Abstract: The aim of this study is to discuss the synthesis of thin films using chemical bath deposition method. In recent years, studies of thin films of different groups have attracted great attention due to their applications are possible in many areas of modern technology. Researchers have deposited binary, ternary and quaternary thin films from aqueous solutions using chemical bath deposition method. Here, the growth of metal sulfide, selenide and telluride thin films has been reported. The influence of deposition parameters on the physical properties of films was investigated. The research findings indicate that an increase in deposition time allows more materials to be deposited onto the substrate. Morphological studies of films show that the films thicknesses were increased as the bath temperature was increased.

Keywords: Chemical bath deposition, chalcogenide, solar cell, thin films

INTRODUCTION

Chalcogenide thin films have attracted a great deal of attention because of they can be used in solar cell, corrosion resistant coating, microelectronics, optics, magnetic, laser devices and gas sensor application. Here, chemical bath deposition method was chosen because of its cost effective and simplicity for the preparation of films on various substrates such as soda lime glass (Prabukanthan et al., 2010; Noikaew et al., 2008), molybdenum coated-soda lime glass (Noikaew et al., 2008; Lugo et al., 2015), corning glass substrate (Lugo et al., 2014), stainless steel (Pavar et al., 2013), indium tin oxide (Zhou et al., 2008; Ordaz-Flores et al., 2006; Herrera et al., 2006), quartz glass (Khallaf et al., 2008), fluoro-doped tin oxide (Barote et al., 2011; Ahire and Sharma, 2006; Bansode and Wagh, 2014; Islam et al., 2012; Zyoud et al., 2013), titanium (Lokhande, 1990) and microscope glass slide (Anuar et al., 2012; Ezugwu et al., 2010; Oladiran et al., 2012; Sadekar, 2014; Al-khayatt and Jaafar, 2014).

According to various scientists, the properties of films can be controlled by different deposition conditions such as pH, bath temperature, deposition time, annealing temperature and concentration of solution. In this review study, an analysis was carried out to study the influence of deposition parameters on the chemical bath deposited films.

Deposition process: Generally, chemical bath deposition method is used to prepare thin films from cations with sulphide, selenide and telluride ions. During the deposition process, the cleaned glass substrate was dipped into chemical bath. In order to investigate the best quality of thin films, the different deposition conditions were carried out during the deposition process.

Effect of deposition parameters: The vast preparation and studies of metal chalcogenide thin films by various researchers worldwide could be grouped into binary, ternary and quaternary compounds. These research activities are mostly related to the study of material properties especially suited to solar cell application.

Influence of the complexing agent: The use of complexing agents is very common in the preparation of thin films through chemical bath deposition process. It is very clear that the quality of thin films depends on the nature of the complexing agent. Agawane et al. (2013) have reported that the ZnSe films produced using sodium citrate was highly uniform if compared to those prepared using hydrazine hydrate based on SEM results. In the XRD patterns, there are five peaks and three peaks could be detected for the CdS films deposited in the presence of ammonia and ethylenediaminetetraacetic acid, respectively (Zhang et al., 2003). The grain size of the ZnS films which prepared in the presence of hydrazine hydrate, triethanolamine and tri-sodium citrate is 66.7, 34.4 and 24.9 nm, respectively (Deepa et al., 2014). In the AFM studies, the CdS film deposited with sodium borohydride showed roughness of 9.33 nm whereas films deposited with hydrazine indicated roughness of 6.33 nm (Carrillo-Castillo et al., 2013).
Influence of bath temperature: As can be seen from the different literature reviews, it is very common to study the influence of the bath temperature on the properties of films range from room temperature to 90°C. Mousa and Ali (2008) have reported that the PbS film thickness and grain size is increased from 217 to 750 nm and from 7 to 15 nm, respectively as the bath temperature was increased from 20 to 50°C. Similar results also have been reported by Ezike and Okoli (2012) and Alias et al. (2014) on the chemical bath deposited CuAlSe$_2$ films and Cu$_3$SnS$_4$ films, respectively.

In the XRD studies, the crystalline orientation improves with the increase of bath temperature as reported by Gonzalez-Panzo et al. (2014). In the other case, Sreedevi and Ramakrishna Reddy (2013) have reported that the intensity of (111) plane increases with the increase in bath temperature from 50-70°C. Also, the number of peaks increased when the bath temperature is increased as shown in XRD patterns. Anuar et al. (2010b) have pointed out that the number of peaks contributed to PbSe increased to three and four, as the bath temperature is increased further to 60 and 80°C.

In terms of photosensitivity behavior, the PbS films deposited at 35°C shows the lowest photo response behaviors are characterized by the formation of the thinnest (815 nm) films. While, the increase of the photosensitivity for the films deposited at 75°C is explained through the formation of the thickest (1313 nm) PbS films (Ho et al., 2013). The In$_2$S$_3$ films were grown by varying the bath temperature from 50 to 90°C. In EDAX analysis, S/In ratio in the layers increased with the increase of bath temperature from 50 to 70°C, reached a maximum at 70°C and then decreased up to 90°C as reported by Gopinath et al. (2013). Lastly, accordingly to research findings, the films prepared at higher bath temperature such as 80°C (Munikrishna Reddy and Vedavathi, 2012; Deshpande et al., 2013) and 75°C (Anuar et al., 2011a) have higher absorption properties if compared to other bath temperatures.

Influence of deposition time: In order to study the influence of deposition time on the properties of thin films, the deposition process was carried out at different periods by researchers. The obtained experimental results conclude that an increase in deposition time allows more materials to be deposited onto substrate and thicker films to be formed. For example, the thickness of CdS (Patil and Pawar, 2014; Abulmakarim et al., 2014) and ZnS (Abdullah et al., 2012) films was varied as the deposition time was increased according to literature reviews, respectively. However, the band gap decreases with increase of film thickness. The band gap values obtained are 2.39, 2.48 and 2.52 eV for the NiSe films deposited for 3, 2 and 1 h, respectively (Anuar et al., 2011b). Shinde et al. (2012a) have reported a similar trend for the chemical bath deposited Cu$_x$S films.

In terms of morphological studies, atomic force microscopy images showed incomplete coverage of material over the surface of substrates for the Cu$_3$SnS$_4$ films prepared at shorter time such as 20 and 40 min (Anuar et al., 2009). This is due to the thin films deposition process on a substrate depends on the formation of nucleation sites and subsequent growth of the films from this centers. Because of the sizes of the grains were noticed to increase as the deposition time was increased during the deposition process. As the deposition time was increased further, the fine polycrystalline materials agglomerates together to form larger grains and the films cover the surface of substrate completely. Also, longer deposition time leads to the formation of more homogeneous film as reported by Patel (2012).

Surface roughness was investigated using atomic force microscopy. The AFM images confirmed that the surface roughness increased with increasing deposition time. The surface roughness of PbS films was 39, 44, 54 and 70 nm for the deposition time 10, 20, 30, 40 min, respectively (Ibrahim, 2014). On the other hand, the influence of deposition time on the absorption characteristic of CuS films has been investigated by Ezenwa (2013). The absorbance value increased gradually with increase in the deposition time from 1 to 5 h.
The influence of annealing process: Annealing is one of the most commonly used surface treatments. It was chosen to improve the crystallinity of the thin films. For instance, the intensity of the peaks increased indicating better crystalline phase in the annealed films such as CdS (Haider et al., 2008; Enriquez and Mathew, 2003) and CdTe (Geethalakshmi and Muthukumarasamy, 2012) films.

Sometimes, phase transformation from mixed phase to stable phase could be observed in annealed films. For example, XRD data revealed that the coexistence of the cubic and hexagonal phases in the as-deposited films while hexagonal phase in CdS annealed films which reported by Pushpalatha et al. (2014). In other cases, the XRD studies exhibit that the deposited layers are mainly consisting of CdS phase. After annealing, metastable cubic phase was transformed into stable hexagonal phase (Mustafa et al., 2012).

Generally, good quality of annealed films could be obtained if compared to as-deposited films. Research findings indicate that increase in annealing temperature increases the grain size continuously along with reduce of strain and dislocation density of the films. PbS films annealed at 573 K indicated the largest crystallite size of 12.72 nm as compared to other temperatures (Oriaku and Osuwa, 2008). Similar behavior also reported by Prem Kumar et al. (2011), indicated that the grain size increases with increasing the annealing temperature from 200 to 400°C.

Ampong et al. (2010) studies the optical absorption spectra of as-deposited CdS thin films and annealed films at 100, 200°C. They have observed that the band gap energy values were 2.1, 2.2 and 2.3 eV, for the sample CdS as-deposited, annealed at 100 and 200°C, respectively. In other words, an increase in band gap with annealing temperature might be attributed to the improvement in crystallinity in the CdS films.

pH: As we know, there was no deposition of films when the solution pH is inappropriate. Therefore, a series of experiments will be conducted in order to determine the best conditions for the deposition process. We can conclude that alkaline media is needed for the chemical bath deposition of PbS (Mousa et al., 2014), CdS (Ahmed et al., 2013; Zhou et al., 2012; Kariper et al., 2011), ZnS (Luque et al., 2015) and CuS (Singh et al., 2013) thin films from solutions. In contrast, Ni₃S₂ (Anuar et al., 2010c), In₄S₃ (Yahmadi et al., 2005), FeS (Anuar et al., 2011d), ZnS (Kang et al., 2010), ZnSe (Anuar et al., 2011c) were prepared from an acidic bath according to literature reviews. In acidic medium, dissociation of thiosulfate takes place and will produce sulfur. Next, the released electrons react with sulphur to form sulfide ions. Finally, these sulfide ions combine with cation ions to form thin films.

Concentration of solution: The influences of solution concentrations towards the properties of the films were investigated by varying the concentration of solutions used in the chemical bath. For example, grain size of CdS films increases with increasing cadmium ion concentration in solution (Hani and Atallah, 2012), meanwhile, it can be seen that depositing films of different concentrations of Sb³⁺ increases the thickness of Sb₂S₃ films (Srikanth et al., 2011). However, further increase in the volume of solution such as sodium thiosulfate caused reduction in thickness of Bi₂S₃ films as reported by Balasubramanian et al. (2012).

In terms of morphology studies, SEM micrographs indicated that the CdS films are covered by spherical grains, whose size decreases and their density increases noticeably when [S]/[Cd] ratio increases (Fouad et al., 2011). In terms of absorbance and transmittance study, transmittance was found to increase with decrease in solution concentration from 0.5M to 0.05 M, while MnS films absorbance value showed the inverse (Usoh and Okujagu, 2014).

In the case of ternary compound such as CdZnS, the influence of zinc content has been studied by many researchers. Visual observation indicated that the films obtained were smooth, uniform, adherent, bright yellow in color and yellowness increases with increasing Zn content (Sanap and Pawar, 2011). Meanwhile, the pH was found to decrease with increasing concentration of zinc as reported by Song and Lee (2009). In terms of optical transmittance study, the transmittance decreased firstly with increasing of Zn:Cd ratio from 1:9 to 3:7, then increased as Zn:Cd ratio is 4:6, lastly decreased with the further increasing of Zn:Cd ratio to 5:5 (Jia et al., 2010). In the XRD patterns, the polycrystalline nature of prepared films was increased when the zinc content is 0.2 and 0.4 (Ravangave and Biradar, 2013).

On the other hand, Ag-In-S thin films were prepared by Chang et al. (2010). The SEM images indicate that when the [Ag]/[In] molar ratio increased, the morphology changed from fiber-like to spinel and to a mixture of fiber like and spinel structures. Anuar et al. (2010d) have been prepared Cu₃SnS₄ films under various concentrations of solutions. The AFM images of the films prepared using 0.05 M CuSO4 show distribution of grains, which covers the surface of the substrate completely. However, as the concentration of copper sulfate was reduced to 0.01 M, the distribution of grains has been reduced.

Band gap: Nowadays, there are various binary, ternary and quaternary thin films have been reported for photovoltaic cells. Because production costs are low in the semiconductor technology and optical band gaps in the range of 1-2 eV match the solar spectrum (Table 2).
Table 2: Band gap energy of various thin films

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Band gap</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe</td>
<td>1.25</td>
<td>Zainal et al. (2004)</td>
</tr>
<tr>
<td>SnS</td>
<td>1.0</td>
<td>Hankare et al. (2008)</td>
</tr>
<tr>
<td>PbSe</td>
<td>1.3</td>
<td>Okeke and Ekpunobi (2010)</td>
</tr>
<tr>
<td>PbS</td>
<td>1.8</td>
<td>Rajathi et al. (2014)</td>
</tr>
<tr>
<td>NiSe</td>
<td>1.61</td>
<td>Hankare et al. (2010)</td>
</tr>
<tr>
<td>CoS</td>
<td>1.13</td>
<td>Mane et al. (2011)</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.8</td>
<td>Gopakumar et al. (2010)</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.45</td>
<td>Laxman et al. (2012)</td>
</tr>
<tr>
<td>SbS 2</td>
<td>1.78</td>
<td>Nair et al. (1998)</td>
</tr>
<tr>
<td>CdZnSe</td>
<td>1.7-2.3</td>
<td>Deo et al. (2014)</td>
</tr>
<tr>
<td>PbMnS</td>
<td>1.5</td>
<td>Joshi et al. (2006)</td>
</tr>
<tr>
<td>Ag-In-S</td>
<td>1.82</td>
<td>Lin et al. (2008)</td>
</tr>
<tr>
<td>HgCd 3+S</td>
<td>1.76</td>
<td>Deshmukh et al. (1998)</td>
</tr>
<tr>
<td>CdMnS</td>
<td>1.45-1.65</td>
<td>Oriaku et al. (2008)</td>
</tr>
<tr>
<td>Cu 4SnS 4</td>
<td>1.04</td>
<td>Bari et al. (2006)</td>
</tr>
<tr>
<td>Ag 3SnS 3</td>
<td>1.28-1.39</td>
<td>Yeh and Cheng (2014)</td>
</tr>
<tr>
<td>Cu 2ZnSnS 4</td>
<td>1.5</td>
<td>Subramaniam et al. (2014)</td>
</tr>
<tr>
<td>Cu 2ZnSnS 4</td>
<td>1.55</td>
<td>Shinde et al. (2012b)</td>
</tr>
<tr>
<td>Ag 3ZnSnS 4</td>
<td>1.2</td>
<td>Yeh and Cheng (2014)</td>
</tr>
<tr>
<td>Cu 2ZnSnS 4</td>
<td>1.6</td>
<td>Kumar et al. (2014)</td>
</tr>
</tbody>
</table>

CONCLUSION

Various thin films were successfully deposited onto substrate using chemical bath deposition technique. Because of its simplicity in the experimental set up involved, scientists are always expanding their investigation in this field in order to produce good quality films. Lastly, this review study presented some research results on how to optimize the chemical bath deposition method to achieve improved quality of thin films deposited on glass substrates.

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