# CIS 층의 정전분무 증착
## On the Electrospray Deposition of CIS layers

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### 1. Introduction

Electrospray deposition (ESD) technique is fast finding its applicability in the field of thin film device manufacturing processes and the ease and cost efficiency attached to ESD process with possible integration with Roll-to-Roll (R2R) fabrication line is the potential future of thin film device manufacturing. With the fast evolution and progressing interest in the concept of green energy production and related devices, the demand of cheap and robust solar cell devices has increased manifolds. Researchers are particularly allured towards the fabrication of thin film flexible and non-flexible solar cells for the primary purposes of their installation on space vehicles, clothings and for household purposes as well.

Second generation solar cells comprising primarily of CdTe and $CuInSe_2$ (CIS) or $CuInGaSe_2$ (CIGS) as the absorber layer are very popular research topics from the view point of thin film photovoltaics than the first and third generation photovoltaics comprising primarily of Silicon based and Organic photovoltaics respectively.

Presently, the more developed and popular chemical or physical vapor deposition methods have generally been used to deposit thin metal films of ~1-2 μm thickness that require sophisticated and expensive vacuum systems. Vacuum-based processes include sputtering & selenization and reactive sputtering [1]. Non-vacuum-based processes include chemical bath deposition [2] and coating of nano-particles thereby deploying them into different deposition mechanisms.

Since late 1990s the electrospray was used for production of solar cells from CdS [3] and CdSe [4]. Films produced by electrospray were homogeneous and composed of agglomerates built of particles smaller than 1 μm.

The achievement of ultra-fine ~1-2 μm thick layer especially for CIS or CIGS is a challenge using non-vacuum deposition techniques and a lot of research is going on in this area. Electrospray ionization is one such technique which has the potential of becoming a reliable cost-effective and robust technique for the processing of thin CIS films for the use in photovoltaics. This work records the deposition of CIS absorber layer with the required thickness and appreciable smoothness of the film to be later deployed for the manufacture of a fully functional solar cell, solely with Electrospray deposition technique. For the purpose of manufacturing CIS based solar cell, nano-particulate copper and Indium metal layers of 1–2 μm have been deposited by electrospray using alcoholic suspension pastes by Kaelin et al. [5]. Yoon et al [6] have suggested nano-particle based approach for the formation of CIS layer. Nano-particles with core–shell structure were used as the precursor material, and binary phases were used as core and shell material in the core–shell structure to maximize the kinetics of CIS formation reaction.

As the name suggests, using ESD implies that the deposition phenomenon should solely be a spray achieved through electrostatic forces. In fact it is an imbalance between the surface forces arising because of the surface tension of the liquid to be sprayed and Maxwell stresses which are induced because of the electric field, that pull the liquid downwards from the capillary into a stable jet which further disintegrates into smaller droplets because of coulomb forces and hence a cloud of charged, mono-dispersed and extremely diminutive (sometimes up to nanometers) droplets are achieved.

The present study describes the successful deposition of CIS nano-particle layers on the conducting ITO coated glass substrates using Electrospray deposition. The CIS nano-particle ink comprises of Polyvinylpyrolidone (PVP) as the surfactant and glycerol is added to increase the viscosity of the ink. Table 1 shows the properties of the CIS-ink. Operating envelope of the ink has been determined experimentally and the layer morphology is examined using scanning electron microscope. Excellent and precise deposition characteristics prove the prowess of ESD in the fabrication of thin film photovoltaics.

Table 1: Ink Properties

| S/N | Properties | Values |
|---|---|---|
| 1 | Glycerol (wt%) | 37.5 |
| 2 | Conductivity (μS/cm) | 58 |
| 3 | Surface tension (N/m) | 0.0337 |
| 4 | Viscosity (Pa.s) | 0.0123 |

### 2. Experiment setup

The schematic diagram of the experimental setup is shown in Fig. 1. A syringe pump (Harvard Apparatus, PHD 2000 Infusion) holds the CIS ink containing syringe (Hamilton, Model 1001GASTIGHT syringe) connected to the 150 μm inner and 300 μm outer diameter metallic capillary (NanoNC, NNC-DN-2230) keeps the minimum required flow rate. A high voltage power source (NanoNC) connected between the capillary and copper plate ground electrode generates highly concentrated electric field at the capillary outlet and generates the largely mono-dispersed electrospray of the CIS nano-particles. A high resolution CCD camera (MotionPro N3) is connected to the main computer and is responsible for the high speed, high resolution capturing of the events going on at the capillary tip i.e. dripping and Taylor- cone formation etc. Teflon tubing is used for the CIS ink supply from the syringe to the nozzle. Metallic nozzle is mounted on an independent plunk capable of moving in the z-direction while the copper plate electrode holding the ITO coated glass substrate, with the ITO coating grounded as well through a copper strip, is attached to the stage which is capable of moving in all the x and y directions so that a uniform spray coating can be formed on whole of the substrate and at adjustable substrate to nozzle tip distances.

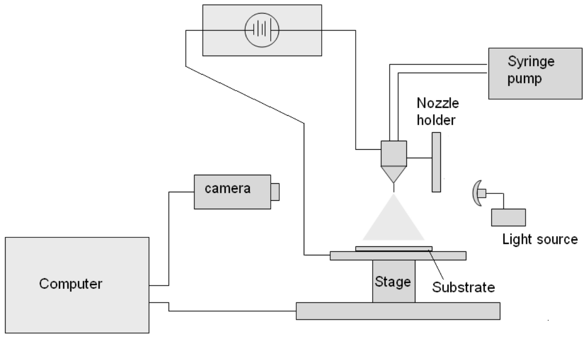



Figure 1: (a) Schematic diagram of ESD system

### 3. Results and Discussion

#### 3.1. Taylor-Cone formation and Operating Envelope

Electrohydrodynamic atomization refers to a process, where a liquid jet breaks up into droplets under influence of electrical forces. Depending on the strength of the electric stresses in the liquid surface relative to the surface tension stress, and depending on the kinetic energy of the liquid leaving the nozzle, different spraying modes can be obtained, namely dripping, micro-dripping, unstable or pulsating cone-jet mode, stable-cone jet mode and the multi-jet mode. There are other modes of spray as well and a detailed note on different spraying modes can be found elsewhere. The main advantage with the cone-jet mode of the electrospray is the larger mono-dispersity of the sprayed particles which carries a lot of importance when dealing with thin solid films. Therefore the emphasis of this study was to achieve the electrospray of the CIS particles with cone-jet mode. An operating envelope has been determined for the operation at different flow-rates and the representative plot of the complete operating envelope is given in figure 2. Figure 3 (a) represents the high-speed camera image of the Taylor-cone recorded at a flow-rate of 100 µl/hr and Figure 3 (b) represents the online digital camera image of the spray being ejected from the nozzle. A symmetric and uniform spray regime is visible which guarantees a smooth and uniform layer deposition.

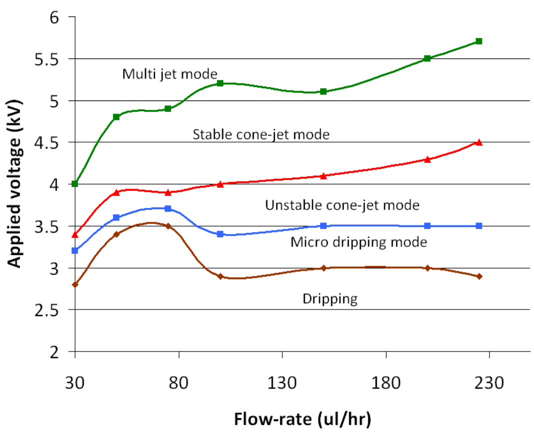
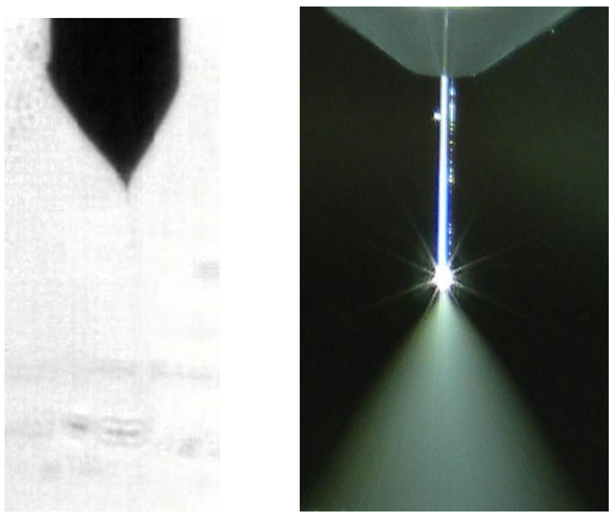



Figure 2: The operating envelope of CIS nano particle ink for the head

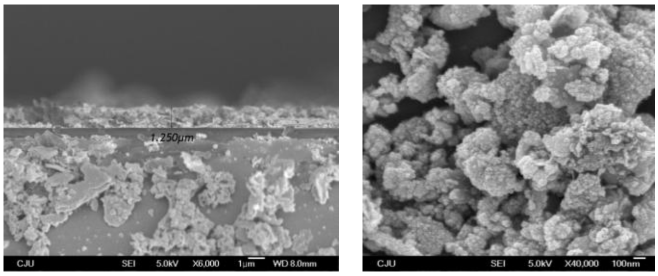


(a) (b)

Figure 3: (a) Online photographs of (a) Taylor-cone and (b) Spray emanating from the nozzle.

### 3.2. Sprayed Layer Characteristics

The deposition was done at a liquid flow rate of 50 µl/hr and at a stable cone-jet voltage of 4.4 kV. The deposited samples were sintered at 100 °C for 30 minutes and then analyzed using a Scanning Electron Microscope (SEM). Fig. 4 (a) represents the side view of the deposited layer and reveals smoothly resting CIS particles' layer with excellent thickness of ~1.25 µm which is in acceptable range for CIS based solar cells (Basol et al. 1996) [7]. Particle integrity is appreciable and particles are flocked together into uniform agglomerates penetrating into each other. The mentioned results were obtained through a single pass of electrospray with the substrate moving at a speed of 2.5 mm/sec. Fig. 4 (b) portrays a surface scan of the deposited layer for CIS deposition. A presentable morphology is revealed with occasional cracks of the film ranging from 100 nm to 500 nm.




(a) (b)

Figure 4 (a) Thickness view and (b) surface morphology of the deposited layer

## 4. Conclusion

Electrospray deposition has been discussed in the backdrop of its feasibility for the deposition of the CIS layer for a CIS based solar cell through a nano-particle based CIS ink. A complete CIS layer has been deposited through electrospray in a single step without involving any other process. Electrospray, being a much cheaper and easy solution for the manufacture of photovoltaics carries a unique advantage of operation at the standard room conditions and does not require expensive deposition equipment. Fine surface morphology and exceptional layer thickness of 1~2 µm are witnessed in this study, which are very important phenomenon for thin film photovoltaics structures and hence establish the viability of ESD for the applications in photovoltaic manufacture.

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