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Electrodeposition of cadmium sulfide

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Abstract: Electrochemical depositions of CdS from different media aqueous, non- aqueous and ionic liquids have been discussed in this **review**. Electrochemical techniques, substrates used for electrodeposition of CdS have been also discussed. All of conditions of the electrodeposition including temperature, pH, solution composition and sulfur source which lead to suitable shape of electrodeposited CdS for using in different applications also have been discussed in this review.

Keywords: Electrodeposition; Cadmium Sulfide; Ionic Liquids; aqueous solutions; non-aqueous solutions.

1. Introduction

II-VI semiconductors such as CdS, ZnS, CdSe, and ZnSe are used as buffer layers in Cu(In,Ga)(S,Se) (CIGS) photovoltaic devices. CdS is the most commonly used buffer layer. CdS is an n-type semiconductor with a band gap of 2.42 eV at room temperature. Thus, CdS thin films have been used widely as window layers in solar cells with an absorber layer of CdTe, Cu_2S, or $CuInSe_2$. So far, CdS thin films have been deposited by various methods, e.g. vapor deposition, spray pyrolysis, chemical bath deposition, and electrochemical deposition. Electrochemical deposition is an attractive method for preparation of thin films in commercial quantities because it uses relatively cheap equipment, enables the deposition in large area and easy control of growth parameters through applied potential, current, pH and temperature of the bath. Many researchers have studied the mechanism of an electrochemical deposition of CdS from aqueous and little from nonaqueous solutions [1-4]. A variety of electrodeposition techniques have been reported for the preparation of CdS films, using anodic oxidation or cathodic reduction. Good results were obtained and the details of this method are reported in this review.

2- CdS thin-film electrodeposition from ionic liquids.

To overcome the limits imposed by the electrochemical breakdown of conventional solvents, new solvents must be used which have larger potential windows. Room temperature ionic liquids (RTIL) fulfill this criterion. Modern non-aluminate RTIL are conducting, are thermally stable to greater than 200 ºC or more, and have low vapor pressures. The greater thermal stability and high conductivity of RTIL gives those advantages over organic solvents such as DMSO. Reline, the RTIL used in the present work, was first developed by Abbott et al. [5] It consists of choline chloride and urea, which form a deep eutectic mixture due to hydrogen bonding interactions between the urea and chloride ions [5]. Reline is conducting, has an electrochemical window of over 2.5 V, and is air and water stable. The large electrochemical window allows access to the electrodeposition of less noble elements which cannot be plated from aqueous solutions. The electrodeposition of CdS from RTIL has been carried out and investigated for its photoelectrochemical properties [6]. 5 mM $CdCl_2$ and excess sulfur were added to the RTIL for the electrodeposition experiments. Sulfur required stirring for 2 h at 100 °C before it fully dissolved to be approximately 30 mM. Fluorine doped Tin Oxide (FTO) Glass and glassy carbon were used as a substrate for the electrodeposition process. Electrochemical deposition of CdS thin films were carried out at 100 °C. Films were deposited for up to 2000 s at fixed potentials. CdS films deposited over a range of potentials between −0.6 to −0.8 V exhibited colors varying from pale transparent yellow (−0.6 V) through to dark brown (−0.8 V). The brown color was attributed to excess cadmium in the films. The as deposited yellow films were of variable quality, some deposits being smooth and continuous whilst others were patchy and flaked off when washed in water. Film thicknesses were typically less than 50 nm. As-deposited yellow CdS films gave n-type photo-responses under illumination. Thin films of CdS electrodeposited with this method give band gap of value 2.72 eV [6].

Thin films of CdS were electrodeposited on FTO coated glass by reduction of a thiosulfate precursor in the presence of Cd(II) ions in methyltributylphosphonium tosylate ionic liquid at 130–150 °C. The data obtained from XRD and band gap measurements suggest the presence of hexagonal CdS crystals [7].

3- Electrodeposition of CdS from non- aqueous solutions

To overcome some of the problems associated with aqueous media. The use of non-aqueous solvents allows the raising of the growth temperature significantly enabling the production of highly crystalline semiconductor materials. Non-aqueous systems with cadmium salt and elemental sulfur dissolved in solvents such as DMSO, DMF, and ethylene glycol have been used, following the method of Baranski and Fawcett. The study of CdS electrodeposition on Hg and Pt electrodes in DMSO solutions using cyclic voltammetry (at stationary electrodes) and pulse polarography (at dropping Hg electrodes) provided evidence that during deposition sulfur is chemisorbed at these electrodes and that formation of at least a monolayer of metal sulfide is probable [8].

The cathodic electrodeposition of cadmium sulphide from a non-aqueous solution bath has been developed. CdS films have been prepared by electrodeposition using elemental sulphur [9] or triphenylstibine sulphide [10] as a sulphur source in dimethyl sulphoxide (DMSO), dimethyl formamide (DMF) , diethylene glycol (DEG) or ethylene glycol (EG) as the Solvent at bath temperatures between 100 and 140 ºC. Edamura and Muto [11] deposited Cu-doped CdS onto ITO galvanostatically at a current density of 1.4 mAcm^{-2} using dimethylsulfoxide solutions at 120 ºC containing $CdCl_2$ (0.055 M), elemental sulfur (0.19 M), and $CuCl_2$ (up to 1 mM). These workers obtained films of hexagonal crystallites with preferred c-axis orientation and with decreasing grain size as Cu content increased. Increasing the Cu content also caused the films to become porous and to adhere poorly to the substrate.

Cadmium sulfide has been electrodeposited from a nonaqueous bath using 0.5M $Na_2S_2O_3$, 0.05M $CdSO_4$, 0.1M EDTA (ethylenediaminetetraacetic acid tetrasodium salt) in ethylene glycol on stainless steel, titanium, and ITO-coated glass. Also hexagonal CdS films had been electrodeposited onto the pervious substrates from non-aqueous bath using ethylene glycol as a solvent at 90 ºC [2, 12]

Cadmium sulphide (CdS) films were deposited from ethylene glycol bath by the pulse plating technique using $CdCl_2$ and S at 90 °C on conducting glass substrates. The films exhibited cubic structure. The peaks increased in height and became sharper as the duty cycle increased. Optical absorption measurements indicated direct band gap values in the range 2.39 – 2.80 eV were obtained as the duty cycle is decreased [13]. Thin films of CdS were electrodeposited on transparent indium-tin-oxide (ITO) conducting glasses by cathodic electrodeposition in non-aqueous solution under galvanostatic conditions. In the preparation of CdS films, an ethylene glycol solution containing 6.7 gl^{-1} cadmium chloride ($CdCl_2$) and 3.3 gl^{-1} sulphur (S) was used [3].

CdS quantum dots (QDs) were electrodeposited from a dimethylsulfoxide (DMSO) solution of 50 mM $Cd(ClO_4)_2.6H_2O$ and 100 mM elemental S, at a temperature of 90 ºC and a constant deposition current of 0.5 mA cm^{-2}. The substrate was a film of (111) textured gold. The initial deposit consisted of very small (about 3 nm) nanocrystals of CdS. With increasing deposit thickness, the crystal size increased and the degree of orientation decreased. Photocurrent spectroscopy and I –V spectroscopy, using a conducting scanning force microscope tip, were used to measure the CdS band gap variations due to size quantization. The latter method also revealed room temperature conductivity peaks assigned to Coulomb charging of the QDs and evidence for charge tunneling into higher discrete energy levels [14].

4- Electrodeposition of CdS from aqueous solutions

Cadmium sulfide has been formed from the anodization of the metal in alkaline sulfide solution [15] and in buffered sulfide solution [16, 17]. It has been deposited cathodically from a solution containing cadmium and thiosulfate ions [1, 18]. Lowering the pH by the addition of dilute H_2SO_4 was shown to cause the decomposition of the $S_2O_3^{2-}$ to form colloidal sulfur and improve the deposition by elimination of the anodic stripping peak in the cyclic voltammogram compared to that observed with thiosulfate at its natural pH of 6.7. The overall electrode reaction is;

$$Cd^{2+} + S_2O_3^{2-} + 2e \leftrightarrow CdS + SO_3^{2-} \quad (1)$$

The electrode material has a significant influence on the formation of the CdS films in terms of both thickness and stoichiometry, although all films tend to contain sulfur-rich regions as well as regions of cadmium-rich CdS. Pulsed electrodeposition has also been used to deposit CdS from solutions of cadmium chloride and sodium thiosulfate at 90 ºC [19] on glass/ITO substrates.

Dennison [20] used both potentiostatic and galvanostatic techniques to deposit CdS and to study the reasons for the degradation in performance of the CdS electrodeposition process and to determine the mechanism of CdS formation. They suggested that along with Eq. (1) a second overall reaction should be considered, namely

$$2Cd^{2+} + S_2O_3^{2-} + 6H^+ + 8e \rightarrow 2CdS + 3H_2O \quad (2)$$

where this cathodic electrodeposition of CdS is performed in acidic solutions at 90 ˚C. Form the obvious equations the total electrons are $2e^-$ per cadmium atom and indicates that CdS formation occurs via a sulfur atom abstraction from $S_2O_3^{2-}$. This reaction was called for, in order to suggest that the reduction of Cd^{2+} is the only electrochemical step, whereby charge is consumed, followed by a subsequent chemical step comprising sulfur association to reduced cadmium. Sulfur is generated by the decomposition of thiosulfate. On the other hand, in the second reaction corresponds to an overall $4e^-$/Cd process where reduction of $S_2O_3^{2-}$ itself must occur as well as that of Cd^{2+}, the former comprising actually the rate-determining step. This route becomes more favorable as pH decreases for it requires additional protons.

Das and Morris [21] prepared CdS/CdTe solar cells by periodic pulse electrodeposition. For CdS deposition they employed a bath of 0.2 M Cd^{2+} (from $CdCl_2$) and 0.01 M $S_2O_3^{2-}$ from sodium thiosulfate at a pH of 2 by adding HCl. The deposited layers were annealed at 400 ºC and XRD spectra showed good CdS and CdTe peaks. The final solar cell efficiency was 10% indicating good-quality layers and junctions.

Demir and Shannon [22, 23] investigated the deposition of CdS on Au via underpotential deposition and found that hexagonal CdS is preferred on both the (111) and (100) low-index planes of Au. It was suggested that Raman scattering might be useful as an in situ method for monitoring film quality during deposition.

Cadmium sulfide has also been deposited on ITO-coated glass using the potentiostatic method [24]. In this work an aqueous solution of 0.2M $CdCl_2.2H_2O$ and 0.01M $Na_2S_2O_3$ adjusted to a pH in the range of 2–3 using HCl was used with a bath temperature of 90 ºC. For pH > 3 the solution produced precipitates of cadmium hydroxide and, for pH < 2, CdS precipitates were produced. Cadmium sulfide was deposited via a co-deposition process obeying the overall reaction of Eq. (2). Between -0.5 and -0.6V versus SCE the resulting films were yellow in color, indicating stoichiometric CdS. Films were annealed at 350 ºC in a hydrogen atmosphere for 30 min. For more negative potentials the films became Cd rich and then essentially metallic. Bath temperature was also found to affect growth significantly with increasing bath temperature resulting in higher growth rates and smoothness and adhesion of the films enhanced. X-ray diffraction analysis of these films showed reflections associated with the hexagonal wurzite α-CdS phase.

Good-quality CdS was obtained with a graphite anode at 90 ºC and a pH of 8. Polycrystalline CdS was obtained as determined by XRD and no post-deposition anneal was employed by these workers.

Goto and co-workers [12] used a bath of 2 mM $CdSO_4$ and 100 mM $Na_2S_2O_3$ at a pH of 2.5 adjusted with H_2SO_4 to deposit CdS films. They studied the effect of the annealing atmosphere (O_2, air, or N_2) using photoluminescence spectroscopy. Annealing in nitrogen resulted in an increasing concentration of native defects as the anneal temperature was raised, while annealing in oxygen resulted in little native defect formation with the oxygen expected to fill any sulfur vacancies formed since it is isoelectronic to S. Annealing in air was similar to annealing in oxygen; however, the photoluminescence line-widths were broader, indicating poorer quality material.

The obtained results in this work indicate which the pulsed current electrochemical method can be used as a confident and controllable method for the electro-synthesis of cadmium sulfide/cadmium nanocomposite and cadmium sulfide in nanofibers forms. When a synthesis is carried out under a pulse frequency of 8 Hz, a pulse height (current amplitude) of 100 mA cm^{-2}, a synthesis solution temperature of 50ºC, an initial cadmium chloride concentration of 0.2 M, sodium thiosulfate concentration of 0.02 M in hydrochloric acid solution with pH of 2, nanocomposite of cadmium sulfide/cadmium in nanofiber form can be obtained. At

high pressure and high temperature, cadmium sulfide nanostructures can be synthesized without any impurity of cadmium [25].
Cadmium sulphide (CdS) films were deposited by the pulse plating technique at room temperature and at different duty cycles in the range of 6–50% using 0.25 M cadmium sulphate and 0.30 M sodium thiosulphate at a deposition potential of -0.75 V (SCE). The total deposition time was kept constant at 1 h. The thickness of the films was around 2.0 µm. X-ray diffraction (XRD) studies indicate the formation of polycrystalline films with the cubic structure. The crystallite size increased from 23.0 to 27.5 nm as the duty cycle increased from 10 to 50%. Optical absorption studies indicated a direct band gap in the range of 2.40–2.80 eV as the duty cycle is decreased [26].

Galvanic method is used for the electrodeposition of CdS. This technique is presented for the deposition of high quality cadmium sulfide (CdS) thin films onto SnO_2 substrates. Single phase films were deposited in a bath of cadmium chloride and sodium thiosulfate at pH = 4 and temperature = 85 °C at a growth rate of 1 nm/min. In the pH range of 3 to 4, the deposition rate is sensitive to cadmium chloride concentration. At higher pH the deposition rate is very low while at lower pH mixed phase films were obtained and homogeneous CdS formation occurred in the bath. CdS/CdTe solar cells with efficiencies over 8% were fabricated using evaporated CdTe to demonstrate the utility of CdS films deposited by this simple technique. The galvanic deposition technique is useful in laboratory settings with limited deposition hardware and limited chemical waste disposal facilities [27].
Cathodic electrodeposition in the presence of Cd-tartrate complex ion as complexing agents in aqueous solution was used to prepare cadmium sulfide thin films deposited on titanium substrates. The effect of deposition periods and solution temperatures towards the crystallinity of the cadmium sulfide thin films were investigated. The deposition process was carried out at –0.800 V by varying the deposition periods (15, 30, 45, 60 and 75 minutes) and solution temperatures (15, 27, 40 and 60 °C). The bath consists of Cd-tartrate complex (0.05 M) and $Na_2S_2O_3$ (0.05 M). The pH of the bath was maintained at 2.5. Deposition for 45 minutes under room temperature is the optimum condition to prepare quality CdS thin films under the current condition. The thin films produced were polycrystalline in nature. The films showed good adherence towards the substrate in the presence of sodium tartrate. The film exhibits direct transition with an energy gap of about 2.30 eV [28].

Miller et al. [15, 29] reported the anodic formation of microcrystalline CdS on polycrystalline Cd metal in a strongly alkaline (pH 14) aqueous sulfide–polysulfide solution (Na_2S, NaOH). The process could be accomplished both galvanostatically and potentiostatically and resulted typically in the development of a yellowish opaque layer of semiconducting, n-type CdS, which was enriched with electrolysis time by hydroxide or oxide species. The formation and stripping of these films were studied by rotating ring-disk electrode (RRDE) voltammetry, under dark and illuminated conditions. It was concluded that although the as-grown anodic films can hardly show optical absorption efficiencies comparable to CdS single crystals or even polycrystalline pressure-sintered electrodes, they are rather stable in the polysulfide environment, thus operating in a manner appropriate to regenerative photoelectrochemical cells. Better optical results could be obtained with different bath composition, e.g., with buffered Na_2S, $NaHCO_3$ solutions of lower pH. Peter studied in detail the growth of anodic CdS films on the Cd electrode in similar solutions [30], as well as the processes that occur at the Cd/solution and CdS/solution interfaces [17]. According to the linear sweep voltammetry, three characteristic regions could be distinguished revealing the essential features of the anodic passivation of cadmium in alkaline sulfide solutions: (a) the monolayer region, with a sharp structured current peak corresponding to the passivation of the metal by two or three monolayers of CdS; (b) the plateau region, in which further growth takes place by high field ionic migration until a thickness of some 5 nm is reached; (c) the transpassive region, in which a less compact layer of CdS thickens rapidly to 500 nm or more.

Growth at constant current appeared to be well described in terms of the Cabrera–Mott model of the high-field–assisted formation of insulating rims. It was noted that when the potential exceeds a critical value (in constant current or potential sweep experiments) the kinetics abruptly change, and a porous or polycrystalline CdS layer forms over the original barrier layer presumably by a diffusion-controlled process. It was not clear why the growth kinetics and mechanism change abruptly at about 5 nm. Remarkably, however, the growth kinetics at an applied constant potential could be described, not by the inverse logarithmic law as would be required by the Cabrera–Mott model, but rather by the so-called direct logarithmic law, according to which charge density at a constant potential imposed across the electrode increases with the logarithm of time. Peter attempted to reconcile this discrepancy in terms of a Cabrera–Mott model of inverse logarithmic law, modified for the change in potential difference across the inner Helmholtz layer, and hence across the oxide film itself. This attempt, however, did not meet with any success, in contrast, e.g., to the case of oxide growth at Pt electrodes, where an equivalent modification brought the galvanostatic and potentiostatic data into full agreement and proved that the same mechanism controlled the growth under both experimental conditions. It would, therefore, appear that different mechanisms control the formation of the CdS films under galvanostatic and potentiostatic modes of growth.

Since amalgam electrodes are more suitable than polycrystalline metal electrodes for the quantitative study of anodic electrocrystallization phenomena, the anodic formation of CdS has been studied on Cd(Hg) electrode in buffered sodium sulfide solutions by means of potential perturbations and capacitance measurements [8]. Comparison of the experimental data with the predictions of a model known to well describe the growth of multiple layers of Cd(OH) on Cd(Hg) showed a significant lack of agreement. It was suggested that in the present case, during deposition and reduction of CdS films on Cd(Hg), phase transformations or recrystallization processes occur. As an attempt to describe in detail the way in which phase transformations may influence the course of electrocrystallization, a qualitative model was assumed involving changes of the crystal orientation of the deposit during film deposition from (10.0) hexagonal to (110) cubic, transforming again to (10.0) at high overpotentials. This recrystallization could be reversed upon decreasing the overpotential, the film structure changing spontaneously to the (110) texture. The mechanism of these electrocrystallization reactions usually consists of the nucleation of 2D centers which grow by the rate-determining addition of new molecules to the expanding perimeter, until overlap becomes significant. That is actually the case for the first monolayer formation of CdS on Cd(Hg) as manifested by current transients which follow closely the behavior predicted for 2D progressive nucleation.

A kinetic description of the initial stages of CdS growth under potentiodynamic conditions at various sweep rates at room temperature as well as under galvanostatic conditions at different temperatures has been attempted by Damjanovic and co-workers [31, 32]. They showed that the same kinetic equation describes the growth of thin anodic sulfide films at Cd electrodes under both galvanostatic and potentiodynamic conditions. For the growth of films up to about 5 nm, it was confirmed that the kinetics is fully accounted for by the model of high-field–assisted formation of ions at the metal/anodic film interface and their migration through the film.

Anodization generally results in the formation of films with limited thickness, uncertain composition, defects, and small crystallite size. Thus, the barrier nature of the n-type semiconducting CdS film obtained in the previous manner makes it too thin to form the basis of Cu_2S/CdS or CdTe/CdS solar cells by the normal dipping process. Hetero-junction cells of low efficiency have, however, been made by anodization followed by vacuum deposition of the added layer (Cu_2S).

The cathodic approach has been investigated actively as a method for the production of thin film CdS, in particular for the fabrication of heterojunction cells. Photoactive CdS films could be grown in alkaline NH_3/NH_4Cl-buffered aqueous solutions containing thiosulfate as sulfur source and complexed Cd^{2+} (EDTA+NH_3), on Ti substrates [33]. The electro-reduction of thiosulfate was considered to proceed as

$S_2O_3^{2-} + 3H_2O + 8e^- \rightarrow 2S^{2-} + 6OH^-$ forming CdS in the presence of Cd(II) ions.

In acidic aqueous solutions of thiosulfate and $CdSO_4$, it was suggested [18] that disproportionation of the thiosulfate ions ($S_2O_3^{2-} \rightarrow S + SO_3^{2-}$) is coupled to electrochemical charge transfer to Cd^{2+}.

In effect, reduction of sulfite is more probable than that of sulfur in the colloidal state, so that considering the disproportionation of thiosulfate in acid solutions may amount to using sulfite, i.e., the anion of sulfurous acid–SO_2 in water. Repeated cycling of a Pt rode in this solution yielded a deep yellow, uniform, translucent film on Pt, containing Cd and S in roughly equal amounts with no detectable contaminants (according to microprobe analysis). The produced layers were thin (< 1 μm) and of poor crystallinity, but photoactive in sulfide, thiosulfate, sulfite, and sulfate solutions.

Optimum conditions for the formation of CdS by the acidic method on metallic Al substrate at 25 °C have been reported as follows: pH 2.3, potential –1 V vs. SCE, and electrolysis time > 2 h [1]. Thermal treatment improved the characteristics of the films and their photovoltaic properties, which were evaluated by evaporating a Cu_2S layer on the CdS/Al film, to form a heterojunction cell. The influence of the deposition substrate on the formation and morphology of CdS was found to be important. The aluminum substrates gave the best results among Pt, Mo, and Al. In the case of molybdenum, surface blocking by adsorbed sulfur was considered. Generally, the experimental results on electrodeposition of CdS in acidic solutions of thiosulfate have implied that CdS growth does not involve underpotential deposition of the less noble element (Cd), as would be required by the theoretical treatments of compound semiconductor electrodeposition. Besides, in the present case, colloidal sulfur is generated in the bulk of solution, giving rise to homogeneous precipitation of CdS in the vessel, so that it is quite difficult to obtain a film with an ordered structure. The same is true for the common chemical bath CdS deposition methods.

Yamaguchi et al. [34] suggested specific electrochemical assistance to a chemical deposition process from an acidic aqueous solution of cadmium chloride and thioacetamide, in order to realize film growth only by the heterogeneous reactions at the film/solution interface. The electrochemical reaction, namely electroreduction of protons at small current densities (several tens of $\mu A\ cm^{-2}$), was used in such a way as to maneuver the chemical formation of CdS to take place preferentially at the substrate surface (ITO-glass), while prohibiting the agglomeration of the fine particles formed homogeneously in the solution phase. The film growth was considered as occurring by an atom-by-atom process generating individual crystallites, so that highly crystallized hexagonal CdS thin films could be developed, consisting of single-crystal CdS particles having hexagonal cylindrical shape. The films could become as thick as 500 nm without suffering from structure disordering. The authors stress in conclusion that an active use of electrochemistry can improve a CBD process drastically. Evidently, their particular approach may be valid also in the deposition of other related compound thin films.

Pulse plating techniques with symmetric or asymmetric waves have been employed for improving the deposition of CdS in acidic aqueous baths of cadmium sulfate and thiosulfate precursors [35, 36]. A better control of sulfur incorporation in the deposits was reported. Formation of the initial layer of CdS involved reaction of Cd(II) ions with the chemisorbed sulfur or with a pre-existing layer of metal sulfide. Actually, it is recognized that two different mechanisms may be involved in the above process. One is related to the reaction of a first deposited metal layer with chalcogen molecules diffusing through the double layer at the interface. The other is related to the precipitation of metal ions on the electrode during the reduction of sulfur. In the first case, after a monolayer of the compound has been plated, the deposition proceeds further according to the second mechanism. However, several factors affect the mechanism of the process, hence the corresponding composition and quality of the produced films. These factors are associated mainly to the complexation effect of the metal ions by the solvent, probable adsorption of electrolyte anions on the electrode surface, and solvent electrolysis. In practical terms, large-scale cracking in the produced films, detrimental to photoelectric applications, was the main drawback of the above method. In order to prevent the appearance of cracks, propylene carbonate (PC) has been used as a solvent, with encouraging results [37]. The mechanism of electrodeposition of CdS in PC solutions containing Cd(II) ions and elemental sulfur has been studied by performing cyclic voltammetry at stationary Pt and Au electrodes [38].

Electrodeposition of cadmium sulfide thin films was realized by the electroreduction of the aqueous thiocyanato complex of Cd^{2+}. Formation of CdS is supposed to proceed via metal-catalyzed ligand reduction. The film thickness increased linearly with the electricity consumed, confirming the electrochemical growth of CdS. The deposition bath was fairly stable and could be used repeatedly to prepare many CdS films. This technique seems to be the only example to achieve purely electrochemical growth of CdS from a single solution. The resultant CdS thin film had a uniform structure in which each grain was made up with single phase crystalline hexagonal CdS. When the deposition was carried out on poly-crystalline Ni, the deposited CdS thin film showed a strong preferential orientation with the c-axis perpendicular to the substrate surface owing to their small lattice mismatch of 4.17%. The aqueous solutions containing 0.08 M $CdCl_2$ and 1 M ammonium or potassium thiocyanate were used as plating baths. The solution of KSCN was acidified to pH 3.2 by adding dilute HCl. An indium tin oxide (ITO) coated glass or a nickel plate was used as the substrate. The bath temperature was maintained at 70°C by a thermostat. A prolonged electrolysis at -0.7 V resulted in the formation of CdS thin film on the substrate [39].

5- Template-electrodeposition preparation of CdS nanostructured and nanowire

Electrodeposition of nanostructures into the pores of nanophase membrane templates has been demonstrated by Martin and co-workers [40, 41] who studied the optical properties of template-synthesized materials and also prepared arrays of micro- and nanoscopic electrodes for fundamental and applied electrochemistry. Chakarvarti and Vetter [42] presented the first templated synthesis of semiconductors, in particular semiconductor–metal heterostructures (Se–Cu) and Se microtubules, by electrodeposition in the etched 2.5 µm pores of a nuclear track filter.

Cubic polycrystalline CdS nanowires were prepared in pores of anodic alumina membrane (AAM) template at room temperature with aqueous solution of $S_2O_3^{2-}$ and Cd^{2+} by template-electrodeposition method, which has advantages of both the template and the electrodeposition. The basic idea behind this method is, on one hand, to make use of the nanosized pores in AAM template for the confinement of growth of nanowires across the diameter, on the other hand, to avoid high temperature, organic reagent and codeposition of S during the preparation of CdS nanowires [43]. The electrodeposition of CdS nanowire arrays was performed at a potential value of -1.05 V referred to the saturated calomel electrode (SCE) in a three-electrode cell at room temperature for 2–3 h. The electrolyte solution was 5 mM $Na_2S_2O_3$, 0.1 M Na_2SO_3, 0.2 M $CdSO_4$ and 0.2 M EDTA in 1 M NH_3-H_2O/NH_4Cl buffer (1:1). In order to avoid codeposition of the insulating elemental S with CdS, so alkaline solution (pH 10) is used during template-electrodeposition of CdS nanowire arrays, see reaction (a), thiosulfate $S_2O_3^{2-}$, can easily be prepared in situ by dissolution of S.

$$S + SO_3^{2-} = S_2O_3^{2-} \qquad (a)$$

Free sulfide ions, for subsequent reaction with Cd^{2+} ions (reaction (c)), can be formed electrochemically by reaction (b) in $S_2O_3^{2-}$ aqueous solution

$$S_2O_3^{2-} + 2e = S^{2-} + SO_3^{2-} \qquad (b)$$

$$S^{2-} + Cd^{2+} = CdS \qquad (c)$$

Cadmium sulfide (CdS) nanowires on porous alumina template have grown by a simple dc electrochemical method. A dimethyl sulfoxide (DMSO) solution of 0.055M $CdCl_2$ and 0.19 M elemental sulphur was used. This solution prevents the corrosion of Al during the deposition. The growth of CdS nanowires was carried out for 2–30 min at solution temperature of 80–160 ºC with a dc bias applied between the PA (porous alumina) electrode and a platinum counter electrode [44].

Cadmium sulfide (CdS) nanocrystal thin films and nanowires have been deposited onto mechanically flexible substrates via dc-electrodeposition, which is a very suitable technique for large area manufacturing. CdS thin films have been deposited onto indium tin oxide (ITO). During the CdS thin film deposition, the ITO and a platinum counter electrode were immersed into a solution containing 0.055 M $CdCl_2$ and 0.19 M elemental sulfur. The deposition voltage was kept constant at 3V dc, while the temperature was varied from 90 to 110 ºC. During the deposition in order to prevent oxide formation, a constant nitrogen flow was maintained. CdS nanowires were deposited on aluminum coated anodized alumina membranes (AAM) using the same method. In this processes, the aluminum coated AAM were also immersed into a solution containing 0.55 M $CdCl_2$ and 0.19 M elemental sulfur. It has been observed that the length and the diameter of the CdS nanowires depend on the deposition time and voltage [45].

Polymer ion tracks foils were used as a template for obtaining electrodeposited cadmium sulfide (CdS) nanowires. CdS nanowires were deposited chronoamperometry at potential of -730 mV by using a solution containing 200 mM $CdCl_2.2H_2O$ and 10 mM $Na_2S_2O_3.5H_2O$. The pH of solution was 2–3, at 85 ºC [46].

CdS nanotubes and nanowires have been synthesized with controlled dimensions by means of template-electrodeposition method in etched ion-track polycarbonate (PC) membranes. The diameters of nanotubes and nanowires are between 20 and 110 nm, and the lengths are up to tens of micrometers. X-ray diffraction (XRD) and selected area electron diffraction (SAED) pattern investigations demonstrate that CdS nanotubes and nanowires are polycrystalline in nature. The deposition of CdS was performed potentiostatically at a potential value of -1 V at 70 ºC for 5–8 h. The electrolyte solution consisted of 0.05

M $CdCl_2$ and 0.01 M thioacetamide (TAA). The pH of this mixture was adjusted to 2.4 by adding appropriate amounts of hydrochloric acid [47].

The fabrication of CdS nanorod arrays on transparent conductive tin-doped In_2O_3 (ITO) glass substrate was achieved by combining electrodeposition and hydrothermal processes. One thin layer of CdS particles on substrates was prepared by electrodeposition as seeds, upon which well-aligned nanorod arrays were hydrothermally grown in large scale [48].

CdS– multi carbon nanotube (MWNT) heterostructure can be obtained by electrochemical deposition. CdS nucleates with a high degree of selectivity at the tip but a small number of particles also form on the body at the higher cathodic potentials. In the electrochemical deposition of CdS, Si wafers with MWNT arrays were used as the working electrode. The Si wafers with MWNT were pretreated in 15 wt. % HNO_3 aqueous solutions for 30 s. Chemical treatment, such as wet oxidation in HNO_3 functionalizes nanotube surfaces with anchor groups, such as hydroxyl, carboxyl, and carbonyl that are necessary to tether metal ions on the tubes and increase the electrochemical activity of the surface of the carbon nanotubes in water solution. After the pretreatment, CdS were cathodically deposited from an aqueous solution of 0.2 M $CdSO_4$ and 0.01 M of $Na_2S_2O_3$. The pH of the solution was kept between 2 and 3, using concentrated hydrochloric acid. Static potentials of −0.8V and −1.5V were applied with respect to the SCE reference electrode during the deposition [49].

Nanostructured CdS was also deposited by electrodeposition on indium tin oxide (ITO)- coated glass. The solution used for this deposition contained 0.055 M $CdCl_2$ and 0.19 M elemental sulfur and was kept at a temperature of 120 ºC. DC electrodeposition was used because of its simplicity as well as uniform deposition results on flat substrates. Electrodeposition was performed at a constant voltage of 2.5 V [50].

An in-situ induction precipitation approach via electrochemical reduction has been successfully used to prepare CdS nano-film on glassy carbon electrode (GCE) surface. A polished GCE was immersed in a relatively optimized solution containing $[Cd^{2+}] = 5.0$ mmol L^{-1}, $S_2O_3^{2-} = 8.0$ mmol L^{-1}, [EDTA] = 28 mmol L^{-1}, for electrochemical deposition with a deposition potential of -1.06 V vs. SCE for 800 s at 15 ºC. The formation process of CdS induced by continuously electrochemical reduction of $S_2O_3^{2-}$ was expressed as follows [51]:

$$S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O$$
$$S + H^+ + 2e^- \rightarrow HS^-$$
$$Cd^{2+} + HS^- \rightarrow CdS + H^+$$

Cadmium sulfide (CdS) nanowires were electrosynthesized within the pores of the anodic alumina membranes (AAM) using underpotential deposition (UPD) through an electrochemical co-deposition at room temperature (25 ºC). Au/anodic alumina membrane (Au/AAM) composite was used as a working electrode for electrodeposition process. The electrolyte for the electrodeposition of CdS nanowires contains amixture of 10 mM $CdSO_4$, 0.1 M EDTA and 2mM Na_2S. The pH of the solution was adjusted to 4.0 ± 0.1 by using CH_3COONa/CH_3COOH buffer. EDTA was used to form a Cd-$EDTA^{2-}$ complex in order to prevent the chemical precipitation of Cd^{2+} and S^{2-} as CdS. The deposition potential for CdS was determined from cyclic voltammetry data of Cd and S in the presence of EDTA. The electrodeposition of CdS nanowires were performed at −500 mV since this potential value is suitable with the UPD of Cd and S. When the electrodeposition was performed for an appropriate time (usually 5–7 h), the nano-channels were completely filled with CdS deposits, and it could be found that the surface of AAM turned yellow because overfilled products covered on the top surface of the AAM. The AAM filled with CdS nanowire arrays. SEM, TEM, and XRD results demonstrated that these CdS nanowires have a uniform diameter and direction of crystal growth. The optical absorption of CdS nanowires exhibits amarked blue-shift compared with that of bulk CdS due to quantum size effect [52].

$Cd(OH)_2$ nanoparticles (NPs) were synthesized on graphite treated with plasma through electrochemical deposition in a solution of CdF_2 saturated with O_2. $Cd(OH)_2$ NPs were formed from reaction of Cd^{2+} in solution with OH^- generated on the graphite after reduction of O_2. The $Cd(OH)_2$ NPs were densely distributed on the surface and converted to form hollow CdS NPs via a thermal reaction with H_2S at 300 ºC. $Cd(OH)_2$ NPs were electrodeposited onto the plasma-treated graphite in a solution of 1.0 mM CdF_2 and 0.1 M NaF adjusted to a desired pH with 0.1 M HCl. Oxygen gas was purged into the solution for 30 min to achieve O_2-saturation. The electrodeposition was operated typically with a potential fixed in a range from −0.55 V to −0.65 V vs SCE. The resulting graphite electrode was rinsed with ethanol and de-ionized water to remove residual adsorbates. For the preparation of CdS NPs, the electrode covered with $Cd(OH)_2$ NPs was heated to 300 ºC, and gaseous H_2S was introduced into the chamber to a pressure 600 mtorr for 30 min. proposed to occur as follows:

$$O_{2(aq)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$$

$$Cd^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)}$$

$Cd(OH)_2$ was converted to CdS via anion exchange as follows [53].

$$Cd(OH)_{2\,(s)} + H_2S_{(g)} \rightarrow CdS_{(s)} + 2H_2O_{(g)}$$

A cadmiumsulfide nanotube (CdS NT) was successfully fabricated by a two-step route consisting of the template free electrochemical deposition of cadmium hydroxide films at 298 K and their subsequent sulfurization by S^{2-} ions. The electrochemical deposition of cadmium hydroxide was performed potentiostatically by the desired potential bias (−0.7 – −1.2 V vs. Ag/AgCl) in $Cd(NO_3)_2$ (0.1 M) at 298 K, using an indium tin oxide (ITO) conducting glass as the working electrode, a platinized Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The distance between the working electrode and the counter electrode was adjusted to ca. 10 mm. The prepared cadmium hydroxide thin films were then reacted with aq. Na_2S (0.1M) for 60 min at 298 K to form CdS. The prepared CdS NT electrode was successfully applied to photo-electrochemical solar cells with high efficiency [54].

One dimensional (1D) cadmium sulphide (CdS) nanostructures have been synthesized by electrochemical template deposition technique, using poly carbonate membranes. The poly carbonate membranes of pore size: 400, 100, and 80 nm have been used. The electrolyte used has 0.1539 g/ 100 ml $CdSO_4.8H_2O$ and 1.2604 g/100 ml Na_2SO_3 in double-distilled de-ionized water. The pH of the electrolyte is adjusted in between 1.65 and 1.80 using concentrated sulphuric acid. The deposition process has been performed between temperatures 40 and 45 ºC and keeping voltage low enough (1.2 V) to avoid side reactions, such as hydrogen evolution. The electrochemical deposition was made to proceed with continuously stirring the electrolyte enabling the unrestricted movement of its ions. On completion of the electrodeposition process, which takes about 30 min CdS nano rods are synthesized in the pores of the polycarbonate membrane, following the reaction between the Cd^{2+} ions and the S^{2-} ions. The initial process possibly involves the conversion of SO_3^{2-} into $S_2O_3^{2-}$ ions. These thiosulphate ions act as the source of sulfur. When electric field (1.2 V) is applied between the anode and the conductive copper tape as the cathode, Cd^{2+} ions enter inside the pores of the membrane while moving towards the cathode. The S^{2-} ions enter the pores by the process of diffusion, leading to the formation of CdS molecules, which nucleate inside the pores of the membrane, there by restricting the dimensions of the nano forms to the shape and size of the pores [55].

6- Conclusions

CdS can be electrodeposited from different media; ionic liquids, non-aqueous and aqueous solutions. For more negative potentials the films became Cd rich and then essentially metallic. Bath temperature was also found to affect growth significantly, with increasing bath temperature resulting in higher growth rates and smoothness and adhesion of the films enhanced. At higher pH the deposition rate is very low while at lower pH mixed phase films were obtained and homogeneous CdS formation occurred in the bath. Complexing agent as an additive in the electrodeposition bath gives good adherence for the CdS deposits towards the substrate. The size and the form of the structure of the electrodeposited CdS depends on the concentrations of Cd^{2+} ions, temperature, substrate composition and form, deposition potential or current time, pH of the deposition bath and the distance between working and counter electrodes.

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