Effects of Reaction Temperatures and Time on Preparation of $Cu_2ZnSnSe_4$ Thin Films

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Abstract. $Cu_2ZnSnSe_4$ thin films were prepared at 160~200 ^oC by spin-coating and chemical co-reduction, the effects of reaction temperature, time and substrates on thin films were investigated. Experimental results show that, the temperature, reaction time and process are the main factors that affect crystal phase and morphology of quaternary compound films. Longer reaction time and higher temperature are in favor of product crystallinity. $Cu_2ZnSnSe_4$ film with sigle phase and good crystallinity was obtained at 200 ^oC by twice reaction. Compared to the product films prepared on glass substrates, the crystallinity of $Cu_2ZnSnSe_4$ film on silicon substrates was slightly better.

Introduction

The conversion efficiency of $Cu_2ZnSnSe_4$ (CZTSe) with good photoelectric properties has been up to 10% reported currently [1]. Therefore CZTSe is very suitable as the solar cell absorption layer material [2]. There are many methods to prepare CZTSe thin films at present such as atomic beam sputtering, thermal evaporation, photochemical deposition, spraying, sol-gel, electrochemical deposition method, etc [3-5]. For Example M. Ganchev et al obtained CZTSe films by selenium method after preparing brass and bronze base layer [6]. In this work, the $Cu_2ZnSnSe_4$ thin films were prepared by spin coating and chemical reduction method, and the effects of time, temperature and substrate on phase formation, crystallization and morphology of the product films were studied.

Experimental

The precursor solutions were prepared by dissolving raw material powders of $CuCl_2{\cdot}2H_2O$, $SnCl_2{\cdot}2H_2O$, $ZnCl_2$ and SeO_2 in stoichiometric proportions of $Cu_2ZnSnSe_4$ into a certain amount of solvent, such as water, alcohol and other solvents. And then the precursor films with certain thickness were obtained by repeated spin coating, drying 4~8 times. And then were put into the reactor filled with 1mL reducing agent hydrazine hydrate and heated at different temperatures for a period of time. The desired product film can be obtained after natural cooling to room temperature and the product sample was taken out and dried. The phases of product samples were characterized by X-ray diffraction (XRD) on a model of Bruker D8. The size and morphology of the products were observed by JSM6380LA electron microscope (SEM).

Results and discussion

The effects of reaction temperature and time on the product films

The phases of product films reacted once at different temperatures

Fig.1 shows XRD patterns of product thin films reacted once at 160 ^oC, 170 ^oC, 180 ^oC and 200 ^oC on glass substrates with ethanol as solvent. According to the standard PDF card No.52-0868 of $Cu_2ZnSnSe_4$, the XRD peaks at 2θ 27.1^o and 45.1^o are corresponding to (112) and (204) crystal planes respectively. Fig.1a, b and c indicate that the crystallinity of product samples obtained at 160 ^oC, 170 ^oC and 180 ^oC was not better than that of obtained at 200 ^oC. It can be seen that the crystallinity of the product film increases with the temperature raising.

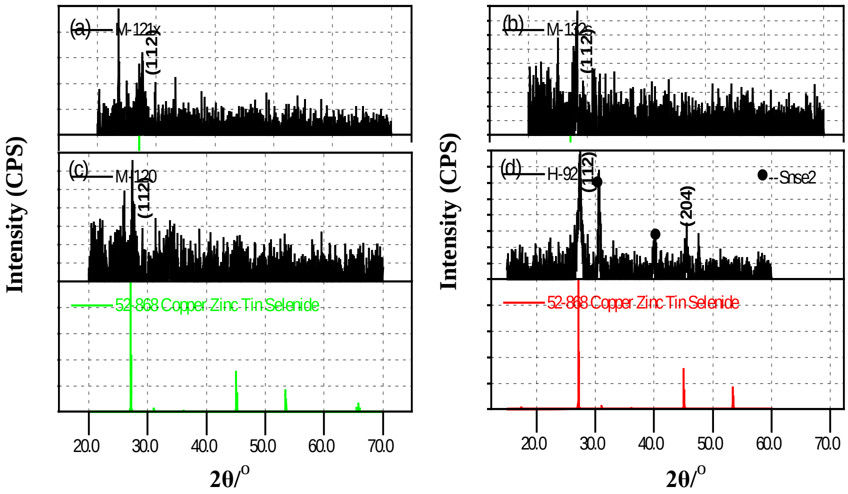

Fig.1 XRD patterns of product thin films reacted once at different temperatures
a) 160 °C b) 170 °C c) 180 °C d) 200 °C

The phases and morphology of product films reacted twice at different temperatures

Fig.2 gives the XRD patterns of product thin films reacted twice at different temperatures of 160 °C, 170 °C, 180 °C and 200 °C on glass substrates with ethanol as solvent. The XRD peaks at 2θ 27.1°, 45.1°and 53.4° are corresponding to (112), (204) and (312) crystal planes respectively. This is similar to the results reported in many works [7,8]. Compared with the results in Fig.1, it can be seen that the reaction times have obvious influence on the crystallization of the products. When the reaction temperature is same, the crystallinity of the samples reacted twice increased than that reacted once. So the reaction times are in favor of the product crystallinity.

The color and morphology of the product films prepared at different reaction temperatures are different in the macro. When the reaction temperature is below 200 °C, the product film shows brownish-black, and combines closely with the substrate; and the black and dense film obtained at 200 °C bonds weakly with the substrate and is easy to fall off. Its large brittleness makes it easily broken and its morphology is similar to that of self-supporting $CuInSe_2$ film prepared by Zhejiang University [9].

Fig.3 shows the SEM images of product thin films reacted twice at different temperatures. It can be seen that the product film surfaces are not continuous with many cracks which decreases with the reaction temperature increasing. The product film obtained at 200 °C shows relatively continuous, uniform and smooth as indicated in Fig.3d.

The effects of reaction time on product films

Fig.4 shows the XRD patterns of product thin films reacted at conditions of 200 °C for different time, ethanol as solvent and spin coating 8 times. The XRD peaks at 2θ 27.1°, 45.1°and 53.4° are corresponding to (112), (204) and (312) crystal planes respectively. It can be clearly seen that the intensity of XRD peaks increased with the time extension. The XRD peaks at 2θ 33.7° and 61.7° correspond to impurity NH_4Cl and Si substrate respectively. The reaction conditions of sample d shown as in Fig.3d are the same as those of sample a. Fig.3d shows that sample a has impurity phase such as $SnSe_2$, Se and $Cu_{1.8}Se$, which was similar to that reported in the literature [10]. Fig.5 shows SEM images of the product thin films reacted at 200 °C for 40 h and 60 h respectively. It indicates that $Cu_2ZnSnSe_4$ films with impurity phase NH_4Cl consist of many small particles.

Conclusions

$Cu_2ZnSnSe_4$ films were prepared by spin-coating and chemical co-reduction at 160 ~200 °C. The temperature, reaction time and process are the main factors that affect the crystal phase and morphology of quaternary compound films. Longer reaction time and higher temperature are in favor of product crystallinity. $Cu_2ZnSnSe_4$ film with sigle phase and good crystallinity was obtained at 200 °C by twice reaction. Compared to the product films prepared on glass substrates, for the cases on silicon substrates, the crystallinity of $Cu_2ZnSnSe_4$ film was slightly better, but it was very easy to generate NH_4Cl impurities and was difficult to obtain $Cu_2ZnSnSe_4$ thin film with pure phase.

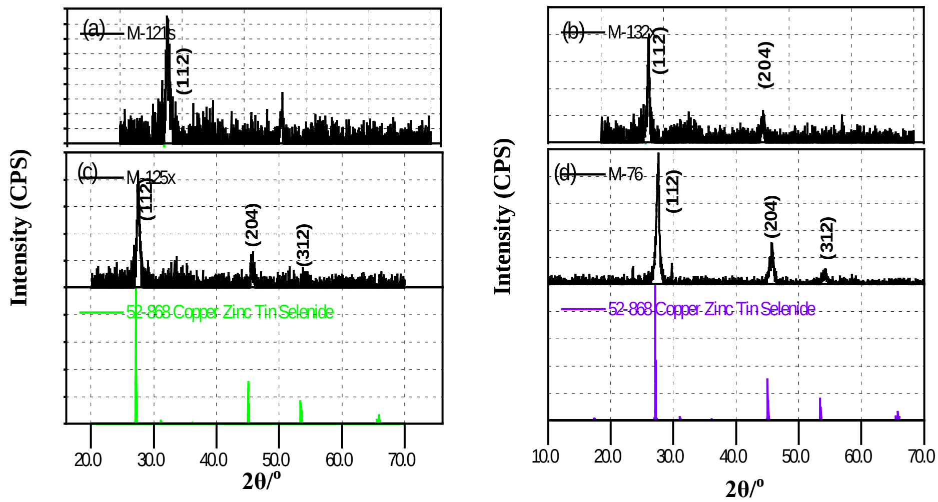

Fig.2 XRD patterns of product thin films reacted twice at different temperatures
a) 160 oC b) 170 oC c) 180 oC d) 200 oC

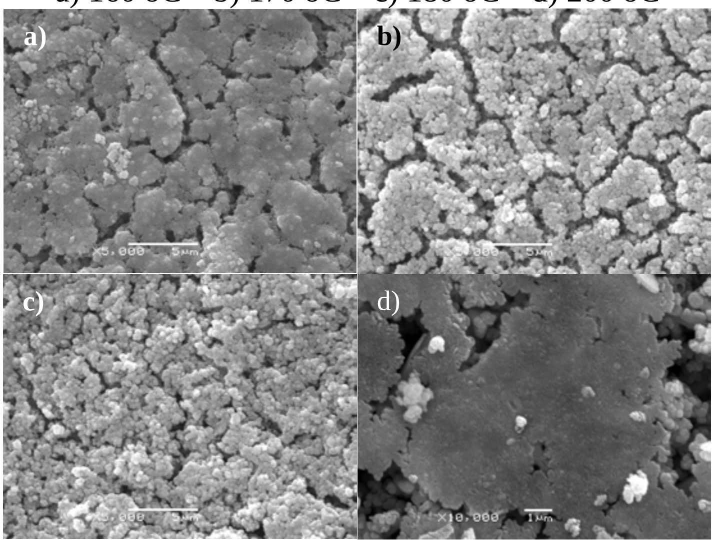

Fig.3 SEM images of product thin films reacted twice at different temperatures
a) 160 oC b) 170 oC c) 180 oC d) 200 oC

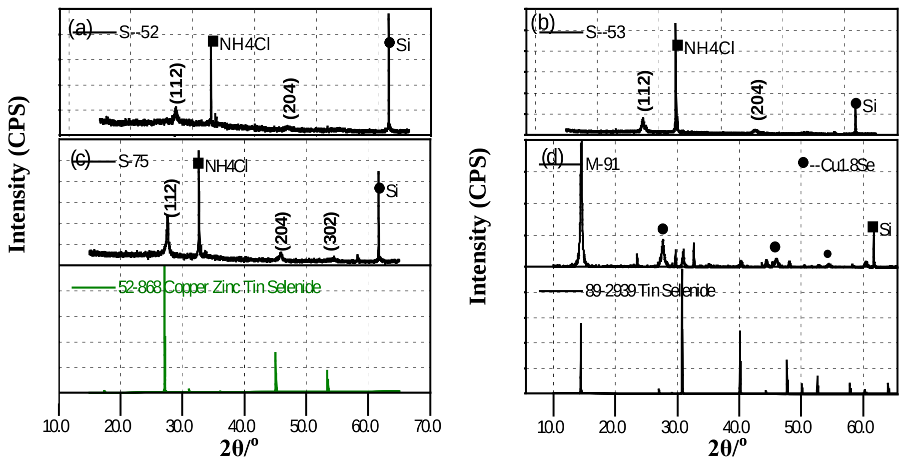

Fig.4 XRD patterns of product thin films reacted at 200 oC for different time
a) 20h b) 40 h c) 60 h d) 20 h

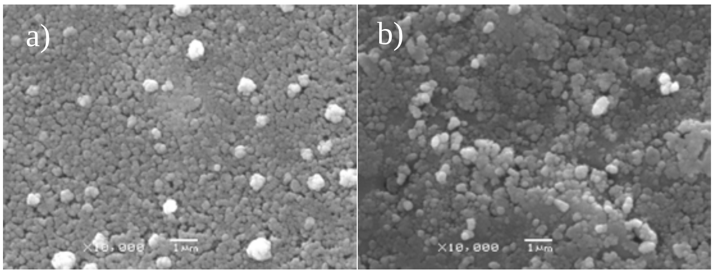

Fig.5 SEM images of the product thin films reacted at 200 oC
a) 40 h b) 60 h

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