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Phases and morphorlogy of $CuFeS_2$ films prepared by electrodeposition

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This work reports one low-priced ways for production of $CuFeS_2$ films on conductive glass surface. $CuFeS_2$ films were prepared by electrodeposition and post-sulfurization treatment at 220 °C for 30 h in N_2 atmosphere for the first time. $CuFeS_2$ films were prepared by electrodeposition with sulfate, ascorbic acid, complexing agent sodium citrate as raw materials. When the deposition potential is -1.0 V and the deposition time is 20 min, $CuFeS_2$ thin films with good phrase formation can be obtained at pH 4 and 0.02M $Na_2S_2O_3·H_2O$. The phase of samples were characterized using X-ray diffraction (XRD). The morphology of samples were characterized via scanning electron microscopy (SEM). The composition of samples were characterized by energy dispersive spectrometer (EDS). The crystallinity of $CuFeS_2$ thin films prepared under these conditions are relatively good. The microcosmic morphology of the samples is flaky crystal. It is shows that post-sulfurization method is helpful for the phase formation of $CuFeS_2$ films electrodeposited.

Keywords: $CuFeS_2$, Thin film, Photoelectric, Electrodeposition, Solar energy.

Introduction

Recently, Chalcopyrite $CuFeS_2$ was classified as indispensable and multi-functional materials [1] due to their abundance [2], their higher conversion efficiency [3], higher absorption coefficients [3] and lower toxicity [2, 3] compared with other semiconducting materials. It was found to be a semiconductor with a zero or narrow band gap [4]. It has been considered as a prospective material with wild applications including energy storage, solar energy generation [5-8]. The preparation methods of optoelectronic materials including chemical co-reducton [9], vacuum evaporation [10], solution-chemical method [11-13], hydro-thermal method [3, 5, 8, 14], electrodeposition [15], flash evaporation technique [4], high energy ball milling [16, 17], thermal-injection synthesis [2] and so on.

Se Hoon Kim studied the influence of surface roughness on the efficiency of a flexible organic solar cell [18]. At the same time, Cuan-Lin Chiu researched the influence of doping iron ions into Cu(In,Ga)Se films [19]. Thin-film batteries also has been studied for a long time. Kegao Liu has prepared many kind of absorption layer films, such as $CuInSe_2$ [20], $CuInS_2$ [21] and ZnS [22] successfully, for example. As a kind of ternary optoelectronic material, $CuFeS_2$ has strict technological requirements in the preparation process, and the process parameters of electrodeposition have great influence on the properties of $CuFeS_2$ preparation [15], so it is necessary to explore an optimum technological condition.

Eelectrodeposition method has the advantages of non-vacuum and low cost, the deposition process can be carried out at room temperature, and a uniform and dense film can be prepared [15]. The thin film can be crystallized by the sulfurization treatment, and the film is crystal structure of chalcopyrite. The electrodeposited $CuFeS_2$ is often prepared by sulfurization treatment to improve the composition and crystallization, thus improving the photoelectric performance of the film.

This work used $CuSO_4·5H_2O$, $(NH_4)_2Fe(SO_4)·6H_2O$, and $Na_2S_2O_3·H_2O$ as the basic raw material, $CuFeS_2$ thin films were prepared by using the constant potential method. The effects of the pH value and the concentration of $Na_2S_2O_3·H_2O$ on the phase formation and morphology of the films were investigated and characterized.

Experimental Details

Solution preparation: 0.01 M $CuSO_4·5H_2O$, 0.01 M $(NH_4)_2Fe(SO_4)·6H_2O$, 0.01 M ascorbic acid, 0.01 M complexing agent sodium citrate and a certain concentration of $Na_2S_2O_3·H_2O$. The $CuFeS_2$ thin films were electrodeposited at different pH and concentrations of $Na_2S_2O_3·H_2O$ on the FTO-coated glass surface. The deposition time was 20 min and deposition potential was -1.0 V. The films were prepared via using electrodeposition and post-sulfurization at 220 °C for 30 h in an N_2 atmosphere. The electrodeposition of thin films was obtained via the PARSTAT 2273 electrochemical workstation. All the experiments can be guaranteed

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to be variable unique.

The crystal structure of samples were analyzed by the Bruker D8 Advance XRD system with Nifiltered Cu-Kα (λ=1.5059 Å). The samples' surface morphology were analyzed by using scanning electron microscope (SEM) with a model of JSM-7610F made by Japan Electronics Co., Ltd. The composition of the film was detected by using energy dispersive spectrometer (EDS) with a model of JSM-7610F made by Japan Electronics Co., Ltd. The resistivity was measured by Four Probe Resistivity Meter.

Results and Discussion

The effect of pH of system on phase formation and morphology of $CuFeS_2$ thin films

The crystal structures of the synthesized products were characterized by XRD. Fig. 1 shows the XRD patterns of $CuFeS_2$ thin films deposited on FTO substrate. FTO substrate is one kind of conductive glass. Through the phase retrieval, it can be seen that there are three peaks at 2θ angles with 29°, 48° and 57°. These three peaks are matched with the three strong peaks of copper iron sulfide. The peaks correspond to (112), (204) and (312) crystal planes of the chalcopyrite structured $CuFeS_2$ (Card No.74-1737) at pH 4, which is in consistent with other reports [5]. Additional peaks resulting from FTO (mostly SnO_2, Card No.46-1088) have been identified as F. Each phase of the sample contains a glass substrate. It may account for the thickness of the film. It can also be observed from the Fig. 1 that the impurity phase CuS (Card No.75-2233) appears in the other samples except the sample with pH 4. Only at pH 4 can the pure phase of the target product be obtained. Therefore, the optimal pH value of the system is 4.

Fig. 2 shows the morphology of the synthetic $CuFeS_2$

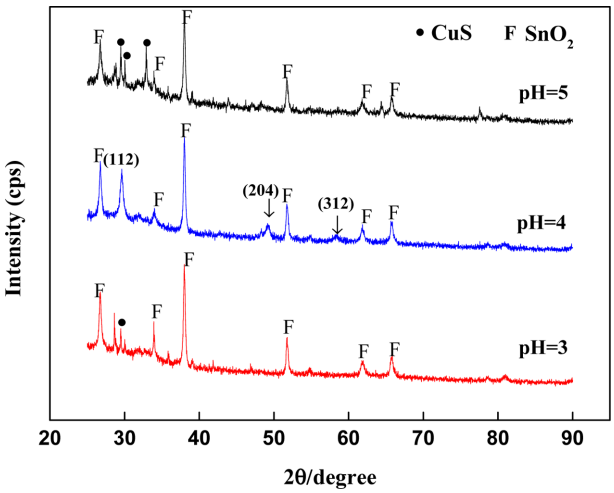

Fig. 1. XRD patterns of thin films prepared at pH 3-5 after sulfurization.

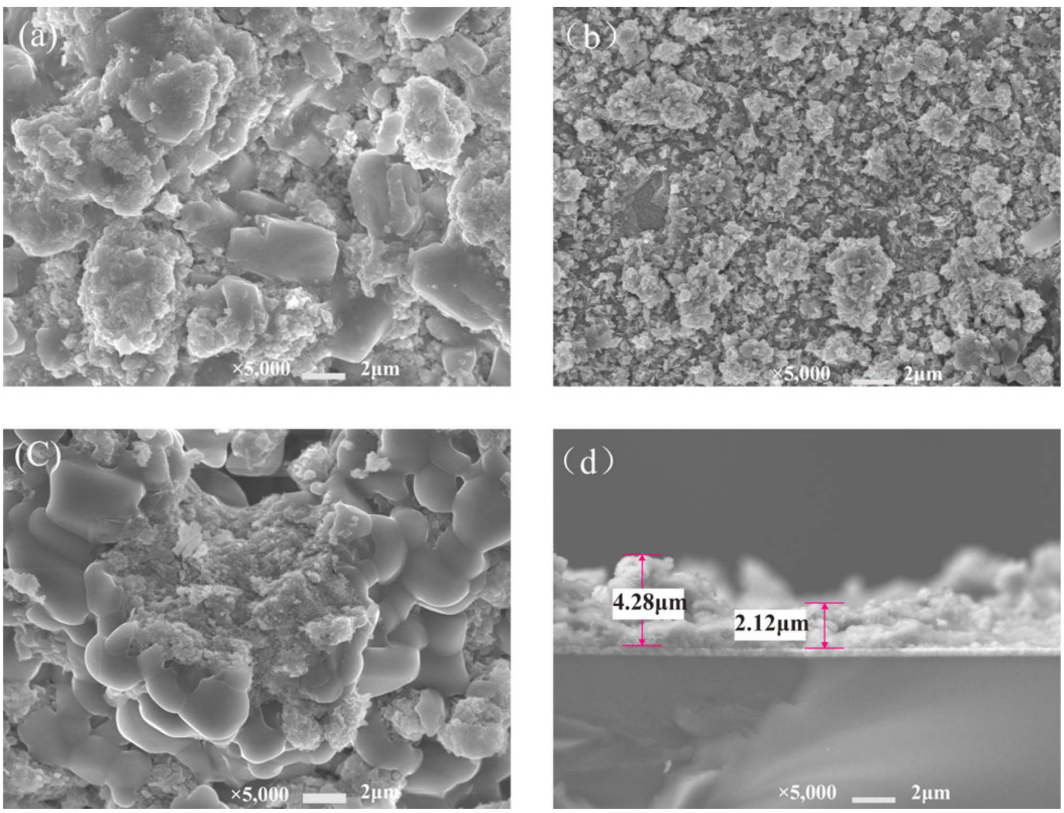

Fig. 2. Morphology of samples prepared by electrodeposition after sulfurization. (a) pH = 3; (b) pH = 4; (c) pH = 5; (d) Cross section of thin film.

prepared by electrodeposition after sulfurization. It was found that the surface of the film was relatively uniform, the degree of crystallization was relatively good, and the particles were relatively small at pH 4. It can be seen the microcosmic morphology of the samples is flaky crystal. The thickness of the thin film varied from 1 to 5 μm.

For the above study, it is concluded that the structure and morphology of films depend on pH mostly.

The effect of concentration of $Na_2S_2O_3 \cdot H_2O$ on phase formation and morphology of $CuFeS_2$ thin films

The crystal structures of the synthesized products were characterized by XRD. Fig. 3 shows XRD patterns of $CuFeS_2$ thin films with different concentration of $Na_2S_2O_3 \cdot H_2O$ after sulfurization. It can be seen that there are three diffraction peaks at 2θ angles with 29°, 48° and 57°, except that the concentration of $Na_2S_2O_3 \cdot H_2O$ is 0.00 M. These three peaks are matched with the three strong peaks of copper iron sulfide. The diffraction peaks correspond to (112), (204) and (312) crystal planes of the chalcopyrite structured $CuFeS_2$ (Card No.74-1737), additional peaks resulting from FTO (mostly SnO_2, Card No.46-1088) have been identified as F. It can also be observed from the Fig. 3 that the impurity phase CuS (Card No.74-1234) appears in sample of 0.01 M and 0.03 M. It is concluded that the purity phase could be prepared when sample's concentration of $Na_2S_2O_3 \cdot H_2O$ is 0.02 M. Therefore, the optimal concentration of $Na_2S_2O_3 \cdot H_2O$ is 0.02 M.

Fig. 4 shows the morphology of the synthetic $CuFeS_2$ prepared by electrodeposition after sulfurization. It was found that all the samples showed flake products except that the concentration of $Na_2S_2O_3 \cdot H_2O$ is 0.00 M. In order to determine the composition of the flake product further, the energy spectrum of the flake target product was detected.

From Fig. 5, it was found that the ratio of copper -

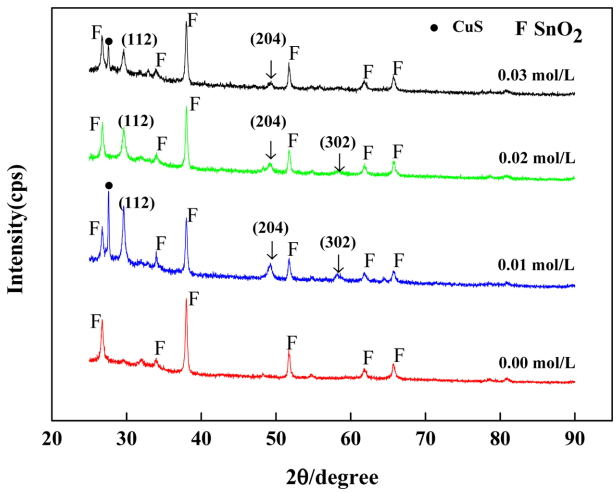

Fig. 3. XRD patterns of thin films prepared with different of $Na_2S_2O_3 \cdot H_2O$ after sulfurization.

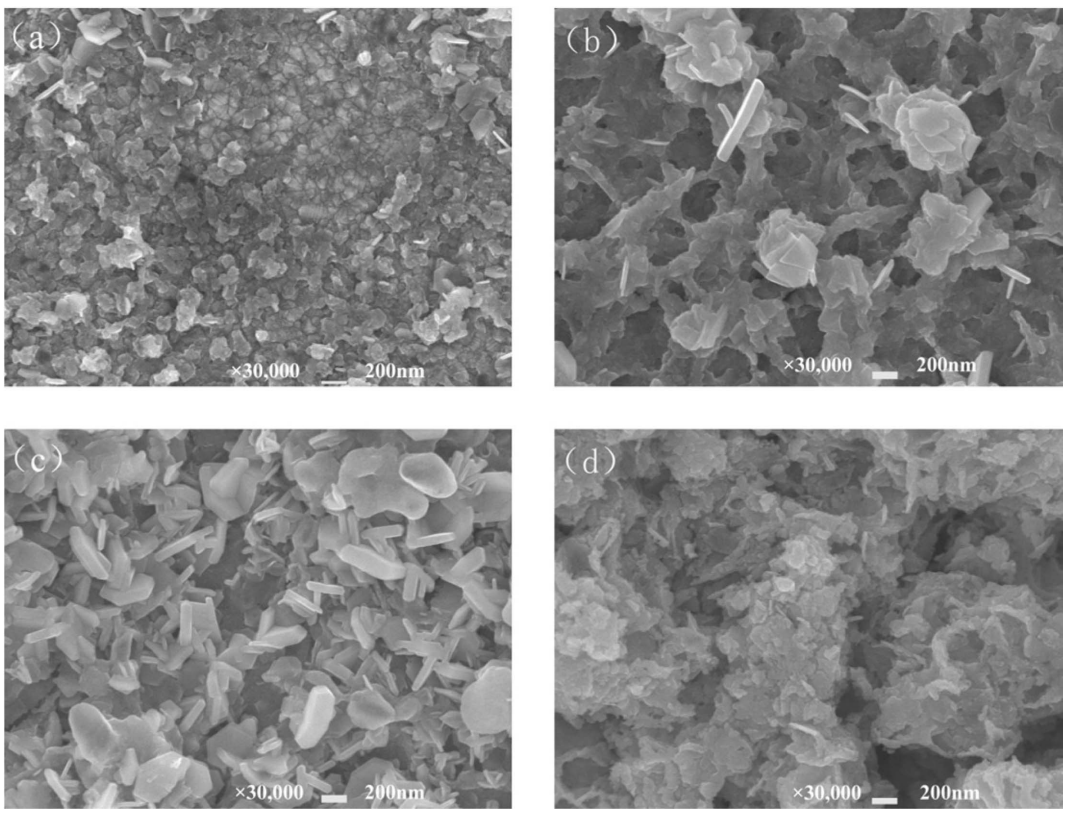

Fig. 4. Morphology of samples prepared by electrodeposition after sulfurization.(a) 0.00 M; (b) 0.01 M; (c) 0.02 M; (d) 0.03 M.

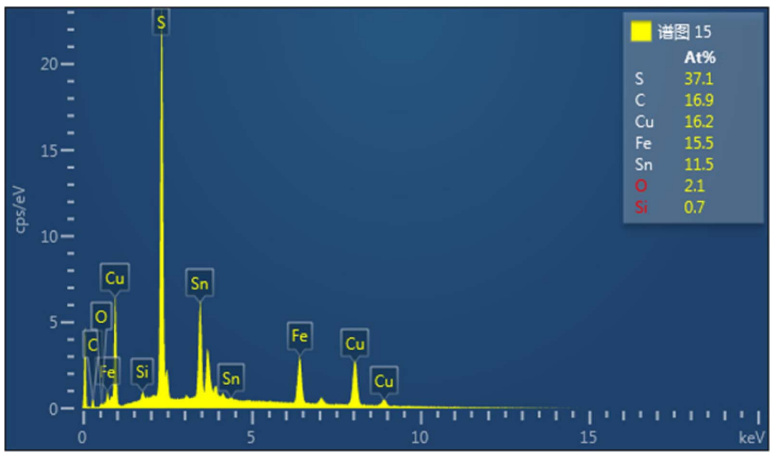

Fig. 5. EDS spectrum showing the elemental composition of synthetic $CuFeS_2$.

iron - sulfur atom was roughly in accordance with the atomic ratio of the target product 1:1:2. The thin film's resistivity is 2.016 Ω·cm.

Conclusions

In summary, $CuFeS_2$ films has been prepared successfully on conductive glass surface by two-step approach: electrodeposition and post-sulfurization. $CuFeS_2$ films were prepared by electrodeposition and post-sulfurization treatment at 220 ºC for 30 h in N_2 atmosphere. There are four highlights in this work. The first one, when deposition potential is -1.0 V and the deposition time is 20 min, $CuFeS_2$ thin films can be obtained at pH 4 and 0.02 M $Na_2S_2O_3·H_2O$. Secondly, the crystallinity of $CuFeS_2$ thin films prepared under these conditions are relatively good. The microcosmic morphology of the samples is flaky crystal by SEM. Furthermore, the sample's phase has been confirmed as chalcopyrite structure. At the same time, the ratio of copper - iron - sulfur atom by EDS was roughly in accordance with the atomic ratio of the target product. These results are meaningful for proving that post-sulfurization is a useful measure for preparation of $CuFeS_2$ films.

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