

Synthesis and size control of CIS powder by the addition of diethylamine in the mechanochemical method

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CIS powder has been highly researched as a material for thick-film photovoltaic cells. CIS can be mass produced and synthesized through the mechanochemical method. Despite the simple process, however, the mechanochemical method has been reported to pose a problem with respect to uniformity as it is difficult to control the particle size and there are remnants of unreacted reactants after synthesis. Thus, in this study, diethylamine was added during the synthesis of CIS powder using the mechanochemical method to control particle size and remove excess reactants to obtain uniform powder. An increase of diethylamine during CIS synthesis led to an enhanced wet milling effect, which in turn decreased the powder size. However, at 22.5 wt.% and above, the mechanochemical energy was insufficient for synthesis, resulting in an observation of the raw materials, In, Se and a small amount of CuSe, without the synthesis of CIS.

Key words: CuInSe₂, Mechanochemical method, Solvent, Particle size.

Introduction

The CuInSe₂ (hereafter CIS) photovoltaic cell, produced using the thick-film process, is considered promising as it is inexpensive and the process is simple [1-4]. Manufacture of a thick-film CIS photovoltaic cell requires nano-sized CIS powder, but there are limited methods of synthesizing CIS as it is not an oxide or metal. Thus, CIS powder has been synthesized using the solvothermal method [5, 6]. The solvothermal method has the advantage of synthesizing a powder with uniform particle size, but this method cannot be used to synthesize a large amount of powder at once and it is also expensive. To solve these problems, research has been conducted to synthesize CIS powder using the mechanochemical method [7, 8]. In the mechanochemical method, a metal source and zirconia balls are placed inside a zirconia jar to synthesize the powder through milling. The powder is synthesized through physical impact between the balls and the source, which makes this process simple and inexpensive, but the resulting particle size is big and some reactants remain unreacted [9, 10].

In order to resolve these issues, diethylamine was added as a solvent during the synthesis of CIS using the mechanochemical method and the changes in the phase and shape of the powder according to the amount of solvent added were observed in this study. The amount of solvent was varied to understand the re-

lationship of the solvent quantity, synthesis of material and particle size, in order to optimize the process conditions in terms of the impact and milling on the raw powder. The aim of this study was to propose the optimal conditions for mass synthesis of uniform CIS powder based on the results of the experiment.

Experimental Methods

The powders of Cu (99.7%), In (99.99%) and Se (99.99%) were used, and the solvent used was diethylamine (99.9%). They are all supplied by Sigma-Aldrich Co. Ltd., Japan. In a glove box with nitrogenous atmosphere, Cu (1.81 g), In (3.44 g) and Se (4.73 g) powder, 60 g of 3 Φ zirconia balls and varying amounts of diethylamine (from 0 to 3 cc) were loaded into a 45 cc zirconia jar. For the zirconia jar, a planetary mill (Pulverisette 7, Fritsch GmbH, Germany) was used. Milling was performed for 1 hr at 300 rpm, after which the powder was dried for 24 hrs at 80 °C.

The crystal structures of synthesized powders were measured by X-ray diffractometer (PANalytical, X'pert pro, Netherlands) and the particle morphologies were observed by field emission scanning electron microscope (LSM-6700F, Jeol, Japan). Surface area of the powder was measured by B. E. T. (ASAP 2420, Micrometrics, U. S. A.).

Result and Discussion

Fig. 1 is the X-ray diffraction patterns of powder synthesized repeatedly through the mechanochemical method without solvent. The results of the repeated

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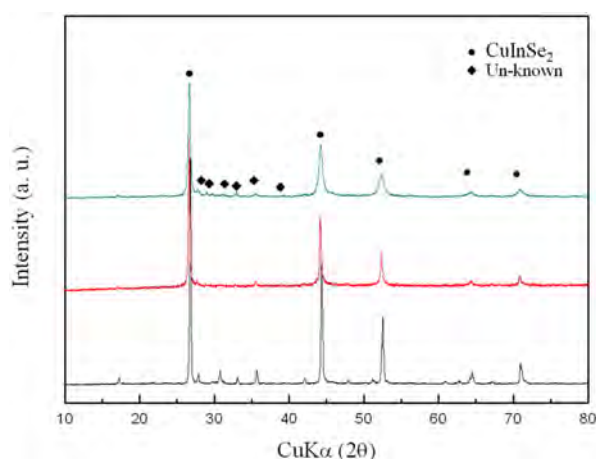


Fig. 1. X-ray diffraction patterns of powder synthesized repeatedly through the mechanochemical method without solvent.

synthesis showed that almost all the synthesized materials were CIS, but there were small amounts of reactants remaining as well as unknown peaks. Also, the peaks of the reactants and the unknown peaks had different peak intensity depending on how many times the process was repeated. As such, synthesis of CIS using the mechanochemical method without solvent results in remnants of reactants and unknown peaks, which is thought to be because the synthesized powder forms large lumps or gets coated on the container walls. The unreacted materials become isolated between the large lumps, and cannot react with other materials even with prolonged milling time. Thus, it was confirmed that it is difficult to synthesize 100% single-phase, uniform CIS powder using the mechanochemical method.

The phase of CIS powder changes easily as it reacts with organic solvents even at room temperature. However, according to Gu [11] *et al.*, milling the CIGS powder with diethylamine, wet milling was possible without any changes to the phase of CIGS. Thus, in the synthesis of CIS using the mechanochemical method, diethylamine was used as a solvent for the milling process to control the particle size. Fig. 2 shows the X-ray diffraction patterns of powder synthesized by the mechanochemical method with the amounts of diethylamine. Synthesis of CIS was observed when the amount of diethylamine was below 22.5 wt.%. However, at 30 wt.%, CIS was not synthesized and a small amount of CuSe and the raw materials, In and Se, were observed. In the mechanochemical method, powder is synthesized through physical impact [12] between the balls inside the container, and the addition of more solvent diminishes the impact. Also, an increase of solvent enhances the milling effect on the powder, resulting in an increase of fine powder. The fine powder, in turn, acts as a buffer and reduces the shock energy occurring in the milling process. In other words, sufficient shock energy between the balls is transferred to the powder for the synthesis of CIS when

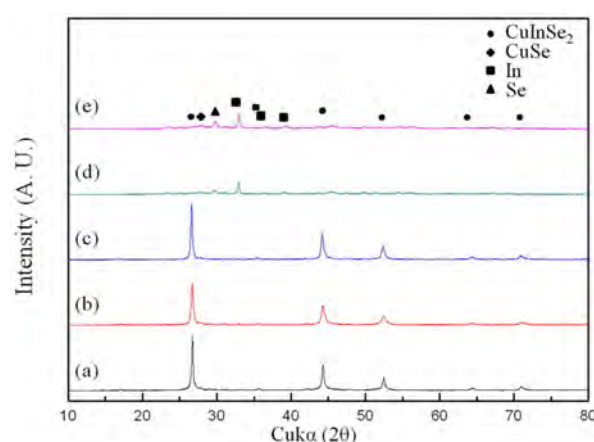


Fig. 2. X-ray diffraction patterns of synthesized powder by mechanochemical method with the solvents of diethylamine; (a) 0 wt.%, (b) 7.5 wt.%, (c) 15 wt.%, (d) 22.5 wt.%, (e) 30 wt.%.

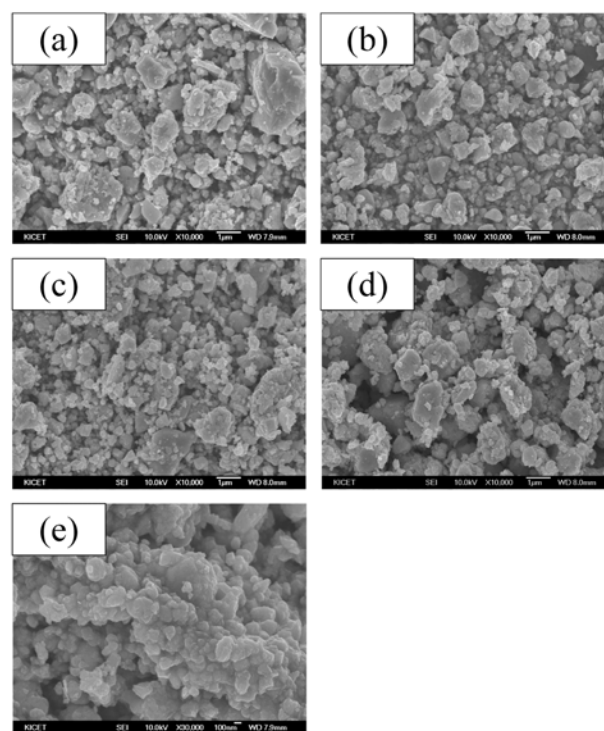


Fig. 3. Morphologies of synthesized powder by mechanochemical method with diethylamine; (a) 0 wt.%, (b) 7.5 wt.%, (c) 15 wt.%, (d) 22.5 wt.%, (e) 30 wt.%.

a small amount of solvent is added. However, when a large amount of solvent is added, the shock energy is reduced due to the solvent itself as well as the resulting milled powder, and this prevents the synthesis of CIS.

Fig. 3 shows the morphologies of powder synthesized by the mechanochemical method with amounts of diethylamine. In Fig. 2(a), which shows the powder synthesized without diethylamine, a significant variation in particle size, from hundreds of nm to dozens of μm , can be observed. As such, powder synthesized using metal materials with high ductility through the mechanochemical method tends to form large lumps.

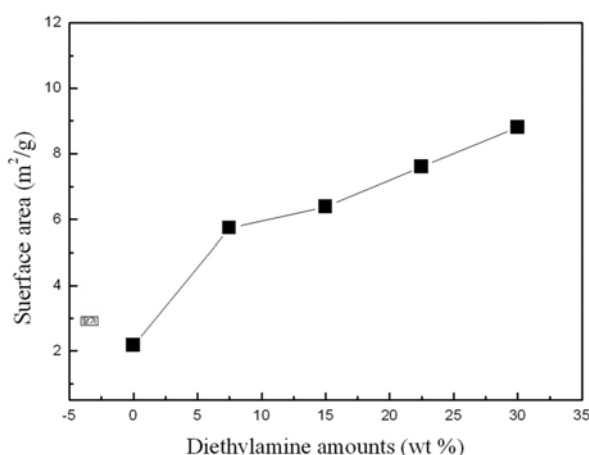


Fig. 4. Specific area of synthesized powder by mechanochemical method with the amounts of diethylamine.

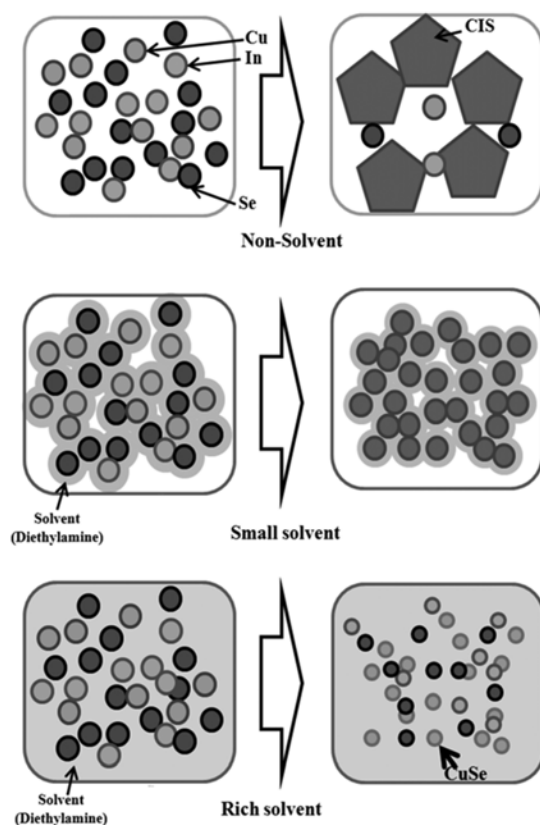


Fig. 5. Schematic diagram of synthesis mechanism and particle size control by the addition of solvent in the mechanochemical method.

However, with an increase of diethylamine, the large particles gradually disappeared and there was an increase of particles smaller than 1 μm . In particular, even at over 30 wt.%, the condition at which synthesis of CIS did not occur, the increase of diethylamine led to a gradual decrease of large particles and an increase of small particles.

Fig. 4 is the specific area of synthesized powder by mechanochemical method with the amounts of diethylamine. Because the particle sizes of the powder

synthesized through the mechanochemical method are unevenly distributed, the milling effect cannot be accurately determined from only the SEM image. Thus, the milling effect was examined through the specific surface area of the powder. It was observed that an increase of diethylamine during the synthesis of CIS resulted in an increase of the specific surface area of the powder. In particular, compared to the condition when the solvent was not added, the specific surface area increased dramatically in the 7.5 wt.% diethylamine condition. At higher than 7.5 wt.%, the specific surface area was observed to increase constantly with an increase of the solvent. As shown in Fig. 2 and the SEM images, the specific surface area increased constantly even with an addition of more than 22.5 wt.% of solvent, at which the synthesis of CIS does not occur. When solvent is added in the mechanochemical method, it becomes coated on the surface of the synthesized powder. This in turn leads to the slipping of powder, preventing the increase in size and the agglomeration phenomenon, for more effective milling [13].

Fig. 5 is the schematic diagram of the synthesis mechanism and particle size control with the addition of solvent by the mechanochemical method. As shown in the Fig., synthesis of CIS using the mechanochemical method without a solvent causes the synthesized powder to form lumps or become coated on the container walls. Also, there are unreacted materials isolated by the lumps of CIS powder. However, when an appropriate amount of solvent is added, the solvent exists between the powder particles and also produces a wet milling effect, resulting in smaller particle size. Also, the unreacted materials can participate in the reaction during the milling process, and as a result, no unreacted materials are observed at the end of the reaction. On the other hand, adding an excess amount of solvent leads to a decrease in particle size due to the enhanced milling effect, but reduces the physical impact of the balls, resulting in the synthesis of a small amount of CuSe and remnants of In and Se.

Summery

The results of the study on the effect of diethylamine on the phase and shape of powder during CIS synthesis using the mechanochemical method are as follows.

1. Synthesis of CIS occurred when the amount of diethylamine added was below 22.5 wt.%, but beyond this point, CIS synthesis did not occur and only a small amount of CuSe and In and Se were observed.
2. During CIS synthesis using the mechanochemical method, an increase of diethylamine enhanced the milling effect regardless of the crystal phase produced, which resulted in a decrease in particle size.
3. During CIS synthesis using the mechanochemical method, adding 22.5 wt.% diethylamine enables mass

synthesis of single-phase, uniform CIS powder with a size of less than 1 μm .

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