Preparation of Ag$_2$S thin films by electro-deposition

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Abstract. Ag$_2$S thin films were fabricated on the ITO-coated glass substrates by cathodically electro-deposition from the mixture solution including 0.01mol·L^{-1} AgNO$_3$ and 0.05 mol·L^{-1} Na$_2$S$_2$O$_3$ with pH=2.5 at room temperature. The microstructure and surface morphology of the films were investigated with the deposition potential (E) varied from -0.23V to -0.28V. The X-ray diffractograms show that the deposited films are monoclinic Ag$_2$S with the relative deviation of cell parameters within 1.5%. The estimated cell parameters of the Ag$_2$S films deposited at E = -0.25V are closest to those of the standard sample. The SEM pictures show that films are uniform with better compactness at more negative deposition potential, but there are some aggregation when the potential up to -0.28V. According to the AFM images, the root mean square (RMS) roughness and grain size decrease with the decreasing of potential absolute value, but they will increase when the deposition potential is too small. The best potential is -0.25V for depositing Ag$_2$S thin films.

Introduction

Since Silver sulfide Ag$_2$S is an important chalcogenides semiconductor compound and appears to be a promising solar absorbing material as its band gap (Eg~1.1 eV) is between 1 and 2 eV [1]. Moreover, Ag$_2$S possesses a unique combination of various properties like high dark ionic or electronic conductivity, photoconductivity and photographic sensitivity in a broad range of wavelengths as well as related photovoltaic and photochromic effects. This reveals that Ag$_2$S thin films as functional materials have wide applications in the contemporary advanced technologies extended over photoconductive and photovoltaic cells, solar selective coatings, ion selective electrodes and membranes to IR detectors, laser recording media, etc [2].

The silver sulphide (Ag$_2$S) thin films have been prepared by many methods, such as chemical bath deposition [3], successive ionic layer adsorption and reaction (SILAR) [4], thermal evaporation [5], electro-deposition [6] and so on. Among these methods, the electro-deposition provides numerous advantages: it just needs simple and inexpensive equipment, and cheep materials; films can be fabricated on larger and irregular substrates; the deposition process can be controlled rather precisely.

The electro-deposition technique is widely applied in the preparing of many kinds of photovoltaic materials, such as CuZnSnS$_4$, CuInS$_2$, SnS, CdS, ZnO, but there are few reports on the Ag$_2$S thin films prepared by electro-deposition. Maybe the silver sulphide nanoparticles tend to form agglomerate, which affects the quality of Ag$_2$S greatly and makes the preparing process of Ag$_2$S thin films much difficult especially in aqueous solutions. To avoid the appearances of agglomerate, researchers found out many methods including: adding the complexing agent [6] and changing the aqueous into nonaqueous medium [7]. But, adding the complexing agent may increase experimental parameters and the non-aqueous medium is expensive or toxic generally. Here we tried to prepare Ag$_2$S thin films by catholically electrodeposition in aqueous solution without complexing agent.

Experiment

The Ag_2S thin films were electrodeposited by using a conventional three-electrode electrochemical system. Indium tin oxide (ITO) coated glass substrates (80–120Ω/□ sheet resistance) were used as the cathode (working electrode) for all depositions. The deposition area was about 2×2 cm^2. A platinum electrode was served as the anode and a saturated calomel electrode (SCE) was used as the reference electrode. The electric power was supplied by a potentiostat of 0–12 V. The electro-deposition bath contained 10mmol/L $AgNO_3$ and 50mmol/L $Na_2S_2O_3$ as precursor sources of Ag and S. The pH value of the solution was adjusted to 3.0 by adding H_2SO_4. The substrates and the platinum electrode were ultrasonically cleaned 20mins with acetone and ethanol in turn, and then rinsed with distilled water prior to each deposition. The thin films were deposited at room temperature. All the chemicals used were analytical grade reagents and the water used was deionized water.

X-ray powder diffraction (XRD) patterns were recorded using a diffractometer (Co Kα, PANalytical, X'Pert, data were converted into Cu Kα). The surface morphological examinations were carried out by employing a Hitachi XL30E scanning electron microscope (SEM) with an energy dispersive X-ray analysis (EDAX) attachment. The AFM 3D images were observed in the contact mode by CSPM 5000s Atomic Force Microscope system.

Results and Discussions

Cyclic voltammetry Cyclic voltammetry (CV) is employed to study the kinetics of the electrochemical reactions in electrolytic bath. Fig.1 shows the cyclic voltammogram on the ITO substrates. The electrolytic solutions contain 0.01M $AgNO_3$ + 0.05M $Na_2S_2O_3$, from the CV program, the suitable deposition potential can be found. In Fig.1, the cathodic current increases gradually up to -0.33V. In the process of experiment, it was discovered that, when the deposition potential is more negative than -0.35V, there is no continuous and compact film on the ITO substrate, and there is much black precipitation under the substrate, thereby the solution becomes suspension. Probably because the K_{sp} of Ag_2S is rather small (1.2×10^{-49}) ,the Ag_2S particles tend to form precipitation and aggregate in the solution, which affects the formation of the Ag_2S film greatly.

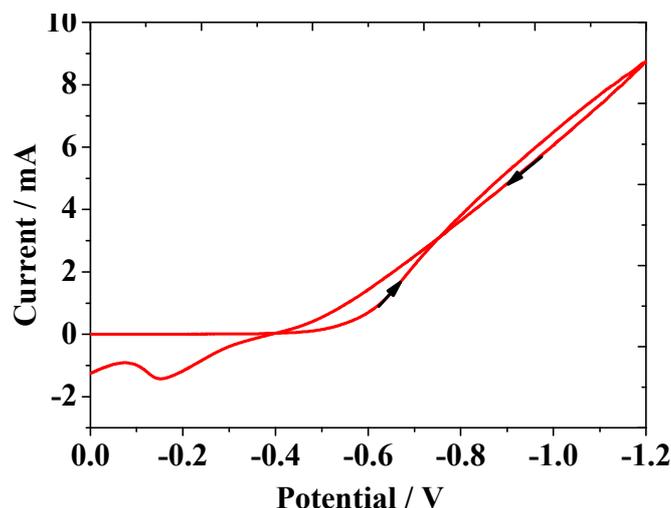Fig. 1. Cyclic voltammogram (CV) on ITO substrate with solution
of 0.01M $AgNO_3$ + 0.05M $Na_2S_2O_3$

Structure of Ag$_2$S films The XRD patterns of the as-deposited thin films on the ITO substrates are shown in Fig. 2. From all the XRD patterns, it can be seen that there are only three peaks in each pattern and these three peaks are all in good agreement with the standard monocline Ag_2S (PDF 75-1060). No peaks of Ag and S are discovered in the spectra. The three peaks occur at 2θ angle of 37.87o, 44.05o and 64.23^o corresponding to d-spacing values 2.3734, 2.0541 and 1.4490Å which are

attributed to planes ($\bar{1}04$), ($\bar{2}02$) and ($\bar{1}35$), respectively. For all the deposits, ($\bar{1}04$) is the preferential orientation.

It appears that the films are well crystallized with narrow peaks indicating large grain sizes. In the figure, peaks ($\bar{1}04$), ($\bar{2}02$) and ($\bar{1}35$) are all detected in all the samples and the peak intensity is increased gradually when the deposition potential changes from -0.28V to -0.23V. But, the deviation between the crystal plane spacings becomes large with the increase of deposition potential absolute value, shown in Table 1. In conclusion, Ag$_2$S thin films can be obtained at these conditions, and the films are best crystallized when the deposition potential is -0.25V.
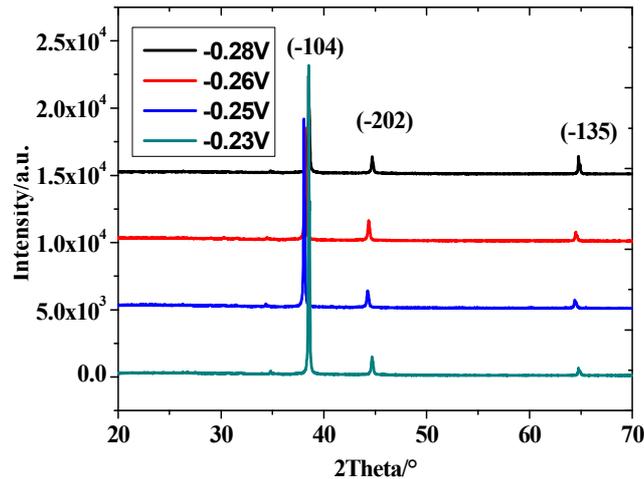

Fig. 2. The XRD patterns of the films deposited at different potentials

Table1. The crystal plane spacings comparison between sample and reference

Deposition potential (V)	d/ Å			Relative deviation $\Delta d/d_{st}$ / (%)		
	d$_{(-104)}$	d$_{(-202)}$	d$_{(-135)}$	d$_{(-104)}$	d$_{(-202)}$	d$_{(-135)}$
-------	2.3709	2.0531	1.4451	0	0	0
-0.28	2.3352	2.0253	1.4382	1.51	1.40	0.48
-0.26	2.3552	2.0408	1.4436	0.66	0.60	0.10
-0.25	2.3734	2.0541	1.4490	0.11	0.05	0.28
-0.23	2.3587	2.0452	1.4440	0.51	0.38	0.08

Morphology of Ag$_2$S films Fig. 3(a), (b) and (c) show the SEM micrographs for the films deposited at various deposition potentials. The SEM images reveal the microstructure of each sample. In Fig. 3 (a), the film is not very compact and uniform with the partial large grains grown on the top of the tiny grains. The morphology and grain size of the samples have no distinct changes when the deposition potential is decreased from -0.23V to -0.25V, but the compactness and uniformity of the film are better. When the deposition potential is up to -0.28V, the grain size becomes much smaller, and the compactness and uniformity of films has improved greatly. But some aggregates appear when the deposition potential absolute value is increased. From these micrographs, the increase of deposition potential absolute value is good for the crystallization, but too high potential will bring precipitation and aggregates.

Table 2 RMS and average size of the Ag$_2$S films deposited at different potentials

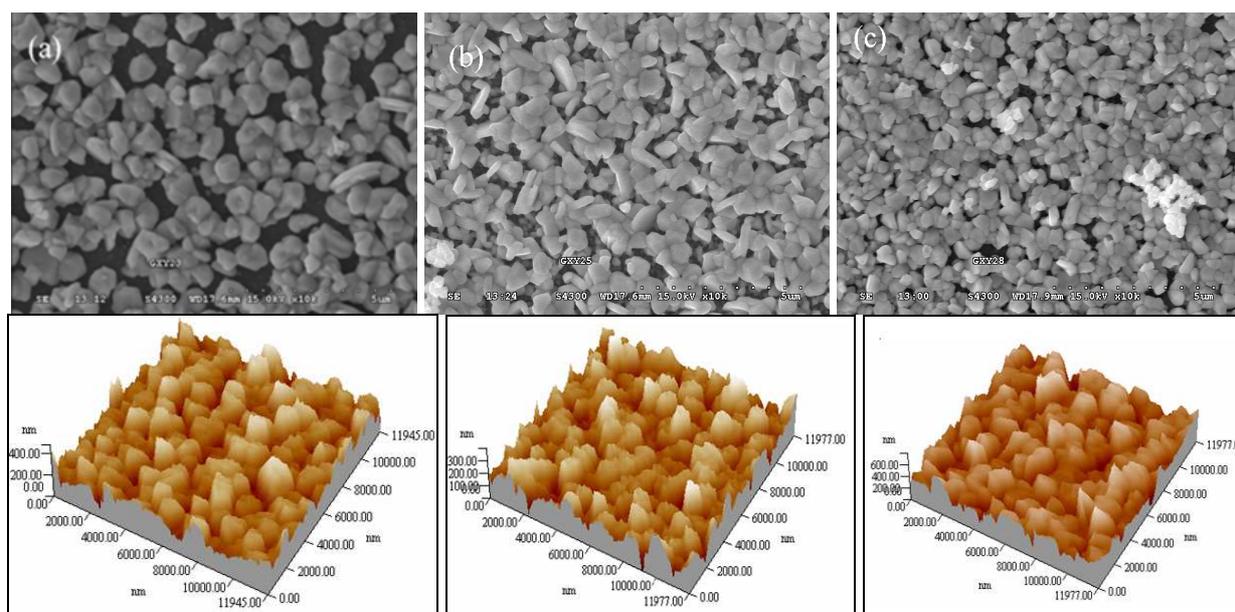| Deposition potential (V vs SCE)	RMS (nm)	Average size (nm)
-0.28	67.1	293
-0.25	58.4	259
-0.23	105	345

Fig.3. SEM and AFM images of the films deposited at various potentials: (a) and (a') E= -0.23V; (b) and (b') E= -0.25V; (c) and (c') E= -0.28V

Summary

Ag_2S thin films were prepared on ITO substrates by cathodically electro-deposition from electrolyte containing $AgNO_3$ and $Na_2S_2O_3$. The structure and morphology of these films deposited at different potential were characterized by XRD, SEM and AFM techniques. The deposited thin films are polycrystalline Ag_2S with monoclinic structure. When the potential changed from –0.28V to - 0.23 V, compared with the standard XRD spectra, the crystal plane spacing deviation between the sample and the standard increases firstly and then decreases. The deposition potential has some impact on the surface morphology of the films with the RMS roughness varied from 67.1 nm, 58.4 nm to 105 nm with the change of deposition potential from –0.28V to -0.23V.

Acknowledgment

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