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The spray-ILGAR® (ion layer gas reaction) method for the deposition of thin semiconductor layers: Process and applications for thin film solar cells

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ABSTRACT

The spray Ion Layer Gas Reaction (ILGAR) process starts with ultrasonic nebulisation of the precursor solution, e.g. $InCl_3$/ethanol for our successful buffer material In_2S_3. In an aerosol assisted chemical vapour deposition (AACVD) type reaction an $In(O,OH,Cl)$ film is deposited on a heated substrate and is subsequently converted to In_2S_3 by H_2S gas. The cycle of these steps is repeated until the required layer thickness is obtained. The robust and reproducible process allows a wide control of composition and morphology.

Results of this "spray-ILGAR" method with respect to process, material properties and its application depositing the buffer layer in chalcopyrite solar cells are reviewed. New aspects such as the investigation of the complex chemical mechanism by mass spectrometry, the process acceleration by the addition of H_2S gas to the aerosol, the controlled deposition of ZnS nano-dot films and finally the latest achievements in process up-scaling are also included.

Solar cells based on industrial $Cu(In,Ga)(S,Se)_2$ absorbers (Avancis GmbH) with a Spray-ILGAR In_2S_3 buffer reached 14.7% efficiency (certified) and 15.3% with a ZnS/In_2S_3 bi-layer buffer comparable to reference cells using standard CdS buffer layers deposited by chemical bath deposition (CBD).

The quasi-dry, vacuum-free ILGAR method for In_2S_3 buffer layers is well suited for industrial in-line production and is capable of not only replacing the standard buffer material (the toxic CdS) but also the often slow CBD process. A tape coater for 10 cm wide steel tape was constructed. It was shown that In_2S_3 layers could be produced with an indium yield better than 30% and a linear production speed of 1m/min. A roll-to-roll pilot production line for electrochemically deposited $Cu(In,Ga)Se_2$ with ILGAR buffer is running in industry (CIS-Solartechnik, Hamburg). A 30x30 cm² prototype of an ILGAR in-line coater developed by Singulus and Helmholtz Zentrum Berlin is currently being optimised. First 30×30 cm² encapsulated modules achieved efficiencies up to 13.0% (CdS buffered reference 13.3%).

1. Introduction

Inorganic thin films find application in a wide field from electronic semiconductor devices, such as sensors and solar cells, to optical and protective coatings of surfaces. As numerous as the applications, are the processes for their deposition. Besides the often expensive physical techniques running under vacuum conditions, various chemical methods exist for the preparation of inorganic thin films. Chemical vapour deposition (CVD), especially metal organic chemical vapour deposition (MOCVD) [1–3], and atomic layer deposition (ALCVD) [4,5] are technically complex, costly and sometimes

too slow. When used on laboratory scale rather simple equipment is needed for the single step methods chemical bath deposition (CBD) [6,7] and spray pyrolysis as well as for the sequential processes such as the sol–gel method [8], Ion Layer Gas Reaction (ILGAR) [9–11] and Successive Ion Layer and Reaction (SILAR) [12]. For the preparation of metal sulphide layers by CBD and spray pyrolysis the starting solution contains the desired metal cation and a sulfide precursor compound, e.g. thiourea or thioacetamide generating hydrogen sulfide or sulfide ions upon heating [13].

Sequential methods consist of at least two steps, one for the deposition of an intermediate precursor film and another, where the reagent and, if necessary, energy are added for the chemical conversion of the precursor to the final composition. In the SILAR process sulfide layers are prepared by successive dipping of a substrate in a metal salt solution and then in a bath of alkali sulfide. This cycle is repeated until the desired layer thickness is obtained. Between these

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dips rinsing steps can be included to improve the homogeneity of the layer, although they can reduce dramatically the deposition rate.

ILGAR is also sequential and cyclic. In contrast it applies the reagent not in solution but as a *gas*, e.g. hydrogen sulfide (H_2S) for metal sulfides [9] and wet ammonia for metal hydroxide/oxide layers [10]. The solid–gas reaction prevents any convective motion of material and allows higher deposition rates, good layer homogeneity and quality. This ILGAR variant with the dipping into a precursor solution is referred to as "*Dip-ILGAR*" [14–16]. It has been successfully used for the deposition of ZnO and ZnS buffer layers for chalcopyrite thin film solar cells [17]. More recently, we *spray* the precursor solution, which is not only much easier for industrial in-line processing but results also in even better homogeneity due to a different chemical mechanism. This paper reviews only the "*Spray-ILGAR*" work with respect to the process and the applications for solar cell components and contains some latest results and developments, concerning the chemical mechanism, the controlled deposition of ZnS nano-dot films as well as the industrial up-scaling.

2. Results

2.1. Spray-ILGAR process

2.1.1. Standard process

Originally ILGAR was carried out by dipping the substrate in a salt solution and subsequently fumigating it with a reactant gas. The adherent liquid film after dipping limited the deposition rate per process cycle to about 1 nm and dipping cannot be integrated very easily in an in-line process. For both reasons the spray application of the starting solution has been established. First *aqueous* $CuCl_2$, $InCl_3$ or $GaCl_3$ solutions were nebulised by a flask immersed in a cheap ultrasonic atomiser as used for room humidification. The generated aerosol was carried in a nitrogen gas stream through a glass tube initially ascending, which allowed the separation of bigger droplets adhering at the wall, before being led downwards to impact the horizontal substrate under an angle of 90° at temperatures below 100 °C. This resulted in a deposition of partially hydrolysed metal chloride precursor film. Periodically, the nebuliser was stopped. After a N_2 purging phase H_2S gas was introduced to the precursor converting it to the corresponding metal sulphide layers. After a second N_2 purging period this process cycle starts from the beginning with the spray step. When a mixed $CuCl_2$, $InCl_3$ and $GaCl_3$ solution was sprayed $Cu(In,Ga)S_2$ layers were obtained after sulfurisation [18].

The layer quality was improved when *alcoholic* solutions were sprayed on hotter substrates (> 200 °C) and a modified set-up was used. This has become our standard Spray-ILGAR process and is explained in more detail, exemplarily for the deposition of In_2S_3, our standard material for solar cell buffers [19]. For a lab scale Spray-ILGAR deposition up to a substrate size of 5×5 cm² the simple equipment is used as shown in Fig. 1. An ethanolic $InCl_3$ solution is nebulised by an ultrasonic atomiser, the generated aerosol is blown under an angle of 45° over the heated substrate (typical temperature 200–250 °C). The flow is homogeneous and laminar. At the substrate the droplets evaporate and decompose forming a precursor film. The following process steps are the same as previously. Thus, one ILGAR process cycle consists of the four steps: spraying-N_2; purging; H_2S sulfurisation; N_2 purging. The layer thickness is controlled by the number of repetitions.

The overall reaction can be written as Eq. (1), the elemental analyses of precursor and final layer carried out by Elastic Recoil Detection and Analysis (ERDA) [19] (Table 1), however, show that a solid $InCl_3$ film is not simply formed during the spray step, which is subsequently sulfurised by H_2S.
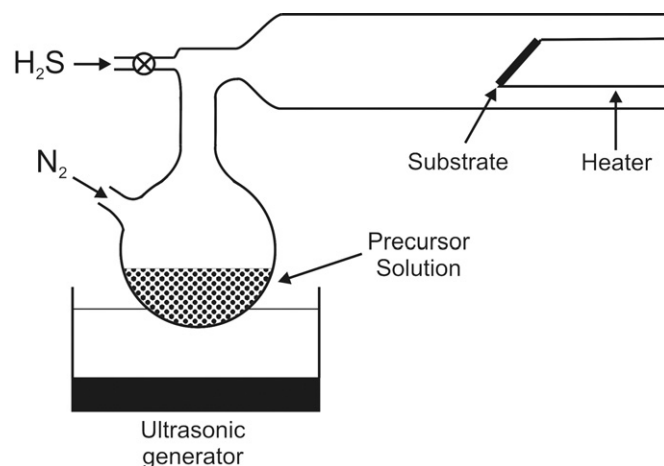
$$2InCl_3 + 3H_2S \rightarrow In_2S_3 + 6HCl \qquad (1)$$

Fig. 1. Scheme of the spray-ILGAR set-up for the deposition of metal sulfide layers on substrates up to 5×5 cm². Reproduced with permission from [19].

Table 1
Spray ILGAR In_2S_3 deposition from ethanolic $InCl_3$ solution. Typical element compositions before (precursor layer) and after sulfurisation (data from ERDA analysis). Reproduced with permission from [19].

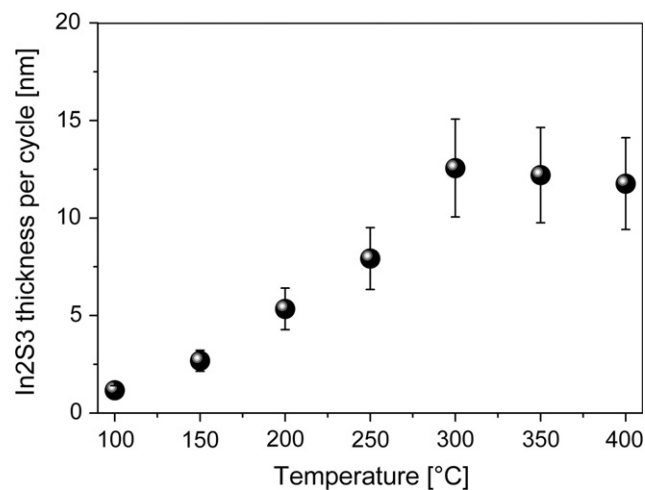|	In (at%)	S (at%)	Cl (at%)	O (at%)	H (at%)	C (at%)
Precursor	24.1	0.0	17.9	33.0	24.7	0.2
After sulfurisation	36.2	46.6	9.0	0.6	6.5	1.1

Fig. 2. Spray ILGAR In_2S_3: thickness per process cycle as a function of substrate temperature. Reproduced with permission from [19].

The precursor layer in fact consists of a mixed indium oxide, hydroxide and chloride In(O,OH,Cl) and even the In_2S_3 layer contains typically 12–20% chlorine. The chlorine comes from the chloride precursor and can be avoided by using, for example, $In(acac)_3$ (indium acetylacetonate).

The spray step is an aerosol assisted chemical vapour deposition (AACVD) at atmospheric pressure and the subsequent sulfurisation a solid/gas reaction. The chemical mechanism is complex and will be discussed in the next section.

At constant N_2 gas flow rate the growth rate increases with increase in temperature up to 300 °C, afterwards it saturates (Fig. 2) [19]. The film growth rate, as a function of precursor concentration, is approximately proportional to $[InCl_3]^{0.4}$, determined by XRF