

Spray-Ion Layer Gas Reaction (ILGAR)—a Novel Low-Cost Process for the Deposition of Chalcopyrite Layers up to the Micrometer Range for Photovoltaic Applications[†]

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A novel variant of the ion layer gas reaction (ILGAR) process is described. Up to now, only layers with a maximum thickness of about 100 nm could be deposited by ILGAR in a reasonable time. Replacing of dipping by spraying on a warm substrate accelerated the application of the precursor solution (e.g., metal chloride in water) by a factor of at least 100. For multinary products, all precursors are applied either simultaneously as a mixed solution or sequentially. In intervals, the spraying is stopped and the reaction gas H₂S is allowed to flow over the substrate. A special, yet simple setup is shown, which allows also a recycling of unconverted precursor. In about an hour time, a micrometer thick layer of mixed or stacked CuS/In₂S₃/(Ga₂S₃) (from CuCl₂, InCl₃ and in some cases GaCl₃, respectively) is deposited. The latter is converted to CuInS₂ (CIS) or Cu(In,Ga)S₂ (CIGS) by annealing in H₂S/Ar at 550 °C. The thermodynamically stable product distribution for this process is calculated. The influence of the process parameters, substrate temperature during precursor deposition, annealing temperature, CuCl₂/InCl₃ ratio and gallium addition, is studied. The layers are used as absorbers in chalcopyrite thin film solar devices. The grain size necessary for this purpose is already sufficient (ca. 0.5–0.7 μm diameter). First solar cells based on spray-ILGAR-CIS and -CIGS have been prepared and compared. The efficiency has already reached 3.4%. An unusual layer morphology is obtained when the substrate temperature is too high (>90 °C). In this case, the layer consists of ideal hollow spheres with a hole in them. An explanation for this phenomenon is given.

Introduction

The chalcopyrite thin film PV-technology is a promising alternative to silicon especially with respect to cost and energy saving production. Cu(In_xGa_{1-x})(S_ySe_{1-y})₂ (CIGS_{Se})-based solar cells have already reached efficiencies of up to 18.8% and 19.2% (for y = 0).¹ The selenium-free absorber CIS (for y = 1) has several advantages, such as replacement of the more toxic selenium, higher voltages, and less efficiency loss at higher temperatures. CIS-based solar cells have shown record efficiencies of 12.7%.²

Most components also of these multilayer devices have to be produced by high-tech and therefore expensive technologies, such as evaporation or sputtering, which require high temperatures or high vacuum or both. In the past, low-tech methods have been proposed, such as spray-pyrolysis³ and electrodeposition⁴ without having found wide application. The recently introduced ion layer gas reaction (ILGAR) is a chemical low-cost method for the deposition of metal sulfide^{5,6} and oxide^{7,8} layers using reactions of metal salts with hydrogen chalcogenides especially at the solid/gas interface, thus allowing also the coating of porous or hollow substrates. This sequential and cyclic process consists of the following steps: (1) application of a precursor salt solution on a substrate; (2) drying of the liquid film; (3) reaction of the resulting solid film with a reactant gas (hydrogen chalcogenide). Steps 1–3 are repeated until the desired layer thickness is obtained.

As an example, for sulfide layers the preparation of ZnS according to the simple eq 1 is given. Metal halides, especially



chlorides, can be converted by hydrogen sulfide at relatively low temperatures, often at room temperature. It is especially advantageous that in addition to the desired metal sulfide only a gaseous byproduct (hydrogen chloride) is generated.

The formation of oxides typically takes place via hydroxides, which are dehydrated at moderately elevated temperatures. In this case, a water/ammonia gas mixture is allowed to flow over the metal salt precursor layer. One characteristic of the ILGAR process is the easy deposition of multilayers or gradient layers.

Up to now, the precursor has been applied by dipping of the substrate in an *organic* solution guaranteeing good wetting and fast and uniform drying. The result is a homogeneous, very adherent, 1–2 nm thick precursor film, which is chemically transformed by the reactant gas in the following process step. Through the use of this “dip-ILGAR” method, buffer layers for chalcopyrite solar cells have already been prepared very reproducibly leading to superior conversion efficiency compared to those with standard CdS buffers.^{9,10} Because after each dip only a precursor film of a certain thickness (depending on the concentration of the precursor solution) remains on the substrate and because this concentration can be increased only in a certain range because of homogeneity problems, only layers of up to about 100 nm thickness can be achieved in a reasonable time. However, in photovoltaics (PV), micrometer layers are also required for absorbers and windows. This paper describes a basic modification of the ILGAR method for the realization of a fast layer growth and an even better suitability for industrial processing. In a first step, we worked on absorber layers. The

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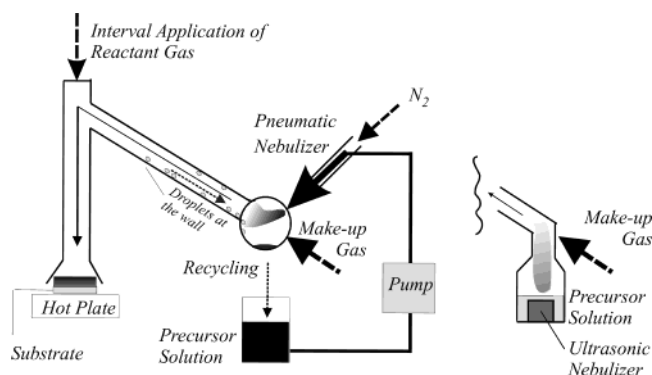


Figure 1. Scheme of experimental setup for metal chalcogenide deposition by spray-ILGAR: (left) with pressure gas nebulizer; (right) with ultrasonic nebulizer. Details are in the text.

preparation of oxide window layers, which is already tested, will be published in a separate paper.

Experimental Section

The experimental setup is custom-made from ordinary glass tubes as shown in Figure 1. A gas pressure sprayer made from a glassblower is fed with nitrogen (5 bar, Linde) and with the precursor solution via a peristaltic pump at a flow of 2 mL/min. Alternatively, an ultrasonic nebulizer (designed for air humidification in the household, Conrad Electronic, Germany) is immersed in the precursor solution. An additional nitrogen stream is introduced as makeup gas. Its flow rate (30 mL/s) has to be adjusted according to the individual geometry of the setup so that the fog is smoothly blown over the substrates (2.5×2.5 cm² glass, covered with 1 μ m of molybdenum when used for solar cells and cleaned with 2-propanol in an ultrasonic bath prior to use). Substrates were heated to 65 °C during deposition. After spraying (1 min for CIS and 0.5 min for CIGS), 5% H₂S in Ar (Messer-Griesheim) is blown onto the substrate for the same period. This cycle is repeated until the desired layer thickness is reached. The sample is then annealed in 5% H₂S in Ar at 550 °C for 1 h. For the deposition in the simultaneous process, an aqueous solution containing 0.5 M CuCl₂ and 0.5 M InCl₃ for CIS and for CIGS also 0.5 M GaCl₃ and 10% ethanol is used. In the latter case 10% ethanol was added to the water. For CIGS in the sequential process, the three solutions containing just one salt but at a concentration of 1.5 M were sprayed successively interrupted by gas reaction steps of the same duration. Chemicals were of analytical grade (Alpha).

A Bruker D8 was used for X-ray diffraction (XRD). Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) measurements were performed with a Leo 430 microscope.

Results and Discussion

The Spray-ILGAR Process. In the novel spray-ILGAR method, the precursor solution is no longer applied by dipping. Now, an aqueous solution (sometimes with 10% ethanol for better wetting) is *sprayed* onto the substrate. This procedure has three main advantages: much faster layer growth, horizontal substrate position, and replacement of at least most of the organic solvent by water. The last two points are of special importance for safe and low-cost industrial in-line production: the substrate must not be removed from the conveyor belt, and the use of water is cheaper and safer.

Figure 1 shows the scheme of the experimental setup. Either a pressurized gas or an ultrasonic sprayer is used to nebulize

the precursor salt solution. We tested both variants. The pressurized gas nebulizer is more robust against corrosion but susceptible to plugging. It must be carefully positioned and adjusted with respect to gas pressure and liquid flow rate, both depending on the salt concentration of the feed solution. Alternatively, a cheap ultrasound nebulizer designed for humidifying of room air was immersed in the solution. Here, it is difficult to protect the sonicator device against corrosion. At present, it is not really clear which sprayer is better.

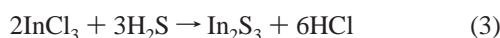
The generated fog is blown by a nitrogen “makeup” stream through a glass tube, initially ascending and then flowing downward onto the substrate. The droplets generated by the sprayer have a certain size distribution. But, the homogeneity of the resulting layer improves with smaller and less disperse drop size. Fortunately, the largest drops stick preferentially to the glass walls. They flow down and can be recycled. The smaller droplets pass the tube and reach the moderately heated substrate where the solvent (mainly water) evaporates and the precursor salt crystallizes leaving a smooth solid layer. It is necessary to stress that, in contrast to spray pyrolysis, no chemical reaction takes place at this time and that the substrate temperature is much lower (below 100 °C).

A simultaneous fog and gas application leads to powder-like layers, which can be easily wiped off because the reaction takes place within the flying droplets. Solid particles reach the substrate. Only a sequential process with separated spray periods and gas periods guarantees very adherent layers, because the precursor salt crystallizes directly on the substrate and into its microstructure. Therefore, the solid film is anchored. In intervals, the spraying is interrupted while the reactant gas is introduced from the top to the solid precursor film on the substrate. The makeup gas is flowing all the time, to prevent access of reactant gas to the drops at the wall and the precursor solution where it would react with the precursor and form precipitates. The parameters concentration and flow rate of the solution, flow rate of the makeup gas, interval frequency, and substrate temperature should be chosen so that (1) a maximum amount of material remains on the substrate and only a minimum escapes with the gas stream beside the substrate (influence on process duration and material loss), (2) the droplets do not dry up during their flight by heat radiation of the substrate (strong influence on layer adhesion), (3) the water evaporates immediately and no liquid film is formed (influence on morphology and homogeneity), and (4) the precursor film is not too thick before the reaction because it must interact with the reactant gas (influence on conversion rate and layer purity).

Most of the parameters have to be optimized individually for each experimental setup. Therefore only general remarks are given. It is clear that the layer growth rate increases with increasing concentration and flow rate of the solution because more salt per time reaches the substrate. However, at the same time, homogeneity and adhesion of the layer deteriorate. Cracks occur when a precursor layer that is too thick is converted by the reactant gas. Layer thickness as a function of makeup gas flow rate goes through a maximum. Initially, more gas transports more fog to the substrate, but beyond the maximum, the aerodynamics pushes the fog stream *over* instead of *against* the warm substrate. The effect of temperature will be discussed in more detail in the following section.

The first applications of spray-ILGAR concerned CuInS₂ and Cu(In,Ga)S₂ as absorber in chalcopyrite thin-film solar cells. The respective selenides or sulfoselenides are also available by ILGAR. However, because of the much higher toxicity of H₂-Se in comparison to H₂S, we concentrated on the sulfides.

Deposition of CuInS₂ (CIS). For the deposition of CIS by spray-ILGAR, a mixed aqueous precursor solution of CuCl₂ and InCl₃ was sprayed onto a molybdenum-coated float glass substrate. Although Cu(I) is required for the CIS molecule, because the Cu(I) compounds are oxidized very rapidly even in the presence of only small amounts of oxygen, for practical reasons the stable Cu(II) precursor was preferred, which is later reduced in the process by H₂S. After 1 min, the feeding pump of the sprayer is stopped and H₂S gas is introduced for 1 min. In this step, the binary sulfides are formed according to eqs 2 and 3. After 25 spray/gas cycles, when the desired layer



thickness of about 2 μm is reached (Figure 2), the sample is annealed in 5% H₂S in Ar for several reasons: (1) for completion of sulfurization because the reaction of InCl₃ at room temperature is slow, (2) for transformation of Cu(II) to Cu(I) according to eq 4, (3) for the formation of the ternary compound



CIS (eq 5), and (4) for crystal growth (important for absorber



layers, where grain boundaries hinder the transport of charge carriers).

Substrate Temperature. A very surprising observation was made when the influence of substrate temperature was studied. Spraying of the precursor solution on substrates at temperatures above 95 °C results in layers consisting of almost ideal hollow spheres with a round opening (Figure 2a). Around the hole, the shell seems to be bent toward the center. This reproducible phenomenon, known also in the field of spray drying, is not limited to CIS; it is also found when ZnO is prepared by spray-ILGAR at too high substrate temperatures. It can be explained in terms of a considerable solvent evaporation already during the flight of the droplets and that occurs preferentially from the drop surface. There the salt concentration increases. During this short time diffusion cannot balance the concentration in the whole drop, the solubility is exceeded, and a solid shell is formed. On the way to the substrate, the temperature rises further. Finally, the increasing vapor pressure leads to an eruption of the liquid content at the weakest point of the crust. The layer close to the opening is drawn back to give the most favored alignment. Of course, such a spherical morphology is not useful for normal thin-film solar cells because of high electrical resistance and insufficient optical density. Nevertheless, one can think of applications in which just such hollow bodies are required, for example, in the pharmaceutical field or for trapping of material. At substrate temperatures below 50 °C, the precursor film does not dry completely. This leads to very irregular and incomplete layers. But, at 65 °C, homogeneous black films are obtained. In the scanning electron microscope (Figure 2b) they appear rather compact with a grain size of about 0.5–0.7 μm.

With the number of spray/gas cycles there is an increase not only in the layer thickness but also in the average grain size (Figure 3). Because the lower part of the layer is heated all the time during the following cycles (i.e., altogether for a longer period than the upper part), the crystals grow and act as a better seed layer for the material deposited afterward.

Annealing Temperature. In the standard preparation of CIS for solar cell absorbers, *metallic* precursors are typically sulfurized at 550 °C.² However, in the ILGAR process *salt* precursors are sulfurized. To get an idea of the thermodynamic situation, thermochemical calculations were performed using ChemSage software,¹¹ which has already been successfully used for the prediction of binary ILGAR-oxide and -sulfide products.¹² The program varies temperature and pressure in the systems of species consisting of the elements Cu/In/S/Cl/H. The calculation employs a technique for the minimization of Gibbs free energy, dG, to calculate multicomponent multiphase chemical equilibria in closed systems containing gaseous and condensed phases. At a given temperature or pressure and at defined element concentrations, the program calculates a set of values for activities, *a_i*, of all species and their concentration, *n_i*, according to eq 6, providing a best fit for the equilibrium condition dG = 0.

$$dG = \sum \mu_i dn_i = \sum (\mu_{i0} + RT \ln a_i) dn_i \quad (6)$$

with *μ_i* = chemical potential of species *i* (*μ_{i0}* under standard conditions).

This procedure has the advantage that the calculations are not based on chemical reaction schemes. However, it is necessary to use well-selected thermochemical data, such as formation energies, entropies, and molar heats with temperature dependences for all stable phases.

According to eqs 2 and 3, six molecules of HCl gas are formed, while only four gas molecules (H₂S) are consumed. In a closed system, this would lead to an increase in pressure. However, ILGAR is typically carried out in open systems, that is, the reactant gas is continuously flowing over the sample and all gaseous reaction products are removed together with the excess reactant gas. For the ChemSage calculations, the reaction parameters have to be adapted to come closer to the conditions in a flowing system, for example, 0.1 bar is assumed to compensate for the net gas formation. Figure 4 shows that between 400 and 640 K CuIn₅S₈ is the only stable CuInS compound, while above 670 K the situation is changed to the benefit of CuInS₂.

Interestingly, X-ray diffractograms (XRD, Figure 5) of ILGAR-CIS layers annealed at various temperatures reveal the existence of CuInS₂ (Roquesite) already at 250 °C. A few signals of CuIn₅S₈ would coincide, but many are missing. Therefore the presence of the latter is unlikely. The peak width (full width at half-maximum, fwhm) of the (112) peak clearly decreases from 1.50° at 250 °C to 0.37° at 550 °C indicating a pronounced crystal growth. Earlier experiments¹³ with dip-ILGAR CdS showed on the basis of optical measurements and the quantum size effect^{14,15} that at room-temperature material consisting of nanoparticles in the range of 5 nm is deposited, which agglomerates upon annealing.

Material for PV-absorbers requires large grains to reduce the shunt paths and recombination at the grain boundaries in the device. All further samples were annealed at 550 °C. Additional experiments must prove whether also lower temperatures yield sufficient crystal quality.

Copper/Indium Ratio. The standard CIS process from metallic precursors works under copper-rich conditions leading to larger grains. This effect was also verified for ILGAR-CIS by a variation of the Cu/In ratio (between 1.0 and 1.5). The fwhm of the (112) XRD peak decreases from 0.37° to 0.23° for Cu/In = 1.0 and Cu/In = 1.5, respectively. EDX measurements were not surprising, revealing the same Cu/In ratio in

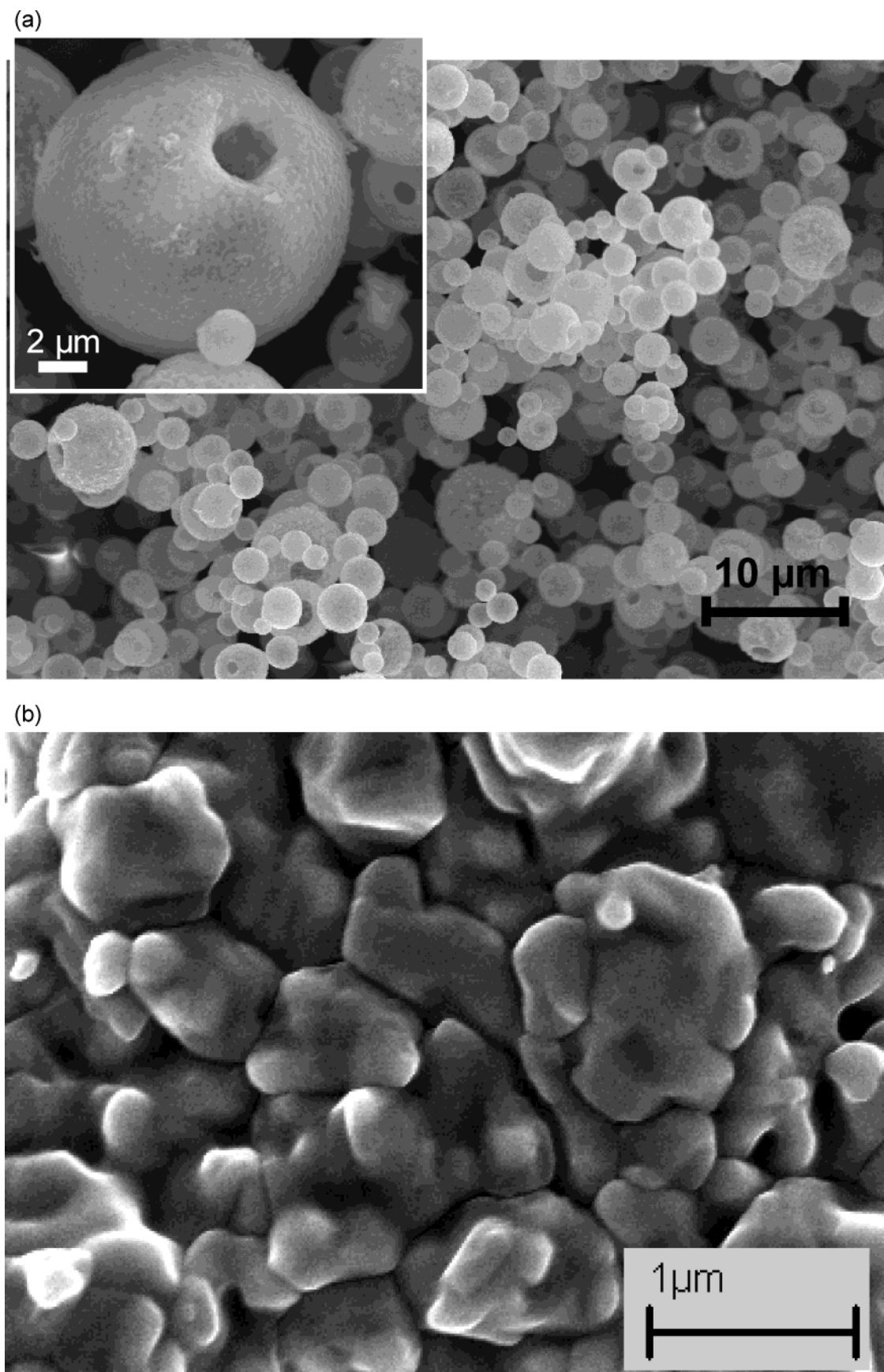


Figure 2. Scanning electron micrographs of layers of CuInS_2 deposited by spray-ILGAR at a substrate temperature of (a) 95 °C and (b) 65 °C.

the final layer as in the precursor bath. The excess of copper forms a CuS phase, which has to be removed by a standard KCN etching.

Deposition of Cu(In,Ga)S_2 (CIGS). It is known that a partial replacement of indium by gallium has a positive effect on grain size and on performance of a resulting solar cell because a wider

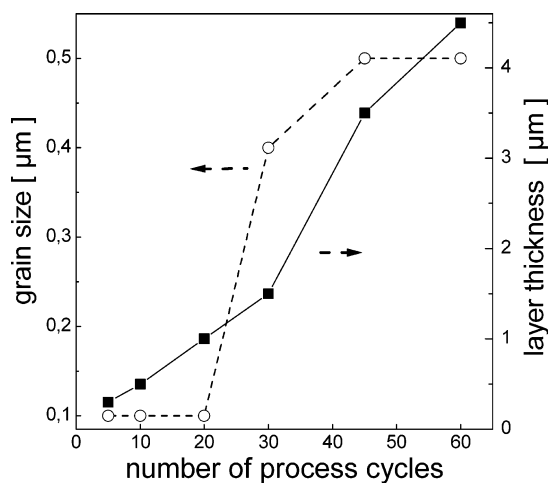


Figure 3. CuInS₂ deposition by simultaneous spray-ILGAR. Layer thickness (determined by profilometry) and average grain size (estimated from SEM) are plotted as a function of the number of spray/gas process cycles.

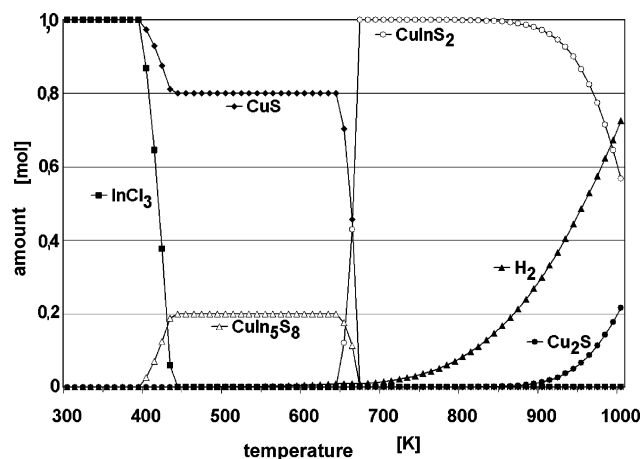


Figure 4. Product distribution in the system Cu/In/Cl/H/S as a function of temperature calculated by ChemSage. Starting amounts were as follows: H₂S (9 mol), CuCl₂ (1 mol), and InCl₃ (1 mol). Pressure was 0.1 bar.

optical band gap. Two spray-ILGAR processes were tested, a simultaneous one, in which a ternary mixture of precursors is used, and a sequential one. In the latter case, CuCl₂, InCl₃, and finally GaCl₃ solutions are sprayed in such a way that the same amount of each species as in the simultaneous variant is deposited. Here, the idea was to mix and reorganize the whole material and favor its grain growth by the diffusion of the compounds through the layer. Indeed, according to SEM, the Ga addition had the expected effect on grain size. The fwhms of the (112) XRD peak of 0.19° and 0.31° for the “sequential” CIGS sample and the “simultaneous” reference, respectively, demonstrate the positive outcome of Ga diffusion.

Solar Cells. First solar cells were prepared consisting of ILGAR-CIS and -CIGS absorbers with 20% excess of copper over indium or indium plus gallium, respectively. The other layers (Mo back contact, CdS buffer layers, ZnO window and Ni/Al front contacts) were prepared by standard processes. Figure 6 shows the $J(V)$ curves for cells with CIS and CIGS absorbers prepared by the simultaneous or simultaneous and sequential process. The cell parameters open circuit voltage (V_{OC}), short circuit density (J_{SC}), fill factor (FF), and efficiency (η) are compiled in Table 1. The advantage of the “sequential” CIGS is obvious. Higher V_{OC} points to a reduced number of shunt paths due to larger grains (compare XRD peak widths).

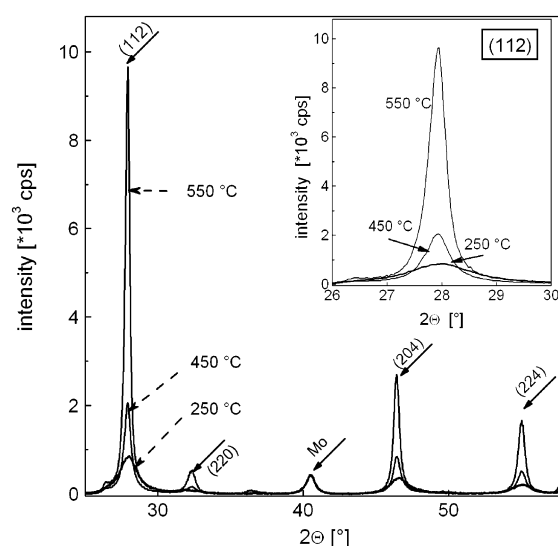


Figure 5. XRD of spray-ILGAR-CIS layers prepared at annealing temperatures of 250, 450, and 550 °C. All peaks except that marked with Mo coincide with those given in the JCPDS database for CIS. The insert shows the (112) peak on an expanded 2θ scale.

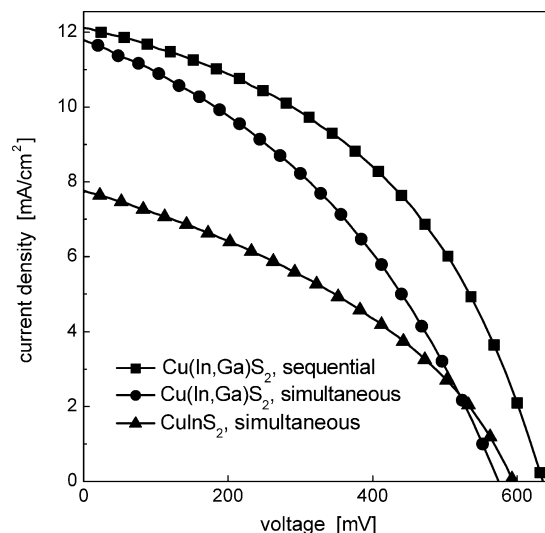


Figure 6. $J(V)$ curves of thin-film solar cells based on spray-ILGAR-CIS (simultaneous process) and -CIGS (simultaneous and sequential process). The corresponding cell parameters are compiled in Table 1.

TABLE 1: Comparison of the Solar Cell Parameters of Solar Cells Based on ILGAR-CIS and ILGAR-CIGS Deposited by the Simultaneous and Sequential Processes

	ILGAR-CIS	ILGAR-CIGS	
	simultaneous	simultaneous	sequential
V_{OC} [mV]	594	574	636
J_{SC} [mA/cm ²]	7.8	11.8	12.1
FF [%]	37.9	37.6	43.9
η [%]	1.7	2.5	3.4

From the improved FF, one can conclude that a better interface is formed. A considerable improvement can be expected by a systematic optimization of Cu/In ratio, layer thickness, and process parameters.

Conclusion and Outlook

It has been shown that CIS and CIGS can be prepared by spray-ILGAR starting from the metal chlorides under low-cost conditions. Cu excess and Ga addition are beneficial for grain growth as in the “classical” process via sulfurization of metal

precursors. The layers are suited for photovoltaic applications. Though the ILGAR absorbers are not yet optimized for this purpose, they yield solar cell efficiencies of up to 3.4%. An improvement by systematic studies seems very likely. Also ZnO layers have been prepared by spray-ILGAR and even doped *n*-ZnO by dip-ILGAR. All layers for solar cells must be optimized first individually, that is, the other layers have to be deposited by standard methods. Finally, all ILGAR layers (absorber, buffer, window) have to be compiled with the goal of a real low-cost "all-ILGAR" solar cell.

It should be mentioned that, in principle, all insoluble metal chalcogenides are available by ILGAR, also mixtures of them with constant or gradient composition. The horizontal substrate position makes spray-ILGAR especially suitable for industrial in-line production or tape coating in a roll-to-roll process. The method is not limited to smooth substrates; also porous ones can be coated. The only precondition for the substrate material is its stability against those chemicals and temperatures being involved during the process. Steel and plastics have been successfully coated. In other words, there are many applications for ILGAR coatings beyond photovoltaics, for example, in the field of catalysis, anticorrosion, antielectrostatic, or mechanical protection.

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