THE GROWTH AND CHARACTERIZATION OF CdS THINFILM BY SOLUTION DEPOSITION TECHNIQUE

BY

MUMA, PETER NSUHATE NGOU
(PG/M.SC/89/8438).

DEPARTMENT OF PHYSICS AND ASTRONOMY
UNIVERSITY OF NIGERIA
NSUKKA

JUNE, 1991

THE GROWTH AND CHARACTERIZATION OF CdS THIN FILM BY SOLUTION DEPOSITION TECHNIQUE

(PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE MASTER OF SCIENCE DEGREE IN PHYSICS).

BY

MUMA, PETER NSUHATE NGOU
(PG/M.SC/89/8438)

SUPERVISOR: DR. C,E. OKEKE

CERTIFICATION

MUMA, PETER NSUHATE NGOU, a Postgraduate Student in the Department of Physics and Astronomy and with the Registration Number PG/M.Sc./89/8438 has satisfactoryly completed the requirements for course and Research-work for the Degree of Master of Science in Experimental solid state physics.

The work embodied in this project report is original and has not been submitted in part or whole for any other diploma or degree of this or any other University.

DR. P.N. OKEKE
Associate Professor of Physics &
Head of Department

DR. C.E. OKEKE
Associate Professor of
Physics, Deputy Dean of
of The Faculty of Physical
Sciences (Supervisor).

DEDICATION

TO ALL PERSONS OF GOODWILL

ACKNOWLEDGEMENT

I wish to appreciate the humane and cordial relationship that has existed during this period of my work, between my supervisor Dr. C.E. OKEKE and myself. In particular, I am grateful for the fatherly approach he has used to see me through.

I am also indepted to my Head of Department DR. P.N. Okeke for his concern and ever ready solutions towards any problem during my stay here.

My most profound gratitude to Matron Ndiyo, Prof. and Mrs. Chimere Ikoku, who have given me the chance of a life time by their love and assistance during my most trying moments.

I cannot thank Mr. Albert N. Ambe and Sister Marrianne Nkwenti enough for the sacrifices (even during this hard times). May I be able to emulate your shinning example.

I am grateful to my darling Agnes Ansa, my daughter Nyuite Essienawann Nsuhate, Mama Therisa Ambe, my mothers,Justice Mbanefo , Mrs. Arit Edem, Pah Chou, my brothers and sisters Mr. I.I. Adie, Langason Bi-Fussina and friends, for the love; the sacrifices, the patience, the encouragement, the prayers, and the concern, during this period especially and always. May the Lord God in his abundant mercies guard and guide you all, as always.

ABSTRACT

We have successfully grown cadmium II sulphide (cdS) thin film on glass substrate, using Tioethanolamine (TEA) as complexing agent, cadmium acetate ($Cd(CH_3COO)_2 \cdot 2H_2O$), Ammonia solution ($NH_3$), and Thiourea ($SC(NH_2)_2$) at a pH of 11.

We have shown that CdS cannot grow in acid medium. We have also successfully characterized CdS thin film with a view of optimizing the growth parameters.

Absorbance measurements revealed a CdS bandgap of 2.43eV. Thickness of the films were measured and an optimum thickness of 15.6×10^{-7}m was obtained after 6 hours of deposition time, using 5ml of 7.45M TEA and 10ml 1M $Cd(CH_3COO)_2 \cdot 2H_2O$, 10ml 1M $SC(NH_2)_2$.

LIST OF TABLES

TABLE OF CONTENTS

TABLE OF CONTENTS CONTD.

CHAPTER ONE

INTRODUCTION

The availability and utilization of energy is the one physical thing that influences our living style most, since energy is the key to industrial development, for the promotion of economic and social well-being of the populace. The energy industry is charged of contrivance, while it professes innocence and the bewildered public is made to pay higher and higher prices for energy without understanding the incredibly complex energy picture. This apart, we are faced with the reality of a fast running out energy resources and the handling of the by-products, when energy is generated.

Whether or not we have enough energy to operate our technological society will involve important decisions and trade-offs by all the elements of our society.

1.1 Why Solar Energy:?

The rate of energy usage keeps escalating due to world population growth and rising material standard of living. That of fossil fuels is relatively alarming since the turn of the century.[1] One may argue that man has the right to develop and use natural resources, but the present generation has no right to use wastefully these resources. Conservation therefore is everybody's watchword.

Man's search for ulternative sources to meet ever

consideration the rapid depletion of fossil-fuel resources. There are many alternatives, but nuclear fusion and solar energy have the brightest long range promises to meet this continual increasing demand.[2]

Nuclear fussion intails putting light atoms together to produce power. Here, problems associated with radiation are minimal and the earth has abundant supply of required major fuels, denterium and tritium. Hence nuclear fussion can be considered the utimate to man's energy problem. Unfortunately, before the turn of the next century man may not be able to modify the world energy picture from this perspective even with recent progress in controlled fusion reactions.[3] Hence, man has turned to the elements. As far as solar energy conversion is concerned, the source is inexhaustable, the process is pollusion free and the technology is available.[4] Man then is faced with the simple problem of harnessing and storing this energy economically to make its usage widespread.

1.2 Prospects Of Solar Energy:

The sun is a hot sphere, ineffect, a nuclear reactor in continuous fusion, combining every four hydrogen nuclei to give one helium nucleus and converting the unbalanced mass to give energy (solar energy). The outer layer of the sun - (the photosphere) emits a continuous spectrum of radiation.[5]

If we consider the sun as a blackbody and a perfect radiator at 5762K, the radiation emitted by the surface of the sun (E_s) is equal to the product of the stefan-Boltzmann

constant(6), the fourth power of the absolute surface temperature (T_s^4) and the surface area (d_s^2).

$$E_s = 6\ d_s^2 T_s^4\ w \qquad - 1.1$$

considering that the earth revolves around the sun with a mean radius R, the surface area of the sphere negotiated is 4 R^2. The irradiance (radiation flux on a unit area of the spherical surface) is given by,

$$G = \frac{6 d_s^2 T_s^4}{4\ R^2}\ wm^{-2} \qquad - 1.2$$

Measurements by National Aeronautics and space Administration give a value of 1352 Wm^{-2} for solar constants (G).[6] This value undergoes atmospherice attenuation before reaching the earth's surface. As the solar spectrum travels through the earth atmosphere, the ionsphere absorbs short wavelengths of the range of x-rays and gamma rays at extremely high attitude. Ozone layer absorbs waves of longer wavelengths of ultraviolet range at 15 to 40Km above the earth's surface. Bonds of infrared range are absorbed by water vapour and carbondioxide.

Sine extraterestial radiation is low while water and carbondioxide absorption is strong, little solar energy reaches the earth's surface. Hence, irradiation on the earth's surface is made up of mainly energies in the wavelength range between 0.29 and 2.5 um. Furthermore as the transmitted portion passes through the atmosphere it is intercepted and scattered in all directions by dry air, water vapour and dust particles. The degree of attenuation is subject to the length of the path and

the characteristics of the medium traversed.

This not withstanding, the amount of solar energy reaching the earth's surface is evident that it is by far our most available energy source. It could make a major impact on our energy economy, by providing space heating, space cooling, and hot water for buildings, producing clean fuels and generating electricity. Let us take the example of the United States of America. In 1976, 18% of 74×10^{15} Btu of energy used was for heating. If 10% of this amount was from the sun, an equivalent of 220 million barrels of oil would have been realized. That is a savings of over one billion dollars would have been realized. Since about 34 billion-trillion Btu. of solar energy falls on American rooftops annually, then the prospects of solar energy are very much there.[7] Also, the developments in solar cell technology is a milestone in solving man's energy crisis.

Solar cells have found greatest application in space exploration activities, where reliability and weight to mass ratio are a major criteria. On earth, there are many alternatives, hence, cost per unit energy ratio is a factor to be considered for solar cells to compete favourably with other alternatives.

A modern power station is of 1000 Mw outpu. For solar cells to generate same, it requires about $40km^2$ of cells which will cover say $80km^2$ of land. Though there are vast land masses not in use that can be useful, the feasibility of reducing cost counts more.[8]

Some of the following methods could aid reduction in cost:

Developing methods of producing cheaper solar cells, like replacing expensive stages in production with cheaper ones, lapping and polishing can be replaced by selective etching in sodium hydroxide solution, screen printing can replace photo-engraving for defining the front electrode. Cells are embeded in silicone elastomer behind either glass or polycarbonate window. The use of cells in conjunction with cheap optical concentrators such as fresnel lenses. The thin film approach. Here, the basic device consists of a thin film of direct gap semiconductor (a few microns) deposited onto a cheap substrate designed for support and ohmic contact. Here we avoid the use of expensive nergy intensive crystal growing processes and require only a small amount of semiconductor leading to an inexpensive solar cell.[9] The availability of cheap materials, either directly through the use of high metallurgical grade products or through some improvement of the ribbon technology may increase the costs of the device itself. Devices with built-in storage capability, if provided at significantly lower costs would open up new markets and may become the basis of extensive technology development.[10]

Some very extensive systems do exist for the utilization of solar energy. Their development and expansion might provide some of the best ways of increasing the contribution of solar energy to the world energy balance. For example, hydroelectric

power, which derives ultimately from solar energy is much in use. Also natural or cultivated photosynthesis provides the great bulk of biomass on the surface of the earth which can be increased in a planned way and would provide additional energy sources.

1.3 Photovoltaics:

A photovoltaic cell, commonly called a solar cell converts electromagnetic (solar) energy directly to electrical energy.[11] No turbines to contend with and no moving parts of any kind.

With the discovery of selenium in 1817 and the preparation of elemental silicon by Berzelius, followed by, the discovery of photoconductivity in selenium in 1873 by Willoughby Smith, this spawned a flurry of activities. These included the discovery of spectral sensitivity of selenium photoconductors, the observation of photovoltaic effect in a solid-state selenium and latter the first selenium photovoltaic cell was described by Fritts. These discoveries laid the foundation for further development of a photovoltaic device technology.

The development of the silicon technology led to the preparation of a single-crystal silicon photovoltaic device. Fabrication processes and further developments and improvements led to their adaptation for better use in space systems until 1974 that terrestial considerations came into play.[12]

Photovoltaic systems ment to provide large amounts of electrical power for terrestial consumption are grouped

frequently into three categories:

1. Small-to-medium-size systems dedicated to individual loads, often with converters attached to or incoporated into a building structure.
2. Ground-based central systems with large collectors serving either a distribution system or large consumers.
3. Space central system, with power transmission to central ground stations.[13]

1.4 The Difference Between Conductors, Semiconductors and Insulators.

Elemental semiconductors are materials with relatively small energy gaps between their valence and conduction bands and with their Fermi levels located somewhere in the gap. The electrical resistivities of semiconductor materials lie between those of metallic conductors and good insulators. The resistivity of metallic conductors is of the order of 10^{-8}RM whereas semiconductor resistivity usually lies in the range of 10^{-2} to 10^{2} m.

The resistance of a semiconductor usually decreases as the temperature rises whereas most metallic conductors would show an increase in resistance. Silicon is the most widely used semiconductor.[14] The crystalline structure of silicon lattice is such that each atom is sorrounded by four neighbours and each of these atoms may be considered to have four electrons in its outter orbital and to share four more, one from each of its neighbours. These eight electrons form covalent bonds between

each pair of electrons appearing as four pairs around the nucleus. At a temperature of $0^{o}K$ all the electrons are attached to their respective nuclei and are not free to take part in the conduction of current. At room temperatures, some of the electrons are able to acquire sufficient energy to be free to move in the lattice. Free electrons are those that have acquired sufficient energy to be able to have a net movement in the lattice. When an electron leaves its position in the lattice, a valancy exists which is called a "hole".

Each time an electron is freed, a hole is formed. This process is called electron-hole generation. The number of electron-hole generated in a particle crystal is a function of temperature and at every given temperature depends on the width of the band gap. Electron-hole pairs are not very desirable in semiconductors.[15] Hence, semiconductors with smaller band gaps, produce more electron-holes and are less desirable than those with larger band gaps. Electron-hole pairs are responsible for uncontrolled, temperature dependent current flow in devices made of such semiconductors.

Let E_V = highest energy in the valence band; E_C = Lowest energy in the conduction band. Then the gap width is given by $E_g = E_C - E_V$, and $E_V < E_F < E_C$. By a relatively small E_g, which may be many times larger than KT, the gap is still small enough that electrons may be found in conduction band states with nonzero probability.[16]

Considering Fig 1. It shows an energy diagram for a semiconductor with E_F (Femi energy) in the middle of the gap and the occupation probability (P_{FD}) at a finite temperature. The tail of P_{FD} is small but not zero at energies below E_V .

In the low temperature limit, all allowed states below E_F would be occupied, and those above E_F would be empty. In elemental semiconductors E_F lies always above the top of the valence band but below the bottom of the conduction band. The E_F in insulators also lies in the gap; however, Eg for insulators is much larger than for semiconductors. Therefore, the probability that an electron would vacate a valence state of the insulator and occupy a conduction state is remote.[17] Diamond for example, has a band gap of 5.4eV, while silicon and Germanium, semiconductors with diamondlike crystalline structure have gaps of 1.11 and 0.67eV respectively at room temperature. At room temperature electrons in the conduction and valence band of both semiconductors and insulators can conduct electricity since these bands are either partially filled or partially empty.

The probability for semiconductors is greater, and electrons occupy the conduction band, leaving vacancies in the valence band. Carrier densities in semiconductors depend on Eg and are sensitive to the temperature through P_{FD} . In metals E_F lies in the conduction band so that there are many available carriers. The range of typical values of conductivity in

metals, semiconductors and insulators is due primarily to the range of charge densities in the respective materials.

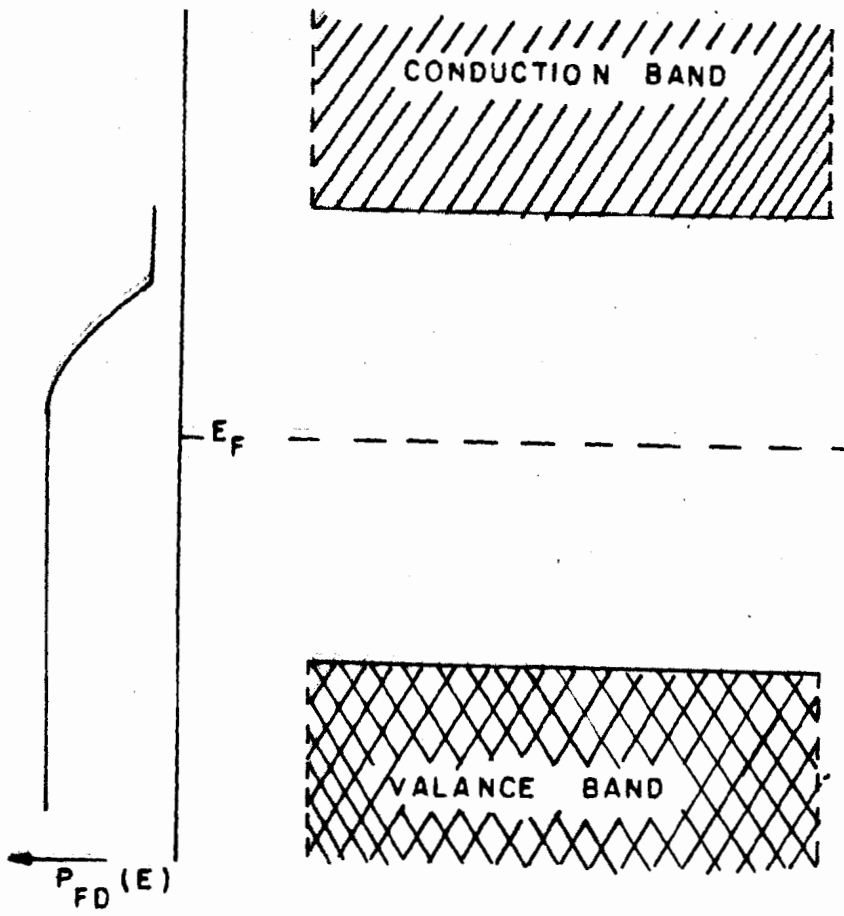


Fig. 1 Energy diagram of an intrinsic semiconductor with $P_{FD}(E)$ (18)

1.5 Selective Surfaces:

In the utilization of glazings in photothermal systems consideration is given to maximizing efficiency. Here, care is taken to make sure that the surface of the absorber - converter has a good absorptance in the solar region and low reflectance (poor emittance) in the thermal region. Such a glazing is said to be selective. This implies that its optical properties are wavelength dependent, varying over a broad spectrum from 0.3 - 20um.[19]

When we talk of selective surfaces, reference is being made to obtaining desired effects by the use of the seperation of incomming solar radiation from the thermal infra red radiation.

Practical selective surfaces ment for solar collectors are expected to produce components that minimize re-radiation losses, thereby increasing thermal efficiency. Heat loss from absorber-converters and glazings can be obtained if they have the following optical characteristics; stability properties; and energy configurations : Optical engineering properties are; reflectance, absorptance, transmittance and emittance. They characterize the interaction of a particular material with incident photon energy.

At the interface of two media, reflection of some of the incident energy occurs. Fresnel's formula gives us the ratio of the intensity of the reflected beam to the incident, where the reflectivity is obtained for the interface that is

polarized with the electric field vector perpendicular and parallel to the plane of the incident beam.

$$R_{11} = \frac{\tan^2(\theta_1-\theta_2)}{\tan^2(\theta_1+\theta_2)} \qquad - 1.3$$

$$R_1 = \frac{\sin^2(\theta_1-\theta_2)}{\sin^2(\theta_1+\theta_2)} \qquad - 1.4$$

The unreflected incident energy at the interface that is not reflected enters the glazing resulting into partial absorption as it penetrates the media. This absorption is given by Bears (Bouger's) law.

$$\frac{dI}{dz} = - KI \qquad - 1.5$$

where I = beam intensity

Z = distance measured in the intensity of the Beam

K = absorption coefficient.[20]

The presence of small amounts of $F_{e_2}\ O_3$ is primarily responsible for solar radiation absorption. The remaining fraction of unabsorbed energy is transmitted (passes through) to the absorber-converter plates of the collector where it may be absorbed, reflected or both, back, to the cover plate.

Materials capable of transmitting radiant energy (diathermanous) their transmission characteristics depend on the wavelength of the incident ratiation. Examples of diathermanous materials are glass and plastics.

Glass is mostly used as window materials in buildings and cover materials in solar collectors. Window glass of the sodalime-silica type usually has 0.15% $F_{e_2}O_3$. In the

infra red spectrum a low % percentage of Fe_2O_3 (0.03-0.07%) is required for higher transmittance. At low transmittance between 0.03 - 0.05% transmittance is more than 90% in the near ultra violet region. It remains high and uniform in the visible region and into the infra red region. At 2.7 m it drops sharply and is opaque at about 4.8 um. Those that contain about 0.50% Fe_2O_3 and are heat absorbing (greenish in the side) in the visible and near infrared regions decrease sharply. Transmittance diminishes especially in the infra red regions with increase thickness. If the iron content is increased so is the effect of tickness.

The selectivity "figure" of coatings at the temperatures at which they are used are measured due to temperature dependence of optical properties of selective surfaces. Temperature dependence results from two main factors. The scattering of electrons due to thermally induced disorder (Optical absorption with phonon creation and absorption) and changes in energy levels caused by disorder. Consideration is also given to pupulation change in conduction and valence bands with temperature in semiconductors.

Selective surfaces should have stable optical and physical properties under long term operation at high temperatures, repeated thermal cycling, short term overheating resulting to failure to extract energy from the collector, environmental corrosion mechanisms, ultra violet degration etc. Unlike glass, transparent plastics, due to their compa-

rative thoughness, flexibility, low cost, type availability, hign transmittance, are usually prefered as cover materials. Though they have relatively low resistance to scratching and abression, easy weathering, cannot withstand high temperatures. At short term, glass looks the most durable low cost material for solar collector covers, its performance experiences the greatest toll in the long run. Specularity and transmittance are important to solar applications. They show minor changes whereas surface morphology, chemical composition of the surface, surface index of refraction and the spectral absorptance are modified by exposure to sunlight and moisture. Hence, commercially produced soda-lime-silica glasses are suitable for solar application. Plastics are affected more by outdoor elements than other materials, especially the ultra violet portion of the solar spectrum. Some however, have good resistance to weathering. For example heat (thermoseting) plastics.

Under ideal conditions, the photon energy which creates electron-hole pair does not use up all this energy to do ideal work. This photon energy ($\hbar w$) is greater than the band gap of the material in question. The fraction that is greater than the band gap is lost as heat irretrivebly. Hence the maximum efficiency for an optimum band gap material is reduced to about 42% by the wide wavelength of the solar spectrum,[21]

Using ideal selective surfaces the solar spectrum can be transformed to a narrow wavelength distribution thereby enhancing the number of electron-hole pairs at the band gap energy of the given material. This can be effected by the use of two selective surfaces attached to a thin metal sheet and placed above a photocell in a vacuum. Here energy is transmitted only by radiation to and from the sheet.[22]

Selective surfaces find application mainly in solar collectors (active and passive), and in building glazings. Solar collectors are made up of a metallic absorber-converter (Opaque) and a transparent window (glazing). The metallic absorber-converter is made up of either metallic or metallized glass, which absorbs maximum radiation emitting minimum thermal radiation. A highly selective surface is one with the highest possible absorption and lowest emittance (by Kirchoff's law).[23] A good example is the labour selective black, made up of a thin film of nickel black on a polished metal substrate. Whereas a selective window is a material that is transparent to sunlight with transmitance and reflectance lying between 1.5 to 3.0 μm. Glass and plastics are good examples. Such substances allow sunlight into a collector at the same time preventing the loss of thermal radiation (infra red) from the absorber. Another type of selective window is the non-reflecting surface. Here the selectivity is in the wrong direction and is used on the window of collectors to avoid reflective losses in incomming sunlight.

Selective surfaces for building glazings are of two types[24]: those with static properties, and those with dynamic properties. In cold climates surfaces with low thermal emittance are used to maintain a warm environment in buildings and in warm climates, through radioactive cooling, in buildings surfaces for solar control are used. Selective surfaces with dynamic properties are used as "smart" windows. They are capable of adjusting, based on the changing demands of the loads in a day or season (cooling, heating or lighting). There are three types of smart windows. Those whose properties change with temperature (thermochromic), those that depend on irradiation (photochromic) and those that change their properties as a result of applied voltage an electric field (electrochromic). The use of chromogenic windows depends on the environment, relative cost and the need. Buildings with appropriate ventilation control systems of window glazings that are designed for either cold or warm climates can have the solar and thermal environment controled.

For cold climates, window glazings absorb radiation into the buildings raising the temperature. Solar transmission (heat gain) during the day is emproved and thermal radiation (heat coss) is reduced during winter. This control can be affected by the use of energy efficient materials. These are materials used for wating glasses allowing transparency for wavelengths between 0.3 - 3.0 μm and opaque for wavelengths between 3.0 - 100.0 um. Here, incident radiation is masimumly

absorbed while thermal radiation is minimized.[25]

Free electron (noble) metals are very effective for use as watings which are transparent at short wavelengths and reflecting at long wavelengths. For example, Cu, Ag, Au. Most other metals show pronounced and undesirable interband absorption within the solar range. This is due to the fact that spectral selectivity is a factor of the free electron properties governing optical properties in the main spectral range. Oxides of some heavily doped oxide semiconductors are also used. They have high luminous transmittance, high infra red reflectance and good electrical conductivity. Here consideration is given such that the band gap be large though to allow transmission up to 0.3 μm and the doped crystal must be such that can be allowed to a level where the watings exhibit free electron-like behaviour beyond a plasma wavelength and the energy gap should not shift-towards the visible range due to doping. Examples of some of the metals doped are Zn, Ca, In, Sn and some combinations.

In our environment the need for cooling buildings cannot be over emphasized. Solar energy passing through glass causes too much heating. To cool such a building one can decrease the through-put of solar energy while maintaining the luminous transmittance. With the use of selective watings, transparent between 0.4 and 0.7 μm and reflecting between 0.7 and 3.0 μm, such that the infrared part of the solar radiation is excluded. The use of radiative cooling materials is also possible.

These are materials that obey the radiative phenomenon. An exposed body at night to the clear sky reaches a temperature (equilibrium) just below that of the ambient air. This results from the exchange of infra red radiation between body and atmospheric cold. This is the same way the earth cools itself,[26] through high transmission "windows in the atmosphere to the cold trosposphere. A significant atmospheric window lies between 8 and 13 um.[27]

Since the properties of low emittance and thermal control watings are static, they lack the possibility of adjusting to the changing demands of buildings, to take care of heating, cooling, and lighting. Hence watings with more dynamic properties are more adaptable. "Heat" and "cold" mirrors, green house glasses, thick films, metal films and multilayer metal films are good examples, as they change based on environmental changes, even though their level of dynamism is highly limited. Due to this limitation, surfaces with optical switching properties called "smart" windows that can be "lured" to introduce required amounts of solar energy, or thermal energy, or visible light are best adaptable. They may be automatic or user operated.

A solar collector must be able to absorb radiation at wavelengths $\lambda \leq 3$ µm which is that at which solar radiation comes. The collector must also avoid radiation of $\lambda \geq 3$ um as it will heat up when exposed to such emitting thermal radiation. Hence for efficient operation at high temperatures

this reradiation must be avoided. Solar absorbing suffaces for warm climates must have low reflectance at $\lambda \lesssim 3$ um and high reflectance at $\lambda \gtrsim 3$ um. To create spectral selectivity (solar-absorbing and solar transmitting or reflecting) surfaces, certain physical mechanism can be exploited. Materials with intrinsic optical properties that show the desired spectral selectivity (synthetic materials) can be used. There are intrinsic solar materials that have the desired selectivity naturally and no need of other materials to augment their wavelength behaviour. They are of various types: intrinsic metallic conductors, intrinsic metallic semiconductors, intrinsic compounds, intrinsic transparent windows. Synthetic materials like the name emplies are modified to obtain desired effects. For the reason that natural intrinsic materials are not easy to find, practical selective surfaces have to be synthesized. This can be achieved by the use of "wavelength discrimination" and "wave-front descrimination" substances.

"Wavelength discrimination" surfaces are highly polished surfaces (usually metal or metallized glass or plastic) that can be obtained through dopping and scattering centres, the use of composite materials, the use of surface watings and surface preparations etc.

"Wave-front discrimination substances make use of physical surface roughness or particulate diameters and distribution to obtain different effects in the visible and infra red

spectral regions. This is obtained in materials by reflective scattering and resonance scattering.

1.6 The Physics Of Photovoltaics:

If we look at a photovoltaic cell as a "black box", then it should be able to absorb photons and create mobile charge carriers that can be induced to flow and generate current in an external load.

Semiconductors, which are the main materials used in photovoltaic cells have the property to absorb photons whose energy is greater than their band gaps, thereby promoting an electron from the valence band to the conduction band and creating a hole in the valence band.[28]

Considering the fact that photovoltaics are ment to tap the energy of the electron, rather than allow the energy to be lost through emission of radiation or dissipation, the cell can be connected to an external circuit, using a semiconductor rectifying device like a p/n homojunction, heterojunction or schottky barrier diode. The potential barrier in the diode serves as a mechanism by which the electron and hole are seperated.

When electromagnetic radiation with photon energies hV Eg (Energy gap) strikes a pln junction, electrons in the valence band acquire enough energy to enter the conduction band, producing electron-hole pairs. The electrons pass down the potential hill created into the n-side, whereas holes go

up into the p-side. In the absence of an external circuit, the n-side is charged up relative to the p-side which results in a reduction of the height of the potential hill, thereby establishing a new equilibrium condition with a potential difference appearing called the open circuit voltage (Voc). The voc is a function of the incident radiation.

Where there is an external circuit , the electrons are lead from the n-side through the external circuit to do useful work and returned to the p-side. Here, they meet and recombine with the holes from the opposite direction. For current to pass, a suitable potential difference is needed since the external circuit has resistance. This potential difference with an energy equivalence of eV is obtained by a difference in Femi levels on bothsides of the junction. The potential hill is reduced to (ΔE-eV), where ΔE is the short-circuit full potential hill.[29] Since the potential hill has been reduced, the junction does not seperate effectively the solar-generated electron-hole pairs as in the short-circuit case. Hence, some of the charge carriers manage to cross the junction in the wrong direction which results in current leakage at the junction and the load current is reduced, compared to the short-circuit current.

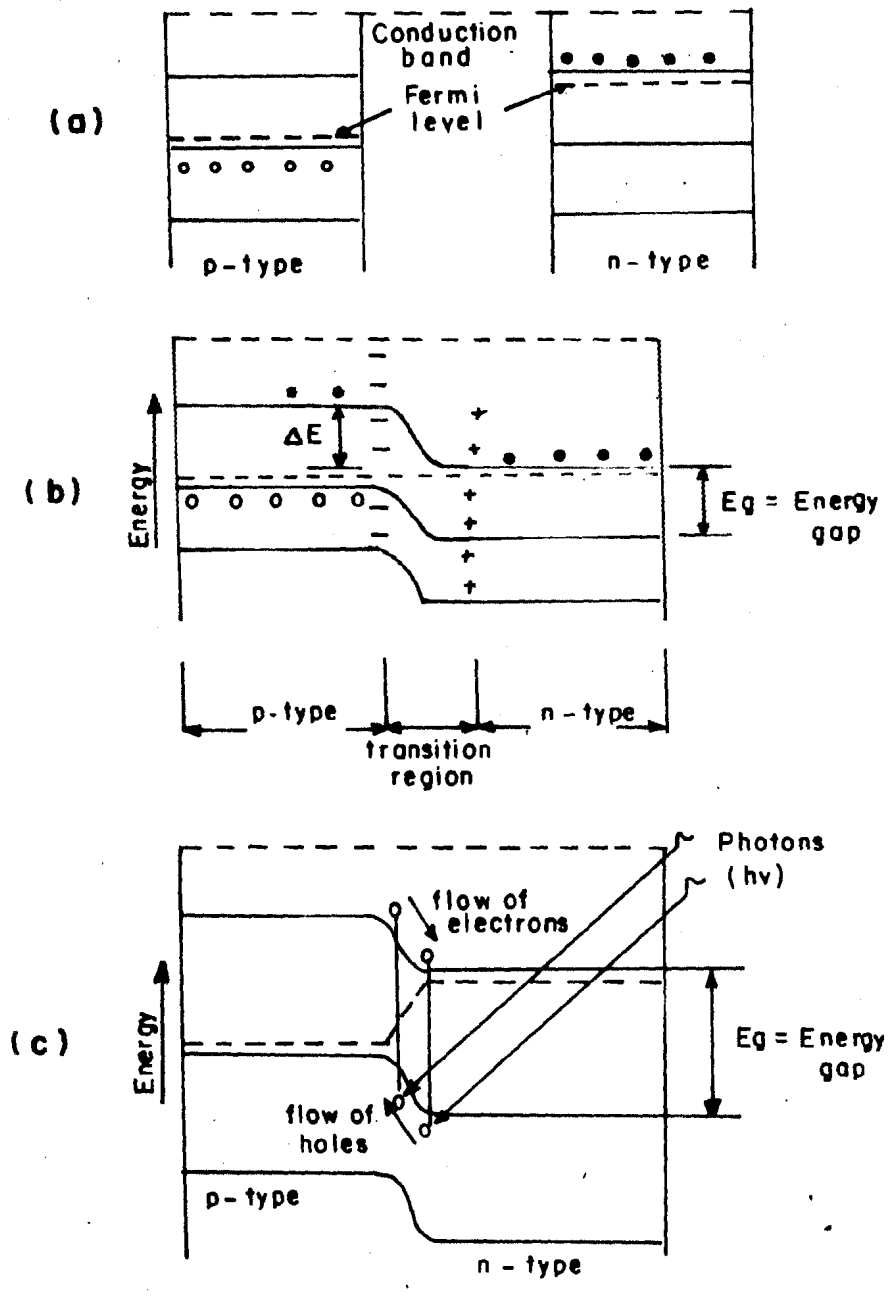


Fig. 2. Energy band diagram of p-n junction (30)

(a) isolated point n-type semiconductor

(b) p-n junction in equilibrium

(c) operation of photovoltaic junction (Energy band diagram)

The performance of a photovoltaic cell is characterized by the open circuit voltage, short circuit current density and the fill factor (FF). Thus, the power conversion efficiency (n) is defined as

$$n = \frac{V_{oc}\ J_{sc}\ FF}{P_{in}} \qquad - 1.6$$

Where Pin is the power density illuminating the device. The fill factor is a measure of the degree to which the current-coltage curve is rectangular and is ideal when it is unity. Carriers move parallel to the junction plane at the surface. For narrow junctions this could be a significant source of series resistance. Series resistance can also result from metal-semiconductor contacts and transport in the bulk semiconductor of the base. Solar illumination intensity (P_{in}) called insolation, depends on atmospheric conditions and the distance the sun's rays travel through the earth's atmosphere. On a clear, bright sunny day with the sun at the zenith, a power density of 100 $mwcm^2$ irradiates the earth's surface. This is described as air mass one (Am1) illumination conditions.[31] The air mass number indicates the distance traversed by the sun's rays through the atmosphere relative to that of normal incidence. Conditions outside the earth's atmosphere are designated Amo ($135mw\bar{m}^2$).

From equation (1.6) we see that when we generate large values of Voc and Jsc, we obtain high efficiency. Unfortunately, these two requirements are not entirely compatible. The Voc cannot exceed the band gap of the semiconductor.

This then implies that for a large Voc we require a semiconductor with large band gap. Since the photocurrent is closely related to the number of photons available for absorption which decreases with increasing gap. For the quantity Voc, Jsc, FF to be maximum, thus defining the material for maximum theoritical efficiency one will notice that a curve of efficiency versus bandgap possesses a fairly broad, maximum which peaks at about 1.5eV. Representing a theoritical efficiency of about 23% for Am1 conditions. Another important optical parameter is absorption coefficient $\alpha(\lambda)$. The reciprocal gives an indication of the thickness of material over which photons of a given wavelength (λ) are absorbed. $\alpha(\lambda)$ is defined through the equation

$$I(x) = I_0 \exp(-\alpha n) \qquad - 1.2$$

Where I(x) = intensity of unabsorbed photons at a depth x in the semiconductor. Values of $\alpha^{-1}(\lambda)$ equal to photon energies just greater than the band gap give a measure of the thickness of semiconductor required for effectively complete absorption of all the usable photons in the spectrum. This is due to the fact that the higher energy photons are more readily absorbed and the density of photons is greater for longer wavelengths. For a material like silicon that has an indirect band gap, so that phonons are needed to mediate the absorption process and consequently the absorption coefficient increases comparatively slowly with energy, with values of the order of $10^4 m^{-1}$ for long wavelengths. This means that a few hundred microns of

silicon are required for complete absorption.

On the contrary, galliun arsenide has a direct bandgap and values of absorption coefficient that rise rapidly to $10^6 m^{-1}$ above the gap, therefore, only a few microns of this material are required in a solar cell.

Since the conversion of solar to electrical energy by photovoltaic cells does not involve thermal energy, it therefore bypasses the carnot limitation on efficiency of heat engines. However, the limitations of the solar cell to only 20-30% stems from other factors. Cell's response to only a portion of the wavelengths available in the solar spectrum. Since photons of wavelengths greater than a given wavelength for a given material do not have sufficient energy to create electron-hole pair, the energy only serves to heat thermally the semiconductor. This effect on the lattice vibrations encourages carriers to surmount the potential hill and cross the junction the wrong way thereby adding to the detrimental influence on the conversion efficiency. To avoid raising the temperature of the semiconductor, the unwanted portion of the incomming radiation spectrum can be reflected and by quick transfer of the excess heat out. Cheap materials can be used as reflectors or refractors. Multiple cells can be used to improve the conversion efficiency, either by putting different solar cells in optical series or reflecting selectively certain wavelengths from the concentrated sunlight onto an appropriate type of solar cell.[32]

1.7 Developments Of Solar Cells:

The advent of space programmes came along with the need for photovoltaic power sources. The available technology and favourable energy gap made silicon the natural choice.[33]

The first silicon cell had a conversion efficiency of 6%. Solar cells for space applications have need to withstand micrometeorites and ionizing radiation. Also choice of n^+/p rather than a p^+/n configuration was necessitated by superior radiation resistance. With a small quantity of lithium diffused into the wafer, more radiation resistance was conferred onto the cell. Further protection was given by the use of glass coverslip, fastened with adhesive to the front surface. Materials such as SiO_x or TiO_2 were used as quarter-wave antireflective wating to enhance cell output. Since high power/weight ratio is next to reliability, experiments were carried out using thinner wafers. Recombination of minority carriers at the rear contact and incomplete absorption of radiation causes cell photocurrent to fall when there is a decrease of wafer thickness. At the end, trade-off between efficiency, weight and strength determines the thickness of wafers.

Studying the relationship between junction diffusion parameters and blue response of the cell,[34] found out that a very low carrier lifetime resulted when the phosphorus surface concentration exceeded $2\times10^{26}m^{-3}$. Radiation absorbed by this layer did not contribute to the photocurrent, but

when the junction depth is reduced from 0.4 um to 0.15 um, the photocurrent increased by about 15%. Also, the following changes had to be made. The antireflective wating of SiO_x was changed to a more transparent Ta_2O_5. Photoengraved closed-spaced front electrode grid was used to reduce series resistance.

Using a quarter-wave antireflection wating, surface reflection loss at a single wavelength can be reduced to a lower value. With the provision of a textured front faced this loss is reduced further in the "Non-reflective cell".

When a (100) silicon surface is selectively etched in hydrazine solution, it assumes the form of an array of square pyramids, such that, when radiation hits the surface twice it is almost completely absorbed. The surface texture causes radiation to traverse the cell obliquely, thereby increasing absorption especially in the case of thin cells. By reflecting minority carriers away from the contact, the diffused region improves both J_{sc} and V_{oc} and also reduces series resistance. It is now generally agreed that all aspects of cell performance except V_{oc} are satisfactory.[35]

It is theoritically predicted that, there is a continuous increase in cell voltage as the resistivity of the wafer reduces, but in practice reducing the resistivity below $10^{-3}\Omega$ m results in no further increase in cell voltage. If some modifications are made, the above described cells are suitable for space and terrestrial use. The schottky barrier

cell can be prepared on finely polycrystalline silicon where grain boundaries might interfere with the usual diffusion process. The interdigitated and vertical multijunction cell have low interval series resistance and are suitable with optical concentrators.

Despite the progress already made, silicon slice technology produced cells are unlikely to meet E.R.D.A. cost goals unless radical changes are made in material and device manufacture in the areas of the present silicon purification process, crystal growth, cutting, lapping, polishing and batch processing of cells.

Attempts to make silicon in sheet form so as to omit subsequent cutting, lapping and polishing stages are in progress.[36] Apart from silicon, gallium arsenide with a band gap of 1.43eV is well matched to the solar spectrum. Though much more costlier than silicon, it performs better than silicon at higher temperatures and intensities due to its larger band-gap.

CHAPTER TWO

THIN FILM MATERIALS

"A thin material created ab-initio, by an atom/molecule/ion/cluster of species-by-atom/molecule/ion/cluster of species condensation process".[37]

The above definition of a thin film, does not arise from the thickness of the film but from the mode of fabrication, how it affects the microstructure and its properties.

Thin film growth takes place by one of the following modes:[38] layer-by-layer; Stranski-kaitcher and 3-deimensional growth of discrete nuclei. Layer-by-layer mode, takes place when either the ad-atoms have little mobility (as in amorphous deposits) or under extreme conditions of very low supersaturation, single crystal structure, or ultrahigh vacuum deposition. When the film after growing like the layer-by-layer mode changes to three dimensional nuclei, we have the stranski-kaitcher mode. The three dimensional growth of discrete nuclei is most common for oriented thin films.

Growth takes places at nucleation sites in the plane of the film and perpendicular to the film.

2.1 Thin Film Deposition Techniques:

In the development of large-area thin film solar cells, emphasis is laid not only to performance criteria but also to their economical viability for terrestial applications. Thus, the need to exploit thin and thick film techniques arises,

such that they satisfy simplicity, cost effectiveness, large-area, uniform and controlled deposition to yield well-defined structural metallurgical and electro-optical properties.

Three steps are involved in thin-film deposition: creation of atomic/molecular/ionic species; transportation of species through medium and condensation of species on substrate. While thin film deposition techniques can be classified under the following headings: Physical vapour deposition (PVD); chemical vapour deposition (CVD); electroless or solution growth and electrochemical deposition (ECD); PVD and CVA techniques have been combined.[39]

2.2 Physical Vapour Deposition:

When a material is heated to a sufficiently high temperature, it produces a desired vapour pressure necessary for the vapour atoms to move across the medium and condense on a substrate to form a thin film. The rate of deposition/condensation is subject to the geometry of the source substrate and condensation coefficients on the surface. When the vapour atoms collide with the risidual gas atoms in the vacuum, they are scattered. The rate at which the gas molecules impinge on the substrate surface is given by the langmuir-Dushman kinetic theory equation.[40]

$$N_e = 3.513 \times 10^{22} P_e/CMT)^{\frac{1}{2}} \text{ molecules } cm^2 s^{-1}$$

where T = temperature, M = molecular weight of vapour species, P_e = equilibrium vapour pressure (in torr) of the evapourant

under saturated-vapour condition.

To avoid film contamination by gas, film deposition is preferable in a vacuum, when the deposition takes place at normal rates between 1 to $10 A^{-1}$. The sticking coefficient of gas atoms at high temperatures makes pressure of 10^{6} torr good enough for deposition of clean films apart from those that are readily oxidizable, hence needing better vacuum conditions.

Apart from S, Se, Te, Bi, Sb, P and As that vapourize in the form of polyatomic clusters depending on vapourization temperature all other elements sublime. Alloys vaporuze accompanied by dissociation or association or both. Thermal decomposition takes place when the various constituents have different volatilities. If they are equally volatile, congruent evapouration takes place. Dissociation tends to be greater at higher evapouration temperatures and lower pressures. Binary-Oxides for example, at high temperatures evapourate by dissociation.

Based on the nature of the deposition process (high supersaturation, condensation kinetics and rapid quenching of absorbed atoms) thin films are naturally thermodynamically nonequilibrium structures. They are fine-grained and have a high concentration of frozen-in structural defects. Where single crystal films are not possible, solar cells applications need large oriented grains or mosaic monocrystals. Mosaic crystals are epitaxially grown in sizes up to tens of micrometers and have small-angle grain boundaries.

Investigations of epitaxially grown solar cell films have been restricted by economic desirability of developing large-area, high-efficiency solar cells by a cheaper process.

In the Hotwall epitaxy technique, one or two aunular vapour sources are used. A cylindrical enclosure is held at a higher temperature than the substrate and the vapours are transported through them. Hence homogenized and equilibrated multicomponent vapours are deposited on the substrate.

When a low-density vapour beam obtained from a high-vapour-pressure in an ultrahigh-vacuum (UHV) is condensed onto a single crystal substrate we have the molecular beam epitaxy. One can derive its best advantages by making use of the UHV analytical technique to obtain information on the structure, topography and composition and its depth profile and the chemical state of the surface of the film during its growth. At low substrate temperatures expitaxial growth of high perfection can be achieved by keeping deposition rates low ($< 1A^{o}S^{-1}$) onto ultraclean substrates. Multilayer structures are obtainable with the use of very slow deposition rates. MBE is a very sophisticated and expensive set up.

When films are vapour deposited on amorphous substrates, they are generally polycrystalline. Thus, under the right conditions, partially textured or oriented films have been made. Smith and Co. deposited textured films of Si on an amorphous substrate (SiO_2) that has a relief pattern of grating lines with the right periodicity and profile

and latter crystalized it with a lasser (6w) in a repeated raster pattern and got a complete orientation of the films over the grating relief along the grating direction. Here, the grating spacing has to be less than the characteristic grain size of the film about to be deposited. This graphoepitaxy technique is still an academic curiousity.

When kinetic ejection is used by bombarding with energetic and nonreactive ions vapour spacies are created. This process called sputtering results from the transfer of momentum between impringing ions and the atoms of the target surface. The process provides a very simple and precise control on the rate of film deposition since the number of sputtered atoms is proportional to the number of ions. At high deposition rates the process becomes inefficient from the energy point of view, as most of the energy is converted to heat, hence a limitation. Sputtering processes are best suited for depositing adherent films of multicomponent materials, even though they are energy intensive.

2.3 Chemical Deposition Technique:

Under the chemical deposition technique we have spray pyrolysis process, solution growth process, screen printing, chemical vapour deposition, exchange reaction, electrodeposition, anodization, electrophoresis.

The spray pyrolysis process intails spraying an aqueous solution that contains soluble salts of the given atoms of a

desired compound on a substrate that is kept at high temperature. When the droplets reach the substrate surface they undergo pyrolytic decomposition, forming a single or cluster of crystallites. The reaction is endothermic. The energy for thermal decomposition and subsequent recombination of the constituent species is provided, by the substrate. Spray deposited films are strongly adherent, hard mechanically, pinholefree and stable with time and temperature up to the temperature of the spray. The rough topography of the films depend on the spray conditions and temperature of the substrate. The diaplet mobilities and chemical reactivities of the various constituents determines the microstructure range from amorphous to micropolycrystalline. Some preferential orientation may be produced resulting from increase in grain size by recrystallization at the temperature above the spray temperature or under some reactive melieu.

The solution growth process, is governed by the solubility product principle, which can be stated thus: In a saturated solution of a weakly soluble compound, the product of the molar concentrations of its ion (ionic product) is a constant at a given temperature. Precipitation takes place when the ionic product exceeds the solubility product. If the reverse is the case, the solid phase dissolves until the ionic product becomes constant.

In screen printing aproach, a paste of the required material is "printed" onto the substrate to define conductor, resistor and device patterns. The substrate is fired under the required time and temperature, yielding rugged components bonded to the substrate. This offers a flexible inexpensive answer to the problems of grid pattern delineation on solar cells, connection of array, and preparation of active semiconductor layers and devices. The device and circuit may be coated for general protection.

In chemical vapour deposition, the substrate is exposed to vapourized compounds or reagent gases which contain constituents of the desired deposited substance, thereby initiating a chemical reaction close to or at the substrate surface. The required material is thus produced as a solid phase reaction product which condenses on the substrate. The chemical reaction can be influenced by the use of heat, light, x-rays, an electric arc, a glow discharge, electron bombardment or catalytic action of the substrate surface. The morphology of the deposited layer is rightly influenced by the nature of the chemical reaction and activation mechanism. When the reaction takes place in the gas phase (homogenous reaction), powdery deposits are formed, hence it is advisable to attain deposition conditions which would make it possible for the reaction to take place near or on the substrate surface (heterogenous reaction).

Exchange reactions, usually called dipping or chemiplating involves the displacing of a Cd ion by 2 Cu ions of the form.

$$CdY + 2\ CuX \quad Cu_2Y + CdX_2$$

where X is a halogen (Cl, Br, or I) and Y a chalogen (S, Se, or Te). The reaction usually is performed in aqueous solution at temperatures between 90 and 100°C. To increase the solubility of CuX, salts like NaCl and NH_4Cl are added. The number of Cu ions in the solution influence strongly the rate of the reaction.

When electricity is passed through an electrolyte it results in chemical changes termed electrolysis. Substances deposited as a result of the passage of electricity on an electrode are called electrodeposits. This phenomenon is governed by the following two laws. The amount of chemical change that takes place when electricity is passed in an electrolyte is proportional to the amount of electricity passed. The two laws can be combined to read $M = IEt/F$. Where M = mass (in grams) of substance deposited; I = current passed (in amperes); E = chemical equivalent weight (in grams); t = reaction time (in seconds); F = Faraday, equal to 96500C (charge required to deposit one equivalent of any ion from a solution). Many metals can be electroplated for electrical contacts in solar cells. For example, Cu, Ag, Au, Ph and Pb. Ag is the best, in view of its outstanding electrical conductivity.

Anodization, a field assisted form of thermal growth where the metal to be oxidized is made an anode and put into an oxygen containing electrolyte which may be aqueous, nonaqueous or fused salt. The growth takes place at constant voltage or current. The pH of the electrolyte influences the coherence of the film obtained. If electrolyte in question is acidic or too alkaline, the film dissolves during growth, rendering it porous. In semiconductors, anodization plays an important role in the production of devices especially in electroshaping, location of p/n junctions, preparation of stable surfaces for semiconductor devices.

Electrophoresis involves the deposition on an electrode of a suspension of electrically charged particles in a liquid medium. The electrodes are then treated by pressurized compaction and heat treatment to dry out traces of the suspension medium and sinter the particles within the film. The advantages of electrophoresis are that, any powder material can be deposited on any conducting substrate; uniform thickness can be obtained even on complicated shapes; thick coatings are possible and thickness can be precisely controlled; codeposits of various materials are possible and in desired proportion; period of deposition is precise and there is no waste.

2.4 Liquid Deposition Technique:

This technique is not a "thin film" deposition technique but is of great promise in making large-area thin layer materials

for solar cells use. It is devided into Liquid Phase Epitaxy and melt spining Technique. In Liquid phase epitaxy, material from a cooling solution is precipitated onto an underlying single crystal substrate. Keeping the solution and substrate apart, contact is made by "tapping" the furnace with solution, or by dipping the substrate into the solution in a vertical furnace. Saturating the solution with growth material at the required growth temperature, it is allowed to cool in contact with substrate surface. Melt spining is used to produce rapidly quenched ribbons at high speeds.

2.5 Thin Film Characterization:

The optical and electronic properties of thin films are highly sensitive to their crystallographic and microstructural characteristics. So also does the structural features of the interface at the junction affect the electronic behaviour of the photovoltaic junction.[41] The one setback in the many developed techniques to study crystals is the fact that each increase in resolution is at the expense of the total area or volume of the examined material.

Some of these techniques are used to monitor the following: crystal structure, microstructural characterization (morphology and structure), compositional analysis, optical characterization (optical constants n and k).

In the study of crystal structure, x-ray diffraction has the singular advantage of not distroying the sample and no

difficult preparations are required. Sample preparations can be tricky for the use of electron diffraction, though films up to about 1000Å thick can be studied. Reflection high-energy electron diffraction (RHEED) can be used for the study of thicker films. Also, the scanning electron microscope (SEM) is a relatively recent crystal structure-sensitive technique. It has a spatial resolution of about 1 um. Diffraction information can be obtained from regions of 50 to 100Å using the scanning transmission electron microscope (STEM).

The study of the morphology and the structure of photovoltaics is possible with the use of various interference and phase constant techniques. For example, optical spot scanning, for the direct study of actual energy conversion of the cell, though spatial resolution is limited to a few tenth of a micrometer. The SEM allows for extension of the resolution. Its versatility results from the long working distance between the final lens and the sample surface, also from its ability to study practically almost any surface. For resolutions that are not even possible with the SEM, the transmission electron microscope (TEM) can be used. Due to the tricky nature of the preparation of samples in such a multilayer device, but once prepared, structural details at atomic resolutions are possible. Combination of TEM and SEM, scanning transmission electron microscope (STEM) can be operated in both transmission and scanning mode, thereby providing better resolution compared

to SEM for surface studies. It also has the capability of performing small-area (50-100Å) diffraction and chemical analysis.

Compositional analysis has been directed towards physical than chemical techniques. Many techniques are based on the detection of characteristic x-ray lines. Short-wavelength x-ray excite the lines in x-ray fluorescence. Here, lateral resolution is poor and lateral and depth resolution can be provided by the use of electron probe microanalyzer (EPMA), SEM or STEM. Solid state detectors are used that have larger acceptance angles and much higher resolution of EDAX for the energy dispersion analysis of emitted x-rays (EDAX). The effects of elastically scattered electrons and secondary fluorescence limits resolution to about 1 μm, whereas for thin samples spatial resolutions of less than 50Å are possible. Auger electron spectroscopy (AES) is available in the scanning mode and yields lateral resolution equal to beam size and depth resolution of from 10 - 30Å. Point-to-point chemical mapping of elemental concentration is possible in the scanning mode. AES has the advantage of high sensitivity to higher elements. We have the secondary ion mass spectroscopy (SIMS) which analysis ions emitted during ion milling from a material. SIMS is a depth-profiling technique. Also, the electron spectroscopy for chemical analysis (ESCA) which is not in general spatially resolving gives depth resolution of 10 - 30Å. AES, ESCA, and SIMS involve ultrahigh-vacuum conditions and

are destructive in depth profiling mode. Rutherford back-scattering (RBS) is nondestructive, but requires an accelerator to provide the probing beam. Castel and Vedel developed an electrochemical analysis of semiconductor materials based on voltametric endpoint detection yielding oxide layer thickness, stoichiometry and equivalent thickness of the semiconductor

Among the variety of techniques to determine the optical constants (n and K), the most commonly used envolves separate determination of n and K from reflectance and transmittance measurements. If multiple reflections are suppressed, the transmittance (T) of a film of index n_1-ik_1 and thickness (t) is given by the relation:

$$T = \frac{6n_o(n_1^2+K_1^2)\ \exp\ (-4\pi k_1 t/\lambda\ )}{[(n_1+1)^2 + K_1^2][(n_o+n_1)^2+K_1^2]} \qquad n_1 > n_o$$

Negleting interference and multiple reflections, T and K are related by

$$T = (1 - K)\ \exp\ (-4\pi K_1 t/\lambda\ ).$$

Absorption coefficient (α) can be determined by measuring K and T, since $\alpha = 4\pi K/\lambda$.

Using a photospectrometer at different wavelengths α can be determined by putting the value of the spectral variation of α in either equations 2.1 or 2.2 below.

$$\alpha = A\ (hV-E_g)^{\frac{1}{2}} \qquad - 2.1$$

$$\alpha = \frac{c(hV+E_p-E_g)^2}{\exp(E_p/KT)-1} + \frac{c(hV-E_p-E_g)^2}{1-\exp(-E_p/KT)} \qquad - 2.2$$

to determine the nature (direct or indirect) of optical transition and the optical gap (E_g).[42]

The electronic characterization of semiconductors entails the determination of resistivity (ρ), mobility of carriers (μn or μp), carrier concentration (n or p), Hall coefficient (R_H), minority carrier diffusion length (L_p or L_n), minority carrier lifetimes (τ_n or τ_p) and their temperature dependence. The methods of measurement include two-point method for resistivity, linear four-point probe method for resistivity, spreading resistance method for resistivity, noncollinear four-point probe method for resistivity, vander Pauw technique for resistivity, Hall coefficient and Hall mobility, Hall effect measurements and Hayness-shockley method for mobility.

CHAPTER THREE

EXPERIMENTAL

3.1 Description of Deposition Technique Used:

The chemical deposition of CdS is based on the release of Cd^{2+} and S^{2-} ions from their compounds in an aqueous solution and their condensation on a substrate (in this case glass) at a pH 10, placed vertically in a bath.

The release of cadinium ions takes place as shown in the following dissociation equilibrium equation.

$$[Cd(TEA)]^{2+} \rightleftharpoons Cd^{2+} + TEA. \qquad 3.1$$

While thiourea $(SCNH_2)_2$ dissociates in alkaline armoniacal medium giving S^{-2} ion as follows,

$$Sc(NH_2)_2 + O\bar{H} \longrightarrow CH_2 + H_2O + SH \qquad - 3.2$$

$$SH^- + OH^- \longrightarrow S^{2-} + H_2O \qquad - 3.3$$

Hence, the Cd^{2+} and S^{2-} ions condense to give CdS obeying the solubility product requirement. The overall reaction is given thus,[43]

$$[Cd(TEA)]^{2+} + Sc(NH_2)_2 + 2OH^- \longrightarrow CdS + TEA + CO(NH_2)_2 + H_2O \quad . \qquad - 3.4$$

As already mentioned, the solution growth process is governed by the solubility product principle. Each concentration term is raised to a power equal to the number of ions as shown by the formula for the compound. Considering $Cd(OH)_2$ in solution, it will hydrolyze as follows:

$$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2(OH) \qquad - 3.5$$

while the ionic product is given by

$$\left[Cd^{2+}\right] \times \left[OH^{-}\right]^2 = \text{constant.} \qquad - 3.6$$

For IP SP, precipitation occurs. If SP > IP, the solid phase will dissolve to establish a constant (equilibrium). A fairly stable complex of the metal ions which provides a controlled number of the free ions can be used to eliminate spantaneous precipitation, thus making it easy to form a thin film by a controlled ion-to-ion reaction of the form.

$$M(A)^{2+} \rightleftharpoons M^{2+} + A \qquad - 3.7$$

At any given temperature the concentration of the free metal ions is given thus:

$$\frac{\left[M^{2+}\right]\left[A\right]}{\left[M(A)^{2+}\right]} = K \qquad - 3.8$$

where K = the instability constant of the complex ion. Also, the concentration of the metal ion can be controlled with the use of an appropriate complexing agent and the temperature of the solution.[44]

Elements	Complexing Agents
Ag	CN^-, NH_3, Cl^-
Cd	CN^-, NH_3, Cl^-, $C_6H_5O_7^{3-}$, $C_4H_4O_6^{2-}$, EDTA
Co	NH_3, CN^-, SCN^-, $C_6H_5O_7^{3-}$, $C_4H_4O_6^{2-}$
Cu	NH_3, Cl^-, CN^-, EDTA
Hg	NH_3, Cl^-, CN^-, EDTA
Mn	$C_2O_4^{2-}$, $C_6H_5O_7^{3-}$, $C_4H_6O_6^{2-}$, CN^-, EDTA
Ni	CN^-, SCN^-, EDTA, NH_3
Pb	EDTA, $C_6H_5O_7^{3-}$, $C_4H_6O_6^{2-}$, OH
Sn	$C_6H_5O_7^{3-}$, $C_4H_6O_6^{2-}$, $C_2O_4^{2-}$, OH
Zn	CN^-, NH_3, EDTA, $C_4H_6O_6^{2-}$, $C_6H_5O_7^{3-}$

Table 3.1
Some ions and their common complexing agents.[45]

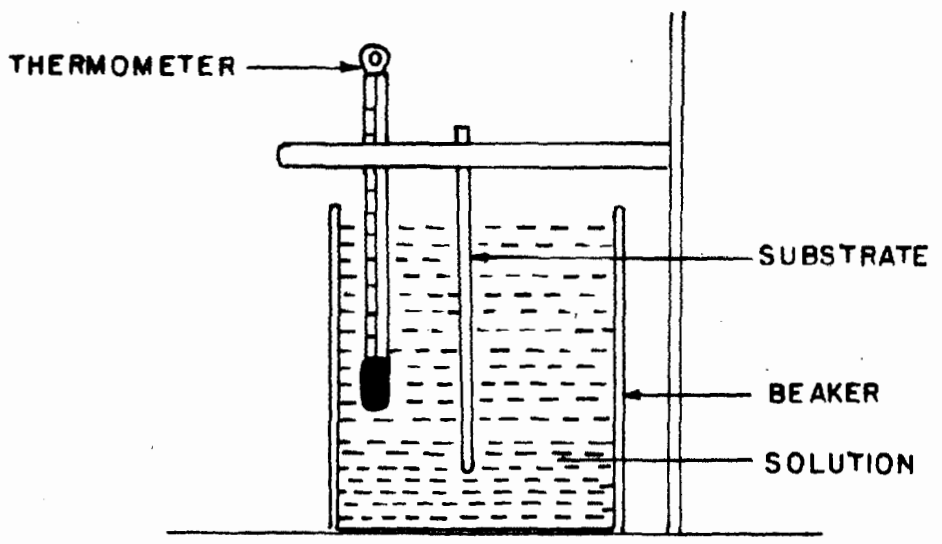


Fig. 3 Experimental arrangement to obtain thin film deposits.

The solution was stirred contineously to keep the temperature uniform while monitoring the thermometer.

An incubation period is needed for the formation of critical nuclei from the system to the clean surface. Growth rate then rises rapidly till when IP =SP. If the substrate is presensitized, there will be no incubation period since nucleation sites already exist on the substrate. The solution itself actually provides nuceation sites. This can be noticed when the substrate are suspended in the solution before forming the complex. The number of nucleation centres, supersaturation of the solution (ratio of IP to SP), and st stiring determine the rate of deposition. While ionic concentration, velocities, nucleation, and growth processes on the substrates, determine growth kinetics. Metal ion (M^{2+}) concentration decreases with increasing concentration of complexing ions, thereby reducing rate of reaction and precipitation. The complex is more stable when pH increases. While free M^{2+} ion concentration reduces, giving a decrease in the deposition rate.

3.2 Ligands:

When an atom or an ion from a metal (commonly) becomes attached directly to a group of neutral molecules or ions, a more or less stable charged aggregate called complex ion is formed. The group of neutral molecules or ions are called ligands or donor groups, said to be complexed or coordinated

to the central ion or acceptor in a first coordination to the central ion or acceptor in a first coordination sphere. For example: $Cu(H_2O)_4^{2+}$, $Cd(TSA)^{2+}$, $Co(NH_3)_4F_2^{+}$ whose coordination number (of the ion) is the number of ligand atoms arranged in definite geometry and bonded directly to the central ion [46, 47, 48, 49, 50]

Even though partial dissociation may take place, complex ions or neutral complexes that make up a complex compound most often retain their identity in solution. Complexes may exchange ligands slowly or rapidly where the former are called nonlabile or inert and the latter are called labile complexes. Here, note should be made between thermodynamic stability and kinetic stability. For example; $Cr(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ have nearly the same average energy per bond, but $Cr(H_2O)_6^{3+}$ exchanges water molecules with the solvent water at a slow measurable rate whereas $Fe(H_2O)_6^{3+}$ exchanges extremely rapidly.[51] The chemistry of coordination compounds is determined by the electronic configuration of the central ion, the donor and acceptor properties of the ligands and the nature of the linkage between ligand and central ion. This can be seen from Werner's theory which states:

> Even when, to judge by the valence number the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valencies may be called into action".[52]

3.3 Reasons For Technique Used:

Though the art of growing crystals must rest essentially on empiricism and extensive firsthand experience, the choice of a particular method and refirement, to meet desired specifications must be based on scientific principles, thermodynamics and kinetics. Crystal growth methods are classified into the following groups; growth from the melt, growth from solution and growth from vapour phase.[53]

The choice of a particular method is governend by certain limitations; those by nature, and those set by properties of the material. For example, yttrium ion garnet (YIG) does not melt congruently, $CaCO_3$, (at atmospheric pressure) sic decomposes before melting, SiO_2 undergoes solid state transformation before melting point at room temperature. Hence none can form crystals from the melt.

Solution growth is simple and inexpensive. It only becomes complex when requirements of instrumentation are imposed due to specifications on purity, size, properties of solvent come into play. Compared to growth from the melt, lower temperatures are required and can lead to lower density of lattice defects. When a crystal of high quality is desired, then, one decides on growth from solution based on the availability of high purity solvent, which is insoluble in the crystal. Impurities in the initial chemicals can be made ineffective by the use of complexing agents. Since film formation has ions as building blocks (as opposed to atoms in

other deposition techniques) they are nearly stoichiometric. Films can also be deposited on all kinds of hydrophilic substrates.(54, 55)

3.4 Deposition Of CdS Thin Film:

CdS films were deposited by reacting cadmium acetate and thiourea in a basic medium. Ammonia solution was used to create the required basic medium and triethanolamine (TEA) as complexing agent.

1M solution of cadmium acetate ($Cd(C_2H_3COO)_2\ Cd.2H_2O$ was prepared by dissolving 26.652gm of the salt in 100ml flask of solution. 1M solution of thiourea was also prepared by dissolving 7.612 gm of the salt in 100ml flask of solution.(56, 57)

10ml of 1M cadmium acetate solution was put in a 100ml beaker and 10ml of 7.45M TEA was added and stirred. 10ml 17.05M ammonia solution was added and the mixture was stirred for a few seconds. 10ml of 1M thiourea solution was added and stirred to give a homogenous solution. Distilled water was added to give 100ml and was stirred for a few seconds and cleaned glass slides were clamped virtically in the baths. The clear solution gradually turned yellow. The slides were latter taken out and washed with distilled water and allowed to dry in air after different time intervals.

The growth of the films was studied as a function of deposition time, TEA concentration, ammonia solution concentration, thiourea concentration as parameters.

3.5 Band Gap Determination (Optical Method):

When an incident beam strikes a semiconductor, electrons absorb photons with energy greater or equal to the energy gap of the semiconducting material thereby migrating from the valence band to the conduction band. This can be written as

$$hV \geqslant Eg \quad ^{58} \qquad - 3.9$$

At the absorption edge, equation (3.9) becomes

$$hV_o = Eg \qquad - 3.10$$

$$Eg = \frac{hc}{\lambda o} \qquad - 3.11$$

where C = velocity of radiation, $_o$ = minimum wavelength at absorption edge, h = Plank's constant and V = transition frequency.

Using equation (2.1) and (2.2), the nature (direct or indirect) of optical transition and the optical gap (E_g) can be determined. Here, values of the spectral variation of the absorption coefficient(α) can be substituted in the equations.

taking $h = 4.144 \cdot 10^{-15}$ eVs ; C = $3.0 \cdot 10^{10} ms^{-1}$

$$Eg(eV) = \frac{1.241}{(um)} \text{ eVm}$$

3.6 Qualitative Analysis Of Deposited Thin Film:

Using a knife, some of the deposited film was scraped into a beaker. Ammonia solution was added to it dropwise. A white precipitate was formed. On adding more ammonia solution the precipitate dissolved. This confirmed the cation test for Cd^{2+}.

About 50mg of the deposited film was put in a beaker and 1ml of dilute hydrochloric acid was added and the mixture warmed gently. An offensive odour emanated from the mixture. When tested with lead acetate paper, the paper turned black. This also confirmed the anion test for sulphide (S^{2-}).[60]

Hence, the film deposited is CdS.

3.7. Measurement Of Film Thickness:

Film thickness was measured by the gravimetric method. The length, breath and width of the film were measured using vernier calipers and micrometer screw gange. The mass of the film deposit was measured by weighing the substrate before and after deposition with August Sauter KG. D-7470 electronic balance.

The thickness of the deposited film is given by the relationship.

$$\text{Thickness of film} = \frac{\text{mass of film}}{\text{density of film} \cdot \text{Area of Film}}$$

since mass of film is given by the product of density and volume of film.

The changes of film thickness against time were studied for various parameters: for two volumes of TEA; two volumes of NH_3 ; and two volumes of $SC(NH_2)_2$.

3.8 Measurement of Absorbance Of Film:

Using the Pye - Unicam Sp-6 spectrophotometer the optical absorption was measured for different reaction baths, to determine wavelengths at which absorption is maximum. A blank glass slide was first scanned through a range of wavelengths and one with deposited film through the same wavelength after zerroing the spectrophotometer.

Graphs of absorbance versus wavelengths were plotted for each sample. The absorption edge was extrapolated from the absorption spectrum and the value of wavelength used to calculate the band gap by substituiting same in equation (3.11).

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Summary of Results:

Time (hrs)	Thickness (m) for 10ml of 7.45M TEA	Thickness (m) for 5ml of 7.45M TEA
2	$1.73 \cdot 10^{-7}$	$3.52 \cdot 10^{-7}$
3	$3.77 \cdot 10^{-7}$	$7.00 \cdot 10^{-7}$
4	$4.63 \cdot 10^{-7}$	$9.36 \cdot 10^{-7}$
5	$7.81 \cdot 10^{-7}$	$13.80 \cdot 10^{-7}$
6	$8.71 \cdot 10^{-7}$	$15.60 \cdot 10^{-7}$

Table I:

Changes in CdS Fil Thickness And Deposition Time For 2 Vol. of TEA.

Time (hrs)	Thickness (m) for 10ml of 17.05M NH_3	Thickness (m) for when no NH_3 was used
2	$1.73 \cdot 10^{-7}$	$1.09 \cdot 10^{-7}$
3	$3.77 \cdot 10^{-7}$	$0.41 \cdot 10^{-7}$
4	$4.63 \cdot 10^{-7}$	$0.73 \cdot 10^{-7}$
5	$7.81 \cdot 10^{-7}$	$0.76 \cdot 10^{-7}$
6	$8.71 \cdot 10^{-7}$	$1.19 \cdot 10^{-7}$

Table 2:

Changes in CdS Film Thickness And Deposition Time For 2 Vol. of NH_3.

Time (hrs)	Thickness (m) for 10ml of 1M $(NH_2)_2$	Thickness (m) for 20ml of 1M $Sc(NH_2)_2$
2	$1.73 \cdot 10^{-7}$	$6.09 \cdot 10^{-7}$
3	$3.77 \cdot 10^{-7}$	$7.97 \cdot 10^{-7}$
4	$4.63 \cdot 10^{-7}$	$9.71 \cdot 10^{-7}$
5	$7.81 \cdot 10^{-7}$	$12.2 \cdot 10^{-7}$
6	$8.71 \cdot 10^{-7}$	$10.9 \cdot 10^{-7}$

Table 3:

Changes in CdS Film Thickness And Deposition Time For 2 Vol. of $Sc(NH_2)_2$.

4.1.1 Film Thickness Versus Time:

The deposition of CdS was observed to take place first rapidly and slows down latter. (Chopra and Das)[61] hold that growth kinetics of a thin film is determined by ion-by-ion deposition of the chalcogenide on nucleation sites on the substrate surface. Since an incubation period is required first, growth is slow and when these sites are established growth is rapid until it attains a terminal thickness where the rate of deposition equals rate of dissolution. That is ionic product (IP) equals solubility product. The period of incubation is absent for presensitized substrates.

4.1.2 Thickness Versus Volume Of TEA:

The changes in thickness for 2 volumes of TEA were studied and this is represented in Fig. 4. The rate of deposition is seen to be more when the volume of TEA is smaller. This goes to confirm the fact that complexing agents turn to regulate the rate of combination of cations and anions in a chemical bath.

4.1.3 Thickness Versus Volume of NH_3:

Ammonia solution was used primarily to regulate and provide the desired pH for the growth of CdS thin film. The study was for (a) 10ml 17.05M NH_3 and (b) no NH_3 used, as represented in Fig 5. It is observed that the rate of growth was much pronounced when the pH was higher. In (a) the pH was 11 while the pH of (b) was 8. Hence one can conclude that CdS thin film grows better in basic media.

4.1.4 Thickness Versus Volume Of Thiourea:

The changes in thickness for two volumes of 1M thiourea solution was studied for (a) 10ml and (b) 20ml as shown in Fig. 6. It was observed that the rate of growth of CdS thin film is influenced by the population of anions in the path. Hence the greater the population the greater the rate of deposition.

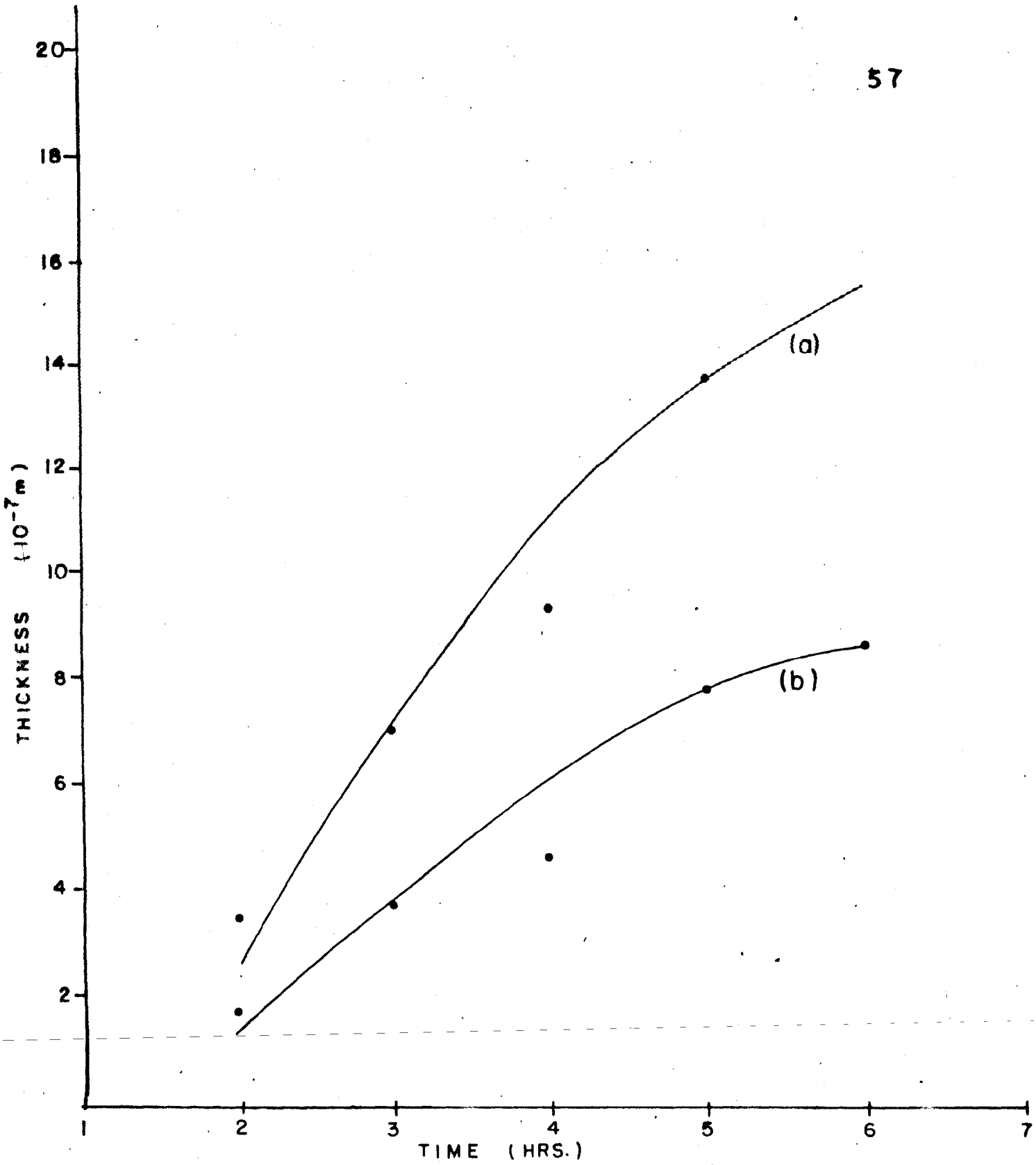


Fig.4 Changes in Cds films thickness and deposition time for 2 volumes of tea (a) 10 ml of 7.45M TEA ; (b) 5ml of 7.45 M TEA

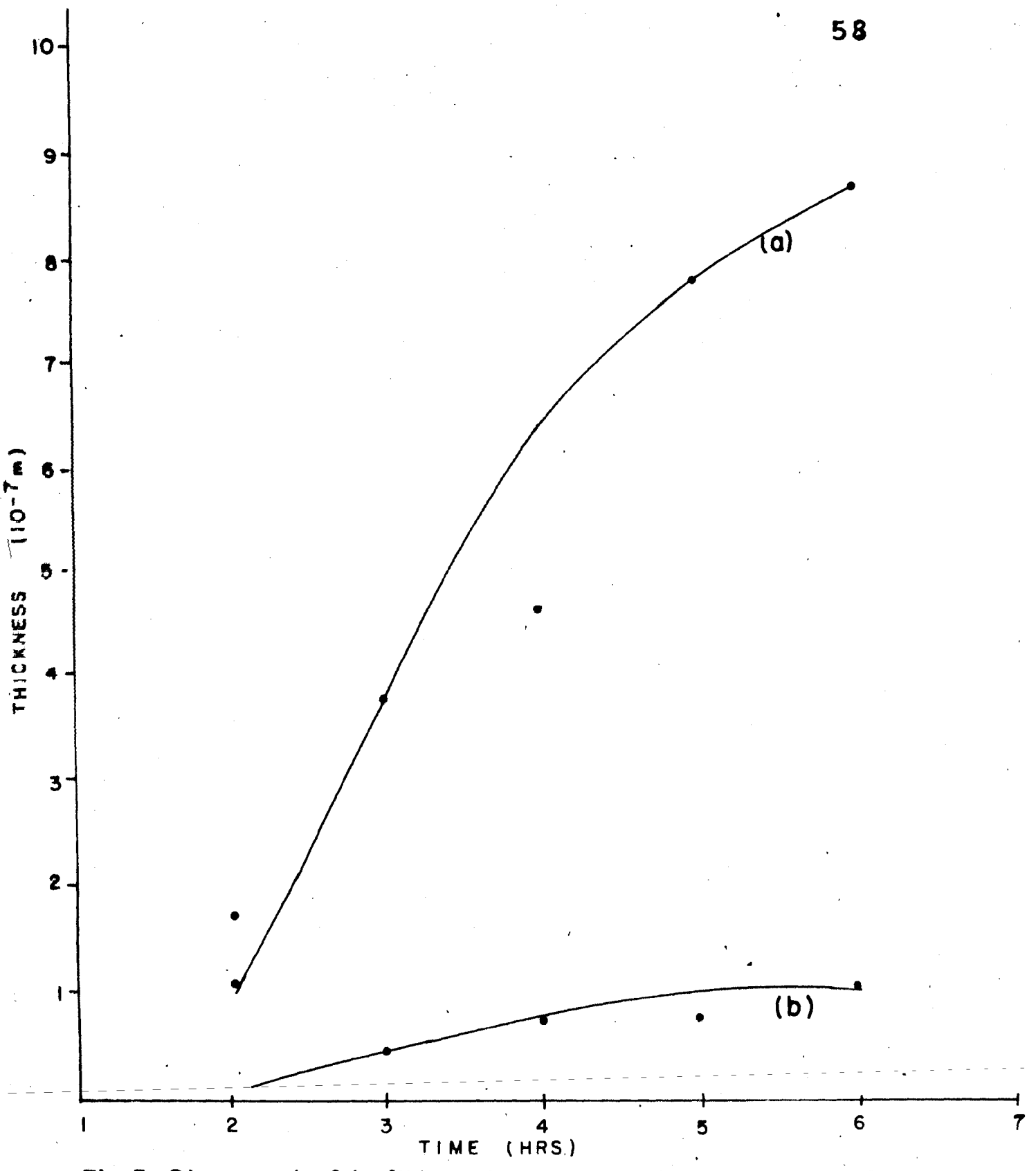


Fig. 5 Changes in Cds films thickness and deposition time for 2 volumes of NH_3: (a) 10 ml of 17.05 M NH_3; (b) No NH_3 used

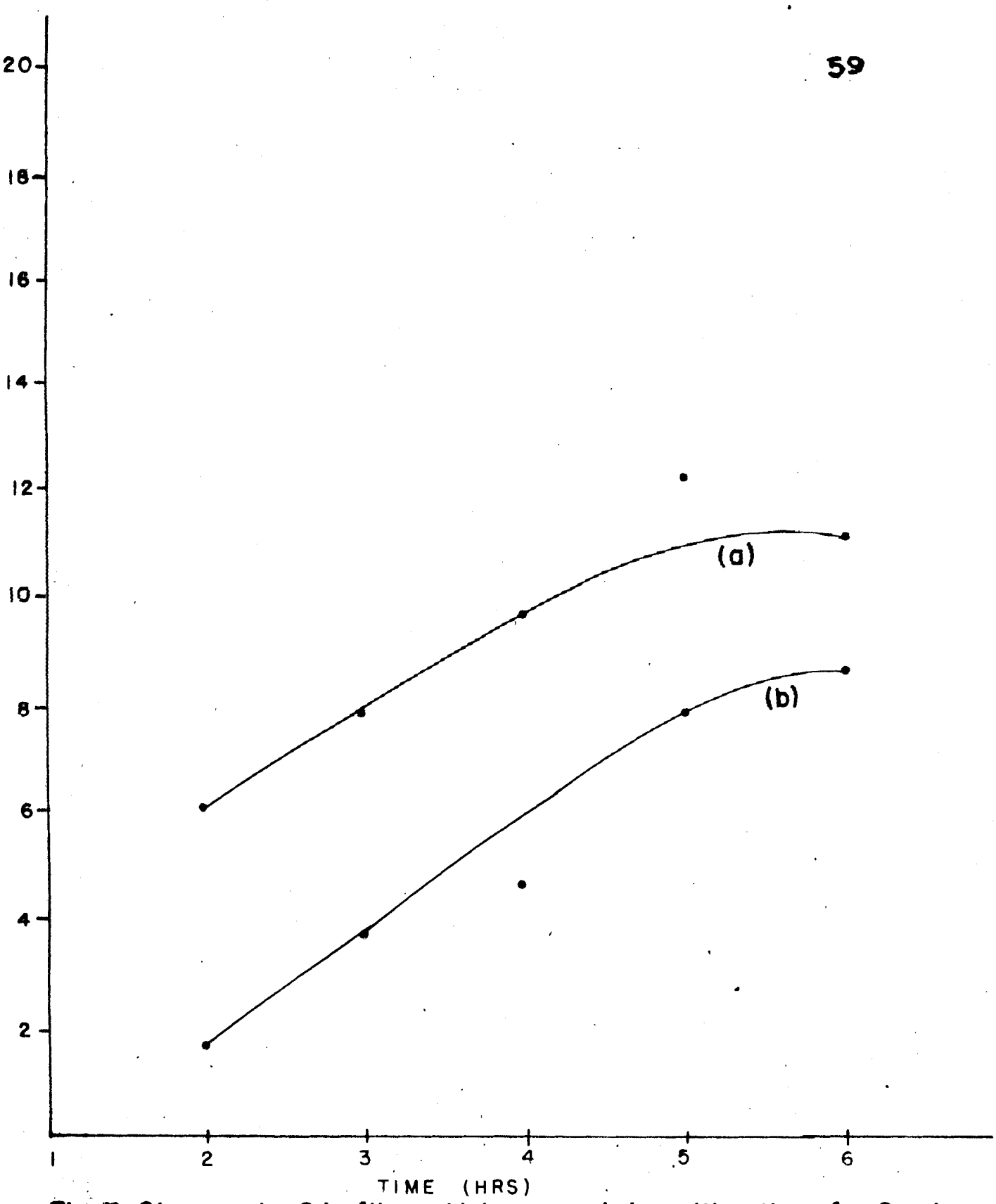


Fig. 6 Changes in Cds films thickness and deposition time for 2 volumes of $SC(NH_2)_2$: (a) 10 ml of $(NH_2)_2$; (b) 20 ml of $SC(NH_2)_2$

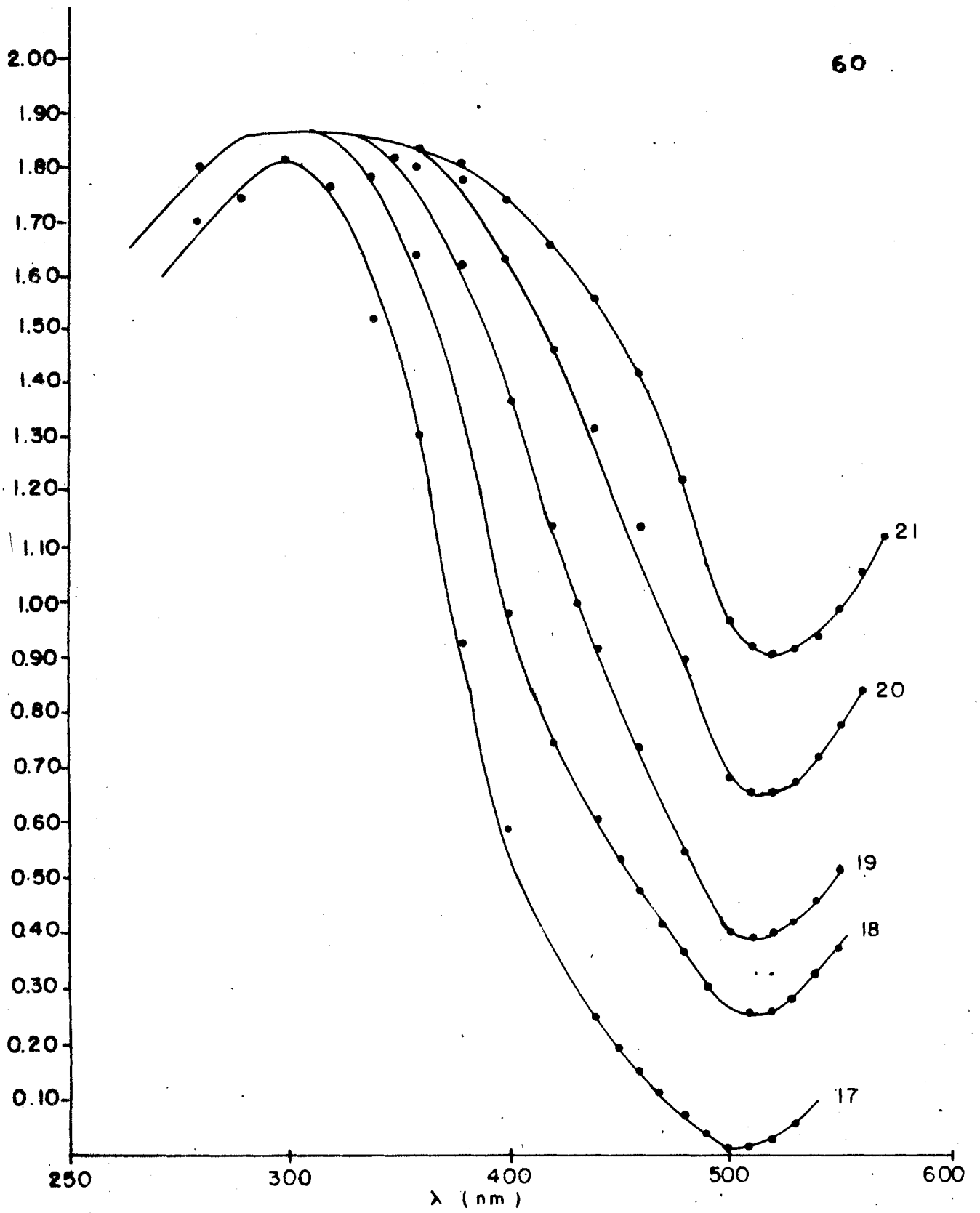


Fig. 7 Absorbance vs wavelength of the same concentration observed over different hours

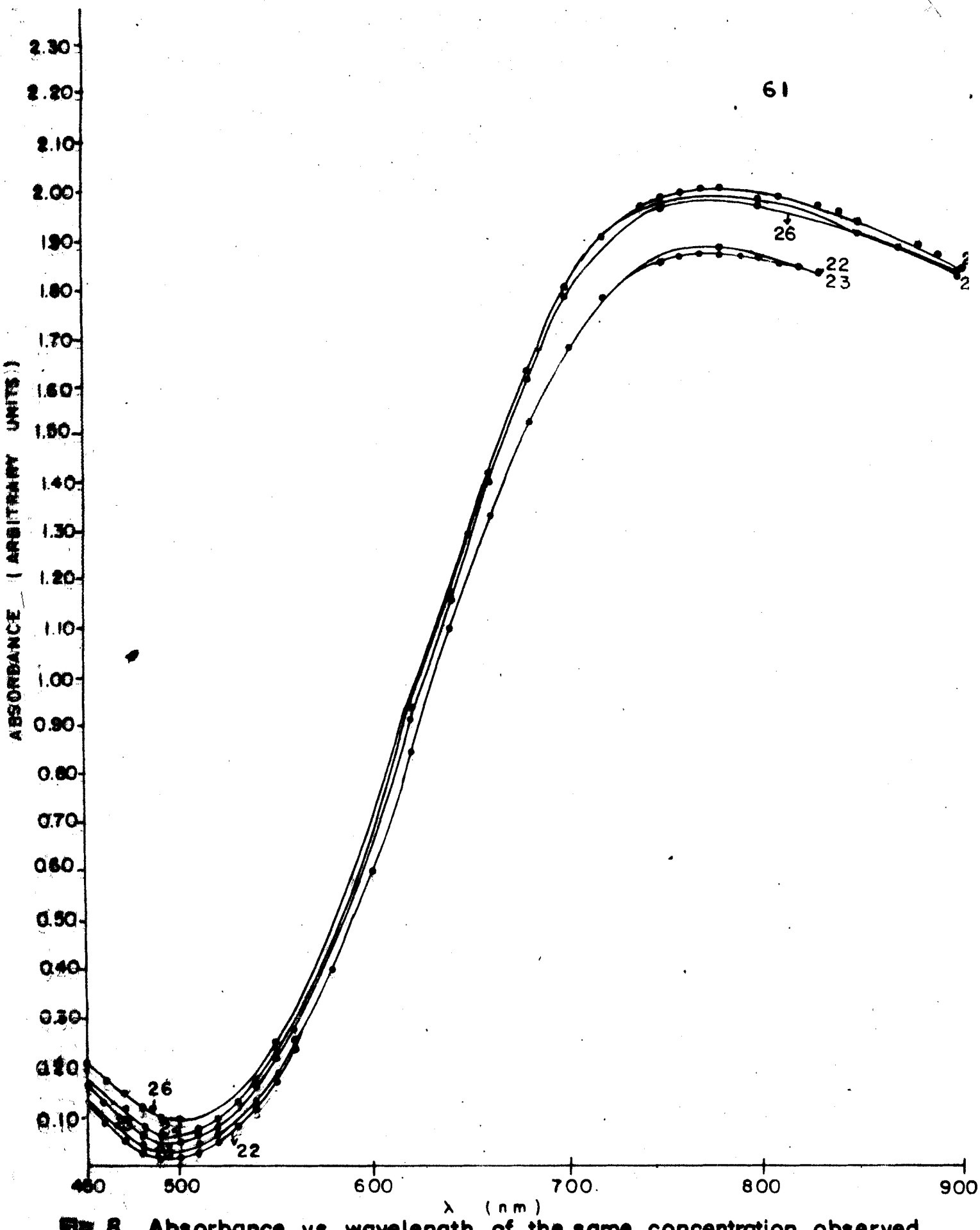


Fig. 8 Absorbance vs wavelength of the same concentration observed over different hours

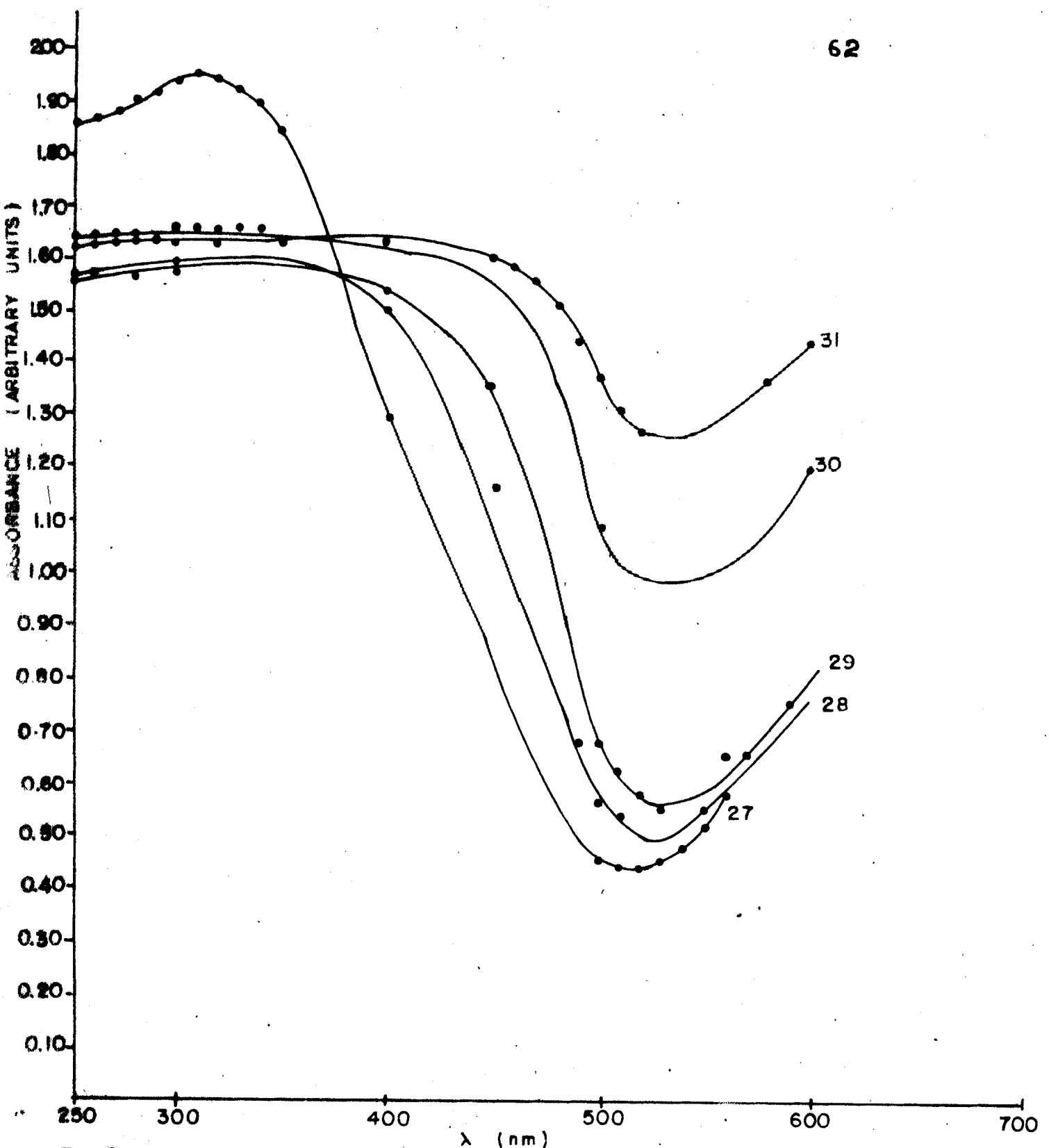


Fig. 9 Absorbance vs wavelength of the same concentration observed over different times

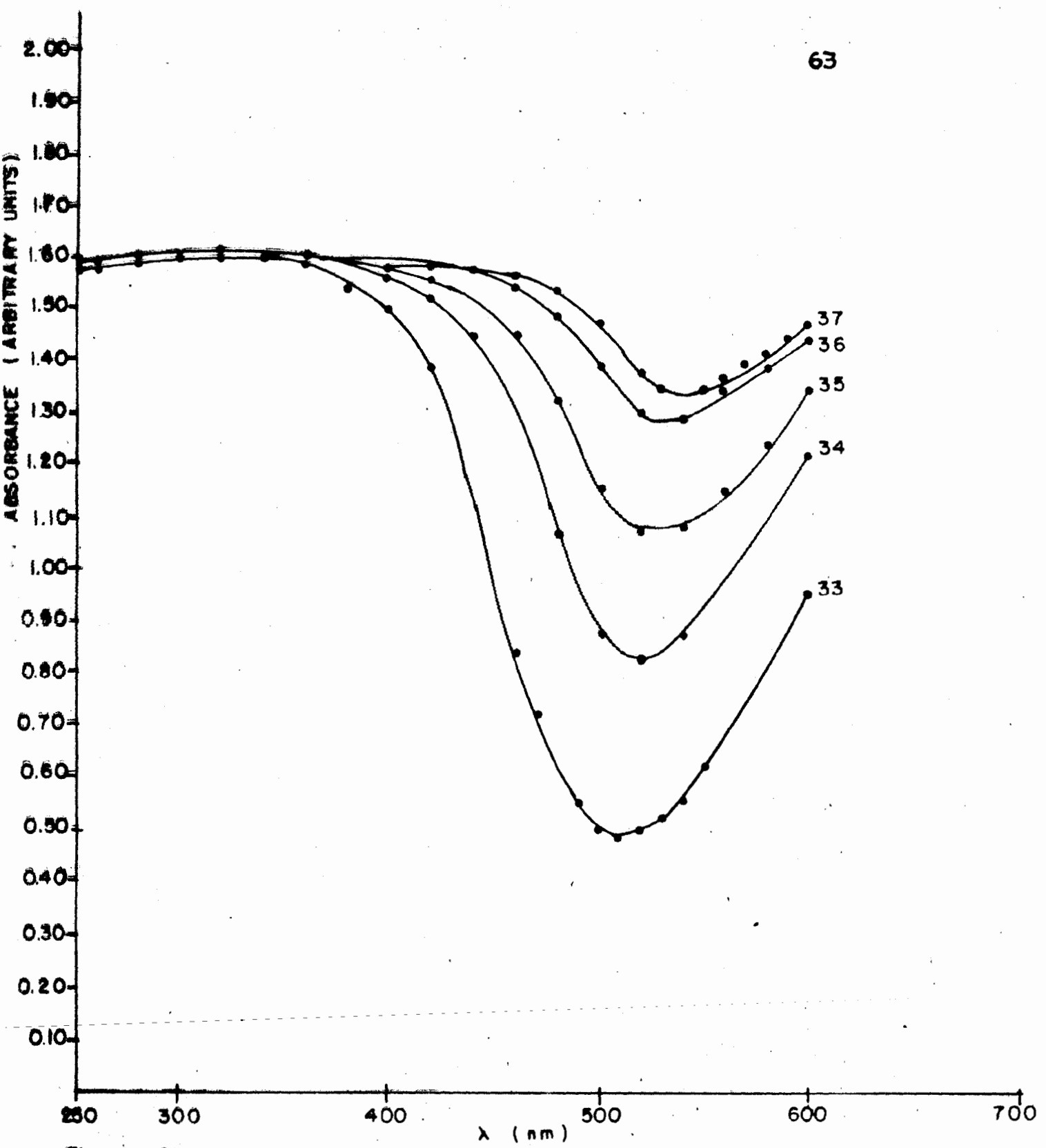


Fig. 10 Absorbance vs wavelength of the same concentration observed over different times

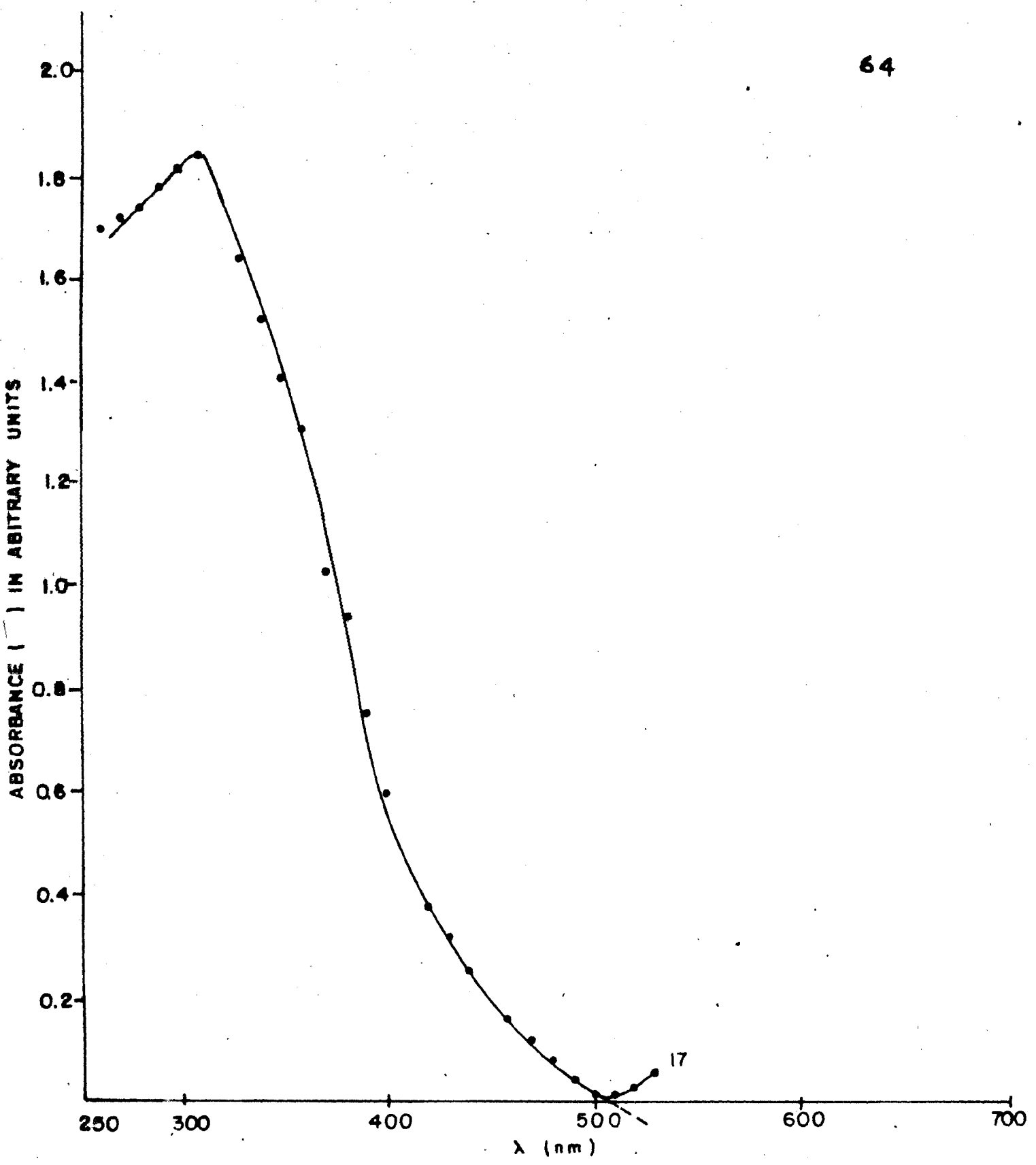


Fig. 11 Absorbance vs wavelength observed over 2 hours

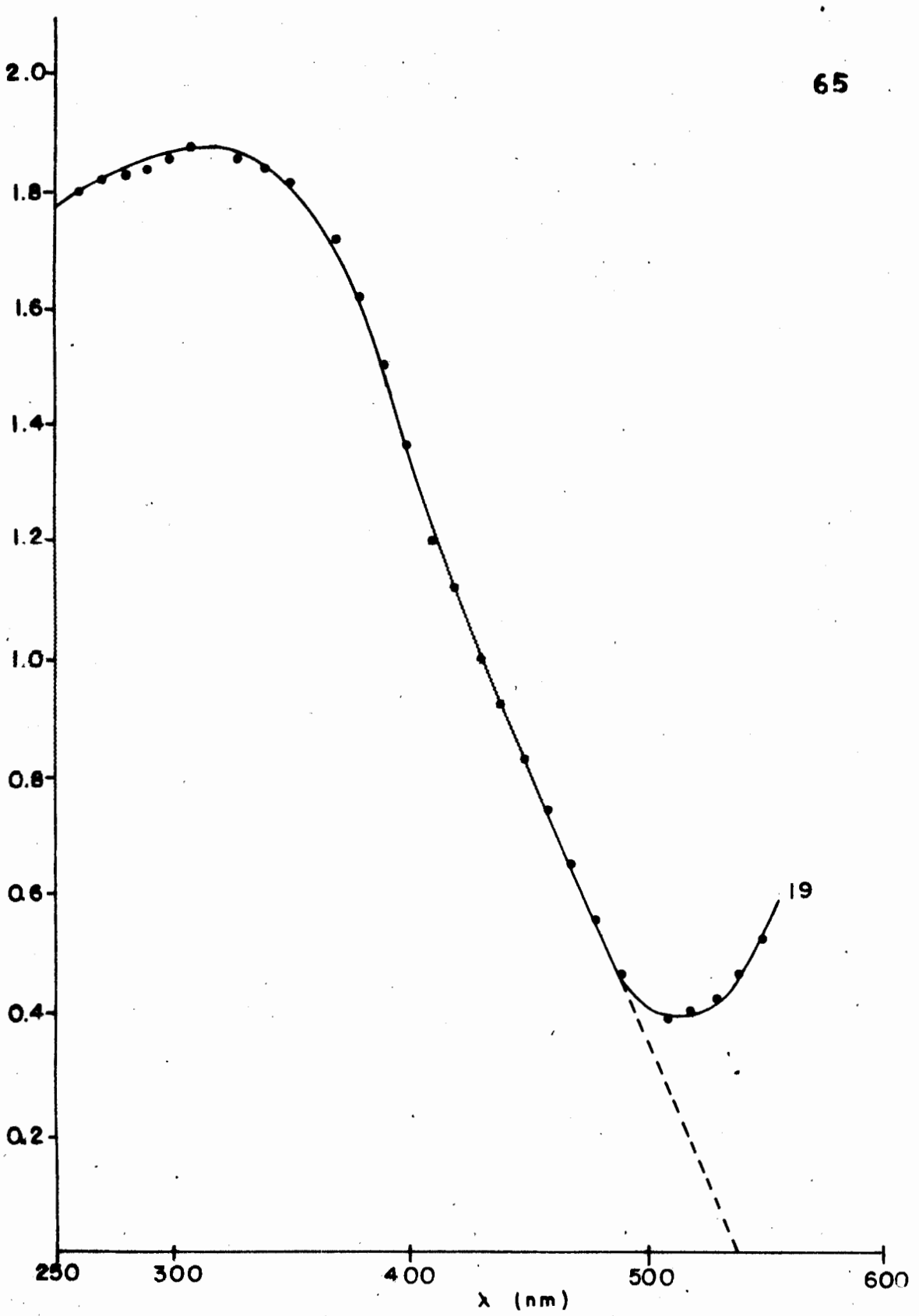


Fig. 12 Absorbance vs wavelength observed over 4 hours

4.2 Absorbance Versus wavelength:

Wevelength (nm)	absorbance(∝) inabitrary units	wavelength (nm)	absorbance(∝) in abitrary units
260	1.70	440	0.25
280	1.74	460	0.16
300	1.82	470	0.12
310	1.84	480	0.08
320	1.76	490	0.04
340	1.52	500	0.02
360	1.30	510	0.02
380	0.93	520	0.03
400	0.59	530	0.06
420	0.37		

Table 4:

Wavelength (nm)	absorbance( ) in abitrary units	Wavelength (nm)	Absorbance ( ) in abitrary unit
260	1.80	420	1.12
280	1.83	440	0.92
300	1.86	460	0.74
310	1.88	480	0.55
320	1.88	500	0.40
330	1.86	510	0.39
340	1.84	520	0.40
360	1.80	530	0.42
380	1.62	540	0.46
400	1.36	550	0.52

Table 5:

The value got by extrapblation from the absorption spectra as shown in Figs. 11 and 12 was used to calculate the band gap.

The value of the band gap got was 2.43 $\pm$ 0.01 eV. This value compared favourably with the characteristic band gap for CdS 2.420eV at 29^{o}C.[62]

Fig. 7 shows curves of absorbance versus wavelength for the same concentration of 10ml 1M $(CH_3COO)_2Cd.2H_2O$, 10ml 7.45M TEA, 10ml 17.05M NH_3, 10ml 1M $SC(NH_2)_2$ observed over a period of 2 to 6 hours.

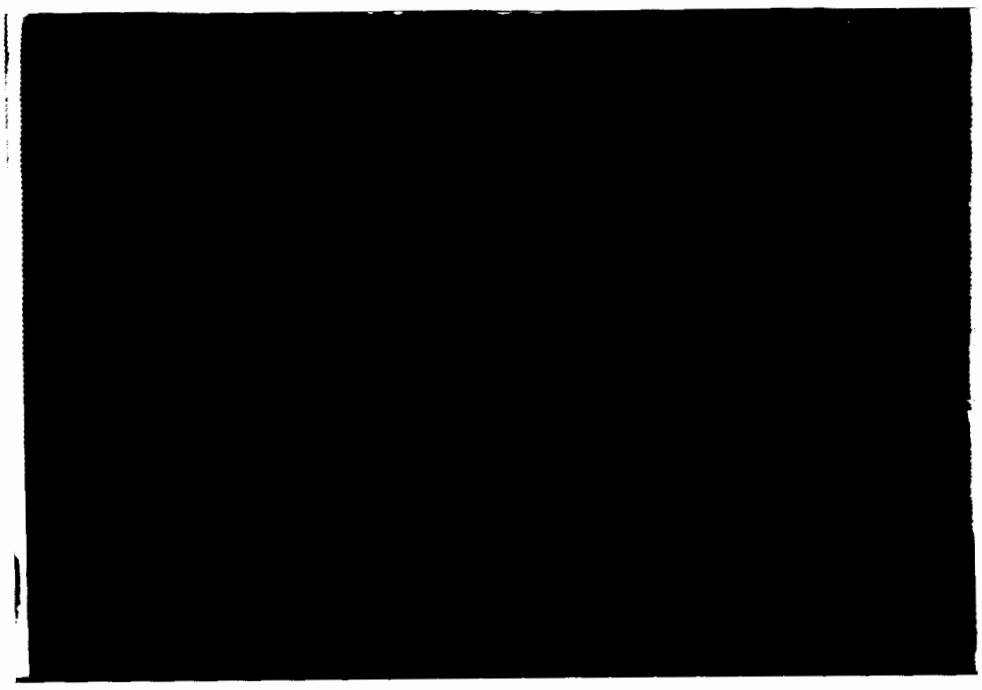
Fig. 8 shows curves of absorbance versus wavelength for the same concentration of 10ml 1M $(CH_3COO)_2Cd.2H_2O$, 10ml 7.45M TEA, 10ml 1M $Sc(NH_2)_2$ and no NH_3 observed over a period of 2 to 6 hours.

Fig. 9 shows curves of absorbance versus wavelength for the same concentration of 10ml 1M $(CH_3COO)_2$ $Cd.2H_2O$, 10ml 7.45M TEA, 10ml 17.05M NH_3 and 20ml 1M $SC(NH_2)_2$ observed over a period of 1 to 6 hours.

Fig. 10 shows curves of absorbance versus wavelength for the same concentration of 10ml 1M $(CH_3COO)_2Cd.2H_2)$, 5ml 7.45M TEA, 10ml 17.05M NH_3, 20ml 1M $Sc(NH_2)_2$ observed over a period of 2 to 6 hours.

Fig 11 and 12 are of the same concentration as Fig. 7, observed over 2 and 4 hours respectively.

The curves in all cases showed the same patter, but for the case where NH_3 was not used. The maximum absorbance for Fig 8 is between 700-800nm while that of the others fall between 250-350nm. This is the ultraviolet region.



PICTURE OF GROWN CdS THIN FILM

4.3 CONCLUSION

Cadmium sulphide (CdS) is a crystalline substance in two solid phases; α-CdS and β-CdS. Both modifications are observed at all temperatures and their coexistance is a function of substrate temperature and thin film thickness. The admixtures of α and β in different proportions account for the colour variations. When in tufts of hair-like needles crystals are yellow, whereas larger crystals are brownish-yellow. This is due to the relative amount of light that is transmitted and reflected.[63, 64]

The deposition of n-type thin film of CdS on glass substrate has been successful. The band gap of 2.43 $\pm$ 0.01eV at 30^{o}C compares favourably with the characteristic bandgap of 2.42eV for CdS.

From eauation (1.6) which states thus:

$$n = \frac{V_{oc}\, J_{sc}\, FF}{P_{in}}$$

we see that large values of Voc and Jsc if generated, yield higher efficiency. Practically this is not the case as Voc cannot exceed the band gap of the semiconductor.[65] Hence materials with larger band gaps generate larger values of Voc and are more efficient. CdS this has the advantage of a large band gap and performance better even at high temperatures and intensities, since semiconductors with larger band gaps generate lesser electron-hole pairs. Electron-hole pairs are responsible for uncontrolled temperature dependent current

flow. The band gap of CdS makes it a potential material for solar cells.

We have also seen that solution growth technique deposits thin films that compare favourably with those produced by other methods. It has the advantage of low cost as it does not require soffisticated equipments.

TEA has also been shown to be a good complexing agent for CdS thin film growth.

Suggestion For Further Study:

Due to the inability to measure other material properties like; resistivity, minority carrier, life-time, carrier recombination velocity, grain size etc, a complete assessment of the film has not been possible. With improved facilities, these properties could be assesed. Also, the variation of film thickness against growth time for other temperatures could be studied.

By carrying on further study, the exact amounts of the substances used could be determined and acertained to yield maximum thickness.

REFERENCES

1. Hsieh, J.S. Solar Energy Engineering, New Jersey: Prentice-Hall Inc. (1986).

2. Ibid.

3. Ibid.

4. Debney, B.T. and Knight, J.R. Contemporary Physics. 19(1978) 1.

5. Hsieh, J.S. Solar Energy Engineering, New Jersey: Prentice-Hall Inc. (1986).

6. Jansen, T.J. Solar Engineering Technology, New Jersey: Prentice-Hall Inc. (1985).

7. Priest, J. Energy For A Technological Soceity. Reading: Addison-Wesley (1979).

8. Bolton, J.R. Solar Power And Fuels, New York: Academic Press Inc. (1977).

9. Debney, B.T. and Knight, J.R. Contemporary Physics 19(1978).

10. Bolton, J.R. Solar Power And Fuels, New York: Academic Press Inc. (1977).

11. Ewers, W.I. Solar Energy. A Biased Guide, Northbrok Illinois: Domus Books Inc. (1979).

12. Kreider, K.F. and Kreith, F. Solar Energy Handbook, New York: McGraw Hill Inc. (1981).

13. Cherry, W.R. "The Generation Of Pollution Free Electrical Power From Solar Energy". Transactions Of The ASME, Journal Of Engineering For Power. (1972).

14. Ahmed, H. and Spreadbury P.J. Electronics For Engineers. Cambridge: Cambridge University Press, 1973.

15. Ibid.

16. Uman, M.F. Introduction To The Physics Of Electronics New Jersey: Prentice-Hall Inc. 1974.

17. Ibid.

18. Ibid.

19. Okujagu, C.U. "Spectral Selective Windows", Unpublished Ph.D Thesis. University of Nigeria, Nsukka (1991).

20. Ibid.

21. Ibid.

22. Jansen, T.J. Solar Engineering Technology, New Jersey: Prentice-Hall Inc. (1985).

23. Okujagu, C.U. "Spectral Selective Windows", Unpublished Ph.D Thesis, University of Nigeria (1991).

24. Hsieh, J.S. Solar Energy Engineering, New Jersey: Prentice-Hall Inc. (1986).

25. Okujagu, C.U. "Spectral Selective Windows", Unpublished Ph.D Thesis. University of Nigeria, Nsukka (1991).

26. Kreider, K.F. and Kreith, F. (eds). Solar Energy Handbook. New York: McGraw-Hill (1981).

27. Okujagu, C.U. "Spectral Selective Windows", Unpublished Ph.D Thesis. University of Nigeria, Nsukka (1991).

28. Debney, B.T. and Knight, J.R. Contemporary Physics 19(1978).

29. Hsieh, J.S. Solar Energy Engineering, New Jersey: Prentice-Hall Inc. (1986).

30. Debney, B.T. and Knight, J.R. Contemporary Physics 19(1978).

31. Ibid.

32. Hsieh, J.S. Solar Energy Engineering, New Jersey: Prentice-Hall Inc. (1986).

33. Priest, J. Energy For A Technological Society, Reading: Addison-Wesley, (1979).

34. Lindmeyer, J. and Allison, J.F. Com. Sat. Technical Review. 3(1973) 1.

35. Debney, B.T. and Knight, J.R. Contemporary Physics 19(1978).

36. Bates, M.E., Locks, F.M. and MLavsky, A.I. Conference Record Of The 9th IEEE Photovoltaic Specialists Conference (1972), 386.

37. Chopra, K.L. and Das, S.R. Thin Film Solar Cells, New York: Phenub. Pub. Co. (1983), 7.

38. Ibid.

39. Ibid, 195

40. Ibid, 197

41. Ibid.

42. Ibid, 187.

43. Okujagu, C.U. "Spectral Selective Windows", Unpublished Ph.D Thesis. University of Nigeria, Nsukka, (1991).

44. Chopra, K.L. and Das, S.R. Thin Film Solar Cells, News YorK: Phenub Pub. Co. (1983) 221.

45. Ibid, 222.

46. Dunn, T.M. McClure, D.S. and Pearson, R.G. Some Aspects Of Crystal Field Theory, New York: Harper and Row Pub. 1965.

47. Figgis, B.N. Introduction To Ligand Fields, New York: Interscience Pub. Inc. (1966).

48. Basola, F. and Pearson, R.G. Mechanisms Of Inorganic Reactions (2nd ed), New York: John Wiley and Sons Inc. (1967).

49. Chaberek, S. and Martell, A.E. Organic Sequestering Agents, New York: John Wiley and Sons Inc. (1959).

50. Langford, C.H. and Gray, H.B. Ligand Substitution Processes, New York: W.A. Benjamin Inc.(1966)

51. Day, M.C.Jr. and Shelbin, J. Theoritical Inorganic Chemistry (2nd ed), New York: Van Nostrand Reinhold Co. (1969).

52. Ibid, 393.

53. Bardsley, W., Hurle, D.J.J. and Mullin, J.B. Crystal Growth: A Tutorial Approach, North-Holland Series in Crystal Growth. Amsterdam: 2(1979).

54. Sharma, N.C., Pandya, D.K. Sehgal, H.K. and Chopra, K.L. Thin Solid Films, 59(1979) 157.

55. Kaldis and Scheel, H.J. (ed). Current Topics In Material Science. "Crystal Growth And Materials ECC G-1" Zurich, Amsterdam: North Holland Pub. Co. (1977).

56. Dean, J.A.(ed). Lange's Handbook Of Chemistry (11th ed), New York: McGraw-Hill Inc. (1973).

57. Treadwell, F.P. Analytical Chemistry, New York: New York: John Wiley and Sons, 1(1937).

58. Chopra, K.L. and Kaus, I. Thin Film Device, Applications. New York: Plenum Press, (1983).

59. Eisbergy, R.M. Fundamentals Of Modern Physics, New York: John Wiley and Sons (1961) 66;68.

60. Bentley, J.B. and Bottomley, G.L. Practical Chemistry, London: Chatto and Windus, (1964) 66.

61. Chopra, K.L. and Das, S.R. Thin Film Solar Cells, New York: Phenub Pub. Co. (1983).

62. Dean, J.A. (ed). Lange's Handbook Of Chemistry. (11th ed), New York: McGraw-Hill Inc. (1973).

63. Mellor, J.W. A comprehensive Treatise On Inorganic And Theoritical Chemistry, London: Longmans 4(1960)593.

64. Brian, R.P. (ed). Crystal Growth. Hungary: (1975) 571.

65. Debney, B.T. and Knight, J.R. Contemporary Physics. 19(1978).