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Rational synthesis of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals with low defect and tuning band gap

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ABSTRACT

Kesterite Cu_2ZnSnS_4 has emerged as promising replacement for CIGS in scalable commercial thin film photovoltaics. Due to the chemical and size similarity of Cu and Zn atom, $[Cu_{Zn}+Zn_{Cu}]$ defect cluster has low formation energy and high concentration in CZTS, which resulting large amount of recombination centers. In this manuscript, $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals were rationally synthesized with low defect and tuning band gap. When 2% of Cu was substituted by Ag, highest apparent carrier concentration and lowest defect were observed. The band gap of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals can be rationally controlled by adjusting Ag/(Cu+Ag) ratio. This work may contribute to enhancing the performance of Cu_2ZnSnS_4-based solar cells and photocatalyst in hydrogen evolution.

1. Introduction

Copper-indium-gallium-selenium (CIGS) thin film photovoltaics are increasingly penetrating the consumer solar panels market due to high power conversion efficiencies and low material utilization [1,2]. However, as the annual production of CIGS photovoltaics increases, the cost and scarcity of In and Ga could become major issues that limit the widespread utilization of CIGS photovoltaics [3]. By replacing In and Ga with Zn and Sn in 50:50 ratio, kesterite Cu_2ZnSnS_4 (CZTS) and related alloy have emerged as promising replacement for CIGS in scalable commercial thin film photovoltaics, because of their optimal band gap, nontoxic and relatively high earth-abundance of constituent elements. An independently certified world-record 12.6% PCE CZTS photovoltaics has been presented [4], yet this value is only half of the record efficiency achieved by CIGS photovoltaics. The performance of CZTS photovoltaics significantly trails that of CIGS photovoltaics is largely due to the deficit in open-circuit voltage (Voc) [5]. Several hypotheses had been proposed to account for this Voc deficit, including carrier recombination in the CZTS(Se) layer and interface with buffer layer [6]. Large amount of native lattice defects which attributed to the increased number of elements in CZTS are responsible for most of carrier recombinations [7]. For example, constituent element of multivalent Sn (II and IV oxidation states) is proved to create deep levels defects [8]. Due to the chemical and size similarity of Cu and Zn atom, $[Cu_{Zn}+Zn_{Cu}]$ defect cluster has low formation energy. High concentration of $[Cu_{Zn}+Zn_{Cu}]$ defect cluster in CZTS results significant disorder of Cu and Zn atom on Cu/Zn sublattice [7,9]. Any attempt which can reduce defects or increase carrier concentration of CZTS may be beneficial for improvement of photovoltaic device as well as other applications. Though it has been proposed that disorder of Cu and Zn atom in CZTSSe could be reduced through low-temperature annealing with extended time [10], there has been no published report of device improvements using this technique. Until now, several chemical strategies had been developed to reduce defects or increase carrier concentration in CZTS materials. For example, sodium doping or treatment is found to increase carrier concentration and/or mobility and passivate deep defects in CZTS [11,12]. For most compound semiconductors, it is commonly accepted substitution of atom from same group in periodic table results in band-gap engineering. Agrawal and Hillhouse reported tunable band gap solar cells by substitution of Sn with Ge which belongs to same group of elements [13]. For the disorder of Cu and Zn atom, it is also a possible method to decrease $[Cu_{Zn}+Zn_{Cu}]$ defect cluster by using same group atom to partially replace Cu or Zn.

Here, we are particularly interest in synthesis of Cu_2ZnSnS_4-based nanocrystals with low defect and tuning band

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structure. In this work, Cu_2ZnSnS_4-based nanocrystals were prepared by reaction of corresponding metal acetates and elemental sulfur in hot oleic acid solution. By replacing parts of copper acetate with equivalent molar amount of silver acetate, a series of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals with different doping levels were obtained. When 2% of Cu was substituted, the highest apparent carrier concentration was observed. The band gap of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals also can be rationally controlled by adjusting the Ag/(Cu+Ag) ratio.

2. Experimental

2.1. Materials and preparation

All materials were all of analytical grade and used as received. In a typical synthesis, 1 mmol of copper acetate (or silver acetate), 0.5 mmol of zinc acetate and 0.5 mmol of tin acetate were added into 8 mL oleic acid and heated to 230 °C. After 2 mL of oleic acid solution containing 2.5 mmol sulfur was injected and maintained at 230 °C for 30 min, Cu_2ZnSnS_4-based nanocrystals were obtained by centrifugation and wash.

2.2. Characterization

The crystallographic structure of product were identified by X-ray diffraction (XRD, Philips X' Pert Pro) with a step size of 0.02° in 2Θ. Raman spectrum was recorded using a LABRAM-1B confocal laser micro-Raman spectrometer at a resolution of 2 cm^{-1}. Transmission electron microscopy (TEM) observations were performed on JEOL JEM-2010 microscope with accelerating voltage of 200 kV. UV–vis reflectance spectra were obtained by using a Lambda 35 UV–vis spectrometer (Perkin-Elmer) with 2 nm resolution. All electrochemical experiments were performed on a CHI 660E workstation.

3. Results and discussion

Powder X-ray diffraction (Fig. 1(a)) shows the prominent peaks observed in synthesized $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals correspond well with tetragonal CZTS (JCPDS no. 26–0575), indicating the synthesized $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals also have a tetragonal crystal structure. The diffraction peaks at 2θ=28, 47 and 57 can be indexed to (112), (220) and (312) planes, matching well with the previously reported values [14,15]. The Raman peak (Fig. 1(b)) at about 333 cm^{-1} also correspond well to single phase of kesterite CZTS. And we did not probe the presence of impurities such as Cu_2S, ZnS, SnS, Cu_3SnS_4 and Ag_2S [15–17]. Low doping level of Ag does not significantly change the XRD and raman peak positions.

As shown in Fig. 2, all $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals are polygon. The size of the $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals vary from 10 to 15 nm with the increasing of Ag content. HRTEM analysis verified the tetragonal structure with lateral facets corresponding to (112) planes. By substituting Cu with Ag, the interplanar spacing of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals increased from 0.31 nm to 0.32 nm for 0% and 10% doping levels due to the larger size of Ag atom compared with that of Cu [18].

The effective carrier concentrations in various $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals were investigated by impedance spectroscopy using Mott-Schottky plots. The $(Cu_{1-x}Ag_x)_2ZnSnS_4$ films were prepared onto a FTO glass by drop casting and used as working electrode. According to Mott-Schottky equation, the carrier concentration is inversely proportional to the slope of C^{-2} vs. E, where C is the space-charge layer capacitance of the film and E is the potential of the electrode [19]. Negative slopes of Mott-Schottky plots indicate that all the synthesized $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals are p-type semiconductors (Fig. 3). It can be seen that the slope of the $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals films decreased first and then increased with the increase of Ag doping levels. When Ag doping level was 2%, the lowest slope was observed, indicating the highest apparent carrier concentration of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals. This phenomenon may be interpreted by intrinsic or weakly n-type conductivity of Ag_2ZnSnS_4 [20].

Fig. 4 shows the band-gap energies of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ obtained from UV and CV methods. It should be noted that all the energy gap are determined by the coordination of the cations as previous report [21]. The band-gap energies of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ estimated from the $[F(R)h\nu]^2$ vs. $h\nu$ plot of reflectance spectra are 1.63, 1.81, 1.92, 1.95, 1.98, 2.02 and 2.1 eV with increase of Ag doping levels. The HOMO energy level (ionization potential Ip) and LUMO energy level (electron affinity Ea) of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ were obtained from cyclic voltammograms [22,23]. The CV scales were carried out in 0.1 M BAPF6/DMF at 50 mV s^{-1} scan rate. The HOMO levels of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals are −4.12, −4.14, −4.14, −4.13, −4.08, −4.09 and −4.10 eV with increase of Ag doping levels, while the LUMO level are −5. 60, −5.82, −5.88, −5.90, −5.93, −5.98 and −6.03 eV, respectively. The gap values (Egap) of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ calculated from the CV measurements are 1.48, 1.68, 1.74, 1.77, 1.85, 1.89 and 1.93 eV, respectively. It

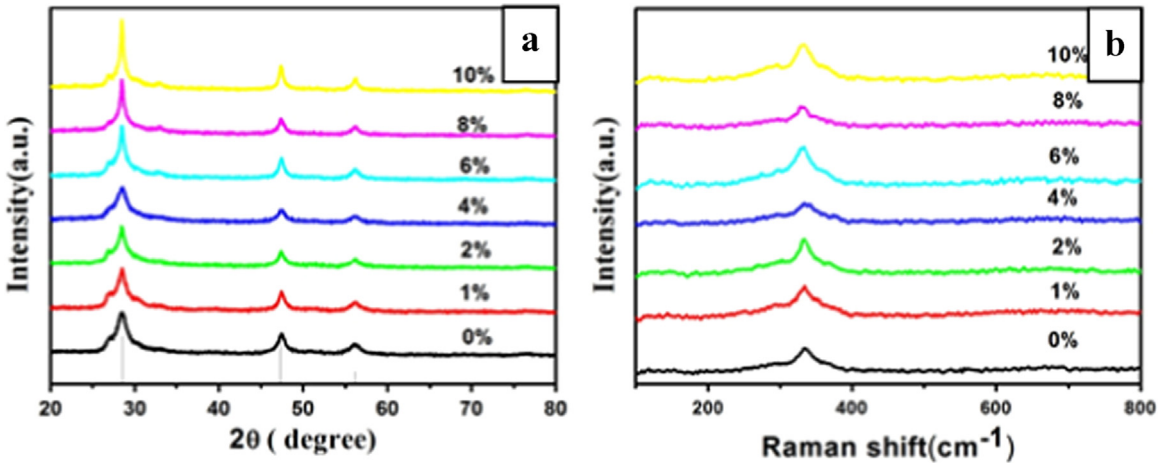

Fig. 1. XRD pattern and Raman spectrum of $(Cu_{1-x}Ag_x)_2ZnSnS_4$ nanocrystals.