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Preparation of polycrystalline ZnSe thin films for solar energy conversion: A literature survey

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ABSTRACT

The present survey describes the different of preparing ZnSe polycrystalline thin films using various substrates which suggest that the different methods employed for preparation of thin film are not of much importance as far as morphology and crystallinity of the films are concerned. All methods described are easy, inexpensive and nonpolluting. Post annealing of this film plays an important role for achieving crystallinity.

KEYWORDS

ZnSe thin films;
Solar energy;
Photoelectrochemical cell;
Semiconductor.

INTRODUCTION

Zinc Selenide is a well known II-VI semiconductor which is a popular opto- electronic semiconducting material having a wide band gap of 2.7eV (direct bad gap). Because of its large band gap it has gained considerable attention for its use as thin film photoanode in photoelectrochemical cells[1, 2]. Therefore ZnSe substitutes CdS in photoelectrochemical cells for an expectation to get higher cell efficiency as it allows transmission of higher energy photons than band gap of CdS (2.4eV)[3]. The first work on ZnSe electrode used as photoelectrode in the form of single crystal was reported by William in the year 1967[4].

ZnSe was used as photoelectrode in the form of single crystal as reported by William in the year 1967[4]. The preparation of ZnSe single crystal is not only very much expensive and tedious but also it is unstable due to photoanodic dissolution which makes it unsuitable for its use in photoelectrochemical cell.

In this paper, we briefly review various methods for preparation of thin film ZnSe semiconductors discussed by various workers.

SELECTION OF SUBSTRATE

The selection of substrate used for deposition of semiconductor material in the form of thin film plays an important role. The substrate chosen for this purpose should exhibit good adhesion to the semiconductor film. It should be electrochemically inert to the electrolyte used in photoelectrochemical cell. The substrates used for deposition of n-type ZnSe semiconductor thin film are conducting glass (SnO_2coated), fluorine doped tin oxide (FTO) coated glass, nickel coated glass, ITO glass, titanium, nickel, non-conducting glass slides, copper, stainless steel, gold etc.

PREPARATION OF THIN FILM

C.D.Lokhande et al[3] prepared ZnSe thin film on FTO coated glass substrate by chemical bath deposition (CBD) method using aqueous solution containing selenourea (0.06M), $ZnSO_4$ (0.5M), ammonia solution (0.7M) and hydragine hydrate (80%). The temperature was maintained at 80^0C.

In the presence of liquid ammonia, $ZnSO_4$ forms Zinc-ammonia complex $(Zn(NH_3)_4^{2+}$. Selenide ions (Se^{2-}) are released from selenourea which react with the above complex to produce ZnSe. The reactions involved in ZnSe growth process have been proposed as follows:

$$Zn(NH_3)_4^{2+} + N_2H_4CSe \rightarrow ZnSe + H_2CN_4 + 4NH_3 + 2H^+ \quad (1)$$

It has been reported that the films were found to be amorphous containing Oxygen and Nitrogen in addition to Zinc and Selenium. However ZnSe films obtained were found to be photoactive due to excess generated electron.

G.Riveros et al[5] prepared polycrystalline ZnSe thin film by electrodeposition method using an electrolytic solution containing 0.2M Zinc sulphate, 10^{-4} -10^{-3}M SeO_2. The pH of the solution was adjusted to 2.4 by adding sulfuric acid. Thin films were deposited potentiostatically on titanium plates; glass substrates coated with fluorine doped tin oxide and ITO glass substrates. From voltammetric study they stated that the well defined peak at - 0.6V is associated with deposition of selenium accoding to the reaction

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (2)$$

Since the deposit is red colored amorphous selenium.

The above reaction is followed by deposition of ZnSe thin film, as the reaction as mentioned below is favored by the free energy change of ZnSe formation i.e Δ.G= - 137kJ/mole.

$$Se + Zn^{2+} + 2e^- \rightarrow ZnSe \quad (3)$$

The ZnSe semiconductor film was found to be p-type with energy gap value (E_g) of 2.6-2.7eV. As far as adherence, morphological and crystallinity properties are concerned, the titanium substrate was found to be better.

For the first time R.Kumaresan et al[6] studied the deposition of polycrystalline thin film of ZnSe by a new technique called photochemical deposition method (PCD) and optimized the growth parameters. Indium-tin oxide (ITO) coated glass substrate was used for deposition which was immersed in the deposition solution near the surface. The deposition was performed from an aqueous solution of Zinc sulphate, sodium selenosulphate and sodium sulphite. The deposition solution and the substrate were illuminated by UV light from the top. The pH of the solution was maintained by adding sulfuric acid.

They proposed that by absorption of UV light the SO_3^{2-} ions get excited and release electron.

$$SO_3^{2-} + h\nu \rightarrow SO_3^- + e^- \quad (4)$$

In acidic medium Selenium is released from selenite ions according to the reaction:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (5)$$

The selenium atoms thus generated and the solvated electrons react with the Zn^{2+} ions (from $ZnSO_4$) to from ZnSe compound according to the reaction:

$$Zn^{2+} + H_2SeO_3 + 4H^+ + 6SO_3^{2-} + h\nu \rightarrow ZnSe + 3H_2O + 3S_2O_6^{2-} \quad (6)$$

The deposition rate, as reported, was found to be low when the substrate was non conducting (glass). The as-deposited films were amorphous in nature which became crystalline on high temperature annealing. The PCD-ZnSe films exhibited stoichiometric composition with uniform nature due to annealing at high temperature.

G.I.Rusu et al[7] prepared ZnSe thin film on glass substrate by physical vapor deposition under vacuum. The films obtained were polycrystalline and the optical band gap energy was found inbetween 2.5 and 2.8eV. The ZnSe thin films were grown by S.Soundeswaran et al[8] potentiostatically using electrodeposition (electrocrystallization) method from an aqueous electrolyte containing 1M $ZnSO_4$ and 100 mM SeO_2 at room temperature. The pH of the solution was maintained at 2.1 using dilute H_2SO_4. The substrates used were titanium plate and ITO coated glass.

The electrochemical equations involving the electrocodeposition of Zn and Se as reported by them are as below:

$$Zn^{2+} + 2e^- = Zn_{(s)} \quad (7)$$

$$SeO_2 + 4H^+ + 4e^- = Se_{(s)} + 2H_2O \quad (8)$$

The key factors for the deposition of ZnSe were stated to be deposition potential and SeO_2 concentra-

tion. The ratio of $[Zn^{2+}]$ /$[SeO_2]$ was made large by adjusting the Zinc deposition potential in such a way that it comes closer to that of deposition potential of Selenium, applying the relations:

$$E_{zn} = E^{o}_{zn} + \frac{RT}{2F}\ln\frac{\alpha^{2+}_{zn}}{\alpha zn}$$
$$= -1.005 + 0.0295\log\frac{\alpha^{2+}_{zn}}{\alpha zn} \quad (9)$$

And

$$E_{se} = E^{o}_{se} + \frac{RT}{4F}\ln\frac{\alpha_{Se}O_2}{\alpha_{Se}} + \frac{RT}{F}\ln\left(\alpha\frac{4}{H+}\right)$$
$$= 0.5 + 0.0148\log\frac{\alpha_{Se}O_2}{\alpha_{se}} - 0.0595\,pH \quad (10)$$

Where $E_{Zn}{}^0$ and $E_{Se}{}^0$ are standard potential of Zinc and selenium respectively (wrt to standard SCE).

The nature of the substrate was found to have strong influence on the nature of the ZnSe deposit. The titanium substrate was found to be superior to other.

Another approach to the deposition of polycrystalline ZnSe thin film is successive ionic layer adsorption and reaction (SILAR) which has been reported by R.B.Kale and C.D.Lakhande[9]. The films have been deposited onto glass substrate at room temperature from an aqueous solutions containing 0.13M sodium selenosulphate (pH =12), 0.25M Zinc acetate complex using 1M tartaric acid.

The formation of ZnSe thin films as reported by SILER method involves the following steps:

Sodium selenosulphate undergoes hydrolysis to produce selenide ions as follows:

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \quad (11)$$
$$HSe^- + OH^- \rightarrow H_2O + Se^{2-} \quad (12)$$

On immersion of the glass substrate in the solution containing Zn^{2+} ions, they (ions) are adsorbed on the surface of the substrate. When such substrate is dipped in a solution containing Se^{2-} ions, ZnSe is formed due to the following reaction:

$$Zn^{2+} + Se^{2-} \rightarrow ZnSe \quad (13)$$

As stated in this method the thickness of thin film depends upon concentration, pH, temperature, number of deposition cycles, rinsing times etc. The thin film of ZnSe on to glass substrate has been visible only after 50 deposition cycles and the thickness of the film is found to be increase linearly with number of deposition cycles and reaches maximum at 150 deposition cycles. The ZnSe thin film has been reported to be uniform, homogeneous and well covered to the substrate.

From optical absorption study they found the film to have band gap energy 2.8eV and room temperature electrical resistivity of the order of 10^7 ohm cm.

Synthesis of ZnSe thin film has been described by[10]. They have adopted the chemical bath deposition (CBD) where ZnSe thin film was synthesized from an alkaline bath on glass substrates. The chemical bath used was an aqueous solution containing 10 ml of (0.2M) $ZnSO_4.7H_2O$, 15 ml of (1M) tartaric acid, 25 ml of(2.8M) ammonia, 25 ml of (2%) hydrazine hydrate and 10 ml of (0.25) sodium selenosulphate. The pH of the resulting solution was 11.45 and temperature was maintained at 333K. The ZnSe thin film was deposited for a time period of 2 hours. They proposed the following growth mechanism.

Zn^{2+} ions in the reaction mixture react with tartaric acid to form water soluble Zn-tartarate complex. Sodium selenosulphate in alkaline medium dissociates to produce selenide ions (Se^{2-}). The metal complex interacts with the Se^{2-} ions to form ZnSe thin film.

$$Zn^{2+} + nA^{2-} \rightarrow [Zn(A)_n] \quad (14)$$
$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \quad (15)$$
$$HSe^- + OH^- \rightarrow Se^{2-} + H_2O \quad (16)$$
$$[Zn(A)_n] + Se^{2-} \rightarrow ZnSe + nA^{2-} \quad (17)$$

Hydrazine hydrate (A) according to the authors might be playing the role of catalyst.

ZnSe thin films deposited using the above methods have been found to be amorphous which on annealing becoming crystalline.

ZnSe thin film has band gap energy of 2.81eV as shown from optical absorption study. The room temperature electrical conductivity of znSe thin film is of the order of 10^{-8} (ohm.cm).

The influence of deposition potential, temperature, concentration of electrolytic bath on crystallinity and composition of ZnSe thin film prepared by electrodeposition method have been studied by[11]. The ZnSe thin film was prepared on conducting glass (FTO) substrate from an aqueous solution containing $ZnSO_4$ and SeO_2.

The electro co-deposition of zinc and selenium was done by using an electrolytic bath containing 50-300

mM of $ZnSO_4$ and 0.2-2 mM of SeO_2 having pH value within range 2 to 3. The deposition was carried out at different temperatures and the deposition potential was varied from -0.6 to -1.2 V versus SCE.

ZnSe thin film was formed electrochemically by following reactions as proposed:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (18)$$

$$Zn^{2+} + 2e^- \rightarrow Zn \quad (19)$$

$$Zn + Se \rightarrow ZnSe \quad (20)$$

They observed that good quality polycrystalline ZnSe is formed at deposition potential of -0.8V versus SCE.

As far as effect of bath composition on structural properties ZnSe thin film is concerned, the concentration of SeO_2 was reported to have a key role to play in the formation of the film by electrodeposition method. With SeO_2 concentration of 1mM was found to be most favorable as far as crystallinity and morphology of thin film is concerned. However concentration of $ZnSO_4$ doesn't affect the structure of the same. As observed by other research workers, here also, the authors reported enhancement of crystalline size with annealing temperature.

It has been reported[11] that the optical band gap of ZnSe thin film at room temperature is 2.67 eV. Excess selenium could be eliminated by annealing the films.

The condition of the electrodeposition of a thin film of polycrystalline ZnSe on Copper substrate from an aqueous bath consisting of 0.001 to 0.008M H_2SeO_3 and 0.1 to 0.8M $ZnSO_4$ solutions with pH = 2 (adjusted by addition of dil. H_2SO_4) at different temperatures such as 25, 50 and 75^{0}C were studied by Remigiusz[12]. From the potentiostatic electrodeposition of ZnSe thin film, they reported that the process was accelerated by an increase of concentration of selenious acid. However the change of amount of zinc ions in the electrolytic bath did not produce any effect on the composition of the film. High temperature could accelerate the deposition process and also improve the quality of the ZnSe thin film coating. Similar observations were reported earlier by workers[11]. They proposed[12] the following mechanism for the formation of ZnSe thin film starting with a reduction responsible for Selenium deposition:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (21)$$

At more negative potential for the reduction of the deposited selenium to H_2Se is possible

$$Se + 2H^+ + 2e^- \rightarrow H_2Se \quad (22)$$

Thin film of ZnSe is formed at the cathode due to the following reaction:

$$Se^0 + Zn^{2+} + 2e^- \rightarrow ZnSe \quad (23)$$

Other competitive electrochemical reactions which are likely to occur during electrolysis, like hydrogen evolution as mentioned in reaction (22). The excess of selenium in the films as reported by them (12) was probably due to chemical reaction between the selenious acid and hydrogen selenide which takes place close to the electrode surface as follows:

$$H_2SeO_3 + 2H_2Se \rightarrow 3Se + 3H_2O \quad (24)$$

They have also reported that higher deposition temperature led to the formation of stable crystallized ZnSe thin films.

P.P.Hankare et al[13] published a paper on photoelectrochemical application of ZnSe thin film prepared by chemical deposition method. Here they used a stainless steel plate as substrate. The efficiency of the PEC cell using sulphide – polysulphide redox electrolyte was found to be 0.13%.

Zn Zhang, Xuezho shi, Chunming Wang[14] studied the mechanism of formation of ZnSe thin film electrochemically on gold-disk electrode. The solutions used for formation of Zinc atomic layers consisted of 2.5 mM $ZnSO_4$ and 0.5M ammonium acetate as supporting electrolyte. The pH of the solution was adjusted at 9 by using ammonium hydroxide. Similarly for selenium deposition they used solution consisting of 2.5 mM H_2SeO_3 and 0.5M Na_2SO_4 as supporting electrolyte, the pH being 4. The blank solution as reported by them consisted of 0.5M Na_2SO_4 (pH = 4).

The mechanism reported by the authors is as follows:

The electrodeposition of selenium atom on to the gold substrate using H_2SeO_3 and Na_2SO_4 solutions may be according to the reduction reaction,

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (25)$$

The bulk selenium undergoes reduction to Se^{2-},

$$Se + 2H^+ \rightarrow H_2Se \quad (26)$$

As reported (13) reaction (26) will be accompanied with a subsequent reaction as follows:

$$2H_2Se + H_2SeO_3 \rightarrow 3Se + 3H_2O \quad (27)$$

The selenium covered gold electrode when dipped in 0.5 M ammonium acetate and 2.5 mM $ZnSO_4$. The

atoms deposited on the electrode react with H2Se to form ZnSe,

$$Zn + H_2Se \rightarrow ZnSe + 2H^+ \quad (28)$$

CONCLUSION

It has been suggested that cathodic electrodeposition is superior in all respect to other methods. Thermal post-deposition treatment i.e. annealing has been found to be very much effective for getting polycrystalline thin film. The optical band gap energy (E_g) at room temperature for ZnSe thin film prepared by different methods has been reported to be 2.5eV to 2.8eV. Neither methods of preparation nor the substrate used play any role to decide optical properties of ZnSe thin films. Out of all the methods mentioned, the PCD (photochemical method) technique is found to be new and potential method for the deposition of polycrystalline ZnSe compound semiconductor thin film.

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