Proceedings of the International Congress on Advances in Applied Physics and Materials Science, Antalya 2011

Deposition and Characterization of CdS, CuS and ZnS Thin Films Deposited by SILAR Method

B. Guzeldir[a], M. Saglam[a] and A. Ates[b]

[a]Department of Physics, Faculty of Sciences, University of Atatürk, Erzurum, Turkey

[b]Department of Material Eng., Faculty of Eng. and Nature Sciences, University of Yıldırım Beyazıt Ankara, Turkey

Cadmium sulfide, copper sulfide and zinc sulfide films were grown on Si(111) substrate by successive ionic layer adsorption and reaction method at room temperature. The crystalline structure and morphology of obtained films were characterized by X-ray diffraction, scanning electronic microscope and energy dispersive X-ray analysis methods. The films were polycrystalline and showed preferred orientation. The surface morphology of these films looked relatively smooth and homogeneous in the scanning electron microscope image. The energy dispersive X-ray analysis spectra showed that the expected elements exist in the thin films.

PACS: 61.05.–a, 61.05.cp, 61.72.uj

1. Introduction

In recent times, surface wetting properties have aroused great interest worldwide both in biological processes and industrial applications. Different chemical techniques such as chemical bath deposition (CBD) [1, 2], spray pyrolysis (SP) [3, 4], electrodeposition [5, 6] etc. have been used to obtain thin films. All these experimental techniques either demand stringent reaction conditions such as high temperature and pressure, and hazardous chemicals or both. Among the different methods for film deposition, the relative simplicity of the successive ionic layer adsorption and reaction (SILAR) method and its potential application for large area deposition make it very attractive. Easy control on film thickness by adjusting number of deposition cycles is the beauty of this method.

In SILAR method, to prepare thin films substrates are immersed into separately placed cationic and anionic precursors and precipitate formation in the solution, i.e. wastage of the material was thus avoided. Also, SILAR can be used to deposit compound materials on a variety of substrates such as insulators, semiconductors, metals.

In this research exploration, we have reported synthesis of CdS, CuS and ZnS thin films onto Si substrates at room temperature by SILAR technique and its room temperature structural characterizations were carried out in detail.

2. Experimental

In this study, to fabricate these thin films, cleaned and polished *n*-type Si semiconductor with (111) orientation and 1–10 Ω cm resistivity was used. The wafer was dipped in i.e. 10 min boiled NH_3+H_2O_2+6H_2O solution and followed by a 10 min HCl+H_2O_2+6H_2O at 60 °C. The native oxide on the front surface of the substrate was removed by HF+H_2O_2 (1:10) solution and then followed by rinse in de-ionized water of 18 MΩ. Cadmium sulfide thin films were deposited using $CdCl_2$, copper sulfide thin films were deposited using $CuCl_2$ and zinc sulfide thin films were deposited using $ZnCl_2$ for cationic solutions. The anionic solution was freshly prepared sodium sulfide (Na_2S) for these films.

The cationic and anionic precursor solutions characteristics: adsorption, reaction and rinsing times were detailed in literature for these thin films [7–9]. One SILAR cycle contained four steps: (a) the substrate was immersed into first reaction containing the aqueous cation precursor, (b) rinsed with water, (c) immersed into the anion solution, and (d) rinsed with water. Figure 1 shows the scheme of SILAR technique for the deposition of CdS, CuS and ZnS thin films.

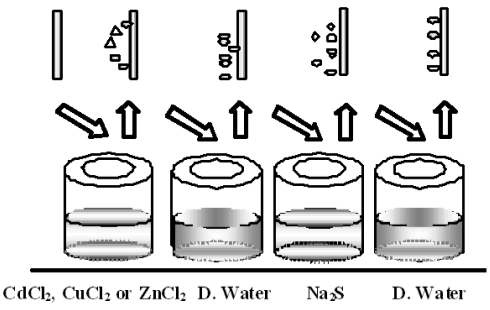

Fig. 1. Experimental scheme for the deposition of CdS, CuS or ZnS thin films.

The structural characterization of the films has been performed by using X-ray diffractometer in the range of scanning angle 20–70° using Rigaku D/Max-IIIC diffractometer. The surface morphology has been inspected by using ZEISS SUPRA 50VP scanning electron microscope with an attached energy dispersive X-ray analysis (EDAX) analyser to qualitatively measure the sample stoichiometry.

3. Results and discussion

The X-ray diffraction patterns (XRD) are analysed to obtain the structural information of thin film. The structural analysis of CdS, CuS and ZnS thin film was carried out by using X-ray diffractometer in the range of scanning angle 20–70°. The X-ray diffraction patterns of the as-grown on single crystal Si(111) substrates are shown in Fig. 2. The CdS films were found to have polycrystalline nature and grown in the hexagonal crystal structure with strongly preferred orientation along the (002) plane parallel to the as-revealed from the XRD studies. The planes (100), (102), (103), (006), (110) and (108) indicate the covellite phase with hexagonal crystal structure for CuS thin film, ZnS thin film has (111), (220) which belong to the cubic phase. The d values, (h, k, l) Miller indices of CdS, CuS and ZnS thin films have been given in Table for grown on Si substrates. All of these results are in agreement with the literature [10–12].

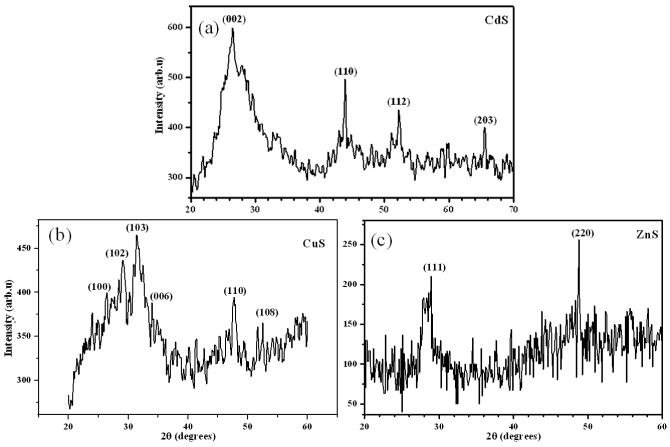

Fig. 2. XRD pattern of thin films grown on n-Si substrate: (a) CdS, (b) CuS, (c) ZnS.

Figure 3 shows SEM images of as-grown CdS, CuS, and ZnS thin films. It is seen that well-crystallized grains in the first image belong to these films. As can be seen in Fig. 3a–c the CdS, CuS and ZnS films were dense, uniform and homogeneous without visible pores and covered well with substrate. From the image of CuS and ZnS thin films, it is clearly seen that the particles forming the films are in nano scale.

One of the important applications of the SEM is to obtain the knowledge of the material composition. This microanalysis mode of SEM replied upon the monitoring

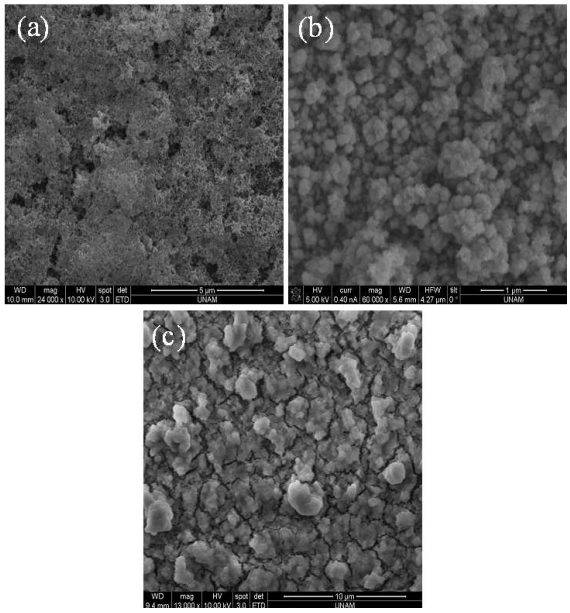

Fig. 3. SEM image of thin films grown on n-Si substrate: (a) CdS, (b) CuS, (c) ZnS.

TABLE

The d values and (h, k, l) Miller indices of CdS, CuS and ZnS thin films for Si substrate.

Samples	(hkl)	d [Å]
CdS	(002)	2.43
	(110)	2.06
	(112)	1.75
	(203)	2.85
CuS	(100)	3.37
	(102)	3.07
	(103)	2.83
	(006)	2.61
	(110)	1.90
	(108)	1.73
ZnS	(111)	3.08
	(220)	1.86

X-rays emitted by surface of the sample under electron irradiation. These X-rays may be collected and analyzed to give information on the elemental compounds present in the sample. The quantitative analysis of the films was carried out by using the EDAX technique to study stoichiometry of films.

Figure 4 shows typical EDAX patterns and details of relative analysis for these thin films. These spectra show the expected elements detected in the thin films. The elemental analysis was carried out only for (CdS) Cd and S the average atomic percentage was found to be 20.82:9.81, for (CuS) Cu and S the average atomic percentage was found to be 27.01:13.23, for (ZnS) Zn

and S the average atomic percentage was found to be 23.44:11.41. Also, small percentage of C, Ca, Mg and O elements is present in the thin films. It is thought that these elements may probably result from Si used as substrate.

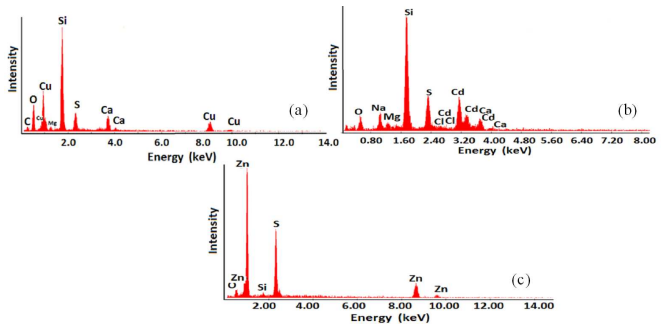

Fig. 4. EDAX spectrum of thin films grown on *n*-Si substrate: (a) CdS, (b) CuS, (c) ZnS.

4. Conclusions

In this study, the SILAR method was used to deposit CdS, CuS and ZnS thin films on Si substrates. Structural properties of these thin films were investigated by XRD, SEM and EDAX methods. The crystal structures of the CdSe, ZnSe and CuSe thin films were investigated by X-ray diffractometer and their main diffraction peaks are found to be in agreement the other studies. The films were found to have polycrystalline, homogeneous structure and covered the substrates well. The EDAX spectra showed that the expected elements exist in these thin films. Some of the thin film with equal distribution of grains, mostly falling in nanometer regime, was clearly seen.

Acknowledgments

We would also like to acknowledge the financial support given by the TUBİTAK Foundation, project No. 108T500.

References

[1] A.S. Khomane, P.P. Hankare, *J. Alloys Comp.* **489**, 605 (2010).

[2] S.S. Kale, C.D. Lokhande, *Mater. Chem. Phys.* **62**, 103 (2000).

[3] A.A. Yadav, M.A. Barote, E.U. Masumdar, *Mater. Chem. Phys.* **121**, 53 (2010).

[4] T. Elango, V. Subramanian, K.R. Murali, *Surf. Coat. Technol.* **123**, 8 (2000).

[5] A.V. Kokate, U.B. Suryavanshi, C.H. Bhosale, *Sol. Energy* **80**, 156 (2006).

[6] M. Izaki, T. Shinagawa, K. Mizuno, Y. Ida, M. Inaba, A. Tasaka, *J. Phys. D* **40**, 3326 (2007).

[7] M. Saglam, A. Ates, B. Güzeldir, A. Astam, M.A. Yıldırım, *J. Alloys Comp.* **484**, 570 (2009).

[8] A. Ates, B. Güzeldir, M. Sağlam, *Mater. Sci. Semicond. Proc.* **14**, 28 (2011).

[9] A. Ates, M. Saglam, B. Güzeldir, M.A. Yıldırım, A. Astam, *J. Opt. Adv. Mater.* **12**, 1466 (2010).

[10] S.V. Bagul, S.D. Chavhan, R. Sharma, *J. Phys. Chem. Solids* **68**, 1623 (2007).

[11] J. Liu, D. Xue, *J. Cryst. Growth* **311**, 500 (2009).

[12] C. Yan, D. Xue, *J. Phys. Chem. B* **110**, 25850 (2006).

[13] S. Prabahar, M. Dhanam, *J. Cryst. Growth* **285**, 41 (2005).