Chapter I

Introduction

1.1. Introduction

The knowledge of physical properties of different materials for their possible applications in the daily life has always been a prime field of interest of the human civilization. The scientists of the present day technologically advanced society are still struggling hard for the fabrication of chief and efficient materials for a variety of technological applications. Condensed Matter Physics is enormously grown since the discovery of a pn-junction; one of the greatest achievements wherein replacement of many circuit elements takes place by a single semiconductor chip, called integrated circuit. The use of semiconductors has enhanced the quality of electronic devices and also reduced their cost and size. As successful as the semiconductor industry has been and as powerful as computers are, there is still a persistent motivation for improvement. More difficult computational problems always lay just out of the reach of current technology, in areas ranging from computational Condensed Matter Physics to weather forecasting to transportation scheduling. Undeniably, computing technology has improved at a more than acceptable rate thus far, with the performance of computers doubling roughly every two years. The recent remarkable progress in the electronic industry is governed by the dictum known as Moore's law [1], which predicts that the density of transistors on an integrated circuit doubles about once every two years. Since the transistor density is a rough measure of the attainable processing power, the consumers gain higher processing capabilities, smaller devices and smaller prices per unit. But the trend described by Moore's Law

is heading toward great difficulties. The reason for this impending cessation of progress is that the conventional approach of improving computers simply making circuit components smaller so they can be placed at higher densities on chips obviously has a limit. So far, manufacturers have been able to keep up with the dictum and increase in transistor density by reducing element size in a planar lithographic process. Current developments show that, with lithographic processes, it will be feasible to decrease structure sizes to the scale of a few nanometers. Soon, the dimensions of an individual device will reach a limit where quantum mechanical processes start to dominate carrier transport. Even now, as a result of interface quality and quantum mechanical effects (such as tunneling), most of the power consumed by modern electronics is wasted on parasitic currents. Thus, a new approach needs to be taken up if computing capabilities are to continue their exceptional progress.

Integrated circuit manufacturing is almost exclusively based on silicon and the material properties of this semiconductor have been well established. Manufacturing techniques are precisely controlled and employed in large-scale productions. For manufacturers, it would be desirable to use elements of standard electronic circuits and extend them for performing novel functions with quantum mechanical effects in mind. One possible alternative approach to improving electronics beyond what can be achieved by miniaturization is to incorporate the detection and manipulation of electron spin. This approach has been termed Spin Electronics, or Spintronics.

One of the most promising possibilities for implementing spintronics requires the use of ferromagnetic semiconductors. Such materials could be easily incorporated into

the current semiconductor electronic approaches and provide the necessary addition of spin sensitivity through various means. However, ferromagnetic semiconductors are rare, especially those with Curie temperatures at or above room temperature (which is desired for practical applications). Accordingly, enormous research efforts over the past decades have been directed towards developing ferromagnetic semiconductors with mixed results. A typical approach that has been taken to synthesize a ferromagnetic semiconductor is to modify a conventional semiconductor by introducing a small amount of magnetic transition metal atoms in an effort to induce ferromagnetic properties while retaining the semiconducting behaviour.

1.2. Dilute Magnetic Semiconductors (DMS)

Semiconductors and magnetic materials are the key compounds in the high-tech electronic industry. To improve the performance and reduce the size of these devices, enormous work is in progress to combine these two materials. The doping of magnetic atoms, transition metal or rare earth atoms, in a semiconductor crystal is called dilute magnetic semiconductor (DMS). The effective use of spin along with charge on electrons in dilute magnetic semiconductors (DMSs) make them ideal candidates for spintronic applications. The unique quality of electron spin, its quantization (up and down states), can be exploited as a natural logic cell with "0"and "1" values [2-7]. The effective use of the electron spin along with its charge makes spin based electronic devices ideal and efficient than the ordinary once. The possible outcomes of spintronics are high performance computers and multi-functional electronic devices. In the present era, the main focus of spintronics are: (i) identification of materials for spin based electronic devices, (ii) synthesis of the

identified materials either in its thin film form or nanostructures, (iii) investigation of physical properties and half metalicity, (iv) analysis of the results and, (v) designing a device or parts of it for technological applications. Most of the materials studied are of the form $A^{II}_{1-x}Mn_xB^{VI}$ [3-6]. Although other materials including $A^{IV}_{1-x}Mn_xB^{VI}$ [3, 4] and more recently $A^{III}_{1-x}Mn_xB^V$ [3, 4], other magnetic ions can be used in the materials, e.g. Fe, Ni, Co, Cr, Eu, etc., each of which give slightly different properties. The presence of localized magnetic moments in the semiconductor lattice significantly affects the electronic properties of the host material due to the exchange interaction between *sp* band electrons and magnetic moments localized on magnetic atom site. In addition, the exchange interaction between the magnetic moments is also present in these materials and depending on the properties of the host material, can lead to whole range of magnetic behaviour from antiferromagnetic to spin glass to ferromagnetic [2-7]. The most significant feature of a DMS is; the state of magnetization modifies the electronic structure through the spin exchange interaction between the local magnetic moments and carriers [2 -12].

Spin-based electronic technology forms the basis for information technology in the modern age by exploiting both the charge and spin of the electrons in semiconductor devices through introducing magnetic elements into nonmagnetic semiconductors to form dilute magnetic semiconductor materials (DMS). When the power of the integrated circuits is switched off, the stored data in these circuits disappears while in magnetic circuits, the magnetic polarization does not leak over time like an electric charge does; as a result, the data are stored even when the power is switched off [3]. No known wearing out mechanism exists, since switching the magnetic polarization

4

does not involve any real movement of electrons or atoms. The semiconductor devices based on spintronics technology or the spintronic devices have the advantages of non-volatility, increased data processing speed, decreased electric power consumption and increased integration densities compared to the classical semiconductor devices [3, 6-13]. These advantages make spin-based electronics one of the most important topics of investigation in the field of a new functional semiconductor devices.

Spin-based devices have many potential applications, such as in the spin field effect transistors (spin-FET), the spin resonant tunneling devices (spin-RTD), spin light-emitting diodes (spin-LEDs), optical switches operating at THz frequencies, encoders, decoders, modulators and quantum bits for quantum computation and communication [6-10]. In a DMS compound, the two important parameters, charge and spin of the electrons are exploited in a single crystal. The interesting physical properties of these compounds like magnetic, magneto-electronic, half-metallic and magneto-optic are expected to play a vital role in the futuristic high-tech spintronic devices. To bring all these properties in a single integrated material and to develop a novel and advanced dilute magnetic semiconductor for spin based electronic applications is a dream of the present days [3, 6-13].

1.2.1. History of spin-based electronics (Spintronics)

All electronic technology we use today is based on the charge and spin of the electrons. Although electronics is developing all the time the charge and spin of an electron are used only separately. But the novel field of spintronics, a promising field of spin based electronics has attracted enormous attention in the recent years [3, 5,

11-16] because it makes use of both (spin and charge) and opens the possibility of developing an entirely new technology with new capabilities and opportunities for applications. One such application is magnetic semiconductors.

Semiconductors and magnetic materials are therefore of importance in the high-tech electronic applications. To improve the performance and reduce the size of these devices, enormous work is in progress, both theoretically and experimentally, to combine these two materials. The doping/alloying of magnetic transition metal or rare earth atoms in a semiconductor crystal is called dilute magnetic semiconductor (DMS). The effective use of spin along with charge on electrons in dilute magnetic semiconductors (DMSs) make them ideal candidates for spintronic applications.

Significant scientific improvements in spintronics have been observed after the discovery of the diluted magnetic semiconductors [3, 5, 12, 16]. The growth techniques of the magnetic semiconductors have been improved significantly over the last two decades. These methods allow today's researchers to fabricate semiconductors in ultra-thin layer form with ultra-high purity and quality. They also provide unprecedented control over their chemical composition and crystallite size with atomic layer precision. At the same time application of these techniques to different materials exhibiting bandgap and lattice parameter engineering results in crafting of semiconductors that suit our needs and help for better understanding of the role of magnetic ions in the semiconductor structures. Doped III-V alloy is formed when III-V semiconductor is doped with a 3d transition element. These DMS materials have attracted a considerable attention for their possible use to increase the efficiency and reduce the size of the electronic devices. The electron spin with its

charge can be exploited in these futuristic spin-based devices, which would help not only in enhancing the device efficiency but also decreasing the size of these devices. A considerable time and money will be saved and complications involved in the growth and characterization processes will be reduced to a great extent. Therefore, it is imperative to use cheaper, easier and simple method to predict important properties of the materials for their possible applications. Because of the direct bandgap nature of these compounds they are optically active and hence are widely used in photonic and optoelectronic devices. The wide bandgap coupled with the direct transition nature make them ideal candidates for optoelectronic applications in a short wave length range. These semiconductors are efficient in high power, high temperature and short wave length electronic devices because of their high thermal conductivity, large bulk moduli and high melting temperature. Thus, these materials are effectively utilized in short wave length LED's, optical detectors and laser diodes. Another very promising group of compounds for DMS applications is II-VI compounds. The presence of magnetic ions in these semiconductor alloys leads to an exchange interaction between the sp band electrons and d electrons associated with Mn^{2+}, resulting in extremely large Zeeman splitting of electronic levels in the presence of an external magnetic field. This selective amplification of spin-dependent properties leads to dramatic new effects, such as the giant Faraday rotation [3, 5, 7], the magnetic-field-induced metal-insulator transition [17] and the formation of bound magnetic polarons [3, 5, 7]. Most of the II-VI-based DMSs display either paramagnetic or spin glass behaviour. Since the Zeeman splitting of the electronic levels is proportional to the magnetization of the material, the splitting decreases

rapidly with temperature when the material is in paramagnetic phase. Therefore the spin LED and other spin based devices can operate only at very low temperature. For that reason, any device based on the giant Zeeman splitting can operate only at very low temperature. There are, however, some reports in the literature about the observations on a ferromagnetic phase strongly p-doped in II-VI DMSs [3, 5, 14, 15-20]. The A^{II}-B^{VI} compounds are grouped according to the element which forms the cations like ZnMnS, ZnMnSe, ZnMnTe, CdCoS, CdCoSe, CdCoTe, ZnCoS, CdMnSe, CdMnTe, HgMnS, HgMnSe and HgMnTe. In II-VI semiconductors, the II element is substituted by an equivalent valence f magnetic transition metal atoms making it possible to achieve a high density of magnetic atoms and to fabricate quantum structures. In such DMS, magneto-optic properties were extensively studied and optical isolators were fabricated using large Faraday Effect [3, 5, 7, 11, 13]. In the early stage of development, it was the II-VI compound semiconductors containing substitutional Mn^{2+} ions which received major attention and consequently these are the most common and thoroughly studied [3, 5, 7, 18-20]. Their unique and fascinating properties triggered tremendous motivation among the researchers to explore the possibilities of using them in many technological applications. The most common DMS are II-VI compounds (viz. CdS, CdTe, ZnS, ZnSe, etc.) with transition metal ions (e.g. Mn, Fe, Co, Ni) substituting original cations and are particularly interesting for this purpose [3, 5, 7, 14, 15]. Nevertheless, II-VI materials are equally competent or even more than III-V compounds for fundamental studies, in which localized spins and holes can be introduced and controlled independently. Recently DMS have attracted new interests because of the possibility to make

quantum computing architecture using spin polarized electron confined in quantum dots as quantum bits [3, 5, 21-23]. To accommodate these frontiers of DMS materials, search for alternative spintronic materials can be sought in two folds; first, search for a completely new material, bit difficult and requires huge efforts and complicated instrumentation and process control. Second, addition of different elements / materials to already known materials leads to the formation of miscible systems. The miscible systems, apart from reducing the system degradation, improve other properties of thin film materials and obey the Vegard's law [12, 14, 15]. This process allows the tailoring of the band gap, structure and morphology of the materials within their miscible limits and a variety of electronic materials can be designed and tailor made to suit a specific property requirement by alloying another phase of suitable characteristics. These doors of the Materials Science have opened a new era to make II-VI compound materials the potential and high performance candidates for their practical and industrial utilities.

1.2.2. Survey of the literature

Cobalt sulfides form a group of II–VI semiconductor materials that are attracting a considerable attention in recent years, although they are most complicated metal chalcogenides. These sulfides are of particular interest due to their unique catalytic, electrical, optical and magnetic properties and their potential applications in solar energy absorbers, ultra-high-density magnetic recording, anodes for Li-ion batteries and catalysts for hydrodesulfurization or dehydrodearomatization [23-29]. Cobalt sulfide exists in a variety of crystalline phases such as : Co_4S_3, Co_9S_8, CoS, $Co_{1-x}S$, Co_3S_4, Co_2S_3 and CoS_2 [24, 30, 31]. Efforts were taken towards synthesis of these

micro and nano crystals with various morphologies, viz. Co_9S_8 and CoS_2 nanoparticles [24, 32], CoS nanowires [33, 34], thin films [12, 35-37], octahedrons of Co_3S_4 [24, 38] and sea urchin-like Co_9S_8 [24, 38]. It is worth noting that Co_3S_4 nanotubes [24, 39] and cobalt sulfide hollow nanocrystals [40] were fabricated based on the Kirkendall effect. Considerable efforts have been focused on depositing cobalt sulfide thin films by various methods such as chemical bath deposition (CBD) [12, 35-37, 41], chemical vapour deposition (CVD) [42], electrochemical deposition (ECD) [27] and Langmuir- Blodgett (LB) methods [43].

A biomolecule-assisted hydrothermal process with universal green chemistry approach was developed to synthesize cobalt sulfide nanowires for applications in supercapacitor [38]. Novel sea-urchin like nano crystals of cubic phase, Co_9S_8, were synthesized via a facile hydrothermal synthetic route [33]. The effects of temperature and reaction time were investigated. The role of optimum conditions was found to be essential for the growth of these nanocrystallites. Formation of cobalt sulfide hollow nanocrystals through a mechanism similar to the Kirkendall Effect has been investigated by Yin et al, [34]. A specific capacitance, as high as 508 F g^{-1} was achieved for CoS nanowires in comparison with the best supercapacitor material, RuO_2 ($\approx$ 700 F g^{-1}). Polycrystalline cobalt disulfide nanoparticles were obtained by Bi et al, [40] from the reaction of aqueous $CoCl_2.6H_2O$ with thiourea in the presence of hydrazine hydrate. The XRD and SAED studies indicated formation of amorphous CoS_2 nanoparticles. The role of hydrazine was found in shaping the rod- or needle-like nanoparticles and the reflux temperature and time were also found to influence the crystallization process. This systematic study demonstrated dependence of

morphology and phase of cobalt disulfide nanoparticles on experimental conditions (solvent, temperature and time, etc.). Reaction at >120°C lead to the fast formation of a single void inside each shell. At intermediate temperatures (100°C - 120°C), formation of the Co_3S_4 phase was observed in a two-step process as: Co sulfidizes into Co_9S_8 which subsequently transforms into Co_3S_4. Wang et al, [41] synthesized nanosized cobalt sulfides through a one-step chemical reaction at room temperature. The outcomes revealed semiconductive nature of CoS. With a reversible capacity of over 300 mAh g^{-1} based on the total mass of the electrode, CoS nanopowder confirmed promising candidature as cathode active materials for lithium-rechargeable batteries. Formation of three-dimensional cobalt sulfide hierarchitectures through a mechanism similar to Ostwald ripening has been investigated by Wang et al, [42]. Electrochemical measurements showed superior supercapacitor performance of CoS nanostructure with high specific capacitance (555 F g^{-1} at 5 mA cm^{-2} and 464 F g^{-1} at 100 mA cm^{-2}) and excellent cycle life in 2 M KOH solution. CuS, CoS, and CuS/CoS onto FTO glass substrates were deposited to function as counter electrodes in polysulfide redox reactions in CdS/CdSe quantum dot–sensitized solar cells (QDSSCs) [43]. Relative to a Pt-electrode, the CuS, CoS, and CuS/CoS electrodes provide greater electrocatalytic activity, higher reflectivity, and lower charge-transfer resistance. Because the CuS/CoS electrode has a smaller internal resistance and higher reflectivity relative to those of the CuS and CoS electrodes, it exhibited a higher fill factor and short-circuit current density. As a result, under illumination of one sun (100 mW.cm^{-2}), the QDSSCs incorporating CuS/CoS counter electrodes provided η = 4.1 ± 0.2 % [43].

Panthi et al, [44], demonstrated in-situ formation of CoS nanoparticles using addition of ammonium sulfide solution to PAN solution containing cobalt acetate. The obtained CoS nanofibers showed enhanced catalytic activity towards dehydrogenation of ammonia borane. Moreover, the hybrid nanofibers were recommended to be utilized as photocatalyst as the nanofibers photo oxidize methelene blue dye in a very short interval. The cobalt sulfide/graphene (GNS) composite nanosheets were prepared by a facile one pot solvothermal route in the presence of graphene oxide sheets [45]. Sphere-like cobalt sulfide particles with an average size of about 150 nm (which are complicated phases of CoS_2, CoS and Co_9S_8) were observed through SEM and TEM. The as-fabricated cobalt sulfide/GNS composite exhibited a very high electrochemical lithium storage reversible capacity around 1018 mAh g^{-1}. Moreover, the cobalt sulfide/GNS composite retained reversible capacity of above 950 mAh g^{-1} after 50 cycles at a current density of 100 mAh g^{-1} thus, proved its excellent cycling durability and high-rate capability. Hierarchical cobalt sulfide crystals with flower-like microstructures were successfully prepared by a simple one-pot solvothermal route, employing $CoCl_2 \cdot 6H_2O$ as a cobalt precursor and KSCN as a sulfur source [46]. The effects of reaction parameters of the solvent and source in CoS synthesis were studied and the decisive role in determining the final morphology was witnessed. Highly efficient and transparent multicomponent catalysts for Dye Sensitized Solar Cells (DSSC's) were obtained by simultaneous electrodeposition of platinum and cobalt-sulfide (Pt:CoS) on conducting glass substrates by Rossi et al, [47]. At equal charge transfer resistances (R_{CT}), the superior transparency of electrodeposited Pt:CoS compared to

ED Pt and ED CoS was attributed to the synergic combination of a very thin CoS layer and a fine dispersion of Pt nanoparticles. DSSC's equipped with electrodeposited Pt:CoS as counter electrode on FTO substrates performed better (by 14%) under back illumination compared to DSSC's equipped with electrodeposited Pt-only and CoS only. CoS thin films were prepared by a spray pyrolysis method on glass substrates at a constant substrate temperature of 300°C [48]. The films were crystalline in nature with hexagonal structure. The optical transmission analysis showed two-step transitions; first, energy gap varied from 1.35 eV to 1.4 eV and for second, 1.96 eV to 2.11 eV, respectively [48]. Huang et al, [49], reported a simple strategy to prepare 2-dimensional cobalt sulfide by the one-step hydrothermal process. The cobalt sulfide sample has a microstructure of interconnected sheets. As the electrode material, the layered cobalt sulfide films exhibited superior performance with high specific capacitances (1314 F g^{-1} at 3A g^{-1}) as well as excellent cycle life (less than 8.3% decrease in specific capacitance after 500 cycles at 3 A g^{-1}). Facile single pot selective stoichiometric synthesis of cobalt sulfide has been carried out by combustion synthesis without using any surfactants, capping agents and inert atmospheric conditions [56]. Paint approach is developed to fabricate CoS counter electrode materials and its performance was tested against Pt counter electrode in QDSSC. Inclusive impedance measurements confirmed the better electrocatalytic activity of cobalt sulfide samples than Pt probably due to the lowest R_{ct} and best activity of present Co_9S_8 phase. The unique layered morphological characteristics of 2D CoS facilitates the infiltration of electrolyte and provide a more active surface when it is evaluated as an electrode material for

biosensors. Huang et al, [51], reported the synthesis of CoS nanosheets by a simple one-step hydrothermal process. A novel electrochemical biosensor for the introduction of CoS nanosheets and AuNPs efficiently accelerated the electron transfer. The as-prepared CoS based biosensors exhibited excellent selectivity and good stability. A facile and rapid method to prepare three-dimensional (3D) flower-like CoS hierarchitectures by microwave assisted heating has been developed recently by Luo et al, [52]. The 3D flower-like CoS architectures constructed by 2-dimensional nanopetals intertwined with each other. A specific capacitance of 586 F g^{-1} was obtained at a charge-discharge current density of 1 A g^{-1}. The CoS nanostructures exhibited excellent cycling stability and maintained 91% of its initial specific capacitance after 1000 cycles. Recently, a facile electrochemical technique has been employed by Ray et al, [53], to fabricate titania nanotube (T-NT)/cobalt sulfide (CoS) composite electrode for high performance supercapacitor application. CV studies indicated that a very high specific capacitance (400-500 F g^{-1}) can be achieved with excellent cycle stability. A very high percentage (80%) of capacitance retention was achieved in these composites even after 1000 charge–discharge cycles. Zinc sulfide (ZnS) is one of the first semiconductors discovered [54], which belongs to the group of II–VI wide band gap semiconductors. Naturally, ZnS is a white -yellow coloured powder or crystal. It has two commonly available allotropes: one with cubic (sphalerite or zinc blende) structure and another with hexagonal (wurtzite) structure [54]. ZnS exhibits high transparency over a wide range of spectrum typically between 250 nm and 380 nm. The electrical resistivity is in the order of 10^4 $\Omega \cdot cm$ with an n-type electrical conductivity. It can be doped as both n– and p–type

semiconductors, which is unusual for the II–VI semiconductors [54, 55]. It is used as a promising material in photonic, optical and several electronic devices. ZnS is considered as one of the most suitable candidates for field emitters [54, 55] and field effect transistors (FETs) [56]. It is an ideal object for fabrication of high-performance sensors [54, 57-60] due to its excellent fluorescence properties and nontoxicity and usefulness for infrared windows [61] and lasers [54, 62, 63]. In addition, a range of solar device applications are made feasible with ZnS thin films, including filters, anti–reflection coatings in silicon based solar cells and buffer layers in chalcopyrite semiconductor–based solar cells [64]. The band gap of ZnS (3.5–3.8 eV) is higher than that of CdS (2.4 eV) which improves the solar cell device efficiency by eliminating absorption losses in the short wavelength region of the solar spectrum [65]. Recently, thin film solar cells based on chemical bath deposition of ZnS(O,OH) buffer layer have achieved an efficiency of 18.6% [66], which makes it a highly competitive alternative to the conventional CdS buffer layer.

1.3. The Thin Films and Thin Film Depositions: Broad Classification

Technological progress of modern society depends on the Materials Science and Engineering community's ability to conceive the novel materials with extraordinary combination of physical and mechanical properties [67, 68]. Modern technology requires thin films for a variety of applications. Thin films are thin material layers ranging from fraction of a nanometer to few micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film designs. The engineering of thin films become complicated by the fact that their Physics is, in some cases, not well understood. In particular, the problem of

stoichiometry and morphology tuning may be hard to solve. Hence, a thin film is defined as a low dimensional material created by condensing one by one atomic/molecular/ionic species of a matter; the thickness is typically less than several microns [70-72].

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronics, photonics and magnetic devices [68-72]. The processing of materials into thin films allows easy integration into various types of devices. The material properties significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic and optical properties. Thin film technologies make use of the fact that the properties can particularly be controlled by the growth conditions and preparation parameters [69, 70]. Thin films are formed mostly by deposition, either by physical or chemical methods and have immense importance in microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, AR coatings, photoconductors, IR detectors, interference filters, solar cells, polarizers, temperature controllers in satellites, super conducting films and anticorrosive and decorative coatings [70].

This is an ever growing field in the physical and chemical sciences, which is the confluence of Materials Science, Surface Science, Applied Physics and Applied Chemistry. Thin film technology has its objectives in the provision for scientific bases for the methods and materials used in thin film electronics. Additionally, it provides a sufficient data in the area of applications to permit for understanding of those aspects of the subject that might still be termed an 'art'. The enormous

flexibility provided by the thin film growth processes allows for the fabrication of desired geometrical, topographical, physical and crystallographic structures into two or lesser dimensions and to study their structure sensitive properties [70-72].

Although the study of thin film phenomena dates back over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of micro-miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage techniques and it is this which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed which have found themselves looking for an application or perhaps more importantly the market. In general, these devices have resulted from research into the physical properties of thin films. Secondly, as well as generating newer ideas for new devices, fundamental research has led to a dramatic improvement in understanding of thin films, surfaces and interfaces. This in turn has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties. The cleanliness and nature of the substrate, the deposition conditions, post deposition heat treatments and thorough surface passivation are the vital process variables in thin film fabrication [70-72]. Therefore, prior through understanding of thin films, it is not really been possible to apply them to real devices. Thirdly, much of the finance for early thin film research originated from space and defense programs to which the device cost is less important than its lightweight and other advantages. The major applications of thin film technology are

not now exclusively in these areas but rather often spread in the domestic sectors in which low cost is essential [11-13, 16, 35, 70-72].

Thin film materials and their technologies have already become a part of semiconductor devices, wireless communication, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, magneto-optic discs, lithography, micro-electromechanical systems (MEMS), multifunctional emerging coatings and other emerging cutting edge technologies [70]. The properties of thin films are extremely sensitive to the method of preparation [11-13, 16]. Several techniques and preparation procedures have been developed depending on the desired film properties and the application. Each method has its own merits and demerits and of course, no one technique can deposit the thin films covering all the desired beneficial aspects such as cost of the equipments, deposition conditions and nature of the substrate material, etc. A variety of thin film materials and their deposition, processing and fabrication techniques, characterization tools and techniques and their structure-property relationships are the key features of the thin film devices and this is the basis for the foundation of a thin film technologies [11-13, 16, 35-37, 69-72]. Underlying the performance and economics of thin film components are the manufacturing techniques that are used to produce the devices. Physical methods cover the deposition techniques which depend on the evapouration or ejection of the material from a source, i.e. evapouration or sputtering, whereas chemical methods

are the specific chemical reactions. Thus chemical reactions depend on the thermal effects as in vapour phase deposition and thermal growth. However, in all these cases, a definite chemical reaction is required to obtain the final product. When one seeks to classify deposition of films by chemical methods, one finds that they are available into two more classes. The first of these classes is concerned with the chemical formation of the film from medium and typical methods are electroplating, chemical reduction plating and vapour phase deposition. A second class is that of the formation of the film from the precursor ingredients, e.g. anodization, gaseous anodization, thermal growth, sputtering, ion beam implantation, CVD, MOCVD and vacuum evapouration. However, there are certain techniques which are only capable of producing thick films and these include screen printing, glazing, electrophoretic deposition, flame spraying and painting. Thin film deposition techniques are broadly classified under two heading as shown below (fig. 1.1) [70, 73].

Figure 1.1. Classification of thin film deposition techniques.

1.3.1. Physical methods

a) Physical vapour deposition

PVD processes proceed with the following sequence of steps:

i)   The solid material to be deposited is physically converted to vapour phase.

ii) The vapour phase is transported across a region of reduced pressure from the source to the substrate.

iii) The vapour condenses on the substrate to form a thin solid film.

The conversion from solid to vapour phase is through the physical dislodgement of the surface atoms by absorbing heat during evapouration or by momentum transfer in sputter deposition.

b) Sputtering

If a surface of target material is bombarded with energetic particles, it is possible to cause ejection of the surface atom, the process is known as sputtering. The ejected atoms can be condensed onto the substrate surface to form a thin solid film. This method has various advantages over normal evapouration techniques in which no container contamination will occur. It is also possible to deposit alloy films which retain the composition of the parent target materials. DC sputtering, radio frequency sputtering and magnetron sputtering are the oldest of sputterings used.

1.3.2. Chemical methods

These methods can be summarized in brief as:

a) Electrodeposition

It is a process of depositing a substance on the electrode by electrolysis; the chemical changes being brought about by the passage of current through an electrolyte. The

phenomenon of electrolysis is governed by the Faraday's laws. When a metal electrode is immersed in a solution containing ions of that metal, a dynamic equilibrium $\bar{M}.M_n + X$ (M- Metal atom and X =S, Se, Te) is set up. The electrode gains a certain charge on itself which attracts oppositely charged ions and molecules holding them at the electrode / electrolyte interface. During deposition ions reach the electrode surface, stabilize on it, release their ligands, release their charges and undergo electrochemical reaction. The factors influencing the electrodeposition process are: current density, bath composition, pH of the electrolyte, temperature of the bath, agitation, electrode shape, etc.

b) Spray pyrolysis

This is a thermally stimulated reaction between the clusters of liquid vapour atoms of different spraying solutions of the desired compound onto a substrate maintained at elevated temperature. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal or cluster of crystallites 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 recrystallization of the crystallites is provided by the hot substrate. The nature of the fine spray droplets depends upon spray nozzle. The growth of a film by a spray pyrolysis is determined by the nature of the substrate and solution as well as spray parameters. The films are generally rough, adherent, mechanically strong, pinhole free and stable with temperature and time. The surface of the substrate gets affected in the spray process and the choice is limited to glass, quartz, ceramics or oxides, nitride or carbide coated substrates.

c) Chemical vapour deposition

Chemical vapour deposition can be defined as a material synthesis method in which the constituents of vapour phase react to form a solid film at the surface. The chemical reaction is an essential characteristic of this method; therefore, besides the control of the usual deposition process variables, the reaction of the reactants must be well understood. Various types of chemical reactions are utilized in CVD for the formation of solid films and pyrolysis, reduction, oxidation, hydrolysis, synthetic chemical transport reaction are the best examples.

d) Anodization

This is an electrolytic method for producing oxide films on the surface of the metals. These metals form the anode that is dipped into a liquid electrolyte such as a salt and/ or acid solution. Oxide ions are attracted to the anode to form a thin layer of metal oxide. On increasing the field strength, more oxide ions diffuse through the oxide layer to the metal surface and hence, the oxide layer grows thicker.

1.3.3. Selection of a deposition process and a chemical solution deposition route

No single technique is ideally suited for preparation of a large area thin film with all the desired properties. Hence choice and selection of a deposition process plays a vital role in the formation of good quality thin films and while selecting a particular technique it should be tested satisfactorily for the following aspects:

a) It should be cost effective.

b) It should be able to deposit the desired material.

c) Should be able to control microstructure and deposition rate.

d) Able to maintain the stoichiometry as that of the starting materials.

e) Should be able for the operation at reduced temperature.

f) No restrictions on depositing materials.

g) Should be easily scale up process.

h) Should be able for masking of the substrates.

i) Should have control on film substrate interface and defects created in the film.

Among the various techniques discussed above, chemical solution deposition technique is employed in the present investigation. Chemical reaction either takes place on the surface of the dipped substrate or in the solution itself, where mixing of the components on the surface to be coated is required. Most of the coatings are formed in a two-step fashion;

i) "Sensitizing" the surface for the nucleation reaction of the adhering coating layer, and ii) Deposition of a coating by selected reactions.

Among the various chemical deposition systems, chemical bath solution deposition has attracted a great deal of attention because of its overriding advantages over the other conventional thin film deposition methods. The chemical bath deposition method for the preparation of thin films has recently been shown to be an attractive technique because of its simplicity, convenience, low cost, low temperature and has been successfully used for depositing ternary metal chalcogenide thin films [11-13, 16, 35-37, 69, 73]. Understanding of the Chemistry and Physics of the various processes involved in a deposition processes has now made possible to obtain undoped/doped, multicomponent semiconductor thin films of usual/unusual and metastable structure. Among the methods suggested in the fig. 1.1, the chemical methods are economical and easier than that of the physical methods. The chemical

solution deposition (CSD or CBD) method is the most popular technique today because a large number of conducting and semiconducting thin films can be prepared by this technique [11-13, 35-37, 69, 73]. It is also popular due to its simplicity and low cost and the thin film can be deposited on different substrates like glass, ceramic, metal, etc. A large studies have been conducted, over about three decades, on chemical solution deposition (CSD) method for the preparation of thin films. Due to excellent productivity of this technique on a large scale and simplicity of the apparatus, it offered a most attractive way for the formation of thin films of oxides, semiconductors, chalcogenides and superconducting oxides, etc.

1.4. The Electrochemical PV Cell

The Becquerel effect (1839) reflected into the origin of solar cell and then different types of solar cells were developed and accordingly classified based on utilization of the solar energy. Depending on the built in potential, due to the difference in Fermi energy levels, solar energy utilization can be classified as shown in fig. 1.2. In semiconductor – semiconductor (S-S) solid state junction cells, two types of junction are formed; a homojunction and a heterojunction. A homojunction cell consists of a shallow junction formed between similar materials either by diffusion of dopant into a monocrystalline semiconductor substrate or by growth of an epitaxial layer onto the substrate. A heterojunction is the interface between two dissimilar materials. The semiconductor – metal (S-M) junction cells are commonly known as Schottky barrier cells and can be fabricated by depositing a semitransparent metal film on the semiconductor surface. The transparent metal film is normally evapourated on a carefully processed semiconductor surface. The MIS and SIS junction cells have a

thin interfacial layer of an insulator between a top inducing contact (metal or semiconductor) and a base semiconductor. The interfacial layer is generally an oxide or the compound which is always an insulator.

The semiconductor- liquid (SL) junction cells consist of a semiconductor photoelectrode dipped into an electrolyte solution along with a suitable counter electrode [73-77]. The counter electrode is a metal or a treated graphite. The charge transfer process at the semiconductor/ electrolyte interface results in band bending at the interface establishing a potential barrier at the interface. These cells are further classified into five groups: 1) photoelectrolytic cells, 2) rechargeable cells, 3) photogalvanic cells, 4) photoelectrocatalytic cells and 5) photoelectrochemical (PEC or PV) cells.

Out of these cells the photoelectrochemical system is easiest one. A PV or PEC effect is defined as one in which irradiation of an electrode/ electrolyte system produce a change in electric potential (at open circuit condition) or in the current flowing in external circuit (under short circuit condition) [74-76]. Early semiconductor electrochemistry studies have shown that the distribution of potential at the semiconductor-electrolyte interface is almost similar to that at a simple p-n junction [74-76]. A direct conversion of solar energy into electrical energy using a semiconductor/ electrolyte interface was first demonstrated by Gerischer. Thus, photoelectrochemical (PV) solar cells, in principle, can be much cheaper than the traditional solid state photovoltaic cells. This is particularly important because of the comparatively low solar radiation power density requiring the use of large area converters. The future prospects of photoelectrochemical solar energy conversion

depend on how completely its potential advantage can be utilized in practice. Secondly, the photoelectrochemical method is convenient in that, one of its versions - photoelectrolysis enables light energy to be directly converted into chemical energy reaction products and thus permits the energy storage problem to be solved along with proper and reliable energy conversion. During the last two-three decades a huge variety of work has been done on photoelectrochemical (PV) systems in search of a suitable and efficient PV-cell.

1.4.1. Basics of a semiconductor-liquid junction

a) Oxidation and reduction processes

The charge transfer across the semiconductor/ electrolyte interface in dark as well as in light results in a net flow of current through the junction. This is the key concepts for working in photoelectrochemical solar cells and reports are available which predict the analogy between the semiconductor and an electrolyte. A process in which substance gains an electron is called a reduction reaction [73-77];

$$OX + \ e^- \ \leftrightarrow \ Red \ E^o \qquad\qquad\qquad .....(1.1)$$

where, OX and Red are oxidized and reduced species and E^o is the standard electrochemical potential. The reverse process of loosing an electron is called an oxidation reaction. In a system where one species loses whereas other gains an electron is called a redox system. If E^o is positive, the reaction proceeds from left to right and when it is negative, the reaction proceeds from right to left. The analogy between the semiconductor and electrolyte can be summarized as;

i) The oxidized and reduced species in an electrolyte are analogous to the conduction and valance bands respectively in semiconductor.

ii)   The term $E_{f,redox}$ can also be explained in a similar manner as that of the semiconductor Fermi level, E_F.

iii)   The energy necessary to transfer an electron from the reduced species to the oxidized one is analogous to the band gap (Eg) of a semiconductor.

iv)   The redox potential is a potential required to transfer an electron from redox species to the vacuum level or vice-versa.

Figure 1.2. Flowchart indicating utilization of solar energy [75, 76].

b) Semiconductor-electrolyte interface

The semiconductor/electrolyte interface review are available in the literature [73-77]. When a semiconductor is dipped into an electrolyte redox couple, as its chemical potential is different from the redox potential (E_{redox}), a new equilibrium is established between the semiconductor and an electrolyte solution by the rearrangement of charges. This results in a strong electric field across the junction. When this semiconductor-electrolyte junction is illuminated with a light having energy greater than the band gap energy of a semiconductor, electron-hole pairs are produced in the depletion layer; charge separation takes place due to the local field present at the interface. The probability of annihilation of a hole with an electron is reduced by this field. This condition will be optimum when the light penetration depth is equal to the depletion layer width. Hence, all the incident light is absorbed in the depletion layer and the maximum number of electron-hole pairs are produced. These separated charges produce a counter field which is maximum at open circuit condition. This is the open circuit photovoltage. The conduction band and valance band bend at the interface due to the counter voltage. The photovoltage is given by the change in the Fermi level as shown in fig.1.3. When a counter electrode is immersed in the electrolyte and connected externally to the semiconductor, the photo generated electrons move into the bulk of a semiconductor; reach the counter electrode through the external circuit to reduce an oxidized species in the electrolyte. The holes are pushed to the electrode surface where they oxidize a species in the electrolyte. The magnitude of the photocurrent depends on the absorption coefficient of the semiconductor, width of the space charge region, hole diffusion length, area of

illuminated electrode, incident photon energy and radiation intensity. Under short circuit condition, the Fermi levels of the semiconductor and the redox electrolyte are equalized and a net charge flows during illumination.
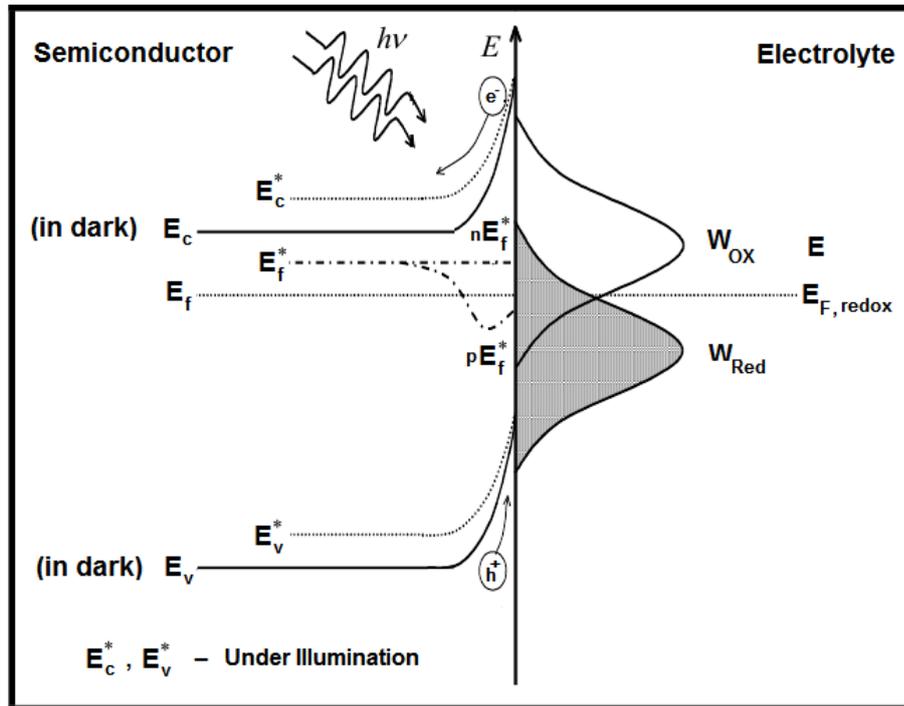

Figure. 1.3. The positions of bands under illumination responsible for photo induced charge transfer**.**

c) Classification of the photoelectrochemical (PEC/PV) solar cells

The electrochemical PV cells are very similar to the Schottky type solid state solar cells. The principle of charge transfer reaction at the semiconductor – electrolyte interface forms the basis of various types of photoelectrochemical solar cells. Depending on the net free energy change (ΔG) in the overall system, the PV-cells are classified into three categories [73, 77].

i) Electrochemical photovoltaic cells ($\Delta G = 0$)

These cells consist of such a redox couple that the total cathodic and anodic reactions

do not lead to the net chemical change, i.e. a change in the net free energy, $\Delta G = 0$. The electrodes do not participate in the chemical reaction, they only serve as a "shuttle" for the charge transfer mechanism. At the semiconductor electrode,
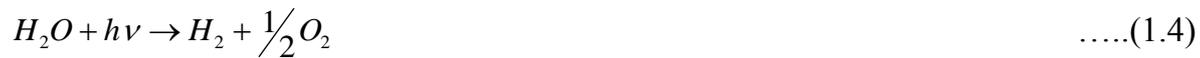
$$(Red)_{solv.} + h^+ \leftrightarrow (OX)_{solv.} \qquad \qquad .....(1.2)$$

At the metal counter electrode,

$$(OX)_{solv.} + e^- \leftrightarrow (Red)_{solv.} \qquad \qquad .....(1.3)$$

The above cell is the regenerative type PV cell useful for direct production of electricity.

ii) Photoelectrolysis cells ($\Delta G > 0$)

Effectively two redox couples are present and a net chemical change takes place in the system by converting the optical energy into an equivalent chemical energy. The photoelectrolysis cells and some electrochemical storage cells belong to this category. Some examples of reactions of this type are;

$$H_2O + h\nu \rightarrow H_2 + \frac{1}{2}O_2 \qquad \qquad .....(1.4)$$

$$CO_2 + H_2O + h\nu \longrightarrow \underset{Chemical\ energy}{(CH_2O)_X} + O_2 \qquad \qquad .....(1.5)$$

iii) Photocatalytic cells ($\Delta G < 0$)

In these cells, similar to the above two redox couples are present such that a net chemical changes take place. Hence $\Delta G < 0$ and the optical energy provides the activation energy for the chemical reaction. Example of this type is photocatalytic reaction as;

$$N_2 + 3H_2 + h\nu \rightarrow 2NH_3 \qquad \qquad .....(1.6)$$

d) Requirements of electrochemical PV cells

The requirements expected for a good PV solar cell are as follows:

i) Semiconductor photoelectrode

Semiconductor photoelectrode used for PV application should satisfy the following requirements:

- It should be of the direct band gap type with high optical absorption coefficient (10^4 to 10^5 cm^{-1}).

- The band gap should be such that, a maximum span of the solar spectrum should be utilized.

- Electrode should be thick enough to absorb all the incident radiation.

- It must be stable against corrosion when dipped into a specific redox electrolyte, both in dark and under illumination. Low band gap semiconductors generally get easily corroded. Therefore, the choice of a semiconductor material is very important for electrochemical PV- solar cells.

- Charge carriers of the material should have high mobility and life time.

- The electrode [contributing to the series (R_s) and shunt (R_{sh}) resistances of a PV-cell] should have low resistance such that R_s of a PV-cell should be as small as possible, whereas R_{sh} should be very large (Ideally $R_s = 0$, $R_{sh} = \infty$).

ii) Electrolyte/redox couple

Another important parameter in the PV- cell is the electrolyte redox couple. Electrolyte consists of the oxidized and reduced species. These ionic species help to transfer the photo generated holes from photo electrode to the counter electrode. The energy levels in the electrolyte are similar to the concept of energy states in the solid and $E_{f,redox}$ is equivalent to the Fermi energy level of a semiconductor. When the

31

semiconductor electrode is immersed into an electrolyte, an equilibrium sets up by the electron exchange at the surface; the Fermi levels of both the semiconductor and electrolyte adjust with each other that produces a barrier at the interface. This barrier depends on the nature of the solution species and the semiconductor. For effective charge transfer at the electrode/ electrolyte interface:

- Reduction-oxidation reactions should occur appropriately at the semiconductor band edges.

- Charge transfer rates of oxidized and reduced species at both semiconductor and counter electrode should be high or effective.

- Oxidized/ reduced species and solvent components should have photo and thermal stability throughout the useable solar spectrum and the operational temperature range.

- The electrolyte should have minimum optical absorption.

- It should be non-corrosive to electrode.

- Ionic conductance of the electrolyte should permit negligible ohmic losses.

- Toxicity, reactivity and cost should be preferably low.

iii) The counter electrode

The counter electrode is also equally important. It must satisfy regenerative processes; the electrolyte species are oxidized at the counter electrode giving no net chemical change in the composition of an electrolyte. The requirements of the counter electrode for better performance of the PV cell are:

- The counter electrode should not react with an electrolyte, i.e. it should be chemically inert.

- It must be electronically active i.e. the charge transfer between the counter electrode and redox species in the electrolyte must be faster and effective.

- When a counter electrode is immersed into the electrolyte, the half-cell potential of the electrode should match with that of the half-cell potential of the semiconductor electrode.

- The counter electrode should have a low overpotential for the reduction reaction.

e) Conversion efficiency and fill factor

PV-cells for solar photon conversion are usually deigned to produce electric power. These cells are designed to be operated at their maximum-power point on the I-V curve to produce maximum electric power at the maximum energy conversion efficiency (η_{max}).

$$\eta_{max} = \frac{I_{max}V_{max}}{i}$$
$$\qquad\qquad .....(1.7)$$

where, i is the incident solar irradiance, I_{max} is the maximum-power point photocurrent density and V_{max} is the maximum power point voltage. The ratio of the maximum power generated and the product of the short-circuit photocurrent density (I_{sc}) and the open- circuit voltage (V_{oc}) is known as the fill factor (F.F). The higher the value of F.F., the better the quality of the device.

$$FF = \frac{I_{max}V_{max}}{I_{sc}V_{oc}}$$
$$\qquad\qquad .....(1.8)$$

1.4.2. Advantages of electrochemical PV cell

a) The fabrication of a PV cell is easy and simple.

b) Many complicated processing steps in the fabrication of a p-n-junction are simplified or eliminated.

c) Growth of a single crystal with large area is not required.

d) Since the junction formation is a spontaneous process randomly oriented crystallites can be used.

e) The large minority carrier diffusion length (LD) of a semiconductor material and the depletion layer width (W) are must.

f) The most important advantage of a PV cell is that it has a facility for chemical storage.

1.5. The CoS and $Co_{1-x}Zn_xS$ Systems: Why?

Semiconductors and magnetic materials are the two main pillars of the present day electronic industry and are the basic building blocks of the solid state electronic devices [1, 4-6]. The wide utility of II-VI semiconductors and their alloys in photonic and optoelectronic devices and their possible applications in the futuristic spintronic devices have made them ideal compounds for investigations. These semiconductors have high melting points, high thermal conductivities, large bulk moduli and wide variations in their electrical and optical properties. They are therefore, effectively used in high-power, high-temperature and high-frequency optoelectronic devices [12, 77] viz. high-frequency light-emitting diodes, optical detectors and laser diodes. Binary compounds (CoS, ZnS, CdS, HgS, PbS, ZnSe, CuSe, etc.) have limited variations in their properties (e.g., structural, electronic, optical and magnetic). Owing to the complex nature of the high-tech photonic and optoelectronic devices, it is highly desirable to search for new materials with variable properties over a wide

range of solar spectrum. To tune these binary compounds for a specific application their property engineering can be made feasible by alloying them with an element of known properties. The formation of an alloy is the easiest technique to modify the physical and structure-morphological relations of a material wherein compounds with different physical properties are brought together to obtain a whole range of the structural disorder that changes the materials properties to a large extent. The new products are of technologically importance. The ternary nature of these materials offers the possibility of tuning the lattice constants and band parameters by varying the magnetic ion concentration of the new entrant [3, 5, 7, 12]. The random distribution of magnetic ions over the cation sublattice leads to an exchange interaction between the *sp* band electrons and *d* electrons. This selective amplification of the spin-dependent properties leads to new dramatic effects, such as the giant Faraday rotation, magnetic-field-induced metal-insulator transitions and the formation of bound magnetic polarons [3, 5, 7, 12]. Recently, Cr- and Co-doped II-VI based DMS's gained a lot of momentum, since their electronic properties are expected to be similar to the III-Mn-V DMS [77]. The previous discussion focused primarily, on the magnetic phenomena that occur upon introducing transition metals into the semiconductors and insulators, but of course other changes take place as well. In particular, the introduction of transition metal impurities can have large effects on the electronic band gaps. Films and nanostructures of II-VI compounds doped with transition metal atoms are widely investigated as diluted magnetic semiconductors (DMS) due to the wide range of technological applications expected

from the coexistence of the optical and electrical semiconductor properties with transition metal room temperature ferromagnetism.

Equally, cobalt sulfide is one of the most complicated transition metal sulfides, which has a number of phases and chemical compositions [24, 35-37]. Therefore, the primary major challenge is that the synthesis of CoS needs to be well-controlled on account of its complex phase diagram. In addition, cobalt ion has a very strong affinity to oxygen. It is difficult to exclude cobalt oxide or cobalt impurities from the resultant materials. Although the research programs are being actively pursued on the semiconductor and metal nano crystals, only a little work has been done on the cobalt sulfides. The difficulties in the controlled synthesis of cobalt sulfides can be caused by their stoichiometries, which are much more complicated than that of other transition-metal sulfides. In this context, cobalt-zinc-sulfide system seems to be an interesting system and has been chosen for the investigations because;

   a) The system $Co_{1-x}Zn_xS$ not studied so far.

   b) The two binary compounds carry technological importances.

   c) Both CoS and ZnS exhibit similar crystal structure.

   d) Zn substitution in CoS can occur with relatively low strain on the semiconductor lattice owing to more or less same four-fold coordinated ionic radii of Zn^{+2} and Co^{+2} ($Zn^{+2} = 0.72$ Å and $Co^{+2} = 0.74$ Å).

   e) Both possess high coefficient of an optical absorption (10^4 cm^{-1}).

   f) The energy gaps of the two component semiconductors [CoS (≈ 1.1 eV) and ZnS (≈ 3.2 eV)] are such that the effective band gap can be tuned to a maximum of the solar spectrum.

g) Both CoS and ZnS can be prepared with a simple, inexpensive and almost no-tedious chemical route involving meaningless consumption of the chemical precursors and electrical energy without the use of sophisticated instrumentation and bulky costlier equipments.

1.6. Problem in Brief and Proposed Plan

Our motivation stems mainly from the modern field of spintronics and solar energy conversion. With questions and problems spinning in our mind like, how will magnetic ions interact? How will the electro-optical and magnetic properties be altered compared with the well-established parent material properties, we have decided to synthesize CoS and $Co_{1-x}Zn_xS$ thin films via an aqueous alkaline chemical route. The primary goal of this work was to determine, how transition metal impurities can be used to modify the electronic band structure of semiconductor (Eg) in such a way to harness the solar energy and for other applications.

To accomplish these goals, we have applied various experimental tools. We synthesized CoS and Zn doped CoS thin films by a novel chemical synthesis technique in an aqueous alkaline environment. The base material was first obtained under stringent conditions (time, temperature, concentrations of ammonia, TEA, speed of the mechanical rotation, pH, etc.) and the reaction mechanism is suggested. The materials growth was then observed and evaluated through the SEM, FESEM, AFM and few of the optical characteristics. The final yield of a chemical deposition was subjected to a variety of characterization techniques and an electrochemical photovoltaic application as a part of this thesis.

Regarding the studies of introducing transition metal impurities into the semiconductor to induce magnetic properties, we first developed and demonstrated a method to add zinc impurity atoms within the host cobalt sulfide lattice. This allowed us to the integration of magnetic element in CoS prepared under optimized conditions.

We then studied the advanced characterizations, viz. XPS and EDAX to determine the constituent elemental analysis of the as-obtained CoS and $Co_{1-x}Zn_xS$ thin film samples. These techniques were unveiled that a part of the zinc atoms were coupled to host CoS lattice to create conditions which propelled the observed results. These findings were again confirmed by the structural analysis using an X-ray diffraction technique.

For the studies on optical characteristics, we investigated these films through the optical techniques. We then used electrical transport measurements to determine the conduction mechanism and to reveal several other important electrical parameters.

Finally, we tested these materials for their application part based on the electrochemical photovoltaics. We fabricated a PV-cell comprising CoS and Co-Zn-S thin films as the active photoelectrodes. These PV-cells were characterized trough the electrical, optical and PV properties and the effects of Zn concentration on the properties of PV-cells were outlined with a special emphasis given to the Zn-concentration in CoS. The results were correlated with the solid state thin film properties. The landmarks of the various studies and observations are summarized in the present Ph.D. dissertation are as under;

Chapter-1 is a brief assessment and historic development of the dilute magnetic semiconductors and thin film technologies. It also describes the significance of the method and choice of the materials with reasoning.

Chapter-2 begins with the description of the deposition method selected. This chapter gives a detailed account of the experimentations performed on the compositional (EDS and XPS), structural (XRD), spectroscopic (FTIR), microscopic (Wettability, SEM, FESEM, AFM and MFM), optical and electrical transport measurements. The design and fabrication of a PV-cell and its characterization needed to examine the cell properties are also discussed.

Chapter-3 is regarding the preparation details, growth mechanism, reaction kinetics, physical observations (colour variation and wettability studies) and a detailed account of the materials composition (EDS and XPS). The effects of various preparation parameters on growth of the material are discussed.

Chapter-4 gives a detailed account of the structural (XRD), microscopic (SEM, FESEM, AFM and MFM) and spectroscopic (FTIR) studies of the CoS and (Co, Zn)S thin films.

Chapter-5 The effect of Zn-concentration on the various properties are outlined. The optical and electrical transport (UV-Vis measurements, electrical conductivity and thermoelectric power measurements) studies of these films are highlighted.

Chapter-6 is an application part of these as-grown materials in electrochemical PV-cells. The matched electrolyte was searched out. The basic charge transfer processes at the electrode /electrolyte interface, both in dark and under illumination, are discussed. This chapter also includes studies on I-V and C-V characteristics in dark,

barrier height measurements and some of the typical optical responses. It also includes important conclusions drawn as a result of incorporation of Zn into CoS.

Chapter-7 is a summary of our hard efforts.

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