



Studies on Synthesis of Silver Bismuth Sulphide and Mercury Bismuth Sulphide Thin Films for Solar Cell application

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Abstract

Dye-sensitized Solar Cells (DSSCs) are a promising candidate for the next generation of renewable photovoltaic sources. There are two types of semiconductor Sensitized Solar Cells (SSCs): Extremely Thin Absorber (ETA) solar cells and liquid-junction semiconductor-sensitized solar cells. Many semiconductor materials, including CdS, CdSe, PbS and Sb₂S₃ have been employed as sensitizers for SSCs. Most of these sensitizers belong to the binary metal chalcogenide systems. Ternary semiconductors are also important materials for solar cells. However, ternary metal chalcogenide SSCs have been much less explored because ternary semiconductors are more difficult to synthesize for there are three elements involved and the stoichiometry of the atoms must be correct. In the present review article, using the doctor blade/spin coating/drop Coating/chemical Bath Deposition (CBD) and Successive Ionic Layer adsorption Reaction (SILAR), thin film deposition of TiO₂ on Fluorine Tin Oxide (FTO) coated glass substrate is carried out. Using Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption Reaction (SILAR) deposition of thin films of AgBiS₂ and HgBiS_x onto Fluorine Tin Oxide (FTO) and TiO₂ is carried out. In the present work, different characterization techniques are used to analyze the TiO₂, AgBiS₂ and HgBiS_x thin films. The characterization were carried out by X-ray diffraction (XRD) for structural study, Scanning Electron Microscopy (SEM) for surface morphology and for

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Introduction

Currently there is a lot of solar research going on in what is being referred to in the industry as Third-generation solar cells. These new generations of solar cells are being made from variety of new materials besides silicon, including nanotubes, silicon wires, solar inks using conventional printing press technologies, organic dyes, and conductive plastics. The ultimate goal is to improve on the solar cells already commercially available – by making solar energy more efficient over a wider band of solar energy (e.g., including infrared), less expensive so it can be used by more and more people, and to develop more and different uses. Third generation solar cells can exceed the theoretical solar conversion efficiency limit for a single energy threshold material. Recently, ternary AgSbS₂ films and nanoparticles were successfully synthesized for use as a sensitizer for SSCs. AgBiS₂ belongs to a group of I–V–VI semiconductors which has important applications in linear and nonlinear optoelectronic devices, thermoelectric devices, and optical recording media. Bulk AgBiS₂ has an energy gap of $E_g = 1.2$ eV, which is close to the optimal gap (1.39 eV) for a solar absorber. It has a high absorption coefficient of $\alpha = 105$ cm⁻¹ (at $\lambda = 600$ nm). These two features give AgBiS₂ the potential to be utilized for a high-efficiency solar absorber.

Chemical bath deposition technique for thin film deposition:

Chemical Bath Deposition (CBD) is a slow process which facilitates better orientation of crystallites with improved grain structure. Depending upon the deposition conditions, film growth can take place by ion-by-ion condensation of the materials on the substrates or by adsorption of the colloidal particles from the solution onto a substrate.

Successive ionic layer adsorption reaction (SILAR)

SILAR is a relative method. In this method, first step is specific adsorption of the most strongly adsorbed ions of the compound to be grown by the substrate immersion in a solution of one of its cationic precursor. The second step is, water rinsing of the excess solution still adhering to the substrate. Third step is chemical reaction between the most strongly specific adsorbed cations and the less strongly adsorbed anions by the subsequent substrate immersion in the solution and finally again water rinsing of the excess solution still adhering to the substrate. This ideally results in a single monolayer of the desired compound. Fig.1 and Fig.2 represents experimental setup for CBD and growth scheme of SILAR method respectively.

This review is divided into two main sections. The theoretical background of CBD and MCB method, doctor blade, spin coating and drop coating method and the survey of chalcogenides thin films deposited by CBD and MCB method are discussed in the first section.

The concentration of pure solid is constant number Since K and K' are constants, the products of KK' is also constant, say K_s . Then equation 2.4 becomes we get, the constant K_s is called solubility product and the expression $C_A^{+} C_B^{-}$ is called as the ionic product. When the solution is saturated the ionic product is equal to the solubility product. When the ionic product exceeds the solubility product, the solution is supersaturated, precipitation occurs and ions combine on the substrate and in the solution to form nuclei. There are three main factors as temperature, solvent and particle size, which affect the solubility product. For any formation of thin film, there is some minimum number of ions or molecules required to produce a stable second phase in contact with a solution called a nucleus. The rate at which nuclei form in a solution is depends upon the degree of super saturation. The rate of nucleation increases exponentially in higher supersaturated solution.

The SILAR method is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR process is intended to grow thin

films of water insoluble ionic or ion covalent compounds of the type K_pA_a by heterogeneous chemical reaction at the solid solution interface between adsorbed cations.

Where, K represents cation, p represents the number of cations, a represents the numerical value of charge on cation, X is a ion in cationic precursors having negative charge, q represents the number of X in cationic precursors and b the numerical value of charges on X , Y the ion which is attached to chalcogen ion, b' the number of Y in the anionic solutions, q' the numerical value of charge on Y , A represents the anion, a' the number of anions. A is the chalcogen ion. In the presence of complexing agent, above reaction can be written as, Where, C is complexing agent. The basis of SILAR growth it consists of at least four different steps: adsorption, rinsing (I), reaction and rinsing (II).

In this first step of SILAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

By repeating these cycles, a thin layer of material, K_pA_a , can be grown. Following the above-mentioned steps the maximum increase in film thickness per one reaction cycle is theoretically one monolayer. This results into a solid layer of the compound K_pA_a . In practice, however, the thickness increase is typically less than or greater than a monolayer. Thus, the process involves an alternate immersion of the substrate in a solution containing a soluble salt of the cation of the compound to be grown. The substrate supporting the growing film is rinsed in highly purified deionized water after each immersion.

The factors affecting the growth phenomena are the quality of the precursor solutions, their pH values, concentrations, counter ions, individual rinsing and dipping times. In addition, complexing agent and pretreatment of the substrate have been shown to affect the SILAR growth.

Doctor Blading or tape casting is an economical method for producing large surface areas film which is very well suited for laboratory work and consists of printing, coating, or spreading paste with a blade onto a substrate in which composition of paste is very important. The paste can be formed by using suitable solvent; the paste drop can be spread by blade. The mesoporous film can form by this method. The desired thin film can be formed by this method by varying applied pressure.

In a spin coating, an excess amount of solution is placed on substrate. The substrate is then rotated at a high speed in order to spread the fluid by centrifugal force. The rotation is continued for some time, with fluid being spun off the edges of the substrate until the desired film thickness is achieved. The solvent is usually volatile providing for its simultaneous evaporation.

In this method a small amount of solution was carefully spread on the surface of sample, and then dried it. TiO_2 is deposited by using this method.

Chalcogenides have received considerable attention during recent years because of their proven and potential applications in a variety of semiconducting devices. TiO_2 , HgS and Ag_2S in the forms of single crystals, sintered pellets and polycrystalline materials have been employed in photoelectrochemical (PEC) cells, where OX and Red are the oxidised and the reduced species and E_0 is the standard electrochemical potential. The reverse process of losing an electron is called an oxidation reaction.

Where one species loses an electron and the other species gains an electron it constitutes a redox system. The electron energy state in the redox electrolyte is an analogy with the concept of energy states in a solid, by the energy change in the reaction this means that we introduce a free electron from infinity into the solution and let it occupy the lowest electron state in an oxidized species without change of the salvation structure. This gives the energy of the unoccupied states. The reverse process gives the energy of the occupied state reduced species).

The probability function for electron states in the redox electrolyte is the sum of occupied and unoccupied states, which is equivalent to the density of states function in the solid. $D_{red}(E)$ and $D_{ox}(E)$ are represented by W_{red} , W_{ox} are given by the

thermal distribution functions of ionic configurations, and Cox and C redare concentrations of ions in the solutions.

At equilibrium, the occupation of these energy states in the redox electrolyte is again given by the Fermi distribution function.

EF redox is electrochemical potential and is related to the mean free energy change per mole electrons in the redox reaction by

Metals and semiconductor can perform redox reactions with electrolytes. The transfer of an electron to or from the solution can take place only in the energy region of the conduction band while the hole transfer can take place in the energy region of the valence band. Such a transfer can occur between two states of the same energy, one empty and one filled.

The redox system may be one of the following types consisting of:

- ions of the same metal in two different states of valence, e.g. Stannous - stannic
- two anions carrying different charges, e.g. ferrocyanide - ferricyanide
- anions and cations of the same metal, e.g. permanganate - manganous ions system
- one or more solids, e.g. lead sulphate - lead dioxide
- Organic compounds, e.g. quinone - hydroquinone

The optical to electrical energy conversion efficiency in a semiconductor/liquid junction cell is given by Photoelectro chemical cells

A typical type of the photocurrent-generated device has a semiconductor in contact with an electrolyte, and this is often referred as photoelectron chemical cells. A photoelectrochemical solar cell (PEC) can generate not only electrical but also electrochemical energy and provide the basis for a system with an energy-storage component (PEC).

Photoelectrochemical systems have the potential to not only convert but also store incident solar energy.

Properties of PEC cells

- Current potential characteristics
- Photovoltaic characteristics
- Photoresponse
- Spectral response
- Speed of response
- Flat band potential.

Literature Review

Huang P C first reported synthesis of AgBiS₂ by successive ionic layer adsorption reaction (SILAR) process. In his work characterization of AgBiS₂, TEM image of several individual AgBiS₂ nanoparticles had an average diameter of 16 nm and are also roughly round in shape. Optical transmission spectra T of 150°C annealed AgBiS₂ (n) nanoparticles with various numbers of SILAR cycles n. The transmission decreased with increasing n, indicating that as n increased, more nanoparticle material was grown on the photo electrode, resulting in enhanced optical absorption. The E_g for n = 4 sample is ~1.32 eV, which is slightly larger than that of bulk AgBiS₂ (1.2 eV). It is interesting to note that this E_g is nearly equal to that of the optimal E_g (1.39 eV) of a solar absorber, a beneficial property for a sensitizer material. The structure of the solar cells included a compact layer, a semiconductor sensitizer layer and a Pt counterelectrode; there was no scattering layer in these samples. Initially, the short-circuit current density (J_{sc}) and power conversion efficiency (η) increased with SILAR cycle (n). The open-circuit voltage (V_{oc}) and fill factor (FF) changed only slightly with n. The best performance was obtained at n = 4, which yielded J_{sc} = 5.76 mA/cm², V_{oc} = 0.16 V, and η = 0.36%, after that, the efficiency started to decrease again. When an Au counterelectrode was used to replace Pt in the cell assembly, the efficiency (η) increased from 0.36 to 0.41%. I-V curves of AgBiS₂ SSCs under various sun intensities

indicated that the efficiency increases with decreasing light intensity. The efficiency at 14.8% sun is $\eta = 0.76\%$, a 43% enhancement compared to $\eta = 0.53\%$ at 1 sun.

The photovoltaic performance of AgBiS₂ SSCs prepared on different thicknesses (5 and 12 μm) of TiO₂ electrode. Thus, it can be said that the two AgBiS₂ cells have the same performance. A thinner TiO₂ film contains a smaller amount of semiconductor material, leading to reduced light harvesting. But it also provides a shorter conducting path for photoelectrons, leading to improved photocurrent collection. From his work Huang P C et al concluded that AgBiS₂ SSCs have several notable features: (a) a high J_{sc} of 7.61 mA/cm²; (b) an E_g (1.32 eV) close to that for an optimal solar absorber. The efficiency of 0.76% (0.148 sun) is respectable, considering that it was first time that the AgBiS₂ SSCs is investigated.

Calva Yanez later reported synthesis of AgBiS₂ absorber layer obtained by SILAR method. Their work demonstrated that use of cubic AgBiS₂ ternary chalcogenide obtained by SILAR methods as absorber layers in hybrid solar cells. By optimizing the number of SILAR cycles, a clean and scalable method renders an absorber material that does not require capping, ligand exchange and passivation steps. Surface photovoltage (SPV) analysis and contact potential difference (CPD) measurements indicated the absence of substantial barriers for majority carrier extraction at the TiO₂/AgBiS₂ interface, as well as a low density of trap states, when compared to binary chalcogenides. Devices reaching 2.85% power conversion efficiency show J_{sc} and V_{oc} values similar to those reported for the record cell based on AgBiS₂ with more complex architecture.

Pejova B synthesized AgBiS₂ using chemical and sonochemical deposition methods. In both approaches, they used reaction system was composed of the following components: silver nitrate, bismuth nitrate and sodium thiosulfate. The first two substances serve as metal ions precursors, whereas the third one plays a double role: as a complexing agent and as a sulfide ion precursor. Because the Bi³⁺ cation has a strong tendency toward hydrolysis, in order to avoid precipitation of BiONO₃, bismuth (III) nitrate was dissolved in a solution of nitric acid ($c(\text{HNO}_3) = 2 \text{ mol/dm}^3$). Best photoelectrical performances of the finally synthesized 3D QD assemblies in thin film form were achieved with initial concentrations of both AgNO₃ and Bi(NO₃)₃ solutions of 0.1 mol dm⁻³, initial concentration of Na₂S₂O₃ solution of 1 mol dm⁻³, keeping the volume ratio of these three species of 1:1:1.

Rodriguez A N reported optical and electrical properties of AgBiS₂ thin films by CBD method. In the said work Ag₂S thin films deposited from chemical baths containing silver thiosulfate complex and dimethylthiourea as a source of sulfide ions. This technique is very similar to that reported for the deposition of CuS thin films. The variations in the crystalline nature of the film with annealing, optical and electrical properties are reported. The deposition of Ag₂S thin films on a chemically deposited Bi₂S₃ thin film and the production of a ternary compound upon heating are also reported. The thin films of AgBiS₂ show good uniformity and adherence on ZnS coated glass substrates. Their optical energy band gap (0.96 – 1.36 eV) is in the desired interval to be used as absorber materials in solar cell structures. The electrical conductivity 10^{-5} to $10^{-2} (\Omega\text{cm})^{-1}$ is in the range required for absorber materials to effectively absorb solar radiation in the depletion region of a junction.

Zhou S reported preparation and photovoltaic properties of AgBiS₂ quantum dots sensitized TiO₂ nanorods photoanodes by electrochemical atomic layer deposition (ECALD) technique. In this work, as a first trial, ECALD has been employed to grow AgBiS₂ ternary quantum dots on a TiO₂ nanorods array substrate. The optical absorption property of TiO₂ NRs was greatly enhanced by sensitizing with the AgBiS₂ QDs, and a photoelectric conversion efficiency of 0.95% was achieved in the QDSSC assembled with AgBiS₂ sensitized TiO₂ NRs photoanode, Pt counter electrode and iodide-based electrolyte by adjusting the ECALD deposition cycle. The conclusion from this work was AgBiS₂ QDs have been successfully fabricated on a rutile TiO₂ NRs array via the route of electrochemical atomic deposition for the first time. By adjusting the deposition cycle, it is convenient to control the coverage of QDs on TiO₂ NRs. A conversion efficiency of 0.95% with a photocurrent of 4.22 mA/cm² and open voltage of 0.53 V has been achieved for the 30 cycle's sample.

In the recent years, interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in solar cells, light emitting diodes and non-linear optical devices has increased. Many reports were available on chemically deposited ternary composite thin films such as, and suggested their applications in the area of energy conversion and solar energy utilization due to the modification in electrical and optical properties. However, there is only one reports on synthesis of $(\text{HgS})_x(\text{Bi}_2\text{S}_3)_{1-x}$, a ternary composite. Also there is much interest in structural, electrical and optical properties of nanostructured semiconductor thin films due to their novelty; their properties are different and often superior to those of conventional coarse-grained polycrystalline bulk materials which are very important for semiconductor industry. The semiconductor material Bi_2S_3 and HgS received great attention since their band gap energies lies close to the range of theoretically attainable energy conversion efficiency. The band gaps of Bi_2S_3 and HgS were reported earlier as 1.3 and 2.4 eV, respectively, which lie in the visible to near-infrared region. The composites of Bi_2S_3 and HgS should have the band gaps in between their characteristic band gaps, which will cover the maximum solar energy spectrum, and therefore it is helpful to get efficient solar energy conversation cell. Various techniques have been employed for Bi_2S_3 and HgS thin film deposition such as chemical bath deposition, SILAR, electro-deposition, spray pyrolysis etc.

Discussion

In the recent years, interest on or semiconductor industry. The semiconductor material Bi_2S_3 and HgS received great attention since their band gap energies lies close to the range of theoretically attainable energy conversion efficiency. The band gaps of Bi_2S_3 and HgS were reported earlier as 1.3 and 2.4 eV, respectively, which lie in the visible to near-infrared region. The composites of Bi_2S_3 and HgS should have the band gaps in between their characteristic band gaps, which will cover the maximum solar energy spectrum, and therefore it is helpful to get efficient solar energy conversation cell. Various techniques have been employed for Bi_2S_3 and HgS thin film deposition such as chemical bath deposition, SILAR, electro-deposition, spray pyrolysis etc.

Brower S W reported synthesis of HgBi_2S_4 by heating 10g of batches of the constituent elements in evacuated sealed silica glass tubes. The specimen was heated to 5000C to partially react the free sulphur. Subsequently the specimen were heated in a rocking furnace to a temperature where the entire content were molten, generally between the 700-10000C and then cooled to room temperature. The specimen was examined by X-ray powder diffraction. The composition of HgBi_2S_4 corresponding to 1:1 molar mixture of HgS and Bi_2S_3 was essentially single phase. This material exhibited photo-voltaic effect. Mercury bismuth sulphide till date is not reported to be synthesized by either CBD or SILAR and hence no literature is available regarding it.

Ubale A U reported electrical, optical and morphological properties of chemically deposited nanostructured $\text{HgS}-\text{Bi}_2\text{S}_3$ composite thin films. The work showed synthesis of nanocrystalline $(\text{HgS})_x(\text{Bi}_2\text{S}_3)_{1-x}$ composite thin films using CBD method. The preparative parameters such as ionic concentration of Hg, Bi and sulphur, temperature and pH were optimized to get good quality thin films on glass. The composition dependent structural, optical, electrical and morphological properties of films were studied by X-ray diffraction, optical absorption, electric conductivity measurements and SEM studies. A simple and convenient CBD method can be employed to deposit good quality $(\text{HgS})_x(\text{Bi}_2\text{S}_3)_{1-x}$ composite thin films. The Bi_2S_3 films are amorphous in nature and crystallinity increases towards HgS . The optical properties show that band gap energy changes from 1.6 to 2.24 eV depending on composition. Decrease in x results in decrease in band gap due to alloying between HgS and the lower band gap Bi_2S_3 . The variation in resistivity and activation energy is also composition dependent.

Mercury sulphide

Mercury sulfide (HgS), a group II–VI compound with cubic phase having bulk band gap about 0.5 eV, which is tunable in the

range of about 1.9–2.6 eV. R S Patil reported nanocrystalline HgS thin films deposited using CBD method at room temperature. The structural, compositional, surface morphological and optical characterizations were carried out for the confirmation of nanocrystalline nature. The nanocrystalline HgS thin films deposited onto FTO substrate were used as photoelectrode in PEC cells and current–voltage (I–V) and photovoltaic power output characteristics were studied. The XRD study showed the face centered cubic structure of HgS thin films. The EDX showed the formation of sulphur rich HgS thin films. The SEM studies indicate the nanocrystalline nature of HgS thin film. The grain size observed from TEM was in good agreement with the value calculated (36 nm) from SEM. The optical band gap of the film was found to be 2.75 eV. The HgS films showed PEC properties in polyiodide electrolyte. S S Kale et al reported HgS films were prepared and the effects of some of the preparative parameters on the properties of HgS thin films were studied with the help of optical absorption XRD, electrical receptivity SEM and TEM techniques. For deposition of HgS films, 0.05 HgCl₂ solution was taken in a beaker, equal volume of 0.1 M Na₂S₂O₃ solution was added to it and clean micro slides were introduced in the beaker. The deposition temperature was varied between 273K and 358 K and deposition time was varied between 45 min and 72 h. It is concluded that the deposition of HgS films at lower temperatures results into smaller grain size and film thickness than at higher deposition temperatures. Due to smaller grain size and film thickness, HgS films show 'blue shift' in band gap energy, E_g, and high electrical resistivity. R A Wagh investigated Fabrication of titanium dioxide (TiO₂) and mercury sulfide (HgS) heterojunction for photo electrochemical study. Their work demonstrated the temporal chemical solution deposition of HgS nanocrystals over spin-coated titanium dioxide for photovoltaic application. The work displayed chemical bath deposition of hexagonal HgS crystals over the anatase TiO₂ photoanode for solar cell application, which is first of its kind. The process of the HgS deposition on the surface of the TiO₂ film was heterogeneous nucleation, which was visibly affected by the deposition time. The appropriate deposition time was determined as 45 min for the TiO₂/HgS heterojunction using electron transfer and lifetime measurements through EIS. For the deposition time beyond 45 min, i.e., 60 min, the photovoltaic properties of TiO₂/HgS-based cell started dropping due to the increased surface-charge recombination.

Bi₂S₃, belonging to the group V–VI, is a promising direct band gap semiconducting material having optical band gap values in the range of 1.3 to 1.7 eV in thin film form. This makes it potentially suitable for photovoltaic applications. A N Kulkarni investigated time dependent synthesis of crystalline Bi₂S₃ and its application as a sensitizer in SnO₂ based solar cells. In this work thin films of Bi₂S₃ with hollow morphology were deposited by chemical bath deposition at room temperature. The structural, morphological and optical properties of Bi₂S₃ films were investigated as a function of deposition time. To study the photovoltaic properties, sensitization of SnO₂ photoanode with Bi₂S₃ was achieved successfully via chemical bath deposition. The solar cell fabricated using SnO₂–Bi₂S₃ photoanode showed an open circuit voltage (VOC) of 357 mV, short circuit current density of (JSC) 740.16 μA cm⁻² and fill factor (F.F.) of 31%. D J Desale synthesized Bi₂S₃ thin films using successive ionic layer adsorption and reaction (SILAR) technique and optimized various preparative parameters, such as ionic concentration, temperature and pH to get good quality film on glass substrate. The X-ray diffraction patterns reveal that Bi₂S₃ thin films have orthorhombic crystal structure. SEM images showed uniform deposition of the material over the entire glass substrate. The optical energy band gap observed to be decreased from 1.69 to 1.62 eV for as deposited and annealed films respectively. The I–V measurement under dark and illumination condition (100W) show annealed Bi₂S₃ thin film gives good photo response. P S Sonawane deposited thin films of Bi₂S₃ by CBD method. From this work it was concluded that the band gap goes on increasing with the increase in % of bismuth in composition that is there is blue shift with the increase of % of bismuth. Particle size goes on increasing with the increase in % of sulphur. The stoichiometric and non-stoichiometric Bi₂S₃ films were observed to be n-type in nature. Number of particles goes on increasing and averaged particle size goes on increasing with the decrease in % of Bi in Bi₂S₃. The band gap energy values are varying from 1.4 to 3.6 eV. The band gap energy value corresponding to stoichiometric Bi₂S₃ was observed to

be 1.71 eV. Films were observed to be nanostructured.

TiO₂/ SnO₂/ ZnO have been investigated for diverse applications in the optical and semiconductor industries because of their interesting semiconducting and dielectric properties. TiO₂ has been especially employed in making different electronic devices, including oxygen sensor, varistor, photo electrode etc. The n- TiO₂, with band gap energy of 3.2 eV absorbs mainly light in UV region and a small amount of light in visible region. However, despite this drawback, the porous and compact TiO₂ layers have found many applications due to its high oxidative power, stability and non-toxicity. The porous TiO₂ film in anatase phase could accomplish the photo catalytic degradation of organic compounds under the radiation of UV. It has many application prospects in the field of environmental protection such as sterilization and sewage disposal. A recent interest is focused on an amphiphilic TiO₂ surface induced by UV irradiation, which is expected to be applicable to windshields and mirrors for vehicles. On the other hand, in the field of alternative energy, a dye-sensitized solar cell is now a hot topic due to its high conversion efficiency produced with a porous TiO₂ electrode which is composed of a few tenths of nanometer-sized particles TiO₂ film with rutile phase. Different types of composite coating films such as TiO₂-CdS, TiO₂-ITO, TiO₂-Al₂O₃, Cd₃ P₂- TiO₂, etc. have been studied for photo-catalytic work and development of photo-electrochemical devices. A compact coating of TiO₂ is useful for arresting photodecomposition of low band gap semiconductor and as a buffer layer in solid solar cells and dye-sensitive solar cells. The nanostructured TiO₂ possess very high effective surface area and the incident photon-to-current conversion efficiency is found to be in excess of 80%. Consequently, a low-cost preparation and fixation of the TiO₂ photo catalyst with small sized particle is necessary for practical applications. From the point of view of practical use, some methods to fix the porous and compact TiO₂ layer have been developed.

Tin Oxide (SnO₂) thin film is one of the important transparent conducting oxides (TCOs) and applied in various fields such as in solar cells, optoelectronic devices, heat mirror, gas sensors, etc due to its electrical and optical transparency in visible light spectrum. It is a wide-gap semiconductor with optical gap around 3.6 eV [25]. The absorption coefficient is in the range of 10⁴ – 10⁵ cm⁻¹.

Zinc oxide (ZnO) is a wide-band gap semiconductor of the II-VI semiconductor group. ZnO has a relatively large direct band gap of ~3.3. Zinc oxide is one of the versatile and important oxide material because of its typical properties such as resistivity control over the range 10⁻³–10⁻⁵ cm, transparency in the visible range, high electrochemical stability, absence of toxicity, abundance in nature, and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes. ZnO thin films have been used in varistor, gas sensors, and solar cell transparent contact fabrications.

Conclusion

In the present review paper, we have described the theoretical background of chemical bath deposition (CBD) for preparation of metal chalcogenide thin films. The CBD method is simple, inexpensive, convenient for large area deposition of metal chalcogenide materials and capable of yielding good quality thin films. We have described the successive ionic layer adsorption reaction method (SILAR) for the deposition binary metal chalcogenide thin films. The SILAR method is a cheap method can be used to prepare metal chalcogenide thin films and wastage of material is avoided as no precipitate is formed during this process.

We have also described the spin coating, doctor blade and drop coating method to deposit thin film of TiO₂ on fluorine tin oxide (FTO) coated glass substrate. We have discussed the theoretical aspects of the photovoltaic cell and the different parameters of the PEC cells. There is a great interest in studying the AgBiS₂, and HgBiS_x thin films deposited by chemical methods for its application as solar storage cells and semiconducting devices.

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