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Evaluation of different deposition conditions on thin films deposited by electrostatic spray deposition using a uniformity test

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ABSTRACT

Copper indium disulphide films were produced by electrostatic spray deposition using a water/alcohol solution of copper chloride ($CuCl_2$), indium chloride ($InCl_3$) and thiourea ($CS(NH_2)_2$) sprayed onto SnO_2:F coated glass substrates. The influence of various deposition parameters, namely substrate temperature (380–450 °C), applied voltage (12–18 kV), solution concentration (0.21–0.49 M), flow rate (25–200 µl/min) and needle–substrate distance (40–70 mm) were investigated. particle image velocimetry measurements were made of the spray cone and correlated with the film uniformity. The film uniformity was measured using an optically based test developed in-house. Results show that the highest concentrated spray solution and lowest deposition temperature produce non-uniform films. In contrast, a needle–substrate distance of 50 mm, and the lowest applied voltage and flow rate resulted in the most uniform films.

1. Introduction

$CuInS_2$ (CIS) is a member of the I–III–VI_2 type semiconductor family and has become one of the most promising polycrystalline materials for solar cell applications. This is due to its near optimum band gap value of 1.42 eV [1], high absorption coefficient [2] and because it is a direct band gap semiconductor [3]. Finally it does not contain any toxic elements and so can be prepared in an open atmosphere with minimal environmental risk. A variety of different methods have been used to prepare CIS thin films such as vacuum thermal evaporation, spray pyrolysis and electrodeposition [4–6]. There remain however, many problems to be solved, such as control of the composition and structure of the as-deposited film, improvement in the electrical and optical properties of the films, as well as the performance of CIS based devices. In order to improve the efficiency of CIS solar cells it is necessary to increase the fundamental understanding of the preparation and deposition processes necessary to produce high quality thin films. This paper studies the effect of some of the fundamental deposition parameters on films grown by the electrostatic spray deposition (ESD) technique. For economic reasons, ESD is an attractive deposition method because of the high deposition rate, large deposition area, minimal chemical waste and low setup cost associated with the technique. Moreover, the technique enables good control of the morphology and stoichiometry of the as-deposited films which is another attractive feature.

The ESD technique makes use of an electrostatic field to generate an aerosol which is attracted to an earthed and heated substrate. The solvent evaporates en route and the chemical precursors react in the vicinity of the hot substrate where suitable films are formed. ESD is an established technique and has been used by other groups to deposit thin metal oxide thin films for rechargeable lithium batteries [7], solid oxide fuel cells [8], biomedical implants [9] and sensors [10].

The quality of the as-deposited samples depends on a series of experimental variables such as deposition temperature, flow rate, potential difference, etc. In order to improve the application of ESD, a greater understanding of the effect of different deposition parameters on the properties of the films is necessary. The same conditions can affect the uniformity of the film thickness, with certain parameters leading to non-uniform depositions. As a uniform film is required for the majority of thin film devices, ensuring thickness uniformity is vital when establishing a new deposition process. During this work, a mathematical relationship is established between the deposition parameters and the degree of uniformity of the thickness of the as-deposited films using a simple, but powerful test.

2. Experimental details

$CuInS_2$ films were deposited using the ESD set up shown in Fig. 1. A positive voltage (Glassman EL40P1 DC supply) was applied between

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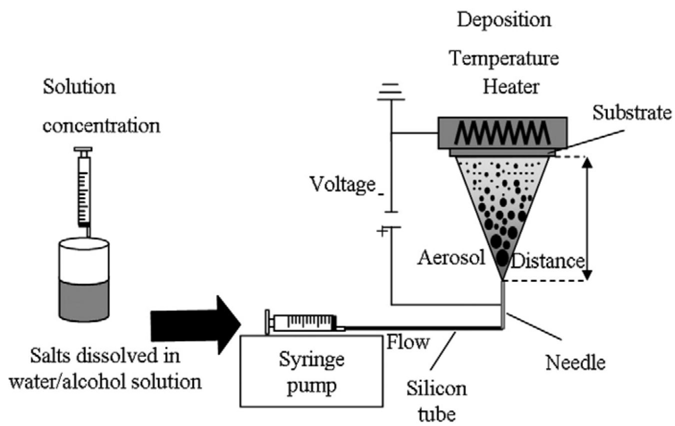

Fig. 1. Schematic of the ESD experimental setup.

the stainless steel needle and an earthed sample holder, and was varied between 12 kV and 18 kV. Due to the potential difference, the solution is atomized at the needle tip and a fine aerosol is generated which is attracted to the earthed substrate. The distance between the needle and substrate was varied between 40 mm and 70 mm. A KD Scientific syringe pump (Model: KDS270) supplied solution through an acid resistant silicon tube to the needle. The flow rate could be changed between 25 and 200 µl/min (±1%), the deposition temperature was controlled via four heating elements and a k-type thermocouple embedded in a stainless steel block which surrounds the substrate. The substrate temperature was set at 380 °C, 410 °C or 450 °C (±5 °C). Water/alcohol solutions $CuCl_2 \cdot {}_2H_2O$ (99.99%, Sigma Aldrich), $InCl_3$ (99.99%, Alfa Aesar) and thiourea (99%, Alfa Aesar) were prepared with concentrations between 0.21 M and 0.49 M while the solution molar ratio was maintained at a constant Cu:In:S = 1:1:5 [13]. Ethanol (80% in volume) was added to reduce the surface tension of the chemical solution and improve the yield of the atomization process. An excess of sulphur was necessary to avoid the formation of insoluble copper–sulphur complexes [11].

Semi-transparent films were deposited onto conductive fluorine–tin–oxide (FTO) coated glass using a fixed spraying volume of 0.2 ml, in order to deposit films of equivalent thickness irrespective of the flow rate.

3. Analytical methods

To evaluate the effect of deposition conditions on the thickness uniformity of $CuInS_2$ thin films, a uniformity test was developed and used in combination with laser-based particle image velocimetry (PIV) measurements. Full details of the test have been described elsewhere [12]; a summary of which, along with a description of the PIV technique is given below.

3.1. Uniformity test

The uniformity test utilises the transmission of light through a semi-transparent sample in order to record the variation in the light absorbed, and hence the thickness uniformity (assuming a uniform film composition), across the specimen. Note that the technique cannot be used for thick/opaque films.

A light-box was used to transmit light through the samples and digital images of the samples were captured and analysed. The test transforms the images into a grey scale matrix and then calculates the thickness of the as-deposited films using the Lambert–Beer's law. From this point, two different but complementary analyses were undertaken:

- Macro uniformity test (MUT) — provides a measure of the overall film coverage. MUT is used to find a numerical value which allows grossly non-uniform samples to be discarded and macroscopically uniform samples to be selected for the second stage of the test
- Micro-uniformity test (µUT) — measures the optical smoothness of the film. It calculates the gradient of the thickness for each point of the matrix. The results are plotted in histograms in which the abscissa represents the gradient while the ordinate represents the normalised frequency of the gradient.

It should be noticed that both tests rely on arbitrarily set limits to dictate whether a film is discarded or not.

3.2. Particle image velocimetry

The two-dimensional PIV system (Fig. 2) used in the tests consisted of a two-dimensional pulsed laser light sheet orientated parallel to the aerosol spray direction and aligned with the centreline of the needle. This illuminated the droplets (particles) in a defined region of the spray and a digital camera recorded images of the particles during each pulse in order to capture a time history of the change in the position of each particle. The behaviour of the flow was then examined by acquiring a series of image pairs at a given frequency (15 Hz pair acquisition rate). Using a small time interval (~50 ms) between the pulses of a pair, individual particles could be identified between frames and the distance and direction of movement of each particle could be analysed in the plane of the light sheet. Spatial correlation techniques were used to process the particle image pairs into two-dimensional velocity vector maps.

3.3. Surface tension and conductivity

The Du Nouy ring method was used to measure the surface tension of the spray solutions. With this technique, a platinum ring is immersed into the solution, and the instrument measures the force necessary to pull out the ring through the liquid surface.

Conductance measurements were performed using a conductivity cell which consists of two platinum electrodes and a conductivity bridge (Wheatstone bridge). The bridge circuit was established such that the solution was one leg of the bridge when the cell was immersed. By

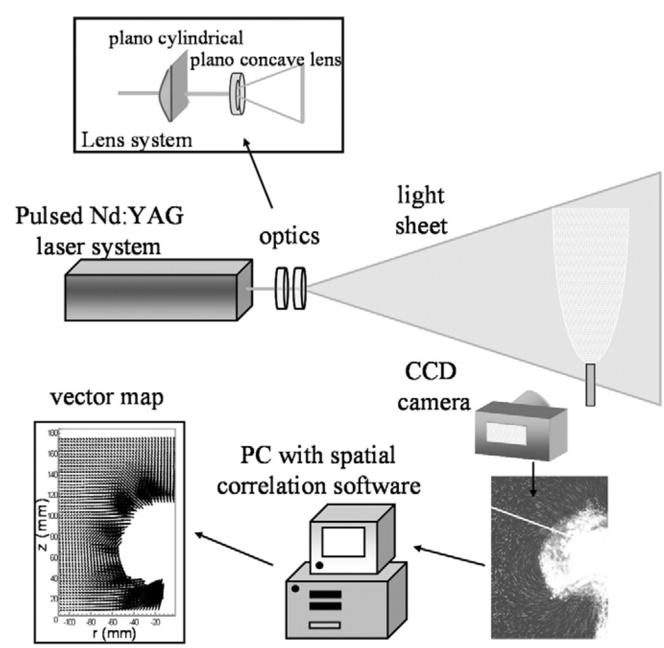

Fig. 2. Schematic of the PIV setup used for recording the direction and velocity of the droplets within the ESD spray cone.