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Structure and morphology evolution in mechanochemical processed $CuInS_2$ powder

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ABSTRACT

$CuInS_2$ powders were synthesized by mechanochemical process from copper, indium and sulfur powders. A self-propagating combustion occurred during the milling process. Phase structure, morphology evolution and component uniformity of Cu–In–S system have been studied by X-ray diffraction, scanning electron microscope and energy dispersive analysis, respectively. Optical property of ball milled $CuInS_2$ has been detected by UV–Vis spectroscopy. The results show that there is no intermetallic phase was observed before the self-propagating combustion though morphology changed obviously during this stage. The detected composition of mixed powder converges toward the original proportion with increased milling as the particle sizes decreased. Homogeneous $CuInS_2$ particles less than 5 μm are obtained after milling 120 min. The reason of mechanically induced self-propagating reaction occurs during milling in this system is also discussed. The UV–Vis absorption spectrum shows the milled $CuInS_2$ has a broad absorption over the entire visible light and extending into the near-infrared region and its band gap is 1.52 eV.

1. Introduction

The I–III–VI_2 ternary semiconductor compounds, has caused wide concern by the application in fabricating solar cells and optoelectronics devices. $CuInS_2$, just like other $CuInSe_2$ based materials, is one of the candidates deserving attention to use for photovoltaic as its suitable band gap [1]. The theoretical solar conversion efficiencies of $CuInS_2$ have been calculated to be 27–32% [2,3]. Moreover, $CuInS_2$ is more environmentally friendly than $CuInSe_2$. $CuInS_2$ particles have been synthesized by several methods, such as colloidal solution-phase growth [4], one-pot route [5], pulse electrodeposition technique [6] and vacuum sintering method [7]. Recently, mechanochemical processing (MCP) has also been used to synthesize $CuInS_2$ particles [8] as its advantages of high energy efficiency, high productivity and short processing cycle time. MCP has also been utilized to synthesize $CuInSe_2$, $CuIn(S,Se)_2$ [9] and $Cu(In,Ga)Se_2$ [10–12] powders, but most of these studies only focused on the use of this preparation method. Though a mechanically-induced self-propagating reaction (MSR) was confirmed to take place in Cu–In–Se system [13], details of MCP are still unclear in other systems. Moreover, Cu–In–S has a longer induction period than Cu–In–Se, so we have enough time to study the structure and morphology changes before combustion to make the reaction mechanism clear.

In this paper, we synthesized $CuInS_2$ powders by MCP and got samples at different ball milling periods. Structure and morphology evolution of Cu–In–S system during MCP, especially before combustion, has been detected and observed. Consequently, copper, indium and sulfur mixture has also been milled in an agate mortar to observe the experimental phenomena, which can help us understand the self-propagating reaction in Cu–In–S system better. Furthermore, the criterion for MSR has been used to explain the reason of combustion took place in Cu–In–S during milling. Moreover, optical property has also been studied.

2. Experimental procedures

$CuInS_2$ was synthesized by milling copper (<20 μm, 4 N), indium (<60 μm, 5 N) and sulfur (<10 μm, 99.5%) mixtures with a given molar ratio Cu:In:S = 1:1:2. The experiments were carried out in an agate vial loaded on a planetary ball mill (KXM-Y-ISP-L) milled for different periods. The ball-to-powder weight ratio and the rotational speed were fixed to 10:1 and 600 rpm, respectively. The milling periods were varied from 10 min to 120 min to study the phase transformation and morphology evolution. In order to determine whether the interrupted ball milling had effect on the structure, another sample was continuously milled for 120 min. In addition, copper, indium and sulfur mixture was milled in an agate mortar to observe the experimental phenomena.

Phase transformation at different milling stages is studied by the X-ray diffraction analyzer (XRD, PW1710, Philips) with Cu Kα radiation ($\lambda = 0.154060$ nm). Morphology and composition change of the samples at different milling periods

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was detected using a scanning electron microscope (20 kV, SEM, JSM-6360LV) and energy dispersive spectroscopy (20 kV, EDS, INCA). Optical absorbance spectra of $CuInS_2$ powders were collected from 350 to 1100 nm by UV–Vis spectroscopy (Lambda 35) to study the influence of Al content on optical properties and estimate the band gap. The powder samples were dispersed in deionized water with a fixed concentration (5 mg/4 ml).

3. Results and discussion

3.1. Phase transformations of Cu–In–S system

The spectra of Cu–In–S mixture ball milled for different periods are shown in Fig. 1. The mixture milled for 30 min shows peaks of the constituent of starting powders. Their position and relative intensities are in good agreement with the pure materials of copper, indium and sulfur (Fig. 1a). There is still no intermetallic phase appears when milling prolongs to 60 min (Fig. 1b). This indicates that the induction period of MSR in Cu–In–S system is more than 60 min. But whether it is intermittent or continuous ball milling after 120 min, most elementary substances are transformed into $CuInS_2$ compounds (Fig. 1c and d). A small amount of indium was detected in this stage. It is not fully involved in the combustion reaction may be due to some of it firmly stuck to the vial wall and the balls. Trace of Cu_2S impurity peaks had also been found after combustion. It can also be seen that continuous milling sample has fewer impurities than the interrupted one in Fig. 1, which may because mechanical energy is accumulated better in the continuous milling.

3.2. Morphology evolutions of Cu–In–S system

Typical stages of morphology evolution of the copper, indium and sulfur mixture before combustive reaction are shown in Fig. 2. The EDS analysis concerned with the morphology of the mixture shows the homogeneous tendency in Fig. 3.

Ductile copper and indium particles get flattened and the brittle sulfur particles get fragmented by the ball-powder-ball collisions after 10 min ball milling. There are lots of small sulfur particles and some large-sized indium and copper particles can be seen in Fig. 2a. It also can be seen that some sulfur granules stuck to or embedded in the large-sized soft metal particle which were larger than 10 μm. This leads EDS detective results greatly deviate from the original proportion of the starting powder (Fig. 3), because the nominal spatial resolution in EDS analysis is about 1–3 μm under typical conditions (energy 20 kV). This case indicates that the mixture is not evenly blended.

Particles are repeatedly flattened, fractured and welded when ball milling goes on. Fracture and welding produce a perpetual exchange of matter between particles and ensure mixing of the various elements of original powders. These fragmented brittle particles tend to become occluded by the ductile constituents and trapped in the ductile copper and indium particles. A layered structure of copper, indium and sulfur is thus formed. The layer structure, like sandwiched, is shown in Fig. 2b.

The layered structure gets convoluted and refined with increased milling. This occurs as ductile materials indium and copper get work hardened and their ductility reduced. Brittle fractures are becoming more common with increasing brittleness. The reactants particle size decreases and becomes more uniform. Agglomerate particles composed of numerous small reactant grains generated at this stage with size of 100 μm (Fig. 2c). The EDS analysis results show a tendency of close to the original proportions, which indicate that the composition becoming homogeneous (Fig. 3).

Interlayer spacing decreases when milling maintained, and brittle insoluble sulfur particles dispersed into the ductile copper and indium matrix. Therefore total interfacial area for diffusion is increased. The existence of polyinterfaces on a nanometric scale can reduce the diffusion length after milling. Indeed, interfacial diffusivities are ~3 orders of magnitude their bulk diffusivities [14]. Finally, coalescence and fragmentation get balance during

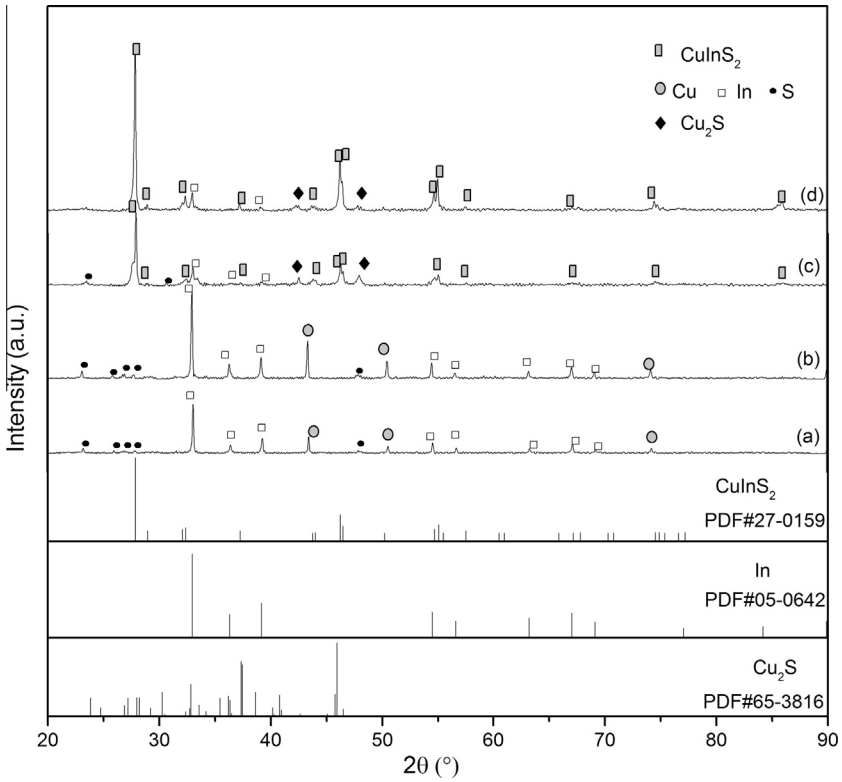

Fig. 1. Diffraction patterns of copper, indium and sulfur powders milled for different periods: (a) 30 min; (b) 60 min; (c) 120 min; (d) continuously milled for 120 min.