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ELECTRODEPOSITION OF TERNARY THIN FILMS: A REVIEW

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ABSTRACT

This review paper summarized the preparation of ternary chalcogenide thin films using electrodeposition method. Electro deposition method is emerged as one of the most preferred deposition technique to produce large area thin films by many researchers. Many efforts are currently directly to generation of binary, ternary and quaternary thin films based on metal sulfide, selenide and telluride using this method.

Keywords *–Electrodeposition; Thin films; Chalcogenide; Solar cells; Semiconductor.*

1. INTRODUCTION

Thin films are considered as the best candidate for applications in optical and photosensitive devices, solar cells and solar selective decorative coatings. Recently, many research groups from all corners of the world have an increasing interest in the investigation and development of ternary chalcogenide thin films. These thin films have been grown by many deposition techniques as listed in Table 1[1-16]. Currently, electro deposition method is considered as one of the most preferred and cheaper deposition method to produce large area thin films[17]. Furthermore, other advantages include simple[18], low cost instrumentation[19], high grow rate, high efficiency of material utilization[20], uniform deposition over substrates, easy control of growth parameters[21], it does not require vacuum chamber[22] and good control over film composition[23].

In this review paper, preparation of ternary thin films include metal sulfide, selenide and telluride by using electrodeposition method will be discussed. The obtained experimental findings will be reported also.

2. LITERATURE SURVEY

Mercury cadmium telluride thin films have been deposited on nickel substrate by Kumaresanet al[24] using $CdCl_2$, $HgCl_2$ and TeO_2. They observe that the cadmium rich content was produced at higher potential. These films display a cauliflower morphology and larger grain size if compared to mercury rich thin films which deposited at lower potential.

The $CdSO_4$, $InCl_3$ and TeO_2 were used to prepare ternary Cd-In-Te films onto SnO_2: F coated glass substrate by Kiran et al[25]. In X-ray diffraction (XRD) analysis, these films display cubic structure with predominant (111) orientation. In optical properties investigations, band gap value was reduced from 1.2 to 1.1 eV as the deposition potential was increased from -0.5 to -0.54 V (SCE), indicating that the band gap changes with the deposition potential.

Copper indium diselenide thin films have direct band gap characteristic, high optical absorption coefficient[26] and high long term stability. In the literature, there are many reports related to the $CuInSe_2$ films growth by electrodeposition technique onto various substrates such as Mo/soda lime glass[27], SnO_2-coated glass[28] and indium tin oxide coated glass[29,30]. On the other hand, some researchers prepare $CuInSe_2$ thin films using various complexing agents such as citric acid[31] and triethanolamine[32] in their research.

$CuInTe_2$ thin films were prepared by Dixit et al[33] using $CuCl_2$, $InCl_3$ and pre-reacted tellurium with nitric acid. In their experiment, acetronitrile was added into electrolytic bath and growth was done at the potentials of -0.35 V and -0.45 V with and without stirring. The films grown under stirring conditions are more oriented in the (112) direction as indicated in XRD patterns. Meanwhile, formation of uniformly covered nano flakes of 40-50 nm could be observed in the films as shown in SEM analysis.

Studies on zinc mercury telluride thin films were carried out by Mahalingamet al[34]. Deposition of films was done using an electrolyte bath contained $ZnSO_4$, $HgCl_2$, and TeO_2 with the pH value varying between 2 and 4. They found that excessive amount of pure tellurium was deposited for the pH below 2.5. However, insufficient tellurium could be detected dissolved in the electrolytic bath when the pH greater than 4. On the other hand, the influence of bath composition also was studied by them. They claim that increased $HgCl_2$ concentration has resulted in high mercury content in the films. However, there was no change of mercury content in the films as the $HgCl_2$ concentration beyond 1mM. The electrical resistivity and the band gap were observed to reduce with increase in the mercury content in the films.

The electrodeposition of molybdenum sulphoselenide thin films on indium tin oxide (ITO) coated glass and stainless steel substrates have been reported by Anandet al[35]. The colour of all the samples were dark grey to black in colour and were adherent to the substrates. These films were characterized by XRD for structural studies and the rhombohedral structure was confirmed.

Electrodeposited cadmium zinc telluride thin films which prepared on SnO_2 substrate have been investigated by Rekha[36]. The films prepared at potential of -0.87V (saturated calomel electrode, SCE) have the cubic structure and uniformly covered with grains of one micron in size as shown in XRD and SEM results. Optical transmission spectra were recorded and the band gap was found about 1.6 eV.

Copper indium disulfide thin films show high absorption coefficient and direct band gap, so that, make them an excellent absorber for solar cells. $CuInS_2$ films were deposited on SnO_2/glass substrate from $InCl_3$, $CuSO_4$ and $Na_2S_2O_3$ as reported by Manfredyet al[37]. A stoichiometric composition and good crystallinity were found for films prepared at potential of -1145 mV (SCE) according to Energy dispersive X-ray (EDX) and XRD results. Zhou et al[38] have reported that the preparation of $CuInS_2$ films on indium tin oxide glass substrate. The XRD analysis indicated that as-deposited $CuInS_2$ films are the major phase at deposition potential of -1000 mV SCE. However, the sample was found to be copper rich in annealed films. In the optical investigations, the band gap and carrier concentration were observed to be 1.43 eV and $4.2 \text{ X } 10^{17}$ cm^{-3}, respectively. Martinez et al[39] have been reported that $CuInS_2$ films were growth on a stainless steel substrate. They conclude that the samples were annealed in a nitrogen atmosphere in order to improve the polycrystallinity of films. Based on their results, the films show *n*-type characteristic as the electrolytic bath has the same concentration $[Cu^{2+}]=[In^{3+}]$. Meanwhile, for different concentrations of copper and indium ions, the films were of the *p*-type.

Cu_4SnS_4 thin films have been prepared under various deposition conditions by Anuar and co-workers. The influence of different bath temperatures (25, 35, 45°C) and deposition periods (15, 30, 45 minutes) on the growth of these films was reported. The atomic force microscopy (AFM) measurement results indicated an increase in the film thickness as the deposition time was increased from 15 min (1269 nm) to 30 min (2016 nm). Furthermore, the AFM images indicated that higher bath temperature leads to larger crystal size[40]. On the other hand, the films were deposited at various deposition potentials, ranging from –400 mV to –1000 mV versus Ag/AgCl in order to determine the optimum conditions. The films were observed to display direct transition in the visible spectrum with a band gap value of about 1.58 eV at –600 mV. Decreasing in deposition potential resulted in an increase in the size of the grains and caused in growth of spherical particles[41]. The influence of pH was studied in their experiments. The films showed good uniformity and exhibited higher absorbance value at pH 1.5[42].

Nowadays, researchers have successfully produced not only ternary thin films, but also quaternary films (Table 2) and binary (Table 3) films using various deposition methods for the applications in optoelectronic and solar cells. The physical and optical properties of thin films were discussed and analyzed in their reports.

Table 1: Ternary thin films prepared by various deposition methods.

Thin films	Deposition method
$Cd_{0.6}Hg_{0.4}Se$[1]	Chemical bath deposition
Ag-In-S[2]	Chemical bath deposition
$CuInS_2$[3]	Chemical bath deposition
Cu_2ZnS_2[4]	Chemical bath deposition
$Ni_3Pb_2S_2$[5]	Chemical bath deposition
Cd-S-Se[6]	Thermal evaporation
Hg-Cd-Te[7]	Thermal evaporation
$Zn_xCd_{(1-x)}Te$[8]	Thermal evaporation
Pb-Te-Ag[9]	Thermal evaporation
Se-Ag-Te[10]	Thermal evaporation
$Ge_{19}Se_{81-x}Sb_x$[11]	Thermal evaporation
$CuInS_2$[12]	Solvothermal reaction
$Cd_{0.9}Zn_{0.1}Te$[13]	Vacuum evaporation
$CuInSe_2$[14]	Hydrothermal method
$CuInS_2$[15]	Spray pyrolysis
Cd-S-In[16]	Spray pyrolysis

Table 2: Quaternary thin films prepared by various deposition methods.

Thin films
Cu_2ZnSnS_4[43]
$MoBiGaSe_5$[44]
$Ag_{1-x}Cu_xInS_2$[45]
CuInSTe[46]
Ag-Zn-Sn-S[47]

Table 3: Quaternary thin films prepared by various deposition methods.

Thin films
MnS_2[48]
CdSe[49]
CuS[50]
Sb_2S_3[51]
ZnS[52]
In_2S_3[53]
ZnSe[54]
PbS[55]
PbSe[56]
SnS_2[57]
NiS[58]
CdS[59]
FeS[60]
Bi_2S_3[61]
SnS[62]
NiSe[63]
MnS[64]
Ni_4S_3[65]
Cu_2S[66]

3. CONCLUSION

Several reports on the electrodeposition of thin films from aqueous solutions have been published and discussed here. Experiment results show that the ternary thin films could be deposited onto various types of substrates and under different growth conditions. Lastly, electrodeposition technique has been selected in this work due to it is a simple process and without vacuum conditions compared with other deposition techniques.

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5. REFERENCES

1. Bhuse VM, Hankare PP, Sonandkar S, Mater. Chem. Phys, 2007, 101: 303-309.
2. Chang W, Wu C, Jeng M, Cheng K, Mater. Chem. Phys, 2010, 120: 307-312.
3. Bini S, Bindu K, Lakshmi M, Kartha CS, Vijayakumar KP, Kashiwaba Y, Abe T, Renewable Energy, 2000, 20: 405-413.
4. Uhuegbu CC, Babatunde EB, Am. J. Sci. Ind. Res., 2010, 1: 397-400.
5. Ho SM, Oriental J. Chem., 2014, 30: 1009-1012.

6. Lalhriat Z, Pratima A, Mater. Chem. Phys, 2015, 162: 813-821.
7. Basharat M, Hannan MA, Shah NA, Ali A, Arif M, Maqsood A, Cryst, Res. Technol., 2007, 42: 817-821.
8. Khairnar UP, Behere SS, Pawar PH, J. Surf. Eng. Mater. Adv. Technol., 2011, 1: 51-55.
9. Manju B, Srashti G, Tripurari ST, Shikha V, Surya KT, Asokan K, Devesh KA, RSC Adv., 2015, 5: 25887-25895.
10. Madhu M, Rashmi C, Anju K, Srivastava KK, Prog. Nat Sci: Mater. Int., 2011, 21: 36-39.
11. Neha S, Sunanda S, Vineet S, Pankaj S, Mater. Chem. Phys, 2012, 136: 967-972.
12. Han S, Kong M, Guo Y, Wang M, Mater. Lett., 2009, 63: 1192-1194.
13. Sridharan M, Mekaladevi M, Narayandass SK, Mangalaraj D, Lee H, Cryst. Res. Technol., 2004, 39: 328-332.
14. Ramkumar J, Ananthakumar S, Babu SM, Sol. Energy. 2014, 106: 177-183.
15. Hussain KMA, Podder J, Saha DK, Ichimura M, Indian J. Pure & Appl. Phys., 2012, 50: 117-122.
16. Shadia JI, Hassan KJ, Riyad NAB, J. Lumin., 2013, 141: 27-32.
17. Thanikaikarasan S, Mahalingam T, Kathalingam A, Moon H, Kim YD, J. New Mater. Electrochem. Syst., 2010, 13: 29-33.
18. Mahalingam T, John VS, Ravi G, Sebastian PJ, Cryst. Res. Technol., 2002, 37: 329-339.
19. Bansal A, Rajaram P, Mater. Lett., 2005, 59: 3666-3671.
20. Cheng K, Meng J, Wang X, Huang Y, Liu J, Xue M, Du Z, Mater. Chem. Phys., 2015, 163: 24-29.
21. Mammadov MN, Aliyev AS, Elrouby M, Int. J. Thin films Sci. Technol., 2012, 1: 43-53.
22. Kashyout AEHB, Ahmed EZ, Meaz T, Nabil M, Amer M, Alexandria Eng. J., 2014, 53: 731-736.
23. Wilman S, Shigeru I, Akio K, Takashi H, Michio M, Electrochim. Acta, 2013, 88: 436-442.
24. Kumaresan R, Babu SM, Ramasamy P, J. Cryst. Growth, 1999, 198-199: 1165-1169.
25. Kiran J, Sharma RK, Kohli S, Sood KN, Rastogi AC, Curr. Appl. Phys., 2003, 3: 251-256.
26. Kashyout AE, Ahmed EZ, Meaz T, Nabil M, Amer M, Alexandria Eng. J., 2014, 53: 731-736.
27. Li J, Zhao X, Xia D, J. Wuhan U. Technol.–Mater. Sci., 2007, 22: 140-143.
28. Wellings JS, Samantilleke AP, Heavens SN, Warren P, Dharmadasa IM, Sol. Energy Mater. Sol. Cells, 2009, 93: 1518-1523.
29. Bouraiou A, Aida MS, Mosbah A, Attaf N, Braz. J. Phys., 2009, 39: 543-546.
30. Meglali O, Bouraiou A, Attaf N, Rev. Energies Renouvelables, 2008, 11: 19-24.
31. Bouabid K, Ihlal A, Manar A, Sdaq A, Outzourhit A, Ameziane EL, J. Phys. IV France, 2005, 123: 47-51.
32. Whang T, Hsieh M, Kao Y, Lee S, Appl. Surf. Sci., 2009, 255: 4600-4605.
33. Dixit P, Kavita D, Ashok KS, Vikas T, Poolla R, Int. J. Mater. Sci. Appl., 2014, 3: 1-5.
34. Mahalingam T, Kathalingam A, Velumani S, Lee S, Moon H, Kim Y, J. New Mater. Electrochem. Syst., 2007, 10: 21-25.
35. Anand TJS, Shariza S, Rosli ZM, Shaaban A, Sivarao, Said MR, Kamaruzaman J, Thiru S, World Appl. Sci. J., 2013, 21: 60-67.
36. Rekha GS, Indian J. Pure & Appl. Phys., 2010, 48: 133-135.
37. Manfredy L, Marquez OP, Marquez J, Lopez-Rivera SA, Martinez Y, Balladores Y, ARPN J. Sci. Technol., 2014, 4: 455-463.
38. Zhou H, Chen X, Adv. Mater. Res., 2013, 690-693: 1659-1663.
39. Martinez AM, Arriaga LG, Fernandez AM, Cano U, Mater. Chem. Phys., 2004, 88: 417-420.
40. Anuar K, Ho SM, Tan WT, Atan S, Kuang Z, Haron MJ, Saravanan N, Solid State Sci. Technol., 2009, 17: 226-237.
41. Anuar K, Ho SM, Tan WT, Atan S, Zulkefly K, Haron MJ, Saravanan N, Chiang Mai U. J. Nat. Sci., 2008, 7: 317-326.
42. KassimA, Nagalingam S, Tee TW, Shariff AM, Kuang D, Haron MJ, Ho SM, An. U. Bucuresti –Chim., Anul XVIII, 2009, Vol I: 59-64.
43. Peng CY, Dhakal TP, Garner S, Cimo P, Lu S, Westgate CR, Thin Solid Films, 2014, 562: 574-577.
44. Patil SP, Mane RM, Kharade RR, Mali SS, Bhosale PN, Digest J. Nanomater. Biostructures, 2012, 7: 237-245.
45. Colantoni A, Longo L, Boubaker K, J. Mater., http://dx.doi.org/10.1155/2014/325271.

46. Bushra AH, Muthafar FA, Duaa AU, Al-Mustansiriyah J. Sci., 2011, 22: 211-221.
47. YehLY, Cheng KW, Thin Solid Films, 2014, 558: 289-293.
48. Anuar K, Abdullah AH, Ho SM, Saravanan N, Av. Quim, 2010, 5: 141-145.
49. Gopakumar N, Anjana P, Vidyadharan PP, J. Mater. Sci., 2010, 45: 6653-6656.
50. Anuar K, Ho SM, Tee WT, Lim KS, Saravanan N, Res. J. Appl. Sci. Eng. Technol. 2011, 3: 513-518.
51. Ezema FI, Ekwealor ABC, Asogwa PU, Ugwuoke PE, Chigbo C, Osuji RU, Turk. J. Phys., 2007, 31: 205-210.
52. Anuar K, Nani R, Ho SM, Int. J. Adv. Eng. Sci. technol., 2011, 7: 169-172.
53. Asenjo B, Guilln C, Chaparro AM, Saucedo E, Bermudez V, Lincot D, Herrero J, Gutirrez MT, J. Phys. Chem. Solids, 2010, 71: 1629-1633.
54. Anuar K, Ho SM, Tan WT, Kelvin, Saravanan N, Eur. J. Appl. Sci., 2011, 3: 75-80.
55. Raniero L, Ferreira CL, Cruz LR, Pinto AL, Alves RMP, Physica B: Condensed Matter, 2010, 405: 1283-1286.
56. Anuar K, Ho SM, Saravanan N, Turk. J. Sci. Technol., 2011, 6: 17-23.
57. Li J, Zhang YC, Zhang M, Mater. Sci. Forum. 2011, 663-665: 104-107.
58. Anuar K, Ho SM, Tan WT, Ngai CF, Am. J. Appl. Sci., 2011, 8: 359-361.
59. Apolinar-Iribe A, Acosta-Enriquez MC, Quevedo-Lopez MA, Ramirez-Bon R, De-Leon A, Castillo SJ, Chalcogenide Lett., 2011, 8: 77-82.
60. Anuar K, Ho SM, Atan S, Saravanan N, Studia UBB. Chemia, 2010, 55: 5-11.
61. Ubale AU, Mater. Chem. Phys., 2010, 121: 555-560.
62. Anuar K, Ho SM, Atan S, Haron MJ, Res. J. Chem. Environ.,2011, 15: 45-48.
63. Hankare PP, Jadhav BV, Garadkar KM, Chate PA, Mulla IS, Delekar SD, J. Alloys Compd., 2010, 490: 228-231.
64. Anuar K, Ho SM, Int. J. Chem. Res.,, 2010, 1: 1-5.
65. Anuar K, Tan WT, Saravanan N, Ho SM, Bangladesh J. Sci. Ind. Res., 2011, 46: 243-246.
66. AnuarK, Ho SM, Lim KS, Saravanan N, Chalcogenide Lett., 2011, 8: 405-410.