OPTIMIZATION STUDY OF COPPER PRECURSORS FOR HIGH QUALITY CuInSe₂ NANOPARTICLES BY WET CHEMICAL ROUTE

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ABSTRACT

High-quality CuInSe₂ nanoparticles have been prepared by the solution phase synthesis procedure utilizing copper acetate or cuprous chloride as the Cu-precursor, indium chloride as the In-precursor and selenium powder as Se precursor, respectively. The synthesis process was optimized to grow 20 to 150 nm sized nanostructures of CuInSe₂, and the Cu to In ratio as well as the kind of Cu-precursor used was found to be most important in determining the structure and property of the nanostructures. The synthesized nanostructures were characterized by TEM (transmission electron microscopy), XRD (X-ray diffraction), PL (photoluminescence) and micro-Raman spectroscopy, and detailed microstructural analyses of synthesized samples were also carried out by selective area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM).

INTRODUCTION

Recently, copper indium diselenide (CIS) and related chalcopyrite alloys are intensively studied worldwide as one of the most promising material system for thin film photovoltaics owing to their unique structural and optoelectronic properties [1, 2]. Solution processed thin film solar cells involving nanocrystal inks have inherent merits in reducing the cost per watt of the fabricated PV modules. Various size, shape and structure nanocrystals are intensively investigated for the formulation of the ink most suitable for PV cell applications. Since the shape, size and structure of the synthesized nanomaterials possess strong correlations with the physical, chemical and optoelectronic properties [3], various synthesis routes have been applied to realize the optimum nanostructure growth for CIS thin film solar cell applications [4, 5]. Among various strategies, the “soft chemistry” route, which is based on a solution process, is an effective method for the chemical synthesis of nanostructural materials with well-controlled shapes, sizes, and structures [6]. In this study, CuInSe₂ nanostructures were synthesized by the solution-phase synthesis method at relatively low temperatures (< 120 °C), using copper acetate or cuprous chloride as the Cu-precursor, indium chloride for the indium precursor and selenium powder as the selenium precursor. The synthesis process conditions including the Cu to In precursor ratio were varied to obtain desired optoelectronic properties.

EXPERIMENTAL

CuInSe₂ nanostructures were synthesized by a low-temperature solution based synthesis method [6]. The molar ratio of precursors (Cu (OOCCH₃)₂/CuCl: InCl₃: Se) were varied around 2:1:2. Anhydrous copper acetate, Cu(OOCCH₃)₂ (or CuCl) and InCl₃ were completely dissolved in solvents after mixing in an inert atmosphere, and Se powder dissolved in solvent was subsequently added to the Cu-In solution and mixed at growth temperatures to grow CuInSe₂ nanostructures at relatively low temperatures (< 120 °C). Refluxing the Cu-In-Se solution under the inert atmosphere was carried out at ~120 °C or lower temperature for the growth. The obtained precipitates were washed with methanol to remove the impurities and then vacuum dried at ~80 °C to finally obtain the CIS nanoparticles. The structural and optoelectronic properties of synthesized CuInSe₂ nanoparticles were characterized by TEM, HR-TEM, EDX, XRD, PL, SAED and Raman spectra.

RESULTS AND DISCUSSION

Figure 1 shows the TEM images of the prepared CIS nanocrystals by using two different Cu-precursors. As shown in the figure, the copper acetate provide the monodispersed CIS nanoparticles of about 150 nm in size, however, the CuCl generate the nanostructures of interconnected network shape in which many small building blocks of less than 20 nm are connected in a large network. The size of nanoparticle building blocks ranges from ~10 nm to 20 nm. The XRD pattern (data...
not shown here) elucidates that the structure of as-synthesized CIS nanocrystals is tetragonal when the copper acetate was used, along with some orthorhombic CuSe$_2$ secondary phase, but the corresponding structure was in cubic phase when CuCl was used as the Cu-precursor again with some orthorhombic CuSe$_2$ secondary phase. The room temperature micro-Raman spectra of the CIS nanostructures grown by using different Cu-precursors exhibit two major characteristic peaks of CuInSe$_2$ with some binary peaks of Cu$_x$Se$_y$ and In$_x$Se$_y$. Raman and PL spectra also elucidate the superior optoelectronic properties of synthesized tetragonal CIS nanoparticles in the case of copper acetate precursor and are in good agreement with the TEM and XRD results. The simple soft chemistry synthesis method for CIS nanostructure preparation developed in this study was very reproducible, and thus it is expected to become a reliable and promising method for CIS nanostructure mass production suited for the development of thin and flexible CuInSe$_2$ based solar cells.

![Figure 1: TEM images of CIS nanostructures using different Cu-precursor: (a) CuCl, (b) Cu(OOCCH$_3$)$_2$.](image)

**SUMMARY**

CuInSe$_2$ nanostructures were successfully synthesized by using two different Cu-precursors, copper acetate and cuprous chloride, respectively. The nanostructures showed tetragonal and cubic crystal phases along with some secondary phases including Cu$_x$Se$_y$ and In$_x$Se$_y$. Depending on the Cu-precursor used, either large mono-dispersed nanoparticles or small individual building blocks of ~10 to 20 nm agglomerated in a large, interconnecting network form were obtained. The shape and size of the nanostructures could be altered by synthesis conditions among which the precursor ratio plays an important role.

**ACKNOWLEDGEMENT**

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (208A251075), and the researchers involved were partially supported by the 2nd phase of the BK21 Program.

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