Review Article

Synthesis of binary metal chalcogenides using SILAR method: Review

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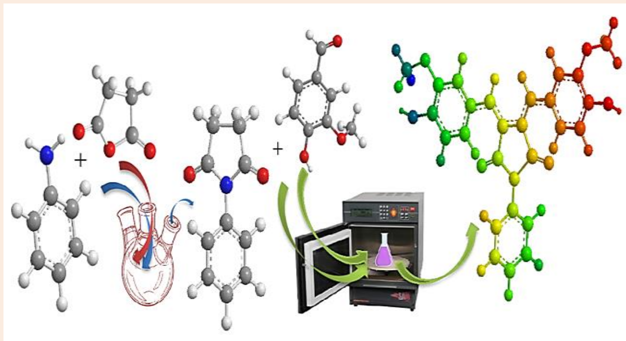
Abstract

The current review summarizes published articles about the preparation of thin films by simple and cheaper successive ionic layer adsorption and reaction method. The films were deposited onto substrate under different deposition conditions. Then, the obtained films were characterized using various analysis methods as discussed in this work. The experimental results will create awareness among the researchers about the quality of thin films.



Keywords: Thin films, solar cells, SILAR deposition method, band gap

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Introduction

Nowadays, successive ionic layer adsorption and reaction (SILAR) deposition method has emerged as an important solution growth technique to prepare various types of thin films. It has many advantages such as simplicity[1], cost effectiveness, easy to control the overall growth rate [2] and less time consuming if compared to other methods [3]. This method based on immersion of the substrate into separately placed cationic and anionic precursors and rinsing between each immersion with ion exchanged water to avoid homogeneous precipitation in the solution [4]. In other words, wastage of the material was avoided as happened in chemical bath deposition method [5].

Since few decades ago, thin films have been used in various optoelectronic devices and photovoltaic technologies include solar cells, sensor devices, electroluminescent devices, and solar control coatings. Because of these reasons, many researchers have worked on various types of thin films using different deposition techniques such as electrodeposition (Table 1), metalorganic chemical vapor deposition (Table 2), RF magnetron sputtering (Table 3), spray pyrolysis deposition (Table 4), chemical bath deposition method (Table 5). The main objective of this work is to study the preparation of thin films using SILAR method, then the obtain films were characterized using various tools. Researchers understand that the growth of thin films onto substrate was mainly depend on deposition conditions such as molar concentration, annealing temperature, pH, dipping time and dipping cycles.

Table 1 Electrodeposition of thin films

Thin films
NiS [6]
ZnSe [7]
Sb_2Se_3 [8]
$SnS_{0.5}Se_{0.5}$ [9]
Cu_4SnS_4 [10]
PbTe [11]
CuS [12]
ZnS [13]

Table 2 Metalorganic chemical vapor deposition of thin films

Thin films
Bi_2Te_3 [14]
Sb_2Te_3 [15]
ZnS [16]

Table 3 Sputter deposition of thin films

Thin films
ZnS [17]
ZnSe [18]
Cu_2ZnSnS_4 [19]
CdS [20]

Table 4 Spray pyrolysis deposition of thin films

Thin films
CuS [21]
ZnS [22]
ZnSe [23]
Cd-In-S [24]

Table 5 Chemical bath deposition of thin films

Thin films
CdSe [25]
ZnSe [26]
Sb_2S_3 [27]
CuS [28]
PbS [29]
PbSe [30]
CdS [31]
SnS [32]
In_2S_3 [33]
ZnS [34]
$ZnIn_2Se_4$ [35]
MnS [36]
$Pb_{1-x}Fe_xS$ [37]
MnS_2 [38]
NiS [39]
$CdS_{1-x}Se_x$ [40]
Cu_4SnS_4[41]
Bi_2S_3[42]
FeS [43]
NiSe [44]
$Ni_3Pb_2S_2$ [45]
SnS_2 [46]
Ni_4S_3[47]
SbCuS [48]
Cu_2S [49]
$CuInSe_2$[50]
$Zn_xCd_{1-x}S$ [51]

Literature survey

Lead sulfide thin films

Lead sulfide thin films prepared using SILAR method by Preetha [52] is observed to be highly crystalline with the size in the range from 22 to 30 nm. In optical studies, they claimed that all the films indicate a gradually increasing absorbance throughout the visible region. It means that these compounds could be used in a photo electrochemical cell. On the other hand, the optimal conditions for the PbS films deposition have been found such as pH of 9.1, dipping time of 10 s and dipping cycles of 10 cycles as suggested by Ersin [53].

Zinc sulfide thin films

Atomic force microscopy (AFM) investigations of zinc sulfide thin films grown on (100) GaAs using SILAR method have been reported by Mika[54]. The AFM images show that the films were smooth with RMS roughness of 0.2 to 1.9 nm depending on the film thickness. On the other hand, ZnS films were prepared by SILAR method using $ZnCl_2$ and Na_2S solutions. The obtained ZnS films show hexagonal structure with size of 1.6 nm[55]. In the optical studies, they conclude that a sharp cut off is observed at 303 nm, corresponds to band gap of 4.08 eV.

Copper sulfide thin films

Copper sulfide thin films have prepared by many researchers using SILAR method. These films could be applied in photothermal conversion, electroconductive electrode, microwave shielding and solar control coating. The influence of molar concentration on the optical properties of CuS films has been investigated by Mani[56]. The band gap reduces from 2.26 to 1.86 eV as molar concentration increases from 0.05 to 0.25 M. The size of the grains increased as the molar concentration increases as shown in atomic force microscopy (AFM) by Elttayef[57]. In addition, they also claimed that the absorbance is higher in the UV-Visible region, but is lower at the near infrared region in such conditions. The similar report in optical studies also could be observed as suggested by Ugwu[58] and Ibiyemi & Tech [59]. The influence of annealing process was investigated by Astam et al. The results indicate that annealing the films at different temperatures ranging from 100 to 400 °C for 45 minutes improved crystallinity as shown in X-ray diffraction (XRD) data.

Zinc selenide thin films

Zinc selenide thin films were deposited onto glass substrate using zinc acetate and sodium selenosulphate solutions by Kale & Lokhande[60]. The obtained films were selenium deficient as indicated in Energy dispersive X-ray (EDX) spectra. The band gap obtained was 2.8 eV and electrical resistivity in the order of 10^7 Ωcm. They also reported the influence of annealing temperature on the properties of films. They found that, cubic phase was transformed into stable polycrystalline hexagonal phase in annealed films as reflected in XRD patterns. Also, depending upon annealing temperature, decrease up to 0.15 eV and 10^2 Ωcm were found in the band gap and electrical resistivity, respectively[61].

Bismuth sulfide thin films

There are many scientists prepared bismuth sulfide thin films using successive ionic layer adsorption and reaction. For example, the growth of Bi_2S_3 thin films on glass slides at room temperature was reported by Ubale[62]. In their experiment, the deposition of Bi_2S_3 films was achieved using bismuth nitrate as cationic and thioacetamide as anionic precursor solutions. The as-deposited films are amorphous in nature as indicated in X-ray diffraction (XRD) pattern. However, the annealed films which prepared at 250 °C for 30 minutes show crystalline with orthorhombic structure. On the other hand, it is seen that resistivity reduces with temperature indicating semiconducting nature of films. Several reasons such as grain boundary discontinuities, presence of surface states and small thickness of films lead to high value of resistivity. The films with lower crystallites may have lower conductivity as compared to the films having bigger crystallites. Desale[3] suggested that the Bi_2S_3 is considered to be a potential candidate for sensor devices due to these films exhibit photoconductivity phenomena. They also reveal that annealed films have good photo response as compared to as-deposited films in *I-V* measurement under dark and illumination conditions. The effect of cationic concentration on the properties of films was investigated by Mageshwari[1]. They conclude that the band gap energy (from 1.81 to 1.25 eV) and activation energy (0.059 to 0.022 eV) reduce with increase in cationic concentration from 0.01 to 0.03 M. This is due to improved grain size and reduction in the defect levels.

Cadmium selenide thin films

Cadmium selenide thin films were used in sensor, solar cell, lasers, thin films transistor, photoconductor and gamma ray detectors. The influence of film thickness on the properties of CdSe films has been studied by Akaltun[2]. Results obtained indicating that the band gap values were reduced from 1.93 to 1.87 eV with increasing film thickness from 255-400 nm. Also, the reducing in resistivity (from 10^6 to 10^2 Ω-cm) with increasing film thickness at room temperature is due to the improvement of the crystallization. On the other hand, hexagonal structures of CdSe thin films have been prepared using SILAR method by Pathan[4]. In the EDX studies, the average atomic percentage of Cd:Se was 55:45, indicating that the sample was slightly cadmium rich.

Cadmium telluride thin films

Cadmium acetate was used as cationic and sodium tellurite as anionic precursor in aqueous medium in order to prepare CdTe thin film using SILAR method by Ubale[63]. In their experimental findings, they obverse that the resistivity is found to be of the order of 411×10^3 Ω-cm at 523 K temperature with an activation energy of ~ 0.2 eV. The XRD pattern and optical absorption studies show that these films are nanocrystalline in nature and have direct band gap with band gap of 1.41 eV. Thickness of CdTe films ranging from 96-312 nm have been prepared by Ubale and Kulkarni[64] using SILAR method. They suggest that increase in grain size from 14.5 to 32.8 nm and decrease in activation energy, electrical resistivity and band gap energy as the thickness was increased.

Tin sulfide and tin disulfide thin films

Tin forms a variety of sulfides such as SnS and SnS_2. These compounds could be used in optoelectronic devices and photoconductive cells. Tin disulfide films have been prepared by Deshpande[65]. They show n-type conductivity with a band gap of 2.22 eV. On the other hand, SnS films have been prepared by Patra[55]. The XRD patterns indicate that orthorhombic structure. In the optical studies, the band gap of 1.32 eV was obtained.

Nickel sulfide thin films

NiS is belongs to VIII-VI compound materials. Generally, they are black in colour and have hexagonal crystal structure (Pathan & Lokhande, 2004). Nickel sulphide thin films were deposited onto various substrates such as glass, fluorine doped tin oxide (FTO) and single crystal Si (111) wafer using SILAR technique (Sartale & Lokhande, 2001). In the XRD analysis, the films deposited onto glass substrate are amorphous while films deposited onto FTO and Si (111) wafer are polycrystalline.

Conclusions

The main aim of this review is to indicate the recent advances in the preparation of thin films using SILAR method. The information as presented in this work might be very useful in the development of chalcogenide thin films in many applications include solar cell, sensor devices and optoelectronic technology.

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