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Application of a substrate bias to control the droplet density on $Cu(In,Ga)Se_2$ thin films grown by Pulsed Electron Deposition

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ABSTRACT

One of the main shortcomings in the fabrication of thin-film solar cells by pulsed high-energy deposition techniques (i.e. Pulsed Laser Deposition or Pulsed Electron Deposition — PED), is the presence of a significant number of particulates on the film surface. This affects the morphological properties of the cell active layers and, ultimately, the performance of the final device. To reduce the density of these defects, we deposited a $Cu(In,Ga)Se_2$ (CIGS) thin film by PED and studied the effect on the film morphology when a DC bias was applied between the substrate and the target.

Our results show that a negative substrate voltage, comprised between 0 and −300 V, can not only reduce the droplet density on the CIGS film surface of about one order of magnitude with respect to the standard unbiased case (from 6×10^5 to 5×10^4 cm^{-2}), but also lower the maximum particulate size and the surface smoothness. When a positive voltage is applied, we observed that a significant increase in the droplet surface density (up to 10^8 cm^{-2}) occurs. The abrupt change in the preferred crystal orientation (switching from (112) to (220)/(204) by applying negative and positive biases, respectively) is also a direct consequence of the applied DC voltage. These results confirm that the external DC bias could be used as an additional parameter to control the physical properties of thin films grown by PED.

1. Introduction

Pulsed energy deposition methods, such as Pulsed Laser Deposition (PLD) and Pulsed Electron Deposition (PED), have been employed for over twenty years in the fabrication of high quality thin film devices. While PLD has been intensively applied in the deposition of a variety of different materials [1–3], PED features and behavior have been hardly studied because of the poor reliability of the pseudo-spark electron beams used in early devices [4]. However, due to the increasing robustness and power of recent pulsed e-beams [5,6] and to the lower costs of the technique when compared to laser sources, PED has gained increasing attention for its industrial scale-up potentials and application to many different thin-film technological families. The PED technique is based on the impingement of a pulsed high-energy electron beam (with a typical power density $>5 \times 10^7$ W/cm^2 [7]) on the surface of a target material. This leads to the ablation and to the subsequent condensation onto a substrate of vapor species with high kinetic energy. The heating of the target surface and the ablation of the species that result from this huge power density occur far from the thermodynamic equilibrium. This event is hence independent on the phase diagram of the target material and allows the congruent evaporation and the preservation of the starting stoichiometry on the growing film. Moreover thanks to the high kinetic energy of the evaporating atoms and ions arriving on the substrate (1–10 eV), well-ordered crystalline films can be obtained even at low substrate temperatures. These unique features of the PED technique allow the deposition of high quality epitaxial films [8,9] and the fabrication of reliable optoelectronic devices based on complex materials, like $YBa_2Cu_3O_7$ [10] and $Cu(In,Ga)Se_2$ (CIGS) [11].

Despite the exclusive advantages involved in the high-energy transfer from the e-beam to the target, the PED technique has critical aspects which are mainly related to the generation of µm-sized particulates and droplets [12–17]. These droplets are expelled from the target surface and, after traveling inside the plasma plume, are finally deposited on the substrate. Because high-performance thin-film semiconducting devices, like for instance CIGS-based solar cells [18], require an extremely smooth surface, the density and the size of the particulates produced by pulsed-energy deposition techniques need to be minimized.

In the case of oxide films deposited by PED, an appropriate selection of electrical parameters has proved to reduce the droplets' presence on the film surface. In this respect the reduction of the cathode voltage [13] and of the external capacitance [19] gave the most satisfactory results. However these solutions are not appropriate in the case of CIGS and

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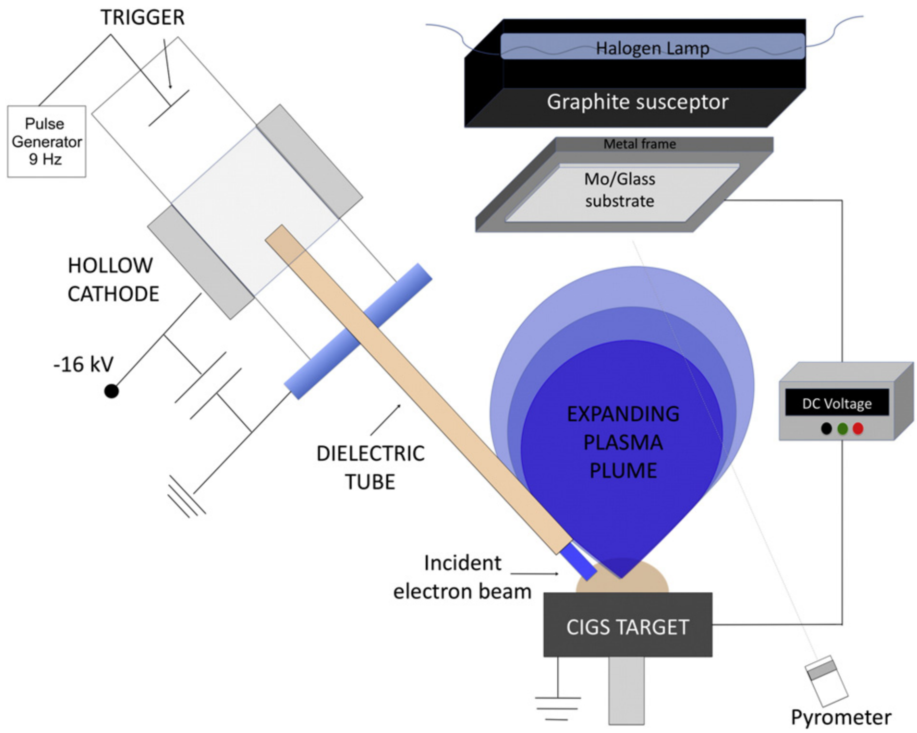

Fig. 1. Representative scheme of the experimental set-up.

$CuGaSe_2$ (CGS), where the film composition is strongly affected by the electrical properties of the electron beam [20]: indeed, in the latter case a power density larger than ~1×10^8 W/cm^2 is needed to avoid the formation of the unwanted $CuGa_3Se_5$ phase, which is detrimental for the operation of the solar cell. In the PLD technique many different technological approaches, like velocity filters [21], off-axis [22] and dual-beam depositions [23] have been attempted in order to minimize the droplet deposition on the substrate. However, because a side effect of these PLD solutions is the reduction of the deposition rate they are not suitable for large-scale applications. Another advantageous route performed in PLD is the application of a DC bias between the target and the substrate. Lubben et al. have shown that a negative substrate bias can significantly diminish the particle density on the film surface [24]. They observed a five-time decrease in the droplet density on a −150 V biased sample with respect to the unbiased one. The authors explain this phenomenon as the result of a negative charge of the droplets that receive an electrostatic repulsion from a negatively biased substrate.

In this paper, we applied Lubben's experimental approach to the PED process to minimize the particulate presence on the surface of the CIGS films. Negative and positive voltages have been applied between the target and the substrate in order to study the dependence of the droplet's density and size on the DC bias. The effects induced by the external field on the structural and compositional properties of the CIGS films have also been analyzed.

2. Experimental details

$Cu(In,Ga)Se_2$ films have been grown using a high vacuum chamber pumped down to a base pressure of ~1.0×10^{-5} Pa and equipped with a commercial PED source (supplied by Neocera Inc.). The discharge voltage was set at 16 kV and the triggered pulse repetition rate at 9 Hz. The capacitance connected to the hollow cathode and the inner diameter of the dielectric tube were 15 nF and 4 mm, respectively. The operation principles of the PED process are reported elsewhere [25]. Argon was used as process gas and kept at a pressure of 5.0×10^{-1} Pa. The target material for the PED ablation was a 10 mm-thick cylindrical piece of polycrystalline CIGS, with a nominal Cu/(In + Ga) ratio of 0.78 and a Ga/(Ga + In) ratio of 0.25. This was synthesized in a modified physical vapor transport reactor starting by elemental species (5 N purity) [11]. The CIGS films were deposited on Mo-coated soda-lime glass substrates (26×26 mm^2 size), located 8 cm away from the target. The substrate was placed under a graphite susceptor, heated by halogen lamps. The substrate temperature was maintained constant at 270 °C and monitored by an optical pyrometer (Raytek Marathon MM). All the CIGS samples were grown by applying the same number of pulses (5×10^4). The substrate holder was a square metal frame, kept in electric contact with the Mo-coated face of the substrate and biased with respect to the grounded target. An external DC voltage, V_{ext}, ranging from −300 V to +200 V, was applied between the substrate and the target (connected to the ground) by means of a DC power generator. A “benchmark” unbiased sample was obtained by electrically insulating the substrate holder in order to compare biased and unbiased CIGS samples. A schematic design of the experimental set-up 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), performed with a Siemens D500 system equipped with a Cu Kα X-ray source (λ = 1.54 Å) in Bragg–Brentano geometry. A Scanning Electron Microscope (SEM, model Philips 515) operating at 25 kV was used for evaluating the film thickness, the surface density of the droplets and their size. Planar SEM images were taken at three different magnifications, 100×, 1000× and 10,000× respectively. The measurement of the film composition was conducted by an Energy Dispersed X-Ray Spectroscopy (EDS) detector mounted on the SEM system. The analysis of the surface roughness was conducted by an Atomic Force Microscopy (AFM, performed by Nanoscope III-Digital Instruments).

3. Results and discussion

3.1. Morphology

The characteristic morphology of an unbiased CIGS film grown by PED is shown in Fig. 2. The film exhibits a great number of spherical