EFFECT OF DEPOSITION TIME ON STRUCTURAL, MORPHOLOGICAL, AND OPTICAL PROPERTIES OF MULTI LAYER THIN FILMS OF (Cd-Zn) S PREPARED BY LOW COST CHEMICAL BATH DEPOSITION

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ABSTRACT

The low-cost chemical bath deposition (CBD) method was used to deposit a ternary Cadmium Zinc Sulfide (Cd-Zn) S thin film on a glass substrate, and its morphological, structural, and optical properties were reported in this paper. When making a composite thin film, Zinc Acetate and Cadmium Acetate are mixed in the right proportions. XRD, SEM, EDX, UV-VIS spectrophotometry, and PL spectroscopy were used to investigate the effect of deposition time on the properties of the fabricated sample. The particles have been seen to be spherical and asymmetrical. For various arrangements of single layer, double layer, and as deposited multilayer thin films of CdS and CdZnS, the polycrystalline growth was confirmed by XRD, with all films exhibiting cubic and hexagonal structures. Some impurities, as well as cadmium, zinc, and sulfur, were found in the EDS tests. The presence of impurities like carbon, oxygen, and nitrogen during film deposition is clearly visible due to the presence of air. The films had thicknesses of 1.20 m. The absorption edge spectra range from 550 to 600 nm, with the CdS thin film having a band gap of 2.52 eV, the CdS- (Cd0.8 Zn0.2) S thin film having a band gap of 2.65 eV, and the CdS- (Cd0.8 Zn0.2)S- (Cd0.5 Zn0.5)S thin film having a band gap of 2.75 eV. PL Spectra shows excitation peak.

Keywords: XRD, SEM, Multilayer, Thin Film, Chemical Bath deposition.
1. INTRODUCTION

In the realm of nanotechnology, thin film technology is the most common and recent emergent technology. The vast array of novel approaches calls for content that meets their needs. Nanotechnology and nanomaterial research have significantly impacted daily life in the last several decades. Semiconducting nanoparticle production, characterization, and applications have recently attracted a lot of attention. Due to the quantum size effect and the huge surface area, when the sizes of semiconducting nanoparticles are reduced to the nanosize range, their electrical and optical properties radically alter. Semiconducting particles can have their conductivity and optical characteristics changed.

The term "thin film" refers to a structure with a two-dimensional regular arrangement or one that is constrained in two directions with respect to the threshold condition. Alternatively, two-dimensional solid materials that are constrained by one thickness (t) direction are also referred to as thin films. When compared to their bulk counterparts, thin film characteristics are different. Thin film technology has advanced significantly in recent years and continues to be used today due to its special technological characteristics. The self-assembly of the component material in the form of solution is the basis for the deposition of the two-dimensional structure, or thin film. Any material or group element may be deposited using a variety of deposition techniques, including chemical growth and nucleation. The nucleation and growth processes are influenced by a number of factors, including deposition duration, solution temperature, rate of deposition, and the chemical composition of the material, or how these factors interact with one another. A thin film is created by depositing a material over a suitable substrate while maintaining the proper conditions, such as the right temperature, duration, and rate of material interaction.

Because their characteristics are intermediate between those of ZnS and CdS, thin films of (Cd Zn)S are intriguing [1–5]. It is regarded as a somewhat practical transparent metal sulphide for use in solar cells as a window. Its UV absorbance is lower and its band gaps are often more than 2.4 eV [1, 5; 6–8]. Cadmium Zinc Sulphide, a ternary compound that belongs to the II-VI group of compounds, with the chemical formula (Cd-ZnS). For broad band-gap windows in heterojunction solar cells and photoconductive devices, (Cd-ZnS) thin films have been widely employed. In solar cell systems where CdS films have been shown to be effective, replacing CdS with the higher band gap ternary compound (Cd-Zn)S has reduced window absorption losses and increased the (Cd-Zn)S's importance as a key component in the field of nanotechnology and thin film based technology. The direct band gap of (Cd-Zn)S, which results in the visible region and is at 2.27 eV, attracted a lot of interest. Due to their high absorption coefficient, they have a wide range of applications, including lasers, buffer layers in thin-film heterojunction solar cells, biological applications, non-linear optical devices, and display devices. Photovoltaic cell with piezoelectric transducer [9-12]

An n-type semiconductor called cadmium sulphide (CdS) is appropriate for use in solar cells made of chalcogenide materials as Cu(In, Ga)Se₂, CdTe, Cu₂ZnSnS₄, and PbS [13–19]. It possesses a high absorption coefficient, a broad band gap energy of 2.42 eV, and good mobility. Thin-film transistors and photosensors are only a couple of the several applications where CdS has tremendous promise [20,21]. Chemical bath deposition (CBD) [17,22–25], vaporisation [26], spray pyrolysis [27], sputtering [28], and sequential ionic layer adsorption and reaction [29] are only a few of the numerous methods used to deposit CdS. CBD, on the other hand, could create CdS thin films with good uniformity and a sizable surface area using a low-cost, low-temperature method. The deposition of several chalcogenides, including CdSe, ZnO, Sb₂Se₅, Bi₂Se₃, ZnS, and CuS, is made possible by CBD in general. Numerous parameters, including pH, precursor concentrations, and bath temperature, can be used to produce materials with a variety of shapes and properties [30–35].

Due to its wide band gap (2.42 eV), high refractive index, thermal and chemical stability, effective transport capabilities, and n-type semiconductor structure, CdS is one of the best options for the window layer in solar cells [36-38]. Cadmium telluride (CdTe), copper indium gallium di-selenide (CuInGaSe₂), and copper zinc and tin sulphide (CuZTS) are utilised as alternatives to cadmium sulphide (CdS) in heterojunction solar cells. Pure cadmium sulphide thin films may absorb light with a wavelength below 512 nm and have a somewhat poor transmittance [42]. However, the performance of this material as a window layer in solar cells might be improved by adjusting the optical band gap energy and electrical conductivity by doping CdS with other elements as Ga [43], Cu [44], B [45], In [46], Sn [47], and Zn [48-51].
Among the aforementioned dopants, Zn has garnered the most attention because it can greatly modify the optical band gap of the compound \((\text{Cd}_x\text{Zn}_{1-x}\text{S})\) [48–52]. The band gap of the II-VI semiconductor \((\text{Cd}_x\text{Zn}_{1-x}\text{S})\) varies depending on its composition, ranging from 2.42 eV for \(\text{CdS}\) to 3.70 eV for \(\text{ZnS}\) [53,54]. Chemical deposition techniques are chosen over physical deposition techniques for the deposition of \(\text{CdZnS}\) thin films due to their cost effectiveness. For the deposition of \(\text{CdZnS}\) thin films, a number of low-cost chemical methodologies and techniques have been reported to date. In particular, Chemical Bath Deposition (CBD) [55,56], Spray Pyrolysis [57,58], Successive Ion Layer Adsorption and Reaction (SILAR) [59], Dip Coating [60], and Ink Screen-Printing [61] have all been mentioned. Because controlled precipitation from a solution over a broad surface is achievable under ambient circumstances, CBD is somewhat more beneficial than the other chemical techniques of deposition [62]. The thin films that are produced are of an equivalent quality to those created using physical deposition techniques. The inclusion of Zn element into \(\text{CdS}\) has been studied in the current study to understand the structural, morphological, and optical features for \(\text{CdZnS}\) thin films.

2. MATERIAL AND METHODS

2.1: Thin Film Preparation

Cadmium acetate and zinc acetate are the mixed in proper proportion. Triethanolamine, 30\% aqueous ammonia solution, thiourea and PVP polymer are added to the cadmium acetate and zinc acetate according to the requirement for the thin film preparation. The thin film was deposited on the glass substrate. The multilayer thin film was deposited on glass slides using the Chemical Bath Deposition (CBD) technique. All the apparatus required to prepare the solution were initially degreased in HCl, followed by acetone and lastly cleaned with triple distilled water. They were allowed to dry in open air. For the first layer deposition of \(\text{CdS}\) bulk thin film, the solution of cadmium acetate, triethanolamine, aqueous ammonia and thiourea was prepared. Instantly the solution is stirred on magnetic stirrer for 60 minutes. The bath temperature was set to 80°C and glass slides were placed vertically in the solution. The deposition of film in chemical bath was carried for 2 hours. The film was taken out from the bath and left to dry at room temperature overnight. The second layer of cadmium sulphide and zinc sulphide was deposited on the first layer. The solution prepared has cadmium acetate and zinc acetate in a certain ratio followed by triethanolamine, aqueous ammonia and thiourea. The stirring time of the solution was one hour. The bath was set to 80°C and the glass slide with earlier deposited thin film of \(\text{CdS}\) was placed vertically in the solution for 2 hours. Similarly the third layer of cadmium sulphide and zinc sulphide (different in concentration ratio from the second layer) was deposited on the second layer. This procedure resulted in the formation of cadmium sulphide and zinc sulphide multilayer bulk thin film.

The similar procedure detailed above for the bulk film deposition was carried for the cadmium sulphide and zinc sulphide multilayer nano thin film deposition. The only difference was pvp which acted as the capping agent for the nano thin film formation. The solution is prepared in the similar manner for all the three films just that before stirring, pvp is added to the solution. The resulting mixture was agitated for 10 min, adjusted to a pH of 10.5, and then placed in an 80°C water bath for 30 min. The same steps were taken to produce (Cd-Zn)S nanostructures where the deposition time varied from 10 to 60 min. The bath was entirely covered throughout the deposition. After deposition of each layer of film, it is left to dry at room temperature. The fabricated samples were uniform, transparent, sticky, and yellow, as presented in Figure 2.

Figure 1: Schematic diagram of CBD technique for growing \((\text{Cd-Zn})\text{S}\) thin film.
Figure 2: Photographic pictures of the fabricated samples at different growth time as written (10, 30 and 60 min).

2.2: Instrumentation
The XRD was used to measure the thin-film structure. X-ray diffraction (XRD) performed by PAN analytical 3 kW X’Pert powder XRD multifunctional diffractometer with Cu Kα radiation source (λ = 1.5406 Å and 2θ range = 20° to 80°). The study was done in National Institute of Technology Raipur Chhattisgarh. This study is powerful tools for the analysis of diffraction peaks ascertained the formation of expected materials and also reveals presence of any impurity or defects. Parameters like crystal size and the lattice constants, lattice strain etc. are then determined and correlated with particle size studies. The morphology properties of the fabricated thin films were examined using scanning electron microscopy (SEM) [JSM-651OLV]. A spectrophotometer and photoluminescence (PL) equipment were used to evaluate optical characteristics.

3. RESULTS AND DISCUSSION

3.1: Analysis of Structural Properties
Figure 3 displays the (Cd-Zn)S thin films' X-ray diffraction patterns at varied deposition periods. It is confirmed that (Cd-Zn)S thin films have formed on the cubic structure (JCPDS #36-1451 card) by the peak at 26.60°, which corresponds to the (111) plane, having the maximum intensity [13]. The peaks connected to planes (110) and (112), which were located at around 44.40° and 52.00°, respectively, indicated that a combination of hexagonal and cubic phases was created [14]. Peak amplitude changes with deposition time, peaking at 10 minutes and subsequently declining. Given that deposition time has a substantial influence on the crystallisation of the film, this implies that the optimal deposition period for maximising crystallinity is 10 min [15]. CdS may have either a more stable or cubic sphalerite crystal structure, depending on the production process [19]. Furthermore, Figure 3 demonstrates that the massive hump in the whole set of X-ray diffraction diagrams near the peak at 26.70° [20] is caused by the glass substrate.
3.2: Study of Morphological Property

SEM was used to analyse the morphology for the production of (Cd-Zn)S thin films. Figure 4 shows top-view SEM images of thin (Cd-Zn)S films that were deposited over a period of 10, 30, and 60 minutes. Each sample resembles a cluster of nanoflakes. Like plant roots, the nanoflakes are intertwined with one another. The samples were found to be perfectly smooth and homogeneous throughout, indicating that the deposited layer was evenly yellowish, adherent, and completely covering the substrate with no pinholes or fractures in any of the coatings. The tiny particles form a porous structure that mimics fibrous material, demonstrating the nanocrystalline nature of the (Cd-Zn)S thin films that are produced. Additionally, thin films are coated in spherical granules, and the density of the particles grows with longer deposition durations. When the minute particles accumulate and cover the whole substrate surface, a homogeneous layer is formed. As the deposition period is increased to 60 minutes, small particles condense into larger clusters that are equally distributed across the films. Shorter periods for ion-by-ion growth, which results in smaller particles, might explain this shape. Conversely, longer times for cluster-by-cluster growth, which has a slower growth rate, would result in lower precursor concentrations. [24,63]. Figure 5 shows EDX analysis for the samples where the ratio of Cd, Zn and S in the composite is extremely similar, which indicates the formation of the same phase of (Cd-Zn)S thin films. There are impurities atoms present on the film. The compositional analysis shows the presence of C, O and N in all the three spectrums however in CdS EDS spectrum Cl and Si are also observed along with C, O and N. The presence of carbon and oxygen may be attributed to air which were incorporated during synthesis.
Figure 4: Top-view SEM images of (Cd-Zn)S thin films at various deposition times.

Figure 5: EDX analysis of (Cd-Zn)S thin films at various deposition times.
3.3: Study of Optical Properties

The band gap values of the (Cd-Zn)S thin films are shown in Figure 6 together with the UV-vis absorption spectra of the manufactured (Cd-Zn)S thin films. All samples feature well-defined absorption band edges about 500 nm. The film exhibits strong increases in optical absorbance and visible region absorption. The design of optical and optoelectronic devices can take use of the significant absorption properties of nanocrystalline CdS and (Cd-Zn)S sheets. The optical absorbance is a potent tool for determining the sample’s optical characteristics and energy gap.

![UV-Vis absorbance spectra of the fabricated (Cd-Zn)S thin film at various deposition times.](image)

3.4: PL Studies

Investigations into photoluminescence (PL) offer significant new information on atomic structure and material quality. Figure 7 shows the PL spectra for (Cd-Zn)S thin films that were recorded under ambient lighting conditions. Defects like vacancies or electron-hole recombination sites were seen in the PL emission and absorption spectra [64]. At ambient temperature, the major peaks emerged at 537 nm (2.30 eV). These might be linked to the shift from the valence band to the conduction band and excitonic transitions, such as pairs recombination and emissions (where excitonic transitions are caused by the defects present in (Cd-Zn)S thin films, such as cadmium interstitials (Cd) or sulphur vacancies (S)). [66]. All deposited (Cd-Zn)S thin films have an emission peak at about 2.3 eV, which is caused by the near-band edge (NBE) emission from free excitons recombining [65]. The obtained optical band gap values closely match the location of the emission peak in the (Cd-Zn)S thin film. As deposition time grows, photoluminescence decreases as a result of the Cd vacancies functioning as acceptors (defects) or centres to capture carriers, which decrease as deposition time rises. As the particle border between them gets wider, such flaws get smaller. The intensity lowers as deposition time rises, indicating greater separation and collecting of charge carriers and less recombination of carriers. The findings demonstrate that (Cd-Zn)S thin films are suitable contenders for solar cells.
4. CONCLUSIONS

In summary, (Cd-Zn)S thin films were effectively created using low-cost and low-temperature chemical bath deposition. Different methodologies were used to characterise the structural, morphological, and optical characteristics of the manufactured samples. The created (Cd-Zn)S thin films have a consistent thin film morphology that is flat and well-adhered to the substrate surface with hierarchical nanoflakes. These thin films are composed of polycrystalline cubic and hexagonal structures. In the case of solar cell applications, this shape could be a suitable choice to improve light absorption. Strong absorption band edges were seen in the thin films in the vicinity of 500 nm, which are connected to (Cd-Zn)S band gap values. According to PL data, the creation of (Cd-Zn) S thin films had a peak at 537 nm, and its intensity dropped as the deposition time rose, suggesting less carrier recombination and more charge carrier separation and collection. Our findings show that (Cd-Zn)S thin films make good candidates for optoelectronic applications, particularly solar cell applications.

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