CHAPTER II
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2.1 Introduction

The recent technology requires various types of thin film materials for a variety of applications /1/. The thin film can be single of multicomponent, alloy/compound or multilayered coatings on substrates of different shapes and sizes /2-4/. The various properties of the thin films can be depending on the applications, high optical/reflection/transmission, hardness, wear resistance, single or polycrystal nature etc. The films with such a versatile properties can be obtained by the techniques of the thin films deposition /3-6/. The structure of the thin films is complex (in view of their applications) which demand tailor-made properties and therefore sophisticated characterisation techniques have emerged out for better understanding of multifarious properties of the thin films. Depending on the property of interest, a host of characterisation tools are available for giving sometimes similar and more often additional and complimentary informations. No one technique is sufficient to characterise a thin film completely even in any one domain such as crystal structure, chemical and physical nature etc. The properties relevant for thin film studies and corresponding characterisation methods are so many that it is impossible to cover all the aspects in any one of the reviews. Further, thin film properties are extremely sensitive to a method of formation and it is quiet obvious that no one technique can deposit the thin film covering all the required and selective properties.

The basic steps involved in a thin film formation process are:

1) creation of material(s) to be deposited in an atomic, molecular or perticulate forms prior to the deposition.

2) transport of the material(s) thus created in the form of a vapour stream or solid or spray etc to the substrate.

3) deposition of the material(s) on the substrate and film growth by a nucleation and growth process.

All the deposition techniques can be distinguished by the way the three basic steps above are effected. One can, in principal, get the films of desired properties by properly modifying these three steps.

2.2 Thin Film Deposition Techniques

Thin film deposition methods have been broadly classified as:

a) Physical Vapour Depositions(PVD), b) Chemical Vapour Depositions(CVD), c) Electroless or Solution Growth Deposition and d) Electrochemical Deposition (ECD).

a] Physical vapour depositions (PVD)

The physical vapour deposition techniques are those in which the material to be deposited is made available in an atomic, molecular or particulate form before being put for deposition. The PVD´s can further be subdivided into:

i) Thermal Evaporation (TE), ii) Electron Beam Evaporation (EBE), iii) Molecular Beam Epitaxy (MBE), iv) Activated Reactive Evaporation (ARE) and v) Ion Plating.

The first three techniques are different in the way the vapour beam is created (step 1). In ARE, step 2 is modified in that the vapour beam is transported through a reactive plasma. In ion plating, conditions at the substrate (step 3) are modified by

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an ion beam. The major advantage of using PVD techniques is that all the above three deposition steps can be independently controlled. However this spells out a warning that the deposition parameters should be carefully monitored and controlled in order to achieve reproducible deposits. The details of all the PVD techniques are beyond the scope of this dissertation.

b] Chemical deposition techniques

Chemical deposition techniques are the most powerful tools for the growth of thin films owing to their versatility for depositing a very large number of elements and compounds at relatively low temperatures /7-10/.

These films can be deposited with required stoichiometry in both vitreous and crystalline layers with a high degree of perfection and purity. Large or small and even or uneven surfaces of all types can be coated with relative ease and the processes are very economical and have been industrially exploited on large scale. The various deposition processes are as follows:

i) Chemical vapour deposition (CVD), ii) Spray pyrolysis, iii) Electrodeposition, iv) Anodization, v) Screen printing, vi) Solution growth or chemical bath deposition (CBD) etc.

A detailed history of each of the above technique is not possible to mention here however, a short account is presented for the sake of understanding.

i) Chemical vapour depositions (CVD)

A CVD is a process in which condensation of compound(s) from the gas phase onto a substrte where reaction occurs to produce a

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solid deposit. A liquid or solid compound to be deposited is made gaseous by volatilization and is caused to flow either by a pressure difference or by the carrier gas to the substrate. The chemical reaction is initiated at or near the substrate surface to produce the desired deposit on the substrate. In some processes the chemical reaction may be activated through an external agency such as heat, R.F.field , light, x-rays, electric field or glow discharge, electron bombardment etc. The morphology, microstructure and adhesion of the deposit is dependent on the nature of the reactions involved. These are thermal decomposition, hydrogen reduction, nitridation, carbidization or oxidation, disproportionation, chemical transport and the combined reactions.

The deposition may be either heterogeneous or homogeneous. The homogeneous depositions produce powdery or flaky deposits. The feasibility of CVD processes can be predicted by studying the thermodynamics of the reactions. The reaction kinetics and the mechanism of film formation are so different in individual processes that a generalised account is not possible. However, some of the important features common to all these methods are: 1) CVD set-ups are simple and fast recycle times are possible, 2) high deposition rates are achieved, 3) deposition of the compounds and multicomponent alloys and control of their stoichiometry is possible, 4) epitaxial layers of high perfection and low impurity content can be grown, 5) objects of complex shapes and geometries can be coated and 6) in-situ chemical vapour etching of the substrates prior to deposition is possible. The factors which are uncommon and affect the deposition,

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uniformity, composition and properties of the thin film layer are:

1) The thermodynamics and reaction kinetics are very complex and are poorly understood.

2) The working temperatures are higher compared to PVD processes.

3) Highly toxic sometimes explosive and corrosive gases and volatile products are involved in the reactions. These may attack the substrate surface and the chamber walls.

4) Higher temperatures lead to diffusion, alloying or to a limited choice of the substrate materials.

5) Uniformity of the deposits and masking of the substrates are usually difficult.

ii) Spray pyrolysis

This is essentially a thermally stimulated reaction between clusters or liquid/vapour atoms of different spraying solutions of the desired compounds onto a substrate maintained at elevated temperatures. The sprayed droplets on reaching the hot substrate undergo pyrolitic decomposition and form a single crystal or clusters of a crystallite of the product. The other volatile byproducts and excess solvents escape in the vapour phase. The thermal energy for decomposition, subsequent recombination of the species, sintering and recrystallisation of the crystallites are provided by the hot substrates.

The chemicals used for this method should be such that the desired thin film material must be obtained as a result of thermally activated reaction between the different species and

remainder of the chemical constituents. The carrier/gas should be volatile at the deposition temperature. Growth of the film by spray pyrolysis is determined by the nature of substrate, chemical nature and concentration of the spraying solutions and spray parameters. The films are in general strong and adherent mechanically hard, pinhole free and stable with time and temperature. The topography of the films is generally rough and independent on spray conditions.

iii) Electrodeposition

It is the process of depositing a substance on an electrode by electrolysis; the chemical changes being brought about by the passage of a current through an electrolyte. Up on immersion of an electrode in a solution containing ions of the electrode itself, a dynamic equilibrium of the kind $E \Longleftrightarrow E^+ + Xe$ (E-electrode atom) is achieved. The electrode gains a certain charge on it which attracts oppositely charged ions and molecules, holding them at the electrode/electrolyte interface. A double layer consisting of an inner layer of water molecules and outer layer of the charge opposite to that on the electrode is formed. During deposition ions reach the electrode surface, stabilise on it, release their ligands and charge and undergo electrochemical reaction. The depletion of the depositing ions from the double layer is compensated by a continuous supply of fresh ions from the bulk of the electrolyte. The transport of ions to the depletion region occur due to the diffusion owing to the concentration gradient and migration owing to the applied electric field and convection currents. The factors influencing the electrodeposition process are : 1) pH of the electrolyte, 2)

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current density, 3) temperature, 4) bath composition, 5) electrode shape and 6) agitation.

iv) Anodization

It is an electrolytic process wherein metal is made the anode in a suitable electrolyte. When an electric current is passed, the surface of the metal is converted into its oxide having decorative, protective or other properties. The cathode is metal or graphite where H_2 involves. The pH of the electrolyte playes an important part in obtaining the coherent films. Thickness of the oxide layer depends on the voltage applied to the metal, temperature of the bath and time of the deposition.

v) Screen printing

Screen printing is essentially a thick film process in which pastes containing the desired material are screen printed by a conventional method onto a suitable substrate to define conductor, resistor or a device pattern. Subsequently, the substrate is kept under appropriate conditions of the time and temperature to yield the rugged components bonded to the substrate. The substrates which have smooth surface, capability of withstanding for higher temperature, mechanical strength, high thermal conductivity and good electric properties and are compatible with the film material paste are used (alumina, beryllia, magnesia, thoria and zirconia). The paste to be used normally consists of : 1) a metallic /resistive/dielectric /semiconducting component in finely divided powder form., 2) bonding agent, 3) an organic suspension medium and, 4) an organic diluent medium. Semiconductors like CdTe, CdS, CdSe etc can be

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deposited by this technique.

2.3 Chemical Deposition Method and Preparation of As$_2$S$_3$ Thin Films

2.3.1 Chemical bath deposition method : Salient features

Various deposition methods are available for thin film praparation and only few are presented in the above article which produce polycrystalline thin films for use in diverse applications. Out of these methods, chemical bath deposition (also known as solution growth deposition, controlled precipitation method, electroless deposition or simply chemical deposition) is relatively inexpensive, simple and convenient method for large area deposition of II-VI and IV-VI compounds/7-10/. The method does not require sophisticated and expensive instrumentations like vacuum system and other cost involving equipments. It can be carried out just in a glass beaker. Only a hot plate and a stirrer are the equipments needed and hence the power consumption is almost negligible. The starting material are commonly avaible and cheap. The chemical bath deposition is ideally suited for large area deposition and can be achieved by using a large volume vessel only. A large number of substrates can be coated in a single run with a proper design. Positioining the substrates in a design along the walls of the reaction vessel is a simple technique to obtain a large number of coatings. Unlike in electrodeposition, electrical conductivity of the substraete is not a hard and fast requirement for this technique. Hence, any insoluble surface to which the solution has free access will be a suitable substrate for deposition. The lower deposition temperature avoids oxidation or corrosion of metallic

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substrates. The method results in pin hole free uniform, adhesive deposits as the solution from which the films are deposited always remains in touch with the substrates. Finally, stoichiometric deposits can easily be obtained since the basic building blocks are ions instead of atoms.

In a chemical deposition method, the film forms slowly which facilitates better orientation of the crystallites with improved grain structure. The quality of the thin films so obtained is dependent on the deposition conditions such as the bath temperature, stirring rate or speed of the substrate rotation, pH, solution concentration and its purity and quality of the substrates.

2.3.2 Growth kinetics

The growth kinetics of this method is two fold: i) first, it proceeds by ion-by-ion condensation at the nucleation sites on the immersed surfaces. The ion-by-ion growth has been reported for PbSe, CdS, CdSe, PbS and HgS thin films /9,10/. ii)secondly, nucleation takes place by adsorption of the colloidal particles and growth takes place as a result of the surface coagulation of these particles giving thin and adherent films. This is known as cluster-by-cluster growth of the films /11/.

The kinetics of film growth depend on various deposition paramerters and the method of formation. In the case of alkaline bath, the growth kinetics is reported to be both by ion-by-ion and cluster-by-cluster of the molecules under different deposition conditions. The ion-by-ion growth results in thin, uniform, hard, adherent and specularly reflcting films where as

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the cluster-by-cluster growth gives thick, powdery, flaky, diffusely reflecting films. Once the nucleation occurs, the deposition rate rises rapidly and becomes almost zero resulting in a terminal thickness of a layer; which is a maximum attainable thickness under given set of experimental conditions. For the nucleation to start at a certain local inhomogeneity, certain time is required referred to as incubation period. On a pre-sensitised substrate, no incubation period for nucleation should observe, since nucleation centres already exist on the substrate. Also when substrates are suspended in a container before forming the complex in the solution, film thickness increases in a manner similar to that of pre-sensitised surface thereby showing that the nuclei for the formation of film are provided by the solution itself /8,10/.

The solution growth method for thin film formation is not only applicable to metal chalcogenides (as mentined earlier) but to oxide thin films too.
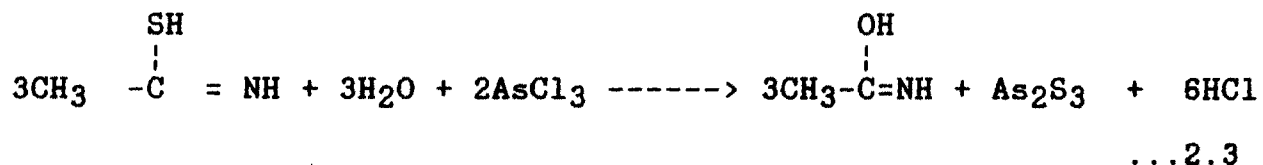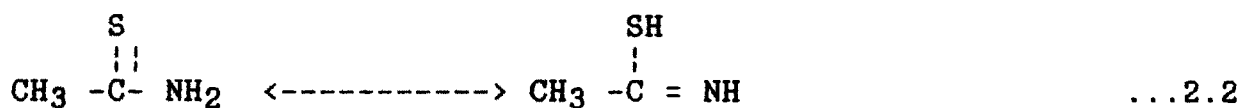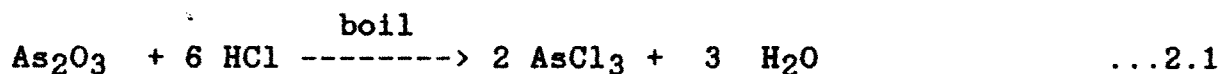
2.3.3 Mechanism of As₂S₃ film formation

The As_2S_3 thin films have been deposited onto the glass substrates by using a chemical bath deposition method that allows the glass substrates to remain in a non-aqueous solution of the reactants. The preparation of the As_2S_3 thin films is carried out in an acidic medium in the presence of a complexing agent and therefore, the formation of As_2S_3 films is made possible on the basis of the slow release of As^{3+} and S^{2-} ions and their subsequent condensation on the substrate support /12/. By this process, the film forms slowly which provides better orientation of the crystallites of arsenic trisulphide with improved grain

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structure. Depending on the deposition conditions (viz. temperature, pH of the solution, solution concentrations and its purity and quality of the substrates) the film growth can take place either by ion-by-ion condensation of the material on the substrates or by the adsorption of the colloidal particles from the solution onto the substrates/12 - 15/. The process of precipitation of As_2S_3 from the solution onto a substrate depends mainly on the formation of nucleus and subsequent growth of the thin film. The concept of nucleation in a solution is that the cluster of the molecules formed undergo rapid decomposition and the decomposed particles combine to grow upto a certain thickness of the film beyond which no further building up of thickness occurs /11,14/. The nucleation starts at some local inhomogeneity when ionic product exceeds the solubility product. Growth of these nuclei by the addition of more and more ions from the solution results in formation of stable nucleoid of the size greater than the critical size and further growth results in the formation of colloidal disperaion. The primary colloids adsorb and sta nucleating forming thin, adherent and reflecting films indicating the cluster by cluster growth of the film.

Actually the film deposition was carried out by the reduction of arsenic using methanol as the reducing agent. For the optimized conditions, bath composition was 0.5 M $AsCl_3$ and 0.5 M thiourea, bath temperature was 30°C, pH of the resulting solution was 2.5 and time of deposition was 96 h. Arsenic trisulphide thin film formation is based on the slow release of As^{3+} and S^{2-} ions in acidic medium (pH 2.5) followed by their

subsequent condensation on the glass substartes. The precipitation of arsenous sulphide from the solution onto the substrate surface depends mainly on the so called "process of nucleation" and its subsequent growth so as to form a continuous thin solid film.The series of chemical reactions proposed for the film formation are;

$$As_2O_3 + 6\ HCl \xrightarrow{\text{boil}} 2\ AsCl_3 + 3\ H_2O \qquad \qquad ...2.1$$

$$CH_3 -\overset{\overset{\displaystyle S}{\|}}{C}- NH_2 \longleftrightarrow CH_3 -\overset{\overset{\displaystyle SH}{|}}{C} = NH \qquad \qquad ...2.2$$

$$3CH_3 -\overset{\overset{\displaystyle SH}{|}}{C} = NH + 3H_2O + 2AsCl_3 \longrightarrow 3CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=NH + As_2S_3 + 6HCl$$

$$...2.3$$

It is clear from the above chemical reactions that the growth rate is affected by the concentrations of the basic source materials and therefore, the concentration of As^{3+} and S^{2-} ions were varied to optimise the conditions for the deposition. The optimum concentrations of As^{3+} and S^{2-} ions were selected as 0.5 M as it is determined from the variation of film thickness with the concentration.

2.3.4 Effect of various preparative conditions on film growth

The rate of deposition and terminal thickness both depend on the number of nucleation centres, supersaturation of the solution and stirring rate. The growth kinetics depend on the concentration of the ions, their velocities and nucleation and various growth processes upon immersed substrates. The effect of

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various deposition conditions on these parameters is discussed below, mainly in relation with the chlacogenide thin films.

The deposition rate and thickness of the film depend on the pH of the reaction mixture, temperature of the reaction bath and concentration of the chemicals used. The optimum conditions for getting adherent, uniform and reproducible As_2S_3 thin film deposits have been obtained by varying the molar concentrations of the starting chemicals, tempearature of the deposition bath, time of the deposition etc. In our case As_2S_3 film formation is carried out under the following optimised conditions:

i) Bath composition- $AsCl_3$ (0.5 M) and thiourea (0.5 M) in the stoichiometric ratio (2:3).

ii) Bath temperature- 30°C.

iii) Deposition time- 96 h.

iv) pH of the solution- 2.5.

a) Nature of the salt

The growth kinetics depend on the nature of the salts/compounds used for the metal and chalcogenide ions. In general, the rates and the terminal thickness are higher for the sulphides than for the corresponding selenides under similar conditions of deposition. The deposiion rate and terminal thickness initially increase with an increase in the chalcogen ion concentration. At higher concentrations, however, precipitation becomes more significant giving rise to decreased film thickness.

b) Complexing agent

An important function of the complexing agent is to supply controlled free metal ions for reduction and may be considered as

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a metal ions buffer. Stability constant indicate affinity of the complexant to the metal ion and their tendency to keep the metal ions in solution even at a pH range where metal hydroxide precipitation is possible. If complex formed is too stable, the reduction of metal ion by weak reductants may be completely inhibited. If the complexant is not sufficiently stable, spontaneous reduction in the bulk of solution will take place if strong reduction agents are used. The complexant selected should not lead in insoluble complexes that are complexed with no charge on them. Negatively charged complexes greatly influence the properties of the metal ion and hence the mechanism of deposition. Acetates, hydroxyacetates, succinates, hydroxypropionates, aminoacetates, aminopropionates, malonates, glycollates, lactates, pyrophosphates, citrates, tartarates, ammonia, ethylene diamine tetraacetic acid (EDTA), quadrol, triethanolamine(TEA), metahnol etc have been used as complexants.

c)pH of the bath

The addition of OH^- i.e increase in pH makes the complex more stable, provided the OH^- ions take part in the complex formation. The metal ion concentration is reduced, leading to a decrease in deposition and increase in terminal thickness with increasing pH value.

d) Bath temperature

Increase of the solution tempearature increases the dissociation of complex and the chalcogen bearing compounds (i.e. S^{2-} ion releasing rate). The increased concentration of metal and chalcogen ions coupled with higher kinetic energy of the ions

result in increase of ion-substrates interaction and yields a higher rate of deposition. Film thickness increases or decreases with increase in the bath temperature depending on the conditions under which films are prepared. At lower values of pH, supersaturation is high even at lower temperature and increases further with increase in temperature. Consequently at sufficiently high supersaturation, precipitation dominates and lower thickness is obtained. At high pH values, precipitation is limited due to the low supersaturation and most of the product is formed on the substrate. With increase in temperature, thermal dissociation of both complex and sulphide ion releasing agent takes place so that more metal and chalcogen ions are available for compound formation and higher thickness of the film is the result.

2.3.5 Preparation of As_2S_3 thin films

Arsenic trisulphide thin film layers have been prepared by a chemical growth process from an acidic medium. The substrate used were spectroscopic grade microslides obtained from blue star, Bombay.

a) Preparation of the substrates

The glass microslides were cut into the dimensions 72x10x2 mm and were utilised as the substrate support. As the stickness of the film layer has a direct bearing on the cleanliness of the substrates, the key precaution taken is the careful cleaning of the substrates. The substrates were cleaned by adopting the following procedure:

i) substrates were first washed with tap water and then boiled in a concentrated chromic acid (0.5 M) for 20 minutes and then kept

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in it for 48 hour.

ii) they were then taken out and washed with double distilled water.

iii) the substrates were again degreased with medium concentrated detergent solution and washed several times with a double distilled water.

iv) Acetone was used to remove water traces if any and the substrates were preserved in the dust free atmosphere.

b) Preparation of the solutions

The chemicals used for the preparation of the As_2S_3 thin films were as follows;

i)   arsenic trioxide (AR-grade) supplied by Loba chem, Bombay.

ii)   thiourea (AR), S-d-Fine Chem Ltd, Bombay.

iii) methanol (AR- grade), E-mark.

iv)   concentrated HCl, Glaxo - Bombay.

Arsenic trioxide was dissolved in a sufficient quantity of the concentrated HCl and a clear solution of $AsCl_3$ (0.5 M) was obtained.

c) Deposition of the As_2S_3 films

The reaction mixture consists of freshly prepared solutions of $AsCl_3$ and thiourea in a volumetric ratio (2:3). They were placed in a beaker 100 ml in capacity and stirred well by a magnetic stirrer so that a clear, homogeneous and faint greenish coloured solution was formed suggesting the formation of a complex containing sulphur and arsenic ions. A specially designed and fabricated substrate holder as shown in Fig.2.1. was used for the positioning the substrates vertically in to the reaction

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bath. The substrate holder was designed such that every mounted surface remains perpendicular to each other so that the proper orientation and churning of the raection mixture could be achieved if the holder is set into motion with a low speed. The steam of the substrate holder was fitted to a motor and for the experimental purpose we adjust the position of the motor so as to dip more than 2/3 portion of the substrates into the reaction mixture. The depostion of As_2S_3 sample was carried out at different temperatures for different time intervals (up to 120 hours). The samples were detached from the substrate holder, washed with double distilled water and preserved in a dark desiccator. The samples were then heat treated (1h) for varios controlled temperatures in a closed tight oven.

Fig.21

5 Cm

1 Cm

B

→S
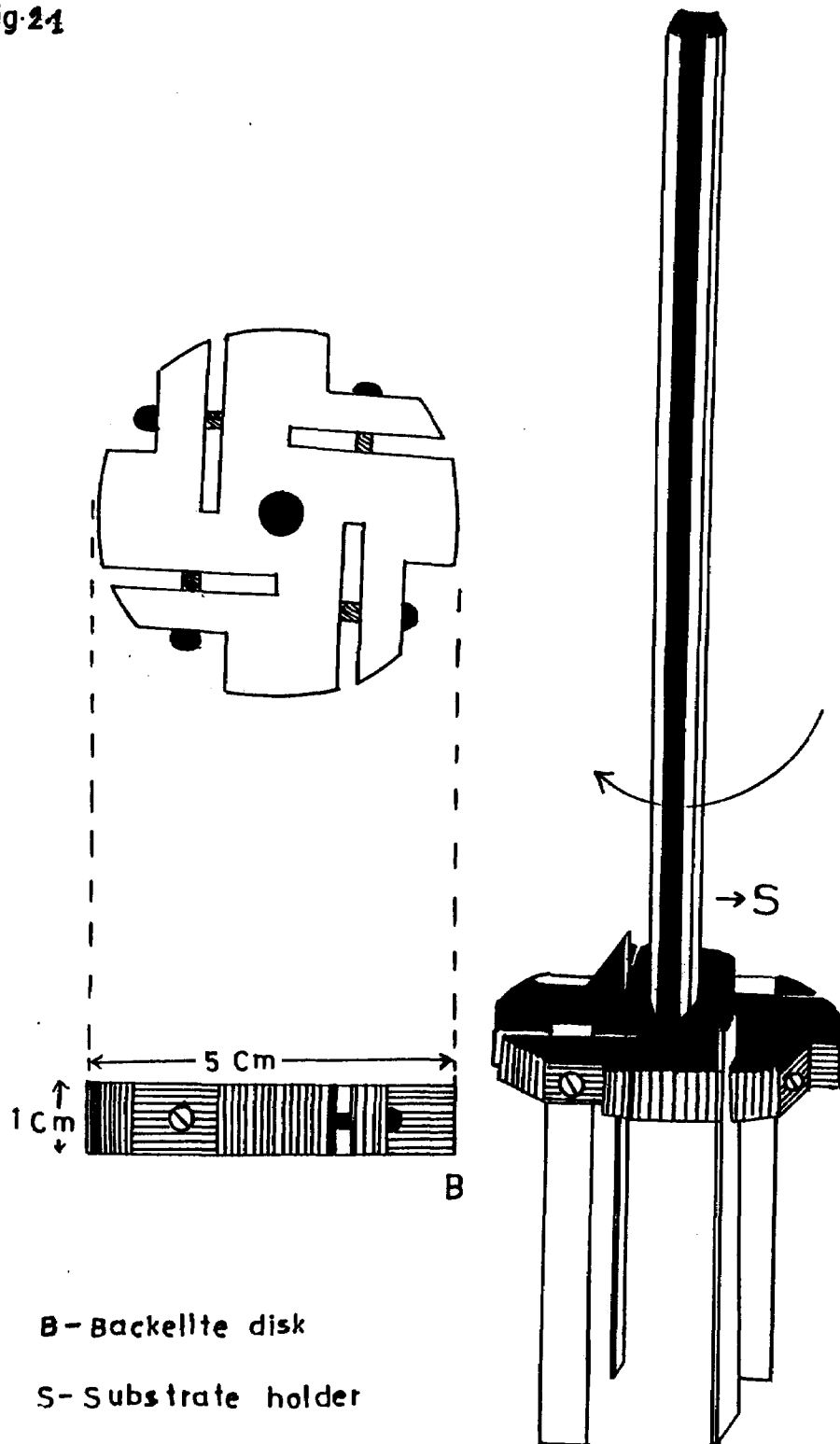
B - Backelite disk

S - Substrate holder

Fig-21 . Design of the substrate holder

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