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Thin film photovoltaic devices prepared with Cu_3BiS_3 ternary compound

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ABSTRACT

Current commercial thin film photovoltaic technologies rely on the use of scarce and/or toxic elements, motivating the necessity to explore new technologies free of critical raw materials. In this work we report the first Cu_3BiS_3 based solar cells with proved photovoltaic activity using standard substrate configuration. The absorbers were synthesized using a sequential process based on metallic stacks evaporation followed by a reactive annealing under S atmosphere. With the optimization of composition (Cu/3: Bi ratio), metallic stack order, annealing parameters and Na doping, we achieve a record conversion efficiency of 0.11%. Combining several characterizations techniques, we show that at this stage of the technology development, issues like composition, secondary phases and morphology cannot explain the low efficiencies obtained with this material. Through a deeper characterization of the devices, we found that most probably, this is related to either, a high doping of the absorber, and/or poor transport charge properties. Understanding and solving these issues, can further help to improve the efficiency of Cu_3BiS_3 based devices towards more competitive conversion efficiencies.

1. Introduction

Solar energy is considered a more relevant alternative for the future generation of sustainable energy. Photovoltaic energy is capable of directly converting solar energy into electricity. Si is the most used material for this type of technology, however, it has the disadvantage of needing a large amount of material for its proper functioning. Due to this, have recently been investigated several materials more suitable for the absorption and conversion of solar energy.

In that sense, there is a general increasing interest for other potential photovoltaic systems, whose components are less polluting and more abundant in the Earth crust, as is the case of Cu_2SnS_3 [1], SnS [2], Sb_2S_3 [3], $CuSbS_2$ [4], $CuBiS_2$ [5], Cu_3BiS_3 (wittichenite) [6], etc. This last compound is found as a mineral in nature and the first deposits were located in Wittichen, Germany. According to various investigations it is a p-type semiconductor [7], with orthorhombic crystal structure [8], presenting fundamental properties suitable for application in solar cells such as: high absorption coefficient (10^{-5} cm^{-1}) and band gap energy with values between 1.4 and 1.7 [7,8]. This favors the application of this material in photovoltaic devices because it is able to efficiently absorb the light in the visible region of the solar spectrum, even with very thin layers.

The synthesis of this material has been reported using various techniques such as chemical bath deposition (CBD) [9], thermal evaporation [10], spray pyrolysis [11], electrodeposition [12] or combining various techniques [6,10]. Nevertheless, and despite the high potential of this material as a photovoltaic absorber, until now there are no experimental reports on photovoltaic devices manufactured and optoelectronically characterized with Cu_3BiS_3. There are reports where the Cu_3BiS_3 material has been incorporated in cells with structures Al/Cu_3BiS_3/In_2S_3/ZnO and Al/Cu_3BiS_3/ZnS/ZnO but they have only been morphologically characterized by TEM to observe the effect of the different buffer layers [13]. On the other hand Yin *et al.*, incorporated the Cu_3BiS_3, on TiO_2/FTO substrates and were characterized photoelectrochemically, presenting conversion efficiencies of 1.281% [14]. Considering the possible relevance of Cu_3BiS_3, in this work we synthesize this compound using a sequential evaporation/annealing technique, reporting the first working photovoltaic devices with Cu_3BiS_3 as absorber material, and discussing about the main efficiency limitations that can further help to increase the conversion efficiency of solar cell devices based on this ternary compound.

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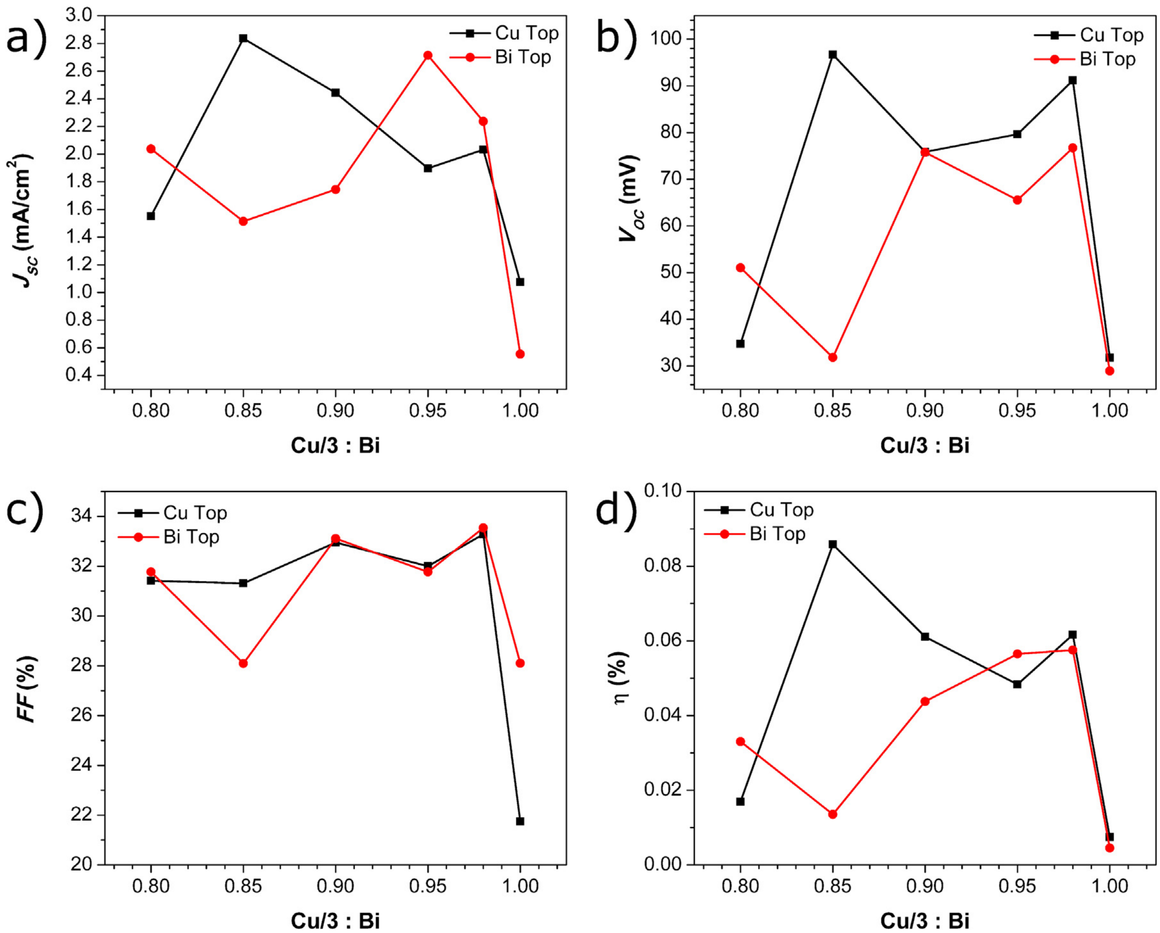

Fig. 1. Evolution of the solar cell parameters a) J_{SC}, b) V_{OC}, c) *FF* and d) η, as function of Cu/3: Bi ratio and metallic stack order.

2. Experimental section

2.1. Metal stack deposition and annealing treatments

Cu_3BiS_3 was synthesized by a sequential process based in the reactive annealing of thermal evaporated metallic layers, onto glass substrates covered with molybdenum (Mo) (800 nm thickness). The Mo layers were deposited using DC magnetron sputtering (Alliance AC450), the deposit conditions used are power = 0.32 kW, I = 0.92 A at a pressure of 1×10^{-3} mbar with deposition time of 13 min. Afterwards, Cu (Copper wire, 1.00 mm dia., 99.9%, Alfa Aesar) and Bi (Bismuth granular, > 99.99%, Sigma Aldrich) metallic layers with different thicknesses were deposited by thermal evaporation technique, using an evaporator Univex 250 Oerlikon. The metals were evaporated varying the stack order including Cu at back and Bi at front, and vice versa. For both structures bismuth thickness was kept constant at 400 nm and copper thickness was varied from 400 nm up to 322 nm (400 nm, 394 nm, 382 nm, 362 nm, 342 nm and 322 nm), in order to test different Cu/3: Bi ratios from stoichiometric one, up to Cu poor conditions (corresponding to Cu/3:Bi = 1.00, 0.98, 0.95, 0.90, 0.85 and 0.80 respectively).

All the reactive annealing processes were carried out in a conventional tubular furnace using a graphite box (volume = 23.5 cm^3). S atmosphere is created inside the graphite box by adding elemental S (Sulfur pieces, 99.99%, Alfa Aesar), and a heating ramp of 20 °C/min were used in all the experiments. In order to optimize the reactive annealing, 1 step and 2 step thermal profiles were studied and compared, varying the maximum temperature of the different steps. Additionally, the S quantity was varied (between 10 and 50 mg). Finally, first attempts for alkali doping (Na doping) were implemented through a pre-annealing deposition of NaF by evaporation. The Na quantity was varied changing the NaF thickness between 5 and 20 nm.

2.2. Material characterization

The thickness of the Cu and Bi layers, and the final composition of the absorbers were measured using X-ray fluorescence (XRF) technique, with a XVD Fischerscope equipment. The structural properties of the different Cu_3BiS_3 films were studied by X-ray diffraction (XRD) technique using a Bruker D8 diffractometer. For the suppression of Kβ radiation a nickel filter was used. Morphological characterization of the surface as well as the cross section was performed by scanning electron microscopy (SEM) using a Zeiss Auriga Series microscope with a 5 kV acceleration voltage.

2.3. Solar cell processing and characterization

Before the fabrication of solar cells and in order to avoid the possible presence of Cu-S secondary phases, KCN etching was performed using a 2% w/v solution during 2 min. Immediately after, CdS buffer layer was deposited (70 nm) by chemical bath deposition [15], followed by the deposition of i-ZnO/ITO (50 nm / 200 nm) window layer by pulsed DC magnetron sputtering (CT100 Alliance Concepts). Individual solar cell of 3×3 mm^2 in area is defined by mechanical scribing using a micro-diamond scriber (MR200 OEG).

Illuminated current – voltage ($J-V$) curves were recorded using Keithley source meter and a Sun 3000 class AAA solar simulator (Abet Technologies, 25 °C, AM1.5 G illumination) calibrated with Si reference cell. External quantum efficiency (*EQE*) characterization was carried out using a Bentham PVE300 system calibrated with Si and Ge