Synthesis and Morphological Evolution of CuGaS$_2$ Nanostructures via a Polyol Method

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Using ethylene glycol as solvent and reductant, CuCl$_2$·2H$_2$O, (NH$_2$)$_2$CS and self-prepared GaCl$_3$ as the starting materials, CuGaS$_2$ nanostructures were synthesized on a large scale at 220 °C. Powder X-ray diffraction, transmission electron microscopy, field-emission scanning electron microscope, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy were used to characterize the products. It demonstrated the evolution of the CuGaS$_2$ particles from spherical assemblies to flowerlike morphology, over time, at 220 °C. Simultaneously, we elucidated the specific roles of reaction temperature, reaction time and solvent in the formation of the final CuGaS$_2$ nanostructures. A possible formation mechanism of CuGaS$_2$ nanostructures was also discussed. The room temperature photoluminescence spectrum showed blue-shift and an increase of intensity, with a decrease in the sizes of CuGaS$_2$ particles.

Key words: Chalcogen, Semiconductor, Nanostructure

I. INTRODUCTION

Recently, one of the important goals of material scientists has been to develop ways of tailoring the structure of materials with unusual and novel forms [1,2]. The preparation techniques and properties of inorganic crystals with biomimetic-like morphologies have attracted a great deal of research interest [3]. The shape and texture of inorganic materials are known to determine their various wide electrical and optical properties [4-6]. These are important in numerous applications, such as catalysis, solar cells, light-emitting diodes and biological labeling. Therefore, studies in shape control and novel methods for self-assembling or surface-assembling molecules for the purposes of generating materials with controlled morphologies and unique properties, have been undertaken in recent years [6,7].

I-III-VI$_2$ chalcopyrite semiconductors are materials having potential applications for optoelectronic and infrared-radiation generation and detection devices [8,9]. CuGaS$_2$ is a chalcopyrite semiconductor with a large direct energy of 2.46 eV, and normally has p-type conductivity in the area of heterojunctions with large direct energy of 2.46 eV, and normally has p-type conductivity in the area of heterojunctions with large direct energy of 2.46 eV, and normally has p-type conductivity. These materials with unusual and novel forms have been undertaken in recent years [6,7].

**II. EXPERIMENTAL PROCEDURE**

All of the chemical reagents used in this experiment were of analytical grade, purchased from Shanghai Chemical Reagents Co., and used without further purification. Anhydrous GaCl$_3$ was prepared from Ga$_2$O$_3$. In a typical experimental procedure, GaCl$_3$ (2 mmol), CuCl$_2$·2H$_2$O (2 mmol), and (NH$_2$)$_2$CS (5 mmol) were put into a Teflon-lined autoclave with capacity of 50 mL, which was then filled with polyol up to 90% of the total volume. The autoclave was sealed and maintained at 200-220 °C for 8-24 h, and then cooled to room temperature naturally. The precipitate was filtered and rinsed with distilled water and absolute ethanol several times. After drying at 60 °C for 4 h, a brown product was obtained.

The X-ray diffraction (XRD) analysis was performed using a Philips X’pert diffractometer with Cu K$_\alpha$ radiation ($\lambda$=0.1541874 nm). The transmission electron microscopy (TEM) images were rendered on a Hitachi Model H-800 with a tungsten filament, using an accelerating voltage of 200 kV. The scanning electron microscope (SEM) and field-emission scanning electron microscopy (FESEM) images of the sample were produced on a Hitachi X-650 scanning electronic microanalyzer and field-emission microscope (JEOL, 7500B, 10 kV), respectively. The high-resolution transmission electron microscopy (HRTEM) image and the corresponding selected area electronic diffraction (SAED) were made on a JEOL 2010 high-resolution transmission electron microscope operating at 200 kV. The X-ray photoelectron...
spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using a nonmonochromatized Mg Kα X-ray as the excitation source. The room temperature photoluminescence (PL) spectrum was recorded on a Fluorolog-3-TAV spectrophotometer. The slit was set to 2.5 nm, and the excitation wavelength was set to 370 nm.

III. RESULTS AND DISCUSSION

The typical XRD pattern of the product prepared in ethylene glycol (EG) at 220 °C for 8 h is shown in Fig.1. All the peaks in Fig.1 can be indexed to tetragonal CuGaS$_2$ with cell parameters $a=5.304$ Å, $c=10.598$ Å, which are very close to the reported data [17]. No obvious impurities are observed in the pattern. The average size of the particles is estimated as 15 nm, based on the Scherrer equation.

![FIG. 1 Powder XRD patterns of CuGaS$_2$ prepared in EG at 220 °C for 8 h.](image)

The quality of the samples is characterized by XPS. The binding energies obtained in the XPS analysis are corrected for specimen charging by referencing the C1s to 284.60 eV. No obvious impurities could be detected in the sample, which indicate that the level of impurities is lower than the resolution limit of XPS (1%). The Cu2p core level spectrum (Fig.2(b)) illustrates that the observed values of the binding energies for Cu2p$_{1/2}$ and Cu2p$_{3/2}$ are in agreement with the published values of bulk for Cu(I) [18]. Besides, the Cu2p$_{3/2}$ satellite peaks characterizing Cu(II), which are usually centered at about 942 eV [19], are absent in Fig.2(b). Therefore, we can conclude that the Cu element existing in the compound CuGaS$_2$ is entirely at Cu(I) state. Figure 2(c) is the typical Ga3d core level spectrum. The S2p core level spectrum (Fig.2(d)) shows a peak located at 161.70 eV, which is also in agreement with the literature.

Figure 3 shows the TEM and HRTEM images of the samples obtained in EG at 220 °C. These images show the evolution of the CuGaS$_2$ particles from spherical assemblies to a flowerlike morphology over time, at 220 °C. When the reaction proceeds for 8 h, the product is composed of spherical assemblies (Fig.3A and Fig.4A). When the reaction runs for 12 h, the sphere-like particles become large (Fig.3B and Fig.4B). The corresponding SAED pattern of a spherical assembly is shown in Fig.3C, signifying a polycrystalline morphology. From the pattern, the reflections of planes 112, 220/204, 312 were clearly seen. The sample obtained at 24 h (Fig.3D and Fig.4C) has large quantities of flower-like particles ranging from 1 μm to 3 μm in diameter. These flowerlike structures are built up by many interlaving flakes with thicknesses of about 80-100 nm. The lattice resolved HRTEM image (Fig.3E) shows that a clear interplanar spacing of about 0.31 nm corresponds to the lattice spacing of (112) planes. The inserted image is the corresponding SAED pattern recorded from one of the flakes of the flowerlike structure. We found that the SAED patterns recorded from both different flakes and different areas of individual flakes were identical.

From the XRD, TEM and FESEM results, it is clear that reaction time has great influence on the phase purity and morphology of the final product with the current technique. When the reaction time is less than 1 h, the reaction is quite incomplete in the final product. In order to obtain phase-pure CuGaS$_2$, the reaction time must be no less than 4 h, and longer reaction time favors the purity and crystallinity of the final product. When the reaction proceeds for 8 h, the product is composed of spherical assemblies. Between 8 and 24 h, the sphere-like particles enlarge eventually becoming flowerlike crystals. Longer treatment time (e.g. 3 days or 4 days) did not significantly affect the crystallinity or the yield of the target products.

In our experiments, it was found that the reaction temperature is also an important factor for the formation of the different morphologies of CuGaS$_2$ crystals. When the reaction temperature was lower than 200 °C, the reaction was incomplete and the products mainly consisted of Cu$_{1.8}$S and other impurities, according to the analysis of XRD. Suitable reaction temperatures for the formation of novel sphere-like and flower-like CuGaS$_2$ structures ranged from 220 °C to 230 °C.

Additionally, the solvent plays another vital role in determining the morphology and the product. In order to investigate the effect of solvent on morphology and product, experiments have been done with vari-
FIG. 2 XPS spectra of the sample: (a) survey spectrum, (b) Cu2p core level spectrum, (c) Ga3d core level spectrum, (d) S2p core level spectrum.

FIG. 3 TEM images of the products at 220 °C for various times: A. 8 h; B. 12 h; C. SAED of B; D. 24 h; E. HRTEM of the flake (inset: the corresponding SAED pattern).
FIG. 4 FESEM images of the products at 220 °C for various times: A. 8 h; B. 12 h; C. 24 h; D. 48 h; inset: the corresponding image in high magnification.

TABLE I Effect of reaction condition on the products (220 °C)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Solvent</th>
<th>Time/h</th>
<th>Products</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene glycol</td>
<td>24</td>
<td>Cu_{1.8}S + CuGaS_{2}</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Ethylene glycol</td>
<td>8</td>
<td>CuGaS_{2}</td>
<td>Spherelike</td>
</tr>
<tr>
<td>3</td>
<td>Ethylene glycol</td>
<td>24</td>
<td>CuGaS_{2}</td>
<td>Flowerlike</td>
</tr>
<tr>
<td>4</td>
<td>Ethanol</td>
<td>24</td>
<td>Cu_{1.8}S + CuGaS_{2}</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>Glycerol</td>
<td>24</td>
<td>CuGaS_{2}</td>
<td>Irregular and flowerlike</td>
</tr>
<tr>
<td>6</td>
<td>1,2-propanediol</td>
<td>24</td>
<td>CuGaS_{2}</td>
<td>Flowerlike</td>
</tr>
<tr>
<td>7</td>
<td>1,4-butanediol</td>
<td>24</td>
<td>Cu_{1.8}S + CuGaS_{2}</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>Diethylene glycol</td>
<td>24</td>
<td>CuGaS_{2}</td>
<td>Flowerlike and sheetlike</td>
</tr>
<tr>
<td>9</td>
<td>Triethylene glycol</td>
<td>24</td>
<td>CuGaS_{2}</td>
<td>Irregular particles</td>
</tr>
</tbody>
</table>

ous polyol. Details of the conditions and results of the experiments are listed in Table I. The SEM images of as-prepared samples with the different solvents are not shown. Flower-like structures were obtained when ethylene glycol or 1,2-propanediol was used as the solvent. When the solvent was replaced by glycerol, irregular flower-like structures were found. Some flakes appeared when diethylene glycol was used as the solvent. Irregular aggregated particles are achieved in triethylene glycol with higher viscosity. In our polyol method, polyol serves as both reducing agent and solvent in this synthesis. Reducing Cu^{2+} to Cu^{+} during the reaction process is beneficial to synthesis of the target products. When ethanol or 1,4-butanediol was used as the solvent, the reaction is incomplete and the products consisted of Cu_{1.8}S and other impurities. This is likely due to the fact that ethylene glycol, triethylene glycol and glycerol are more effective reducing agents than ethanol or 1,4-butanediol, which effects the formation of the target products. In ethanol or 1,4-butanediol, Cu^{2+} cannot completely be reduce to Cu^{+}, and produces Cu_{1.8}S and other impurities during the reaction process.

It is well known that physicochemical properties of a solvent such as polarity, viscosity and softness will strongly influence the solubility, reactivity and the transporting behavior of the reactants [20]. In the present system, the viscosity and boiling point of the solvents affect the structure of the final product, and the best solvents for obtaining uniform flower-like nanostructures are ethylene glycol and 1,2-propanediol, both have viscosity and boiling points which are relatively low. Relatively low viscosity and boiling point are helpful in the dissolution and diffusion of particles. There-
fore, small particles can easily transform into flower-like nanostructures by dissolution and diffusion. If we used solvents of higher viscosity and boiling point, such as diethylene glycol, triethylene glycol and glycerol, we cannot obtain the flower-like nanostructures. As a result, we think that using ethylene glycol or 1,2-propanediol as the solvent is requisite in the formation the flowerlike CuGaS$_2$ nanostructures.

From the above results, a possible formation mechanism of the flowerlike nanostructures and their evolution are described as follows: (i) some primary nuclei were formed while elevating the reaction temperature to 220 °C. The initial nuclei rapidly aggregated into spherelike particles because of the sample surface area of a sphere for a given volume and the physicochemical properties of solvent. (ii) the spherelike particles served as seeds and grew larger. After a period of rapid growth, the concentration of reactants decreased. There was an equilibrium of nucleation and dissolution. (iii) with protracted reaction time (e.g. 12 h or more), the flowerlike nanostructures were produced on a large-scale at the expense of the small particles, due to the difference between large particles and the small particles, according to Gibbs-Thomson law [21]. More studies are required to clarify the growth mechanism of these nanocrystals.

The room temperature photoluminescence (PL) emission spectra of the CuGaS$_2$ nanocrystals were measured using a 370 nm excitation wavelength. Figure 5 shows the variation of the fluorescence spectrum of the samples obtained in EG at 220 °C for various reaction times. The emission peaks are located around 420/435, 440, 445 nm, respectively. From the figure, it can be seen that the samples exhibit blue band emission peaks at 420-445 nm. A 55-80 nm blue shift relative to bulk CuGaS$_2$, which exhibits a strong emission band peaking at ~500 nm [13], was observed. The blue shift resulted from quantum-confinement effects, which have been well documented [22]. When the reaction time is increased from 8 h to 24 h (causing the average size of the particles to grow from approximate 15 nm to 80 nm), the emission peaks generally lose their intensity under the same measurement conditions. It is well known that the PL properties of the nanoparticles are strongly dependent on their morphologies, surface states, size distribution and surface passivation [23,24]. The changes in the sizes and microstructures of the products cause modification of electronic structures and influence the carriers excited from the valence band to the conduction band, which then relax their energy on the product surfaces leading the variations in luminescence. In the PL spectra, one of the noticeable features was the split of the emission peak into two lines when the nanocrystals were prepared at 220 °C for 8 h. The split of the exciton band also has been observed at low temperature in ZnO nanoparticles [25], GaN/AlGaN quantum wells [26] and (Cd, Mn)Te self-organized dots [27]. The split of exciton band possibly originates from the radiative recombination of the quantum-confined electron-heavy hole excitons and electron-split-off hole excitons [28]. The exact origin of the split of exciton band is not clear at present. Further investigation is required.

IV. CONCLUSION

In summary, CuGaS$_2$ nanocrystallites with different morphologies have been synthesized via a polyol method. XRD, TEM, FESEM, HRTEM, XPS and PL were used to characterize the samples. It was found that reaction time, reaction temperature and solvent play important roles in the formation of the final CuGaS$_2$ nanocrystallites with different morphologies. This method may be extended to prepare novel nanostructures of other materials. Room temperature PL emission of the CuGaS$_2$ nanocrystals with different morphologies has also been investigated and the results reveal that all these samples showed blue band emission.

V. ACKNOWLEDGMENT

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