SYNTHESIS AND SIGNIFICANCE OF NANOMATERIALS WITH EMPHASIS ON ZNS AND CDS THIN FILMS

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Abstract

One facet of this evolution is the emergence of thin films, which are not two-dimensional due to the dimensional growth constraint. This has several uses across various fields. Variety of materials, including metals, semiconductors, insulators, dielectrics, and many more, may be used to make thin films, and they can be manufactured in a number of different methods. There are several suggested methods for the configuration of films. The deposited quality with the least degree of compositional change [1] and the most repeatable characteristics can also be improved using new techniques. With the right thin film production procedure, thin film properties and flexibility may be obtained. Chemical deposition techniques are commonly used to make thin films because of their adaptability in depositing a wide range of compounds, as well as their ability to control synthesis parameters at low deposition temperatures [2-3].

Keywords: thin films, application, dimensional growth, Chemical deposition technique, synthesis parameters

Introduction

The different thin film preparation procedures are distinguished by how the above-mentioned fundamental phases are modified. In theory, by modifying the above mentioned techniques, thin films with the required properties might be produced. The melting point of the materials, as well as their stability, purity, dissociation constants [4-6] in solutions and other deposit characteristics, all have an impact on the preparative procedure used. All of these preparative characteristics can be controlled in a variety of ways. With a high degree of preparation and purity, the films can be deposited in vitreous and crystalline layers with the required stoichiometry. Nanoscience and nanotechnology are concerned with the production, characterization, research and use of nanostructured materials. Nanomaterials are made up of well-organized components that are at least 100 nanometers in size and it's the most popular length measure for describing the size of a single molecule [7-9]. Nanomaterials have very different physical and chemical properties than atomic-molecular or bulk materials of the same composition. For materials in this size range, a transition from atoms or molecules to bulk form occurs resulting in some unexpected characteristics. Nanoscience is founded on the uniqueness of nanostructures characteristics of configuration, energetic, response, dynamics and chemistry. Nanostructure properties and reactions may be controlled, allowing for the creation of new devices and technologies.

There are many conventional energy sources such as the sun, wind, geothermal; hydropower and bio fuels that may be used to provide basic human requirements. However rising demand and an increasing reliance on fossil fuels to supply that need have a variety of negative environmental repercussions. Coal, gas, oil and uranium are all nonrenewable resources that are rapidly decreasing. Due to the widespread use of nonrenewable fuels, the energy industry is under pressure to shift away from carbon-emitting activities toward solar, nuclear and other environmentally friendly options. The desire for sustainable energy has renewed interest in electrochemical-based power sources such as batteries, super capacitors and fuel cells on a global scale. Concerns about ion and electron transport that are dependent on the geometry of active electrode materials are critical for enhancing device [10] manufacturing efficiency.

Semiconductors with a wide range of optoelectronic characteristics have come a long way in recent years and their prominence in research and technology is expanding as a result of innovative uses in devices like light sources. LEDs, laser diodes (LDs), integrated circuits (ICs) and photo detectors [11-13] are all examples of light-emitting diodes (LEDs). The II-VI and III-V group semiconductors and alloys were employed for fascinating applications among the different unique semiconductor materials produced. In the correct proportions, elements from groups II and VI of the periodic table CdS, ZnS, ZnSe, ZnTe, and other II-VI semiconductor compounds are included in the table (e.g. CdS, ZnS, ZnSe, ZnTe). These semiconductors have a rather large band gap with a number of qualities that make them more useful than other costly materials. In general, a big band gap suggests a higher energy electrical component. A large separation between the bands are employed in semiconducting lasers and light emitting diodes as the electronic transition energy is reduced over the whole spectrum of these materials They may now emit in both the visible and ultraviolet UV spectrums. These materials are also exceedingly ionic due to their high degree of ionicity. A powerful electro-optical and electromechanical coupling [14] is possible. Wurtzite and zinc blende tetrahedral crystals are found in semiconductors of the III-V group. Infrared to ultraviolet wavelengths are covered by II-VI semiconductors with linear band gaps. The visible spectrum includes the ultraviolet region as well as the whole visible spectrum.

Recent researches on solar cells fabrication aimed towards lowering the fabrication cost in order to decrease the price of the energy obtained. The researches were directed to use thin films technology for solar cell fabrication. Suitable materials should be easily prepared and inexpensive, show stable behavior over long periods of operation. The high cost and the difficulty to obtain single crystal semiconductors give a great interest to polycrystalline semiconductors, including a wider range of compounds which could be used in different applications. ZnS is an n-type II–VI compound with a wide band gap (3.5eV–3.7eV) at room temperature. It is a promising material for future applications such as window layers of solar cells and coatings which are sensitive to UV light. It is an excellent host material for electroluminescent phosphors and it is being commercially used for electroluminescent displays. Various techniques, such as sputtering, chemical vapor deposition, spray pyrolysis, electrodeposition, successive ionic adsorption and reaction and chemical bath deposition have been used to prepare metal sulphide thin films.

1.1Chemical Bath Deposition Technique

The schematic diagram and photograph of an experimental set-up for the deposition of thin films using the chemical bath deposition technique are shown in Figure1. Water bath, chemical reaction bath constant speed motor cum regulator, substrate and substrate holder is all included. It was kept in the water bath to maintain the temperature of the main reaction bath. A magnetic stirrer was placed in the primary reaction bath and constantly swirled the solution during the deposition duration to ensure uniform deposition over the substrate. As a substrate, glass slides were employed. The pH electrode was put into the reaction beaker for pH monitoring in order to maintain the pH.

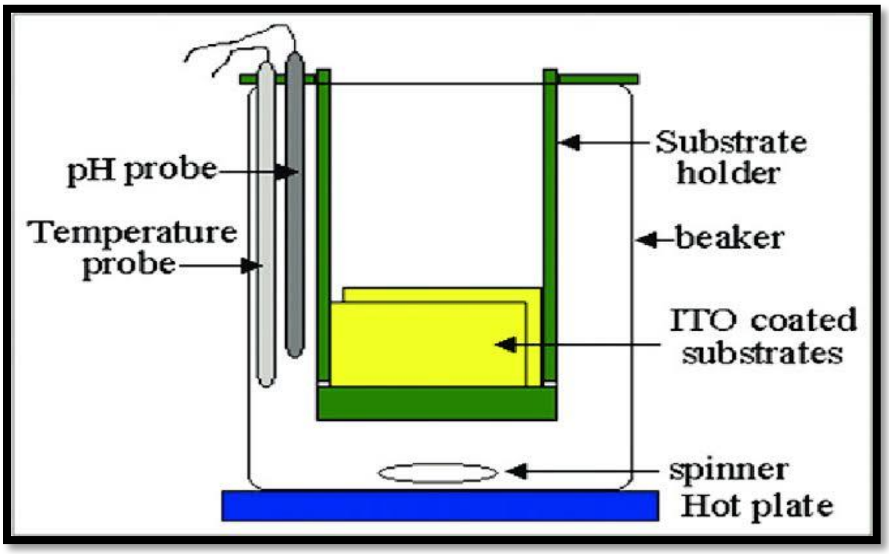


Figure.1: Schematic Diagram of Experimental Set-Up for the Chemical Bath Deposition Technique

Chemical bath deposition (CBD), which is well known as a prevalent low-temperature aqueous technique for depositing large-area thin films of semiconductors, has been recognized as the simplest and most economical one. CBD is a technique in which thin films are deposited on substrates immersed in dilute solutions containing metal ions and the chalcogenide source. Chemical deposition of ZnS thin films has been carried out in aqueous alkaline baths by many workers [15]. In most of these works an ammoniacal solution and one complementary complexing agent for the cation have been used. Dona and

Herrero [16] deposited ZnS film using ammonia and hydrazine hydrate as complexing agent. The importance of ternary complexes (two ligands and one metal) for the deposition of ZnS has been studied by O'Brien reported the influence of NH_3 concentration in the properties of chemical bath deposited ZnS films. A detailed investigation has been made by Mokili et al. on the growth of ZnS thin film on addition of ammine. The effects of ammonium salt on the chemical bath deposition of ZnS thin film have been studied by Oladeji and Chow. Tri sodium citrate has also been used as complexing agent in the deposition of ZnS thin film by Cheng et al and Johnston et al.

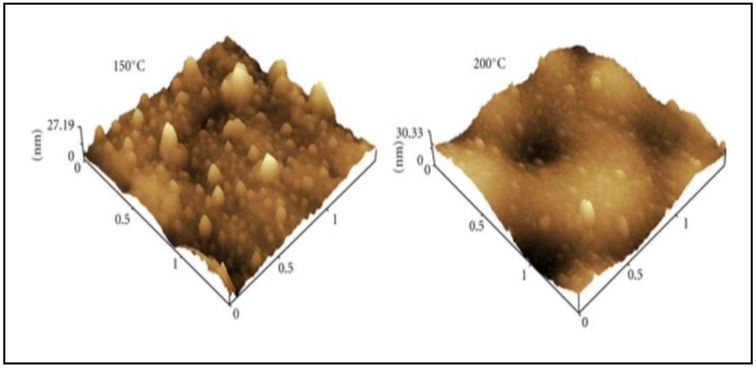


Figure.2: AFM images (scan area: 1.50 μm × 1.50 μm) of thin films forms of ZnS quantum dots heat-treated at 150°C and 200°C.

Nanotechnology is predicted to revolutionize all the sectors of human utility, in addition to electronics and optoelectronics. The recent availability of ground-breaking devices like STM and AFM, FESEM, Raman Spectrometer and others has increased interest in this field. These tools approach enables investigation of material characteristics with atomic-level resolution. Such technological achievements are intrinsically tied to pioneering researches that have uncovered unique physical features of material at a point in between the micro and macro level.

The discovery of carbon-based nanotubes in 1990 spurred a new surge of interest in the topic. This finding inspired a frenzy of study into additional one-dimensional nanostructures, which are materials having one dimensional growth which is much common than all others. 2D growth ways are restricted to the nano range. Nanowires, nanobelts, nanorods and nanotubes are examples of one-dimensional nanostructures. Only one of the two rapid growth orientations is constrained within nanoscale dimensions in two-dimensional nanostructures. Nanosheets and self-assembled monolayers are two examples. All orientations are limited to nanoscale dimensions in zero-dimensional nanostructures. For instance, quantum dots and nanoparticles may exhibit this. The materials are limited to the nanoscale, which significantly improves or modifies their characteristics, making them all fascinating.

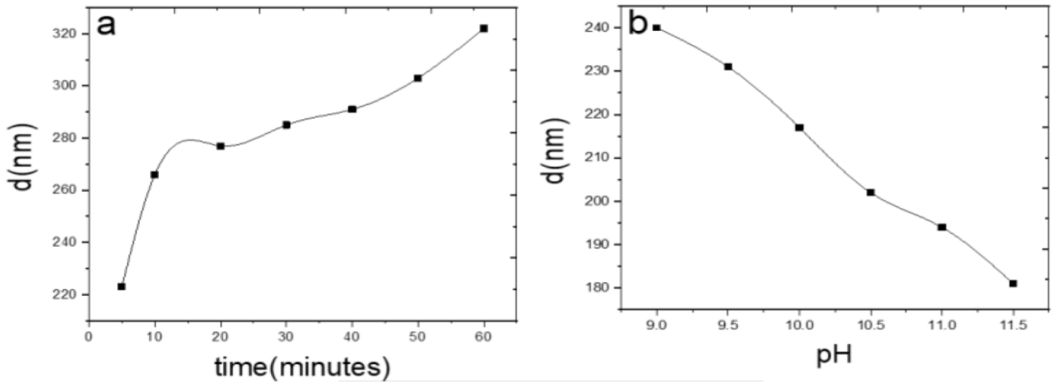
1.2 Nanoscale interactions

For the last decade, nanotechnology research has concentrated on improving control over these materials. Nanoscale interactions are controlled by fundamental physical and chemical principles that are not completely understood. This is why a substantial amount of the research is devoted to finding novel properties, structures and morphologies for manufacturing devices which have a long-term technical efficiency. Since they make it much simpler to produce precise patterns and architectures of nanomaterials and scale up nanostructure production for commercial usage, positioning and patterning nanostructures will be essential for incorporating them into device manufacture [17]. Despite substantial advancements in nanomaterial deployment, rational control and design of their characteristics have remained challenging. In this situation, one of nanotechnologies biggest benefits is also one of its worst drawbacks. A material's characteristics can alter significantly by altering the size with few nanometers, opening the door to a wide variety of new designs and originality. However, even a tiny variation in a material's size may have a big influence on how it behaves, severely reducing the amount of room for mistake.

When analyzing the physical (or chemical) properties of a material on a nanoscale, the dimension and other qualities have a significant relationship. For instance, a small shift of 5 nm can cause their luminescence to shift from the red to the blue end of the visible light spectrum. For the production and application of nanomaterials, the accuracy required for altering dimensionality within a few nanometers or less is crucial. Nanotechnology has the ability to change the types and scope of functions that are accessible as well as how materials and products are made. With less than 1000 commercial nanotechnology-based products already on the market worldwide, it has already had a substantial commercial influence. This number will undoubtedly increase in the future. Today's electronics are built on the foundation of semiconductors. The semiconductor transistor has been widely used in the information, computing and communication industries since its inception. Later on, the focus switched to semiconductor device miniaturization in order to increase integration, functionality and energy efficiency. As a result of these efforts, semiconductors have developed from basics to the modified forms which are capable of managing high magnitude of currents at a micrometer range. The present era is focusing on the development of nano size materials which can be operated directly at the sub atomic level. The spacing between bands (bandgap) and the number of electrons filling the bands define whether a material is a metal, semiconductor or insulator. Metals may carry electricity because they have unbound electrons and partly filled valence band [18]. When a material is in the form of nanocrystals, the chemistry of the crystal lattice is greatly influenced by the nature of the matter which is redefined as a result of the highly strained facade atoms. The atoms are predominantly subjected to tensile lattice strain. The unstrained bulk bonds to the lattice of (a) tensile surface strain and (b) compressive lattice strain. If the breaking process is extended until the crystal size is extremely small, surface bonding will win out over bulk bonding. This cross-over occurs at a crystal size of a few hundred nanometers or less, according to most experimental and theoretical study. This is one of the most fascinating examples of the supremacy of surface atoms. The kind of atomic bonding in a crystal lattice has a big impact on its chemistry. When a material is in the form of nanocrystals, the features of the material change as a result of the highly strained surface atoms. In other words, the strained bonds of the surface atoms define the material's properties and the atoms are subjected to primarily tensile lattice strain.

2.1 Science of Thin film

Thin film science and technology has been rapidly developing in recent years due to its variety of applications in diverse sectors like electronic industries, solar power utilization and space science, production of high memory computer elements, various types of sensors and other thin film based devices over the last few decades. Thin film physics has evolved into a complete discipline in its own right. Thin film substances have properties that are radically different from their bulk counterparts. The nature of the substrate, temperature, temperature of the source, rate of deposition, nature and pressure of residual gas in the vacuum chamber, obliquity of the incident vapor stream, impurities and defects incorporated in films during deposition, ageing and above all film thickness are all factors that influence the structure and other physical properties of thin films [19]. The dependence of properties on thickness is quite strong in ultra-thin films. Thin-film physics arose from early scientific interest about the behavior of two-dimensional materials and the widespread use of thin-film devices, particularly in the electronics sector, assisted in the development of thin-film technology. Variation of thickness of ZnS thin film with different parameters is shown in fig.3. Lattice defects, stacking faults, twinning, atomic organization disorders, dislocations, grain boundaries and other native defects exist in all solid thin films, whether created by vacuum deposition or other processes. These parameters have an impact on the mechanical, electrical, optical and other photo electronic features of the films. Once again, layer thickness and growth method appear to affect structure or structure-sensitive properties. As a result, a basic understanding of the structure and microstructure of diverse thin films as well as their possible impact on other features is necessary.



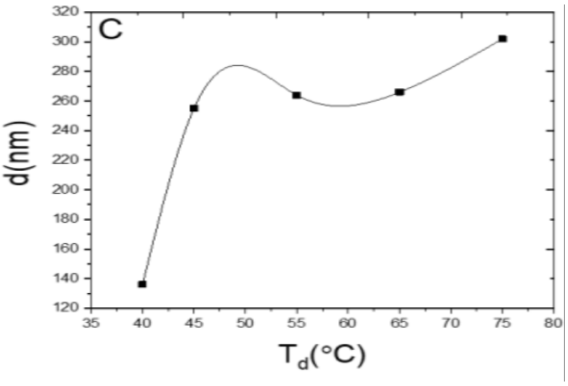


Figure.3: Variation of thickness of ZnS thin films as a function of (a) deposition time $t_{d,}$ (b) pH of the solution, (c) deposition temperature T_d

In the thin film growth process, there should be enough time in between the two following depositions of atoms and layers for them to occupy the lowest practicable potential energy configuration with regard to the surface and further on adhered layers. All of the atoms (or molecules) in a thermodynamically stable film should be at their locations of lowest potential energy, and additional atoms (or molecules) will energetically take up places and orientations compatible with nearby atoms on the substrate or with earlier layers that have been placed. As a result, newly inserted atoms or molecules will take up dwelling designated by the substrate and previously deposited layers energetically stipulated occupancy sites. The vapor atoms are adsorbed by vander walls forces on the substrate and migrate or diffuse along the substrate surface from one potential well to another because of intrinsic kinetic energy or that produced by the substrate. In the process of migration the absorbed species or monomers clashes together, creating subcritical or critical nuclei or clusters that release condensation heat. Nucleation is the process of addition, adsorption and migration that results in the development of stable clusters and critical nuclei.

2.2 The II-VI compound semiconductors

Nanodimensional states of materials engrossed lot of consideration from academics recently because of their exceptional physical and chemical characteristics. Due to their possible application in contemporary technologies, they are a viable choice for the production of electronic, optoelectronic, storage, phosphor and photo catalytic materials [20]. Over the past two decades they have undergone extensive research in order to identify their fundamental properties and provide the foundation for further technology advancements. The II -VI materials and related alloys are the most commonly studied among various materials, particularly III-V, IV-VI and II-V as a result of their unique and outstanding features. Semiconductors like CdO, CdTe, CdSe, ZnSe, ZnMgTe, ZnO, HgS and others are currently being researched. They have multi applications and varied uses as they have excellent physical and chemical characteristics in their nano dimensional form. CdS & ZnS are the most regarded and studied substances in this regard. When impurity atoms are doped there occur significant changes in their intrinsic properties. The transition metal group-member impurity atoms significantly affect the physical and chemical characteristics of the host system. Mn^{+2} and Ni^{+2} ions serve as the dopant elements, whereas CdS and ZnS nanomaterials serve as the host materials. One of the most significant materials utilised in photonics research is zinc sulphide, a transparent semiconductor [1] with a relatively broad band gap (3.8 eV). ZnS has the potential to be used in a wide range of applications, including electroluminescent devices, solar cells, and other optoelectronic devices. ZnS nanostructures inonedimension are appealing as prospects for electrical and optoelectronic nanodevices. ZnS may be crystallized in either the Zinc blende or wurtzite structures; however wurtzite is probably the most beneficial for industrial applications [2] due to its non-central symmetry and polar surface. Wet chemical precipitation is used to encapsulate the impurity components in the host matrices. The medium is adjusted to pH values of 9.0, 10.0 and 11.0 using liquid ammonia medium and the doping levels are set at 5, 10 and 15 weight percent. $Cd_{1-x}M_xS$ is synthesized using a wet chemical method at room temperature with x = 5%, 10%, and 15% wt. and M is metal like Mn or Ni. The pH values of the medium are 9.0, 10.0 and 11.0. Numerous tests are performed on the IV samples to determine their quality. The cubic zinc blende and hexagonal wurtzite structures are expressed in the form $Cd_{1-x}Mn_xS$ and $Cd_{1-x}Ni_xS$, respectively. The crystal structure of the unit cell is always the same as that of a bigger chunk of the crystal, so a given bulk of crystal may be studied using just a small representative sample thereof. Six lattice constants are generally required to define the shape and size of a unit cell. These are its axial lengths (lengths of the edges of the unit cell along its major axes), which are usually denoted as *a*, *b*, and *c*, and its inter-axial angles, which are usually denoted by *alpha* (α), *beta* (β), and *gamma* (γ). In some crystal structures, however, the edge lengths along all axes are equal (a=b=c), so only one lattice constant is used for its dimensional description, *a*. Lattice constant values and knowledge of crystal structure are needed to calculate distances between neighboring atoms in a crystal, as well as in determining some of the crystal's important physical and electrical properties. Note that, depending on the crystal structure, the distance between two neighboring atoms in a lattice may be less than the lattice constant. Figure 4 shows the lattice parameters of a unit cell.

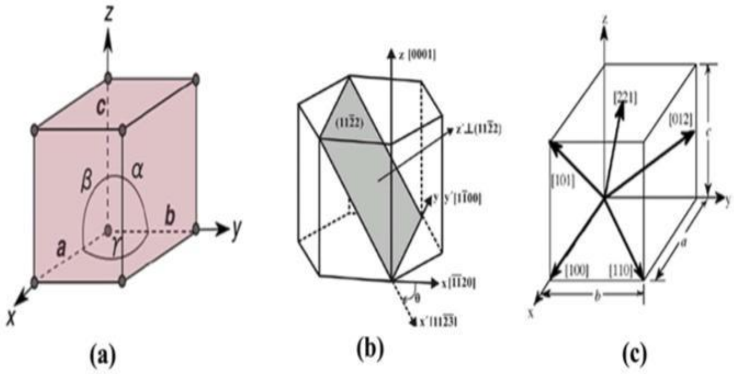


Figure 4: A unit cell with lattice parameters

a) X, Y and Z coordinate axes showing axial lengths and interaxial angles

b) Hexagonal parameters

c) Cubic parameters**.**

Conclusion:

The microelectronics and optoelectronics sectors are among economy's most powerful technical drivers, as seen by the rapid expansion of communication and information processing, storage and display applications. Thin films are now widely used in a variety of applications, including energy generation and conservation, biotechnology, optical, decorative, anticorrosive and wear-resistant coatings. Semiconducting thin films are crucial in the various stages of electronic device construction and specialized functioning. Manipulation of thin film characteristics to produce desired optical spectra is important for photovoltaic and optoelectronic device applications. The current research focuses on the synthesis and characterization of non-toxic Zns and CdS thin films with a low band gap. Both ZnS and CdS are environmentally friendly semiconductors with outstanding optical characteristics, making them ideal for buffer layers [21] in TFSCs, infrared windows and ultraviolet/visible light producing LEDs. In this study efforts were made to customize the characteristics of these materials primarily optical properties, by altering deposition conditions, doping and post-deposition treatments.

The research is important because it influences the stability of electronic equipment that is subjected to radiation, energetic particles and other environmental factors. XRD, XRF, SEM, HRTEM, AFM, UV-visible spectrophotometer, fluorescence spectrophotometer, Raman microscope and FTIR equipment were used to characterize the materials. Other equipments such as FESEM, NSOM and XPS offer further information on material behavior. The Rutherford backscattering spectrometry (RBS) technique may be used to analyze surface layers and precisely estimate the thickness of film materials. We have also looked at doped ZnS and CdS materials to see whether they offer better optical characteristics. Doping reduces particle size which improves luminescence efficiency as a result; doped materials are more effective in device applications.

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