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Pb-doped Cu_3Se_2 nanosheets: Electrochemical synthesis, structural features and optoelectronic properties

Fatemeh Monjezi[a,b], Farid Jamali-Sheini[c,*], Ramin Yousefi[d]

[a] Department of Physics, Science and Research Branch, Islamic Azad University, Ahvaz, Iran
[b] Department of Physics, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran
[c] Advanced Surface Engineering and Nano Materials Research Center, Department of Physics, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran
[d] Department of Physics, Masjed-Soleiman Branch, Islamic Azad University (I.A.U), Masjed-Soleiman, Iran

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ABSTRACT

Thin films of nanostructured un- and lead (Pb)-doped copper selenide (Cu_3Se_2) with various Pb concentrations were grown on fluorine-doped tin oxide (FTO) glass substrates through an electrochemical deposition method. The structural, optical, electrical and photovoltaic properties of the deposited films were studied using different techniques. The X-ray diffraction (XRD) patterns showed polycrystalline tetragonal structures for the Cu_3Se_2 nanostructures and the field emission scanning electron microscopy (FESEM) images exhibited that all deposited Cu_3Se_2 films contain nanosheets. The nanosheets of the Pb-doped samples were observed to be bent and fractured at edges. Furthermore, photoluminescence (PL) analysis of Cu_3Se_2 unraveled three emission bands in the ultraviolet, green and infrared regions and outlined a shift towards lower wavelengths (blue shift) for the near band edge (NBE) of the Pb-doped samples, compared with the un-doped sample. Also, the absorption spectra of the samples were analyzed to determine the optical energy band gap of the samples, which resulted in the value of 1.65 eV for the un-doped sample and demonstrated an increase in the optical energy band gap of Cu_3Se_2 upon adding Pb dopant and increasing its concentration. Finally, evaluation of the films as the absorber layer of solar cells indicated that there is a minimum amount of strain in the sample with the highest dopant concentration, which affects its solar cell efficiency, positively.

1. Introduction

To decrease dependency on finite natural resources and fossil fuels, which destroy the environment, many attempts have been focused on reducing the costs of energy production from renewable resources, such as solar, water and wind energy. Studying energy conversion in materials by using solid-state semiconductor components has provided a wide field of research for developing the technology of renewable energies (Hochbaum and Yang, 2009).

Thin film solar cells have emerged in the market since late 1970s simultaneous with the emergence of solar calculators, which used to work with a thin film of amorphous silicon (Si). After the initial emergence, in the previous decade, development of thin films resulted in the second generation of solar cells. Due to the wide application of semiconductor-based thin films in solar cells and the need of using cheaper materials for lowering fabrication costs, thin film solar cells have become particularly important. Thin films can be grown on different kinds of substrates, e.g. glass, stainless steel and plastic, through various methods including chemical bath deposition (CBD), electrodeposition, flash evaporation and spray pyrolysis. These deposition techniques can be also used in other fields, such as corrosion resistant coating, microelectronics, optics, magnetic devices and gas sensors (Song et al., 2014; Ho and Anand, 2015).

Copper selenide is a *p-type* semiconductor metal-chalcogenide compound (Pejova and Grozdanov, 2001; Urmila et al., 2011), which belongs to the I-VI group (Urmila et al., 2011) and can be used in solar cells, optical filters, optoelectric systems (Li et al., 2013), coatings of solar cells (Garcia et al., 1999a, 1999b), thermoelectric convertors (Hankare et al., 2003) and microwave shielding coatings (Grozdanov, 1994a, 1994b). It exists in a wide range of different structures and phases that have roots in its various stoichiometric forms and the non-stoichiometric form of $Cu_{2-x}Se$ (Li et al., 2013). Since copper selenide can be in a wide variety of stoichiometric states, might contain crystal defects and can be influenced by quantum confinement effect, it has various band gap energies that have not been defined well. Thin films of copper selenide are often in the forms of CuSe, Cu_2Se and Cu_3Se_2 and their band gap energies lie within the range of 1.0–2.3 eV (Palve et al., 2017).

* Corresponding author.
E-mail address: faridjamali@iauahvaz.ac.ir (F. Jamali-Sheini).

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To date, several methods have been used to prepare thin films of copper selenide including CBD (Garcia et al., 1999a, 1999b), thermal evaporation (Liew et al., 2009), electroless deposition (Haram and Santhanam, 1995), pulsed laser deposition (PLD) (Xue et al., 2006), sonochemical (Ohtani et al., 1998) and electrodeposition (Thouin et al., 1993; Urmila et al., 2011). Garia et al. employed a CBD method to grow thin films of $Cu_{2-x}Se$ and CuSe with cubic and hexagonal structures. These films were found to have high electrical conductivity and their direct energy gap values were reported as 2.2 eV (Garcia et al., 1999a, 1999b). Xue et al. developed three types of copper selenide thin films with $CuSe_2$, CuSe and Cu_2Se phases through PLD in argon. They found that the ratio of selenium in their target phase and temperature of the substrate are the deterministic factors for the structure and properties of their deposited thin films (Xue et al., 2006). The method of thermal evaporation was used for preparing thin films of copper selenide by Liew et al. that investigated the electrical, morphological and structural properties of the prepared thin films (Liew et al., 2009). Also, the technique of electrolysis has been reported for depositing thin films on fluorine-doped tin oxide (FTO) glass substrates by a research group (Grozdanov, 1994a, 1994b). Among different methods of growing and depositing thin films, electrodeposition is one of the simplest, most flexible and cheapest methods, which has the advantages of high speed of deposition, cheap price, low deposition temperature and the possibility of creating compound structures, compared with vacuum-based methods (Rong et al., 2012). Dhasade et al. deposited thin films of copper selenide through electrodeposition, successfully. Their scanning electron microscope (SEM) images showed some CuSe nanorods with polycrystalline structures and revealed that the size of the nanorods depends on the starting concentration of the mixed materials. They found out that the energy band gap of copper selenide depends on its stoichiometry. So that, the optical band gap energies of their deposited CuSe thin films varied from 2.35 to 2.54 eV (Dhasade et al., 2015).

According to previous studies, the concentration of the utilized precursor or surfactant affects the structural, morphological and optical properties of deposited copper selenide thin films while these properties play a key role in performance of optoelectrical devices. That is why engineers need some basic knowledge about properties of thin films to devise solar cells (Dhasade et al., 2015) and it is very important to evaluate the effect of different synthesis parameters and dopants on structural and morphologic properties of thin films. In addition, suitability of many atoms for doping thin films has not been investigated and requires careful experimentations. In this respect, this study applies electrodeposition through fixed potential to deposit copper selenide thin films on FTO substrates. Then, the effect of different concentrations of lead metal, as a potential dopant, on the structural, morphological and optical properties of the films is investigated. After that, the doped nanosheets are used to fabricate solar cells and explore their activities for solar cell applications.

2. Experimental

2.1. Synthesis

To obtain un-doped copper selenide, an electrolyte solution containing 10 mM $CuCl_2$ and 10 mM Na_2SeO_3 was prepared. It should be noted that the utilized Se precursor, i.e. Na_2SeO_3, is an unstable compound. The primary pH of the solution (about 4.6) was reduced to 2 by adding diluted H_2SO_4, gently. The required FTO glass substrate and platinum electrode were subsequently cleaned through 480 s ultrasonication in acetone and alcohol and, then, rinsing with water. For deposition of copper selenide on the FTO substrate, an electrodeposition process in a three-electrode cell was conducted. The electrodes included a FTO working electrode (cathode) with 2×1 cm^2 dimension and below 15 Ω/□ sheet resistance, an anode electrode made of platinum and a calomel reference electrode. The temperature of the cell electrolyte was kept about 50 °C. The electrochemical process was

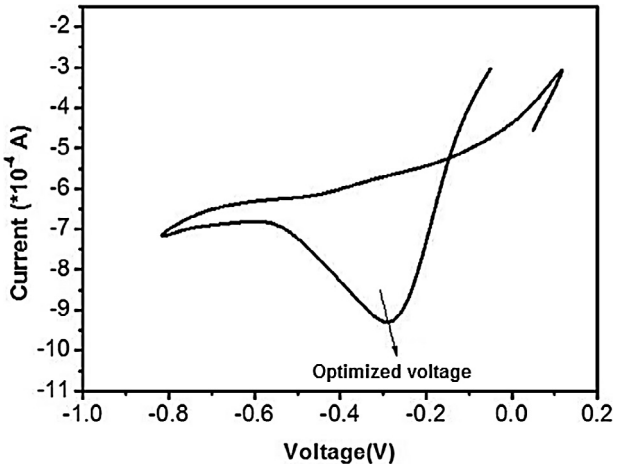

Fig. 1. CV plot for obtaining optimum deposition potential of Cu_3Se_2 films.

controlled by a computer and Metrohm Autolab system. Deposition time for each sample was considered as 20 min. The deposition potential was determined as −0.25 V, according to cyclic voltammetry (CV) experiment (Fig. 1). After finishing deposition, the substrate was removed from the electrolyte solution, rinsed with distilled water and dried in the air. In the case of the Pb-doped samples, 0.0278, 0.051 or 0.071 g Pb (equivalent to 2%, 4% and 6% Pb) were added to the electrolyte solution. The other steps were conducted similar to those of preparing the un-doped sample. The color of the deposited films was dark-brown for all samples.

Eqs. (1)–(7) describe the possible reactions that can occur on the working electrode during the electrochemical synthesis process. Eqs. (1)–(3) are related to decomposition of the raw materials while Eqs. (4)–(7) refer to simultaneous distribution of various Cu_xSe compounds on the substrate (Lippkow and Strehblow, 1998).

$$Na_2SeO_3 + H_2O \rightarrow Na2^{+2} + SeO_3{}^{-2} \quad (1)$$

$$CuCl_2 + H_2O \rightarrow Cu^{+2} + Cl_2{}^{-2} \quad (2)$$

$$H_2SO_4 \rightarrow H_2{}^{+2} + SO_4{}^{-2} \quad (3)$$

$$Cu^{+2} + SeO_3{}^{-2} + 6H^+ + 6e^- cCuSe + 3H_2O \quad (4)$$

$$Cu^{+2} + CuSe + 2e^- \rightleftharpoons Cu_2Se \quad (5)$$

$$2Cu^{+2} + SeO_3{}^{-2} + 6H^+ + 8e^- \rightleftharpoons Cu_2Se + 3H_2O \quad (6)$$

$$3Cu^{+2} + 2SeO_3{}^{-2} + 12H^+ + 14e^- \rightleftharpoons Cu_3Se_2 + 6H_2O \quad (7)$$

It is assumed that the formation and oxidation of different copper selenide compounds under various functional conditions can be concerned as a single-step process. Therefore, based on Eqs. (4)–(6), each of the CuSe, Cu_2Se and Cu_3Se_2 phases can be obtained directly.

2.2. Solar cell fabrication

First, an electron transport film made of titanium oxide (TiO_2) was considered. Then, an active layer made of the main material, i.e. the electrodeposited film of Cu_3Se_2, was deposited. Lastly, a contact film made of aluminum (Al) was deposited through thermal evaporation. The details of preparing the film are as follows. An electrolyte solution of 40 mM $TiCl_4$ was prepared for deposition of the electron transport layer. The optimal deposition voltage was determined as −0.65 V using cyclic voltammetry. Electrodeposition of the electron transport film was carried out at room temperature and continued for 30 min. After deposition, the film was dried in the air and then for phase purity (anatase TiO_2), the film was annealed for 1 h in a box furnace. Finally, the absorber Cu_3Se_2 film was deposited by the aforementioned electrochemical method. Finally, Al contacts were deposited using resistive