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Multi-phase structures of boron-doped copper tin sulfide nanoparticles synthesized by chemical bath deposition for optoelectronic devices

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ABSTRACT

We investigated the influence of boron doping on the structural, optical, and electrical properties of copper tin sulfide (CTS) nanoparticles coated on a WO_3 surface and synthesized using chemical bath deposition. Boron doping at concentrations of 0.5, 1.0, 1.5, and 2.0 wt% was investigated. The X-ray diffraction pattern of CTS showed the presence of monoclinic $Cu_2Sn_3S_7$, cubic Cu_2SnS_3, and orthorhombic Cu_4SnS_4. Boron doping influenced the preferred orientation of the nanoparticles for all phase structures and produced a lattice strain effect and changes in the dislocation density. Increasing the concentration of boron in CTS from 0.5 wt% to 2.0 wt% reduced the band gap for all phases of CTS from 1.46 to 1.29 eV and reduced the optical transmittance. Optical constants, such as the refractive index, extinction coefficient, and dissipation factor, were also obtained for B-doped CTS. The dispersion behavior of the refractive index was investigated in terms of a single oscillator model and the physical parameters were determined. Fourier transform infrared spectroscopy confirmed the successful synthesis of CTS nanoparticles. Cyclic voltammetry indicated that optimum boron doping (<1.5 wt% for all phases) resulted in desirable p-n junction behavior for optoelectronic applications.

1. Introduction

Development of emerging semiconductor materials for use in optoelectronic devices has presented many challenges regarding appropriate materials selection. Materials with suitable optical and electrical properties must be environmentally friendly, cost-effective, highly efficient, and scalable. In optoelectronic devices, such as solar cells, conductive semiconductor nanoparticles are a very important component for harvesting light and generating electrons via photoconductivity over a broad-band spectrum. Previous studies have investigated the properties of binary materials, such as CdS [1], CdTe [2], CdSe [3], In_2S_3 [4], and $Cu_{2-x}S$ [5]. Recently, ternary compound semiconductors, such as $CuInS_2$ [6], $CdSe_xTe_{1-x}$ [7], $CuInSe_2$ [8], and $CuGaS_2$ [9], have been investigated due to the formation of Schottky junctions, which increase the electrical conductivity compared to that of binary compounds.

Copper tin sulfide (CTS) has recently been investigated as a ternary optical material for optoelectronic devices [10]. It belongs to the I_2-IV-VI_3 chalcogenide family and has an absorption coefficient of 10^4 cm^{-1}, similar to that of other solar absorbers such as $Cu(In,Ga)Se_2$ (CIGS). CTS is a p-type semiconductor, has an energy band gap of 1.2 eV, an electrical conductivity of 0.5–10 $\Omega^{-1}cm^{-1}$, and a hole concentration of 10^{17}-10^{18} cm^{-1} [11]. In previous studies, Cu_4SnS_4 was synthesized using various methods, such as spray pyrolysis, spin coating, sulfurization, successive ionic layer adsorption and reaction (SILAR), and co-evaporation [12–16]. Most researchers have synthesized CTS thin film absorbers with energy band gaps in the range 0.9–1.77 eV (0.9–1.75 eV for cubic phases and 1.35 eV for tetragonal phases [17]). These synthesized thin films showed optical and electrical properties suitable for several applications, including transparent conducting electrodes, lithium-ion battery materials, catalysts, photodetectors, and solid-state chemical sensors [18–22].

If we narrow the focus of bulk semiconductor materials to nanomaterials, the required optical and electrical properties become strongly dependent on the morphological characteristics of the starting material, i.e., size, shape, and size distribution. Furthermore, the addition of a dopant to the semiconductor may also improve the performance of the material. Generally, doping with metals such as Ga [23], Zn [24], Mn [25], Cu [26], or

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Ag [27] increases the number of *n*-type carriers in a p-type semiconductor. Previous studies showed that doping with metals generated thermal instability and induced electron-hole pair recombination, which is detrimental for solar cell applications [28]. As an alternative, researchers have explored doping with non-metal elements, which improves the photocatalytic activity by producing a trap state in the semiconductor absorber, improves the quality of the crystal structure, and suppresses carrier recombination [29]. Boron (in the form of B^{3+}) is a potential non-metal dopant as it has the smallest ionic radius (0.023 nm) compared to the ionic radii of Cu^{2+} (0.094 nm), Sn^{2+} (0.118 nm), and S^{2-} (0.184 nm) and highest electronegativity of the possible candidate elements [30–32].

This study reports the first synthesis of a CTS material fabricated from nanoparticles (NPs) coated on a WO_3 film using chemical bath deposition (CBD) at room temperature with controlled deposition times. Various concentrations of boron doping were investigated. The structural morphologies, optical and electrical properties were characterized to determine the suitability of the compounds for optoelectronic devices. The findings are expected to provide a reference for further development of low-cost synthesis methods for new ternary semiconductor materials with multi-phase structures for future applications.

2. Materials and methods

A tungsten oxide (WO_3) film was prepared by mixing 1.414 g WO_3 nanopowder (particle size ~35–40 nm, ≥99.0% purity, ACROS Organics) with 0.7 g ethyl cellulose (48.0–49.5% (w/w) ethoxyl basis, Sigma-Aldrich) in 7 mL alpha-terpineol (90%, technical grade, Sigma-Aldrich). Then, the mixed precursors were dissolved in 10 mL ethanol and stirred for 30 min. The WO_3 solution was coated onto a cleaned silicate glass or a fluorine-doped tin oxide glass substrate (sheet resistance ~ 13 Ω/□) using a doctor blade technique and sintered in an oven at ambient condition at 450 °C for 30 min.

The boron-doped CTS nanoparticles (B^{3+}-doped CTS NPs) were synthesized using the three precursor solutions with an equal concentration of 0.05 M $Cu(NO_3)\cdot 3H_2O$ (99.5% purity, Loba Chemie) and $SnCl_2$ (98% purity, Sigma-Aldrich) in ethanol and a 0.05 M $Na_2S\cdot 9H_2O$ (Analytical grade, Carlo Erba Reagents) in methanol/water (7:3 v/v) solution. Boron powder (particle size ~2 μm, 99% purity, Merck) was added to the mixed solutions as a dopant in various concentrations (0.5, 1.0, 1.5, and 2.0 wt %) and stirred for 90 min at 25 °C. Next, the WO_3 film was dipped into the solution using chemical bath deposition (CBD) [33] for 30 min and then the excess Cu—Sn—S mixture was thoroughly rinsed off the WO_3 film using ethanol and dried on a hot plate at 60–70 °C.

The synthesized NPs were characterized using a field-emission scanning electron microscope (SEM; JEOL, JSM-6301F) and a transmission electron microscope (TEM; Philip TECNAI 12). X-ray diffraction (XRD) was performed using Cu Kα radiation at a wavelength of 1.5406 Å operating at 40 kV and 30 mA (D8 Advance, Bruker AXS, Germany) with $2\theta = 20^{\circ}$–80° for determining the diffraction patterns of the crystal lattice. Optical absorption spectra were measured in the wavelength range of 300–1100 nm using a UV–Vis spectrometer (Lambda 25, Perkin Elmer).

The electrical properties of the ternary materials with various boron concentrations were investigated. An electrochemical analyzer (PGSTAT101, Metrohm Autolab) with a scan rate of 0.1 V/s was used with B-doped CTS-coated WO_3 films as a working electrode and a Cu_2S counter electrode in a polysulfide electrolyte consisting of 0.5 M Na_2S, 2 M S, 0.2 M KCl, and 0.5 M NaOH dispersed in a methanol/water (7:3 v/v) solution. A Ag/AgCl electrode was used as the reference electrode, a potential was applied between the working electrode and the reference electrode, and the current density was obtained from cyclic voltammetry (CV) oxidation–reduction curves.

3. Results and discussion

3.1. Microstructure

To understand the effect of boron doping on the structure of the CTS, the morphology and lattice spacings of the synthesized nanoparticles were analyzed. Fig. 1(a) shows a TEM image of bare WO_3 NPs with diameters of ~50–130 nm. The CTS coated on the WO_3 surface showed an interconnected structure (Fig. 1(b)), which is advantageous for enhancing carrier mobility in the material. The individual NPs of CTS

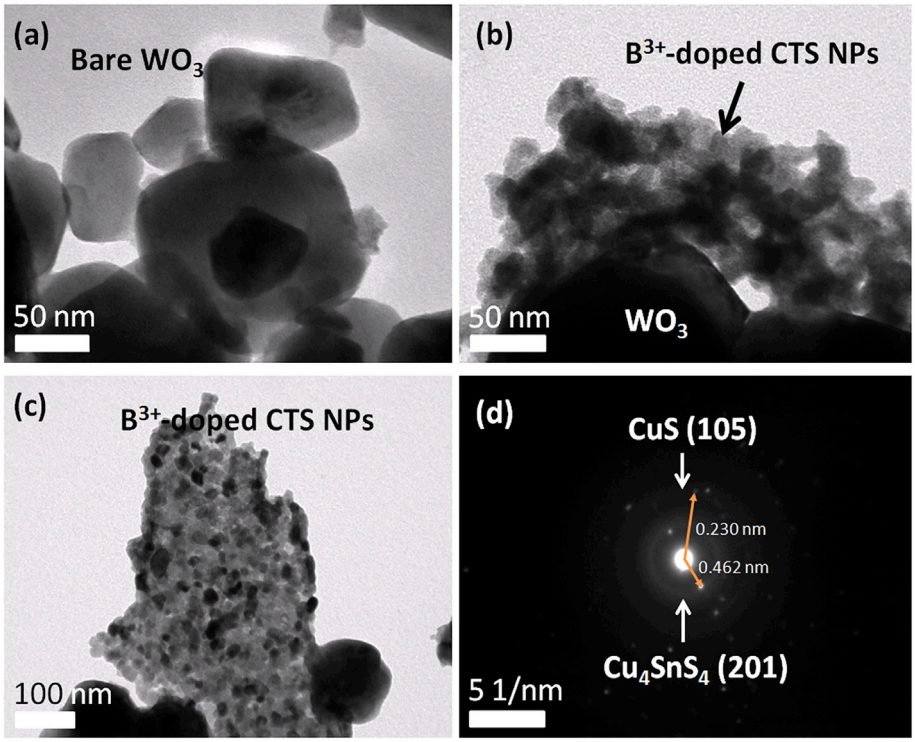

Fig. 1. TEM micrographs of (a) a bare WO_3 film and (b,c) B-doped CTS NPs. (d) SAED pattern of an individual NP.