Characterization of CuInS₂ Films Prepared by Electroplating and Sulfurization

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ABSTRACT: As a ternary compound, CuInS₂ with band gap about 1.5 eV, has chalcopyrite crystal structure, high absorption coefficient and low toxicity of sulfur, therefore, CuInS₂ is a promising absorbing layer used in solar cells with thin films. Electroplating method has many advantages of low cost and easy operation etc. CuInS₂ precursor samples were prepared by electroplating with raw materials of CuCl₂ · 2H₂O, InCl₃ and Na₂S₂O₃ · 5H₂O etc., and the precursor films were heat treated in sulfur atmosphere. The phases of product samples were determined by X-ray diffraction (XRD) and the surface morphology was observed by scanning electron microscopy (SEM), and the elemental content of the film was analyzed by energy dispersive spectroscopy (EDS). Results show that uniform and dense CuInS₂ precursor films can be obtained under conditions of CuCl₂ · 2H₂O, InCl₃, Na₂S₂O₃ · 5H₂O and C₆H₅Na₃O₇ · 2H₂O with contents of 10 mmol/L, 10 mmol/L, 100 mmol/L and 1.25 mmol/L respectively, ph 3.5 and deposition potential −1.0 V. CuInS₂ film with good crystallinity was obtained by sulfurizing precursor film at 350 ºC for 6h, has different XRD peaks for (112), (024/220) and (116/132) crystal planes respectively. Many lumps with uniform size are found, and there are little holes distributing on the surface after heat treatment. The precursor and sulfurized films were all found containing copper, indium and sulfur elements. It is found that the sulfur content in the films was obviously increased after sulfurizing.

1. INTRODUCTION

CuInS₂ is one ternary compound semiconductor material [1] with about 1.5 eV band gap. It shows the advantages of high conversion-efficiency, good stability and without light induced attenuation effect, and has better band gap width compared to the CuInSe₂. In addition, the toxicity of sulfur is low. Therefore, CuInS₂ becomes one of the most promising candidate materials for solar cells.

For preparing CuInS₂ films, the common methods consist of evaporation [2], sputtering [3], electrodeposition [4,5], chemical bath deposition [6], spray deposition [7], solvothermal [8,9] and molecular beam epitaxy [10], etc. Electrodeposition with low cost is easy to achieve large area deposition, so domestic and foreign researchers have used electrodeposition to prepare CuInS₂ films [11]. But there are also some problems, such as the potential of copper, indium and sulfur differ greatly, it is difficult to realize co-deposition. It is found that the CuInS₂ film has poor quality with many holes and sulfur is difficult to enter the film. Chemical composition is difficult to be controlled, and CuS impurity phase is easily generated in preparation process [12,13]. Therefore, it is a significant topic to select suitable electrical deposition process to prepare uniform and compact CuInS₂ films. In the present study of CuInS₂ films prepared by electrodeposition, heat treatment or annealing of product films was carried out, and further optimization of electrodeposition and heat treatment process has become the primary problem in preparation of CuInS₂ films.

CuInS₂ precursor films were prepared with CuCl₂ · 2H₂O, InCl₃ and Na₂S₂O₃ · 5H₂O as raw materials, and then the precursors were heat treated in sulfur atmosphere, the effects of electrodeposition and sulfurization parameters on the surface morphology and phases of product samples were studied, and the composition of precursor and sulfurized film were compared.

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1544-8053/17/01 S089-04
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2. EXPERIMENTAL DETAILS

For preparing CuInS\(_2\) precursor films, the solution was prepared with 10 mmol/L CuCl\(_2\).2H\(_2\)O, 10 mmol/L InCl\(_3\), 100 mmol/L Na\(_2\)S\(_2\)O\(_3\).5H\(_2\)O and 1.25 mmol/L C\(_6\)H\(_5\)Na\(_3\)O\(_7\).2H\(_2\)O. The precursor films were deposited under conditions of deposition potential –1.0 V, 30 min and glass-substrates with SnO\(_2\) layer at room temperature after pretreatment. Put precursor films prepared by optimum electroplating process into tube furnace with hydrazine hydrate. The precursor film was not in contact with hydrazine hydrate, and the sulfur powder was added into hydrazine hydrate, then precursor films were sulfurized in a sealed tube furnace for 3~9 hours at 250~400ºC respectively to obtain CuInS\(_2\) films. The optimum sulfurization process was determined. The phases of sample films were characterized by x-ray diffraction on the Bruker D8 instrument. The morphology of product samples was analyzed by scanning electron microscope. The elemental contents of the samples were analyzed by the energy spectrum analyzer with scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. The Effects of Sulfurization Process on Phase Formation of CuInS\(_2\) Films

3.1.1 Phase Formation of CuInS\(_2\) Films at Different Sulfurization Temperatures for 3h

Figure 1 shows the XRD patterns of product sample films sulfurized at different temperatures for 3h respectively. It can be seen that, the precursor films without sulfurization do not have XRD peaks for CuInS\(_2\) phase except SnO\(_2\) phase belonged to the glass substrates with conducting layer, and only the wide and low diffraction peak at around 42° appears. Compared with the No.23-208 standard XRD card, the target product phase of CuInS\(_2\) can be obtained by sulfurizing. The XRD peaks of CuInS\(_2\) samples correspond to crystal planes of (112), (024/220) and (116/132) respectively.

When holding for 3h at different temperatures, the sulfurization effect is not obvious at 250ºC, and only the diffraction peak at 42° is slightly higher. At 300ºC except CuInS\(_2\) phase there still are impurity phase CuS with a diffraction peak near 42°. The target product CuInS\(_2\) phase was obtained at 350ºC and 400ºC, and the crystallinity was better at 400ºC, and the peak was more acute. It is concluded that when the sulfurization time is 3h, 400ºC is more favorable to get a good crystal CuInS\(_2\).

3.1.2. The Phases of CuInS\(_2\) Films Obtained at Different Sulfurization Temperatures

Figure 2 gives the XRD patterns of product sample films sulfurized for 6h at different temperatures respectively. It indicates that, CuInS\(_2\) phase can be obtained at 250ºC, 300ºC, 350ºC and 400ºC. There are diffraction peaks at about 42° when the film samples were sulfurized at 250ºC and 300ºC. The pure phase CuInS\(_2\) can be obtained at 350ºC and 400ºC according to the XRD patterns, and the crystallinity is better and the diffraction peak is sharper at 350ºC than at 400ºC, and the diffraction peak at 32.408° is corresponding to the
CuInS$_2$ crystal plane (020). It is concluded that it is more favorable to get CuInS$_2$ with good crystallinity under the conditions of sulfurization time 6h and heating temperature 350°C.

3.1.3. The Effect of Sulfurization Temperature on Phases of CuInS$_2$ Samples by Heat Treatment for 3h

Figure 3 shows the XRD patterns of product samples sulfurized for 9h at different temperatures respectively. CuInS$_2$ phase can be obtained at 250°C, 300°C, 350°C and 400°C. There are impurities phase CuS at 300°C and 350°C with XRD peaks at 42°. The pure phase CuInS$_2$ can be obtained at 250°C and 400°C. The crystallinity is better and the peak is sharper at 400°C, and the diffraction peak around 32.408° is corresponding to the CuInS$_2$ crystal plane (020). It is more conducive to obtain CuInS$_2$ with good crystallinity when the sulfurization time is 9h at 400°C.

In summary, CuInS$_2$ thin films with good crystallinity can be obtained from the precursor films sulfurized at 350°C for 6h or 400°C for 9h. Since high temperature and long sulfurization time increase the energy consumption, sulfurizing at 350°C for 6h can be considered as the optimum heat treatment process.

3.2. The Effect of Sulfurization Process on the Morphology of CuInS$_2$ Films

Figure 4(a) gives the surface morphology of CuInS$_2$ precursor film, and Figure 4(b) gives the morphology of CuInS$_2$ film obtained by sulfurizing at 350°C for 6h. In Figure 4(a) the precursor film shows smooth surface with uniform particles with diameters of about 0.5 μm. While Figure 4(b) shows that blocks with more uniform size distributed on the surface, and there are little holes on the surface after heat treatment.

3.3. The Composition of CuInS$_2$ Films Prepared by Sulfurization Process

Table 1 shows the contents of main elements in CuInS$_2$ precursor films, which are determined by the electron beam. The mass fractions of copper, indium and sulfur are 77.29%, 22.15% and 0.56% respectively, and their atomic fraction is 85.26%, 13.52% and 1.22% respectively in this micro area. It indicates that the precursor film does contain copper, indium and sulfur from the qualitative analysis.
CuInS2 deposition time 30 min and solution temperature 25ºC, respectively, pH 3.5, deposition potential –1.0 V, 10 mmol/L, 10 mmol/L, 100 mmol/L and 1.25 mmol/L.

Table 2 shows the element content of CuInS2 which was sulfurized at 350ºC for 6h, and it is the element content of sample in micro area which is beaten by the electron beam. The mass fraction of copper, indium and sulfur is 80.14%, 17.33% and 2.52% respectively, and atomic fraction is 84.60%, 10.13% and 5.28% respectively in this micro area. In the whole range of the film, it can be concluded that there are three kinds elements of copper, indium and sulfur, and the content of sulfur is significantly higher than that of the precursor film.

5. ACKNOWLEDGEMENTS
The National Natural Science Foundation of China (No. 51272140) supported the experiments for this article financially.

6. REFERENCES
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