



CuSbSe₂ thin film solar cells with ~4% conversion efficiency grown by low-temperature pulsed electron deposition

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ABSTRACT

CuSb(S,Se)₂ is emerging as an alternative absorber for thin film photovoltaics, for its intrinsic p-type conductivity, tunable energy bandgap (1.0 ÷ 1.6 eV), high absorption coefficient > 10⁴ cm⁻¹ and very low cost of the constituent elements. In this work, we studied the structural, compositional and electro-optical properties of CuSbSe₂ (CAsE) films grown by Low Temperature Pulsed Electron Deposition (LTPED), a developing technology in thin film photovoltaics. We proved that stoichiometric or Cu-poor CAsE films can be obtained at low temperature (< 200 °C) from a stoichiometric target with no need for post-deposition treatments to adjust the stoichiometry. Solar cells based on Cu-poor and stoichiometric CAsE absorbers exhibit a similar open circuit voltage (~290 ÷ 310 mV), while the J_{SC} increases from ~3 mA/cm² up to ~20 mA/cm² as the Cu/Sb ratio increases from 0.55 to 0.95. A low FF ~40% still limits the performance of all the cells indicating that the standard architecture of thin film solar cells, currently used for CIGS and CdTe devices, need to be significantly reviewed. The results of the structural and optoelectrical characterization presented in this paper show that J_{SC}, V_{OC} and FF can all be improved as a result of the optimization of the device architecture. The best of the LTPED-grown CAsE cells obtained so far, reached an efficiency of 3.8%, very close to the state of the art reported so far in literature.

1. Introduction

Renewable energy sources have an enormous potential to meet the global growing energy demand and gradually replace fossil fuels. Among them, solar energy is already the cheapest source of electric power in large part of the world and is expected to play an increasingly important role in the energy industry. Although photovoltaic (PV) cells based on crystalline silicon are still monopolizing the market for their high PV conversion efficiency and low production costs, thin film solar cells based on efficient light absorbers are at the center of the interest for their suitability for flexible PV technology that could open opportunities in the emerging fields of the building- and product-integrated PV (BIPV & PIPV). Thin film solar cells (TFSC) using inorganic semiconductors compounds have been intensively explored. Materials with direct bandgap (E_G) value in the range ~1.0 ÷ 1.5 eV and absorption coefficient > 10⁴ cm⁻¹, such as CdTe, chalcopyrite Cu(In,Ga)Se₂ (CIGS) and kesterite CuZnSn(S,Se)₂ (CZTS), are the most promising candidates for thin-film PV applications [1].

TFSC with CdTe and CIGS as absorber layers are already on the

market, with reported record efficiencies, at laboratory scale, of ~22% [2] and ~23% [3], respectively. However, the toxicity issues related to Cd, the scarcity of In and the cost of Ga [4] represent serious limitations to their widespread diffusion. Hence, earth abundant and non-toxic compound semiconductors such as CZTS have been considered as possible candidates although, up to now, a maximum efficiency of ~12.6% has been reported [5]. Moreover, the composition control of this quaternary alloy has proved to be very difficult, thus hindering its further efficiency growth.

Consequently, earth-abundant absorbers with a less complicated structure but with the same opto-electronic properties are attracting a great attention. Chalcostibite CuSb(S,Se)₂ (CAS) has been recently considered for PV as well as thermoelectric applications [6,7]. Theoretical calculations have revealed that CuSbSe₂ (CAsE) exhibits a very high absorption coefficient (~10⁵ cm⁻¹) [8], few hundreds of meV just after the band gap (~1.0 eV) [9]. CAsE can be considered chemically similar but structurally different from chalcopyrite CIS, in which scarce indium is replaced with the less expensive Sb. Unlike CIS that exhibits tetragonal bonding [10], CAsE exists in the orthorhombic layered

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structure, where the “lone pair” electronic configuration on Sb distorts the tetragonal bonding, leading to the formation of layered structure without any dangling bonds, usually responsible of the carrier recombination at the grain boundaries [11]. Therefore, the CAsE structure appears to be more defect tolerant than CIS/CIGS, since Cu vacancies are the only structural defects thermodynamically favored at low growth temperature [12]. Since these V_{Cu} act as shallow acceptor dopants within the CAsE bandgap, p-type conductivity can be intrinsically controlled only by generating such point defects, without undesired electrical compensation mechanisms given by donor defects, or the addition of extrinsic doping (i.e. sodium).

Mechanical alloying and solvothermal syntheses are used to grow bulk CAsE crystals, while thin films are deposited by chemical bath deposition [13], thermal [14,15] and e-beam evaporation [16], electrodeposition [17], spin coating [18] and co-sputtering techniques [19]. Very few publications reported the fabrication of CAsE-based solar cells with PV efficiency > 3% [20,21], and a record value of 4.7% [22].

In this work, we report the deposition of CAsE thin films by the Low-Temperature Pulsed Electron Deposition (LTPED) technique. LTPED is a high energy growth method, based on the sudden ablation of a polycrystalline target, by which complex materials can be deposited at very low substrate temperature [23]. High quality CIGS with solar cell PV efficiencies up to 17% have been grown by LTPED at temperature of 250–300 °C and without any post-growth selenization process [24], in form of both polycrystalline [25,26] and epitaxial [27] films. LTPED-grown CAsE solar cells have been realized with the same standard cell architecture of CIGS-based cells [28]. Although the PV conversion efficiency obtained so far is still modest (~4%), the detailed structural and optoelectrical characterization of thin films confirm that CAsE is indeed a promising absorber material for TFSC, with great room for improvement.

2. Experimental

CAsE films were grown in a high vacuum chamber equipped with a LTPED source (Neocera PEBS-20), pumped down to a base pressure of $\sim 1.0 \times 10^{-5}$ Pa. During the deposition process, Ar gas (5 N purity) was introduced at a pressure of up to 0.2 Pa to enable the electron beam discharge and the ablation of the target. The PED targets were obtained by cutting a polycrystalline CAsE ingot in 8 mm-thick disks. The ingot was synthesized in a modified physical vapour transport reactor as reported in [29], starting by 99.9% pure elements. The 1 μ m-thick CAsE films were deposited directly onto uncoated and Mo-coated soda-lime glass substrates (25 \times 25 mm² size), located at a distance of 7.5 cm from the target. The substrates were mounted on a graphite susceptor heated by halogen lamps to a temperature ranging from room temperature (RT) to 250 °C as measured by a thermocouple placed on the substrate surface. The thickness of the films was monitored in-situ by IR thermography [30]. The typical CAsE deposition rates were ~ 3.5 μ m/h. The radiation emitted from the excited species in the LTPED plume was analyzed by optical emission spectroscopy (OES), using a mini-spectrometer (Hamamatsu TM series).

Similarly to CIGS-based TFSC, the devices were completed by growing a CdS buffer layer by Chemical Bath Deposition (CBD) at a maximum temperature of 65 °C. The top undoped i-ZnO and the Al-doped ZnO were deposited by RF Magnetron Sputtering (Angstrom Sciences) at RT and 120 W in Ar atmosphere (0.5 Pa). The typical architecture of the CAsE-based TFSC is shown in Fig. 1.

The structural properties of the samples, including their crystalline quality and lattice preferential orientations, were characterized by X-ray Diffraction (XRD) with a Siemens D500 (Siemens, Berlin, Germany) system in a Bragg–Brentano geometry. The morphological analysis of the samples was analyzed by Atomic Force Microscopy (AFM, model Dimension-3100 from Digital Instruments, Santa Barbara, United States) and Scanning Electron Microscopy (SEM, model Philips 515,

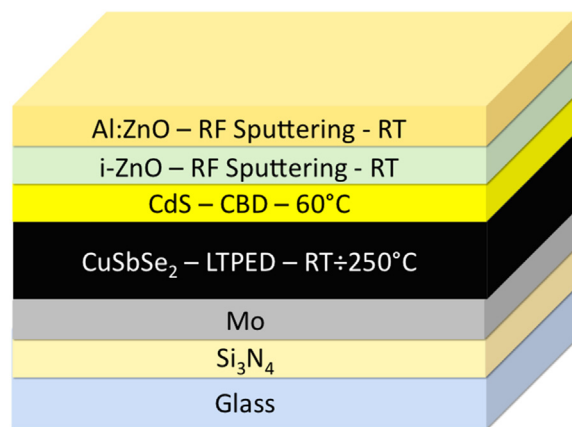


Fig. 1. Schematic representation of the architecture of a CAsE-based solar cell.

Eindhoven, The Netherlands) operating at 25 kV and equipped with an Energy Dispersive X-Ray Spectrometer (EDS) “Phoenix” detector for compositional analysis. Raman measurements were carried out by using a micro-Raman apparatus (Horiba Jobin–Yvon Labram) equipped with a confocal microscope (Olympus BH-4) with 4 \times , 10 \times , 50 \times and 100 \times ULWD objectives, a 20 mW He–Ne laser emitting at 632.8 nm, an edge filter, a 256 \times 1024 pixel CCD detector, a 1800 grooves/mm grating and a density filter wheel. The instrument was calibrated before each measurement using the silicon Raman peak of 520.6 cm⁻¹. The spectra were recorded using the 100 \times objective for 30 s and 4 repetitions. Peak fitting was carried out using a Lorentzian function. The optical properties of CAsE films deposited on glass were assessed by a UV–VIS spectrophotometer (JASCO V-530). Electrical measurements were carried out by Hall Effect in Van Der Pauw geometry for determining carrier density, mobility and CAsE conductivity. The current–voltage (I–V) characteristics of the solar cells were measured by a multimeter (Keithley model 2614B) at 25 °C under a AAB class solar simulator (ABET SUN 2000) with AM1.5G irradiance. Capacitance–Voltage (C–V) and thermal admittance spectroscopy (TAS) measurements were performed using a 4192A HP impedance analyzer at frequencies ranging from 1 kHz to 2 MHz. The amplitude of the test signal was 35 mV. The TAS spectrum was recorded in the 90 \div 300 K temperature range while cooling down. A parallel equivalent circuit model was used to obtain an independent measurement of both the conductance and the capacitance. A quantitative electron beam induced current (EBIC) analysis was carried out in a Cambridge-360 SEM fitted with a current amplifier and a high-resolution digital image acquisition system. A sequence of digital maps of the EBIC signal, generated by a 30 kV electron beam while scanning the solar cell top surface, was collected with a beam current of 400 pA. Each image was processed to obtain a statistical distribution of the EBIC gain (generated current/beam current) over the 2048 \times 1536 pixels of the map.

3. Results and discussion

3.1. Composition, structure and morphology

As already discussed in the case of CuGaSe₂ [26], the chemical composition of the LTPED plasma plume is determined by the effects of two conflicting processes: thermal evaporation and ablation [31]. Thermal evaporation is a near-equilibrium process occurring at the surface of the target. Therefore, the vapour composition is strictly related to the phase diagram of the materials at the surface. In the case of incongruently melting materials, the chemical composition of the vapour does not necessarily match the composition of the target and may hence cause the film to deviate from stoichiometry. On the other hand, ablation is an out-of-equilibrium process involving a region of the target that is instantaneously brought to a plasma state by the electron beam,

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