the oxide thicknesses varying between 7 and 170 μm ,

and type II, a 2 mm thick natural growth Cu_2O single crystal.

The results were interpreted assuming exciton migration and field-induced dissociation at the semiconductor metal interface. A model has been developed to simulate the variation of the photocurrent spectra as a function of the oxide sample thickness. The excitonic diffusion length of the type I samples was found to increase as the temperature was decreased and saturate at a value of about 50 μm for temperatures below 80 K. In the Type II sample, the diffusion length of excitons increased rapidly as the temperature was decreased, due to its low impurity and defect concentration. At $T = 2$ K the diffusion length in the type II sample was of the order of 1 mm.

STATEMENT OF ORIGINALITY

Given below is a list of work done during the course of this study, which to the best of the author's knowledge, had not been previously undertaken :

- 1) Growth of micron thick Ag_2O films on Ag by anodic oxidation.
- 2) Photovoltaic response spectra of $\text{Ag}/\text{Ag}_2\text{O}/\text{Au}$ (Ohmic) cells of anodically grown Ag_2O on Ag, and determination of the barrier height for Ag, Al and Pt.
- 3) Photovoltaic response spectra of Ag-Cu micron thick mixed oxides, grown anodically on Ag-Cu alloys.
- 4) The development of a new method to measure the diffusion length (L) of excitons using the photovoltaic effect.

The above work led to the publication of 4 referred papers :

- 1) E. Tselepis, E. Fortin and A. Mysyrowicz "Exciton-mediated Photovoltaic effect in $\text{Cu}_2\text{O}/\text{Cu}$ ", to appear in Physical Review Letters, vol 59, Nov. 2nd 1987.

- 2) E. Tselepis and E. Fortin "Photovoltaic study of anodically grown oxide films on Ag-Cu alloys", accepted (July 87) in Thin Solid Films.
- 3) E. Fortin and E. Tselepis "Exciton diffusion in thin Cu_2O films" accepted (June 87) in Thin Solid Films, also to appear at the 7th International conference of thin films, to take place at New Delhi, India, in December 1987.
- 4) E. Tselepis and E. Fortin "Preparation and photovoltaic properties of anodically grown Ag_2O films", Journal of Materials Science, 21, 985, (1986).

Papers related to the above work were presented at the following conferences :

- _ 7th International conference of thin films,
New Delhi, India, December 1987.
- _ C.A.P conference, Toronto Univ., June 1987.
- _ A.C.F.A.S conference, Ottawa Univ., May 1987.
- _ C.A.P conference, Sherbrooke Univ., June 1984.
- _ Ottawa-Carleton Graduate student Symposium,
Ottawa Univ., March 1987. (oral presentation)
- _ A.P.S conference, New Orleans, March 1988
(to be presented).

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INTRODUCTION

There is increasingly growing attention and research in oxide materials due to their interesting physical properties . Oxide materials are extensively implemented in microelectronics and optoelectronics as well as in other fields , despite the fact that they usually present technological difficulties in terms of purity and defect concentration , associated with their complex structure in comparison to that of elemental and some binary compound semiconductors. The recent discovery of the high T_c rare earth copper oxide compound superconductor opens a vast new field of development and relevant applications.

In the present work the photovoltaic effect (PV) at the metal-oxide semiconductor junction (Schottky junction) was used to study some electro-optical properties of Ag_2O , Cu_2O and their alloy films, grown anodically or thermally. The growth of micrometer thick films on Cu and Ag by thermal or anodic oxidation is very convenient because :

- 1) it provides a "natural" rectifying junction at the metal oxide/metal interface which is never exposed to the atmosphere after its preparation, thus avoiding contamination problems,
- 2) mechanical stability even for very thin films, and
- 3) simplicity in the preparation and in controlling the oxide thickness which is achieved usually by the duration of the oxidation.

Ag_2O and Cu_2O are the only two compounds that have the Cuprite (M_2O) crystalline structure. A fairly large effort by the "Solar Cell" scientific community was devoted over the years to make an efficient Cu_2O cell (see review article [1]), but without significant success. The study of Ag_2O stemmed from the fact that it has an energy gap value appealing for solar cell applications [2-5] and that very little was known of its semiconducting and photovoltaic properties. The study of anodic oxidation of the Ag-Cu metallic alloys was motivated by the possibility of growing Ag-Cu mixed oxides with large concentration of Ag. So far, Ag concentrations up to 2% at. have been added to thermally grown Cu_2O [6-8].

The photovoltaic effect which will be extensively used in this work, was discovered about 150 years ago by Becquerel (in 1839). It involves the creation of a voltage following the absorption of light in an inhomogeneous material system. The three following processes are necessary for the creation of the photovoltaic effect:

- 1) generation of electrons and holes by radiation, in excess of thermal equilibrium,
- 2) separation of excess charges of opposite charge sign at some electrostatic inhomogeneity (like a metal-semiconductor or a p-n junction),
- 3) the carriers generated must be mobile and stay in their excited state longer than the time required to travel to the charge separating junction.

The variation of the photovoltaic response as a function of wavelength, sample thickness and temperature yields a wealth of information concerning the material's properties. One could determine the following:

- a) energy gap of the semiconductor and its variation with temperature,
- b) the Schottky (Metal - Semiconductor) barrier height of the semiconductor with different metals, and
- c) under certain conditions (see chapter 5) the absorption coefficient or the diffusion length of excitons and free carriers.

In this thesis chapter 1 examines the general background in oxidation techniques, the PV effect, and the metal/semiconductor junction Physics. Chapter 2 presents the experimental apparatus and techniques. In the rest of the chapters, the photovoltaic effect was utilized as a probe to study various properties of the oxides grown. The third chapter deals with the preparation and photovoltaic properties of anodic Ag_2O . The possibility of making a Schottky junction solar cell was examined. The properties of the oxide films grown by anodic oxidation on Ag-Cu alloys were studied in chapter 4. Finally, in chapter 5 a novel method is described to obtain the diffusion length of excitons in thermally grown Cu_2O films on Cu samples. That was achieved by measuring the variation of the photovoltaic current with respect to the Cu_2O film thickness. In order to confirm our results, the model developed was applied to a high

purity natural growth single Cu_2O crystal, for which the $n=1$ yellow series exciton lifetimes and diffusion coefficients were measured before [9,10].

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GENERAL BACKGROUND ON OXIDATION TECHNIQUES OF Ag , Cu AND ON PV EFFECT

In this chapter the general background relevant to all the work dealt with in this thesis is presented. Namely, Oxidation techniques used to grow samples, as well as the physics of the photovoltaic effect and metal-semiconductor junctions. Each following chapter may also include background relevant to its particular subject.

1. OXIDATION

The extensive application of oxide films in technology necessitates continuous improvement in oxidation methods which will insure the desired reproducibility and controlled properties of these films. Certain experimental techniques are well in advance of the theory in this field and in those cases the preparation of oxide films becomes to a great extent an art.

In this work two oxidation methods have been used ; thermal and anodic oxidation. Thermal oxidation is a process that is very well understood. As for anodic oxidation, even though it is simple in principle, the choice of electrolyte, the growth of good quality and of films with reproducible properties, is not obvious.

1. 1. THERMAL OXIDATION

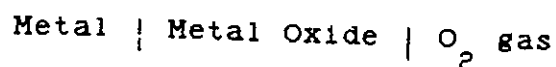
In this section the transport mechanisms through a growing P-type semiconductor oxide layer are described. More information on high temperature oxidation of metals can be found in a book by N. Birks and G.H. Meier [1] and the references therein.

1. 1. 1. Mechanisms of oxidation :

To discuss the mechanisms of oxidation at a metallic slab, let us consider the following equation :



The solid reaction product Metal Oxide will separate the two reactants as shown below ,



In order for the reaction to proceed, one or both reactants must penetrate the scale (oxide layer). Therefore, either the metal must be transported through the oxide, to the oxide - gas interface or oxygen must be transported to the oxide - metal interface and react there. Thus for the oxidation to proceed, it is necessary to assume transport process through the oxide. Wagner [2] developed the theory of " high temperature oxidation of metals" assuming that diffusion of ions across the growing oxide was the rate determining factor in the oxidation process. It was also found that when diffusion through a scale is the rate determining process, then the scale thickness increases

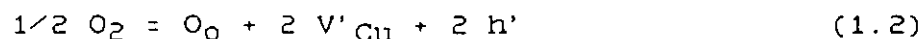
proportionally to the square root of the oxidation time. This is called the parabolic law and it is represented by the following equation :

$$\frac{\text{thickness}}{(\text{time})^{1/2}} = \text{Constant.} \quad (1.1)$$

Since most metal oxides tend to be ionic in nature, ions are considered to be the transport entities through the growing solids. Oxides can be divided into stoichiometric and non-stoichiometric crystals. By non-stoichiometric it is implied that the metal to oxygen atom ratio is not exactly that given by the chemical formula. Non-stoichiometric oxides will show either p-type or n-type behaviour. A p-type oxide semiconductor may arise from either a metal deficit or an excess of non-metal (Oxygen).

1.1.2. Thermal oxidation of Cu to Cu₂O :

Since Cu₂O was the only oxide grown thermally, let us consider briefly the oxidation mechanism of Cu to Cu₂O. Copper oxide is a p-type semiconductor forming cation vacancies and holes. The formation of these defects may be represented by the following equation :



However, it is also possible for the vacancies and holes to associate producing uncharged copper vacancies, according to :



The formation of a neutral cation vacancy may also be represented by combining the last 2 equations, as :



Mrowec et al. [3,4] have investigated the oxidation of Cu to Cu_2O at temperatures higher than 900 °C and they found that the predominant (96 to 97%) transport defect species in Cu_2O are the neutral cation vacancies mentioned earlier. Further discussion on the thermal oxidation of Cu to Cu_2O will be presented in chapter 5 (see section 5.3.3).

1.2. ANODIC OXIDATION

Anodic oxidation is basically an electrolysis process. Two metal electrodes are submerged into the electrolyte (solution) bath, and nucleation of an oxide film occurs on the anode when the appropriate voltage is applied. The nucleation occurs at preferred sites and the oxide first grows laterally and then increases in thickness. When the growing oxide forms a continuous film then the voltage required to continue the same growth rate would have to be increased with the thickness of the film. If the film is breaking up as it grows, then the voltage necessary to continue the oxide growth is the same as the initial voltage since a clean electrode surface is continuously exposed.

In the case of a continuous film, the oxide can grow only when either oxygen ions from the electrolyte and/or metal ions from the anode, migrate through the growing film. Therefore the oxide growth depends on the ionic conductance of the oxide material. It also depends on the electric field set up in the oxide and consequently on the applied voltage. Due to the voltage drop through the solution, and at the interface between the oxide and the electrolyte [5] , the potential difference across the oxide is not equal to the applied voltage between the two electrodes (see figure 1.1). To distinguish the applied voltage to that across the oxide, from the term "overvoltage" was introduced

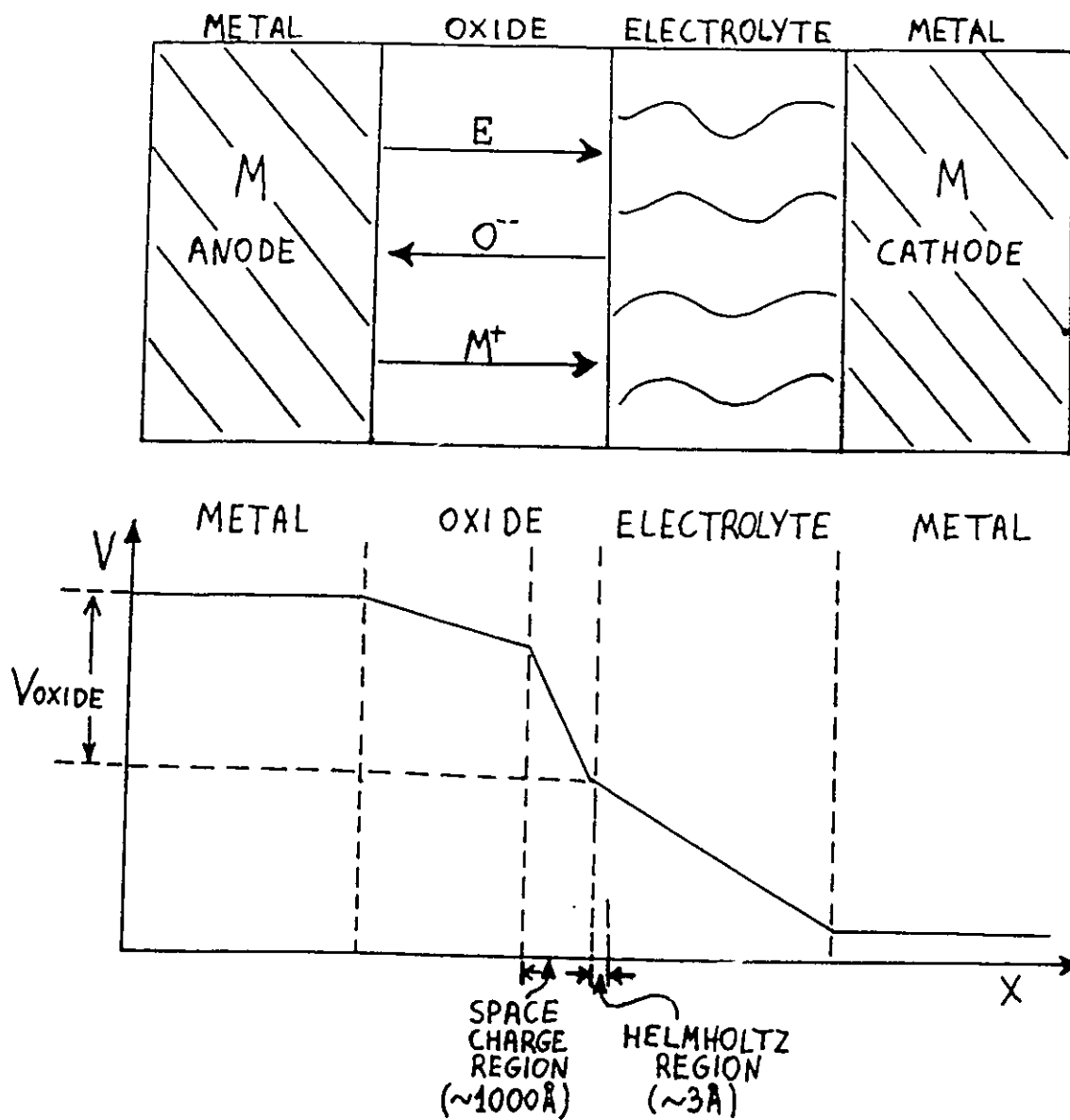


Figure 1.1: Potential difference distribution across a growing oxide film.

in the literature. This is defined as the voltage over the theoretically calculated open-circuit potential for an oxidation reaction at equilibrium. Therefore the overvoltage is a measure of the driving force available to make the oxide grow. A significant portion of the applied voltage appears across a region in the oxide next to the oxide/electrolyte interface, called the space charge region as in figure 1.1, where uncompensated impurities or trapped holes or electrons reside. The remaining applied voltage appears across the Helmholtz layer and the rest of the electrolyte.

The two basic methods for the formation of an oxide film are : 1) oxidation at constant current, and 2) at constant voltage.

1.2.1. Constant current (referred in the literature as galvanostatic condition) :

During continuous film growth at constant current each new layer of oxide thickness dD requires an extra potential dV to be added to maintain the field in the oxide and hence the current. The differential field strength dV/dD does not usually vary with the increasing thickness of the oxide.

1.2.2. Constant voltage (potentiostatic condition) :

The film growth causes a continuous decrease in the field strength. Therefore the ionic current falls. As that current falls, the rate at which the field decreases drops too. Eventually the rate of growth is so small that for any practical

purpose the thickness may be said to have reached a limiting value.

According to the above, it would seem that an oxide of any chosen thickness could be grown, given enough time. But this is not the case. In the anodic oxidation process, after a certain amount of charge has been passed, the ionic current decreases and the film growth ceases. This state is called passivation. Complete anodic passivation of a metal may be said to have occurred when either metal ions cease to emerge from the grown oxide surface and/or adsorbed anions cannot be discharged at the oxide/electrolyte interface. Under these conditions, the voltage between the anode and the electrolyte rises and either a different reaction takes over (such as metal valency change) or the voltage reaches oxygen evolution values (that is electrolysis of the water). Therefore, there is usually an upper limit to the attainable oxide thickness with this technique. This sometimes could be the limiting factor here, because in our case micrometer thick oxide samples are needed in order to have appreciable absorption of energy gap light, which is needed to investigate semiconducting and photovoltaic properties of the oxide semiconductor.

The growth mechanisms were previously discussed briefly and a few definitions were given to make it easier for the reader to follow. More information about all aspects of anodic oxidation can be found in excellent reviews by L. Young [6] and by D.A. Vermilyea [7].

1. 3. METAL-SEMICONDUCTOR JUNCTION (Schottky junction) [8, 9].

In this section the contact of a metal with a semiconductor, which results in a rectifying junction is discussed. In 1938 Schottky [10] suggested that a potential barrier could arise from stable space charge in the semiconductor alone. When a metal is making an intimate contact with the semiconductor the Fermi levels in the two materials must coincide at thermal equilibrium. Let's now examine the formation of a metal/p-type semiconductor junction (since all oxides studied in this work are p-type semiconductors) for the two following cases :

- 1) Ideal junction, and
- 2) Surface state controlled junction [11,12].

1. 3. 1. Ideal junction :

In a p-type semiconductor the Fermi level relative to that of the metal has to rise or fall by an amount equal to the absolute value of the difference of the two work functions (assuming no surface states).

a) Consider the case when the metal work function is smaller than that of the semiconductor ($\phi_m < \phi_{sc}$), figure 1.2a. Mentally, bring together the metal and the semiconductor until the distance between them is very small. At that point a flow of holes from the semiconductor into the metal is established (or of electrons from

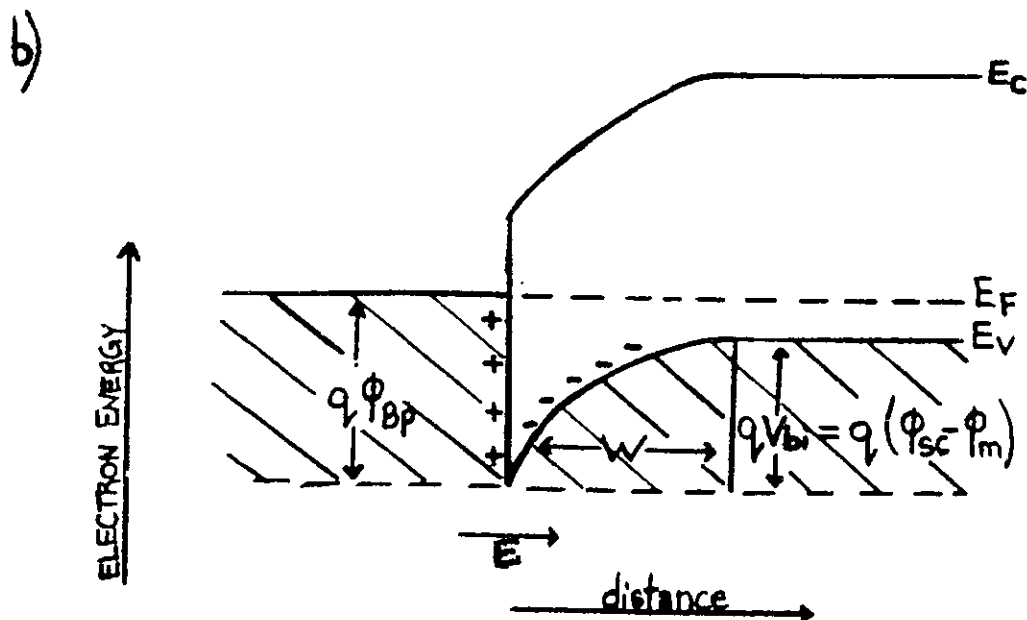
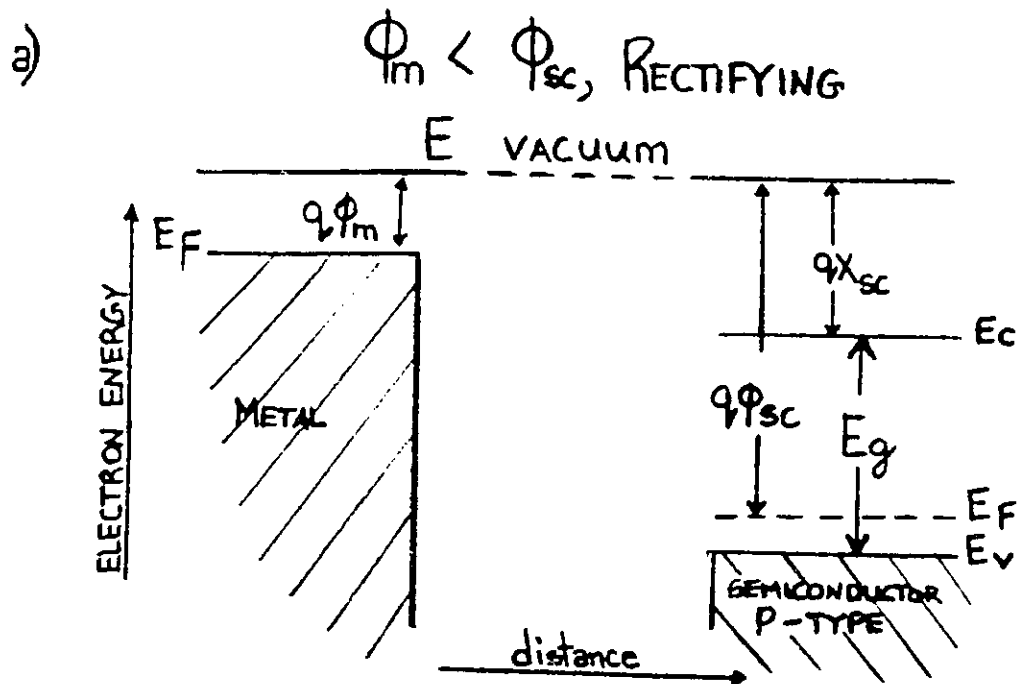


Figure 1.2: Metal/p-type semiconductor work function relation, $\phi_m < \phi_{sc}$ (rectifying contact).
a) non-equilibrium condition (separated by some distance)
b) equilibrium (intimate contact)

the metal into the semiconductor). The transfer of holes creates a region in the semiconductor that is depleted of holes and hence bears a negative space charge (called depletion region) due to uncompensated acceptor levels. On the metal side, the surface bears a positive charge. The charge densities in the semiconductor and the metal surface produce an electric field E located almost entirely in the semiconductor depletion region. The electric field E corresponds to a gradient of electrostatic potential and to a hole potential energy across the depletion layer as shown in figure 1.2a. As the distance between the metal and the semiconductor vanishes the limiting case is obtained, figure 1.2b, where the value of the barrier height $q\phi_{bp}$ (neglecting the image force lowering , which is called the Schottky effect) is given by :

$$q\phi_{bp} = E_g - q(\phi_m - X_{sc}) \quad (1.5)$$

where : qX_{sc} is the electron affinity measured from the bottom of the conduction band to the vacuum level.

E_g is the energy gap.

b) If $\phi_m > \phi_{sc}$, figure 1.3, then there is no barrier to the current flow of holes and the contact is considered ohmic.

$$\phi_m > \phi_{sc}, \text{ Ohmic}$$

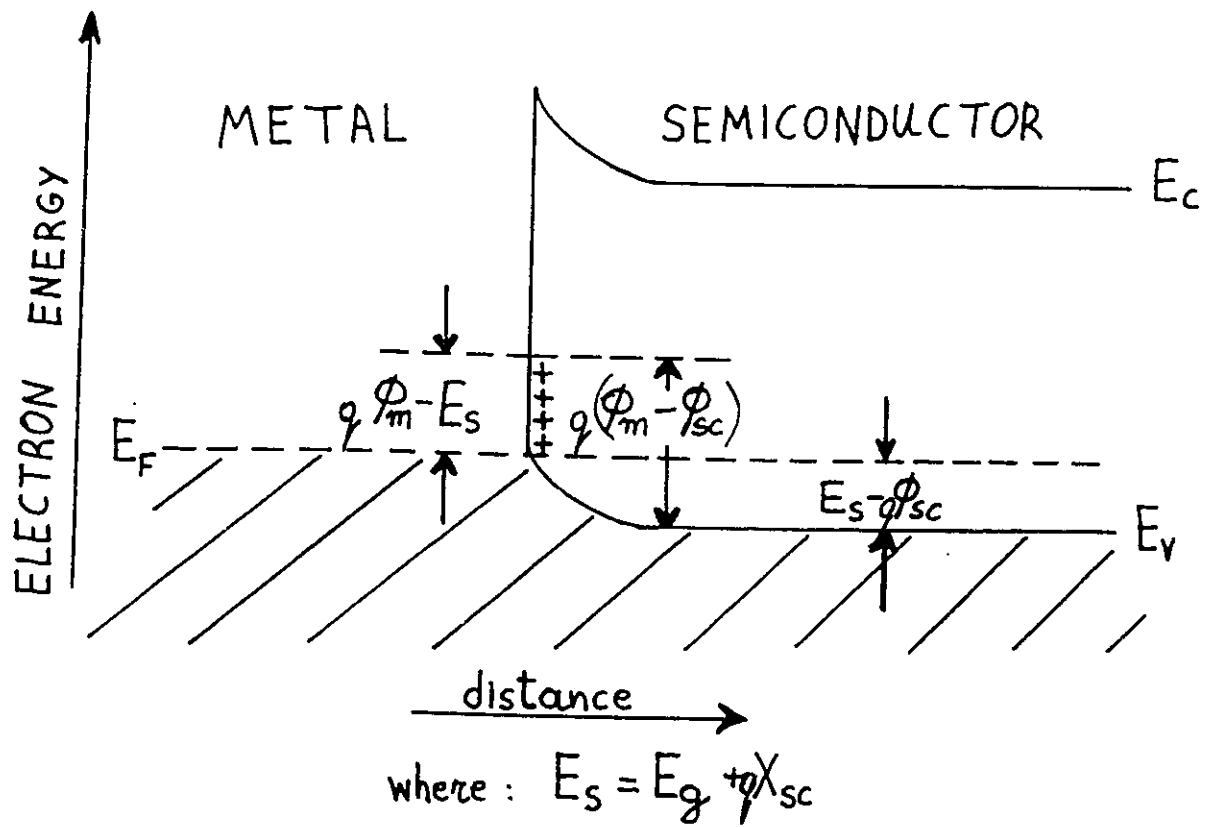


Figure 1.3: Metal/p-type semiconductor work function relation, $\phi_m > \phi_{sc}$ (Ohmic contact).

The reverse of all the above holds for a n-type semiconductor. That is, if $\phi_m > \phi_{sc}$ the junction is rectifying and if $\phi_m < \phi_{sc}$ then the junction is ohmic.

1.3.2. Surface state controlled junction :

a) Surface states and their effect at the semiconductor surface :

Surface states arise due to the interruption of the periodic lattice structure at the surface of the semiconductor crystal, introducing energy levels in the forbidden gap. The wavefunction for such states is localized in space near the surface. Historically, surface states have been classified into fast and slow states [13]. The fast states are associated with the surface states of the semiconductor and exchange charge rapidly with the conduction and valence bands of the semiconductor (in 10^{-6} sec or less). The surface properties of a particular crystal will therefore depend on the density and energy distribution of the surface states.

The slow states, generally found on real crystals, are associated with adsorbed species at the semiconductor surface. The transition times with the bulk semiconductor are long (of the order of seconds). Surface states carry charge in a way similar to donor and acceptor states of a semiconductor. In the following discussion the effects of donor surface states on the junction will be considered, without inquiring as to their identity and nature.

Let's examine now the surface band structure of a p-type semiconductor with donor surface states. It is assumed that at equilibrium, all of the surface donors are ionized, having given up their electrons to acceptor states in the bulk. The result is a positive surface charge and a region of negative space charge in the bulk, the latter being due to fixed ionized acceptors. Because of the space charge, the electrostatic potential is lower in the bulk than it is at the surface, by an amount ϕ_s (ϕ_s the surface potential). This in turn means that the electron energy at the surface is lower by an amount ($e \phi_s$) than it is in the bulk. The net result is that the energy bands are bent downwards at the surface, relative to the bulk as shown in figure 1.4. Notice that the surface donor energy is above the Fermi level at the surface because, in this case, all of the surface donors are empty. Consider the case when the number of surface states is very large (so that not all of the donors are ionized) and all of which lie at roughly the same energy Δ below the conduction band edge, figure 1.5a. Electrons flow from the surface donors into the p-type semiconductor bulk until the Fermi level at the surface coincides with the surface donor energy. This means that some of the surface donors remain un-ionized (still occupied by electrons), thus fixing the position of the Fermi level at an energy Δ below the conduction band. In figure 1.5b the equilibrium case is shown, where the Fermi level is pinned at a donor surface state and it is independent of the doping in the p-type bulk.

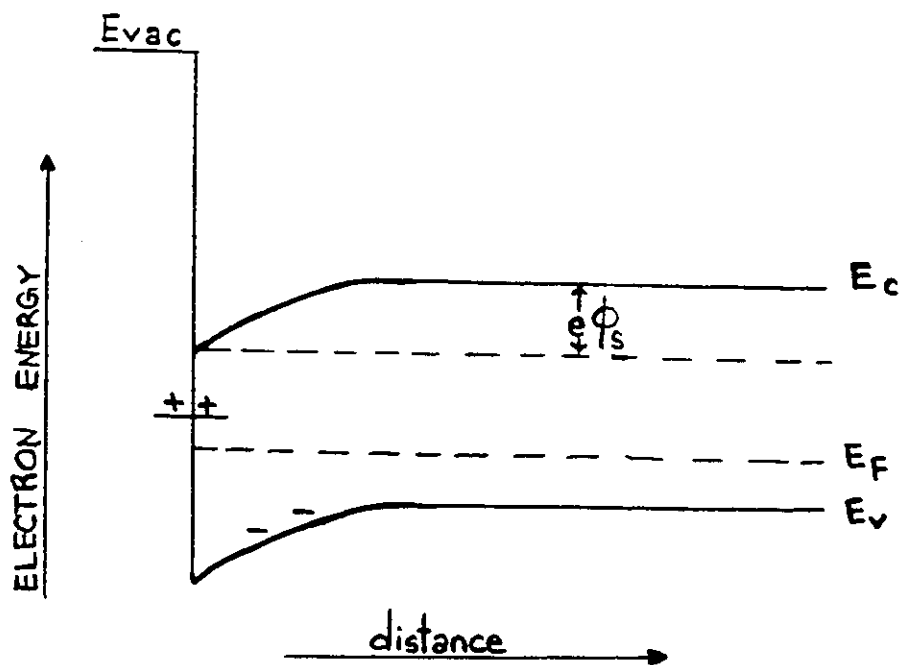


Figure 1.4: Band structure, at equilibrium, of a p-type semiconductor surface with ionized donor surface states.

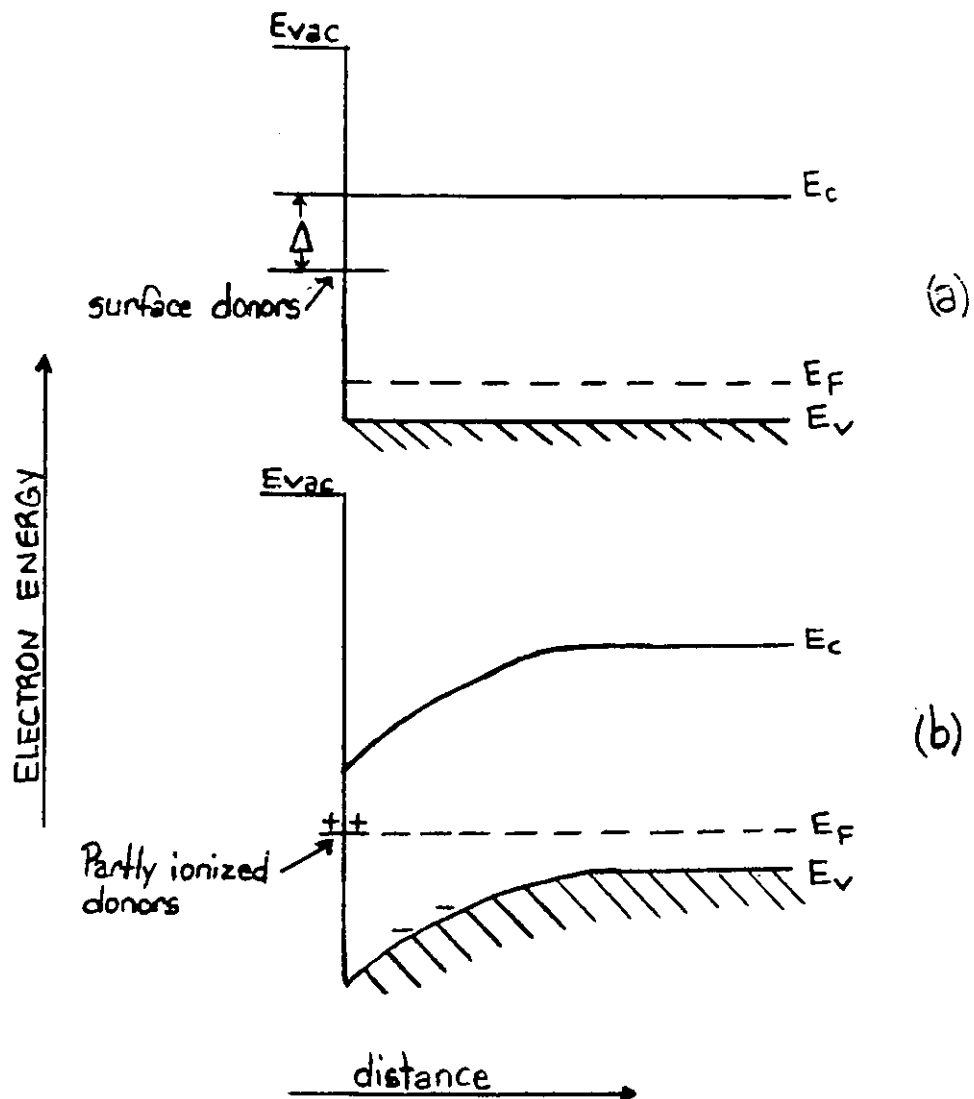


Figure 1.5: Band diagram of a p-type semiconductor with donor surface states,
a) introducing donor states at an energy Δ below the conduction band
b) band diagram after equilibrium

b) Surface state controlled M-SC junction : [11,12]

It is established now . that a well defined transition exists between the interface properties corresponding to "ionic" materials (small number of surface states) and those corresponding to "covalent" materials (large number of surface states) [14]. Apparently, in ionic semiconductors the wavefunctions of the electrons associated with the cations and anions do not overlap sufficiently to create surface states with energies near the center of the energy gap, which if present would control the barrier height. In our case, it seems that barriers on both Ag_2O and Cu_2O are surface state controlled, as will later become apparent from the results.

Assuming that the surface states are present on the semiconductor surface and that the density of these states is sufficiently large to accomodate all the surface charge resulting from the contact between the metal and the semiconductor, then the Fermi level of the metal will adjust itself to coincide with that of the semiconductor, figure 1.6. In that case, the barrier height is determined by the semiconductor surface states and the doping of the bulk semiconductor, thus making it independent of the metal work function. Hence the barrier will be equal to $E_g - \Delta$, figure 1.6.

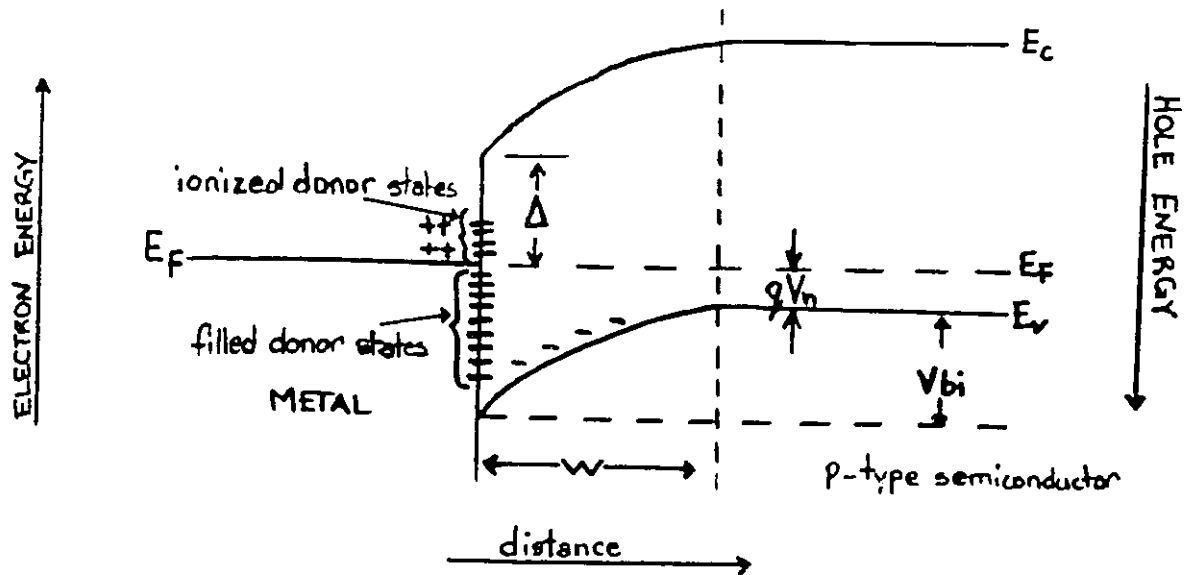


Figure 1.6: Equilibrium band diagram between a metal and a p-type semiconductor with a large number of donor surface states.

1. 4. PHOTOVOLTAIC EFFECT : [15,16]

Whenever photoexcitation creates electron-hole pairs in the vicinity of a junction, the built-in electric field separates the electrons from the holes and a potential V_{pv} is developed across the illuminated junction. This is called the photovoltaic effect and the photovoltage V_{pv} developed, appears in the same way as if a forward voltage of the same amplitude was applied across the junction.

Let's examine in more detail a metal/p-type semiconductor junction and how the photovoltaic effect is created. In figure 1.7a, a Schottky junction in the backcell configuration (light goes through the semiconductor before reaching the junction) is presented. This geometry was used in most of the experiments performed here. Consider a Schottky junction in equilibrium (figure 1.7b), with an energy barrier $e V_{bi}$ (V_{bi} is the built-in potential) and a built-in electric field E . The junction is then illuminated by radiation of energy greater than the energy gap, creating electron-hole pairs. The electrons are swept down the energy barrier by the built-in electric field in the direction opposite to the field and the holes in the field direction. The net result is the separation of the photogenerated electrons and holes, as shown in figure 1.7b. The separated carriers set-up an electric field E' in the direction opposite to the built-in electric field E . The net electric field across the junction is

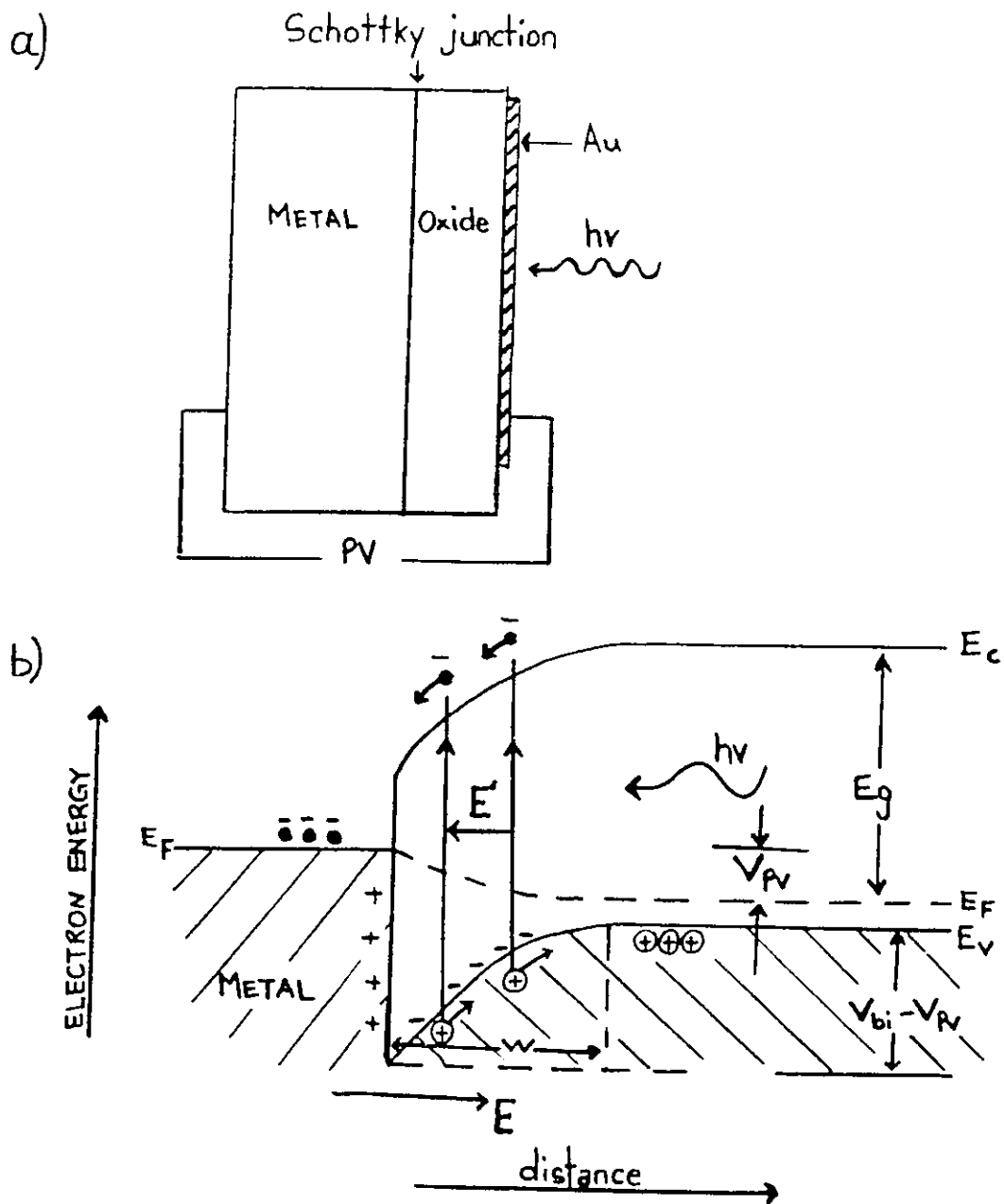


Figure 1.7 a) Schottky junction in the backcell configuration,
b) Equilibrium band diagram under illumination with light of energy larger than E_g .

now reduced to $E - E'$, which in turn means that the electrostatic potential between the metal and semiconductor is reduced to $V_{bi} - V_{pv}$, as seen by the holes from the bulk of the semiconductor. Therefore the result is the development of an open circuit voltage V_{pv} in the forward direction across the illuminated junction. Notice that the maximum photovoltage V_{pv} that can be obtained is equal to V_{bi} , which in turn cannot be larger than E_g/e . If an external conductor is added between the metal and the semiconductor, completing the circuit, a current (I_{pv}) due to light generated electron-hole pairs will be observed. The photovoltaic response measurements were made as a function of light wavelength, to be called from now on photovoltaic spectra.

The photovoltaic spectrum for an ideal metal/semiconductor system is expected to be related to the wavelength-dependent absorption coefficient (α), which is a property of the semiconductor. Such a spectrum could provide us with the optical energy gap (E_g). The energy gap's signature in a photovoltaic spectrum is the drastic decrease in the response at the energy gap value, because the semiconductor becomes essentially transparent to light of energies lower than E_g . This in turn is justified by the fact that the absorption coefficient decreases drastically too. In fact, there is an approximate method to obtain the energy gap from a photoresponse spectrum, called the Moss criterion, this method is further discussed and explained in section 3.8. For energies above the energy gap the PV response does not usually follow $\alpha(\lambda)$, because there are

artificial reasons that alter the idealized PV response. These are associated with the semiconductor material quality, homogeneity and the metal/semiconductor junction quality. In the following section the Schottky junction current-transport theories are briefly presented, in order to indicate the parameters which the photocurrent, generated by band to band excitation, in a real metal/semiconductor system depends on.

1.4.1. Current - transport theory of Schottky junctions : [17]

The current transport in a metal - semiconductor junction is mainly due to the majority carriers in contrast to a p-n junction where the minority carriers are responsible for the current. There are 3 different approaches to the current-transport mechanism :

- 1) The isothermal thermionic emission theory by Bethe [18] ,
- 2) the isothermal diffusion theory by Schottky [10] , and
- 3) a general theory developed by Crowell and Sze, [19] ,
which incorporates the above two theories.

The complete expression of current density J to voltage V characteristics , as developed by the third theory above is :

$$J = A^{**} T^2 \exp(-q\phi_{bp}/K_B T) [\exp(qV_A/K_B T) - 1] \quad (1.6)$$

Where: $A^{**} = f_p f_q A^* / (1 + f_p f_q v_r/v_d)$

ϕ_{bp} : the barrier height formed between a metal and a p-type semiconductor

V_A : the external voltage applied to the metal/semiconductor system, or the voltage (V_{pv}) observed when the semiconductor is illuminated

K_B : Boltzman's constant

A^* : effective Richardson constant, $A^* = 4\pi qm^*K_B^2/h^3$

f_p : probability of electron emission over the potential energy maximum.

f_q : theoretical ratio of the total current flow considering tunneling and quantum - mechanical reflection, to the current flow neglecting these effects.

v_r : effective recombination velocity at the potential energy maximum.

v_d : effective diffusion velocity associated with the transport of electrons from the edge of the depletion layer to the potential energy maximum.

1.4.2. Expression for the depletion layer width, w , [20]

When a metal and a semiconductor make an intimate contact, the energies of the conduction and valence bands of the semiconductor are brought into a definite relationship with the Fermi level in the metal, as shown in figure 1.8a. This relationship serves as a boundary condition on the solution of the Poisson equation in the semiconductor, in the same manner as for a p-n junction.

Under the abrupt approximation (that is when the impurity concentration changes abruptly from acceptor to donor states then one obtains an abrupt junction), in a metal/semiconductor system most of the space charge resides in the semiconductor, as shown in figure 1.8b. Therefore, the depletion width for the metal-semiconductor barrier is the same as that of the one-sided abrupt p-n junction [20] :

for $0 < x < w \Rightarrow \rho \approx q(N_A - N_D)$, and

for $x > w \Rightarrow \rho \approx 0$, $E = dV/dx = 0$, figures 1.8b, c.

Therefore the depletion width, w , is given by the following equation :

$$w = \left[\frac{2 \epsilon_s (V_{bi} - V_A - K_B T/q)}{q |N_A - N_D|} \right]^{1/2} \quad (1.7)$$

Note that, V_A can be either positive (forward bias) or negative (reverse bias).

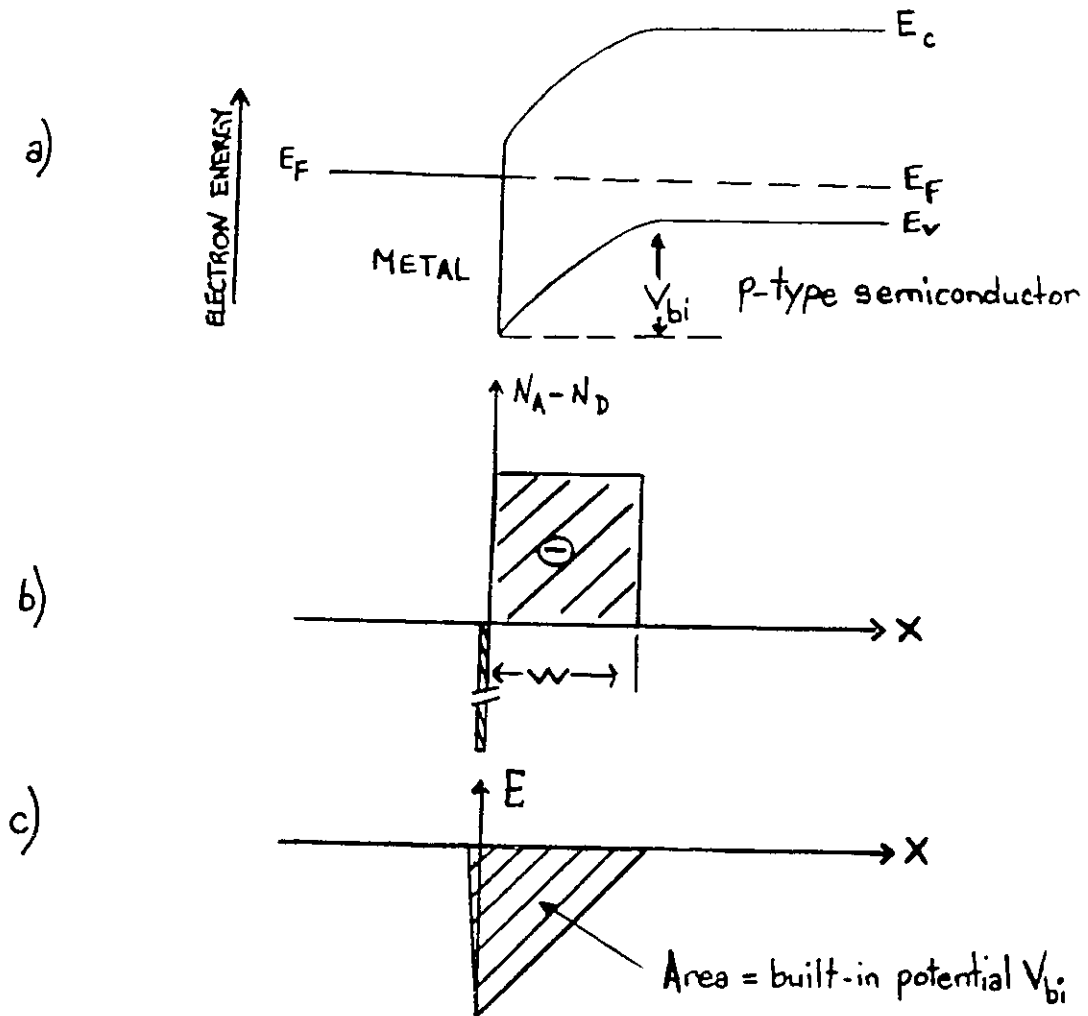


Figure 1.8 a) Equilibrium band diagram between a metal and a p-type semiconductor
 b) Concentration of uncompensated ionized acceptors as a function of distance
 c) Electric field distribution as a function of distance

where :

V_A : applied voltage
 V_{bi} : built-in voltage
 N_A : concentration of ionized acceptor states
 N_D : concentration of ionized donor states
 ϵ_s : static dielectric constant
 ρ : charge density

1.4.3. Barrier height measurements :

There are basically 4 methods used to measure the barrier height (ϕ_B) [21, 22] of a metal-semiconductor junction :

1) Current - voltage : The barrier could be obtained from the I-V curve of the junction. The intercept on the current axis, that is for $V_A = 0$, then the current density in the forward direction in equation (1.6) will be :

$$J_F = A^{**} T^2 \exp(-q\phi_B/K_B T)$$

and the barrier height can now be obtained from the following equation,

$$\phi_B = K_B T / q \ln(A^{**} T^2 / J_F) \quad (1.8)$$

Note, that the value of ϕ_B is not very sensitive to the choice of A^{**} .

2) Activation energy : The barrier height can be determined from the activation energy plot for the metal/semiconductor junction for a fixed forward bias voltage (V_A). The barrier height can be estimated from the slope of a plot of $\ln J$ versus $1/K_B T$, which is equal to $q(\phi_B - V_A)$.

3) Capacitance - Voltage : The barrier height can also be determined by capacitance measurements. When a small A.C. voltage is superimposed upon a D.C. bias, charges of one sign are induced on the metal surface and charges of the opposite sign in the semiconductor. The relationship between C (capacitance) and V (voltage) is given by the following equation : [21]

$$C = \frac{\delta Q}{\delta V} = \left[\frac{q \epsilon_s N}{2(V_{bi} - V_A - K_B T/q)} \right]^{1/2} = \frac{\epsilon_s}{w} \quad (1.9)$$

where, N : the ionized impurity density

ϵ_s : static dielectric constant

w : depletion region width

The intercept on the voltage axis of a plot of $1/C^2$ against the applied voltage (V_A), yields the barrier height from the following equation,

$$\phi_B = V_i + V_n + K_B T/q - \Delta\phi$$

where, V_i : the voltage axis intercept

qV_n : the depth of the Fermi level below the conduction band for a n-type semiconductor, or the energy difference between the top of the valence band and the Fermi level for a p-type semiconductor

$\Delta\phi$: the image force barrier lowering (Schottky effect)

4) Photoelectric effect:

The photoelectric effect method to obtain the barrier height has been used throughout this work. This method was preferred over the others, because it is the most accurate [23] and directly related to the work done here.

Consider the case when light of energy smaller than that of the band gap, but larger than the barrier height is incident onto the sample, as illustrated in figure 1.9. Light then, is absorbed in the vicinity of the metal-semiconductor junction, and the net effect is excitation of holes over the barrier from the metal into the semiconductor.

The photocurrent I per absorbed photon as a function of the photon energy $h\nu$ is given by the Fowler theory [24] :

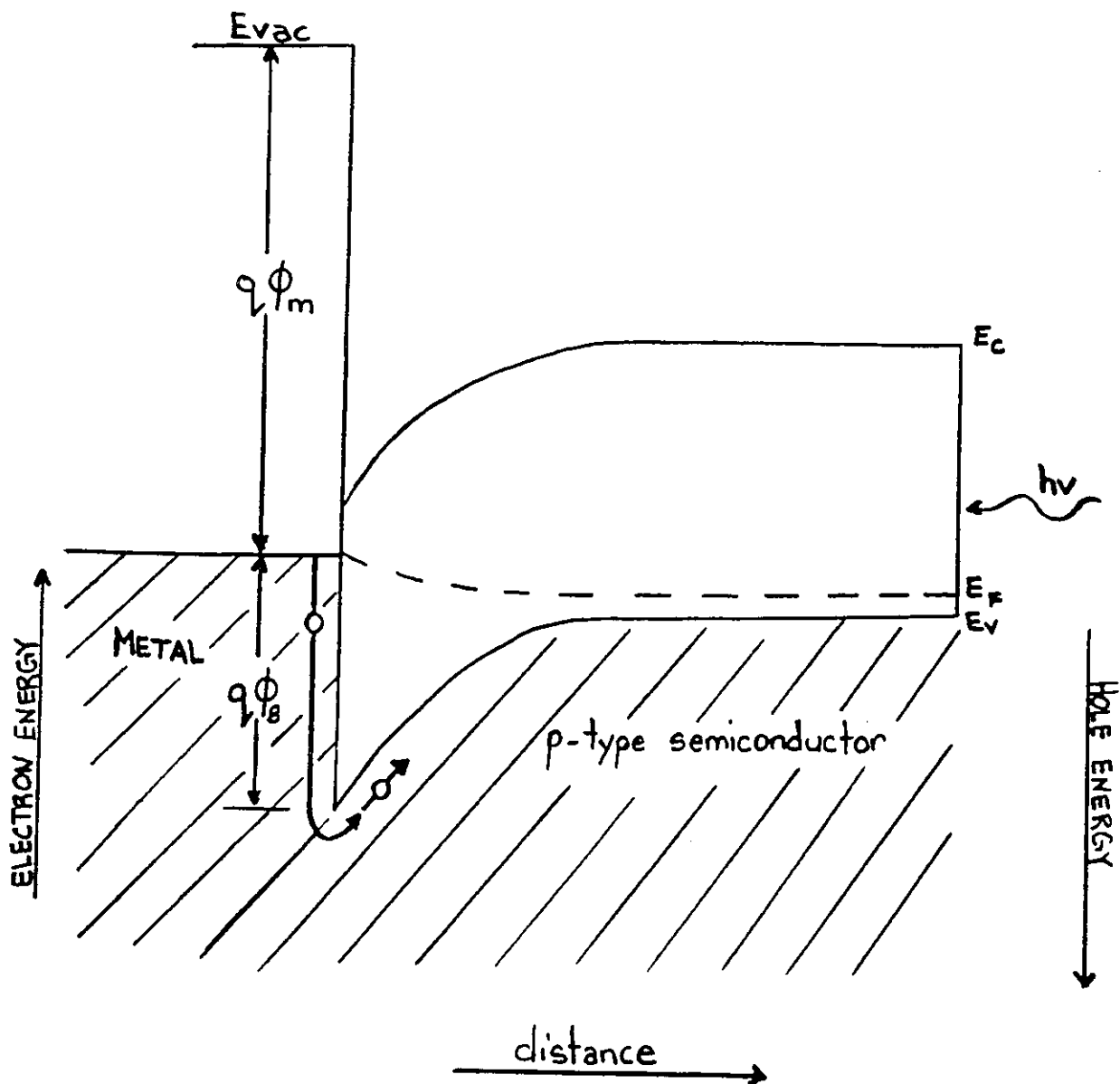


Figure 1.9: Equilibrium band diagram of a Schottky junction under illumination, with light of energy that could excite holes over the metal/semiconductor barrier.

$$I = T^2 / (E_s - hv)^{1/2} \left[x^2/2 + \pi^2/6 - (e^{-x} - e^{-2x/4} + e^{-3x/9} - \dots) \right] \quad (1.10)$$

for $x \geq 0$, where : $x = h(v - v_0) / K_B T$

where :

$h\nu_0$: is the barrier height energy $q\phi_B$

$E_s = q(\phi_m + \phi_B)$, for a p-type semiconductor, figure 1.9, or

$E_s = E_F + q\phi_B$, for a n-type semiconductor the Fermi level E_F is measured from the bottom of the metal conduction band.

Under the conditions :

$x > 3$ (this condition assures that thermal effects are minimized),

$E_s - hv \gg 0$ (this makes for a slow varying term as a function of incident light energy), and

$$q\phi_B < hv < E_g$$

Then, equation (1.10) reduces to [24] :

$$I = \frac{(hv - h\nu_0)^2}{2K_B (E_s - hv)^{1/2}}, \text{ thus } (I) \text{ is proportional to } (hv - h\nu_0)^2$$

$$\text{or } \sqrt{I} \approx hv - q\phi_B \quad (1.11)$$

Thus, a plot of the square root of the photocurrent versus the photon energy would yield a straight line, which extrapolated on the energy axis would give directly the barrier height.

1.5. CONCLUSION:

In this first chapter a) we reviewed the oxidation methods that were used to grow samples; b) the Physics of an ideal and a surface states controlled Schottky junctions were studied; c) the photovoltaic effect and the possibility of determining the energy gap from a PV spectrum was presented, while the current-transport theories were discussed. An expression for the calculation of the depletion width, w , was presented and finally the dependence of the photocurrent on incident photon energy was examined, providing a way to measure the barrier height. The background information presented in this chapter provides the basis for the understanding of the experiments to follow.

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CHAPTER 2

2. GENERAL EXPERIMENTAL APPARATUS AND TECHNIQUES

In this chapter the apparatus, that was common to most of the experiments performed, are described. Sample preparation techniques as well as experimental set-ups particular to individual chapters are only going to be discussed in the relevant chapters. The general apparatus used can be divided into 4 parts: 1) the optical set-up, 2) the photosignal detection techniques, 3) the cryostat used for experiments at liquid Nitrogen temperature, and 4) the sample characterization techniques (X-ray diffraction, sample thickness measurements, etc.)

2.1. THE OPTICAL SET-UP :

The need for photovoltaic spectra necessitated the use of monochromators. Two of them were available, first a high resolution Macpherson for low light intensity work, and second a Bausch&Lomb of lower resolution but of higher light output than the Macpherson. The description of the monochromators follows :

2.1.1. a high resolution Macpherson 2061, 1 meter, of Czerny Turner optical design, mated with a 788 Macpherson Microdrive. The grating used was holographic with 1200 grooves/mm with a spectral resolution at the exit slit of 0.8 nm/mm. Its working

spectral range extended between 400 and 1200 nm, to cover the required wavelength range for the E_g and ϕ_B of Cu_2O , Ag_2O and their alloys. Figure 2.1 shows a top view of the optical set-up. The light source used was a 42 Watt quartz-iodine lamp focused through a set of mirrors to the entrance slit. The light was usually chopped at a frequency of 77 Hz, before entering the monochromator. Filters placed at the exit slit were used to cut off the second order radiation. A beam splitter was used to reflect a small portion of the output radiation to a flat spectral response detector, (usually a Si detector with a flat response over the spectral range between 450 and 950 nm) to correct for the varying light output intensity of the monochromator. Figure 2.2 shows the light output intensity of the monochromator as a function of the wavelength. The curves represent the convolution of the quartz-iodine lamp output intensity modulated by the efficiency of the 1200 groove/mm grating and all the other optical elements used (mirrors, etc.). Curve "a" shows the spectral response as it comes out of the spectrometer without a polarizer, obtained with the use of a Si flat spectral response detector. For curves "b" and "c", a polarizer was placed at the exit slit with its plane of polarization parallel and perpendicular, with respect to the vertical axis of the exit slit, respectively. The light was left unpolarized for all the experiments performed (curve "a"). The widely varying light output of the spectrometer with the wavelength, which was due to a relatively poor quality but very expensive grating from the American Holographic company, made necessary the use of a flat spectral response detector for

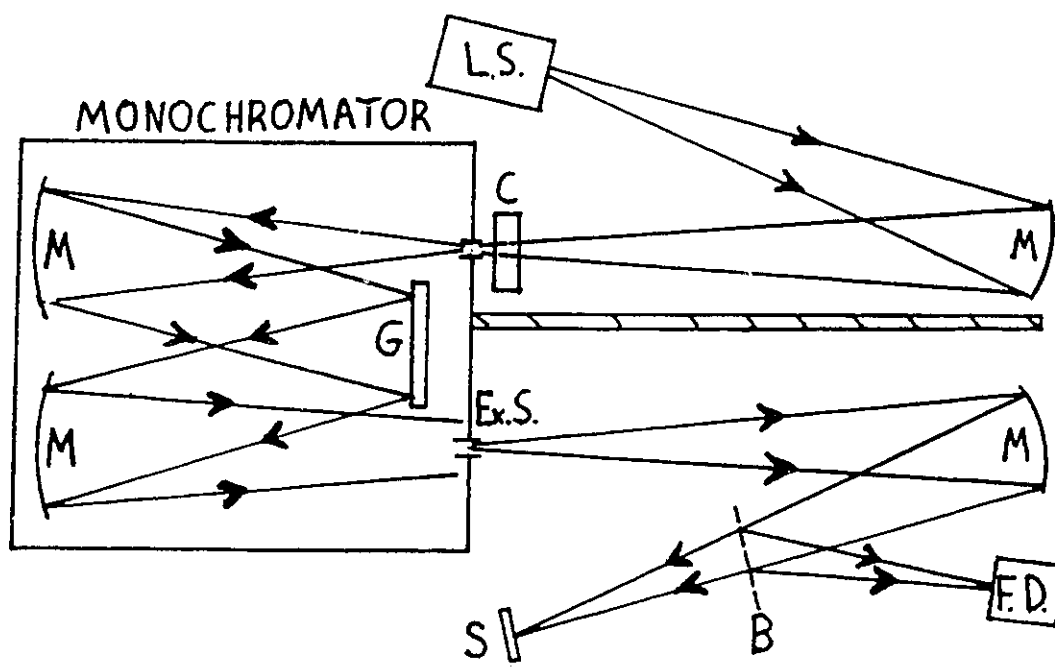


Figure 2.1: Top view of the optical set-up :
 L.S. : light source, M : mirror, C : chopper,
 G : grating, Ex. S. : exit slit, S : sample,
 B : partially transparent-reflecting glass,
 F.D. : flat response detector.

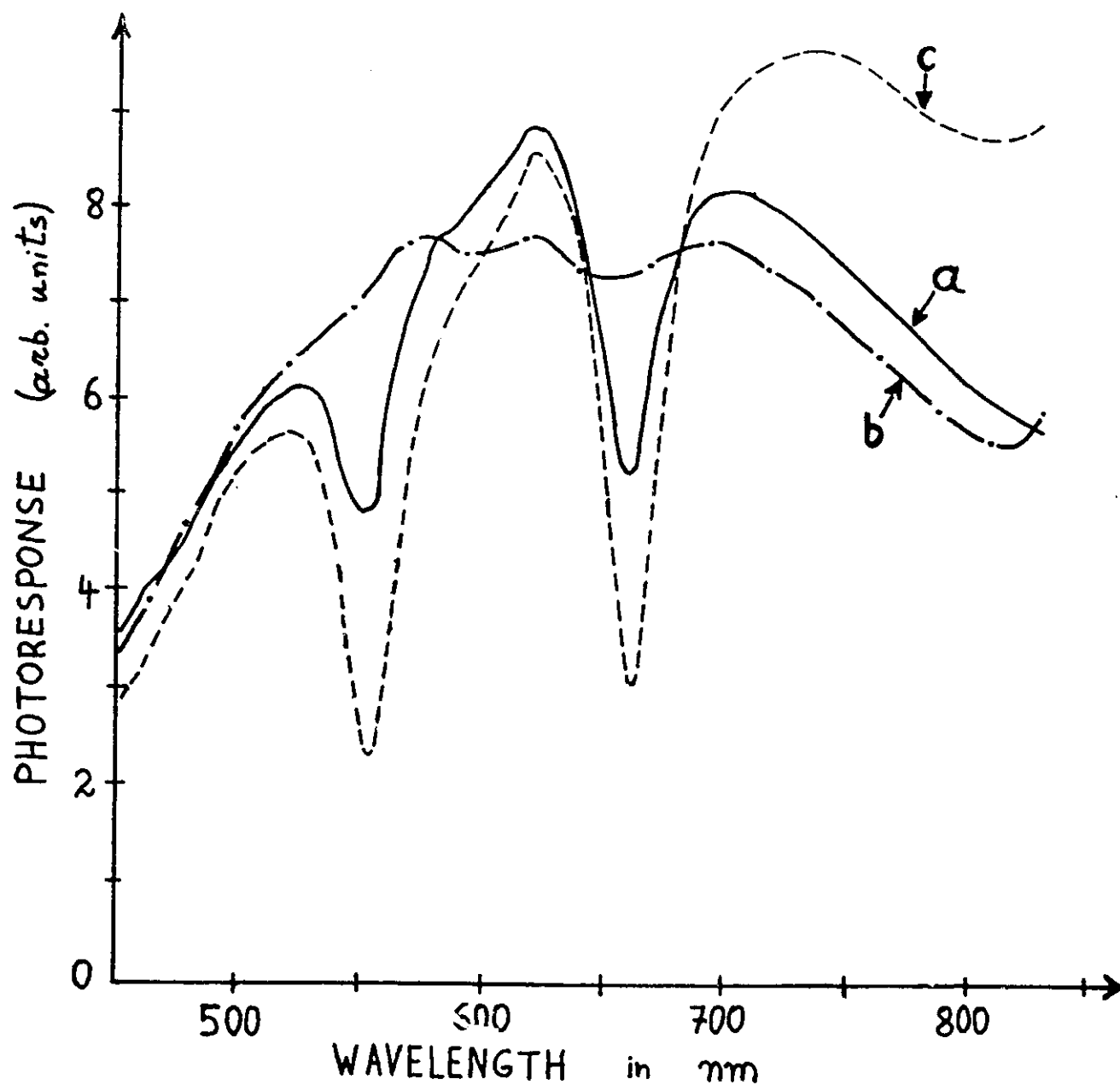


Figure 2.2: Light output intensity of the Macpherson monochromator as a function of wavelength.

Curves : a without polarizer
 b axis of polarization parallel w.r.t. the vertical axis of the exit slit
 c axis of polarization perpendicular w.r.t. the vertical axis of the exit slit

normalization purposes. The above combination of lamp and grating provided a light power output of about $3 \cdot 10^{-7}$ W/cm² and a flux of $\approx 10^{12}$ photons/sec cm², at 600 nm with both slits set at 0.8 mm, corresponding to an output bandwidth of 0.7 nm.

2.1.2. A low resolution Bausch&Lomb monochromator with a 42 Watt quartz-iodine lamp. In this case the wavelength was changed manually. Three gratings were available with the following working spectral ranges and spectral resolutions :

a) 350 to 800 nm, with 6.4 nm/mm b) 700 to 1600 nm, with 12.8 nm/mm c) 1400 to 3200 nm, with 25.6 nm/mm. The grating commonly used was the one with the working spectral range between 350 and 800 nm, set for a 10 nm bandwidth. Its light power output at 600 nm, with the entrance and exit slits set at 4 and 2 mm (12 nm bandwidth) respectively, is about $3 \cdot 10^{-4}$ W/cm² resulting in a flux of $\approx 10^{15}$ photons/sec cm². By placing a mirror where the grating usually sits, this monochromator was also used as an approximate solar spectrum simulator for the evaluation of solar cell characteristics, with a power of 50 mW/cm².

2.2. PHOTOSIGNAL DETECTION TECHNIQUES :

2.2.1. Phase sensitive detection :

The photosignal from the sample was fed into a lock-in amplifier (A), figure 2.3, an EG&G PARC, model 124A with an input impedance of $10^8 \Omega$. Using a beam splitter a small portion of the incident radiation was reflected onto a Si flat spectral response detector, whose signal was fed to a second Lock-in amplifier (B), a PAR model 122. The division of the first signal (A) by the second (B), corrected for the variation of light output intensity of the monochromator, provided that both the sample and flat detector signals were linear with the monochromator light output variation. The resulting signal was then recorded on a Watanabe XY recorder, model WX4421.

In order to maximize the signal to noise ratio without losing any information, the electronic time constant had to be matched with the wavelength scanning speed and the spectral resolution (slit opening) of the monochromator. Care was taken so that the photocurrent was always measured with both lock-ins. The impedance of our samples, at temperatures below 200 K were of the order of 10^9 to $10^{12} \Omega$. The input impedance of the sample lock-in was $10^8 \Omega$. In that case, it is valid to say that the short-circuit photocurrent was measured. For temperatures above 200 K, care was taken so that the photocurrent is still measured. This was achieved by measuring the voltage drop across an external resistor

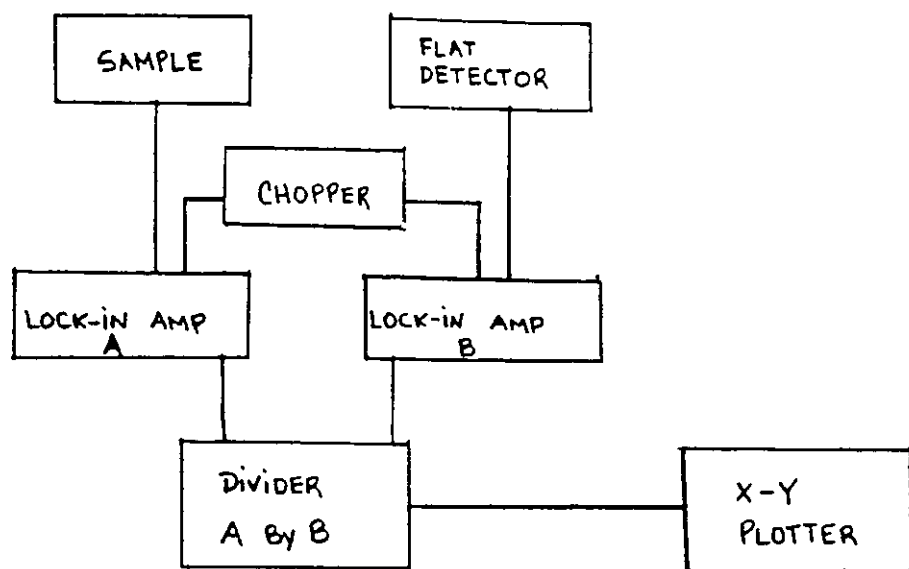


Figure 2.3: Photosignal detection equipment.

of appropriate value, connected in series to the sample circuit.

Whenever the Bausch-Lomb monochromator was used together with the chopper and a lock-in amplifier, the varying output light intensity of the monochromator was corrected manually with the use of calibration tables.

2.2.2. D.C. technique : (the light was not chopped)

Whenever high light intensity was needed and good spectral resolution was not necessary, the Bausch - Lomb monochromator was used along with a Keithley 602 electrometer, in order to obtain low resolution preliminary spectra.

2.3. LIQUID NITROGEN OPTICAL CRYOSTAT :

This was a very simple and effective cryostat keeping a constant temperature, about 5 to 10 K above the liquid nitrogen temperature (77 K) [1]. The sample was mounted onto the bottom tail piece (D), as shown in figure 2.4, and fixed in place by thermal compound. The sample was illuminated through the window (H). The inner part of the tail (C) was surrounded by vacuum and it was in contact with the liquid nitrogen bath (A), as shown in figure 2.4. The temperature was measured with an Omega flat shaped platinum-resistance thermometer mounted onto the bottom tail piece (D), next to the sample. The leads connected to the sample and temperature detector leave the vacuum chamber via a feed-through unit (I). This cryostat is not suitable for work as a function of temperature, because during the period of time (usually 5 minutes)

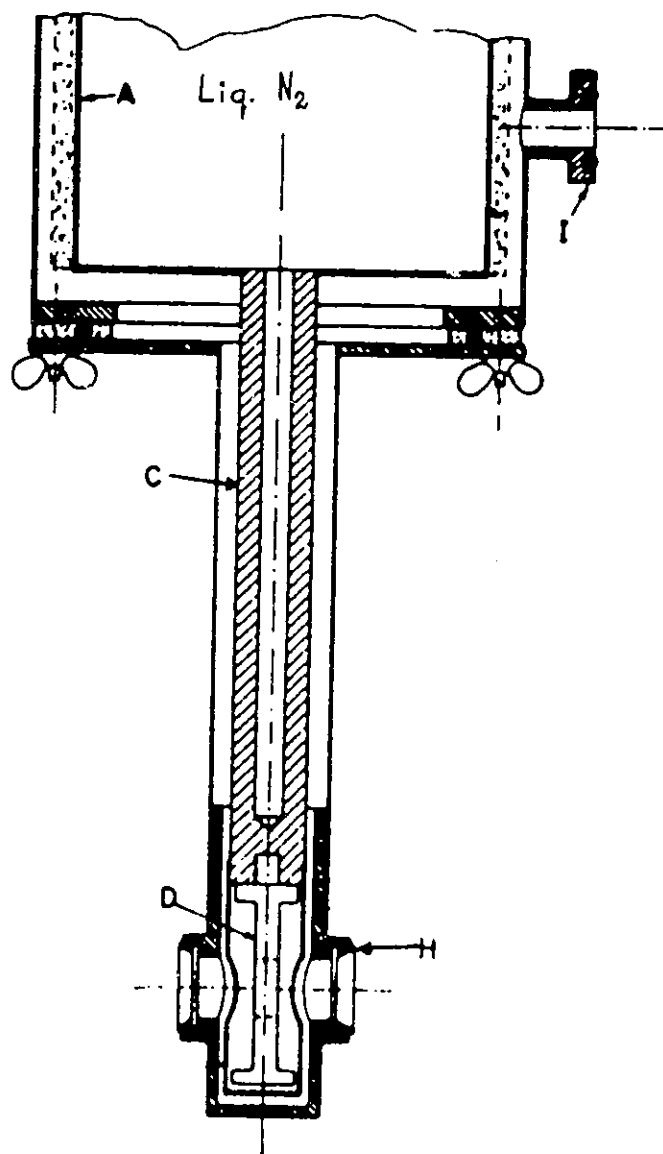


Figure 2.4: View of liquid nitrogen optical cryostat.

needed to obtain the PV spectrum the temperature increases considerably after liquid nitrogen has been removed. This is especially true for the first 100 K above the liquid nitrogen temperature. Therefore, this cryostat can only be used for rough work in terms of PV spectra as a function of temperature.

2.4. SAMPLE CHARACTERIZATION TECHNIQUES :

The sample characterization techniques described here, examine a) the identity and purity of the oxides grown and b) determine the oxide layer's thickness.

X-ray powder diffraction :

The composition of the oxide layers grown by anodic oxidation and that of a few samples grown by thermal oxidation were examined by X-ray powder diffraction, using a Debye - Scherrer camera. The powder was carefully scraped off to avoid any particles from the substrate, on which the samples were grown. The X-ray diffraction technique is capable of detecting a second phase within a host material, if it is present in concentration higher than 1% at. of the host material.

Oxide layer thickness measurements :

The following 3 methods were used to estimate the grown oxide layer thickness :

1) Coulombmetric method : This method was only used for oxides grown by anodic oxidation. The number of moles of oxide grown could be measured by the total charge Q consumed to form the oxide layer, assuming 100% efficiency. If the density d of the oxide is known, and the area A can be measured, then for an oxide with the chemical formula, Me_xO_y , whose molecular weight is M , the Faraday law yields its thickness t :

$$t = \frac{Q M}{2 y F d A} , \quad F : \text{Faraday constant.} \quad (2.1)$$

2) Gravimetric method : In this case the oxide layer thickness was determined by chemically dissolving the oxide (with NH_4OH , in the case of Cu_2O) without affecting the metal substrate. By weighing the sample before and after the oxide removal, its thickness was calculated, provided its density and area were known.

3) Optical microscope method : A Zeiss microscope, model 20T, was used to measure the oxide layer thickness at a step made on the surface of the sample exposing the substrate. With the microscope set at its highest magnification (X 500), the depth of focus was providing a resolution of the order of 2 μm . The procedure for measuring the thickness was the following : two successive readings of the vertical position of the focus plane were taken-off a fine drive (indexed in divisions of 5 μm) by focusing first on the oxide surface and then on the substrate surface.

REFERENCE OF CHAPTER 2

- 1) E. Fortin, The Rev. of Scient. Instrum., 41, 1252, (1970).

PREPARATION AND PHOTOVOLTAIC PROPERTIES OF ANODICALLY GROWN

Ag₂O FILMS

3. INTRODUCTION :

There is very little experimental work done on the semiconducting and photovoltaic properties of Ag₂O [1-4]. E. Fortin et al. [1] studied the photoconductivity of Ag₂O samples prepared : a) by pressing Ag₂O powder against cellulose backing, and b) by cathodic sputtering of Ag in an Oxygen atmosphere. Ag₂O was found to be a sensitive photoconductor regardless of method of preparation, and the energy gap was determined to be about 1.5 eV at room temperature. S. Mitaray et al. [2,3] studied the photoconductivity of Ag₂O thin films prepared : a) by chemical reaction of Ag with AgO, and b) by sputtering. They observed improvement of the crystalline state of the oxide with annealing. They deduced that Ag₂O is a p-type semiconductor, from the variation of the adsorbed mass of certain gases on the oxide surface. F.I. Kreingold et al. [4] obtained exciton absorption and luminescence spectra of Ag₂O crystals at 77 and 4.2 K. The present work will be the first time that photovoltaic spectra of anodically grown polycrystalline Ag₂O are studied. The work was motivated by the fact that Ag₂O has a direct energy gap of about 1.4 eV [1,4,5] making it perfectly suited for absorption of the solar spectrum [6]. Therefore, the photovoltaic properties of

anodically grown Ag_2O were investigated and the possibility of making a Schottky junction Ag_2O solar cell was examined.

Ag_2O is the only structural analogue of Cu_2O . While Cu_2O has been prepared thermally as well as anodically [7,8], Ag_2O has not been prepared thermally because very high Oxygen pressures are required, making the process very difficult. In the polycrystalline form, Ag_2O has a dark grey to brown colour, its specific resistivity is of the order of $10^8 \Omega\text{cm}^{-1}$ [9]. The silver oxide starts decomposing around 160°C in 1 Atm. of air [9]; this is due to the low dissociation energy of the bond between the Silver and Oxygen atoms (which is about 1.5 eV) .

The crystalline structure of Ag_2O , figure 3.1a,b, consists of a body - centred cubic arrangement of oxygen ions which results in a structure where each oxygen ion occupies the center of a tetrahedron of Ag ions (as in figure 3.1a), interpenetrated by a face - centred cubic arrangement of Ag ions as in the metal (figure 3.1b). The interatomic distances are : $d(\text{Ag}-\text{Ag}) = 3.336 \text{ \AA}$ and $d(\text{Ag}-\text{O}) = 2.043 \text{ \AA}$. Therefore , Ag_2O has the $\text{Pn}3\text{m}$ structure and the Octahedron, O_h^1 , point group symmetry.

In the following sections, the methods and techniques used to grow anodic Ag_2O films of relatively good quality, are first presented. Second, the photovoltaic properties are considered, allowing the determination of the band gap and the conductivity type of the material. Finally the barrier height of some metals with Ag_2O is measured.

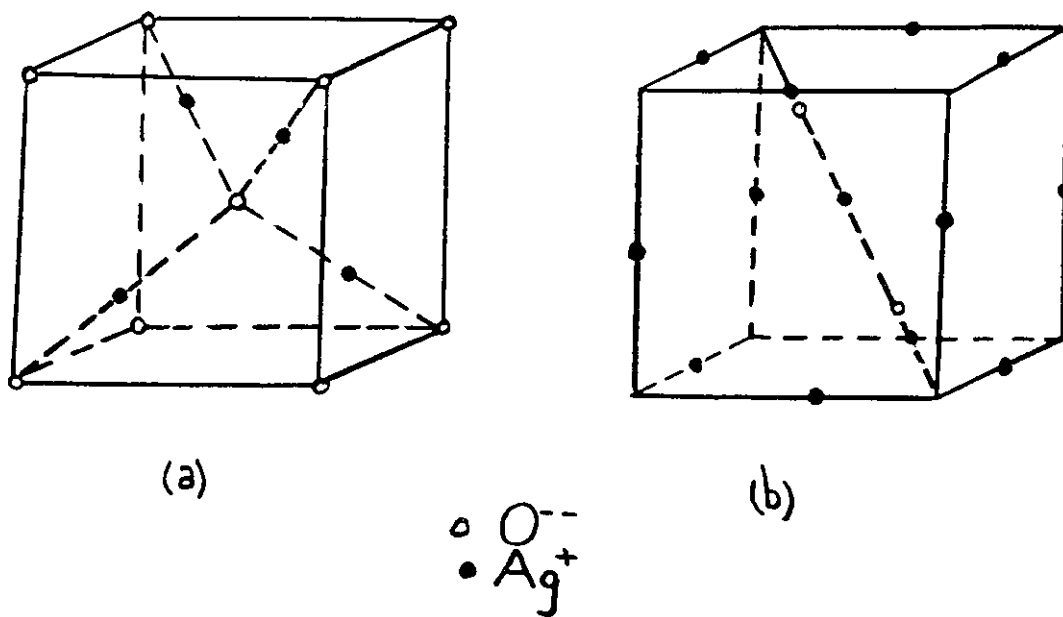


Figure 3.1: The crystalline structure of Ag_2O
a and b sublattices of the Ag_2O structure.

3.1. OXIDATION METHODS :

The book "Oxide Semiconductors" by Z.M. Jarzebski [10] describes and gives references for various oxide preparation methods . Listed below there are 5 preparation methods known to grow Ag_2O :

- 1) HYDROTHERMAL SYNTHESIS : usually used to grow single crystals of maximum volume of 1 to 2 mm^3 [11,12] .
- 2) CHEMICAL REACTION : Ag_2O is formed by a precipitate on making a soluble silver salt alkaline solution [9] .
- 3) REACTIVE SPUTTERING : Ag_2O is formed by cathodic sputtering of Ag in an oxygen atmosphere [1,13] .
- 4) ANODIC OXIDATION : a silver anode is introduced in an electrolytic bath with the appropriate solution .
A current is passed and the Ag anode is oxidized [14] .
- 5) THERMAL OXIDATION : it is a direct reaction of Ag at a very high Oxygen pressure [15] .

The anodic oxidation method was preferred over the other methods due to the following reasons :

- a) oxidation working conditions are relatively easily controlled ;
- b) it provides micrometer thick oxide films and a "natural" rectifying junction between Ag_2O and Ag, which is never exposed to the atmosphere after the oxidation.

c) the prospect of making polycrystalline samples of any lateral desired dimensions , an important consideration for solar panel construction; and d) mechanical stability because the oxide films are grown on a Ag substrate.

Even though there has been quite a large amount of research work on anodic oxidation of Ag to Ag_2O by electrochemists [16 - 22] , their interest is focused to very thin (a few tens of nanometers thick) oxide films to investigate reaction potentials and oxide growth kinetics . In two cases [23,24], there were attempts to make electrical and photoelectrical measurements without significant results. The goal here, of the anodic oxidation method, is to grow compact micrometer - thick polycrystalline oxide films with the largest possible individual crystals on a silver substrate .

3.2. SAMPLE PREPARATION :

The silver used came in the form of sheets of 0.5 mm thickness and 99.99% atomic purity . The sheets were cut in rectangular electrodes of dimensions 3.75 cm x 1.25 cm . Before introducing the Ag electrodes into the solution , they were degreased with ethanol and then polished .

Two polishing procedures were available to us :

- 1) Since the Ag surface was usually already smooth and relatively clean, silverware polish was used to clean it and remove any contaminants (like, silver sulfide) from the surface. Then, it was rinsed with distilled water and finally dried with ethanol.

This procedure leaves the Ag surface reasonably clean with minute scratches .

- 2) Chemical polishing : The solution used consists of 10 ml of 50% H_2O_2 and 40 ml of 29% NH_4OH . The Ag electrodes were dipped into the solution for 30 - 60 seconds, then rinsed with distilled water and finally dried with ethanol . This procedure leaves the silver surface very clean but slightly undulated and pitted .

A combination of the two above polishing procedures , namely #1 first and #2 second , was providing the cleanest Ag surface. This combination was used to prepare the Ag surface prior to oxidation.

3. 3. OXIDATION SET-UP :

In figure 3.2, the experimental set-up used for Ag oxidation, is presented. It consists of a heating plate (H.P.) with temperature controls and a magnetic flywheel used to rotate the stirring dipole (S) inside the solution bath (B). The Ag electrodes were mounted parallel to each other on a holder, spaced 0.5 cm apart. A Hg/HgO [23] reference electrode was connected electrically with the working solution, via the HgO solution through a Haber - Luggin capillary (H.L.). One of the capillary ends was placed 1 to 2 mm away from the anode and the other end in the HgO solution. Therefore, in this way the potential difference developed between the anode and the reference electrode could be monitored and compared to the standard H_2 electrode .

The selection of the reference electrode depends on the working solution and the anodized metal. For solutions with $PH > 9$ and Ag, as in this case, the Hg/HgO reference electrode is preferred. In the case when the solution was not stirred, the solution bath (B) was introduced into a "Haake L" temperature controlling bath, capable of providing temperatures between room temperature and $95^{\circ}C$, with an accuracy of $\pm 0.5^{\circ}C$ about the set temperature. When the heating plate was used the solution was stirred with a dipole covered with PVC to avoid solution contamination. Temperatures up to $90^{\circ}C$ were obtained, kept within 1 to $2^{\circ}C$ of the desired temperature during the oxidation.

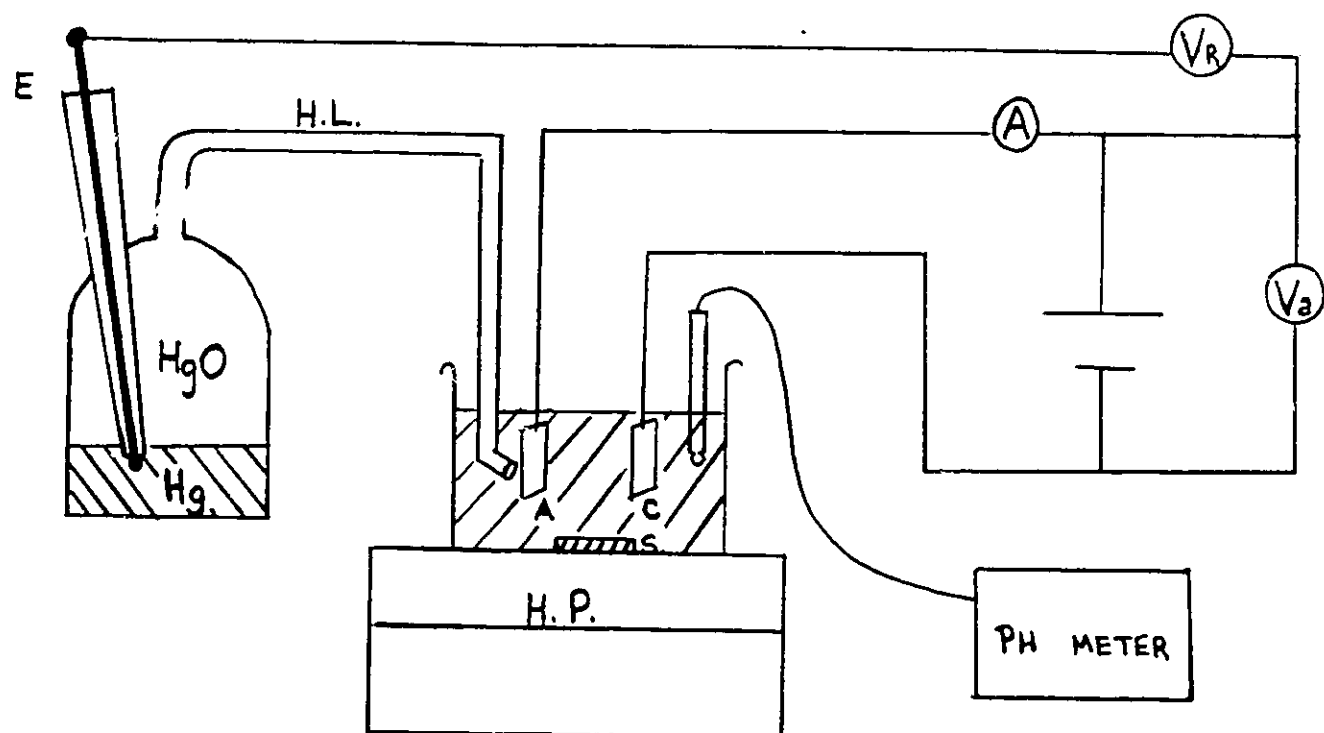


Figure 3.2: Anodic oxidation set-up.

A time period of about 30 minutes was usually needed for the solution temperature to be stabilized. Stirring kept the temperature of the solution constant throughout its volume while at the same time preventing the accumulation of oxidized constituents and supplying sufficient reactants for a critical reaction on the electrode. This way, the equilibrium potential would not increase, leading to an early passivation before the desired thickness and uniform electrode coverage were obtained.

3.3.1. POTENTIAL VERSUS TIME DIAGRAM :

During the Ag anodic oxidation cycle, there are 2 very well defined plateaus [14,26] in the potential versus time diagram (at constant current density), figure 3.3. The first plateau represents the oxidation of Ag^0 to Ag^+ or of Ag to Ag_2O and the second that of Ag^+ to Ag^{++} or of Ag_2O to AgO . Going from the first to the second plateau there is a very sharp increase in the potential difference at the oxide/solution interface, indicating the transition from Ag_2O to AgO . During preliminary galvanostatic (constant current density) runs it was noticed that these features are kept intact in the voltage (voltage monitored between the anode and cathode) versus time diagrams, (see section 1.2). Except for a number of preliminary runs, the reference electrode was not used, since the goal here was to grow Ag_2O and not to get involved with the detailed electrochemical aspects of the problem. An additional reason for not using a reference electrode was the possibility of contaminating the working solution.

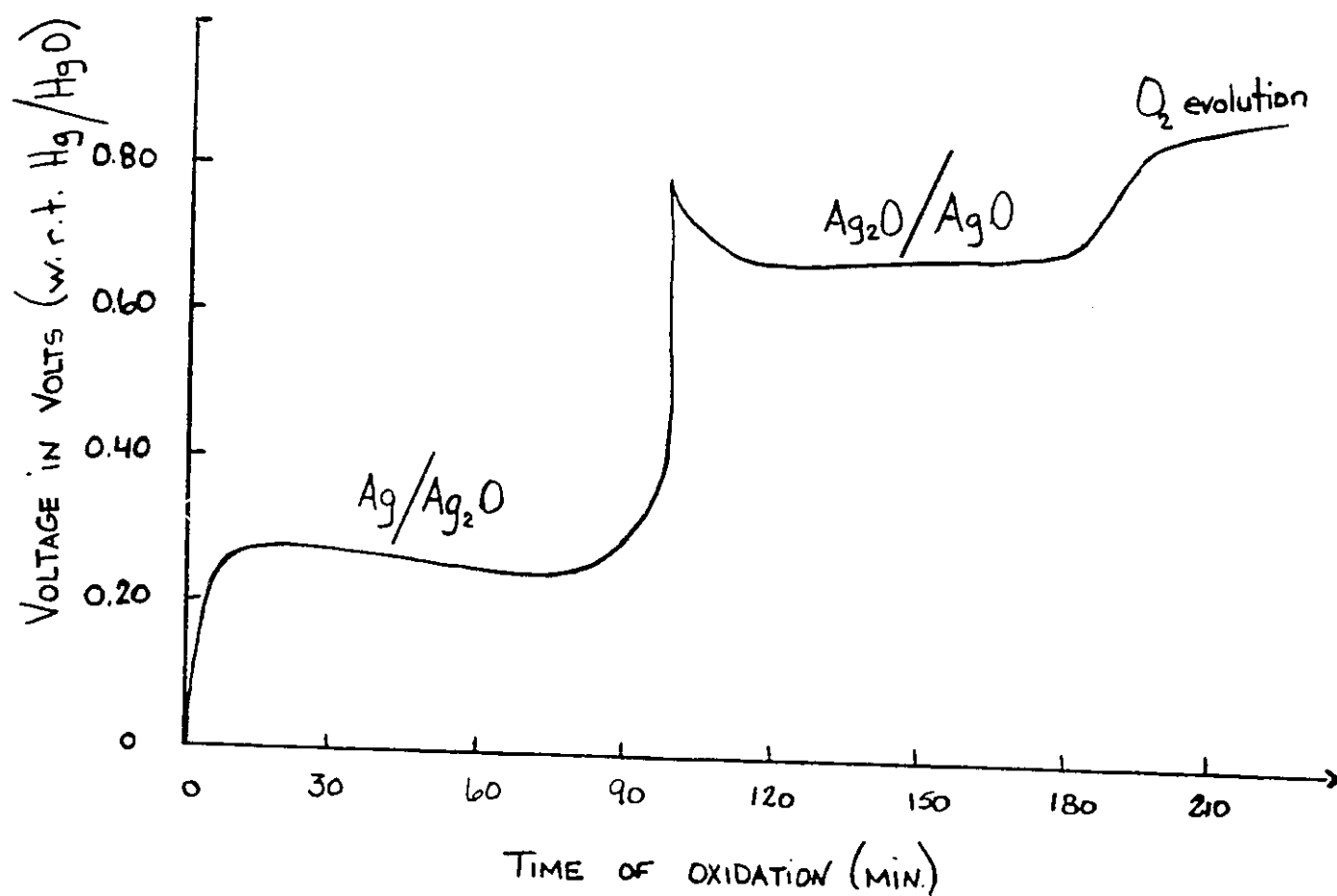
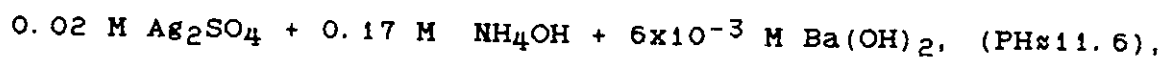


Figure 3.3: Potential versus time diagram of the anodic oxidation cycle of Ag.

3.3.2. OXIDIZING SOLUTIONS AND EFFECT ON THE GROWN OXIDES :

All solutions were prepared from reagent grade or A. C. S. quality chemicals and distilled water. The first solution used was the equivalent for Ag to that used for anodically grown Cu_2O [5] , (Ag_2SO_4 , NaCl , LiCl) , but this approach did not work because the compounds were reacting with the precipitation of AgCl . Then Ag_2SO_4 alone was tried, but that resulted in a very thin oxide layer (submicrometer thickness) and no photovoltaic response due to the incomplete coverage of the metallic surface.

After the above initial approaches, the potential versus PH equilibrium diagram of Ag [27], figure 3.4, was used as a guide to select appropriate operating conditions so that oxidation would proceed within the area of Ag_2O stability. Having figure 3.4 as a guide, alkaline solutions of NaOH and KOH were tried. The PH values of these solutions varied from 11 to 14 and the temperature ranged between 20 and 90°C. Those solutions resulted in the first significant growth of Ag_2O . The Ag electrode coverage, however, was often incomplete and the resulting cells gave little photovoltaic response. Finally, the solution that gave the best results and was used to grow the oxides on which this work was based, consisted of :



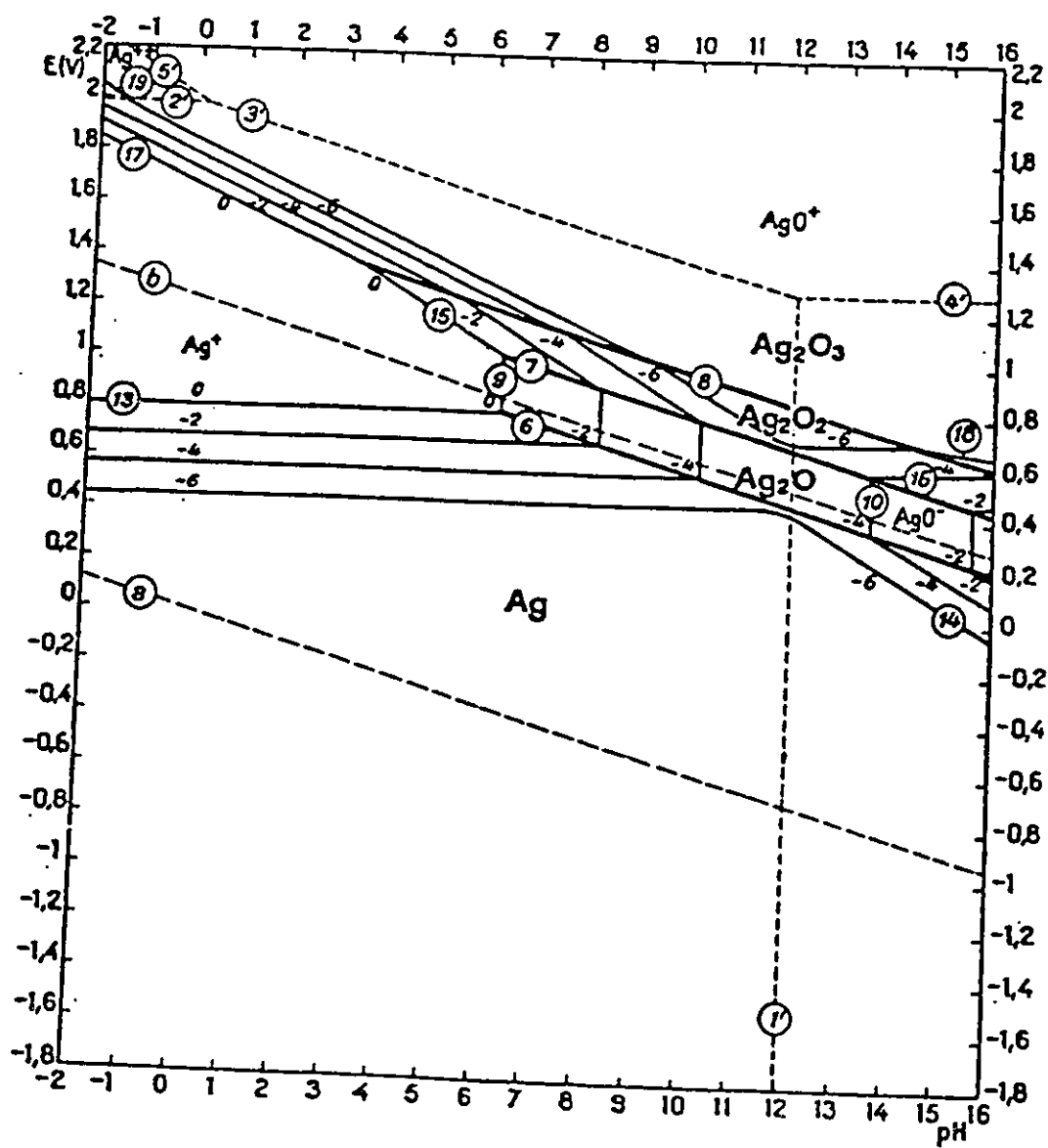


Figure 3.4: Potential versus PH equilibrium phase diagram of Ag (27).

saturated with Ag_2O powder , (the amount of powder determined by the solubility of Ag^+ in NH_4OH obtained from tables [28]), at room temperature . Typical operating conditions were : light stirring, constant current density of about $2\text{mA}/\text{cm}^2$ and oxidation duration of 1 to 3 hours , at room temperature ($\approx 25^\circ\text{C}$) .

The evolution of the above solution to its final composition took the preparation and testing of about 100 samples. Since then 50 more samples were grown and tested . Besides the solution composition, other oxidation parameters were varied for optimization of the quality of the grown oxides : the working solution temperature, the stirring effect, current density, effect of Ag electrode treatment prior to oxidation. In fact, little effect of Ag surface treatment was observed when the above solution was used. On the contrary, when NaOH and KOH solutions were used Ag_2O crystallite-nucleation patterns were observed, under the microscope, running along minute scratches present on the Ag surface prior to oxidation .

There is general agreement in the literature [16,23, 24,29] that oxidation starts as a dissolution - precipitation process, in the case of hydroxide solutions. There are indications, however, that a parallel mechanism of a compact film formation exists as a result of a direct interfacial reaction [23,29 - 31]; therefore, there is evidence for a dual layer oxide with absorbed oxygen at the oxide - solution interface. In the solution used here, Ag_2SO_4 acts as a supplier of Ag^+ ions to the

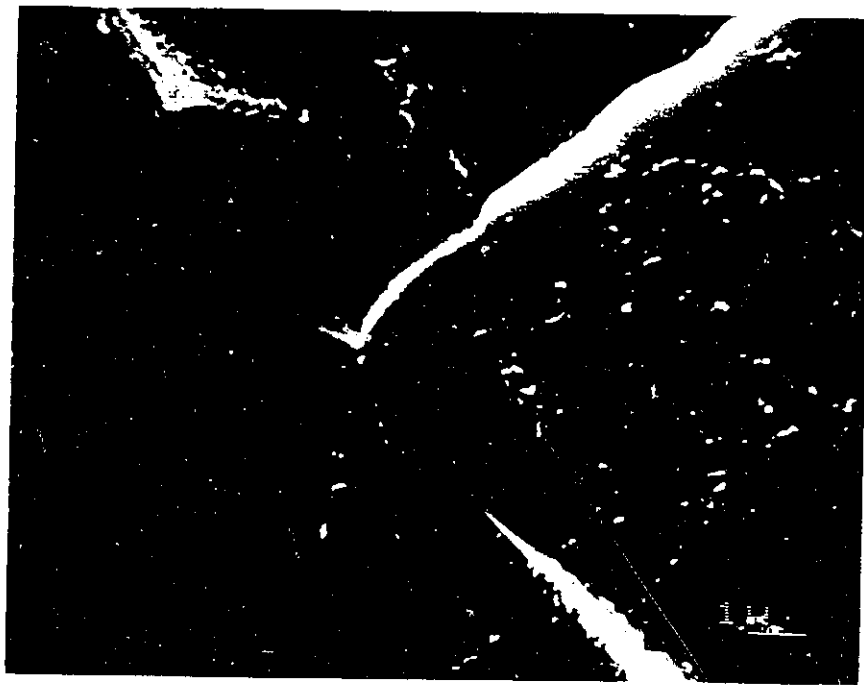
solution, NH_4OH is responsible for the initial dissolution - precipitation mechanism, while keeping the PH within the desired range. $\text{Ba}(\text{OH})_2$ is added to absorb any carbon, carbon monoxide or dioxide in the solution, to form an insoluble precipitate BaCO_3 , thus preventing Ag_2O from absorbing any carbon during its formation. The dissolution - precipitation process consists of Ag^+ dissolution and oxide deposition on the anode, initially in the form of islands which were grown from phase nucleation centres. This is referred in the literature as the "primary layer" [30]. The thickness of this layer is of the order of a few tens of nanometres and the coverage is not complete. Further dissolution of Ag^+ from the silver electrode becomes increasingly difficult as the primary layer expands and thickens. Consequently, the secondary layer [30] starts building up with Ag^+ diffusion through the oxide. The secondary layer consists of primary centres that are reported in the literature to grow laterally up to 1 μm [30]. In the present case they grow 5 to 20 μm wide, overlapping each other covering completely the silver surface. Therefore, a new process has taken over, leading to larger crystallites. This process is possibly either the direct interfacial reaction mentioned above or a precipitation process due to the composition of the solution. The prospect of having a dual oxide layer has to be investigated because it could possibly affect in a negative way the photovoltaic properties of the oxide.

Finally, in an effort to improve the silver surface condition prior to oxidation and study its influence on the oxide film, Ag electrodes were annealed at 860°C in air for several hours before anodizing. This way single silver crystals, some of area 1 to 2 mm², were formed. It was noticed that the oxide crystallites on some of those silver crystals grew in the form of flat mosaic, instead of the pyramidal texture of previous samples. Therefore, the texture of the oxide film appears to depend on the orientation of the silver crystals on the electrode, as was mentioned by Fleischmann et al. [29]. Films prepared as mentioned above give stronger photovoltaic signals and exhibit better electrical stability.

3.4.CHARACTERIZATION OF Ag_2O FILMS :

In order to make sure that the grown oxide was definitely Ag_2O . The following material characterization techniques were used : X-ray powder diffraction, S.E.M. (Scanning Electron Microprobe) analysis, and Auger analysis.

X-ray powder photographs of Ag_2O scraped off the samples showed no evidence of other silver oxide phases, to the degree of resolution this technique provides. Therefore, techniques of higher sensitivity had to be tried. S.E.M. and Auger analysis were attempted, but due to the low bond dissociation energy between Ag and O ($\text{Ag} - \text{O} \approx 1.5 \text{ eV}$), Ag_2O was partially reduced under the electron probing beams. However, the scanning electron microscope, at the University of Ottawa Chemistry department, provided a few impressive "electron" photographs of the oxide film, photo 1 a,b; while the Auger analysis, performed at the NRC, identified sulfur, chlorine and carbon as trace impurities present in the oxide, see figure 3.5. The exact proportions of Ag_2O and impurity concentration could not be deduced, due to the lack of normalization standards for Ag_2O .



Photos 1 a,b: Surface of anodically grown Ag_2O taken with an "electron" scanning microscope.

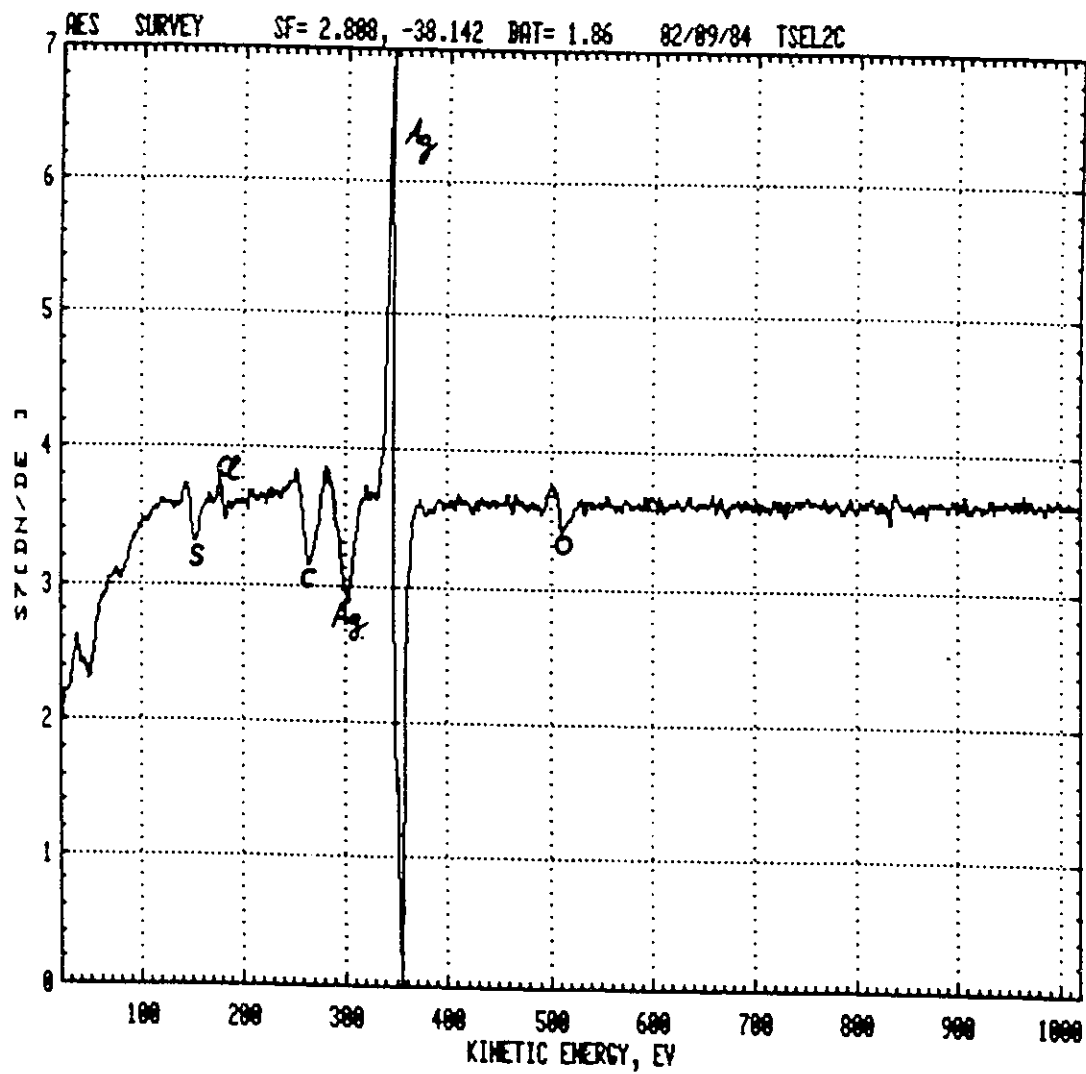


Figure 3.5: Print-out of the Auger analysis of anodically grown Ag_2O .

The thickness of the oxide films was estimated by 2 of the 3 methods described in section 2.4 :

- 1) Coulomb - metric method : assuming 100 % efficiency of the oxidation process an upper limit for the oxide thickness is obtained,
- 2) Optical microscope method : observation of an Ag_2O film cross-section under an optical microscope .

The average oxide sample thicknesses ranged from 1 to over 10 μm usually varying locally due to the relief of its pyramidal polycrystalline texture.

3. 5. PHOTOVOLTAIC PROPERTIES :

The photovoltaic properties of the metal / anodic Ag_2O Schottky junctions were examined by PV spectra taken at room temperature. Such measurements can yield the energy gap and determine the metal-semiconductor barrier height for different metals. The metallic contacts, on top of Ag_2O , were deposited in a Veeco cryopumped evaporator at a pressure of 5 to 8 10^{-6} torr. The thickness of the evaporated metallic films (intended either to give an Ohmic or a rectifying contact) ranged between 7 and 10 nm, thus allowing the light to reach the metal/oxide interface without appreciable absorption. The oxide films grown exhibited specific resistivities ranging between 10^6 and $10^8 \Omega\text{cm}$ at room temperature.

Ag_2O is considered to be a p-type semiconductor by analogy to Cu_2O and there is experimental evidence to support it [3, 5] (although D. B. Gibbs et al. [24] claim that they obtained n-type samples). In this work Ag_2O was found to be p-type, as determined by comparison of the sign of its PV signal to that of an equivalent p-type $\text{Cu}_2\text{O}/\text{Cu}$ cell. Ag_2O has a direct energy gap of about 1.4 eV making it an excellent candidate for absorption of the solar spectrum [33]. Unfortunately the material's instability poses serious problems.

3.6. THE SCHOTTKY-JUNCTION AS A PHOTOVOLTAIC CELL : [34, 35]

In figure 3.6a,b a p-type PV cell under illumination is presented. When the rectifying junction is illuminated through the semiconductor side, it is called a backcell and when it is illuminated from the metal side, frontcell (see figure 3.6a).

In the frontcell configuration the metal must be thin to allow substantial amount of the incident light to reach the semiconductor. The metal film is usually about 10 nm thick. In the backcell as well as in the front cell configuration, the oxide has to be thick enough to absorb most of the solar spectrum and of such thickness that most of the photoexcited carriers may diffuse towards the junction before recombining. Therefore, there are two very important conditions that have to be met in order to obtain an effective PV cell :

The semiconductor film thickness should be :

- 1) of the order of $1/\alpha$, so that most of the incident light is absorbed in it (where α the absorption coefficient is usually of the order of 10^4 cm^{-1} for a direct band gap semiconductor, this corresponds to a thickness of 1 - 2 μm) ;
- 2) of the order of $(L + w)$, usually $L \gg w$, $L = (D \tau)^{1/2}$, where, L : diffusion length, D : diffusion coefficient and τ : the photoexcited carrier lifetime and w : the depletion region width.

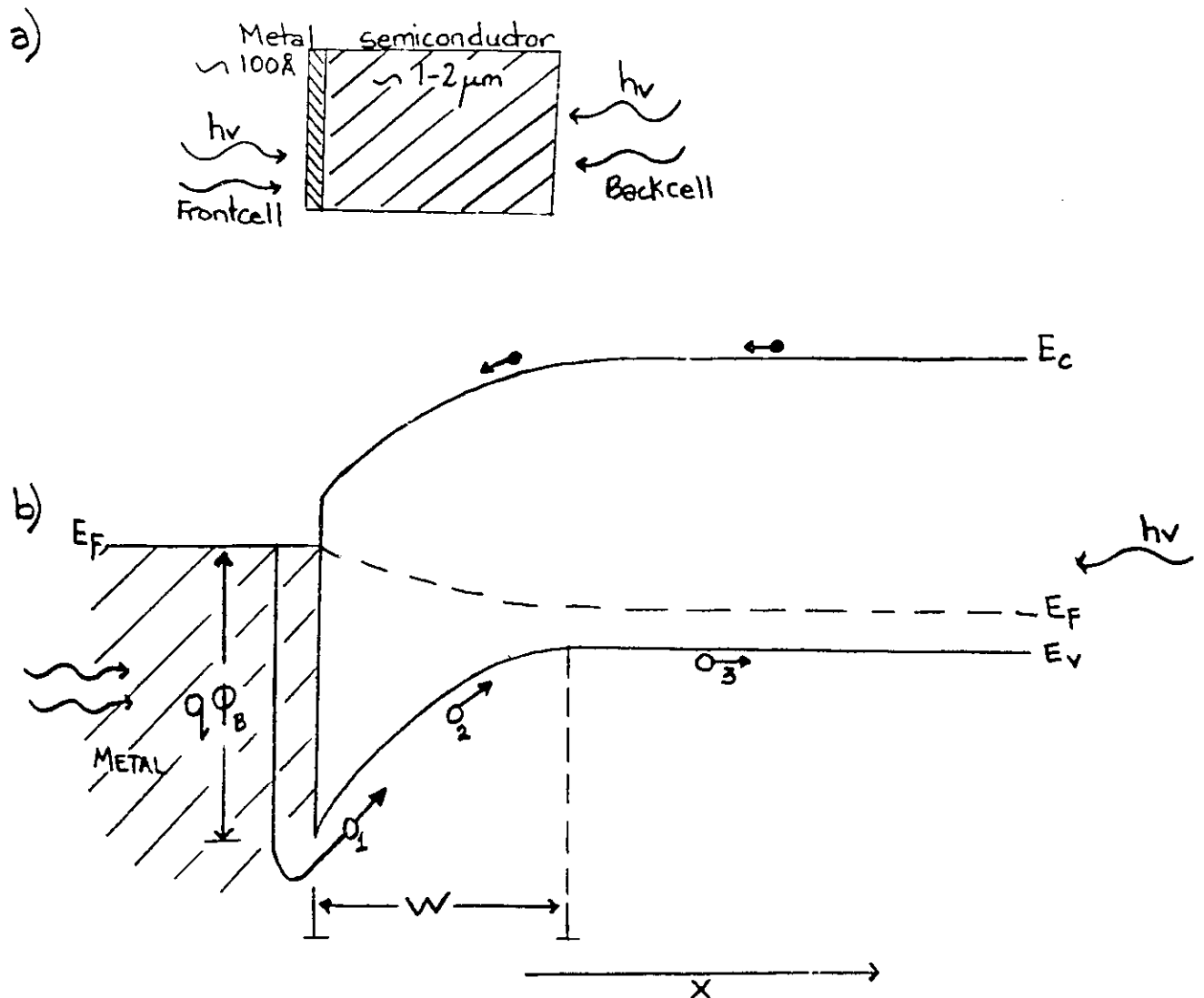


Figure 3.6: a) Frontcell and backcell illumination geometries of a Schottky junction.
 b) Equilibrium band diagram of a Schottky junction under illumination, illustrating the 3 current producing absorption processes.

Usually one is not limited by the fundamental diffusion length but by a reduced L , due to a decrease of the carriers lifetime, stemming from the number of recombination centres formed by a given preparation method of the semiconductor (grain boundaries, trap centres, surface states etc.). In general, there are 3 photocurrent components produced by the light absorbed. Assuming a front cell configuration, as in figure 3.6a,b light of energy $\phi_B < h\nu < E_g$ can be absorbed in the metal and excite holes over the barrier into the semiconductor (process 1, figure 3.6b). The dependence of process 1 to the incident light energy is used to measure the barrier height (see section 1.4.3). Short wavelength light ($h\nu \gg E_g$) reaching the semiconductor is mainly absorbed in the depletion region, w , (process 2). Longer wavelength light ($h\nu \approx E_g$) is absorbed in the bulk region of the semiconductor (process 3). For PV cell applications the photoexcitation of carriers from the metal into the semiconductor contributes less than 1% to the total photocurrent and therefore can be neglected. Thus, the total photocurrent generated will be the sum of the contributions from processes 2 and 3.

The advantages of a Schottky junction over other types of junctions are :

- 1) low temperature processing because no high temperature diffusion is required (although this is not always true) ,
- 2) adaptability to polycrystalline and thin film solar cells ,
- 3) high radiation resistance due to high electric field near the surface (in the frontcell configuration) ,

4) high current output and good spectral response , due to the presence of the depletion region right at the semiconductor surface which can substantially reduce the effects of low lifetime and high recombination velocity near the surface .

3.7. SOLAR CELL PARAMETERS :

Since the possibility of making an Ag_2O Schottky junction PV cell for solar applications will be examined, let us introduce some of the solar cell evaluation parameters. In figure 3.7a,b, the equivalent circuit and the current versus voltage (I - V) behaviour of an ideal solar cell are presented. The equivalent circuit, in figure 3.7a, is made of a current component I_L generated by light, a diode with a current component $I_S(\exp(qV/KT) - 1)$ and three resistances : R_S (in series), R_{Sh} (in parallel) and R_L (the load resistance). The I - V behaviour of a PV cell is expressed by the following equation :

$$I = I_S (\exp[qV/K_B T] - 1) - I_L \quad (3.1)$$

The above equation was deduced by applying the first law of Kirchoff at the point A in figure 3.7a.

where : $I_S = A^* T^2 \exp[-\phi_B / K_B T]$, called the saturation current

$$A^* = \frac{4\pi q m^* K_B^2}{h^3} \text{ , called the effective Richardson constant}$$

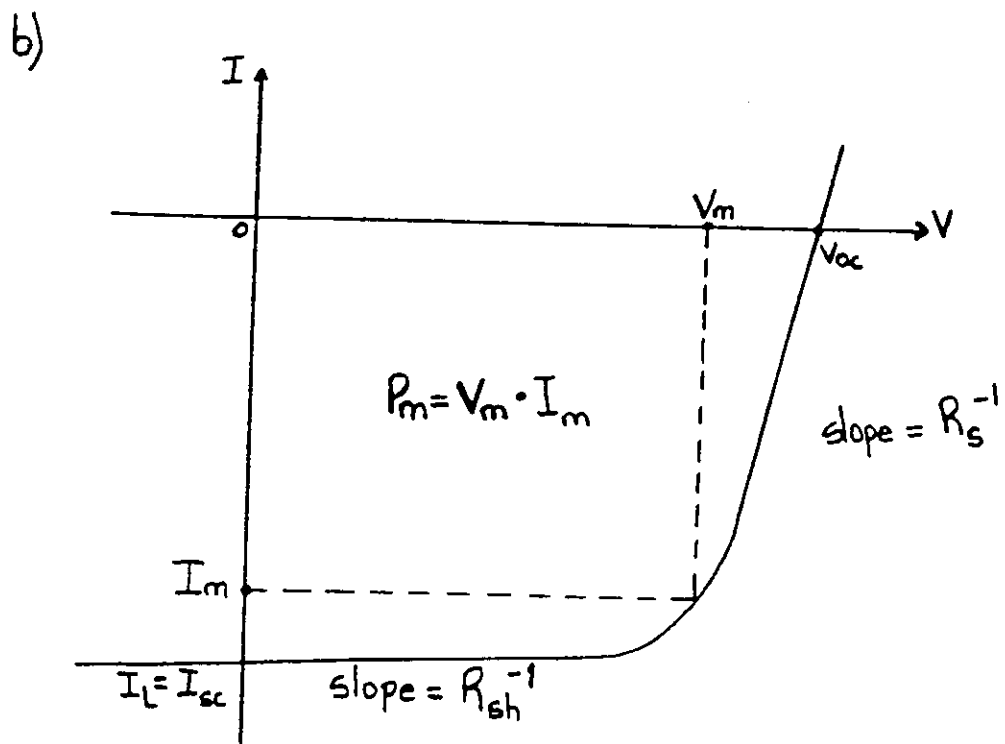
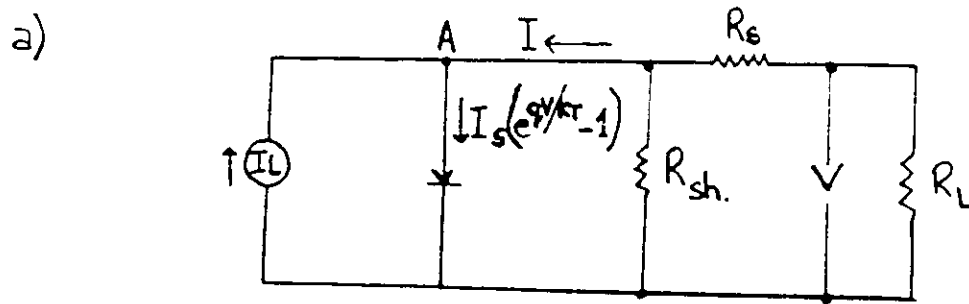


Figure 3.7: a) solar cell equivalent circuit,
b) ideal current-voltage behaviour.

Where ,

K_B : Boltzman's constant

h : Plank's constant

q : electron's charge

m^* : effective mass of carriers

T : temperature

ϕ_B : barrier height

I_L : current that results from the photoexcited carriers,

it is proportional to the number of absorbed photons

Is.c. : the short circuit current is equal to I_L

Vo.c. : the open circuit voltage is obtained by setting $I = 0$ in equation (3.1).

Therefore , the open circuit voltage will be :

$$Vo.c. = K_B T / q \ln(I_L / I_S + 1) \approx K_B T / q \ln(I_L / I_S) \quad (3.2)$$

Under load conditions the maximum power output P_m will be, $P_m = V_m I_m$, as it is illustrated in figure 3.7b.

where : V_m and I_m are the maximum voltage and current under load.

The best Au(Ohmic)/Ag₂O/Ag cells gave a Vo.c. of over 150 mV and Js.c. $\approx 100 \mu A/cm^2$ under 50 mW/cm² illumination with a quartz iodine lamp. The above Schottky barrier cells are not efficient solar cells. In part because of the polycrystalline structure of the Ag₂O film, which creates a large number of grain boundaries thus reducing the recombination time.

3.8. PHOTOVOLTAIC SPECTRA :

A large number of PV spectra, of more than 150 samples were taken with different rectifying metal contacts, such as Al and Pt in the frontcell geometry and Ag usually in the backcell configuration. Figures 3.8, 3.9 and 3.10 present typical PV spectra. Figure 3.8, shows the spectrum of an Ag/Ag₂O/Ag sandwich with an estimated Ag₂O film thickness of the order of 1 μ m. In this case two junctions are opposed to each other. For $\lambda < 540$ nm the front junction is active while for $\lambda > 540$ nm the back junction takes over, as indicated by the sign reversal of the photosignal. The sign reversal is due to the fact that short wavelength light (of large absorption coefficient) is absorbed close to the front surface, thus the front junction is active. For longer wavelengths, as the absorption coefficient decreases, light is now mostly absorbed in the bulk of the semiconductor, therefore the back junction photosignal contribution dominates that of the front. In figure 3.9, the PV spectrum of the same oxide sample, as in figure 3.8, is presented, but this time an evaporated Au film was chosen, which gives an Ohmic contact (Ohmic Au/Ag₂O/Ag). Notice the large photoresponse in the short wavelength range indicating that the oxide film has a thickness of the order of $1/\alpha + L$. Considering the Moss criterion [35] the energy gap is estimated to be around 1.44 eV. In figure 3.10 the PV spectrum of a thicker oxide sample is presented again in the

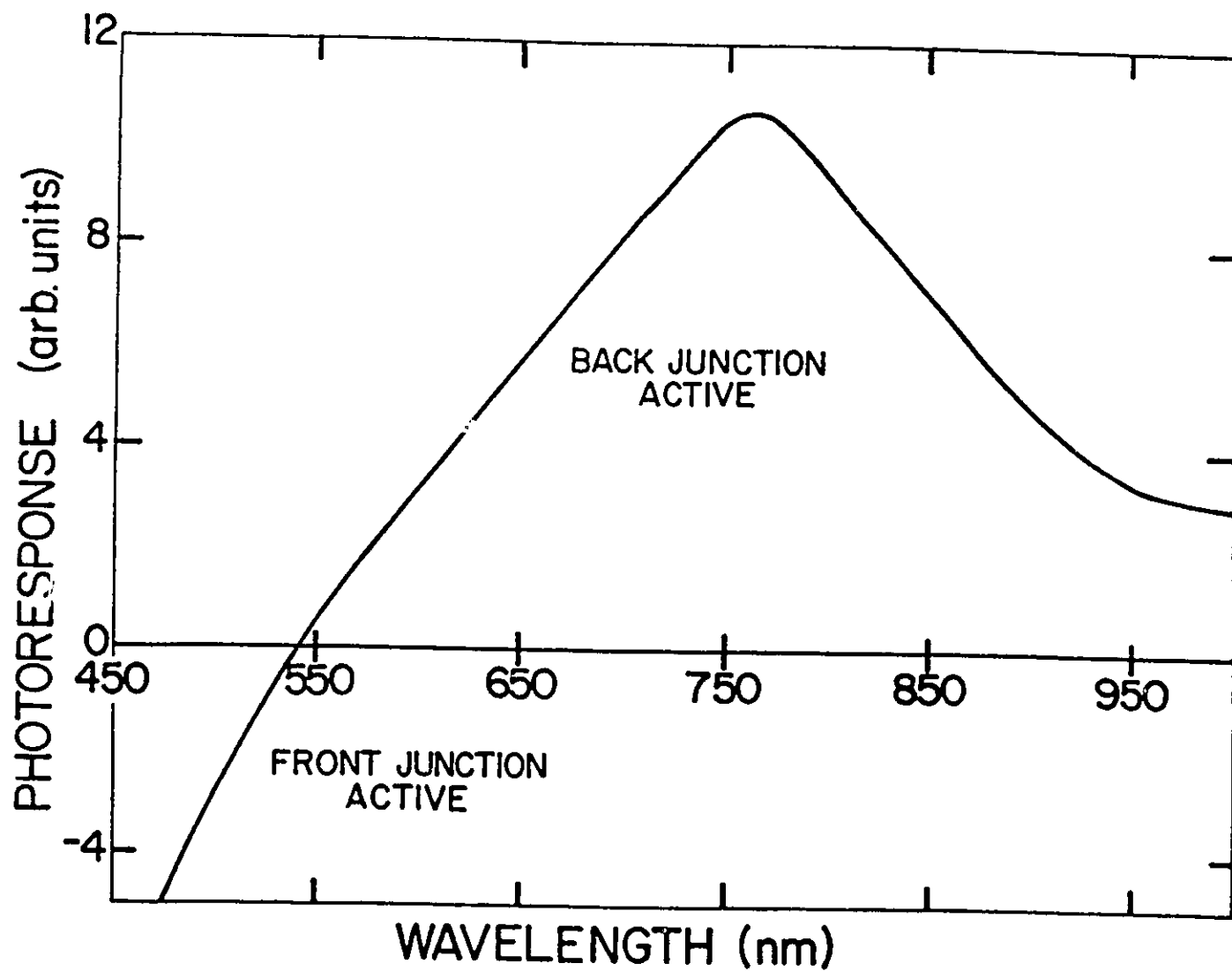


Figure 3.8: Photovoltaic spectrum of a Ag/Ag₂O/Ag sandwich (two opposed junctions).

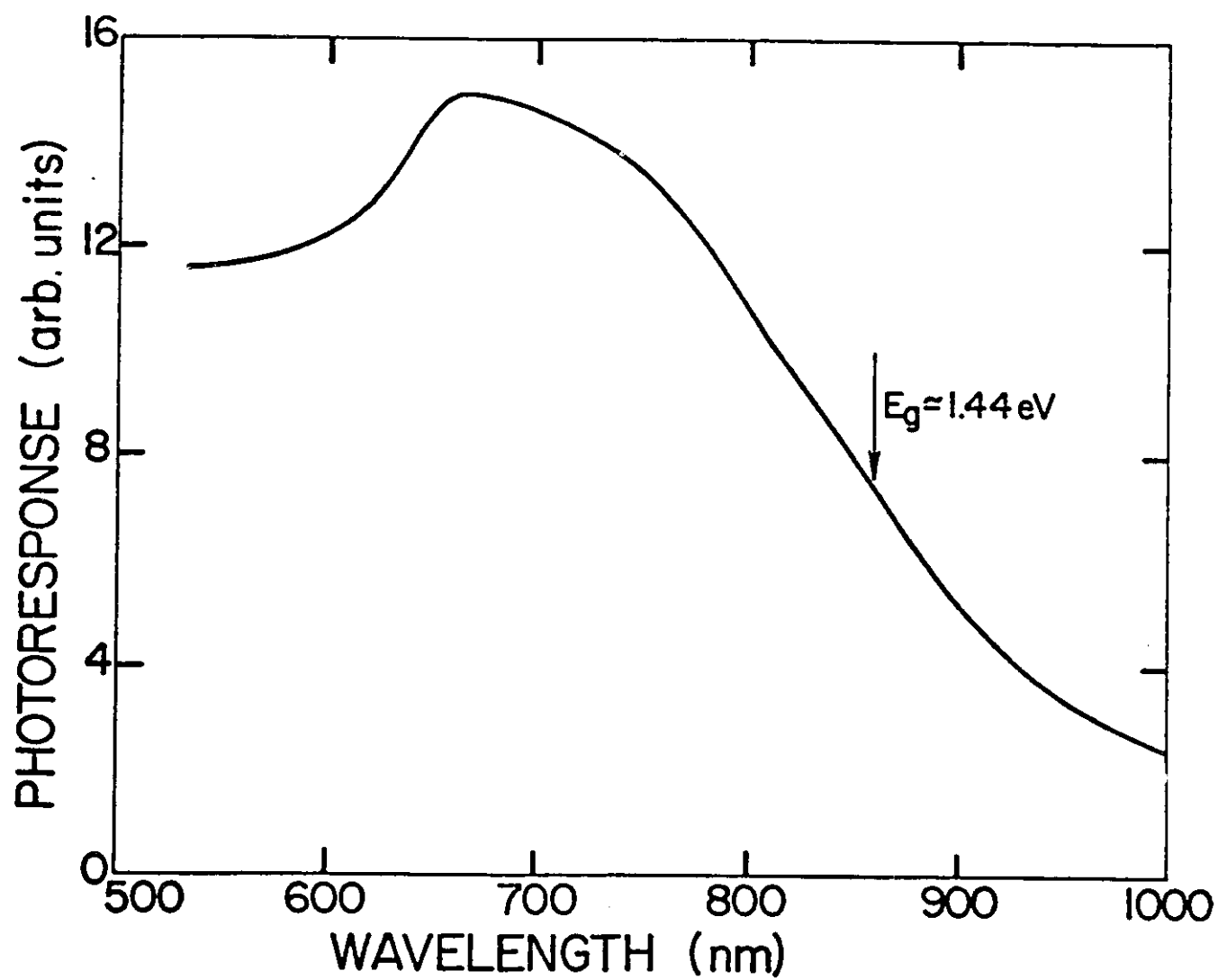


Figure 3.9: Photovoltaic spectrum of a Au/Ag₂O/Ag cell with an Ag₂O film thickness of about 1 μm .

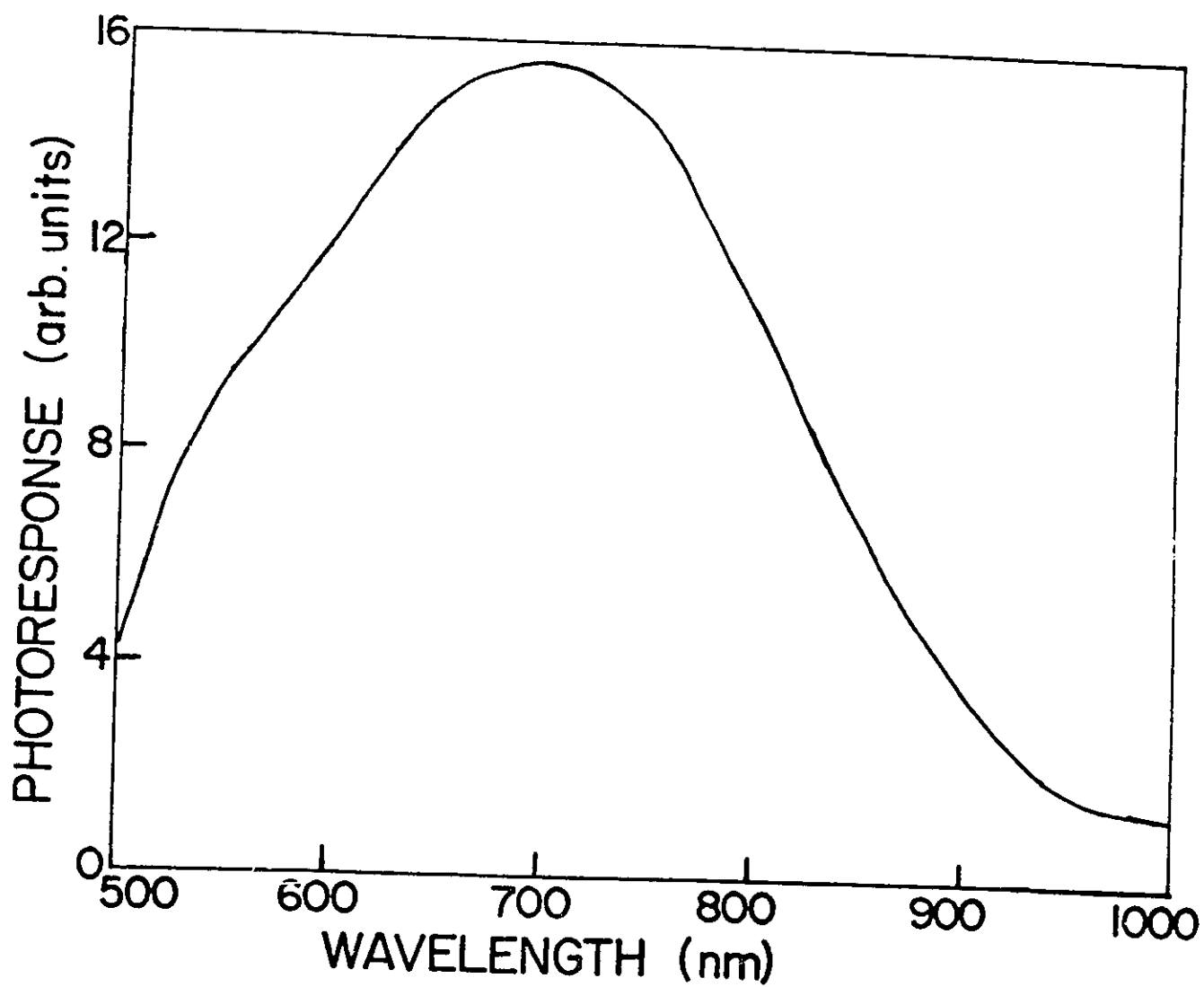


Figure 3.10: Photovoltaic spectrum of a Au/Ag₂O/Ag cell with an Ag₂O film thickness of about 10 μ m.

Au/Ag₂O/Ag(backcell) sandwich configuration. Comparing figures 3.9 and 3.10 the difference in thickness between the two oxide samples is apparent in their different short wavelength photoresponse. Short wavelength light is absorbed close to the front surface, therefore the photocreated carriers would have to migrate towards the back junction, in order to contribute to the photosignal. Assuming that the semiconductor layer thickness of a Schottky backcell is of the order of the free carrier diffusion length, then its photoresponse in the short wavelength spectral region (which corresponds to a large absorption coefficient region) will be enhanced compared to that of an equivalent backcell with a thicker semiconductor layer.

Even though Ag₂O is a direct bandgap semiconductor, no steep decrease in the photoresponse was observed below the energy gap. In the PV spectra of figures 3.8 , 3.9 and 3.10 there is a spectral spread of 100 to 150 nm between the peak response and the half maximum photoresponse , where the bandgap is taken to be according to the Moss criterion [36] . This relatively long tail could be due to impurities (sulphur , chloride , carbon) and structural defects in the oxide, resulting in an energy level distribution extending well into the gap ; at the same time , variable oxygen concentration across the oxide film would cause grading of the bandgap . Applying the Moss criterion , the value of the Ag₂O bandgap , averaged over a large number of samples is 1.42 ± 0.04 eV .

In the following table the various values of the Ag_2O energy gap appearing in the literature are presented. The energy gap values range between 1.2 and 1.85 eV. The energy gap value obtained in this work is in close agreement with four of the six values (# 2, 3, 4, 6) presented in table 1, suggesting that these values are the most reliable.

TABLE 1

#	ENERGY GAP in eV	METHOD OF OXIDE PREPARATION	REFERENCE #
1	1.85	-----	2
2	1.4 - 1.5	Sputtering	5
3	1.33	Chemical Reaction	37
4	1.42	Hydrothermal Synthesis	4
5	1.2	Compressed Powder	1
6	1.5	Sputtering	1
	1.42 ± 0.04	Anodic Oxidation	38

The PV spectra discussed here were taken with fast chopped light techniques (chopping frequency higher than 75 Hz), masking a number of slow PV effects, such as the evolution of photosignal with time (over seconds and some times even signal polarity reversal). Such effects have been observed in anodically grown Cu_2O as well [7] and remain largely unexplained.

grown Cu_2O as well [7] and remain largely unexplained.

3.9. SCHOTTKY BARRIER MEASUREMENTS :

For thin ($\approx 1 \mu\text{m}$) oxide films the back junction of $\text{Ag}_2\text{O}/\text{Ag}$ was usually active under illumination with light of energy close to the bandgap. For certain samples, usually of thicker oxide films (oxide thickness about $10 \mu\text{m}$), the front junction was active even for light energies below the gap, making possible to determine the barrier heights of various metals with Ag_2O . The reason for such an unusual behaviour could be due to : 1) a front rectifying junction of superior quality compared to the back one, and 2) although less likely, the possibility that the polycrystalline texture of the oxide film could increase the path of the multiply scattered light [39], thus artificially increase light absorption .

The barrier heights of Ag , Al and Pt were obtained using the photoelectric method, as discussed in section 1.4.3 . This method was preferred because the barrier height values are directly derived from PV spectra and more importantly do not necessitate the application of any voltage to the electrically fragile cells . The observed barrier heights are :

$0.90 \pm 0.02 \text{ eV}$ for $\text{Ag}_2\text{O}/\text{Ag}$, (figure 3.11) ,

$0.93 \pm 0.02 \text{ eV}$ for $\text{Al}/\text{Ag}_2\text{O}$, (figure 3.12) ,

$0.95 \pm 0.02 \text{ eV}$ for $\text{Pt}/\text{Ag}_2\text{O}$, (figure 3.13) .

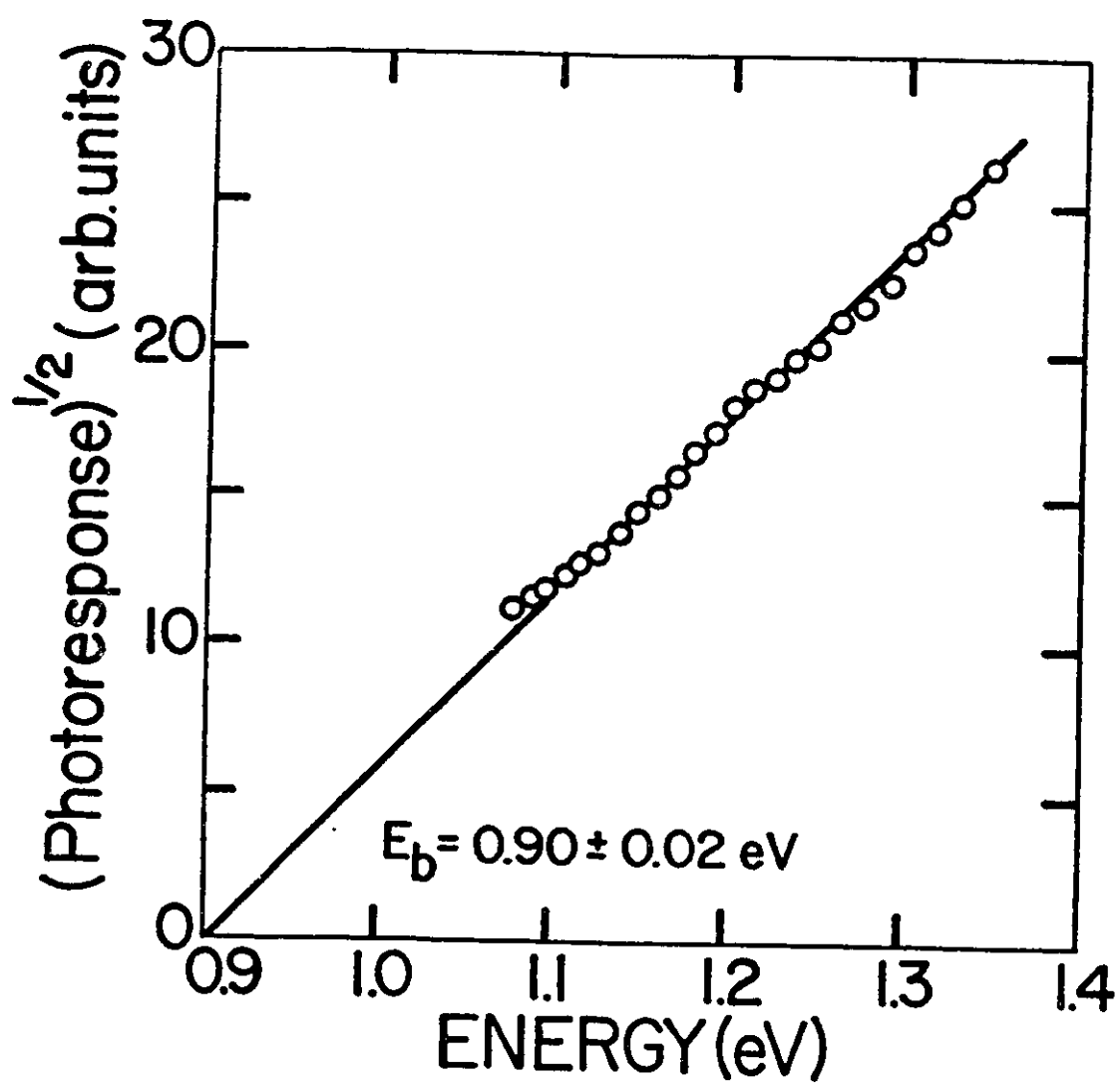


Figure 3.11: Barrier height determination of a $\text{Ag}_2\text{O}/\text{Ag}$ junction

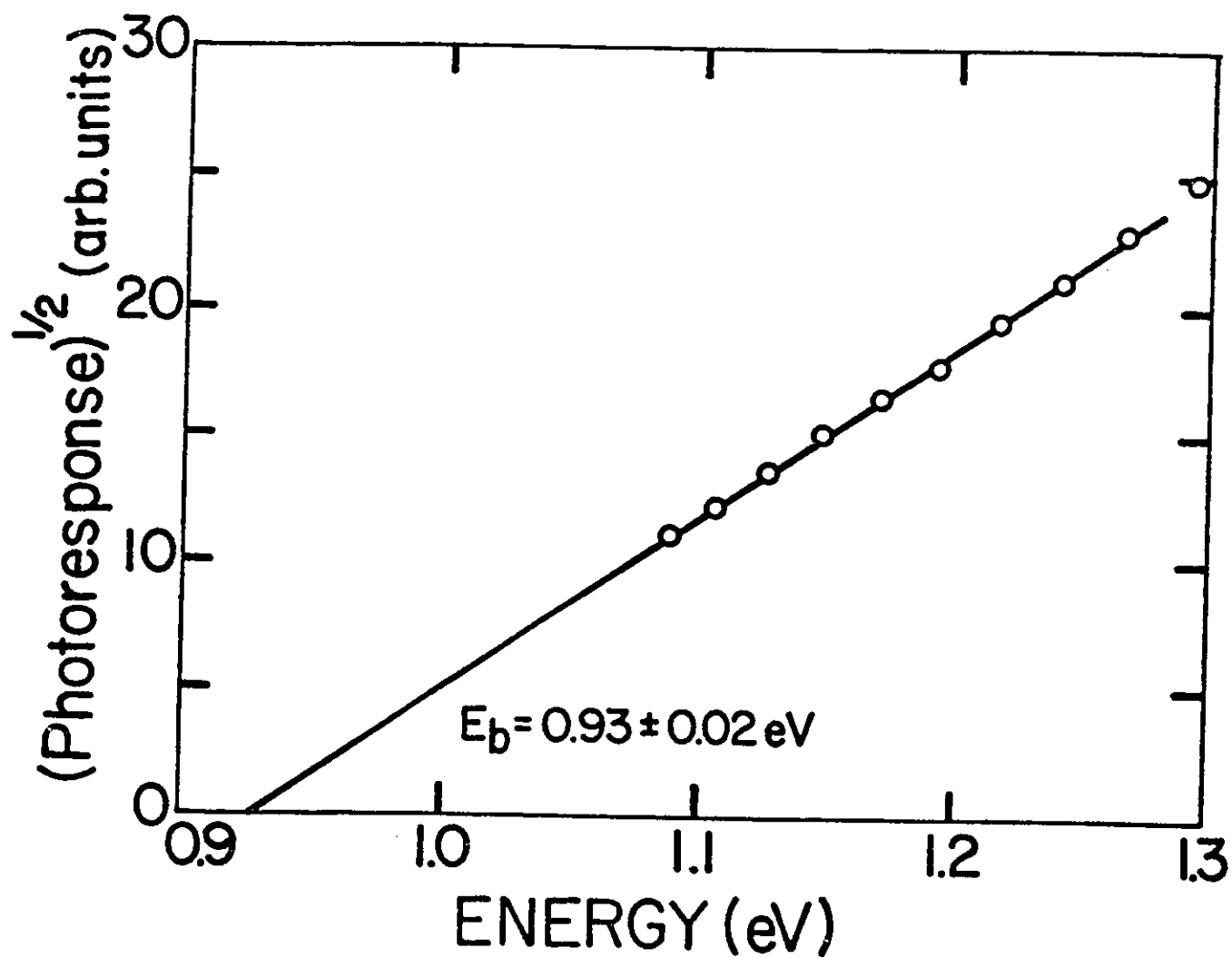


Figure 3.12: Barrier height determination of a Al/Ag₂O junction.

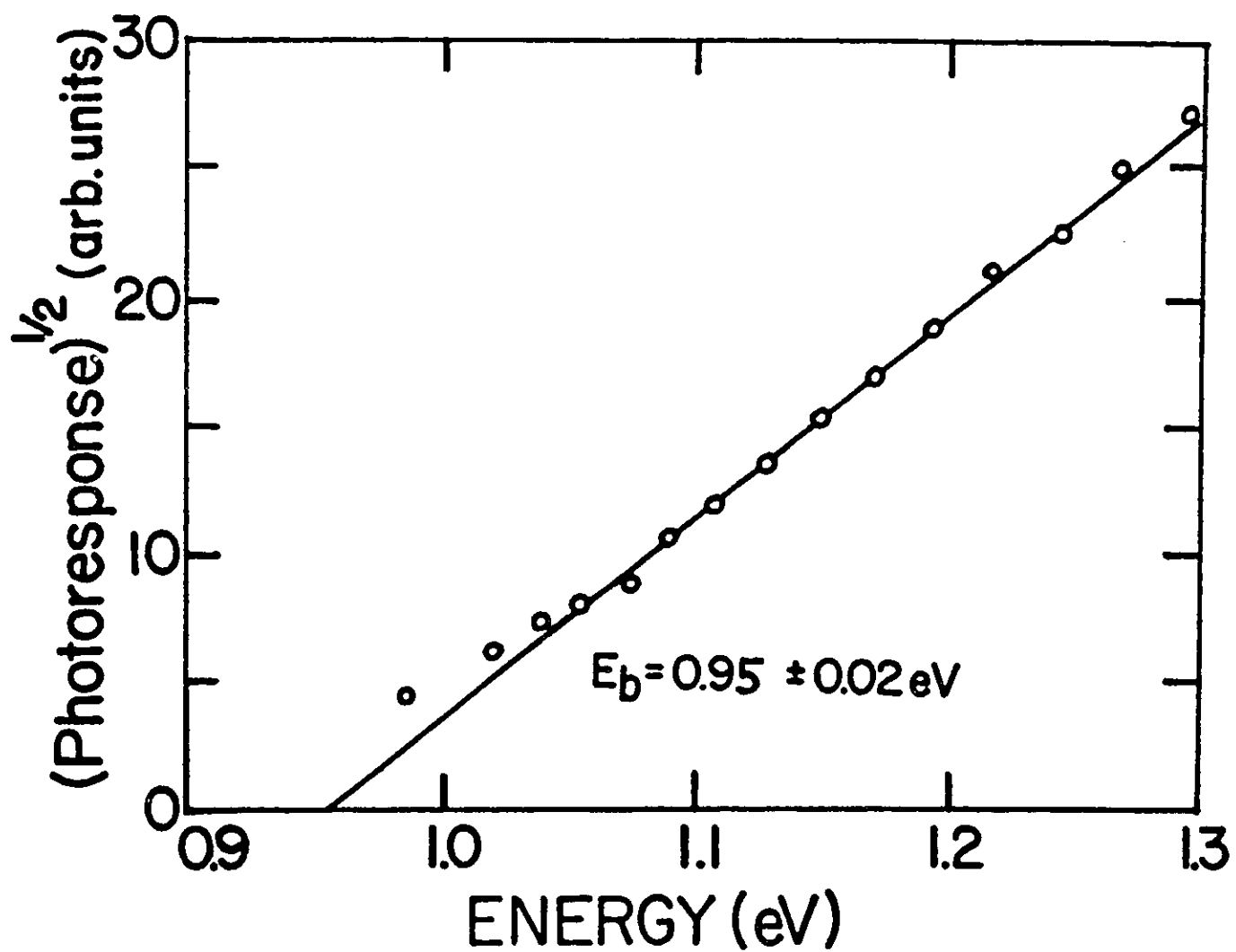


Figure 3.13: Barrier height determination of a Pt/Ag₂O junction.

Gold was found to be Ohmic, when evaporated under conditions which do not cause oxide reduction (these conditions are : pressure of the order of 6×10^{-6} torr and evaporation rate of 0.1 - 0.05 nm/sec, for a 7 to 10 nm film) .

From theoretical considerations, when no surface states are present the barrier height is determined by the metal work function (ϕ_m) for a given semiconductor. In this case for a p - type semiconductor a rectifying junction is obtained whenever ϕ_m is less than ϕ_{sc} (see section 1.3.1). Otherwise, if surface states are present, the barrier height is not sensitive to the metal work function (see section 1.3.2). The work functions for Al, Ag and Pt are respectively : 4.2, 4.3 and 5.4 eV. It would then be expected that the Pt/Ag₂O junction be less rectifying than those of Al and Ag but this is not evident from the experimental data. Metals of lower work functions like In and Mg were evaporated on Ag₂O but without success in obtaining PV spectra.

The barrier heights obtained indicate that most likely the barrier is surface state controlled or as for Cu₂O [40] the front barrier is dictated by both surface states and in parallel by a partial reduction of the Ag₂O surface induced by the evaporated metals and subsequent interdiffusion phenomena .

3.10. CONCLUSION :

In this chapter we investigated the photovoltaic properties of p-type Ag_2O films grown anodically on Ag. The Schottky junction of Ag_2O seems to be surface state controlled with the Fermi level pinned approximately 0.9 eV above the valence band. The energy gap of the grown oxide samples was determined from PV spectra to be 1.42 ± 0.04 eV at room temperature. So far the Ag_2O Schottky junction cells are not efficient solar cells, mainly because of the polycrystalline structure of the grown films, with a large number of grain boundaries which reduce the free carrier recombination lifetime. Difficulties also arise from electrical breakdown and poor thermal stability of the oxide films. With improvement of the oxide film quality more fundamental studies could be attempted on Ag_2O , such as gap variation with temperature and excitonic studies.

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CHAPTER 4

PHOTOVOLTAIC STUDY OF ANODICALLY GROWN OXIDE FILMS

ON Ag-Cu ALLOYS

4. INTRODUCTION

In this chapter the photovoltaic effect is used again to characterize, together with X-ray powder diffraction analysis, the oxide films grown by anodic oxidation on Ag-Cu alloys. Cu_2O [1] and Ag_2O (see chapter 3) [2] films have been grown anodically and studied using the photovoltaic effect. Since both oxides have the same crystalline structure [3], there is an interesting possibility of growing a substitutional type of Ag-Cu mixed oxide. Thermal oxidation of Cu followed by doping with Ag concentrations up to 2% atomic in Cu_2O , were carried out by Schwab et al. [4,5]. Hayashi et al. [6] thermally oxidized Ag-Cu alloys too. The Ag concentration in the grown oxide was again no more than 2% atomic. The above groups studied the influence of a small amount of Ag doping in the excitonic structure of Cu_2O by absorption measurements at low temperature. Thermally it is not likely possible to obtain a mixed oxide, because as the above studies here indicated, one cannot have a high concentration of substitutional Ag in Cu_2O nor of Cu in Ag_2O . The former is due to the fact that Ag_2O is unstable [7] at $T > 160^\circ\text{C}$ at atmospheric pressure.

Anodic oxidation, being a relatively low temperature oxidation process, may thus be the only possible way one could grow a mixed oxide ($\text{Ag}_2\text{xCu}_{2(1-\text{X})}\text{O}$) with a large concentration of Ag. The metallic alloys used here as starting material were usually rapidly quenched from the melt in the hope of obtaining a single or metastable phase, and thus eventually a single phase mixed oxide. Micrometer thick oxide films were grown on the metallic alloy substrate using a variety of solutions. The films were characterized by X-ray powder diffraction and by studying their photovoltaic spectra at room temperature.

In the following sections, we first discuss the Ag-Cu alloy preparation method, the oxidizing solutions used and the grown oxide characterization procedures and results. Second, the photovoltaic spectra of a few representative samples are presented, showing the transition in photoresponse from Ag_2O to Cu_2O . Finally, a discussion of the results and a conclusion close this chapter.

4.1. EXPERIMENTAL

4.1.1. Metallic alloy preparation :

Ag-Cu alloys (phase diagram figure 4.1, [8]) of various concentrations were prepared by melting Ag and Cu of 99.99% at. purity , in an Argon or Nitrogen atmosphere at 1100 °C , inside a sealed quartz tube . The molten metallic alloys were rapidly cooled by submerging the quartz tube in water . Thin rectangular metallic samples were prepared for oxidation by the following procedure :

- a) rolling down the alloy pellet ,
- b) polishing mechanically with increasingly finer powders ,
- c) etching chemically in $\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ (1 : 4 parts) ,
- and d) cleaning with distilled water in an ultrasonic bath .

The alloys were analyzed by X-ray diffraction , which indicated that for concentrations of Ag and Cu up to 8% at. a single phase metastable alloy was obtained (see phase diagram [8]) . A two phase system (Ag and Cu phase) was usually obtained if the concentration of one of the alloy components was higher than 8% atomic . For one of the prepared metallic alloys (Ag 37% / Cu 63% at.) there were indications of a third crystalline phase (metastable Ag/Cu phase) : as evidenced by X-ray diffraction the lattice parameter of the metastable phase was :
 $a = 3.75 \pm 0.01 \text{ \AA}$, corresponding to Ag 25% / Cu 75% atomic [9] .

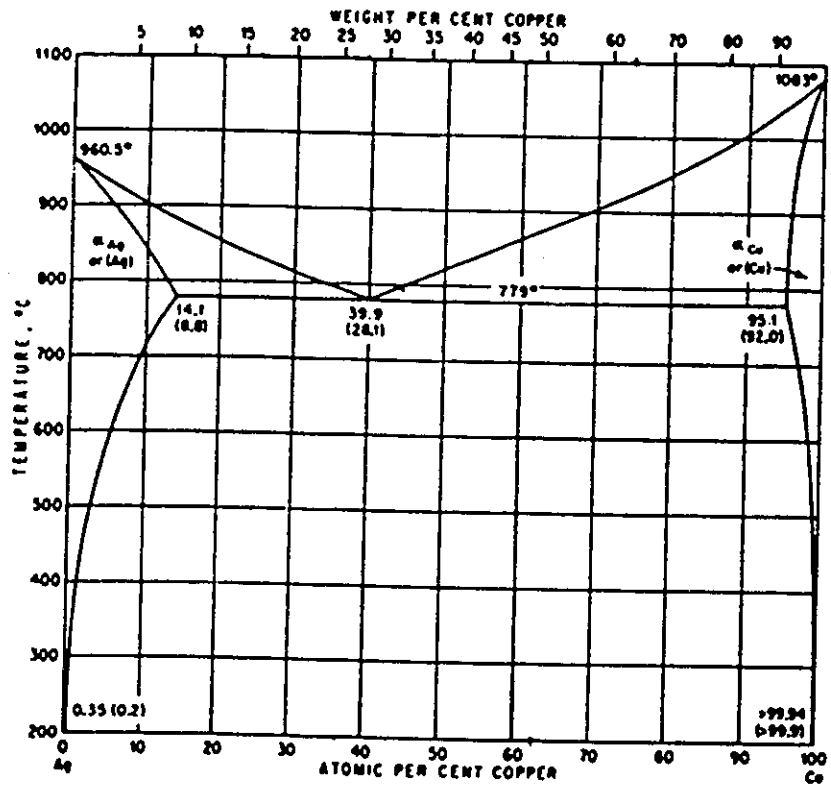


Figure 4.1: Ag-Cu alloy phase diagram (8).

4.1.2. Anodic oxidation conditions :

The oxidizing solutions and conditions used , were those that have been previously found to grow relatively good quality micrometer thick Cu_2O [1] and Ag_2O (see section 3.3.2) [2] films :

(S1) : $0.01 \text{ M CuSO}_4 + 0.005 \text{ M NaCl} + 0.005 \text{ M LiCl}$, ($\text{PH} \approx 5.2$) ;

Oxidizing conditions : Constant current : $2-3 \text{ mA/cm}^2$,

Duration : 1-2 hours, $T : 80-85^\circ\text{C}$.

(S2) : $0.02 \text{ M Ag}_2\text{SO}_4 + 0.17 \text{ M NH}_4\text{OH}$, ($\text{PH} \approx 11.8$) ;

Oxidizing conditions : Constant current : $3-4 \text{ mA/cm}^2$,

Duration : 2-3 hours, $T : 25-45^\circ\text{C}$,

slow stirring.

(S3) : 2 M NaOH , ($\text{PH} \approx 14$) .

Oxidizing conditions : Constant current : $0.2-0.3 \text{ mA/cm}^2$ or

Constant voltage : $0.20-0.25 \text{ V}$,

Duration : 3-4 hours, $T : 40-45^\circ\text{C}$,

fast stirring.

Solution (S1) favours Cu_2O growth while (S2) and (S3) favour Ag_2O . All solutions were prepared using reagent grade chemicals and distilled water , and were saturated with both Ag_2O and Cu_2O powders during oxidation to avoid dissolving any of the oxides grown .

A major difficulty is that there are no conditions in the potential-PH diagrams of the Ag , Cu - H₂O systems [10] that would favour equally well the growth of Ag₂O and Cu₂O . The above potential-PH diagrams however are only valid for solution (S3) . The particular composition of solutions (S1) , (S2) and the as yet unknown film formation mechanisms associated with them may possibly allow mixed oxide growth .

4.1.3.Characterization of the grown oxide films :

The oxides were examined by X-ray diffraction of powder samples scraped off the films , revealing the nature of their constituents . The characteristics of several samples of various Ag - Cu concentrations , oxidized in the three solutions available, are presented in Table 1. In general, whenever the metallic alloy was 2-phase and oxidized in a solution favouring either Ag₂O or Cu₂O , the oxide predominantly grown was that favoured by the solution . A mixed oxide was usually obtained when the metallic alloy was single - phase . There was evidence that compounds from the solution were incorporated in small amounts in the oxide during oxidation. Several samples showed the presence of AgO and AgCl at the same time , particularly for those metallic alloys oxidized in solution (S1) .

Examination with an optical microscope revealed that all 2 and 3 phase metallic alloy samples were totally covered by an oxide film when oxidized in solution (S1) . With solutions (S2)

TABLE 1

SAMPLE #	SOLUTION #	COMPOSITION OF METALLIC ALLOY in % atomic of Ag / Cu	PREDOMINANT OXIDE(S) GROWN	PHOTOVOLTAGE (50 mW/cm ²) in mV	ENERGY GAP in eV	COMMENTS
1	(S2)	100 / 0, S.P.	Ag ₂ O	100	1.42±.03	Ref.#2
2	(S2)	96.5/3.5, S.P.	Mixed oxide AgO	0.11	1.52±.05	
3	(S3)	96.5/3.5, S.P.	Mixed oxide AgO	0.10	1.61±.05	
4	(S1)	91.5/8.5, S.P.	Mixed oxide	100	1.85±.03	Photo-memory effects
5	(S1)	37 / 63 ^a , T.P. 25 / 75 ^b	Cu ₂ O Mixed oxide	130	2.02±.03 1.80±.10	Traces of AgCl, Ag, AgO
6	(S2)	37 / 63 ^a , T.P. 25 / 75 ^b	Ag ₂ O	—	—	Cu-phase not oxidized
7	(S3)	37 / 63 ^a , T.P. 25 / 75 ^b	Ag ₂ O	0.15	—	Cu-phase covered by thin oxide
8	(S1)	17 / 83, D.P.	Cu ₂ O AgO	1.2	2.02±.03	Traces of AgCl
9	(S1)	1 / 99, S.P.	Cu ₂ O	220	2.00±.03	
10	(S1)	0 / 100, S.P.	Cu ₂ O	250	2.02±.03	Ref.#1

S.P. : Single phase .

D.P. : Double phase .

T.P. : Three phases .

a : Composition as it was before alloying .

b : Composition of metastable phase [9] .

and (S3) oxide coverage was completely only on the Ag-phase, while the Cu-phase was only covered by a very thin film, these almost bare regions (usually 5 to 10 μm in diameter and a few hundred $\text{\AA}$ thick) acted as electrical shorting paths preventing any photovoltaic measurements (samples 6 and 7 in table 1). The single phase metallic alloys were always covered by an oxide film in all three solutions .

4.2. PHOTOVOLTAIC SPECTRA :

A gold semi-transparent film 7 to 8 nm thick was evaporated onto the oxide film surface , to serve as an ohmic contact for the photovoltaic measurements. Figure 4.2 shows the sample in the backcell configuration, which was used for the PV measurements throughout this chapter. The magnitude of the photovoltage obtained by illumination with a 50 mW/cm² quartz-iodine lamp , suggested to a certain extent the structural quality of the oxides grown . The lower the photovoltage (Table 1), the larger the number of defects and low resistance paths in the oxide film. The samples that exhibited rectification were usually a few micrometers thick, the oxide thickness varying locally due to the relief of the pyramidal polycrystalline texture.

The photoresponse spectra of the metallic alloy - oxide junction were taken using chopped radiation from a Bausch-Lomb high intensity monochromator with 10 nm of bandwidth. The photosignal was detected with a phase sensitive amplifier, again avoiding charging effects [1] associated with D.C. measurements . The energy gaps were deduced from the photovoltaic spectra , using the Moss criterion [11] and they were indicative of the nature of the oxides grown. The polarity of the photosignal, when compared to that of either Ag₂O [2,12,13] or Cu₂O [14] which are known to be p-type semiconductors, indicated that all grown oxide samples were p-type .

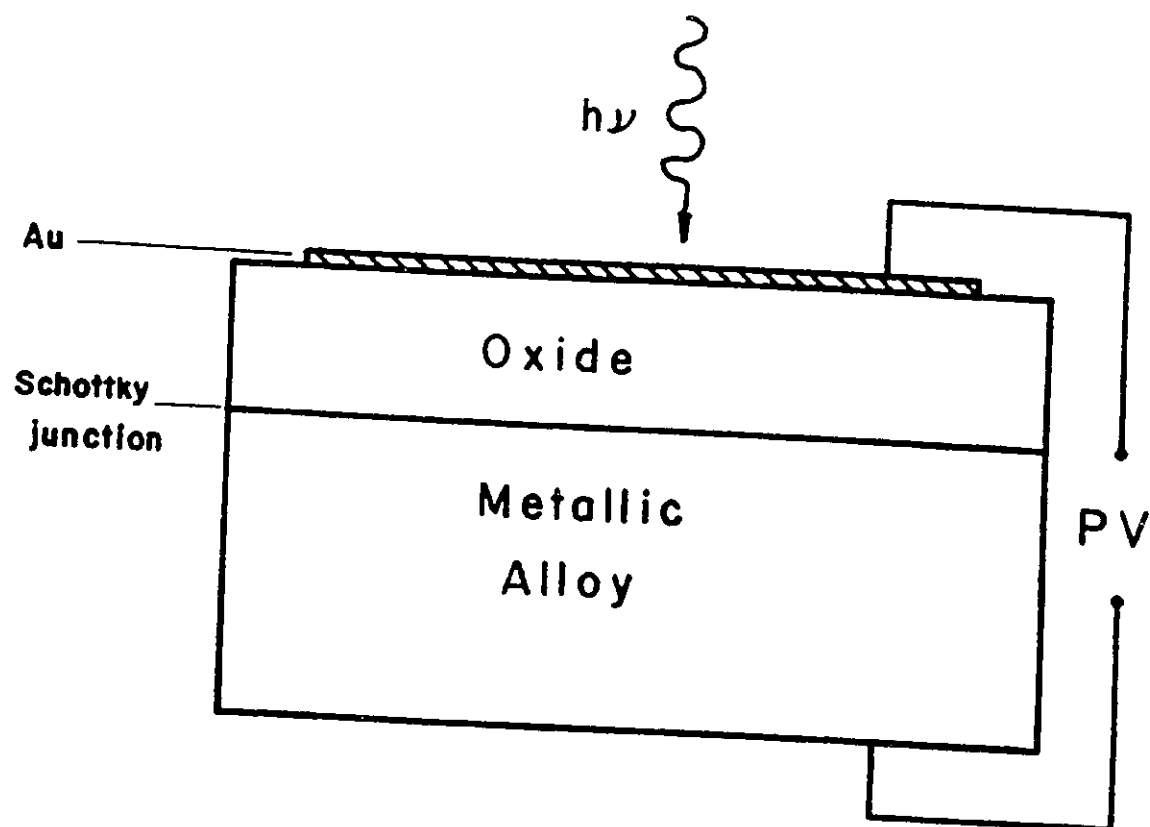


Figure 4.2: Sample configuration for photovoltaic measurements.

In figure 4.3, a number of photovoltaic spectra are presented, showing a representative change in response for the various samples (the number attributed to each curve corresponds to the same sample number in Table 1) as one moves from Cu_2O (curve #10) to Ag_2O (curve #1). The dashed line section of the photoresponse curves #2 and #3 is due to the presence of AgO ($E_g \approx 2.2$ eV) in the grown oxide films as was indicated by X-ray powder diffraction.

Figure 4.4 illustrates the energy gap variation of the various grown oxide films as a function of the Cu atomic percentage in the metallic alloy they were grown from. Note, that for sample #5 two energy gap values are presented. The evidence for these values comes from the photovoltaic spectrum. It showed a typical Cu_2O photoresponse curve, plus a second one of reverse polarity at longer wavelengths : that second curve could be attributed to a second phase in the sample, possibly a mixed Ag-Cu oxide, as the band gap value suggests. When a photovoltaic spectrum was repeated on the same sample a week later, the second curve was missing, indicating that the mixed oxide was in fact unstable. The error bars of the energy gap are determined by both the scatter in the data and the accuracy of the method they were determined from (Moss criterion). The solid line between the energy gaps of pure Ag_2O and Cu_2O represents the suggested theoretical energy gap variation, assuming that : a) both Ag and Cu are readily oxidized without any preference towards one or the other by the solutions used, b) Ag and Cu are interchangeable in

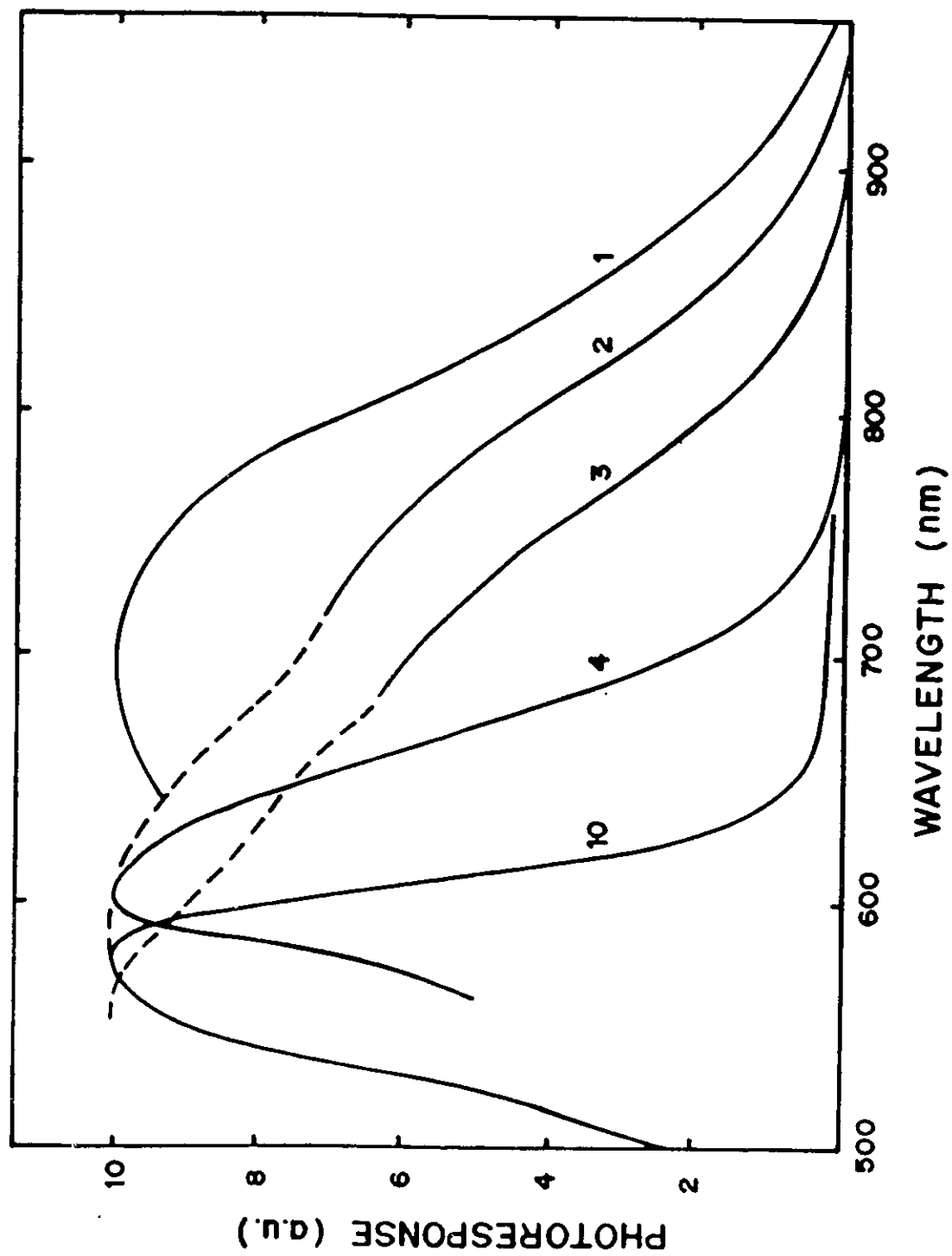


Figure 4.3: Normalized photoresponse spectra for various oxide films. The sample numbers are as in table 1.

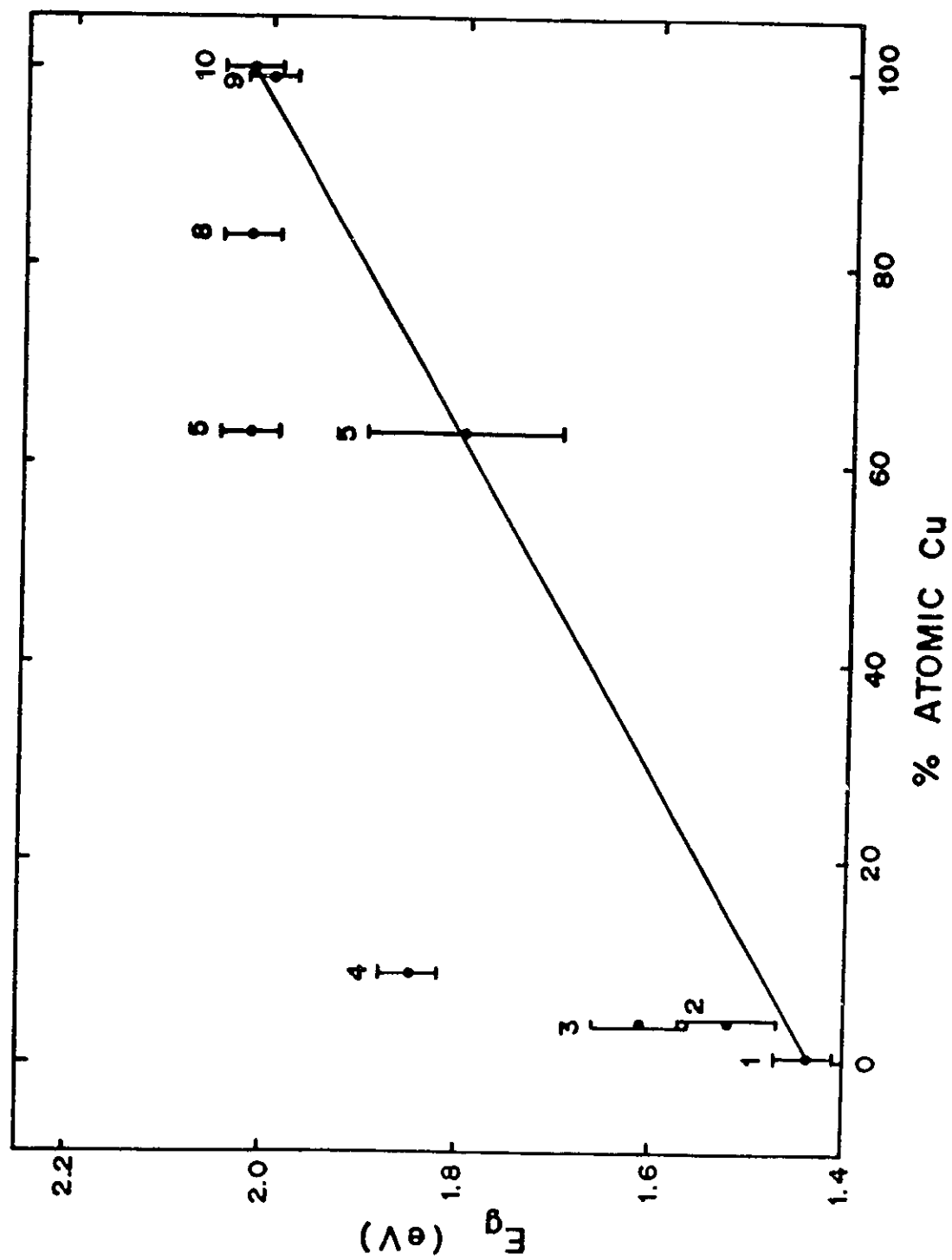


Figure 4.4: Energy gap of the oxide films as a function of the metallic alloy composition. The sample numbers are as in table 1.

the mixed oxide lattice . It is evident from Figure 4.4 , that there is always more Cu in the oxide grown than expected from the existing Cu concentration in the metallic alloy , suggesting that Cu is more easily oxidized than Ag .

4.3. DISCUSSION

Considering the difference in chemical stability between Cu_2O and Ag_2O one could obtain a tentative explanation of certain of the observed phenomena . For Cu and its oxides in air , CuO is the most stable followed by Cu_2O and Cu . In the case of the Ag oxides - air system the opposite order is valid , that is , Ag is the most stable followed by Ag_2O and AgO . Therefore , a Ag-Cu mixed oxide would tend to dissociate into CuO and Ag . But the dissociation of Cu_2O to CuO is a very slow process at room temperature , thus Cu_2O along with Ag are more likely to be the dissociation products of the mixed oxide . In turn , the reduced Ag in the oxide creates low resistance paths "killing" the photovoltaic response . This is mostly the case for oxides grown with solution (S1) as evidenced by X-ray powder diffraction. Solutions (S2) and (S3) seem to grow more stable oxides on a Ag-rich single phase metallic alloy .

It should also be noted, that photomemory and photosignal evolution effects have been observed for the oxides grown here, as they have been previously observed for anodically oxidized Cu [1] and Ag (see chapter 3) [2], indicating that indeed structural and compositional changes are occurring in the alloy oxides with ageing.

4.4. CONCLUSION

The oxide films grown by anodic oxidation of Ag-Cu alloys were characterized by their photovoltaic response and by X-ray powder diffraction analysis. Single phase metallic alloys yielded single phase oxides, while metallic alloys of 2 or 3 Ag-Cu phases yielded more than one oxide phase. The composition and the stability of the semiconducting oxide films were influenced by the nature of the oxidizing solution as much as by the composition of the metallic alloy they were grown from. Some of the problems associated with anodic oxidation of the Ag-Cu alloys are :

a) non-reproducible photoresponse spectra in the case of samples grown in solution (S1) (evolution of the photoresponse curve shape over a period of a few days after oxidation was completed) ,

b) electrical shorting paths were developed a few days after growth. The multiphase oxide samples dissociated to Cu_2O and Ag or the Cu_2O present induced the dissociation of the mixed oxide when solution (S1) was used. Shorting paths were also present, when 2 and 3-phase metallic alloys were oxidized in solutions (S2) and (S3), due to very thin oxide regions on the Cu-rich metallic phase.

c) ambiguity in interpreting the results when more than one crystalline phase was grown .

The results of this study suggest that the metastable mixed oxides grown seem to have a lifetime of a few days when a second oxide phase is present. It may be interesting to try the anodization and photovoltaic study, described in this chapter, on metastable Ag-Cu metallic alloys resulting from ultra-fast quenching techniques.

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CHAPTER 5

EXCITON - MEDIATED PHOTOVOLTAIC EFFECT IN Cu_2O AND ESTIMATION OF THE 1S YELLOW EXCITON DIFFUSION LENGTH

5. 1. INTRODUCTION:

In order to investigate the role of excitons in the photovoltaic response of Cu_2O , photovoltaic spectra of the $\text{Cu}_2\text{O}/\text{Cu}$ junction were taken at temperatures below 300 K down to 2 K, in the spectral range of the yellow excitonic series. The photovoltaic response is attributed to the diffusion of the n=1 yellow series excitons and their subsequent dissociation at the high electric field metal-semiconductor interface. A simple method is described to measure the diffusion length of the n=1 excitons or of any other particles that satisfy the same physical conditions.

The diffusion length values for excitons in a natural growth Cu_2O , reported here, are in agreement with the diffusion length obtained from diffusion coefficient values and 1S exciton lifetimes appearing in the articles by A. Mysyrowicz et al. and D.P. Trauernicht et al. [1,2], provided that the excitons are in thermal equilibrium with the lattice. The above experimental results answer the long existing question of exciton diffusion in Cu_2O [3,4] and provide evidence for the mechanism responsible for photovoltaic current generation in this system.

Interest in the photovoltaic (PV) effect results, is further increased by the fact that excitons in Cu_2O have been shown to display a high quantum degeneracy of the Bose type [5,6], and so raising the possibility of a lossless transport of current energy via exciton superfluidity. It is interesting to find that an exciton mediated superconductivity mechanism, that would yield a high T_c , was proposed 15 years ago [7]. Thus, the photovoltaic effect may provide a simple method for the study of energy transport via exciton migration and measurements for the diffusion length.

In this work two types of samples have been examined. The first series of experiments were performed on polycrystalline Cu_2O films of thickness varying between 5 and 170 μm . This range of thicknesses was chosen to ensure considerable absorption of the $n = 2, 3, \dots$ yellow series excitons as well as part of the $n=1$ indirect absorption band (see section 5.2.3 and figures 5.4, 5.14, 5.15). The Cu_2O films were grown by thermal oxidation on high purity copper [8], while gold was evaporated on Cu_2O to provide an Ohmic contact, forming an (Ohmic)Au/ Cu_2O /Cu photovoltaic backcell. In the second part, photovoltaic spectra of a high purity, natural growth, single crystal were studied, for which the $n=1$ yellow series exciton lifetimes and diffusion coefficients were determined from photoluminescence measurements [1,2]. For the latter sample, PV spectra, in both the backcell and frontcell geometries, were taken.

5.2. BACKGROUND:

In this section the theoretical background on excitons and the information available in the literature are presented and discussed, so that later the analysis of the experimental results is easily understood.

5.2.1. THEORY OF EXCITONS: [9,10,11]

The exciton is a quantum of electronic excitation energy, created by the absorption of a photon, traveling in a periodic structure. It is made of an electron (e^-) excited to the conduction band, leaving behind it in the valence band, a hole (h^+) to which it remains bound in real space by the Coulomb interaction of their opposite charges. Bound electron-hole pair states, known as excitons, are the lowest energy electronic excitations in weakly excited pure semiconductors. The exciton transports energy, although its charge is zero and its motion is characterized by the center of mass wavevector (K).

Excitons are usually distinguished in two limiting cases according to the relative magnitude of the exciton's radius with respect to the lattice interatomic distances.

1) FRENKEL exciton (tightly bound) [12] : This exciton may be so localized that the e and h are almost located on the same atom or molecule, therefore $r_{ex} \approx d$, figure 5.1a (where r_{ex} : exciton radius and d : interatomic spacing). One could consider the Frenkel exciton to propagate through the lattice with a wavevector K by resonant transfer of energy (hopping process) between adjacent

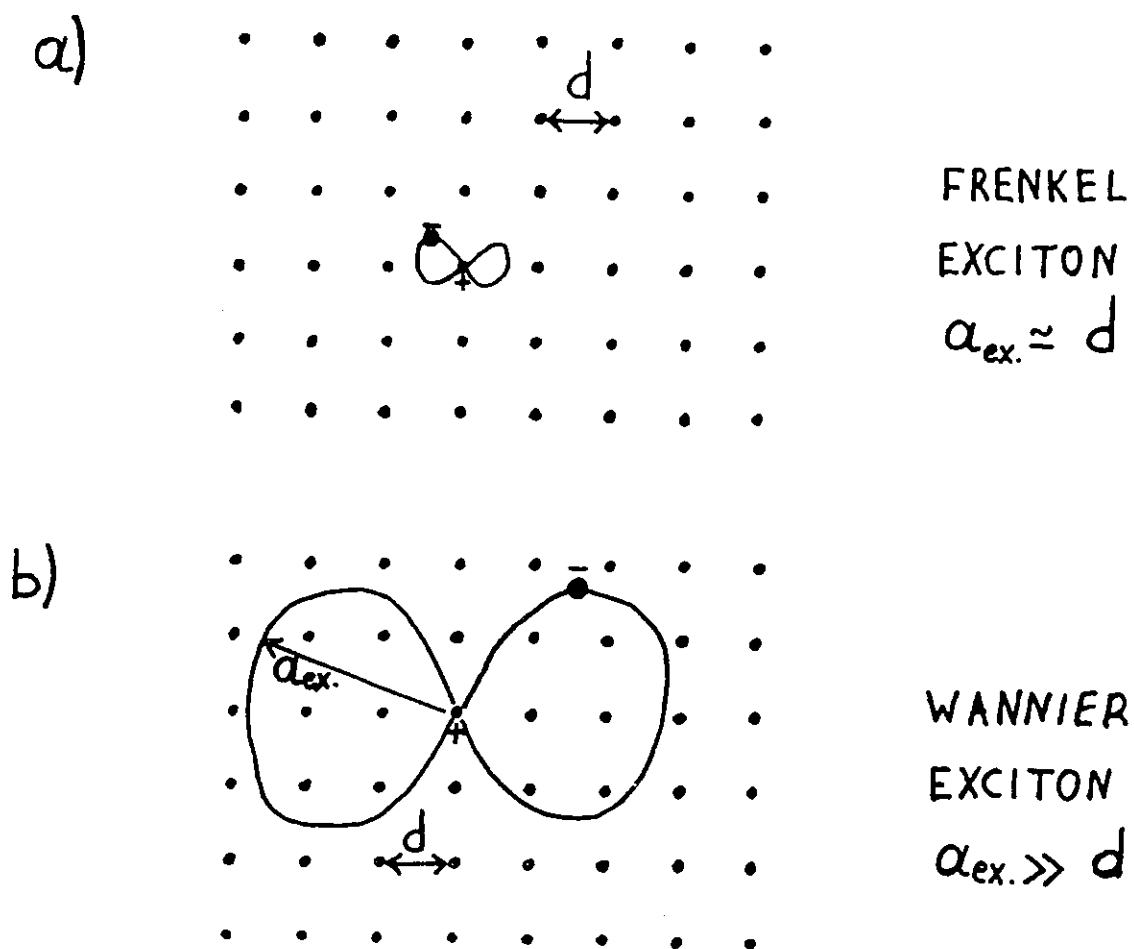


Figure 5.1: Schematic illustration of a p-state exciton as :
 a) a Frenkel exciton,
 b) a Wannier exciton,
 in a lattice of interatomic spacing d .

atoms or molecules. Such excitons are usually present in insulators and organic molecules.

2) WANNIER exciton (weakly bound) [13] : Weakly bound $e - h$ pair whose envelope wavefunction extends over many atoms, therefore $r_{ex} \gg d$, figure 5.1b. In this case, due to the "large" orbit of the exciton, one has to a good approximation an electron and a hole separated by a dielectric medium (ϵ). This situation is realized in Cu_2O and in fact for most semiconductors.

Since we are dealing with Cu_2O , a brief discussion will follow on the Wannier excited states and the commonly used approximations.

Let us assume parabolic conduction (C) and valence (V) bands with isotropic effective masses m_e^* , m_h^* and their minimum and maximum at $k=0$, respectively. In figure 5.2a, the transition from A to B creates an exciton with a translational wave vector K . The total energy of the exciton in the center of mass (translational motion) system is presented in figure 5.2b, where the (zero) ground state of the crystal in the ideal case, is taken when the valence band is full and the conduction band empty. Since the photon wavevector is very small compared to the reciprocal of the lattice vector, only those excited states with $K \approx 0$ contribute to the optical absorption spectra. These spectra consist of a series of discrete lines followed by the ionization continuum. Calculating the set of energy levels for the exciton is the same problem as that for the Hydrogen atom, modified to account for the masses involved and the medium within which the electron and hole

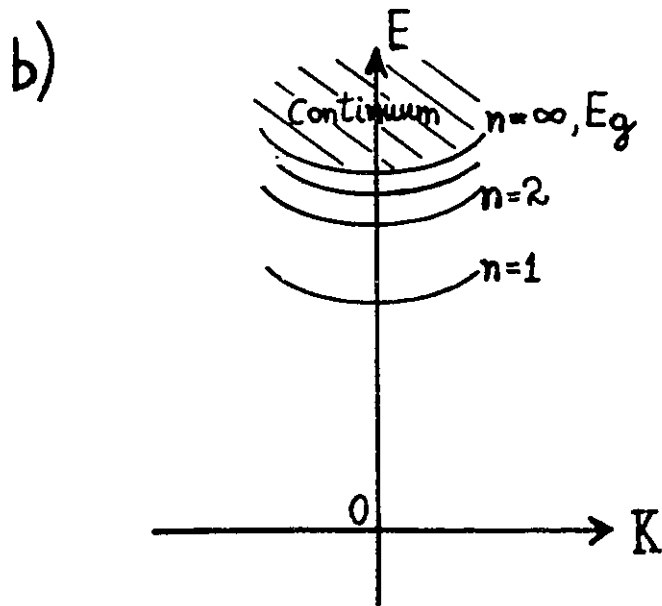
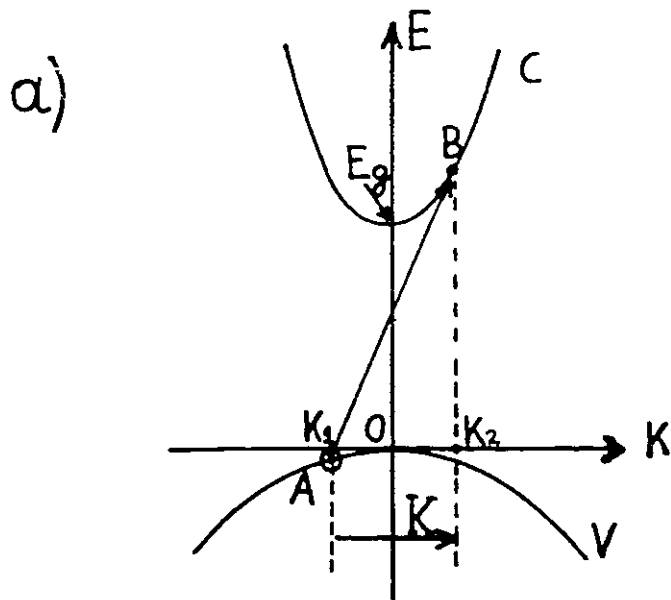


Figure 5.2: Energy versus wave vector diagrams :

- a) One-particle representation,
 - b) Two-particle (excitonic state) representation.
- K : center of mass wave vector.

are interacting. Therefore, in the center of mass system (figure 5.2b) the total energy of the exciton will be :

$$E_n(K) = E_g - \frac{\mu e^4}{2 \epsilon^2 \hbar^2 n^2} + \frac{(\hbar K)^2}{2(m_e^* + m_h^*)} \quad (5.1)$$

where, μ : the reduced mass, $\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$
 ϵ : the dielectric constant
 n : the principal quantum number

In equation (5.1), the second term represents the binding energy (E_b) of the exciton (called also excitonic Rydberg, R_{exc}), while the third term gives the kinetic energy of the exciton. Therefore the binding energy of the exciton is given by :

$$E_{bn} = \frac{\mu e^4}{2 \epsilon^2 \hbar^2 n^2} \implies E_{bn} = \frac{1}{2 n^2 \epsilon^2} \left[\frac{\mu}{m_e} \right] R_H$$

where, R_H : the Rydberg of the Hydrogen atom, $R_H = 13.6$ eV
 m_e : the free electron mass.

Assuming Bohr's model, the radius of an exciton, that is the distance from the nucleus where one is most likely to find the e^- , is given by [14] :

$$r(n) = \frac{\epsilon m_e r_B n^2}{\mu}$$

Where, r_B : the Bohr radius, $r_B = 0.53$ Å.

5. 2. 2. Cu₂O BAND STRUCTURE AND EXCITONIC SERIES:

The Cu₂O crystal structure is cubic with two molecules per unit cell and O_h⁴ is its space group symmetry [15]. It has a direct energy gap at the Γ point (K=0) (figure 5.2a) and inversion symmetry so that all states have definite parity. As a result of the 2 valence and conduction bands, see figures 5.3 5.4, excitonic series are observed in Cu₂O. Let us focus now on the yellow excitonic series, which is the result of interaction between the uppermost d-like valence (Γ_7^+) and the lowest s-like conduction (Γ_6^+) bands, both of positive parity [16]. The 1S transition is forbidden by parity. This transition is only allowed in the quadrupole approximation. Since s-like excitons cannot be created, the first (lowest lying in energy) yellow series excitonic state in the dipole approximation, is the 2P state. The binding energy of the P yellow series excitons is given by :

$$E_{bn} = \frac{1}{n^2 \epsilon_s^2} \left[-\frac{\mu}{m_e} \right] R_H \quad (5.2)$$

where, $R_H = 13.6 \text{ eV}$

$\epsilon_s \approx 7.2 \epsilon_0$, static dielectric constant

$\epsilon_0 = 8.85 \cdot 10^{-12} \text{ C}^2/\text{N m}^2$, permittivity of free space

$\mu = 0.37 m_e$, [17a]

$$\text{Therefore: } E_{bn} = \frac{0.37 \cdot 13.6 \text{ eV}}{(7.2)^2 \epsilon_0^2 n^2} \approx \frac{0.097 \text{ eV}}{n^2} , \text{ with } n=2,3,\dots \quad (5.3)$$

The experimentally determined total energy (in eV) of the yellow P excitonic states, as a function of temperature (T in degrees Kelvin) at K=0 is given by : [18,19]

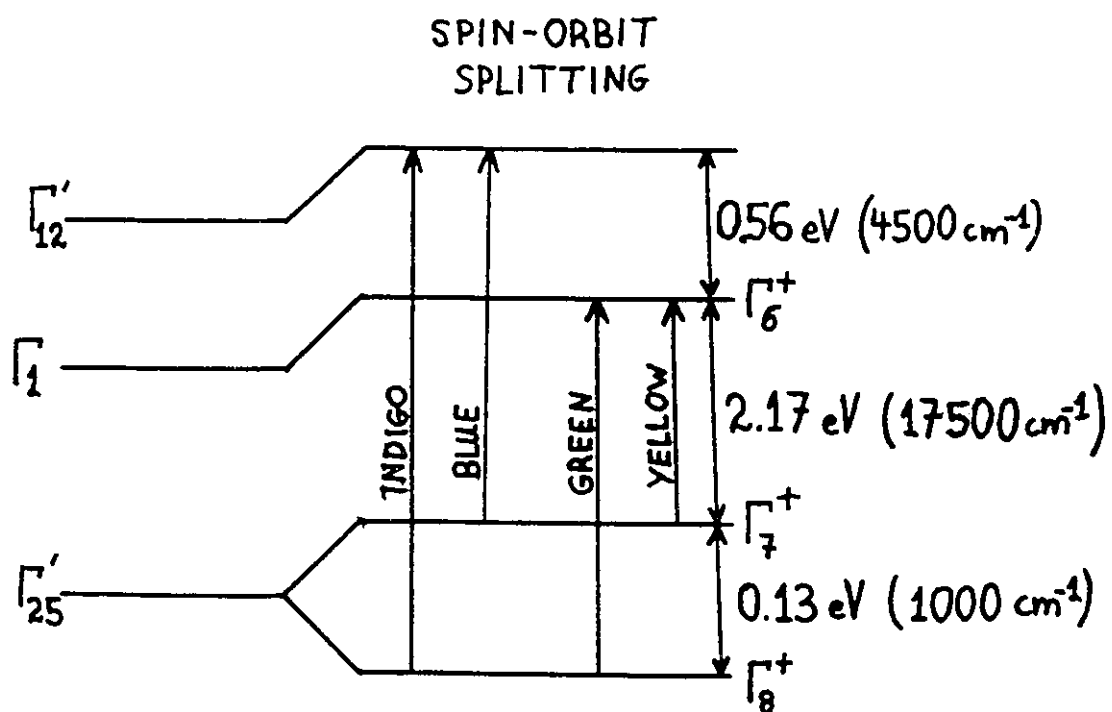


Figure 5.3: Band diagram of Cu_2O at the Γ point, $T = 0 \text{ K}$.

$$E_{yn} = 2.172 (1 - 1.871 \cdot 10^{-5} T - 3.521 \cdot 10^{-7} T^2) - \frac{0.097}{n^2} \quad (5.4)$$

The binding energy for the 1S exciton is found experimentally to be 0.14 eV. The discrepancy between the binding energy obtained for $n = 1$ in equation (5.4) and the one observed experimentally, is due to the fact that the static dielectric constant (in eq. 5.3) although it is good for $n \geq 2$, it is not appropriate for $n = 1$. This is due to the fact that the 1S orbit is of the order of the crystal lattice spacing ($r_{1S} \approx 10 \text{ \AA}$), thus the electron screening is not as effective. To obtain the experimentally observed binding energy of the 1S exciton, a smaller value for ϵ_s has to be substituted in equation (5.3).

Although the 1S transition is optically forbidden in the dipole approximation, electric dipole excitation of the 1S exciton is possible with the cooperation of a phonon (indirect transition) of the right symmetry and parity (Γ_{12}^-). While the 1S exciton's binding energy is 140 meV, the e-h exchange energy is also as large as 12 meV [20]. The e-h exchange interaction removes the degeneracy between the triply degenerate Γ_{25}^+ (orthoexciton) and the non-degenerate Γ_2^+ (paraexciton) states, the paraexciton lying lower by 12 meV.

5. 2. 3. DISCUSSION BASED ON TYPICAL Cu_2O ABSORPTION SPECTRA:

Experimental absorption spectra of Cu_2O are available in the literature at various temperatures [21 - 23]. Here, we are going to discuss some typical absorption spectra (figure 5.4), concentrating in the wavelength region of our interest. The optical absorption spectrum of cuprous oxide begins in the red with two absorption edges separated by 208 cm^{-1} ($2h\nu_0 \approx 26 \text{ meV}$, this is twice the energy of the phonon involved in the indirect transition, see figure 5.4 curve T_1). These absorption edges correspond to indirect transitions, where a phonon is either absorbed or emitted for momentum and energy conservation. At low temperatures a line spectrum appears on top of the red continuum, figure 5.4 curve T_2 . The lines result from the excitonic series. At room temperature the lattice phonon energy ($KT \approx 0.025 \text{ eV}$) is large enough to dissociate all the yellow series excitons, except the 1S level which has a binding energy of $\approx 0.14 \text{ eV}$ (the binding energy of the $n=2$ exciton is about 0.024 eV). The whole spectrum shifts to higher energies as the temperature of the lattice decreases. In figure 5.4, curve T_3 , presents the lowest lattice temperature when only one of the two red edges, the edge due to phonon emission is observed, because there is no significant number of lattice phonons at this temperature to contribute for the phonon-assisted absorption process.

Notice also, that as the temperature is decreased the exciton linewidth becomes finer as their lifetime increases.

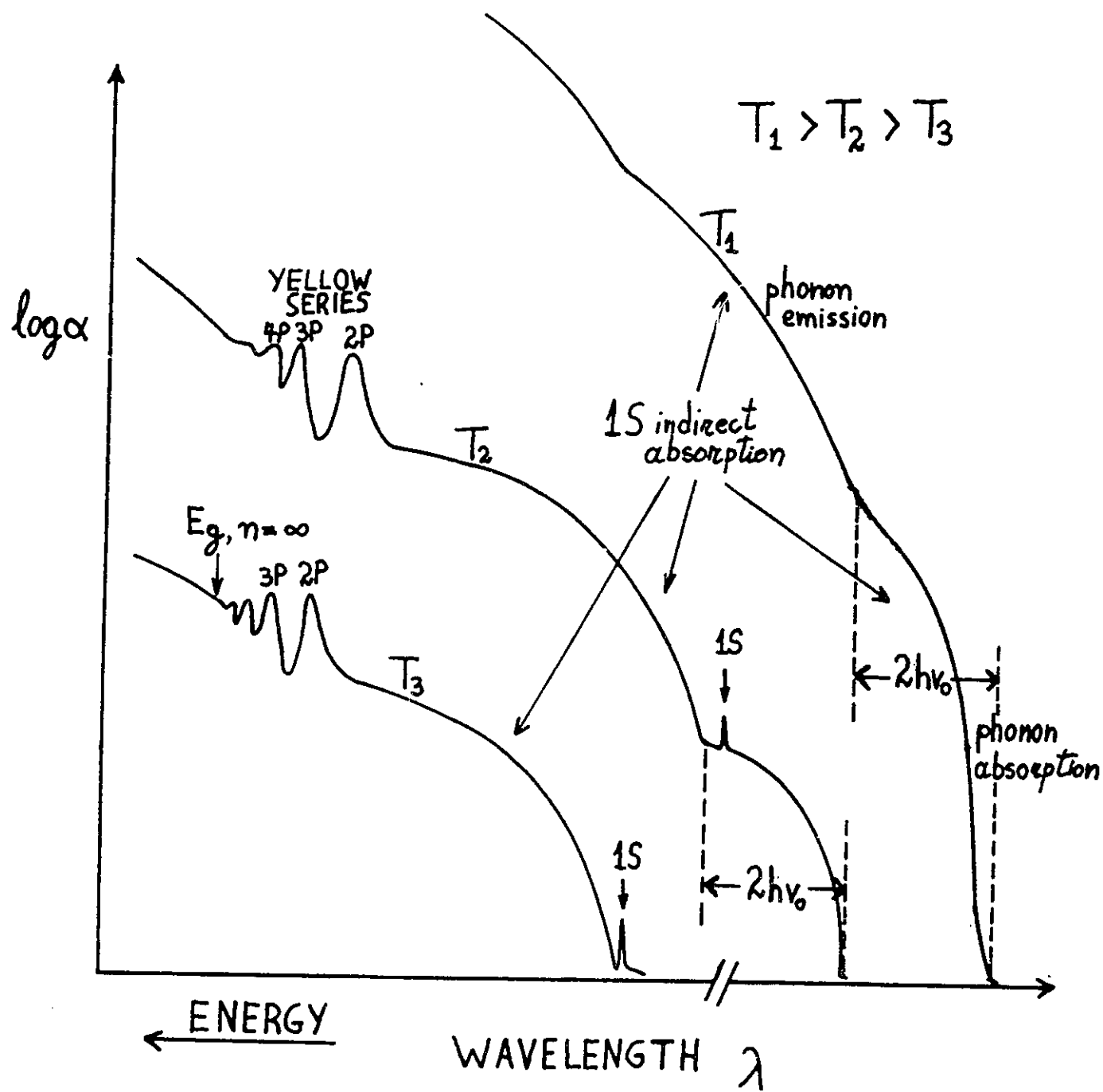


Figure 5.4: Typical Cu_2O optical absorption spectrum, where : $T_1 > T_2 > T_3$.

5.2.4. ELECTRIC FIELD EFFECT ON EXCITONS AND THE DEPLETION REGION OF A SCHOTTKY JUNCTION:

In this section the effects of electric fields on excitons and the depletion region of a Schottky junction will be discussed :

The exciton is a neutral particle when viewed macroscopically. If a high electric field is acting upon it, the exciton could be polarized or even dissociated. To estimate the average electric field necessary to dissociate an exciton a familiar concept from Atomic Physics is used. This is the so called "field ionization", and it occurs when the potential energy across the diameter d of an orbit (in this case the electron around the positively charged hole) is of the order of the binding energy.

$$U = E_{bn} = e E d$$

where, U : the potential energy

E_{bn} : the binding energy

e : electron's charge

E : electric field

d : diameter of excitonic orbit

As the electric field is increased, the lifetime of a given excitonic state decreases against dissociation and its linewidth becomes correspondingly larger [24,25]. In fact, for a

given excitonic series, as the field is increased, the higher order excitons will be first washed out due to their lower binding energies. In the case of the yellow excitonic series of Cu_2O , the $n=1$ state requires an electric field of the order of 10^5 - 10^6 V/cm to be field ionized, while the $n=2$ state requires about $2 \cdot 10^4$ V/cm.

To deal with electric field effects on excitons in a $\text{Cu}_2\text{O}/\text{Cu}$ sample, two cases have to be distinguished:

- 1) The application of an external bias, which results in a field across the semiconductor modifying the depletion region,
- 2) the internal electric fields : a) around ionized imperfections in the semiconductor and b) at the metal/semiconductor interface (DIPOLE LAYER).

1) EXTERNALLY APPLIED ELECTRIC FIELD:

When a bias is applied to a metal/semiconductor system (or to any other junction) obtaining the electric field is not as simple as dividing the applied bias by the sample thickness. In such a system, there are regions of very different resistivities. For a metal/semiconductor system at least two regions can be distinguished. These are : a) the bulk of the semiconductor and b) the depletion region. Since the depletion region is depleted of free carriers, then it will have higher resistivity than the bulk. Therefore, the biases V_B (in the bulk), V_D (in the depletion region) and the associated electric fields E_B , E_D will be given by:

$$V_{\text{applied}} = (\rho_B(t-w) + \rho_D w) \frac{I}{\text{Area}} = V_B + V_D$$

$$\text{thus, } E_B = \frac{V_B}{(t-w)} \quad \text{and} \quad E_D = \frac{V_D}{w}$$

where, I : current

ρ_B, ρ_D : the resistivity in the bulk and the depletion region of the semiconductor respectively

t : the semiconductor sample thickness

w : depletion region width

The equation that gives the depletion region width of a Schottky junction is (see section 1.4.2) :

$$w = \left[\frac{2 \epsilon_s (V_{bi} - V_{\text{applied}})}{e (N_A - N_D)} \right]^{1/2} \quad (5.5)$$

where, ϵ_s : static dielectric constant

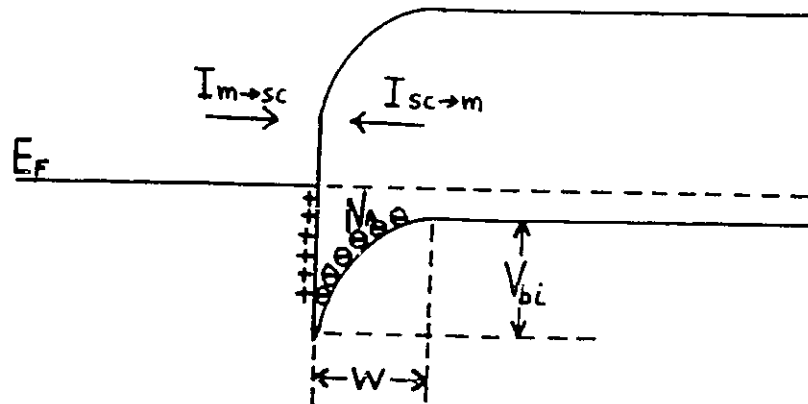
V_{bi} : built-in electric voltage

N_A, N_D : density of ionized acceptor and donor states respectively

In figure 5.5, a Schottky junction is presented with a) no bias, b) forward (V_F) and c) reverse bias (V_R). In this case we assume that the depletion region resistivity is larger than the bulk and thus a large portion of the bias is applied there. In figure 5.5a, the currents across the junction due to thermionic emission (I_{m-sc}, I_{sc-m}) from and into the semiconductor are equal, while the current densities inside the semiconductor due to diffusion (J_D) and drift field (J_F) are equal too, canceling each

a)

NO BIAS, $J_D = J_F$



b)

FORWARD BIAS, $J_D \approx J_F$

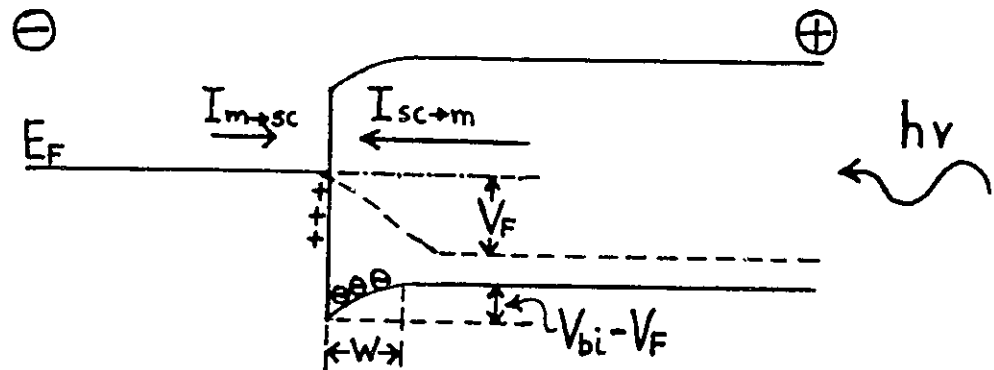


Figure 5.5: Equilibrium band diagram of a metal/p-type semiconductor junction, for :

- a) No bias ($V=0$).
- b) Forward bias (V_F), under illumination.

c) REVERSE BIAS, $J_D < J_F$

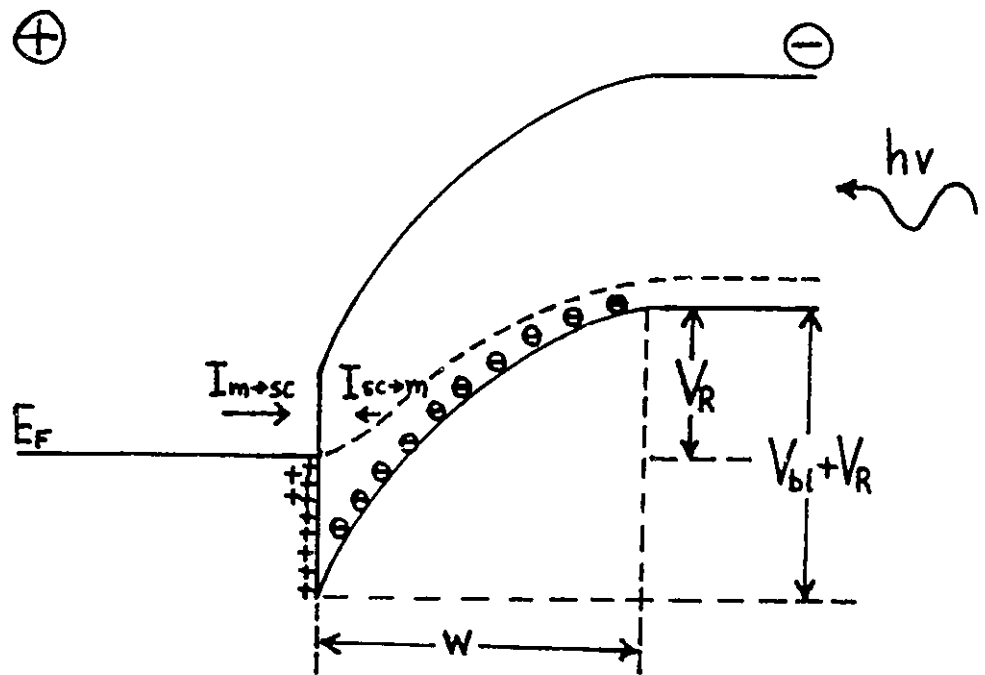


Figure 5.5: c) Reverse bias (V_R), under illumination.

other out. When a forward voltage is applied, figure 5.5b, the depletion width decreases according to equation (5.5), while (in darkness) across the junction the thermionic emission current I_{sc-m} will be larger than I_{m-sc} , because the barrier that the holes inside the semiconductor have to overcome has decreased to $(V_{bi} - V_F)$. Note also, that the electric field at the junction decreases, becoming zero when the flat band condition is reached ($V_{bi} = V_F$). If carriers are photogenerated under forward bias, the net current will be in the direction towards the metal, because $J_D \geq J_F$. When a reverse bias is applied, figure 5.5c, the depletion width increases and the current component I_{sc-m} decreases accordingly. The electric field at the junction increases, since w does not increase as fast as $(V_{bi} + V_R)$ in equation (5.5), therefore $J_D < J_F$. That also leads to increased collection efficiency, due to the larger electric field in the semiconductor.

In all the above cases, I_{m-sc} , (figure 5.4), remains constant to first approximation, provided that the temperature is constant, while tunneling and image-force barrier lowering effects are considered negligible.

2) INTERNAL ELECTRIC FIELDS:

a) Internal electric fields can be created : from charged impurities in a lattice and at crystal boundaries. These fields usually are larger than externally applied ones, because the potential difference is smaller, the sample

thickness they are applied upon, are of the order of interatomic distances.

b) Dipole layer at the $\text{Cu}_2\text{O}/\text{Cu}$ interface

In the case of a $\text{Cu}_2\text{O}/\text{Cu}$ junction, a very thin dipole layer of the order of 10 to 50 nm (depicted as region C in figure 5.6) is present at the $\text{Cu}_2\text{O}/\text{Cu}$ interface, as was evidenced by Auger spectroscopy [27]. The interfacial region between Cu_2O and Cu consists of a defective copper-rich Cu_2O negatively charged layer, produced by the reaction resulting from the contact of Cu_2O with all metals except Au [27]. Considering that the dipole layer is about 50 nm thick and the potential difference across it is about 0.3 V (26), then an electric field of the order of 10^5 V/cm (10^7 V/m) can be expected. Note that the dipole layer is not the depletion region normally obtained at a junction. In fact as is shown in figure 5.6, the $\text{Cu}_2\text{O}/\text{Cu}$ junction has both a dipole layer (C) and a depletion region (W). The barrier height is primarily determined by a high density of donor surface states, as was first proposed by Bardeen [28], most likely to be associated with an oxygen vacancy [29] lying approximately 0.7 eV above the valence band, figure 5.6 (see also section 1.3.2).

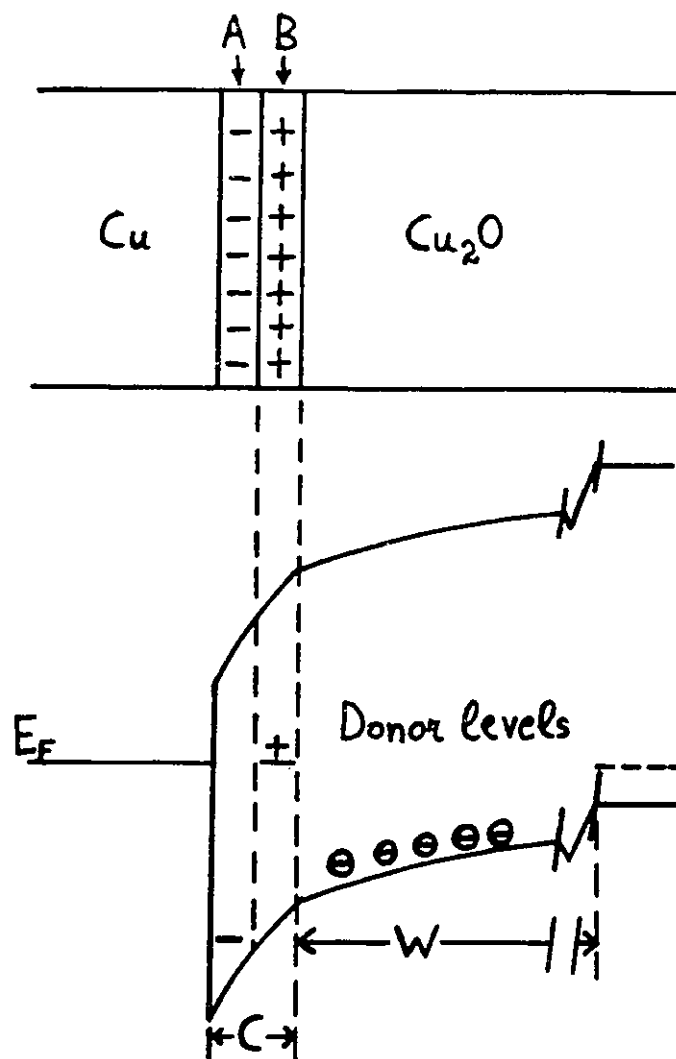


Figure 5.6: Model of the Cu/Cu₂O barrier (26).

- A : copper-rich Cu₂O region with large density of acceptor states.
- B : Cu₂O region with large density of O-vacancies (donor states).
- C : dipole layer.

5.2.5. EXCITON DECAY MECHANISMS:

In this section we are going to discuss the most likely channels for exciton decay in a low density system (therefore there is no interaction between excitons). The mechanisms responsible are : 1) Radiative decay, 2) dissociation into an electron and hole, and 3) self-trapping and trapping of excitons.

1) RADIATIVE DECAY :

An exciton may decay into a photon, and some momentum- and energy-conserving phonon, according to spontaneous transition probabilities.

2) DISSOCIATION INTO AN e^-h^+ PAIR :

This is the only mechanism that will be detectable by photoconductivity and the photovoltaic effect. The dissociation can be caused by several mechanisms :

- a) phonon interaction,
- b) defect interaction,
- c) exciton-mediated ionization of imperfections, and
- d) field ionization.

In the next section, the above mechanisms are discussed because they could be responsible for the photovoltaic current observed.

3) SELF-TRAPPING AND TRAPPING OF EXCITONS :

Self-trapping results from large exciton-phonon coupling which is manifested in localization of the exciton at some definite site. Three channels for decay of the exciton can be

expected : luminescence occurring with a Stokes shift; radiationless decay with a burst of phonons; and transfer of the exciton either to another site of the perfect lattice, in which case we have "hopping" transport, or transfer to a defect site at which any of the above processes could be repeated. An exciton can also be trapped by a defect with an appropriately large capture cross section, without having the benefit of strong phonon interactions. Then one has produced an excited state of the defect, whose decay products can be observed.

5. 2. 6. POSSIBLE CURRENT GENERATING PROCESSES FROM EXCITONS :

Since the exciton is electrically neutral, it carries no current. In real crystals however, one usually observes photoconductivity as a result of optical absorption in the Cu_2O exciton spectral region [3,30]. In order that the excitons produce current, it is necessary to somehow break up the exciton into free carriers. The possible current generating mechanisms are now presented :

1) DISSOCIATION BY PHONONS : In a pure crystal, phonons are the principal perturbation required for the breakup of an exciton. The phonons and the kinetic energy of the exciton must supply the energy needed for the dissociation, which is the exciton's binding energy. This mechanism has been studied by Lipnik [31] and Goodman et al. [32]. Lipnik treated the Wannier exciton in Cu_2O and other crystals, and obtained a relation for the excitonic lifetime against dissociation by a single-phonon process.

- 2) DEFECT INTERACTION : Exciton interaction with stationary defects is a possible current generating mechanism. The case of dissociation resulting from collisions with neutral impurities has been considered by Lipnik [31], who concludes quantitatively that for most impurity densities phonon dissociation will be the dominant mechanism.
- 3) IONIZATION OF IMPURITIES BY AN EXCITON : In this process an exciton disappears giving its entire energy to a free carrier ejected from a state in the gap. So far, this process has been considered to be the one responsible for the photoconductivity observed in Cu_2O [3,30] at low temperatures.
- 4) FIELD IONIZATION OF EXCITONS : Field ionization of the exciton is possible when an electric field E establishes a potential energy difference across the exciton's orbit, which is of the order of its binding energy. Therefore, the possibility that the excitons could be dissociated at the high electric field region ($\approx 10^5$ V/cm) in the $\text{Cu}_2\text{O}/\text{Cu}$ interface is most attractive. This last mechanism, as will become clear later, provides us with a probe that can be used to study the possibility of excitonic diffusion in Cu_2O .

5.2.7. GEOMETRY OF THE SAMPLES :

An idealized experiment to detect the transport of excitons , in analogy to what D.L. Dexter et al. [34] has described, requires an appropriate geometry. The incident light has to be absorbed close to the surface (figure 5.7) in a thickness $1/\alpha$ (a distance equal to the reciprocal of the absorption coefficient). If a suitable exciton detector is placed at the other end of the sample, then varying the sample thickness would give one a relation between the detection efficiency and the sample thickness. It will then be related to the excitons diffusion length, provided that the diffusion length L of the excitons is larger than $1/\alpha$. It will still be necessary to eliminate all possibilities other than the exciton as the particle responsible for the energy transfer. It is also required that the detector active region be much smaller than L . In order to fulfill the experimental requirements laid down above, the thickness of the Cu_2O films, which were thermally grown on copper sheets, was varied between 5 and 170 μm . A gold Ohmic semi-transparent electrode was evaporated on the Cu_2O surface forming a backcell photovoltaic cell. The geometry of our samples is shown in figure 5.7.

In this work, the detector of excitons is the high electric field region of the dipole layer (see section 5.2.4 and figure 5.6). While the sample thickness t is still required to be larger than L (in order to obtain L from the experimental data),

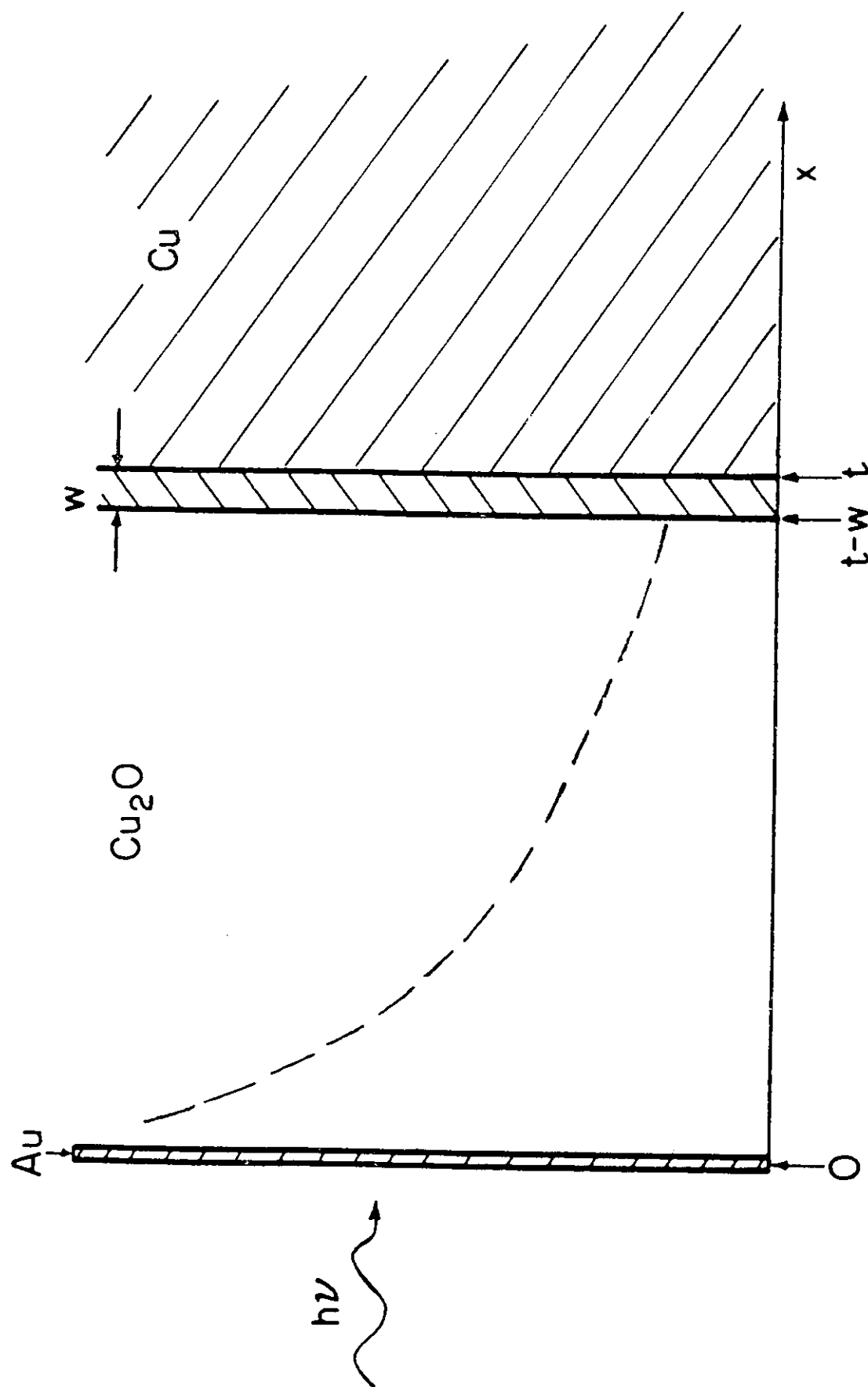


Figure 5.7: Sample configuration for photovoltaic measurements. The dashed exponentially decreasing line, from the Au side to the Cu side, represents the light absorption profile in the oxide film.

the model to be presented in the following section will be able to predict the detection efficiency for appropriate combinations of the parameters t , L , α and w . From now on the dipole layer thickness is referred to as w .

5.2.8. DESCRIPTION OF THE MODEL DEVELOPPED TO PREDICT EXCITONIC DIFFUSION IN Cu_2O :

A novel model is described capable to predict the diffusion length of excitons, using the Photovoltaic Effect, measured in the backcell configuration, at the $\text{Cu}_2\text{O}/\text{Cu}$ junction (see section 1.4). Note, that for all discussions to follow, the exciton transport mechanism to be verified, is the so called "wave-packet" transport [33]. Such a transport is defined as the time interval between scattering of the initial polariton into nonradiative states (mostly exciton-like) and its decay into some other form (a free pair, a photon, phonons, etc...). In this experiment, it is the free carriers that we are going to detect after the decay of the excitons. Therefore care has to be taken so that the majority of the carriers counted are those generated from excitons in the dipole layer. The experimentally measured quantity is the photocurrent. In the steady state case and in the appropriate spectral range, the absorbed light creates an exponential profile of excitons, which depends on α , extending from the illuminated surface inside the sample. Then, the excitons created diffuse towards the back Cu electrode. Depending on the relative magnitudes of $1/\alpha$ (absorption length), of L (diffusion length) and of t which will be varied (t : the Cu_2O film thickness), a certain fraction of the photogenerated excitons will "make it" to the $\text{Cu}_2\text{O}/\text{Cu}$ interface. There, they will be dissociated by the high electric field dipole layer w (see

figure 5.7) into free electron-hole pairs, and collected to produce photocurrent. Note, that a second region of electric field also exists (depletion layer), but has no effect on the excitons, since the electric field in that layer is considerably weaker than the dipole layer field.

5.2.9. DERIVATION OF THE EXCITONIC PHOTOCURRENT:

An exciton-mediated photocurrent in this system will be comprised of two contributions, a direct one from excitons photogenerated in the dipole layer (J_{Direct}) at the $\text{Cu}_2\text{O}/\text{Cu}$ interface, and the other ($J_{\text{Diff.}}$) stemming from diffusion of excitons, created in the semiconductor volume, to the dipole layer region where they will be dissociated to electron-hole pairs and produce photocurrent. The contribution J_{Direct} is due to light absorption and exciton creation in the dipole layer. Therefore,

$$J_{\text{Direct}} = q \alpha \phi \int_{t-w}^t e^{-\alpha x} dx = -q \phi \left[e^{-\alpha t} - e^{-\alpha(t-w)} \right]$$

$$\text{thus, } J_{\text{Direct}} = q \phi e^{-\alpha t} (e^{\alpha w} - 1) . \quad (5.6)$$

where, α is the absorption coefficient at a given wavelength λ ; $L = (D \tau)^{1/2}$, the excitonic diffusion length, with τ the exciton recombination time and D its diffusion coefficient; t the semiconductor total thickness; w the width of the dipole layer; q the electron charge; ϕ the incident photon flux, taking reflection losses at the input surface into account.

The contribution of J_{Direct} will be usually negligible because the dipole layer (w) is very thin (10 to 50 nm).

To calculate the diffusion current $J_{\text{Diff.}}$, the diffusion equation is set up for the steady state case and solved under the appropriate boundary conditions [35]. From Lambert's law of absorption, one obtains the number of photons absorbed per unit time per unit area of a film thickness dx , at a distance x below the surface, thus : $g(x) dx = \alpha \phi e^{-\alpha x} dx$. This number is equal to that of photogenerated excitons. The continuity equation for an excess of excitons $N(x)$ (above the equilibrium density) in the steady state case is then :

$$-\frac{N(x)}{\tau} + D \frac{\partial^2 N(x)}{\partial x^2} + \alpha \phi e^{-\alpha x} = 0 \quad (5.7)$$

The general solution of this inhomogeneous differential equation is :

$$N(x) = A e^{x/L} + B e^{-x/L} - \frac{\alpha L^2 \phi e^{-\alpha x}}{D (\alpha^2 L^2 - 1)} \quad (5.8)$$

The constants A and B can be determined by the following set of boundary conditions, (see figure 5.7) :

$$1) \text{ at } x=0, \quad D \left[\frac{\partial N}{\partial x} \right] = S N(0), \quad (5.9)$$

$$2) \text{ at } x=t-w+\Delta x, \quad N(t-w+\Delta x) = 0, \quad (5.10)$$

where, S is the surface recombination velocity.

Boundary condition #2 implies that although the exciton concentration $N(x)$ is not zero at $x = t-w$, it becomes zero within a very short distance Δx inside the dipole layer " w ". Since

Δx is infinitesimally small compared to the thickness "t", it is neglected from now on.

The application of the boundary conditions results in a system of two linear equations, the solution of which is :

$$N(x, \lambda) = \frac{\alpha \tau \phi}{(\alpha^2 L^2 - 1)} \left[e^{-x/L} [e^{-(t-w)(\alpha - 1/L)} - e^{-(\alpha - 1/L)x}] + \right. \\ \left. + [(SL/D + 1)(e^{-(t-w)(\alpha - 1/L)} - 1) - (\alpha L - 1)] \left[\frac{\sinh \{-(t-w-x)/L\}}{\cosh(t-w/L) + SL/D \sinh(t-w/L)} \right] \right] \quad (5.11)$$

The current density delivered in the external circuit after the excitons dissociate in the dipole layer (w), will be given by :

$$J = q D \left[\frac{\partial N}{\partial x} \right]_{x=t-w} \quad (5.12)$$

Thus :

$$J_{\text{Diff.}} = \frac{q \phi \alpha L}{(\alpha^2 L^2 - 1)} \left[(\alpha L - 1) e^{-\alpha(t-w)} + \right. \\ \left. + \frac{e^{-(t-w)(\alpha - 1/L)} - \alpha L + (SL/D) [e^{-(t-w)(\alpha - 1/L)} - 1]}{\cosh(t-w/L) + \frac{(SL/D)}{D} \sinh(t-w/L)} \right] \quad (5.13)$$

Notice that for $\alpha L = 1$ equation (5.13) appears to be indeterminate. But if the above equation is expanded, in the limit when $\alpha L = 1$, then $J_{\text{Diff.}}$ will be given by :

$$J_{\text{Diff.}} = \frac{q \phi}{2} \left[e^{-(t-w/L)} - \frac{1 + (1 + SL/D)(t-w/L)}{\cosh(t-w/L) + (SL/D) \sinh(t-w/L)} \right] \quad (5.14)$$

Considering that the recombination rate of excitons at the illuminated surface (front surface) is negligible, then as $S \rightarrow 0$, equation (5.13) reduces to :

$$J_{\text{Diff.}} = \Theta q \phi \left[\frac{\alpha L}{(\alpha^2 L^2 - 1)} \{ (\alpha L - 1) e^{-\alpha(t-w)} + \frac{e^{-(t-w)(\alpha - 1/L)} - \alpha L}{\cosh(t-w/L)} \} \right] \quad (5.15)$$

Therefore, the total photocurrent, for a certain wavelength, is given by the sum of equations (5.6) and (5.15) :

$$J_{\text{TOTAL}} = J_{\text{Diff.}} + J_{\text{Direct}}$$

$$J_{\text{TOTAL}} = \Theta q \phi \left[\frac{\alpha L}{(\alpha^2 L^2 - 1)} \{ (\alpha L - 1) e^{-\alpha(t-w)} + \frac{e^{-(t-w)(\alpha - 1/L)} - \alpha L}{\cosh(t-w/L)} \} + (e^{\alpha w} - 1) e^{-\alpha t} \right], \quad (5.16)$$

where, Θ is an overall efficiency factor depending on sample and junction quality.

Reflection at the semiconductor/metal interface has not been included. It has the effect of increasing the direct contribution by a factor of ≈ 2 , when $1/\alpha \geq t$.

Three cases could be distinguished under the following assumptions :

- a) $t \geq L$ and $1/\alpha$, for a given wavelength,
- b) $w \ll L$ and t , for a given λ .

CASE 1: Provided that $L \gg 1/\alpha$, ($\alpha L \gg 1$), while omitting the J_{Direct} contribution as negligible, because of assumption b, then equation (5.16) reduces to :

$$\begin{aligned} J_{\text{TOTAL}} &= 2 \theta q \phi e^{-t/L} \\ &= J_0 e^{-t/L} \end{aligned} \quad (5.17)$$

where, $J_0 = 2 \theta q \phi$, a constant.

Therefore, $\frac{\ln (J_{\text{TOTAL}}/J_0)}{t} = - \frac{1}{L}$ (5.18)

One could now obtain the exciton diffusion length by plotting the photocurrent for a given temperature, wavelength corresponding to that exciton and illumination condition, as a function of the total sample (semiconductor) thickness.

CASE 2: If $L \ll 1/\alpha$, then equation (5.15) reduces to :

$$J_{\text{TOTAL}} = 2 \theta q \phi e^{-\alpha t} \quad (5.19)$$

A graph of $\ln (J_{\text{TOTAL}}/J_0)$ as a function of thickness, yields the absorption coefficient α .

CASE 3: If $L \approx 1/\alpha$, then the whole equation (5.15) has to be used in order to find the variation of J_{TOTAL} as a function of sample thickness. When one of the parameters α or L is known, it is possible to obtain the second one by fitting the experimental data to the equation.

Using equation (5.15) two graphs, figure 5.8a,b, of $\ln(J_{\text{TOTAL}}/J_0)$ versus t (oxide thickness) were generated in order to test the above limiting cases 1 and 2. The following values for the parameters α and L were taken.

In the case of figure 5.8a, α is taken to be 750 cm^{-1} (where $1/\alpha \approx 14 \text{ }\mu\text{m}$) and $L = 50\mu\text{m}$, thus the condition $L \gg 1/\alpha$ (CASE 1) is valid. The slope obtained for $t \geq L$ corresponds to the inverse of the diffusion length, as it is clear from equation (5.18). For curve 8b, α was taken again to be 750 cm^{-1} , while L was taken $5 \text{ }\mu\text{m}$, therefore $L \ll 1/\alpha$. The slope corresponds to the absorption coefficient, as it is evident from equation (5.19) in CASE 2.

Equation (5.16) could also be used to generate graphs of J_{TOTAL} as a function of wavelength by making use of the absorption coefficient values derived from experimental absorption spectra. The generated graphs could then be compared with the experimentally obtained photocurrent spectra.

This concludes the section of theoretical background. In the following sections of this chapter, the sample preparation procedure, the experimental set-up and results are presented.

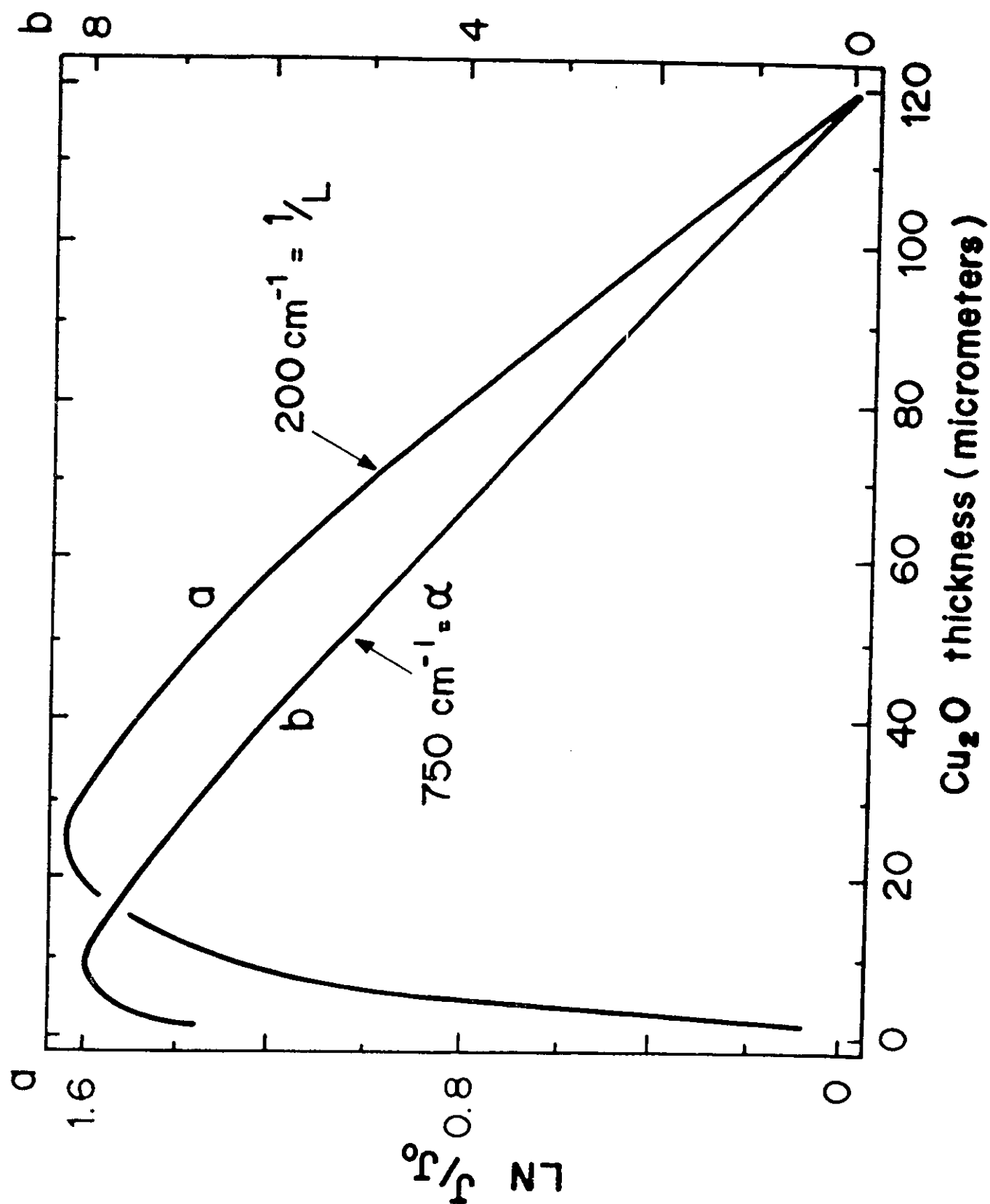


Figure 5.8: Computer generated diagrams using equation (5.15)

a) $\alpha = 750 \text{ cm}^{-1}$, $L = 50 \text{ } \mu\text{m}$ (case 1).

b) $\alpha = 750 \text{ cm}^{-1}$, $L = 5 \text{ } \mu\text{m}$ (case 2).

5.3. SAMPLE PREPARATION:

5.3.1. INTRODUCTION:

Two types of samples have been examined in the various experiments. The samples used for the first series of experiments were Cu_2O films of different thicknesses grown by thermal oxidation of high purity copper (type I samples, see also section 1.1). The second part of this work studies a natural growth Cu_2O single crystal, provided to us by A. Mysyrowicz. This chapter contains a description of the oxidation process, apparatus and the Cu_2O sample treatment before they are finally ready for experimental work.

5.3.2. COPPER TREATMENT AND THERMAL OXIDATION: (type I samples)

Copper square platelets $1.2 \times 1.2 \text{ cm}^2$ were cut from 0.8 mm thick sheets of 99.99% at. purity. They were degreased with ethanol and then manually polished with succesively finer grade carborundum papers (400 - 600 grade). Then, they were washed with distilled water and finally annealed in vacuum (better than 10^{-4} torr) at about 1030°C for 3 to 4 hours, in order to etch the surface thermally and induce crystalline growth in the copper. After annealing, the Cu platelets were usually kept in a vacuum container prior to thermal oxidation. This was done in order to avoid the formation of undetermined oxides in the air. Then, the Cu platelets were placed flat inside a fused quartz tube, mounted horizontally. A Lindberg microprocessor-controlled furnace could

be rolled in to surround the quartz tube. One end of the tube was sealed, while the other was mounted to an Oxygen-feed / rotary pump system, combined with a liquid N_2 trap. The system was operated manually between 760 and 10^{-4} torr, although automatic operation was possible with the use of a MKS Baratron the associated electronics and electric valves.

Pure Oxygen was admitted all at once into the tube from a reservoir. At the end of the oxidation, the rotary pump evacuated the tube, going to effective vacuum within a few seconds. The oxidation pressure and temperature were 55 ± 5 torr and 980 ± 20 °C respectively. The oxide layer thickness was controlled by the time of oxidation. Heating of the Cu samples to the temperature of oxidation and cooling after oxidation were done in vacuum. After the completion of oxidation, a gold layer 7 to 10 nm thick was evaporated onto the Cu_2O film, providing a semitransparent Ohmic contact of approximately 0.3 cm^2 area. Either Cu or Au fine leads were fixed with silver paint onto the gold film and onto the back Cu, which was exposed by removing the oxide at one of the corners of the sample. Therefore, a $Au(\text{Ohmic})/Cu_2O/Cu$ backcell was formed.

The thickness of the thermally grown oxide layers was measured primarily by method # 3, as described in chapter 2, section 4. To evaluate the accuracy of method # 3, the oxide thickness was also occasionally measured by method # 2.

5.3.3. OXIDATION RATE OF COPPER:

To obtain an oxide layer in the micrometer range in a reasonable time, moderate Oxygen pressures ($P_O > 10$ torr) are required, and that in turn requires a high temperature of oxidation ($T > 900^\circ\text{C}$) in order to remain in the Cu_2O region of the Cu- Cu_2O -CuO phase diagram, figure 5.9 [36]. Figure 5.10 shows the Cu_2O film thickness variation with time of oxidation, under the Oxygen pressure and temperature that these samples were grown at. For oxidation times less than 10 seconds, the oxide thickness is hard to control, because one is limited primarily by the time the pump takes to remove Oxygen after the oxidizing period, and also by one's reaction time in opening the valves. Since samples of thickness less than 10 μm were not necessary for this work, the system's evacuation speed was considered adequate. It is interesting to note, that the slope in figure 5.10 is $1/2$, as it is expected from the "parabolic law" of film growth (see also section 1.1), when the rate determining process in the oxide growth is diffusion of atoms (neutral cation vacancies in the case of oxidized Cu) across the growing oxide film.

5.3.4. NATURAL GROWTH SINGLE CRYSTAL: (type II sample)

This crystal was provided by A. Mysyrowicz in order to confirm the interpretation of the photovoltaic effect. It is a high purity, natural growth single crystal, for which values of exciton lifetimes and diffusion coefficients are available [1,2]. The crystal is a parallelepiped with two horizontal (100) faces

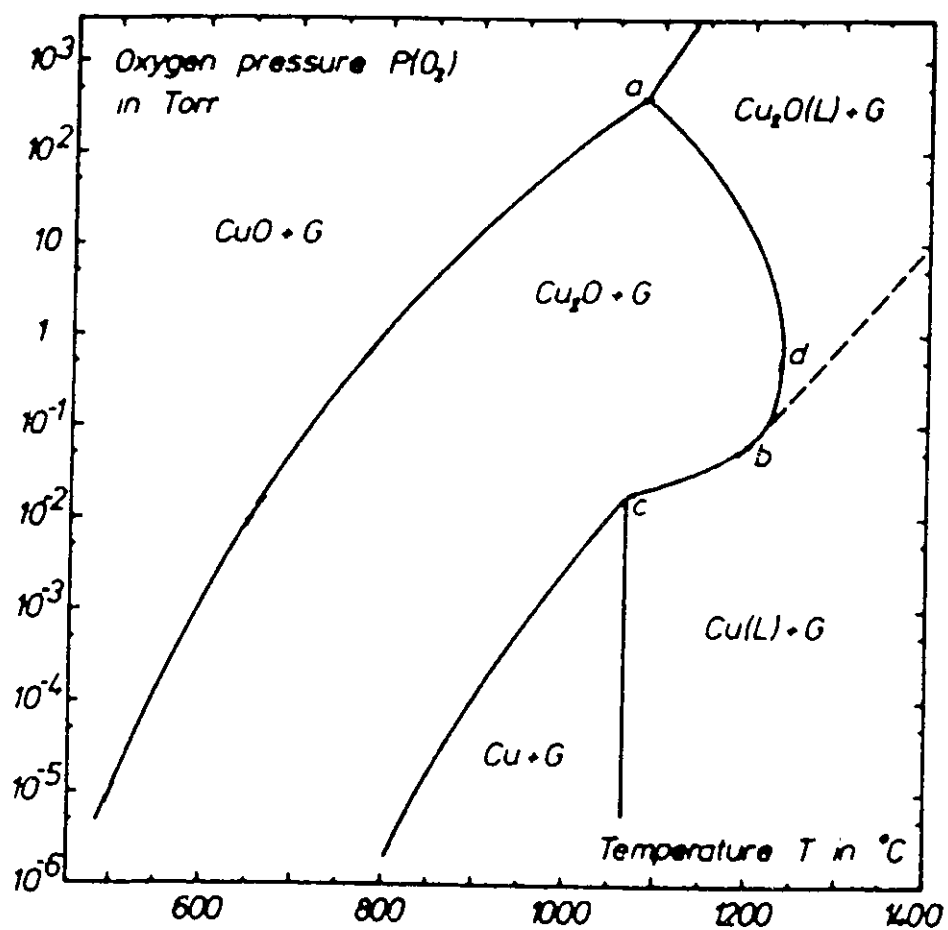


Figure 5.9: Oxygen pressure versus temperature diagram of the Cu-Oxygen system (36).

(L) : Liquid phase, (G) : Gas phase.

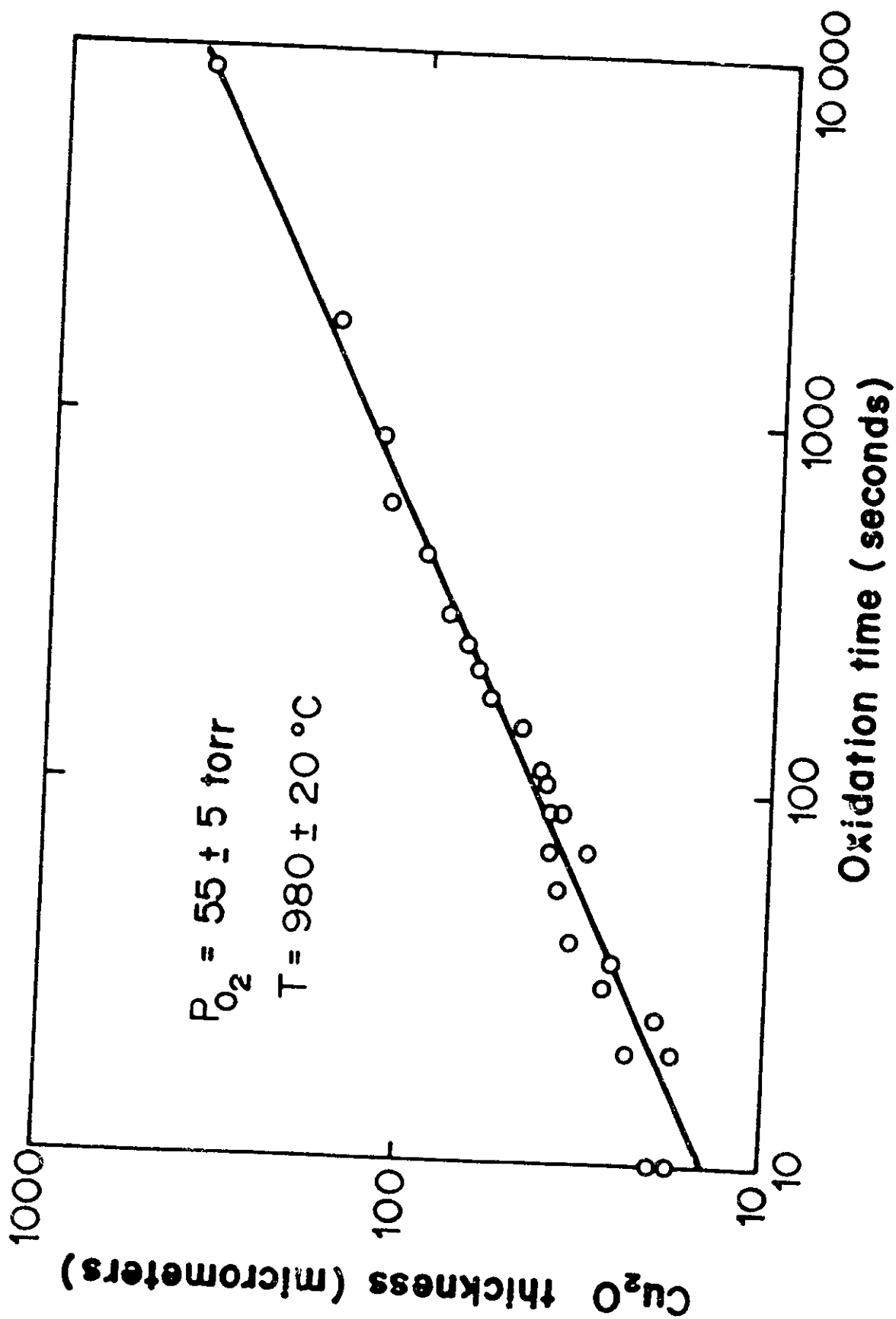


Figure 5.10: Cu_2O film thickness as a function of the oxidation time, for $P_{O_2} = 55 \pm 5 \text{ torr}$ and $T = 980 \pm 20 \text{ }^\circ\text{C}$.

and four vertical (110) faces. Its dimensions are presented in figure 5.11. The crystal came without any metallic contacts onto it. Before evaporating the metallic contacts, it was etched and cleaned using a procedure based on the one reported by L.C. Olsen et al. [26]. The procedure followed for the surface preparation is presented below, in table 1 :

TABLE : 1

SURFACE PREPARATION PROCEDURE

STEP	OPERATION
1	Rinse in distilled water
2	Soak for 1 min in methanol with a final 20 sec in an ultrasonic cleaning bath
3	Etching for 3 min in HBF_4 (etching rate : $\approx 5 \mu\text{m}/\text{min}$)
4	Repeat step 1
5	Repeat step 2
6	Soak for 1.5 min in 2% vol. Bromine-methanol solution with a final 30 sec in ultrasonic cleaner
7	Repeat step 2
8	Repeat step 6
9	Repeat step 2
10	Repeat step 2
11	Rinse in distilled water
12	Blow dry with He (or N_2)

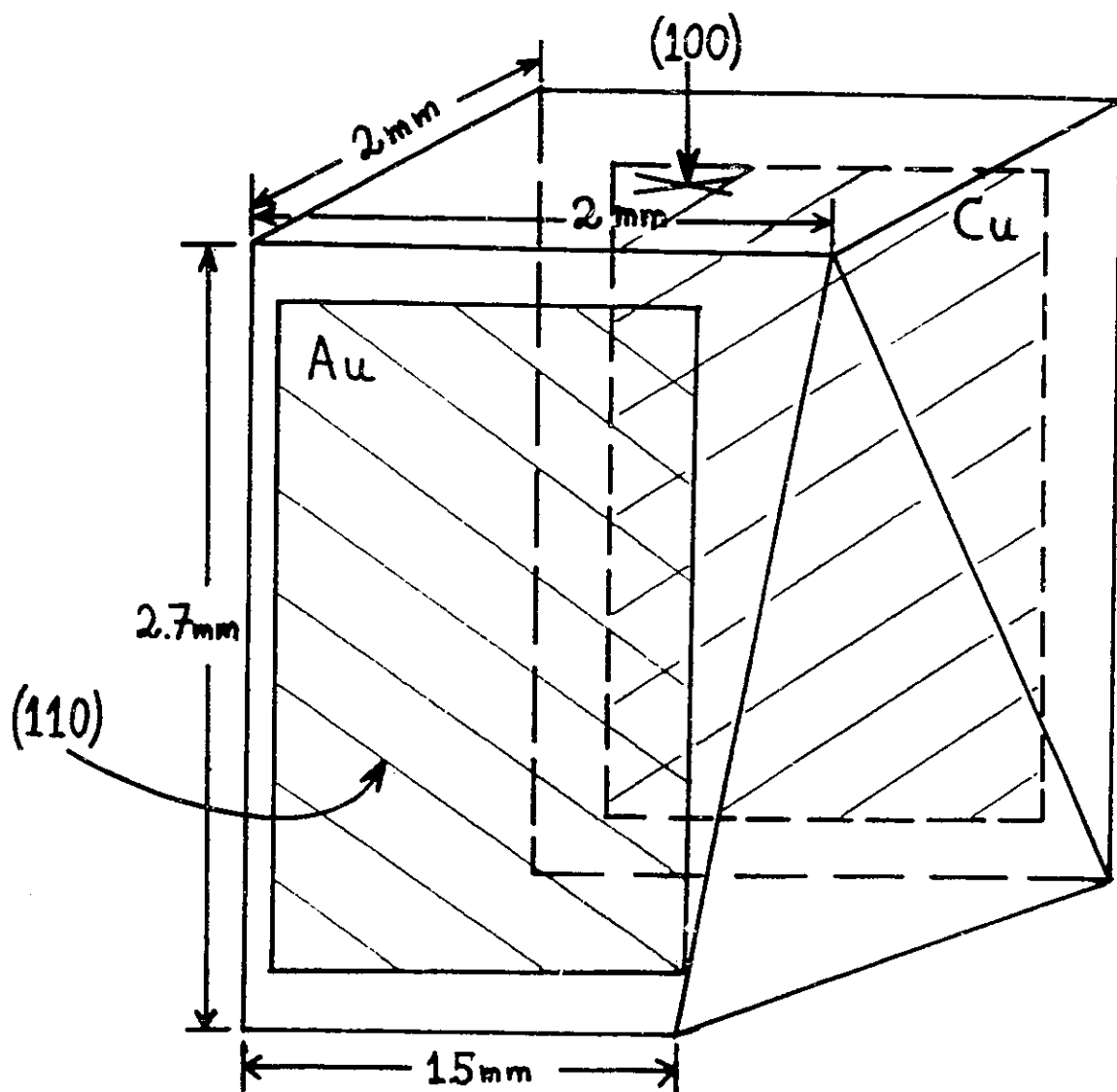


Figure 5.11: Physical dimensions and orientation of the natural-growth Cu_2O single crystal.

Right after the crystal was cleaned, the metallic contacts were evaporated on two opposite (110) faces, as shown in figure 5.11. Semitransparent 8nm thick Cu (rectifying) and Au (Ohmic) contacts were evaporated so that the sample can be used for PV measurements in both the frontcell and backcell geometries. The lateral dimensions of the contacts were 1.5 by 2.3 mm. The evaporation rate was such as to avoid any Cu_2O reduction. The sample was kept in vacuum until it was mounted on a holder, which then was screwed onto the sample rod of the optical cryostat.

5.4. EXPERIMENTAL SET-UP:

All the electro-optical measurements concerning the work in this chapter were performed using the Macpherson 2061 monochromator, set for a spectral resolution of 0.7 nm. The light was chopped at a frequency of 77 Hz. The photosignal detection technique and the optical set-up were presented and discussed in sections 2.2.1 and 2.1.1 respectively. For the low temperature measurements two optical cryostats were used :

- 1) A liquid Nitrogen cryostat used for a few measurements at $T \approx 80$ K (see section 2.3), before the variable temperature cryostat discussed below was received.
- 2) A variable temperature Janis "SuperVaritemp" optical cryostat model 8CNDT, together with a Lakeshore Cryotronics automatic temperature controller, model DRC-80C-M.

In figure 5.12, a diagram of the Janis cryostat is shown. The temperature was automatically controlled with the help of two matched Silicon diode temperature sensors, placed one on top of the Helium vaporizer (F) and the other at the sample zone (I) (see figure 5.12). The temperature could be varied from room down to liquid He temperature and even lower when pumping on liquid He. Actually the lowest temperature achieved was 1.9 K, using an old mechanical pump. According to the lowest temperature obtained, its pumping speed was of the order of 10 cfm. Therefore, higher pumping speed would be required to further lower

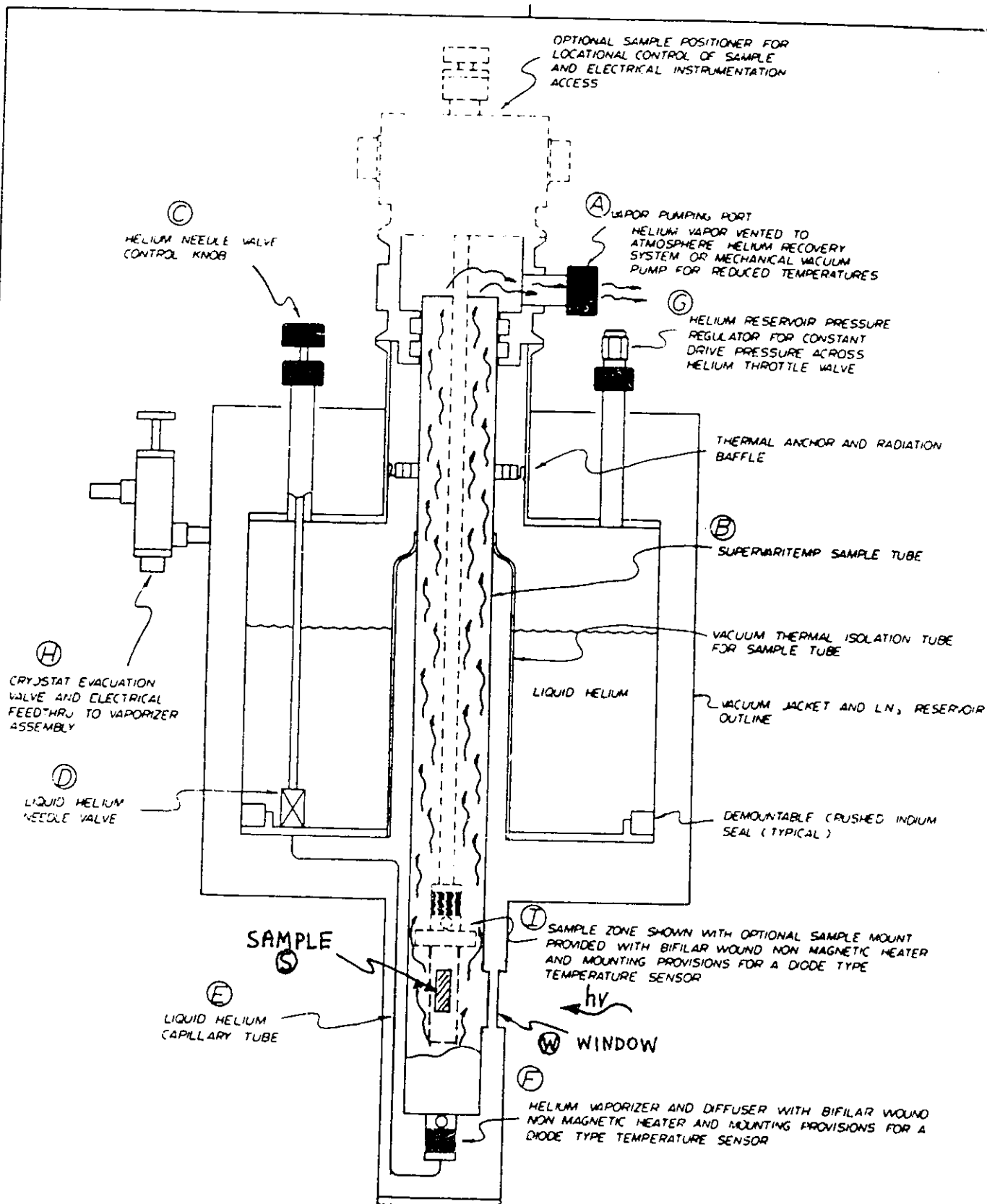


Figure 5.12: Diagram of the Janis "Supervaritemp" optical cryostat used for measurements down to 2 K.

the temperature inside the cryostat.

The sample was mounted on a Cu holder, which was then bolted onto the central rod (I) facing the window (W). The sample was cooled down by the cold He vapour, which was vaporized as liquid He was coming out of the capillary tube (E) at the bottom of the sample tube (F). The automatic temperature controller was not used during the course of measurements because the temperature sampling by the controller added noise to the signal. This noise was overloading the preamplifier of the Lock-in, when the sensitivity was set below 200 μ V. To avoid this problem the temperature was first stabilized with the automatic controller at a given temperature. Then, either a D.C. power supply was connected to the vaporizer coil to maintain that temperature, or when the temperature could be maintained for about 5 minutes within a couple of degrees Kelvin, the controller was turned off and a PV spectrum was taken. The latter method was only possible for temperatures above 100 K. More information on the operating instructions of this cryostat can be found in the manual that comes with the cryostat.

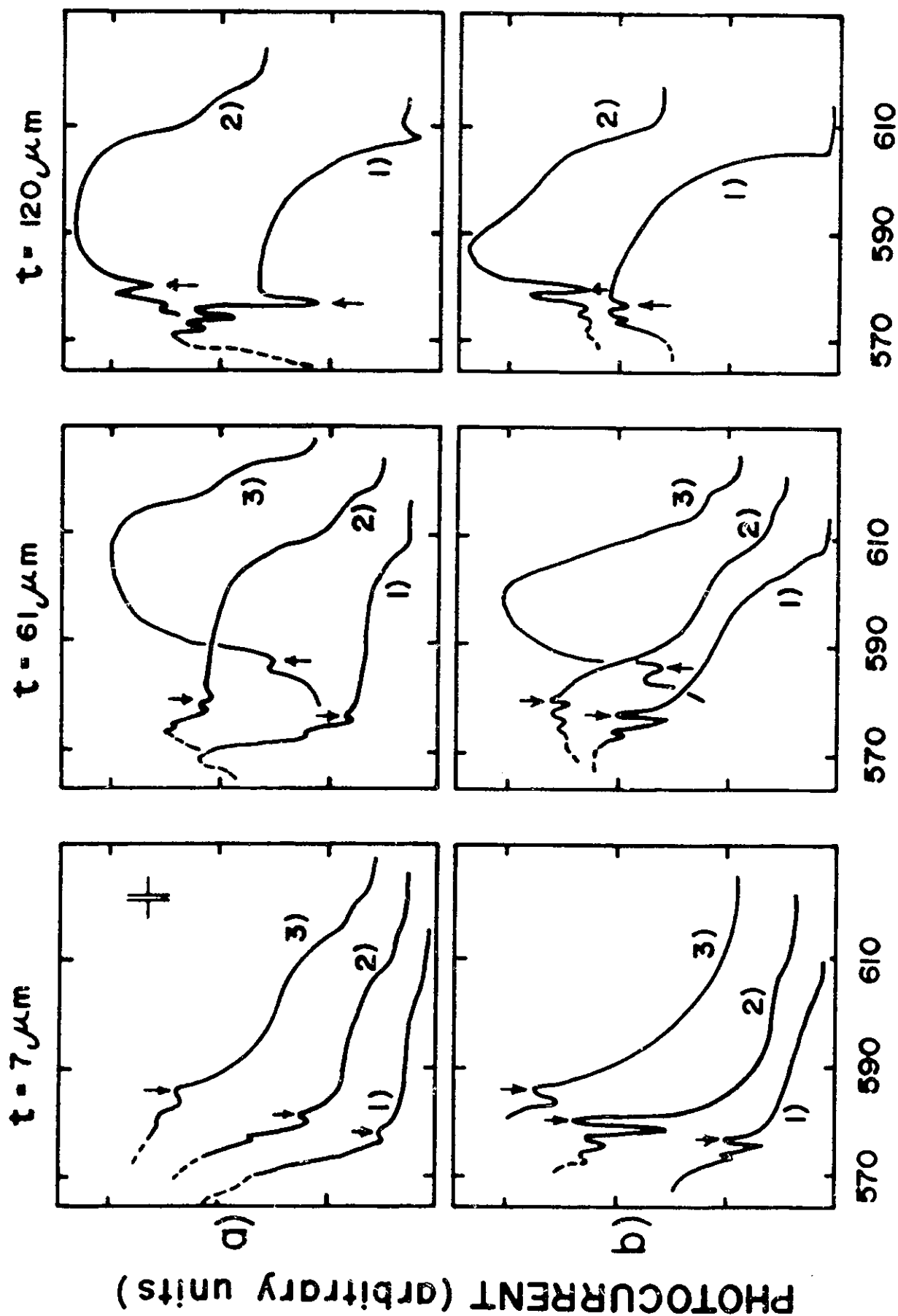
5.5. EXPERIMENTAL RESULTS:

The results will be divided in two sections. In the first, the experimental results obtained with samples (type I) consisting of thermally grown Cu_2O on Cu are going to be discussed and analyzed. In the second section, in order to further confirm the interpretation of the photovoltaic effect, the PV spectra of a high purity natural growth Cu_2O single crystal are examined and analyzed.

THERMALLY GROWN Cu_2O : (type I samples)

5.5.1. PHOTOVOLTAIC SPECTRA AS A FUNCTION OF Cu_2O THICKNESS AND TEMPERATURE:

Cu_2O films of different thicknesses have been grown by thermal oxidation of high purity copper [8]. The photovoltaic cells prepared were of the following form, $\text{Au(Ohmic)}/\text{Cu}_2\text{O}/\text{Cu}$, that means the Schottky junction of $\text{Cu}_2\text{O}/\text{Cu}$ was at the back of the sample (backcells). Therefore, the photovoltaic cell was illuminated from the Au side, see figure 5.7. The PV spectra were recorded at 4 temperatures : 170, 80, 6 and 2 degrees Kelvin. The sample resistance varied between 10^9 and 10^{12} Ohms, depending on the sample thickness and temperature. The photovoltaic response was recorded with a lock-in amplifier of $10^8 \Omega$ input impedance, thus in effect the photocurrent was measured as a function of light wavelength for all sample thicknesses. In figure 5.13a, the



WAVELENGTH (nm)

Figure 5.13: a) Experimentally obtained photovoltaic spectra of type I samples.

b) Computer generated spectra using equation (5.16), at 1) $T = 6 \text{ K}$, 2) $T = 80 \text{ K}$, and 3) $T = 120 \text{ K}$ for $3 \text{ Cu}_2\text{O}$ film thicknesses: 7, 61 and $120 \mu\text{m}$.

experimentally obtained photocurrent spectra for 3 different Cu_2O thicknesses $t = 7, 61, \text{ and } 120 \text{ }\mu\text{m}$ are presented. Curves 1, 2, 3 correspond to 3 temperatures $T = 6 \text{ K}, 80 \text{ K}$ and 170 K , respectively. The dotted part of the lines correspond to the ionization continuum above the band gap.

It is clearly apparent in figure 5.13a, that a current is detected even if the electron-hole pairs are photocreated in the semiconductor, directly in the form of excitons. The spectral region beyond the dotted line in figure 5.13a corresponds to the yellow excitonic series below the semiconductor band gap (see figure 5.4). Excitons created inside the $n=1$ phonon-assisted absorption band, in higher terms of the yellow series, quickly thermalize to the bottom of the $n=1$ band [37] for good quality samples and convert into long-lived optically inactive paraexcitons [1]. Given the large binding energy of the paraexcitons ($E_b \approx 0.14 \text{ eV}$), and low sample temperature, thermal dissociation of the $n=1$ paraexcitons into free carriers is highly unlikely. Furthermore, if ejection of free carriers from states in the bandgap is considered, the results cannot be explained, because the free carrier diffusion length has been estimated by A. Coret [38] to be less than $10 \text{ }\mu\text{m}$ at $T = 77 \text{ K}$. The diffusion length necessary to reproduce the experimental spectra at $T = 80 \text{ K}$ is at least 5 times larger. Therefore, it seems that diffusion of free carriers in the bulk of Cu_2O is not responsible for the photocurrent observed.

Figure 5.13b, presents the calculated photovoltaic spectra using equation (5.16), which was developed from the diffusion theory (see section 5.2.9). The absorption coefficient values used to generate the spectra in figure 5.13b, were taken from S. Nikitine et al. [22], for $T = 6$ K, and from I. Pastrnyak [21] for $T = 80$ K and $T = 170$ K. The absorption spectra are shown in figures 5.14 and 5.15, respectively (the arrows indicate the yellow series excitons). The sample thickness t was measured by method # 3 (discussed in section 2.4), while w was taken to be less than $1 \mu\text{m}$ (see section 5.2.4). The diffusion length L was an adjustable parameter in order to obtain the best agreement between experiment and theory. The spectral shapes seem to become insensitive to the value of L , for $L > t$, as it can also be predicted from equation (5.16).

Any model should also account for the behaviour observed at the position of the $n=2$ exciton, where a positive or negative structure appears in the photovoltaic spectra, depending on the sample temperature and thickness. It is possible to understand the main features of the photovoltaic spectra of figure 5.13a, assuming that the external current results from a field-induced dissociation of excitons in a narrow region at the metal/semiconductor interface (the dipole layer, see section 5.2.4). Comparing the experimentally obtained spectra in figure 5.13a with the computer generated spectra of figure 5.13b, it is evident that the general features are well reproduced by the model

presented in section 5.2.9, including the reversal in the structures observed at $n=2$ or higher order terms of the yellow series. The divergence in the agreement between experiment and theory, for wavelengths that correspond to an absorption length ($1/\alpha$) larger than the sample thickness, is due to the fact that light reflection at the Cu surface was neglected. As a first order approximation, one may assume that the effect of light reflection would double the photocurrent at those wavelengths, because the light is reflected from the $\text{Cu}_2\text{O}/\text{Cu}$ interface back towards the oxide.

The physical origin of the $n=2$ reversed structure can be understood as follows. If the sum of the diffusion length L and the absorption length $1/\alpha$ ($L + 1/\alpha$) is smaller than the sample thickness $t-w$, then a decrease of the photocurrent will occur upon an increase of the absorption coefficient α . That would mean, that an increasing fraction of excitons which are formed closer (large α) to the front Au-covered surface have to diffuse for a longer distance, thus recombining before reaching the dissociation region. Therefore, they do not contribute as much to the signal as those excitons that were created inside the semiconductor (smaller α) and have to travel a shorter distance to the dissociation region. These conditions are met for the $n=2$ structure and the sharp absorption lines of the yellow series higher terms, either in the case of thicker samples, or if the underlying background absorption from the $n=1$ phonon-assisted continuum has sufficiently increased because of the temperature.

The latter can be verified in figure 5.13a, where the inversion of the $n=2$ structure is clearly apparent at $T = 170$ K (curve 3) for the sample of thickness $61 \mu\text{m}$, while at $T = 6$ K (curve 1), the $n=2$ is still positive. Notice, that at $T = 80$ K (curve 2) for the same sample thickness ($t = 61 \mu\text{m}$), the $n=2$ structure is going through the transition to become negative. Also note, that for small thicknesses ($t = 7 \mu\text{m}$) the generated photovoltaic spectra tend to reproduce the excitonic absorption spectra. The experimental data differ however, in the sense that the $n = 2, 3, \dots$ excitonic structures appear markedly reduced with respect to their corresponding structures in absorption spectra (see figures 5.14 and 5.15). This can be explained in view of the fact, that for the thinner oxide sample all excitons are now created in a high electric field region, since the field of the regular depletion region has increased because the sample thickness decreased. It is well known, that the presence of a large field leads to broadening and a reduction of the excitonic oscillator strength, especially for higher order of excitonic terms [24,25] (see section 5.2.4). No attempt has been made to include this effect in the theoretical fits. Finally note, that the diffusion length, as extracted from best spectral fits, increases with decreasing temperature, but only slightly between 80 and 6 K.

The photovoltaic spectra taken at $T = 2$ K, are not presented because they have exactly the same shape as those taken at $T = 6$ K. This result adds further support to the fact that the excitonic diffusion length is saturated due to large number of

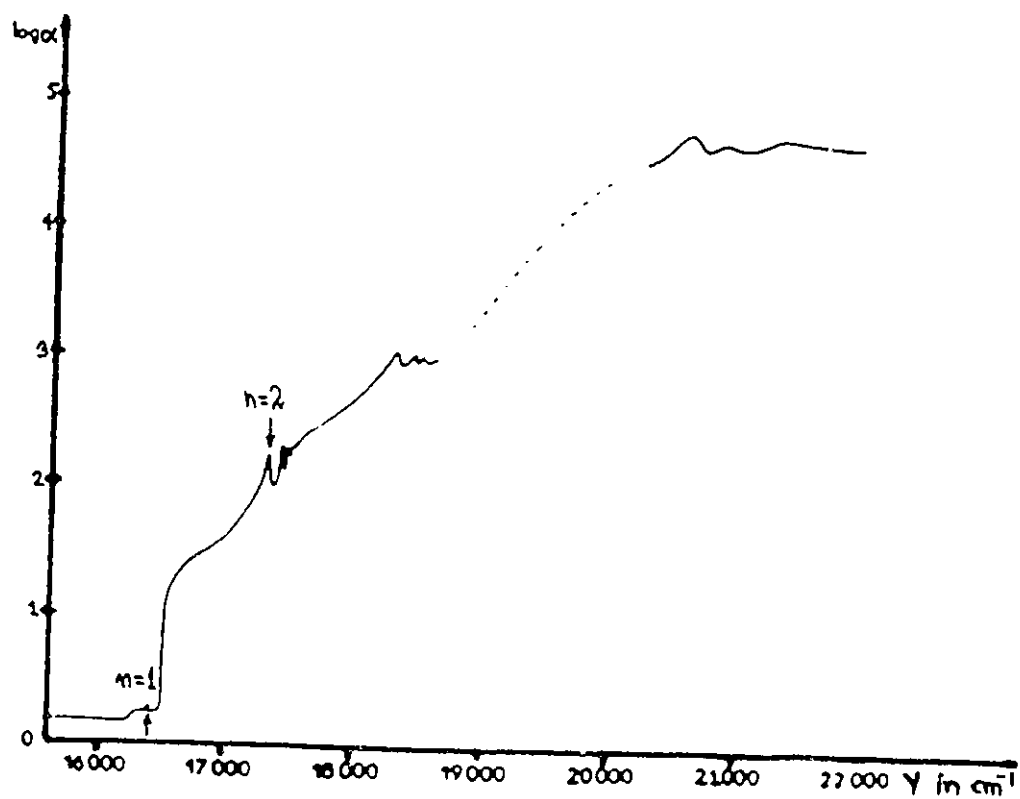


Figure 5.14: Absorption spectrum of Cu_2O at $T = 4.2 \text{ K}$ (22).

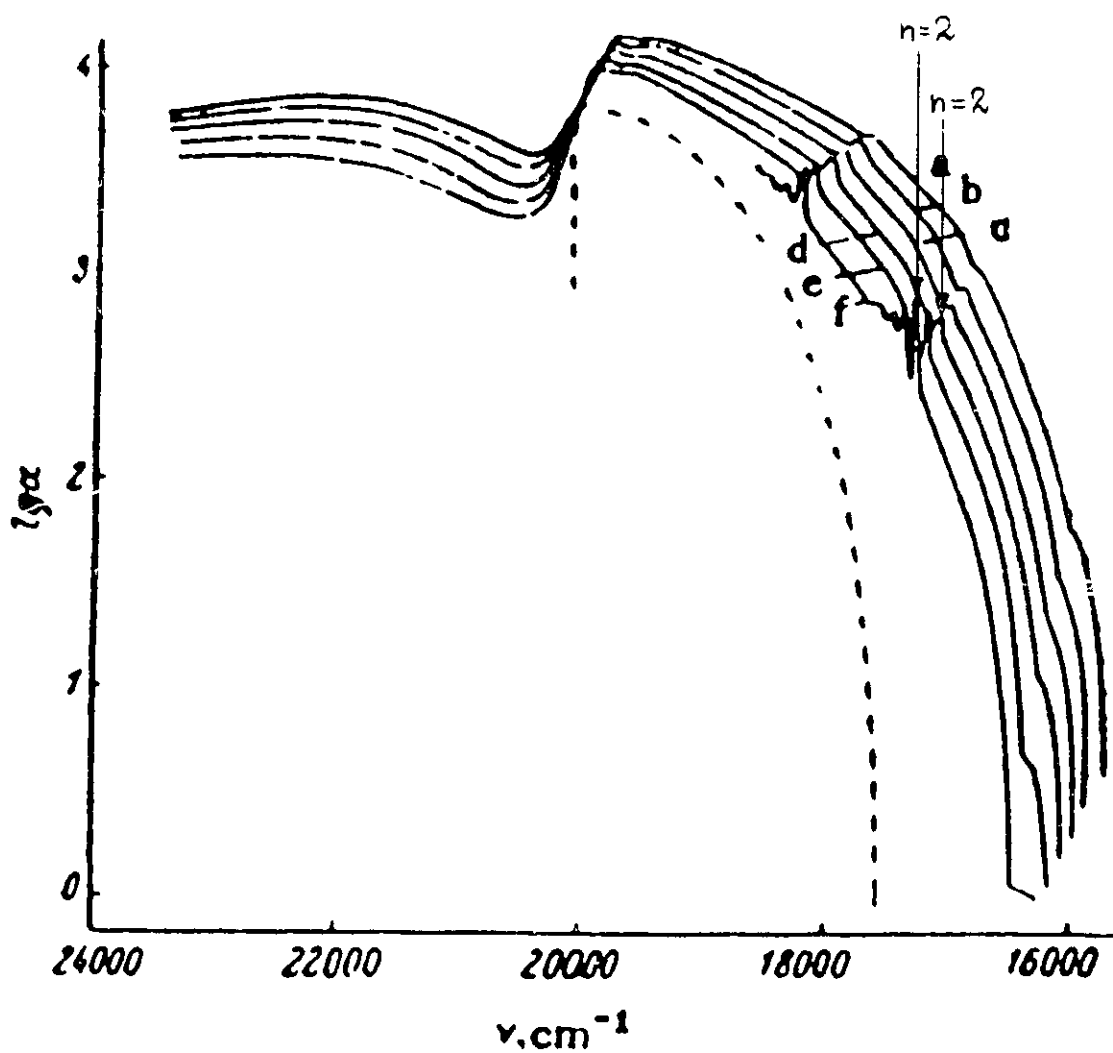


Figure 5.15: Absorption spectra of Cu_2O (21), at :
a) $T=300$ K, b) $T=260$ K, c) $T=220$ K,
d) $T=170$ K, e) $T=140$ K and f) $T=77$ K.

recombination centers at temperatures below 80 K. This will also become evident when the results of a better quality crystal are presented later. Additional measurements discussed below show that the diffusion length reaches a limiting value of $L \approx 45 \text{ } \mu\text{m}$ at $T \approx 80 \text{ K}$, in this kind of material (type I).

One can also extract exciton diffusion lengths using the photovoltaic effect without relying on a detailed knowledge of the exciton absorption spectra. This can be achieved by plotting the measured photocurrent as a function of sample thickness for a given wavelength, at a constant temperature and illumination condition. As it is shown in section 5.2.9, for case 1, equation (5.15) reduces to equation (5.17).

Therefore, provided that $1/\alpha \ll L, t$:

$$\frac{\ln(J_{\text{TOTAL}}/J_0)}{t} = - \frac{1}{L}$$

Such plots are shown in figure 5.16a,b for $T = 80 \text{ K}$. Figure 5.16a was obtained using the constant temperature liquid nitrogen cryostat, while for 16b the Janis variable temperature cryostat was used. The slope obtained from both curves (figures 5.16a,b) is about 200 cm^{-1} , which corresponds to a diffusion length of $50 \text{ } \mu\text{m}$ (case 1, see section 5.2.9). Figures 5.17 and 5.18 show also the logarithm of the photocurrent versus sample thickness at $T = 6 \text{ K}$ and $T = 170 \text{ K}$, respectively. In figures 5.16, 5.17 and 5.18 the wavelength corresponding to the peak of the $n=2$ structure was used to monitor the photocurrent variation. In fact, the same result is obtained even if the wavelength is

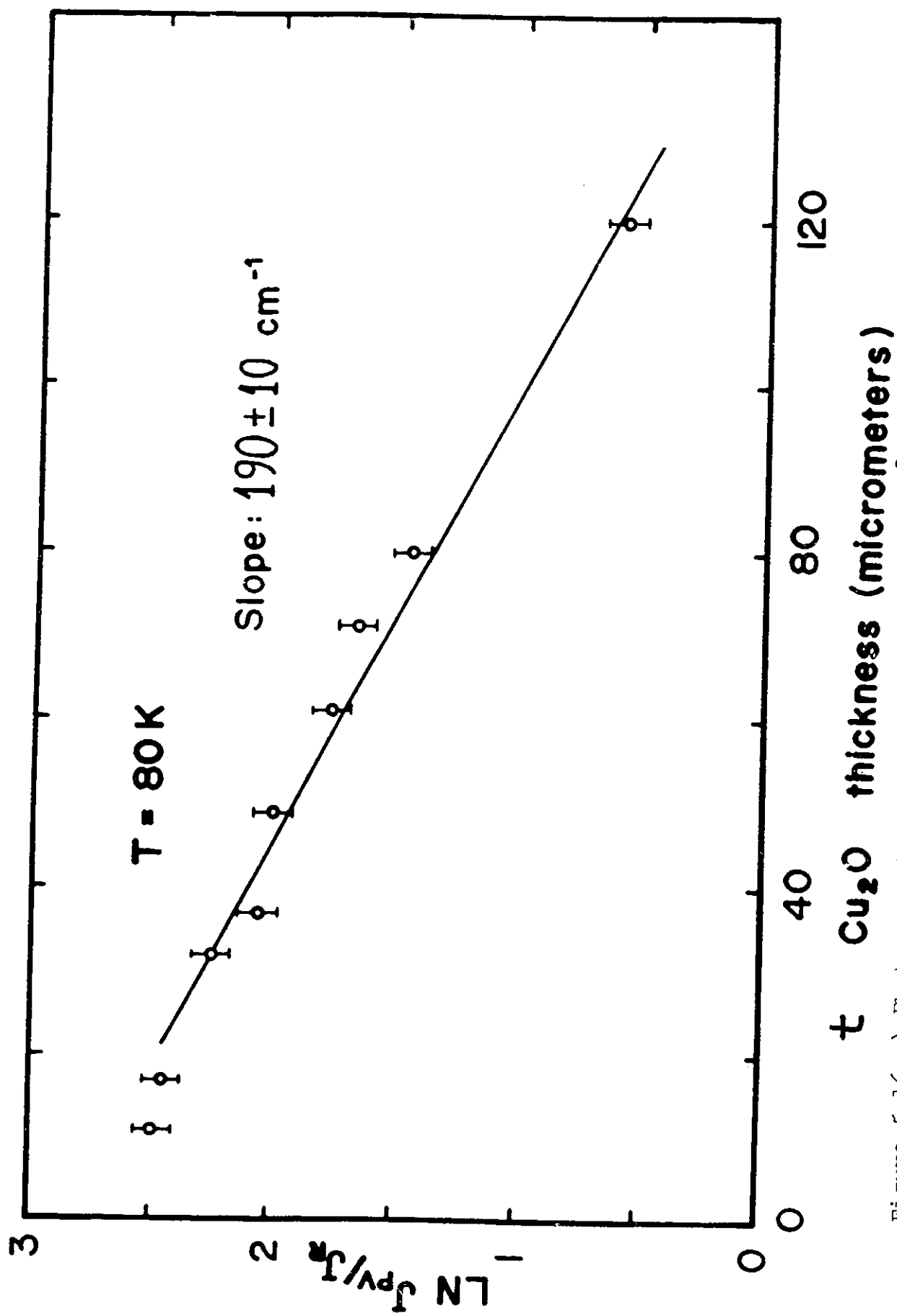


Figure 5.16 a) Photocurrent versus oxide thickness for λ corresponding to the $n=2$ yellow exciton. $T=80 \text{ K}$, data points obtained using the liquid nitrogen optical cryostat.

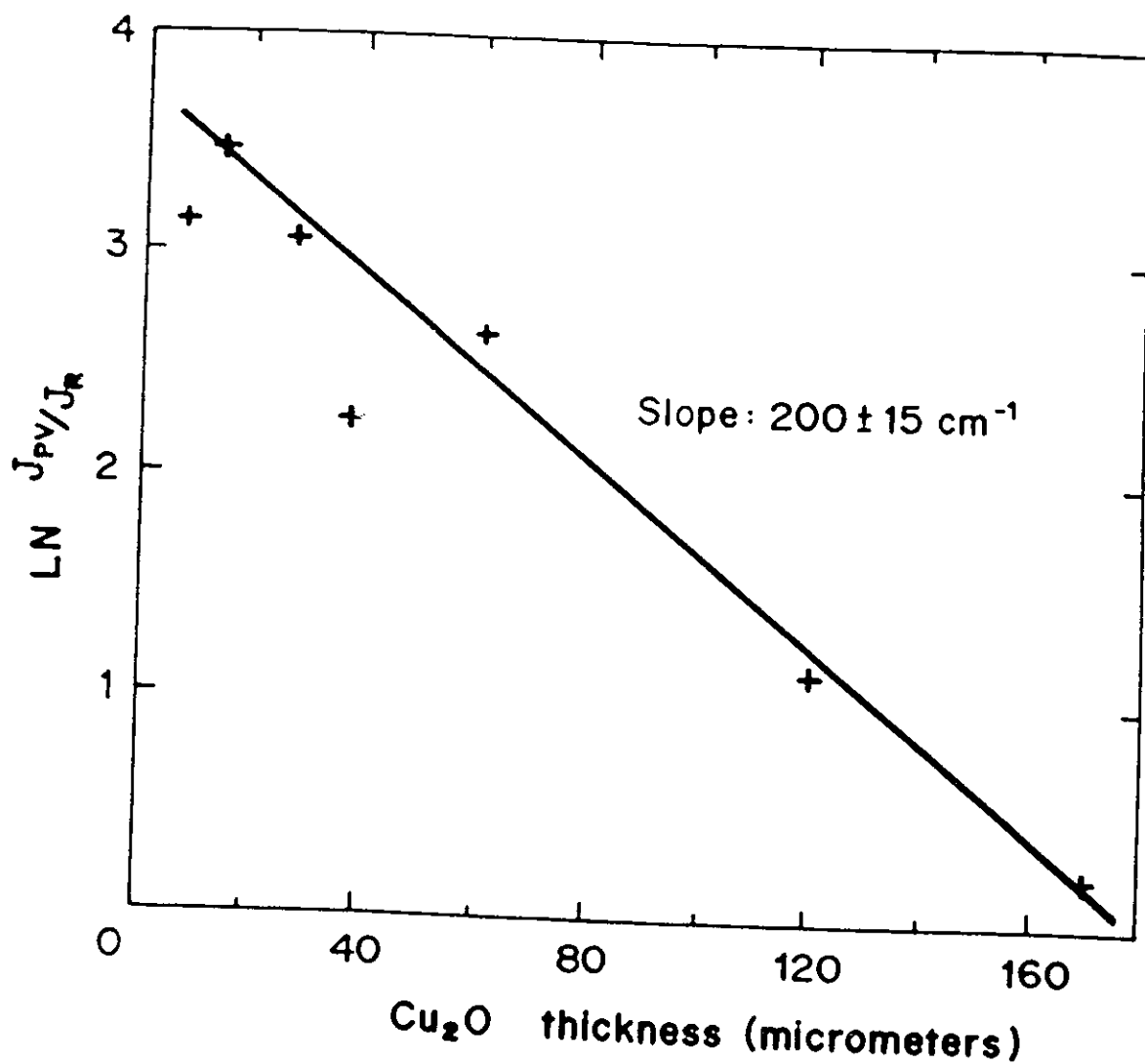


Figure 5.16 b) Photocurrent versus oxide thickness for λ corresponding to the $n=2$ yellow exciton. $T=80 \text{ K}$, data points obtained using the Janis cryostat.

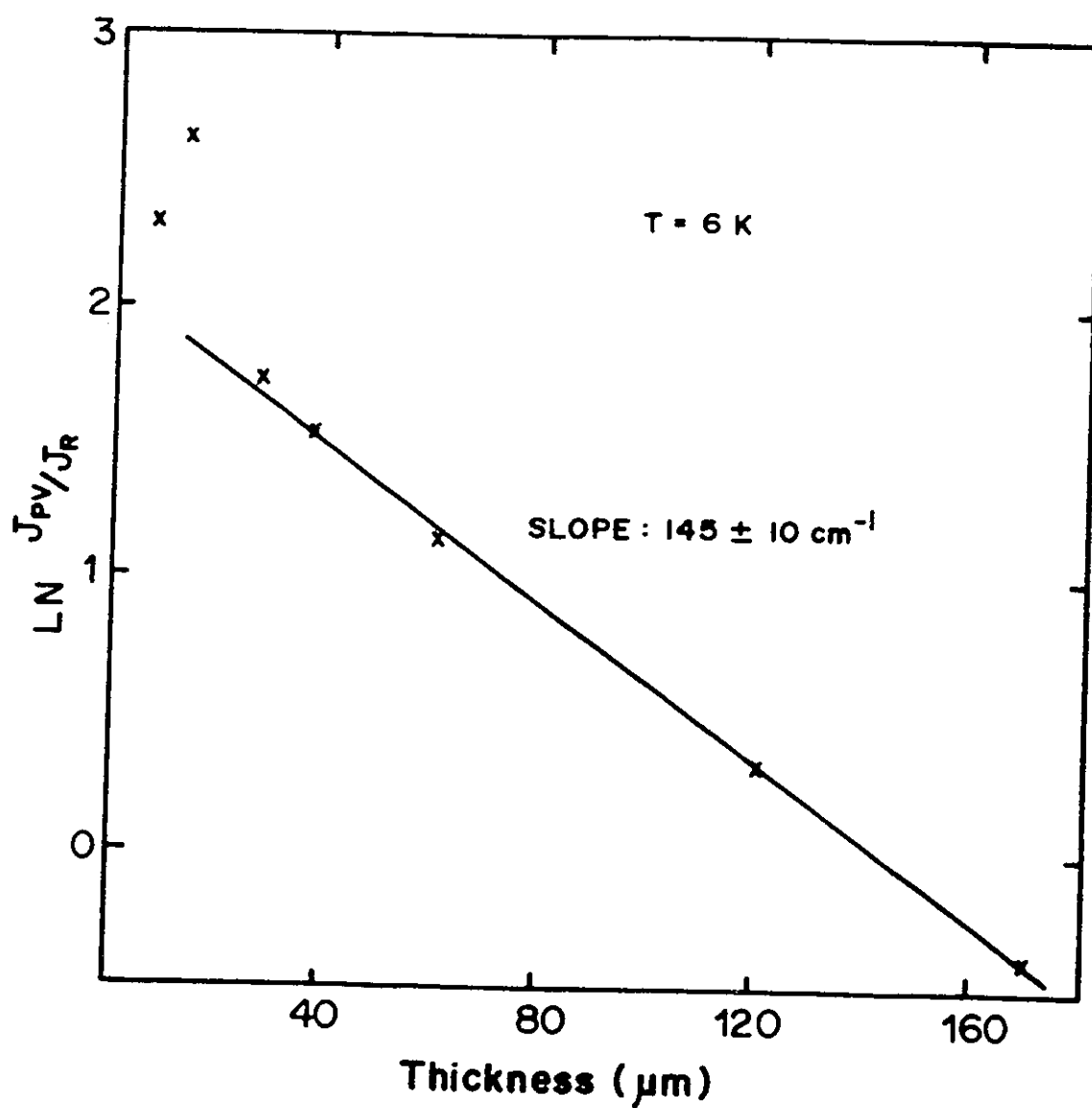


Figure 5.17: Photocurrent versus oxide thickness at $T=6 \text{ K}$,
 (λ corresponding to the $n=2$ yellow exciton).

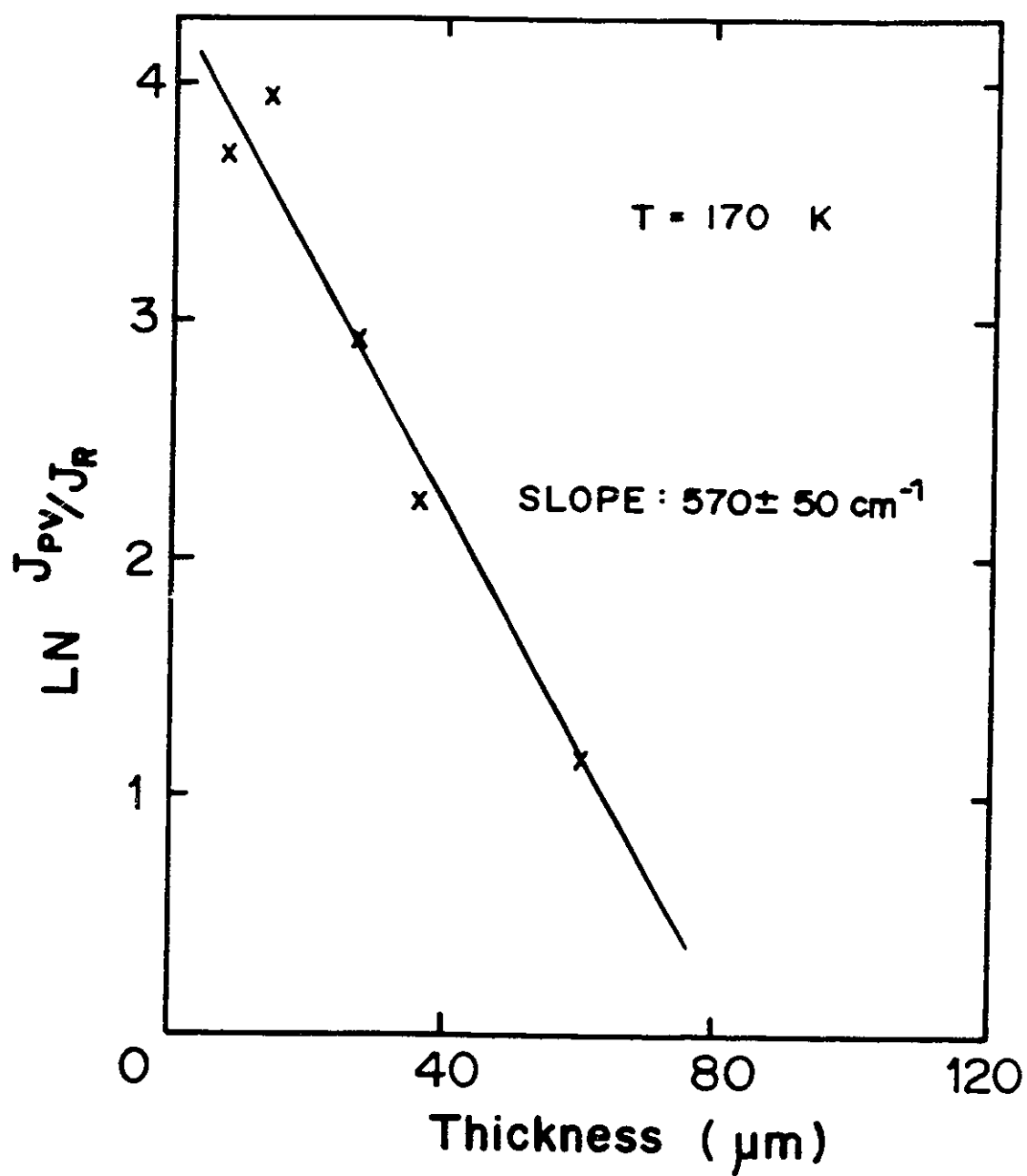


Figure 5.18: Photocurrent versus oxide thickness at $T=170 \text{ K}$,
(λ corresponding to the $n=2$ yellow exciton).

chosen around the $n=2$ structure, because a change of the region where the exciton is created inside the sample (for $t > L$) or a small change in its kinetic energy does not alter its behaviour (further discussion on this matter follows). In the following table the experimental results obtained from figures 5.16, 5.17, 5.18 are summarized :

TABLE 2

	CASE 3	CASE 1	CASE 3
T (in K)	6	80	170
L_{exp} (in μm)	70 ± 5	45 ± 5	18 ± 3
$1/\alpha$ (in μm)	38 ± 2	14 ± 1	16 ± 1
L_{act} (in μm)	45 ± 5	45 ± 5	16 ± 4

The cases presented in the above table correspond to the different situations developed in section 5.2.9. Notice, that at $T = 6$ K and especially at $T = 170$ K the condition $L \gg 1/\alpha$ is not satisfied. Thus the slope obtained experimentally from a plot of photocurrent versus sample thickness does not correspond to the actual diffusion length. To find the actual diffusion length presented in the last row of Table 2, a best fit of equation (5.15) to the experimental data was made (case 3, see section 5.2.9). At $T = 80$ K, the condition of case 1 is satisfied, and thus the inverse of the slope corresponds to the diffusion length.

Note, that $J_0 = 2 e q \phi$ in equation (5.17) is a constant for a given sample. It is expected though, that ϕ (the quantum efficiency factor) would vary from sample to sample. This fact has to be taken into account in order to have reproducible results. Assuming that the semiconducting material quality is the same, then one has to correct for the $\text{Cu}_2\text{O}/\text{Cu}$ junction quality, which depends on the preparation of the Cu surface prior to oxidation and exact oxidation conditions. To account for the junction quality, a spectral region has to be chosen where the photocurrent depends on the barrier height (see section 1.4.3). This is in fact the spectral region beyond the $n=1$ phonon-assisted absorption band, where the absorption coefficient is very small and most of the current results from absorption at the $\text{Cu}_2\text{O}/\text{Cu}$ interface with subsequent carrier emission over the barrier. The following correction procedure was used for the photocurrent in all the figures involving $\ln(J_{\text{pv}}/J_{\text{R}})$ versus sample thickness. The photocurrent (J_{pv}) was measured at a wavelength of interest and then was divided by the photocurrent (J_{R}) taken in the spectral region beyond the $n = 1$ phonon-assisted absorption band. For example, at $T = 6$ K, the photocurrent at the wavelength of interest for each sample, was divided by its photocurrent response taken at 615 nm, while at $T = 80$ K it was taken at 620 nm because the absorption band shifts with temperature. Without the correction procedure there is a significant scatter of data points. After the correction is performed the data scatter is reduced considerably. The result can be seen in figures 5.16a,b, 5.17,

5.18. Figures 5.16a and 5.16b were obtained at different times, 5.16a using the constant temperature liquid nitrogen cryostat and 5.16b using the variable temperature Janis cryostat. The scatter of data points is more pronounced in figure 5.16b because use of the variable temperature cryostat was made, thus resulting in a greater temperature difference between samples than that of the constant temperature cryostat. The results obtained in both cases agree with each other. Figures 5.17 and 5.18 were obtained using the Janis cryostat. At $T = 170 \text{ K}$ the slope was $145 \pm 10 \text{ cm}^{-1}$, and at $T = 6 \text{ K}$ the slope was $570 \pm 50 \text{ cm}^{-1}$, respectively.

5.5.2. EFFECT OF THE ELECTRIC FIELD ON THE PV SPECTRA:

The effect of externally applied electric field on the PV spectra at liquid Nitrogen and room temperatures was studied. It has already been discussed in section 5.2.4, that there are two internal electric field regions associated with the $\text{Cu}_2\text{O}/\text{Cu}$ junction. First, the dipole layer, which is estimated to be $10 - 50 \text{ nm}$ thick with an internal high electric field of the order of 10^5 V/cm . Second, the region associated with the depletion region of an ideal Schottky junction. This region usually extends over microns and the electric field is of the order of a few hundred Volts/cm. The externally applied voltage produced across the sample a maximum electric field of $\approx 1.6 \text{ KV/cm}$. This field was not large enough to significantly affect the $n=2$ structure, as shown in figure 5.19 under reverse bias for a $37 \text{ }\mu\text{m}$ thick oxide sample. The external field however, was sufficient to have an

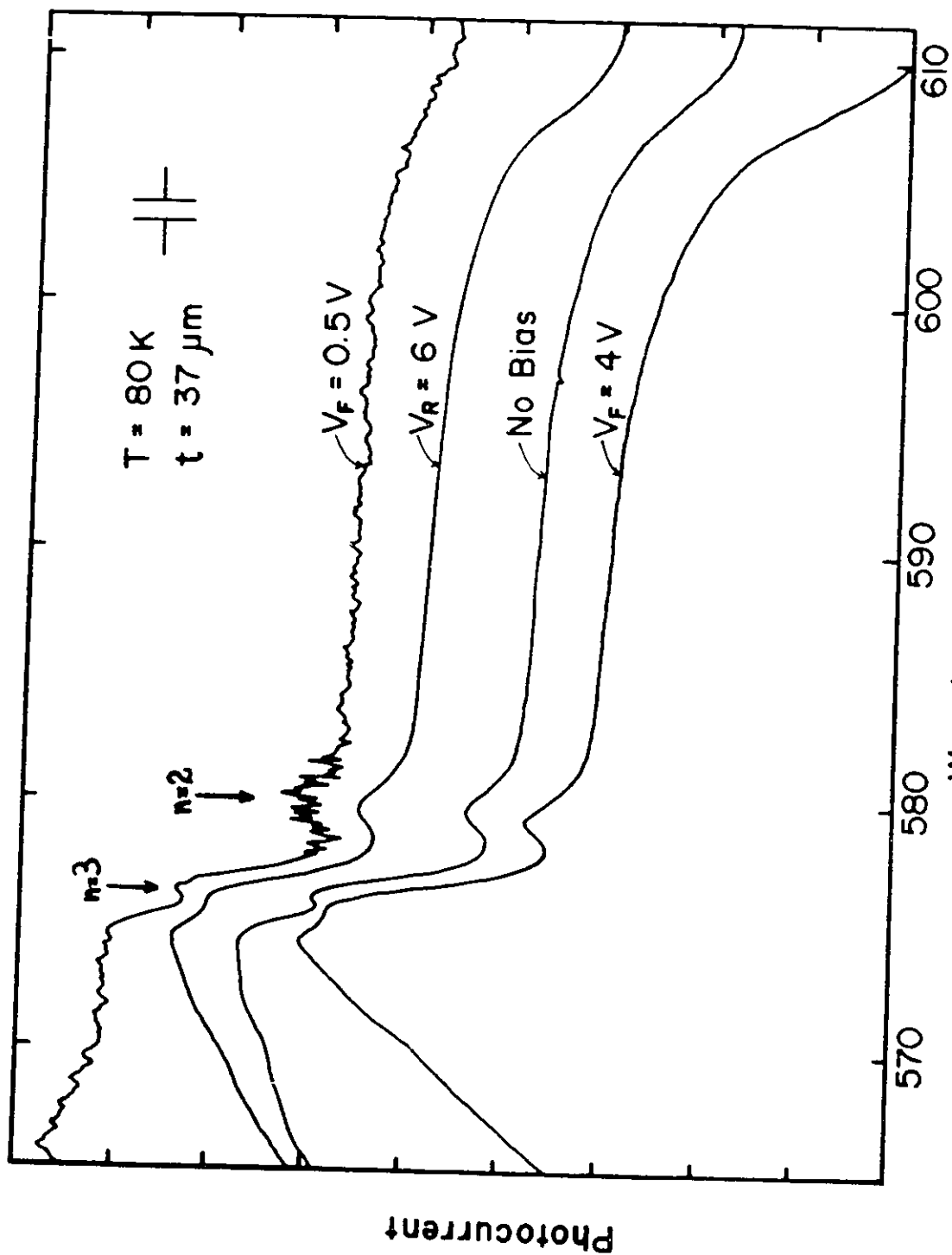


Figure 5.19: Photovoltaic spectra at $T = 80 \text{ K}$ for a $37 \mu\text{m}$ thick Cu_2O film, under :

a) No bias, b) Reverse bias, $V_R = 6 \text{ V}$, c) Forward bias, $V_F = 0.5 \text{ V}$ and
 d) Forward bias, $V_F = 4 \text{ V}$.

effect on the $n=3$ excitonic structure. Note, that under forward bias, as the flat band condition (for $V_{bi} \approx V_F$) is approached, all excitonic features remain unaffected. At a forward voltage of about 0.55 V the polarity of the photocurrent reversed as shown in figure 5.20, indicating that the built-in potential (V_{bi}) associated with the depletion region is about 0.5 V at $T = 80$ K. As the forward voltage is further increased, the bands are bending in the opposite direction as if the semiconductor was n-type. At this point, the $n=3$ excitonic feature starts disappearing again (figure 5.20).

The electric field has the effect of mixing the energy states available to the excitons before they are formed. The mixing of states is larger for the low binding energy excitons ($n \geq 2$). Therefore, this effect will be more pronounced for the excitonic structures of the higher order terms. The second effect of the electric field is to dissociate the excitons when the potential energy across the orbit of the exciton becomes of the order of the exciton's binding energy. It is experimentally observed that the $n=3$ structure is affected by the relatively low externally applied electric field, while no effect is observed for the $n=2$ exciton and neither for the large background of the 1S excitons. One could then deduce that, not all $n \geq 2$ excitons convert into 1S excitons, which are only sensitive to high electric fields ($\approx 10^5$ V/cm).

Therefore, in light of the above let us address again the question : is there diffusion of excitons rather than free

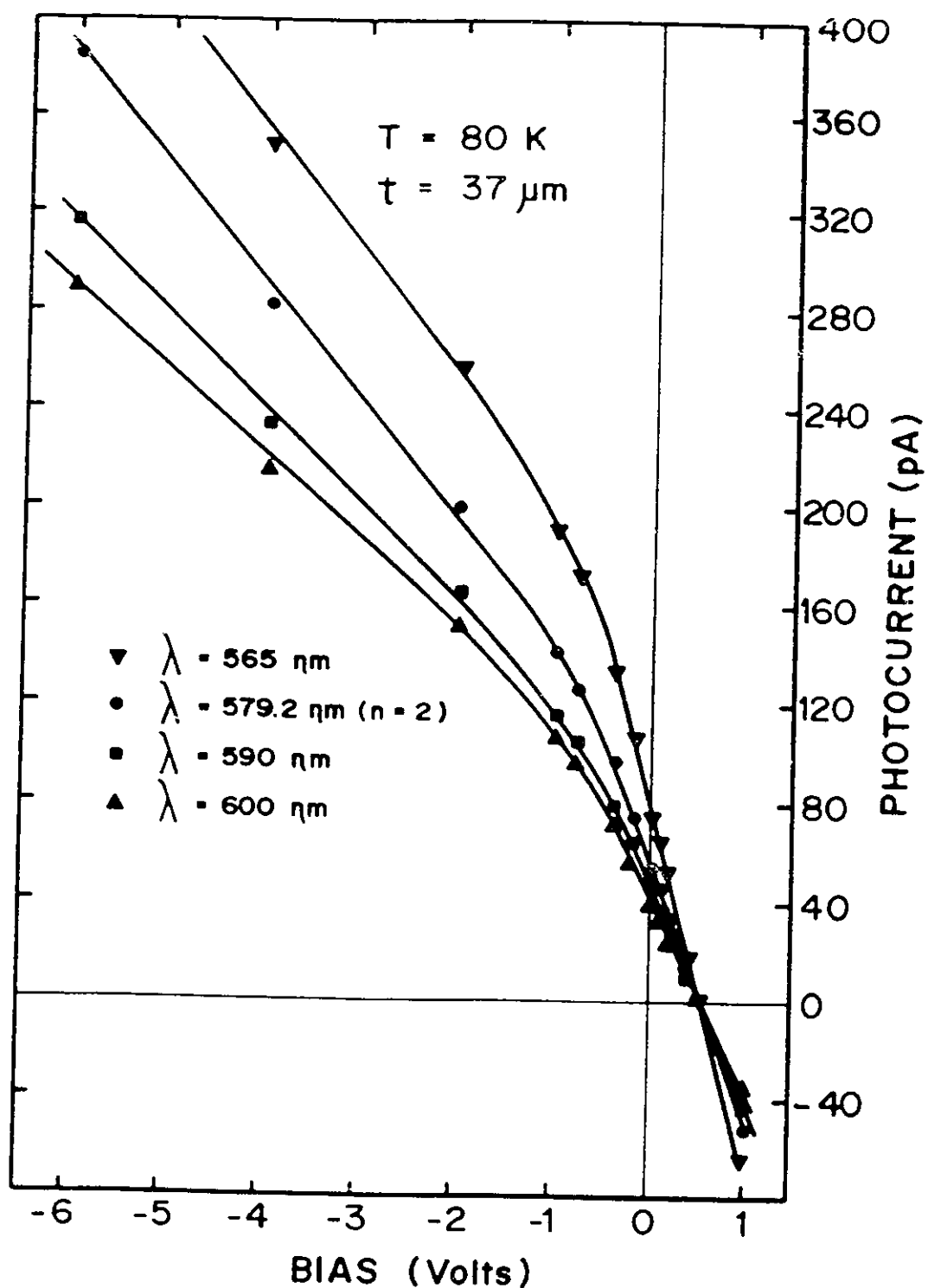


Figure 5.20: Photocurrent versus bias voltage at $T=80 \text{ K}$ for a $37 \mu\text{m}$ thick Cu_2O film, at 4 different wavelengths of illumination.

carriers ? For that matter, let us assume that a large fraction of the photocreated $n=2$ excitons were dissociated into free carriers, then it would be expected that the shape of the $n=2$ structure would be washed-out as the forward voltage V_F was approaching the flat band condition ($V_{bi} \approx V_F$), effectively decreasing the collecting efficiency of the free carriers, because now there is no electric field at the metal/semiconductor junction to sweep the free carriers. Therefore, there is supporting evidence that $1S$ excitons diffuse towards the Cu_2O/Cu back junction, where they are field dissociated. The reason the photosignal increases with reverse bias (figure 5.20) has nothing to do with the electric field effect, but rather with the fact that one is dealing with a poor diode. For an ideal diode, the photocurrent is expected to saturate as the reverse bias is increased.

5.5.3. INFRARED PV RESPONSE WITH AND WITHOUT APPLIED BIAS:

The spectral region referred to as "infrared" in this section, corresponds to the barrier spectral response region of the Cu/Cu_2O junction (due to process 1, $h\nu < E_g$, in figure 3.6b). The infrared response of the thermally grown samples in the backcell configuration, $Au/Cu_2O/Cu$, was examined with and without a reverse bias at room and liquid Nitrogen temperatures. The application of reverse bias onto the junction is of interest, because it improves the signal to noise ratio, and possibly enhances the processes usually masked by the carrier emission over

the metal/semiconductor barrier, thus allowing one to investigate states within the energy gap. The results are presented in case they might become useful for possible later experiments to be performed in the infrared spectral region, for example : two-photon absorption experiments. The Cu_2O sample used for this experiment was 61 μm thick. Care was taken in order to measure the photocurrent, while the second order radiation of the grating was cut off by appropriate filters. In figure 5.21, two spectra are presented showing the photocurrent as a function of wavelength at room temperature, in the spectral region beyond the fundamental absorption edge, for a $\text{Cu}_2\text{O}/\text{Cu}$ junction with and without bias. The dashed line spectrum was taken while 8.3 Volts of reverse bias were applied onto the sample. At this point it is tempting to attribute the observed maximum in the response curve to the polarization of the copper inclusions in the oxide, as was proposed by Weichman et al. [39], who obtained a similar spectrum with absorption measurements. Figure 5.22 presents the PV spectra with and without reverse bias at $T = 80 \text{ K}$. Notice, that the signal polarity for the non-biased spectrum was reversed around $\lambda = 750 \text{ nm}$ and remained negative for longer wavelengths compared to the polarity for $\lambda < 750 \text{ nm}$. In figure 5.23 the PV spectrum of the same sample is shown under reverse bias, at $T = 80 \text{ K}$, close to the fundamental absorption edge of Cu_2O . The hump observed around 650 nm was also observed without applying a bias. Therefore, no definite conclusion for the presence of the Cu inclusions can be drawn at $T = 80 \text{ K}$. Although this is not the

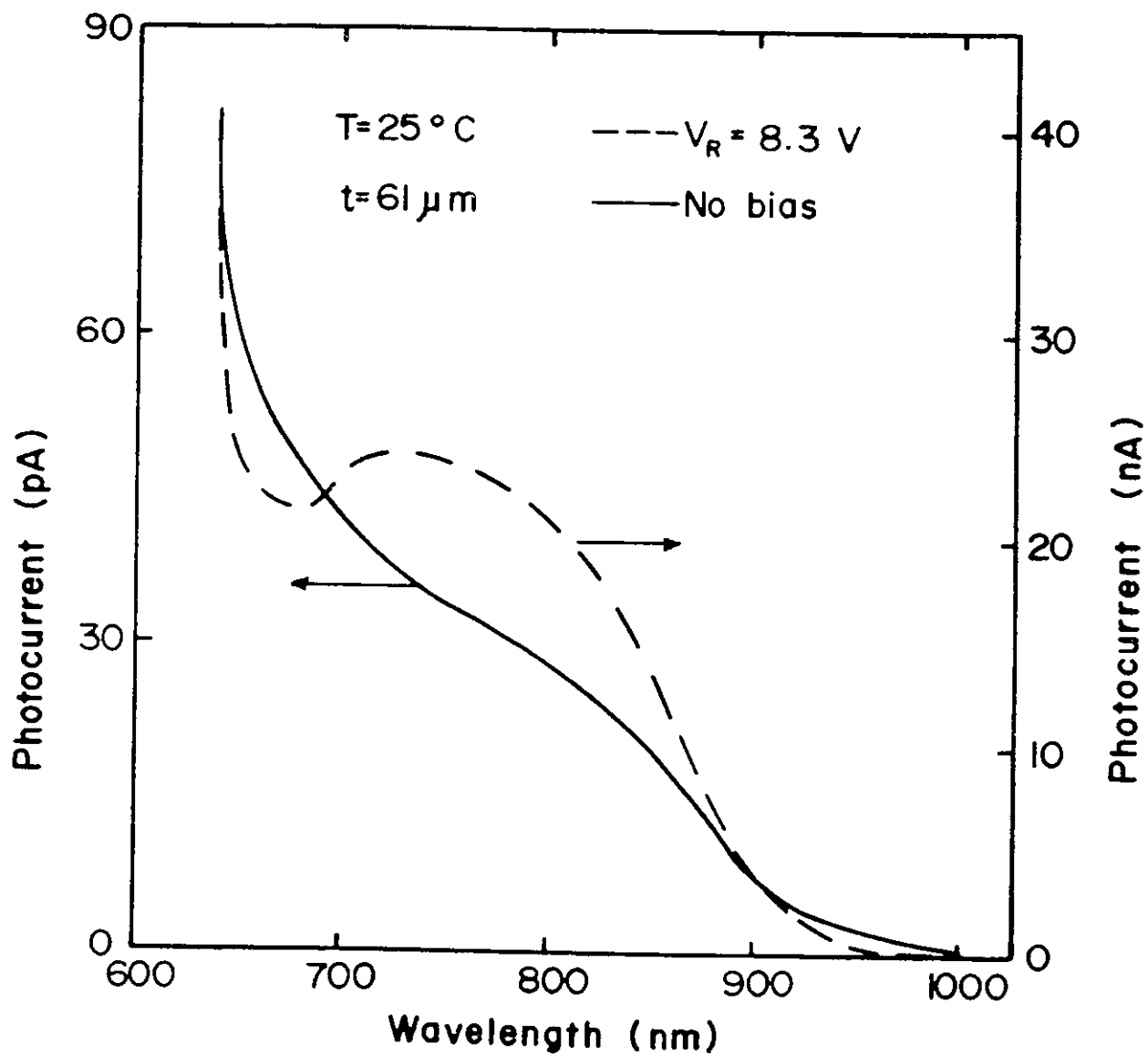


Figure 5.21: Photocurrent versus wavelength recorded at room temperature for a $61\ \mu\text{m}$ thick Cu_2O film.
 Solid line : No bias. Dashed line : $V_R = 8.3\ \text{V}$.

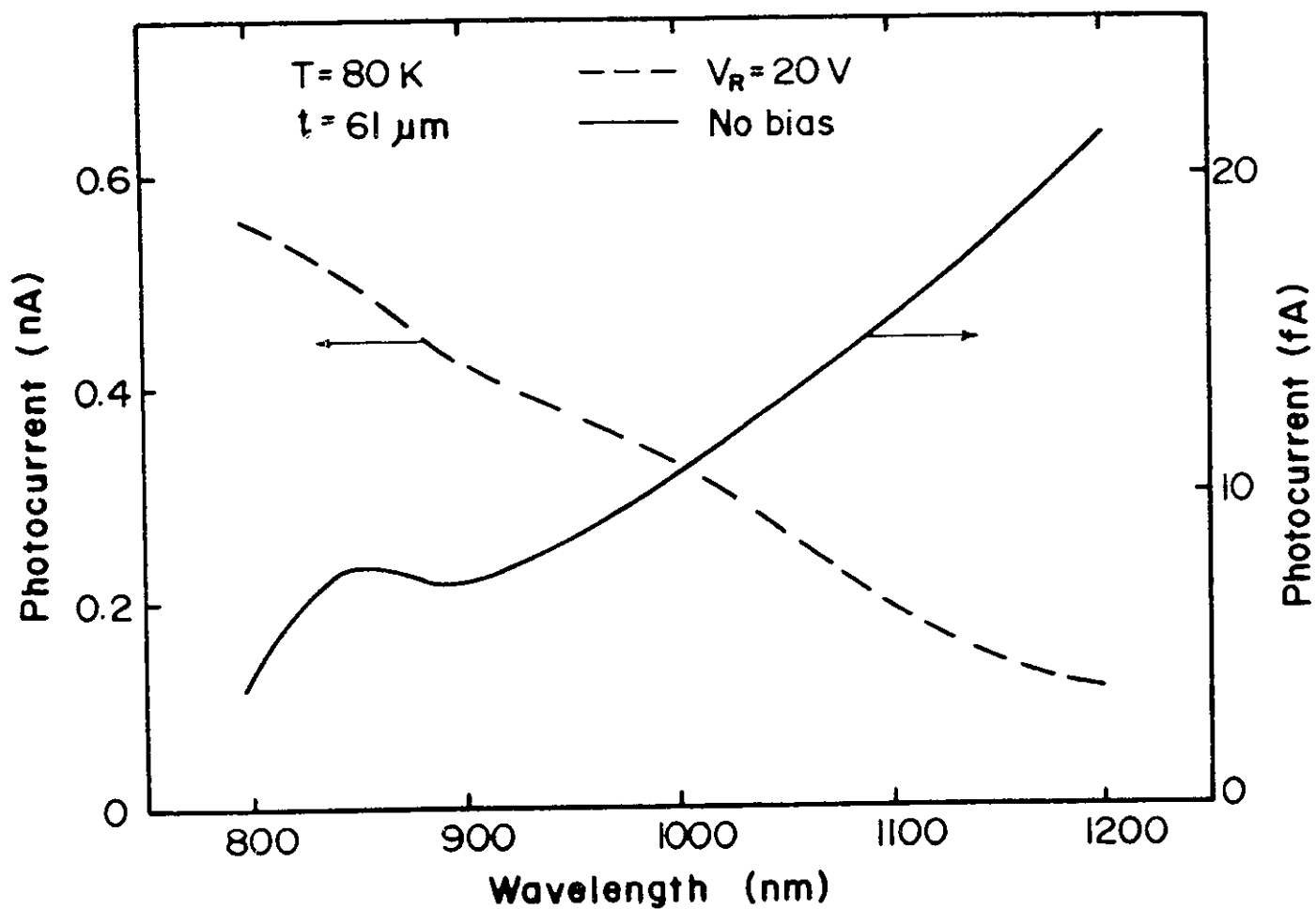


Figure 5.22: Photocurrent versus wavelength at $T = 80 \text{ K}$ for a $61 \mu\text{m}$ thick Cu_2O film. Solid line : No bias. Dashed line : $V_R = 20 \text{ V}$.

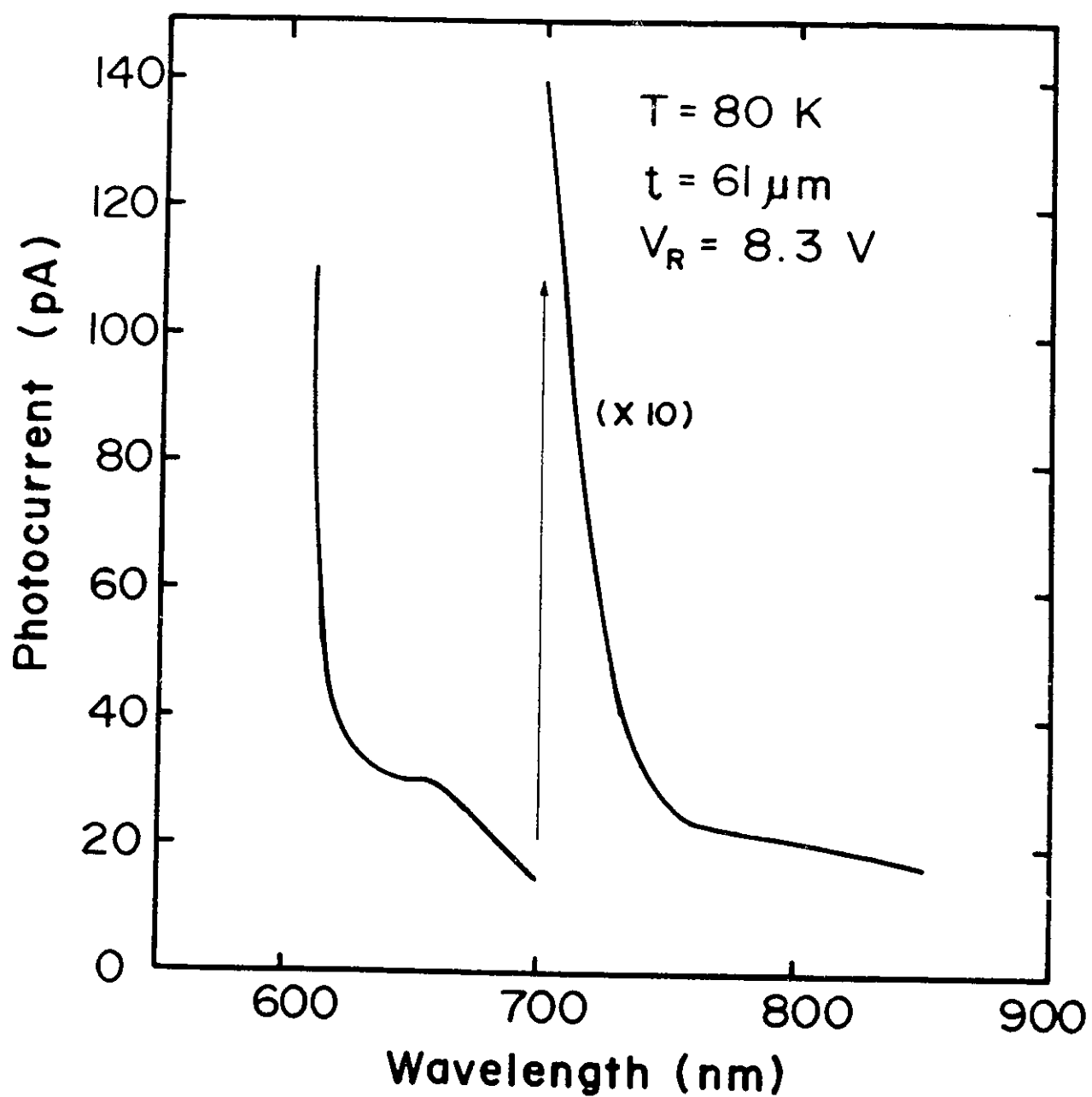


Figure 5.23: Photocurrent versus wavelength at $T = 80 \text{ K}$ for a $61 \mu\text{m}$ thick Cu_2O film, under 8.3 Volts of reverse bias.

scope of this work, that is to investigate by PV the possibility of Cu inclusions being present in our oxide samples, a study for that purpose would require to follow the approach of Weichman et al. [39].

5.5.4. GENERAL DISCUSSION OF THE RESULTS OF TYPE I SAMPLES :

Let us now summarize and discuss the evidence available from the literature and that obtained from the experimental results analyzed in this chapter so far.

- 1) The $n=2$ excitonic state and those of higher order too, have a short lifetime, of the order of 10^{-12} seconds at $T = 80$ K, as the calculation below will show, using the theory of natural line-width of atomic spectra and the Ladenburg formula [40].

$$\tau \approx \frac{\lambda^2}{c \Delta\lambda} = \frac{(580 \cdot 10^{-9})^2 \text{ m}^2}{3 \cdot 10^8 \text{ m/sec } 10^{-9} \text{ m}} = 10^{-12} \text{ sec}$$

where, λ is the wavelength of interest (here the $n = 2$ absorption peak at $T = 80$ K), c the speed of light and $\Delta\lambda$ is the linewidth at half maximum taken to be 1 nm, as evidenced from the PV spectra in figure 5.13a.

- 2) The $1S$ exciton has a lifetime of about 10^{-9} sec in these samples at $T \leq 80$ K, [41].
- 3) The free carriers have a diffusion length of less than 10 μm and a lifetime of the order of $2 \cdot 10^{-8}$ sec at $T \approx 80$ K [38].
- 4) The $1S$ and $n=2$ excitons due to their high binding energies are not dissociated thermally in significant numbers at temperatures below 170 K.

5) It was experimentally found that the diffusion length saturates at $T \leq 80$ K (see table 2 in section 5.5.1).

Assuming that excitons are in thermal equilibrium with the lattice, then in order to obtain an excitonic diffusion length of the order of $L \approx 45 \mu\text{m}$ at $T = 80$ K, the lifetime needed for the 1S to travel that distance (diffusion length) will be :

$$\tau = \frac{L^2}{D} = \frac{(45 \times 10^{-4})^2 \text{ cm}^2}{20 \text{ cm}^2/\text{sec}} \approx 1.0 \mu\text{sec} \quad (5.20)$$

The diffusion coefficient (D) value was obtained from measurements made by D.P. Trauernicht et al. [2] on a natural growth high quality Cu_2O crystal. Therefore, the D value should be higher than the one observed in thermally grown (type I) lower quality samples. The lifetime obtained from equation (5.20) is in disagreement with evidence # 2, which states that the 1S exciton lifetime is about 10^{-9} sec. If a smaller D value was to be considered, then the disagreement would be even worse. On the other hand, there is experimental evidence in Cu_2O [41] that when the exciton lifetime is short ($10^{-9} - 10^{-10}$ sec), the equilibrium distribution in the exciton system will not be reached during its lifetime. In this case the steady state kinetic energy distribution will strongly depend on the initial energy at which the excitons are generated. In fact, in the case of indirect exciton absorption, as for the 1S exciton in Cu_2O , excitons with very large kinetic energies [42] can be created. The exciton wave vector is compensated by the one of a simultaneously created

or absorbed optical phonon (Γ_{12}^-). As discussed by Permogorov [43], the kinetic energy of excitons created by indirect exciton absorption can be surprisingly high and can even exceed the exciton binding energy by several times (hot exciton). Such excitons have a high probability of nonradiative decay, that strongly depends on the defect concentration, which is usually of the order of 10^8 to 10^{10} sec^{-1} (the inverse of the exciton lifetime is used as a measure of the probability) [43]. If the lifetime of the "hot exciton" is of the order of 10^{-9} - 10^{-10} seconds then a certain fraction of the excitons may diffuse before thermal equilibrium is reached through interaction with optical and acoustic phonons. As follows from theoretical calculations [44], the probability per unit time for an exciton to change its kinetic energy by an amount KT is 10^9 to 10^{10} sec^{-1} . It seems that an intermediate case is established in this system, where all the above processes are likely to occur.

Assuming that a hot 1S exciton has a kinetic energy as large as its binding energy, let us calculate how far it will travel.

Its velocity (v) will be :

$$E_K = \frac{\hbar^2 k^2}{2 M} \quad , \quad v = \frac{\hbar k}{M} \quad \Rightarrow \quad v = (2 E_K / M)^{1/2} \quad (5.21)$$

$$v = \left[\frac{2 \times 0.14 \times 1.6 \times 10^{-19} \text{ J}}{3 \times 9.1 \times 10^{-31} \text{ Kg}} \right]^{1/2} \approx 1.28 \times 10^5 \text{ m/sec}$$

where, E_K : Kinetic energy of the exciton

M : effective mass of the exciton, $M = 3 m_e$ [17b]

p : momentum in K-space, $p = \hbar k$

Thus, an exciton with such a velocity (1.28×10^5 m/sec), would travel during its lifetime ($\tau \approx 10^{-9}$ sec) a distance d ($d = v \tau$).

$$d = v \tau = 1.28 \times 10^5 \text{ m/sec} \times 10^{-9} \text{ sec} = 128 \text{ } \mu\text{m}$$

Therefore, the above estimated distance justifies the diffusion length obtained experimentally. In view of the previous discussion and considering the evidence points 1 to 5, the following explanation seems to fit everything together: "hot IS excitons" with large kinetic energy are photogenerated in Cu_2O , live for 10^{-9} to 10^{-10} sec and manage to diffuse on the average $\approx 50 \text{ } \mu\text{m}$ at $T \leq 80 \text{ K}$, limited by the defect concentration in the type I oxide samples. At temperatures above 80 K, the faster thermalization of the excitons limits their diffusion length.

5.5.5. NATURAL GROWTH Cu_2O SINGLE CRYSTAL : (type II sample)

To further confirm the interpretation of the photovoltaic effect, the PV spectra of a high purity natural growth single crystal were studied, for which values of exciton lifetimes and diffusion coefficients are available [12]. Two thin semitransparent metallic contacts were evaporated on the two (110) opposed faces, of the 2 mm thick crystal shown in figure 5.11. One of the contacts was Ohmic (Au) and the second one was rectifying

(Cu). This way, we were able to take PV spectra both in the frontcell and backcell configurations in order to compare them and draw conclusions.

5. 5. 6. Cu₂O/Cu JUNCTION CHARACTERIZATION AND COMPARISON BETWEEN TYPE I AND TYPE II SAMPLES :

In order to characterize the single crystal Cu₂O/Cu junction and compare with the type I polycrystalline samples the open circuit voltage (V_{OC}) and the short circuit current density ($J_{SC} = I_{SC}/Area$) were measured (see section 3.7), as well as the barrier height between the Cu₂O single crystal and Cu, at room temperature. For that purpose the Bausch-Lomb monochromator was used, either modified to a white light source of 50 mW/cm² power for V_{OC} and J_{SC} measurements (see section 2.1.2), or with the near infrared grating of spectral range 700 - 1600 nm for barrier measurements. The results are :

TYPE I SAMPLES

BACKCELL geometry : V_{OC} ranged between 100 and 10 mV

J_{SC} " " 100 and 0.1 $\mu A/cm^2$

The thinner samples gave the larger V_{OC} and J_{SC} values.

TYPE II SAMPLE

FRONTCELL geometry : $V_{OC} = 190$ mV, $J_{SC} = 10 \mu A/cm^2$

BACKCELL geometry : $V_{OC} = 235$ mV, $J_{SC} = 5 \mu A/cm^2$

These values are very good given the oxide's 2 mm thickness.

Figure 5.24 presents the square root of the photocurrent as a function of the incident light energy, in order to obtain the barrier height between Cu and Cu₂O. The solid line corresponds to the Cu₂O single crystal illuminated in the backcell configuration, while the dashed lines correspond to a Au/Cu₂O/Cu backcell polycrystalline sample. Notice, that the polycrystalline type I sample seems to point at 2 barrier height values, one at 0.97 ± 0.02 eV and the second at 0.78 ± 0.02 eV, both values falling within the generally accepted range of 0.7 to 1.0 eV [26,45]. As for the single (type II) crystal one barrier height value of 0.70 ± 0.02 eV is obtained, in good agreement with the barrier height value of a single crystal Cu₂O/Cu junction measured by J.A. Assimos et al. [45]. The above results indicate that the Cu₂O single crystal sample (type II) is indeed of superior quality compared to type I samples given its thickness of 2mm, which is atleast 10 times larger than the thicker type I sample.

5.5.7. PV SPECTRA AS A FUNCTION OF TEMPERATURE :

The photovoltaic spectra were recorded only as a function of temperature, because measurements as a function of oxide thickness would destroy the rare single crystal. The photocurrent was measured across a 10^8 Ohm external resistor for temperatures below 100 K, while the sample resistance was higher

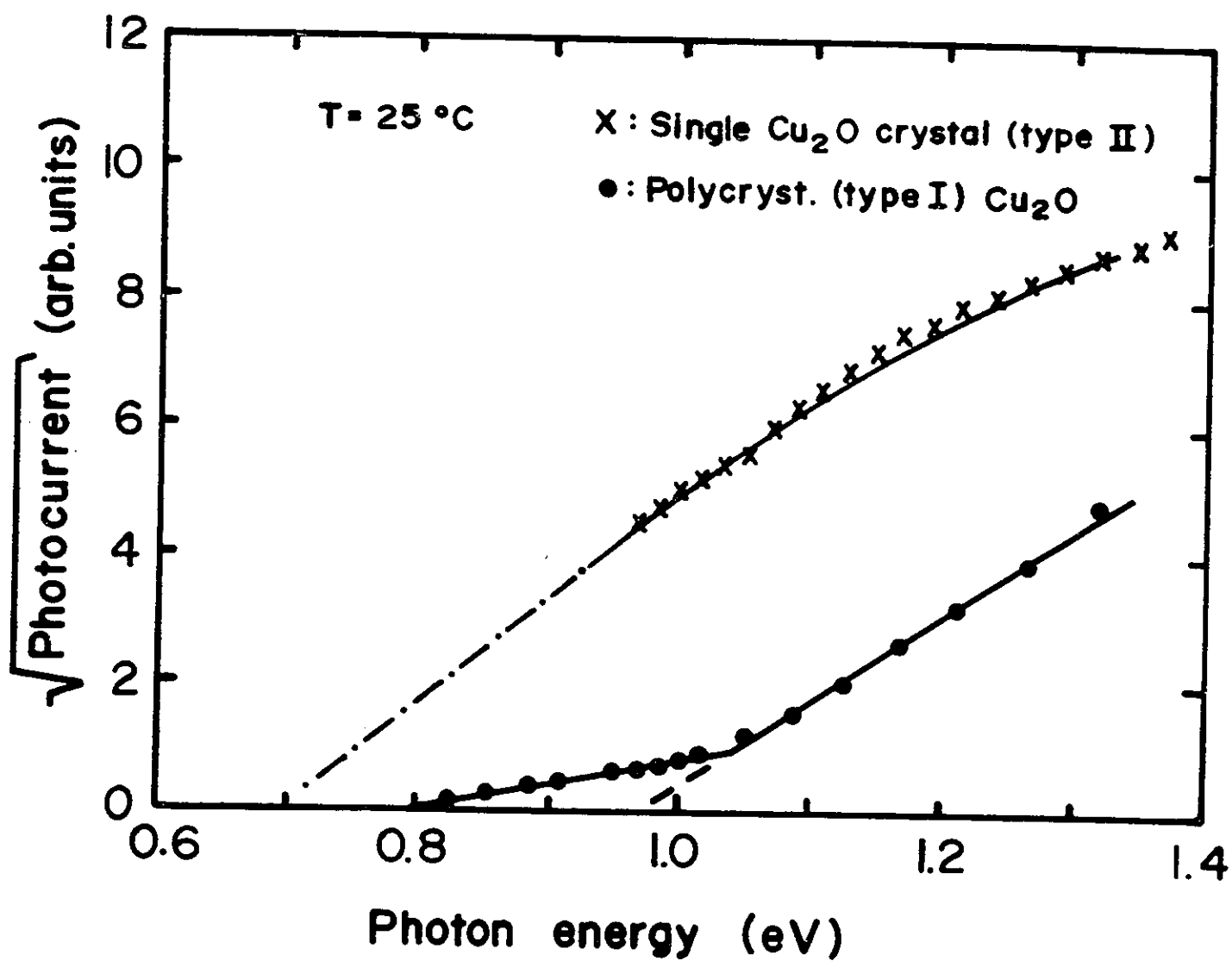


Figure 5.24: Barrier height determination at room temperature of :
 Dot-dashed line: Natural-growth Cu₂O/Cu junction.
 Solid line : Thermally grown Cu₂O/Cu junction.

than 10^{11} Ohms. At higher temperatures an appropriate resistor was used, for example at $T = 277$ K the current was measured across a 10^5 Ohm resistor, the sample resistance being larger than 10^7 Ohm, thus insuring that I_{pv} is always measured.

Figure 5.25 shows the PV spectra taken in the backcell geometry at the following temperatures : $T = 2.1 \pm 0.1$, 5.0 ± 0.1 , 10.6 ± 0.5 and 16 ± 1 K. It was observed that the photocurrent signal in the flat response spectral region between 575 and 605 nm increases with temperature. As for $\lambda < 572$ nm (that is for higher energies, starting from the bottom of the Cu_2O conduction band), there is a sharp increase in the photocurrent at all temperatures, up to 5 times the signal obtained in the 575 to 605 nm spectral region, suggesting perhaps that a large free carrier transport mechanism takes place.

In figure 5.26 PV spectra, again in the backcell geometry, higher temperature runs (at $T = 25 \pm 1$, 35 ± 1 , 50 ± 1 and 97 ± 1 K), are presented. Notice, that as the temperature is increased the shoulder below $\lambda = 573$ nm becomes less pronounced and the background response between 575 and 600 nm is reduced compared to the response for $\lambda > 600$ nm. This is an indication that as the temperature increases the exciton diffusion length decreases. The photoresponse in the long wavelength side of 600 nm follows the absorption coefficient, as is evident from the shape of the PV spectra, which in that range reproduce the phonon-assisted bands.

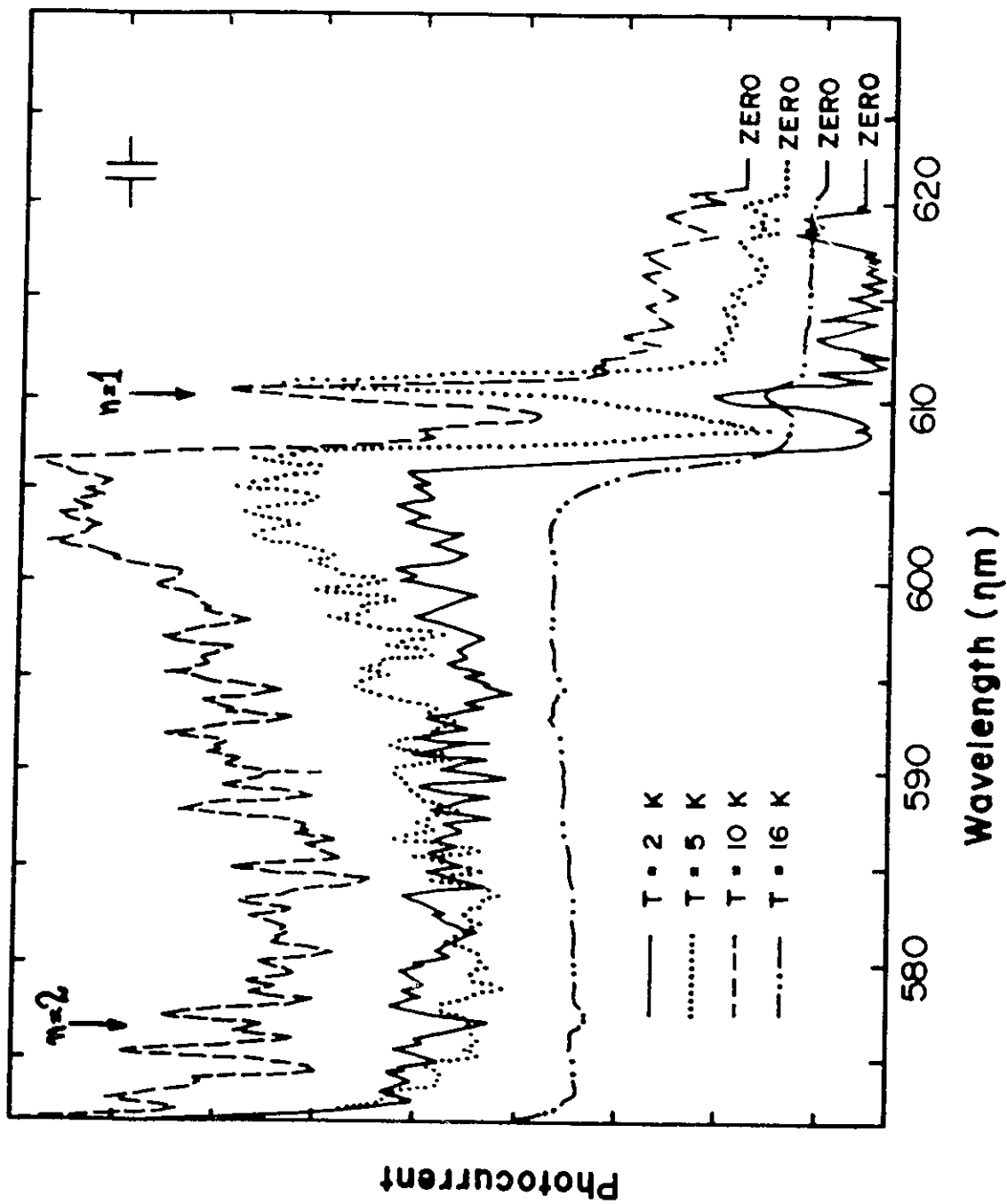


Figure 5.25: Photovoltaic spectra recorded on a 2 mm thick natural-growth Cu_2O single crystal, in the backcell geometry, at $T = 2, 5, 10$ and 16 K .

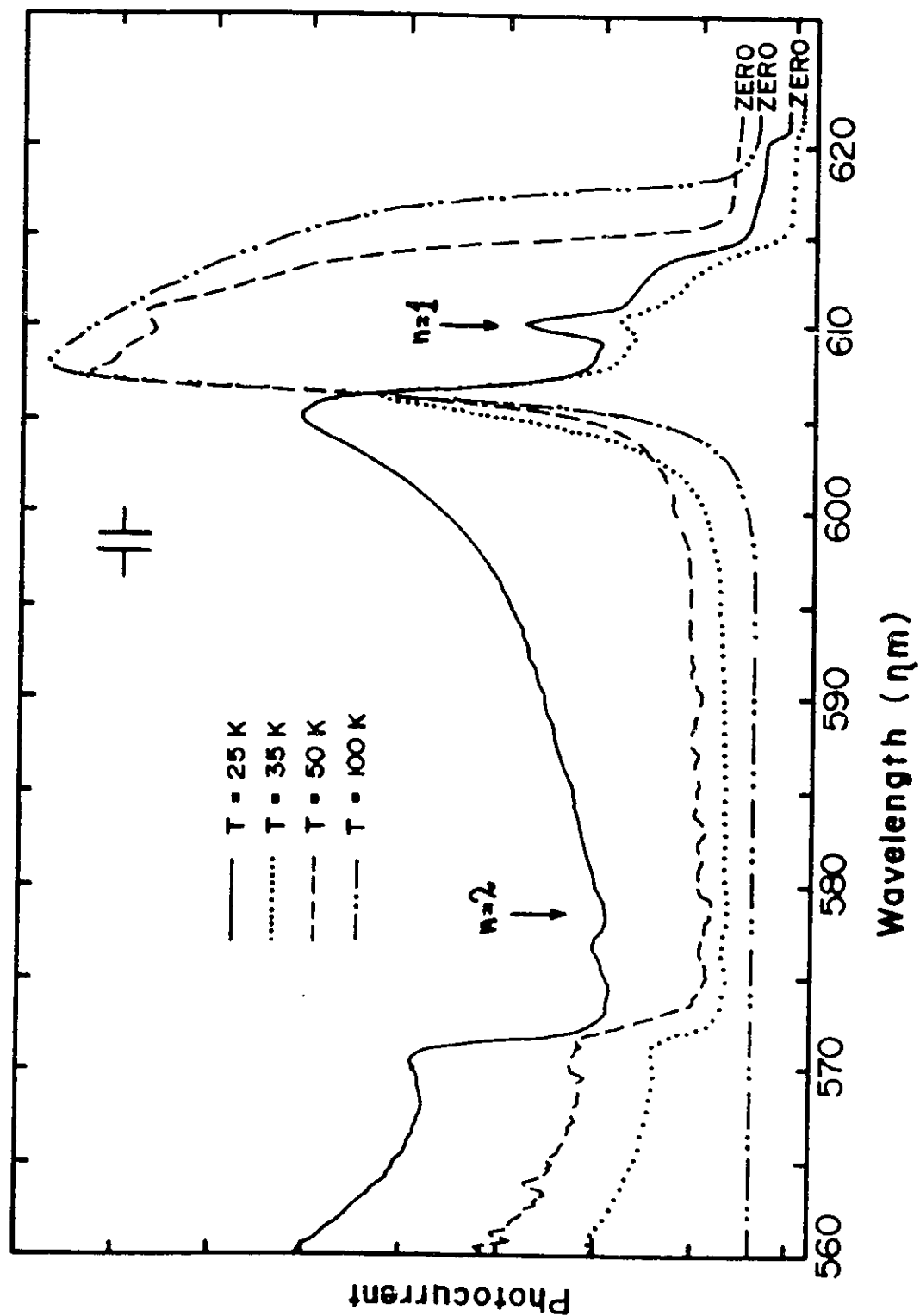


Figure 5.26: Photovoltaic spectra recorded on a 2 mm thick natural-growth Cu_2O single crystal, in the backcell geometry, at $T = 25, 35, 50$ and 100 K .

The flat response in the spectral region between 580 and 600 nm, for the PV spectra taken at $T = 2, 16, 35$ and 50 K further indicates that the photoresponse has no relation to the absorption length $1/\alpha$ (or absorption coefficient), which in fact is smaller than the diffusion length of the 1S exciton, in that spectral range. Notice that, at $T = 100$ K the photosignal for $\lambda < 600$ nm is practically zero, because the diffusion and absorption lengths are much smaller than the sample thickness. At that temperature, a photoresponse is only observed at wavelengths where $1/\alpha$ becomes comparable to the oxide thickness. As the temperature is decreased, L increases (see figure 5.26, $T = 50$ K) and a constant background starts rising for $\lambda < 600$ nm. At the same time the absorption coefficient (α) decreases too, thus $1/\alpha$ (absorption length) penetrates further within the oxide film (see figure 5.26, $T = 25$ K). Note also that, below $T = 20$ K the absorption coefficient does not change significantly. The shape of the PV spectrum taken at $T = 16$ K provides evidence (as the analysis will indicate in the next section) that the diffusion length (L) is larger than $1/\alpha$ for all wavelengths below $\lambda = 605$ nm. Since α does not change appreciably and L is expected to increase in this sample, the shape of the PV spectra taken at $T = 10$ and 5 K does not follow that of $T = 16$ K, as it would be expected. The response shape of the spectrum taken at $T = 16$ K reappears again at $T = 2$ K. One way to explain this discrepancy would be to consider that the temperature during the time that the spectrum

was taken, which is now designated to be 16 K, was in fact lower. But it is the author's opinion that the temperature was indeed 16 K. Therefore, the above discrepancy cannot be explained physically at this point.

5. 5. 8. DETERMINATION OF THE DIFFUSION LENGTH OF THE 1S YELLOW EXCITON

In order to get an idea of the exciton diffusion lengths involved in this sample, let us look in details at a few representative spectra at $T = 72$ K and $T = 2$ K, shown in figure 5.27. Consider first the solid line spectrum at $T = 72$ K, taken in the backcell geometry. Although its shape is different from those of synthetic (type I) samples of figure 5.13a, it reflects the same physical situation, if one takes into account the much larger oxide thickness $t = 2$ mm as compared to the oxide thickness of the samples presented in figure 5.13a. Only those 1S excitons created deep into the bulk by light with wavelength at the edge of the $n=1$ exciton phonon-assisted absorption continuum contribute to the signal, giving rise to a photocurrent in a limited spectral range. By contrast, the photovoltaic spectrum obtained in the front cell geometry displays the wide ranged behaviour of a very thin sample, as expected (see dotted line spectrum in figure 5.27a). The dashed line curve in figure 5.27a was computer generated using equation (5.16), where w was taken less than $1 \mu\text{m}$. The value of $L = 50 \mu\text{m}$ introduced into equation (5.16) to fit the spectrum, taken in the backcell geometry, is in good agreement with the calculated value

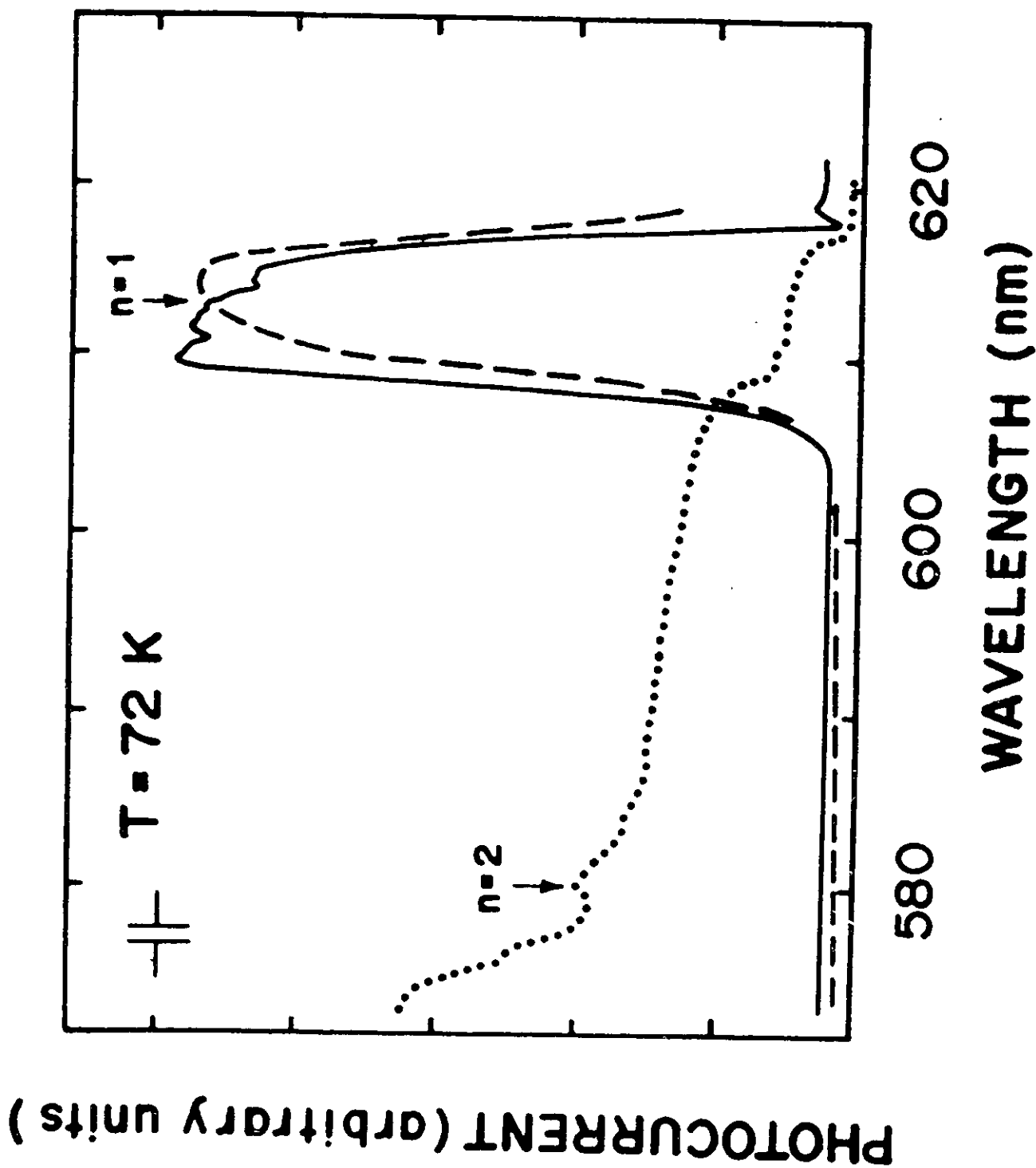


Figure 5.27 a) Photovoltaic spectra recorded on a 2 mm thick natural-growth Cu_2O single crystal. At $T=72\text{ K}$, solid line : experimental spectrum in the backcell geometry, dashed line : computer generated curve for backcell geometry with L taken $50\text{ }\mu\text{m}$ and dot-dashed line : experimentally obtained spectrum in the frontcell geometry.

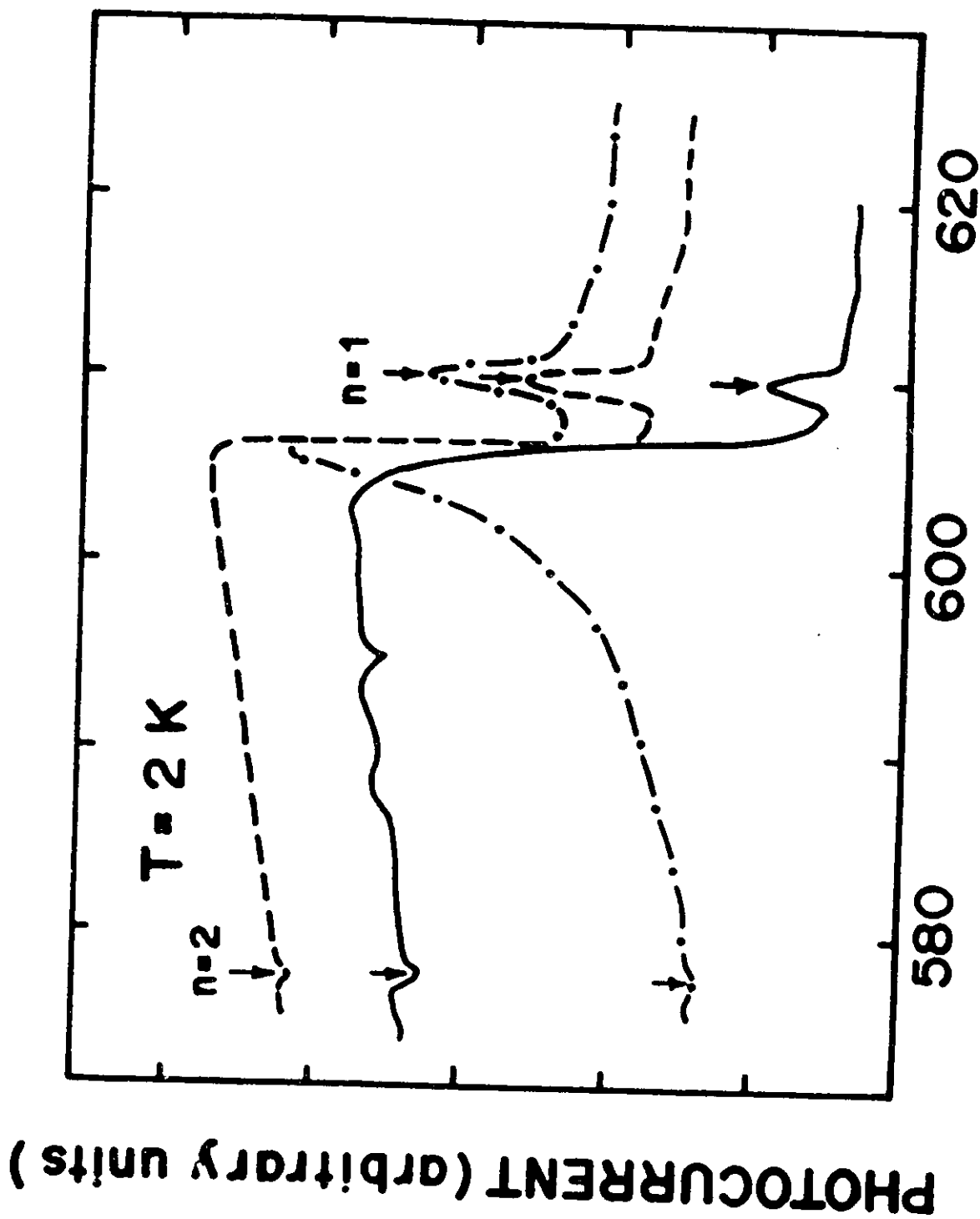


Figure 5.27 b) Photovoltaic spectra on a 2 mm thick natural-growth Cu_2O single crystal. At $T = 2 \text{ K}$, spectra recorded in the backcell geometry, solid line : experimental curve, dashed line and dot-dashed line computer generated curves with $L = 1500 \mu\text{m}$ and $L = 500 \mu\text{m}$, respectively.

using the relation $L = (\tau D)^{1/2}$, where $\tau = 1.7 \mu\text{sec}$ is the exciton lifetime at $T = 70 \text{ K}$ [1] and $D = 20 \text{ cm}^2/\text{sec}$ the diffusion coefficient obtained from D.P. Trauernicht et al. [2]. The absorption coefficient values used for the above fit were taken from the absorption spectrum of I. Pastrnyak [21] at $T = 77 \text{ K}$ (see figure 5.15), as it was done for the polycrystalline (type I) samples (see section 5.5.1 and figure 5.13b).

The photovoltaic spectra recorded below $T = 70 \text{ K}$ differ markedly from those of the polycrystalline samples, even after appropriate scaling for the sample thickness t . These spectra can be fitted by introducing exciton diffusion lengths which increase rapidly with decreasing temperature and which reach values comparable to the sample thickness at $T = 2 \text{ K}$. In figure 5.27b all spectra are taken in the backcell geometry. The solid line presents a PV spectrum at $T = 2 \text{ K}$, while the dashed and dot-dashed lines show computer generated curves obtained using equation (5.15). The absorption coefficient values for both the dashed and dot-dashed line curves were taken from the absorption spectrum of S. Nikitine et al. [22] (see figure 5.14), while the values used for the diffusion length were $L = 1500 \mu\text{m}$ and $L = 500 \mu\text{m}$ respectively. In figure 5.28, the fitted diffusion length values {using equation (5.15)} to the experimental spectra, shown in figures 5.25 and 5.26, are presented as a function of the temperature the experimental spectrum was taken at. The absorption coefficient values used for the PV spectra fits, between $T = 2$ and 35 K , were those reported by S. Nikitine et al. at $T = 4.2 \text{ K}$ [22].

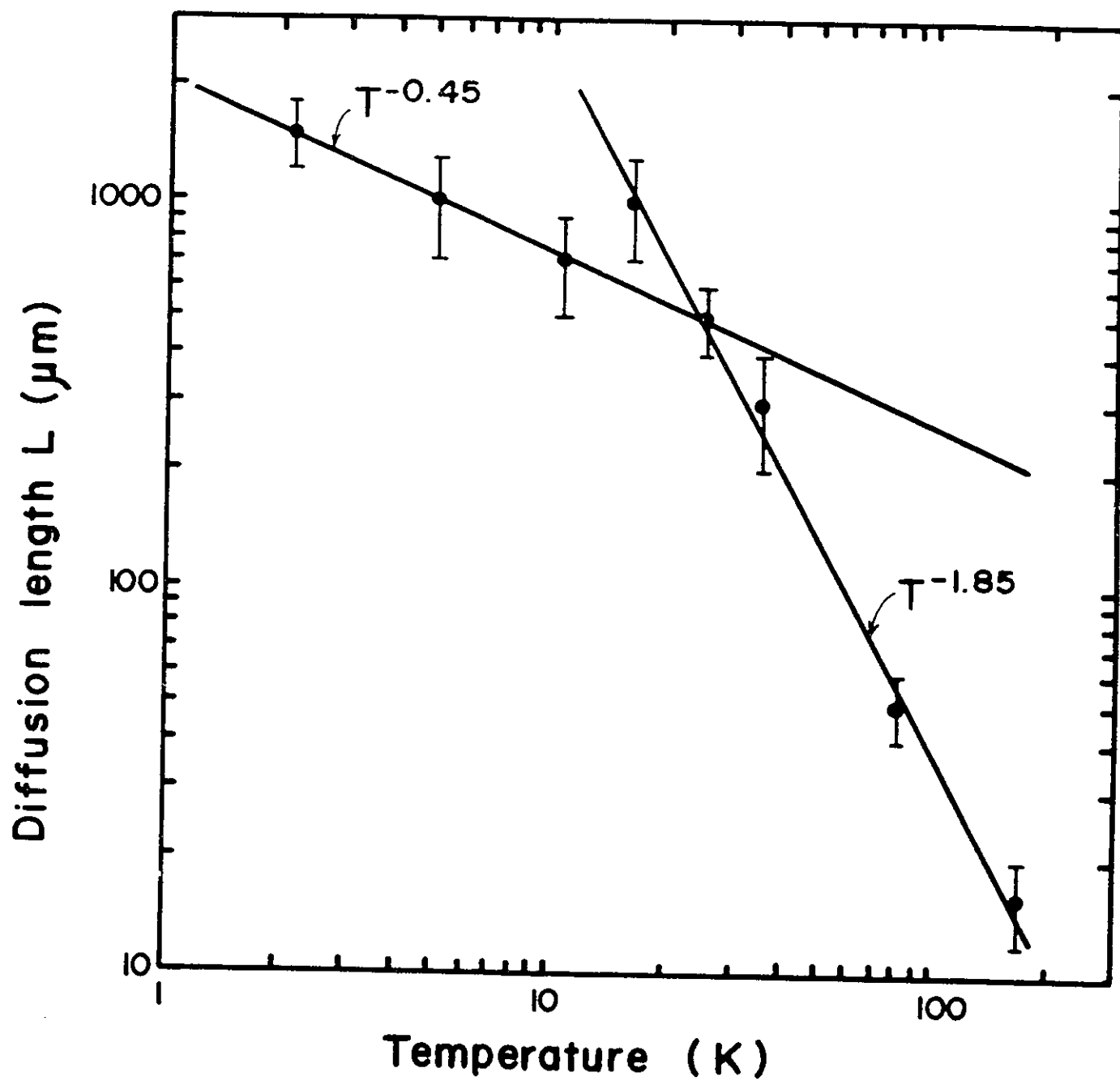


Figure 5.28: Diffusion length of the 1S yellow exciton versus sample temperature.

At higher temperatures the shape of the computer generated PV spectra was insensitive to the diffusion length value, when the latter was taken to be less than 200 μm . This can be understood if one considers the 2 mm thickness of the crystal and the absorption profile of Cu_2O . In figure 28, it was possible to use the diffusion length values of type I samples (see section 5.1.1 and table 2) at $T = 80$ and 170 K, because at those temperatures the diffusion length is not limited by the impurity concentration. When the fitted diffusion lengths were plotted in a log-log graph, two slopes were distinguished as it has been reported for the diffusion coefficient D (for paraexcitons) in a similar sample [2]. Although the trend (in reference [2]) is the same as the one found here, the diffusion length rate of change does not agree with the theory. In reference [2] the steep increase of D with temperature was explained in terms of exciton diffusion coupled with LA phonon scattering down to about 6 K. At sufficiently low temperatures ($T < 6$ K), the exciton thermal velocity becomes comparable or even smaller than the sound velocity, thereby effectively decoupling excitons from the lattice. Such a behaviour, however, is only expected to occur in sufficiently pure crystals like the natural growth single crystal discussed in this section, for which scattering by defects seems to be negligible down to 1.2 K (the lowest temperature tried by D.P. Trauernicht et al. [2]). This is apparently not the case for the polycrystalline thermally grown (type I) samples discussed in sections 5.5.1 to 5.5.4. The impurity concentration in the type I samples seems to be so large, that the transition from phonon scattering to

impurity dominated scattering occurs at about 80 K, thus limiting the recombination lifetime of the excitons and in turn their diffusion length at lower temperatures. A repeat of the experimental spectra and improvement of the PV spectra fits, using more accurate absorption coefficient values, would be required in order to be more confident about the results presented in figure 28.

In conclusion, the experimental results were interpreted assuming exciton migration and field induced dissociation at the metal/semiconductor interface. The photocurrent variation at low temperatures in Cu_2O samples of different thicknesses and the photovoltaic spectrum of a known thickness Cu_2O sample were used to determine exciton diffusion lengths. Therefore, the above type of measurements may possibly provide a simple method for detecting exciton diffusion lengths in other materials where $L > 1/\alpha$.

5. 6. CONCLUSION :

In this chapter the photovoltaic effect of the $\text{Cu}_2\text{O}/\text{Cu}$ junction was investigated at low temperatures in two types of samples. First polycrystalline Cu_2O films were thermally grown on Cu and the photovoltaic spectra in the spectral range of the yellow exciton series were recorded. The photocurrent variation as a function of sample thickness yielded the diffusion length of the $n=1$ yellow exciton with the help of an equation for the photogenerated current that was developed from the continuity equation. This type of measurement seems to provide a simple new method for the study of exciton migration. This method can prove especially valuable if the lowest lying excitonic states are optically inactive, preventing the use of techniques based on luminescence detection. Second a high purity natural growth Cu_2O single crystal was used to take photovoltaic spectra at various temperatures down to 2 K. The experimental results for both types of samples were interpreted assuming exciton migration and field-induced dissociation at the semiconductor/metal interface. The diffusion length for the polycrystalline thermally grown samples (type I) saturated around 80 K, due to the large defect concentration, while that of the natural growth single crystal (type II sample) kept increasing rapidly as the temperature was decreased down to 2 K. It would be expected, that annealing of the thermally grown type I samples would improve the crystalline structure of Cu_2O and in turn the diffusion length of excitons would saturate at a lower temperature.

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CHAPTER 6

GENERAL CONCLUSION

The purpose of this work was to study some electro-optical properties of Ag_2O , Cu_2O and their mixed oxide films, using the photovoltaic effect at the metal/oxide semiconductor junction. The micrometer thick oxide films were grown anodically on Ag and Ag-Cu alloys and thermally on Cu. The photovoltaic effect has many advantages over absorption, photoconductivity and photoluminescence techniques that could be used for certain of the experiments performed here. These advantages are : a) the samples do not have to be self supporting : in this case they are grown on metals ; therefore, we have increased mechanical stability ; b) relatively easily grown micrometer thick films can be used for such studies, thus samples of large dimensions are not necessary, and c) the photovoltaic effect across the metal/oxide semiconductor junction acts as a detector, eliminating the need for detectors in the spectral region of interest.

Ag_2O and Cu_2O are the only two compounds that have the cuprite (M_2O) crystalline structure, both exhibit p-type conductivity and their energy gaps are approximately 1.4 and 2.0 eV respectively at room temperature.

The preparation and photovoltaic properties, at room temperature, of anodically grown Ag_2O were presented and discussed

in chapter 3. This study proved that, although the anodic oxidation method is simple in principle, the large number of oxidation variables make it complex in practice. The polycrystalline structure of the grown oxide films, resulted in a large number of grain boundaries, that seemed to reduce the free carrier recombination lifetime making for a poor Ag/Ag₂O photovoltaic cell. The barrier height of Ag₂O with various metals (Ag, Pt, Al) was measured and it was found to be pinned around 0.9 eV above the valence band. The oxide films had poor thermal and electrical stability. The film quality would have to be improved in order to study fundamental properties of Ag₂O with PV at low temperatures.

Since both Ag₂O and Cu₂O have the same crystalline structure, the possibility of growing Ag-Cu mixed oxides by anodic oxidation was examined. Attempts so far to thermally grow mixed oxides, with Ag concentration in the oxide of more than 2% atomic, have failed. The oxide films grown here were characterized by their energy gap value, obtained from PV spectra, and by X-ray powder diffraction analysis. It was found that the mixed oxides were unstable in the presence of other oxide phases and Cu. Relatively more stable mixed oxides were grown from solutions S2 and S3 (see section 4.1.2), provided that the oxidized metallic alloy was single phase.

Finally, the photovoltaic spectra of the Cu₂O/Cu junction were taken at low temperatures for two types of samples : a) thermally grown Cu₂O films on Cu and b) a natural growth Cu₂O single crystal onto which Cu and Au were evaporated in order to

form rectifying and Ohmic contacts, respectively. The purpose here was to investigate the role of excitons in the photovoltaic effect and measure the diffusion length of excitons, if possible, with the help of a model developed to simulate the variation of the photocurrent response as a function of the oxide sample thickness. The results suggested, that in the yellow exciton series spectral region, excitons diffuse over micrometer long distances and predominantly dissociate into electron-hole pairs at the $\text{Cu}_2\text{O}/\text{Cu}$ interface region (referred to here as the "dipole layer", see section 5.2.4). Although, the excitonic diffusion length in the thermally grown type I samples saturates at a value of $\approx 50 \mu\text{m}$ as the temperature is decreased, the diffusion length of excitons in the natural growth Cu_2O single crystal increases rapidly. This is due to the very low impurity and defect concentration in the single crystal of Cu_2O as compared to the thermally grown polycrystalline Cu_2O samples.

BIOGRAPHICAL NOTE

Efstathios TSELEPIS was born on March 24, 1958 in Athens, Hellas. He graduated from Lycée Leonin High School in 1976. In 1977 he was admitted to KATTE. (Vocational College in Athens) in Field Surveying. In 1979 he came to Canada. In 1982, obtained his Bachelor of Science in Physics from Ottawa University. He then chose to remain in the same University and work in solid state physics, with Dr. E. Fortin, towards a doctoral degree.

During the course of these studies he had the opportunity to be the co-author of the following publications :

- 1) E. Tselepis, E. Fortin and A. Mysyrowicz "Exciton-mediated Photovoltaic effect in $\text{Cu}_2\text{O}/\text{Cu}$ ", to appear in Physical Review Letters, vol 59, Nov. 2nd 1987.
- 2) E. Tselepis and E. Fortin "Photovoltaic study of anodically grown oxide films on Ag-Cu alloys", accepted (July 87) in Thin Solid Films.
- 3) E. Fortin and E. Tselepis "Exciton diffusion in thin Cu_2O films" accepted (June 87) in Thin Solid Films, also to appear at the 7th International conference of thin films, to take place at New Delhi, India, in December 1987.
- 4) E. Tselepis and E. Fortin "Preparation and photovoltaic properties of anodically grown Ag_2O films", Journal of Materials Science, 21, 985, (1986).

Papers related to the above work were presented at the following conferences :

- _ 7th International conference of thin films,
New Delhi, India, December 1987.
- _ C.A.P conference, Toronto Univ., June 1987.
- _ A.C.F.A.S conference, Ottawa Univ., May 1987.
- _ C.A.P conference, Sherbrooke Univ., June 1984.
- _ Ottawa-Carleton Graduate student Symposium,
Ottawa Univ., March 1987. (oral presentation)
- _ A.P.S conference, New Orleans, March 1988,
(to be presented).