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Role of Complexing Agent in Chemical Bath Deposition of Thin Films: A Review

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ABSTRACT

Background: An economical and simple chemical bath deposition technique for depositing various types of thin films has been reported by many researchers**. Objective:** In this work, the main objective is to investigate the role of complexing agent in the chemical bath deposited thin films. **Results:** As we know, complexing agent is one of the crucial chemical additives in preparation of thin films. Therefore, the influence of the complexing agent on the structural, optical, surface morphological and electrical properties of films was highlighted. The obtained films were characterized using various tools such as SEM, AFM, XRD, EDX and UV-Visible spectrophotometer**. Conclusion:** The experimental findings indicated that the films prepared in the presence of complexing agent were good quality thin films.

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INTRODUCTION

Complexing agent is one of the deposition conditions plays an important role in the processing of the thin films. Thin films have been prepared using various chemical techniques including electro deposition (Table 1), chemical bath deposition (Table 2), spray pyrolysis (Table 3) and successive ionic layer adsorption and reaction (Table 4). The obtained films have been widely used in a variety of applications such as solar cells, solar selective coatings, laser materials, sensors, photoconductors, optical mass memories and anti-reflection coating.

The aim of this work is to study the effect of using various types of complexing agents by different researchers. The films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy, UV-Visible spectrophotometer, and energy dispersive X-ray (EDX).

Literature Survey:

CdS thin films have been deposited using chemical bath deposition method by Soundeswaran *et al*. (2004) in the presence of complexing agent. They have confirmed that the addition of ammonium sulphate to the chemical bath results in the growth of uniform films and the substrate is fully covered. However, the addition of ammonium sulphate beyond 0.25% did not show any further significant influence in the deposition.

PbS films have been grown on soda lime glass substrate by Preetha *et al*. (2015) using chemical bath deposition method in the presence of various complexing agents such as triethanolamine (TEA), diethanolamine (DEA) and hexamine. In the XRD studies, DEA complexed films has very low crystallinity, while strong diffraction peaks are obtained for the films prepared in the presence of hexamine. In the SEM studies, the surface is observed to be densely packed with larger grains for the films prepared in the presence of TEA and hexamine. However, the surface becomes less dense for the films prepare in the presence of diethanolamine.

The influence of complexing agents such as hydrazine and hydrazine–ammonia on the properties of chemical bath deposited PbS films was reported by Carrillo-Castillo *et al*. (2014). They found that these complexing agents reduce the deposition rate because of higher complexation and slow generation of lead ions improving the morphology of films. They also concluded that the films indicated an ohmic behavior in the metal-semiconductor interface with resistivity values in the order from 0.4 to 65 Ωcm which is very promising to integrate the material in the fabrication of electronic devices.

The quality of chemical bath deposited Cu_4SnS_4 films is influenced by the presence of complexing

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agent such as Na_2EDTA (disodium ethylene diamine tetra-acetate) was reported by Anuar *et al*. (2010a). They suggested that deposition at concentration of 0.05 M of Na_2EDTA proved to offer reasonably good films. This is because of these films showed good uniformity, good surface coverage with bigger grains and produced higher absorbance value if compared to other samples. PbS were prepared from chemical bath containing lead nitrate, thiourea and Na_2EDTA by Ezenwa (2013). The films obtained have high transmittance in the visible or near infrared regions. However, transmittance of the film reduces with the increase in film thickness.

ZnS films were prepared at pH 10 using chemical bath deposition method in the presence of tri-sodium citrate as complexing agent by Agawane *et al*. (2012). They revealed that an increase in the concentration of complexing agent causes to an improvement of the uniformity of films, decrease in the grain size and RMS value as shown in field emission scanning electron microscopy (FESEM) studies and atomic force microscopy, respectively.

Table 1: Electro deposition of thin films.

Thin films	References
Sb_2Se_3	Ngo *et al*., 2014
ZnSe	Mahalingam *et al*., 2007
PbTe	Xiao *et al*., 2006
CuS	Thanikaikarasan *et al*., 2010
NiS	Bharathi *et al*., 2014
$SnS_{0.5}Se_{0.5}$	Subramanian *et al*., 2003
Cu_4SnS_4	Kassim *et al*., 2010

Table 2: Chemical bath deposition of thin films.

Thin films	References
Ni_4S_3	Anuar *et al*., 2010e
Cu_4SnS_4	Anuar *et al*., 2010f
Cu_2S	Anuar *et al*., 2011c
NiSe	Anuar *et al*., 2011d
ZnSe	Anuar *et al*., 2011e
Bi_2S_3	Ahire & Sharma, 2006
CdS	Ahmed *et al*., 2013
Cu_3SnS_4	Alias *et al*., 2014
Cobalt sulphide	Mane *et al*., 2011
CdSe	Gopakumar *et al*., 2010
CdTe	Laxman *et al*., 2012
$Ni_3Pb_2S_2$	Ho, 2015
Ag-Zn-Sn-S	Yeh & Cheng, 2014
Cu_2ZnSnS_4	Subramaniam *et al*., 2014

Table 3: successive ionic layer adsorption and reaction deposition of thin films.

Thin films	References
CdS	Guzeldir *et al*., 2012
CuS	Guzeldir *et al*., 2012
ZnS	Guzeldir *et al*., 2012
CdSe	Panthan *et al*., 2002
SnS_2	Sankapal *et al*., 2000

Table 4: Spray pyrolysis of thin films.

Thin films	References
CuS	Isac *et al*., 2007
ZnS	Zeng *et al*., 2013 Dedova *et al*., 2005
Cd-In-S	Shadia *et al*., 2013
CdSe	Betkar & Bagde, 2012

In recent times, triethanolamine (TEA) was used as complexing agents by many researchers to prepare various types of thin films. The film deposited with 10 ml TEA showed good uniformity, good surface coverage with bigger grains and produced higher absorbance value as reported by Okereke *et al*. (2012). The band gap energy of Sb_2S_3 films was found to reduce from 1.8 eV to 1.4 eV as the deposition time increases from 12 h to 48 h as reported by Jeroh and Okoli (2012). In the XRD studies, Anuar *et al*. (2011a) conclude that the NiS peaks increased with the rise in concentration of TEA up to 0.1M. However, the NiS peaks dropped for the films deposited at higher concentration of TEA (0.2M). Sangamesha *et al*. (2013) reported on the preparation and optical properties of CuS films in the presence of TEA. The TEA serves as complexing agent to chelate with copper ions. The deposition of CuS films is based on the slow release of Cu^{2+} and S^{2-} ions in the solution, then, condensed on to the glass substrates.

Acetic acid was used as complexing agent in order to prepare the In_2S_3 films using chemical bath deposition method by Gopinath and Ramakrishna

Reddy (2013). The obtained results reveal that the granular density decreases, and grain size increases with increasing the acetic acid concentration. In addition, the optical studies show that the band gap values varied in the range of 2.87-3.32 eV with the change of concentration of complexing agent.

Nitrilotriacetic acid (NTA) was employed as a complexing agent to deposit CdS films on substrate by Khallaf *et al*. (2008). They demonstrated that high quality CdS films could be deposited on soda lime glass substrate in the presence of nitrilotriacetic acid. On the other hand, they also reported that the thickness becomes maximum at [NTA]/[Cd] ratio of 4, which is more than four times the thickness at [NTA]/[Cd] ratio =2.

Chemical bath deposited MnS films were prepared from manganese acetate and thiourea solutions by Dhandayuthapani *et al*. (2015). The presence of both γ and β-MnS phases could be observed in XRD patterns for the films prepared in the presence of ethylenediamine tetra acetic acid (EDTA) which serves as a complexing agent. Photoluminescence investigation indicated the optical quality of films and the band edge emission was detected at 360 nm. On the other hand, micro-raman investigation confirms the enhancement in crystallization of the MnS films because of the effect of molar ratio of precursor solutions.

There are many literature reviews report that the preparation of various types of thin films using tartaric acid as a complexing agent. SnS films were prepared using tartaric acid under various bath temperatures using chemical bath deposition method by Gedi and Kotte (2013). The intensity of (111) plane increases with the increase in bath temperature that varied in the range 50-70 °C. On the other hand, PbS films with thickness of 400-992 nm were prepared by Ho *et al*. (2014) in the presence of tartaric acid. The band gap was reduced from 1.35 to 1.15 eV with increasing the film thickness. A well adherent CdSe films have been prepared by Fekadu *et al*. (2015) in the presence of tartaric acid as complexing agent. EDX confirmed that the atomic percentage of Cd:Se is 49.4:50.6, which is close to 1:1. The grain size was obtained about 4nm by using Debye-Scherrer equation. CuS films were synthesized from chemical bath containing copper sulphate, thiourea and tartaric acid by Anuar *et al*. (2011b) XRD data reveal that the films are polycrystalline with hexagonal structure. SEM analysis indicated that all grains uniformly distributed over the surface of substrate.

Ammonia was used as complexing agents to form a cadmium complex, which slowly releases cadmium ions for subsequent reaction with S^{2-} ions. The influence of ammonia as complexing agent on electrical and optical properties of CdS has been reported by Munikrishna and Nagendra (2013). They observe that the carrier concentration varied from $1.83X10^6$ to $1.026X10^6$ cm^{-3} when ammonia concentration is changed from 0.5 M to 2.5 M. The band gap was 1.92 eV and 2.65 eV for the films prepared using 0.5 M and 2.5 M, respectively as indicated in optical analysis. Fouad *et al*. (2011) have reported that the CdS films obtained are n-type conductivity semiconductor. In addition, these films exhibited excellent transmittance of about 80% in visible and near infrared regions. On the other hand, Ezenwa (2012) reported that lead selenide films were deposited on glass substrates in the presence of ammonia. The results show that the films have the highest absorbance at wavelength range of 300 to 500 nm. However, the absorbance generally decreases with increase in wavelength.

The sodium tartrate was acted as a complexing agent in order to chelate with manganese, iron and zinc ions to produce MnS_2, FeS and ZnS films by Anuar and other workers. The obtained MnS_2 films have cubic structure in XRD studies (Anuar *et al*., 2010b). Also, they conclude that the grain sizes become bigger with the increasing deposition time according to AFM analysis. On the other hand, the obtained FeS films which prepared using higher concentration of solution indicated the higher number of FeS peaks in XRD patterns if compared with other concentrations Anuar *et al*., 2010c). Meanwhile, the substrate was covered completely for the ZnS films prepared at pH 2, indicating more nucleation sites had formed as compared to other pH values (Anuar *et al*., 2010d).

Conclusion:

Researchers have successfully deposited various types of thin films using chemical bath deposition method in the presence of complexing agent. These complexing agents including sodium tartrate, ammonia, tartaric acid, ethylenediamine tetra acetic acid, Na_2EDTA, triethanolamine, acetic acid, hydrazine, ammonium sulphate, diethanolamine and hexamine . The experimental findings indicated that these films were good quality thin films if compared to those prepared in the absence of complexing agent.

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