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Thin Film CIGS Solar Cells with a Novel Low Cost Process

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Abstract

Novel manufacturing routes for efficient and low-cost Cu(In,Ga)Se_2 (called CIGS) thin film solar cells are explored and patented. CIGS has proven its suitability for highly efficient and extremely stable solar cells. The low-cost methods allow impurity free material synthesis, fast large-area deposition, high material utilization and a very short energy payback time with drastically lower manufacturing costs. Two non-vacuum, solution-based approaches are investigated to deposit thin layers of CIGS. The first approach considers incorporation of copper into indium gallium selenide precursor layers by ion-exchange from aqueous or organic solutions. Organic solutions provide faster copper incorporation and do not corrode the metal back contact. Solar cells processed from selenized precursor films exhibit efficiencies of up to 4.1%. The second approach with paste coating of inorganic salt solution results in a solar cell efficiency of 4% (record 6.7%), where further improvements are hindered by the presence of the residual carbon layer. Using alternative organic binders, pre-deposited selenium layers, non-binder recipes helps to avoid the carbon layer although the obtained layers are inhomogeneous and contain impurity phases. A patent for the ion-exchange approach is pending, and the obtained research results on the paste coating approach will be scrutinized during new European FP7 project “NOVA-CIGS”.

1. State of the Art

Thin film solar cells based with the direct band gap absorber Cu(In,Ga)Se_2 (hereafter CIGS) have proven to yield high conversion efficiency already close to classical crystalline Si cells that require 100 times thicker absorbers for complete sun light utilization. Record efficiency of 20% for CIGS solar cells on glass substrates nearly approaches the maximum 25.0% for classical crystalline c-Si cells [1]. The CIGS solar cell is a stack of Mo (back contact), CIGS (absorber), CdS or ZnS or InS (buffer), ZnO/ZnO:Al (transparent conducting oxide (TCO) front contact) layers deposited in that sequence on glass or foil substrates. While the materials and deposition processes for back- and front- electrical contacts and the buffer layers are well established, the processing of CIGS layer and its interfacing with adjacent layers are the keys to the solar cell efficiency, yield, and throughput. Current industrial production of CIGS absorbers relies on the so-called three-stage vacuum evaporation of individual metals, which results in relatively slow processing speed and requires very sophisticated and expensive vacuum equipment.

A major breakthrough in CIGS industrialization could be achieved when simple and non-vacuum production equipment and processing steps could produce reasonably efficient (>10%) solar

modules. Advantages of non-vacuum based processing over conventional vacuum deposition are:

- Significantly lower equipment and maintenance costs
- Easy scale-up for large area processing
- Lower thermal budget and shorter energy pay back time
- Nearly 100% material utilization in case of paste coating (only 40-60% in conventional processing)

The CIGS material has already shown viability for synthesis with simple low-cost equipment. Thus, efficiencies up to 13.6% were obtained by the US companies ISET and Unisun [2] where and 12.2% was achieved by IBM [3]. The former process involves conversion of metal powders into metal oxide precursors which are converted to CIGS by first reduction to metal and then to selenides. The latter process is based on the dissolution of selenides in hydrazine solvent with subsequent annealing. Both commercialized technologies, however, rely on the utilization of highly hazardous process materials H_2Se or hydrazine, respectively. In contrast, it is desirable to focus on simpler and safer manufacturing processes, albeit the so-far achieved conversion efficiencies are lower, on the order of 4-7%.

Laboratory for Thin Films and Photovoltaics at Empa (formerly part of the Thin Film Physics group at ETHZ) has already developed a non-vacuum process based on solution deposition with efficiencies up to 6.7% [4]. This process was based on inorganic salt material dispersed in an organic matrix which was applied on the substrates as thick films by low-cost methods doctor blade and screen printing. Despite an organic impurity layer forming between the substrate and the CIGS absorber, the CIGS layer showed very good opto-electronical properties. However, the open-circuit voltage and fill factor were limited because of the carbon layer between the CIGS and Mo interface, arising from the use of an organic binder, ethylcelluluse, during the paste formulation.

2. Objectives

The overall goal of this work is to explore and investigate novel low-cost processes for the production of thin film $Cu(In,Ga)Se_2$ solar cells. The solution-based method has a potential in reducing equipment cost (simple, non-vacuum, mostly self-adjustable composition control, does not require sophisticated in-situ process monitoring), increasing production speed (no pumping to high-vacuum, fast deposition speed) and reducing material wastage (high material utilization due to solution processing). Additionally, the overall thermal budget of the complete process is expected to be significantly lower than most of the conventionally used processes, which in turn will reduce the energy pay-back time of the solar cells.

In order to achieve the project goal, the following scientific and technological objectives should be addressed:

1. Develop a solution-based process of producing thin CIGS layers free of carbon, metal oxides and other impurity phases.
2. Investigate the influence of different deposition parameters on morphology, composition, and grain structure of the CIGS layers in order to obtain a suitable absorber.
3. Demonstrate the potential of the novel absorber deposition process by developing CIGS solar cells on $5x5cm^2$ glass substrates.
4. Prepare a research roadmap for the European Consortium project with industrial participation.

The concept is based on a previous success of the Thin Film Physics group at ETHZ in developing 4-6% efficient solar cells using paste coating a solution with inorganic salts. The developed process has shown two bottlenecks, namely a limited CIGS thickness insufficient for complete absorption of solar spectrum and a residual organic layer at the CIGS/back contact interface.

Two alternative solution-based approaches are explored in the present project in order to diminish or completely avoid the parasitic carbon layer:

Approach I. Ion exchange method

The innovative process (patent is pending) to grow CIGS absorber layer consists of the diffusion of Cu+ ions from a solution into an $(In,Ga)_2Se_3$ precursor layer and subsequent thermal annealing in an inert or Se containing atmosphere to produce CIGS layers [5-7]. This process completely avoids the formation of the carbon layer because no organic binder material is used to deposit the $(In,Ga)_2Se_3$ precursor.

The proposed ion exchange method has certain similarities with the vacuum-based 3-stage evaporation, where $(In,Ga)_2Se_3$ films are exposed to a flux of Cu and Se atoms at temperatures >540°C during the second stage, leading to the formation of $Cu(In,Ga)Se_2$ and Cu_2Se [8]. An alternative route to incorporate copper, which allows large-area non-vacuum processing, is to use copper ion exchange reactions at low temperatures (≤200°C). Most notable perhaps is the Clevite process used to make CdS/Cu_2S solar cells. In this process, Cu^+ ions in an aqueous solution of CuCl exchange places with Cd^{2+} ions in a CdS layer to form a surface layer of Cu_2S.

Further, the $(In,Ga)_2Se_3$ precursor can be deposited by non-vacuum methods like paste coating and spray pyrolysis. Advanced spraying techniques with high material utilization and homogenous material deposition (e.g. ultrasonic spraying) can be applied. This technique was successfully tested for thin In_2S_3 buffer layers and resulted in good surface coverage and no pinhole formation.

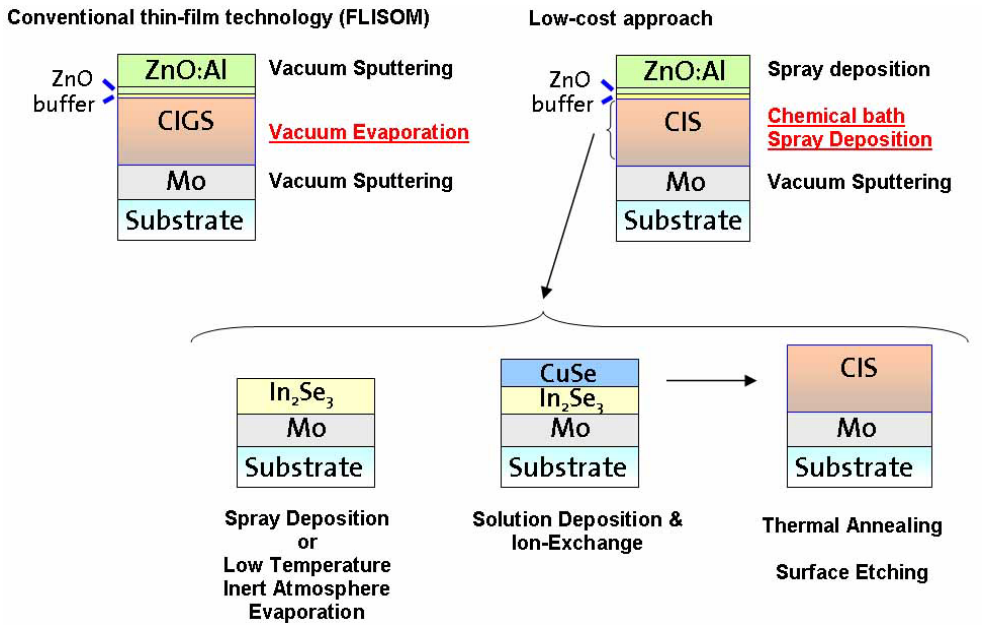

***Figure 1**: Schematic of the novel solution ion-exchange method (right) as compared to conventional vacuum evaporation (left). The CIGS solar cell structure is also shown*

Approach II. Paste coating with or without alternative binders

The methodology of this approach is the same as for earlier-developed coating of pastes containing inorganic salts and ethylcellulose as the binder material [4]. The paste is deposited on Mo-coated glass by doctor-blade technique, dried, and selenized in Se atmosphere (Fig. 2).

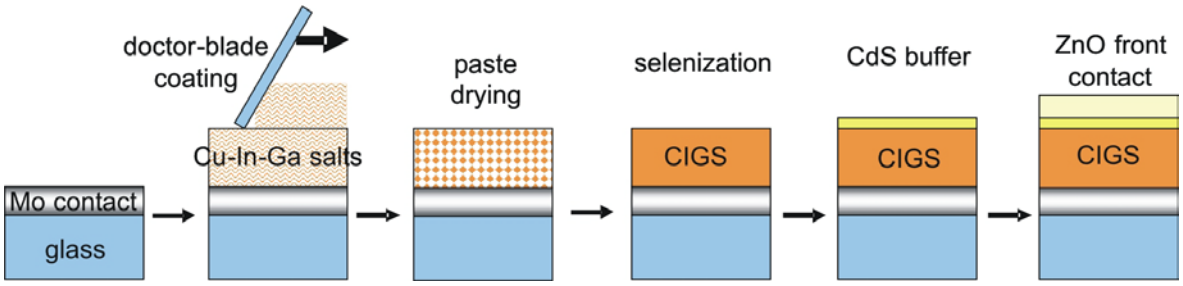

Figure 2: *Flow-chart of the CIGS solar cell fabrication with non-vacuum paste coating of CIGS layers.*

Several alternative solution-based recipes are explored in order to diminish or completely avoid the parasitic carbon layer. First, the precursor paste is applied onto a pre-deposited layer of selenium to induce the CIGS nucleation in the "bottom-up" approach. Second, an alternative organic binder, PMMA, is tested in view of its theoretically complete thermal degradation without char residues. Finally, solutions without organic binders or with alternative solvents, like carbon disulfide, are investigated.

3. Experimental

Deposition of precursor layers

Approach I. Ion exchange method. The Cu incorporation process was performed with $(In,Ga)_2Se_3$ (IGS) layers deposited onto 5x5cm^2 molybdenum-coated soda lime glass substrates. The Mo was deposited by DC sputtering and the IGS layers were deposited by co-evaporation of the elements. The In and Ga were evaporated from line sources, an excess of Se was provided from an effusion cell, and substrate temperature was maintained at 400°C. Throughout deposition the substrates moved back and forth over the line sources, 15 passes were typically required to deposit the ≈2 micron thick layers used in this work. Vacuum deposition was used to provide a high degree of control over the IGS layers, however, it would be desirable in future work to use a non-vacuum technique to deposit these layers.

Graded copper-indium-selenium precursor films were prepared by suspending the indium selenide layers in an aqueous solution of $CuSO_4$ (0.2M) and acetic acid (0.2M) for 1 hour. The acetic acid was required to prevent the formation of copper hydroxide precipitates. The solutions were stirred constantly and heated from room temperature to boiling point whilst the indium selenide films were immersed. After immersion in the copper solution the films were rinsed thoroughly in deionised water and dried.

Some disadvantageous aspects of the aqueous solutions could be eliminated by changing the solution chemistry of the ion-exchange process. Copper-indium-gallium-selenium precursor films were prepared by suspending indium gallium selenide layers in a cuprous ethylene glycol solution containing 0.6M CuCl and 1M NaCl. Using a high boiling point alcohol allows rising a reaction temperature up to 190°C. The relatively high concentration of NaCl is stabilising the solution and improving the solubility of the copper salt.

Approach II. Paste coating with or without alternative binders. Precursor pastes were prepared by dissolving appropriate quantities of copper nitrate hemipentahydrate, indium chloride and gallium nitrate hydrate in methanol for cellulose-containing pastes. In case of PMMA-containing pastes only chloride salts were used. The precursor composition is adjusted to a metal ratio Cu/In/Ga of 1/0.9/0.4 with a concentration of 1 mmol copper atoms per gram methanol. In parallel, a higher viscosity paste with organic binder is prepared: ethylcellulose (EC) or polymethylmethacrylate (PMMA) grains are dissolved in 1-pentanol or chloroform, respectively. The pastes are mixed in different weight ratios to yield a precursor paste with suitable rheology for doctor blade coating.

1-mm-thick soda-lime glass substrate of 5x5 cm^2 is coated with a 400-nm-thick molybdenum layer by conventional dc-sputtering. The spacers defining the distance between the blade

and the Mo-coated glass consisted of two stripes of scotch (approx. 50 μm thickness), applied on both sides of the substrate. In a one-pass movement, the precursor paste is evenly distributed on the substrate surface. The sample is then put on a hotplate and heated to 80-480^{o}C for a few minutes to evaporate the alcohol and burn the organic binder.

Selenization

In order to fully convert the Cu-In-Ga precursor into the CIGS phase, the samples prepared by two approaches were annealed in a tubular two-temperature zone selenization reactor. A continuous flux of nitrogen carries the evaporated selenium from the first temperature zone to the sample in the reaction zone. The sample temperature is ramped up to 560-600 ^{o}C and held there for 10 min, whereas the selenium source is held at a temperature of ~400 ^{o}C during selenization.

Cell processing

Solar cells were processed by applying a 50 nm CdS layer by conventional chemical bath deposition and an i-ZnO/ZnO:Al transparent front contact by rf-sputtering.

Characterization

The resulting CIGS layers are investigated by optical microscopy, Stylus profilometry, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray fluorescence spectroscopy (XRF), Raman spectroscopy, secondary ion mass-spectroscopy (SIMS), and X-ray diffraction measurements (XRD). The solar cell performance is evaluated by measureing current–voltage (IV) characteristics under simulated AM1.5 conditions and external quantum efficiency (QE) measurements.

4. Results and Discussions

Approach I. Ion exchange method

Ion exchange in aqueous solutions [5]

During immersion in the copper solution the Mo exposed around the border of the samples was removed from the substrate. This is due to oxidation of the Mo into soluble molybdenum oxide. When viewed through the substrate glass, it was evident that areas of the Mo underneath the In_2Se_3 had been removed as well. This is thought to be due to pin holes in the In_2Se_3 layers allowing contact of the solution and Mo. This degradation of the back contact limited the thickness of the In_2Se_3 layers into which relevant quantities of copper could be incorporated.

Substrate	Cu	In	Se
Glass	0.5	45.1	54.4
FTO/Glass	1.2	43.5	55.3
ITO/Glass	0.8	43.7	55.5
Glass (Mo in bath)	5.7	38.0	56.3
Mo/Glass	26.1	28.5	45.4

***Table 1**: Composition of resulting layers after immersion of In_2Se_3 layers on various substrate materials into the copper solution. Sufficient copper incorporation was only obtained for substrate materials containing a molybdenum layer.*

When In_2Se_3 layers deposited onto bare soda lime glasses were immersed in the copper solution no ion-exchange reaction occurred and the composition and appearance of the films remained unchanged (to within the accuracy of the EDX measurements). The same was true for In_2Se_3 layers deposited onto FTO/glass and ITO/glass substrates. When a small piece of Mo/glass was included into the bath, limited incorporation of Cu into the In_2Se_3 layer was observed (Table 1).

XRD diffractograms are displayed in Figure 3 for samples at three stages of processing. All peaks in the as deposited In_2Se_3 precursor layer were indexed to the JCPDS files 40-1407 (hexagonal γ-In_2Se_3), 71-0250 (hexagonal In_2Se_3, calculated) and 42-1120 (Mo). After immersion in the copper solution the In_2Se_3 peaks weaken in intensity (relative to the Mo (110) peak). Two additional peaks are present in the diffractogram at this stage, one at 26.8° and the other at 44.5°. Both of these peaks are associated with fcc β-$Cu_{2-x}Se$. The formation of copper selenide with copper in its monovalent state requires that another species in the bath is oxidised. The dependence of the ion-exchange process on the presence of Mo in the bath suggests that the reduction of Cu^{2+} ions to Cu^{+} is performed by oxidation of Mo.

After selenization, all peaks were indexed to JCPDS file 40-1487 ($CuInSe_2$). The chalcopyrite peaks (101), (103), (211) and (105/213) are all observed. No significant preferred orientation is calculated from the XRD diffractogram of the selenized sample. There is no evidence of secondary oxide or selenide phases in the diffractogram.

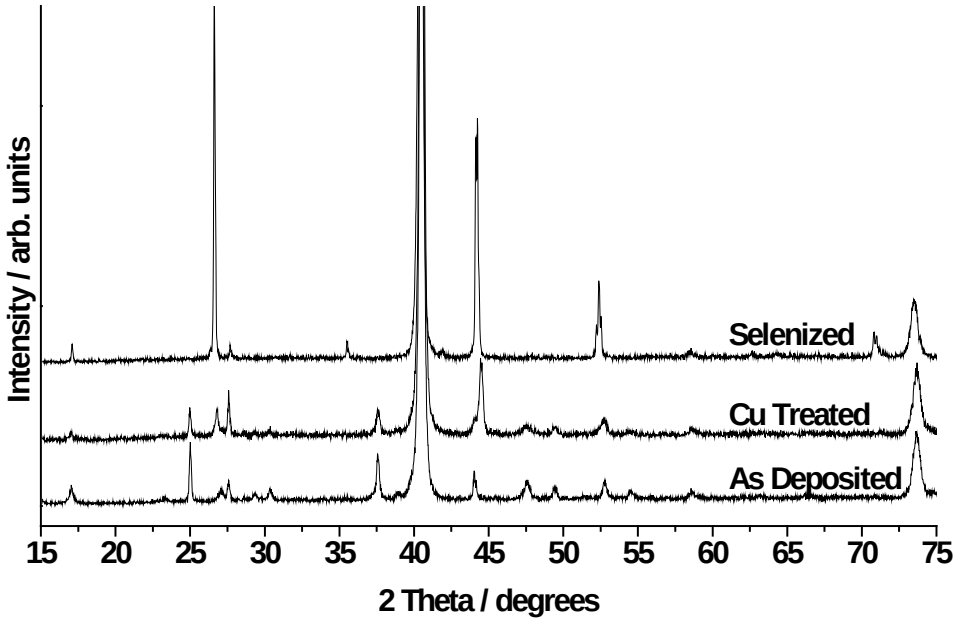

Figure 3: *XRD patterns of an as deposited In_2Se_3 layer, an In_2Se_3 layer after copper in-diffusion and the same layer after the heat treatment in selenium atmosphere (selenization) showing the formed phases after each process sequence.*

XPS measurements on the copper-treated sample showed that it had a graded composition, with highest Cu concentration corresponding to minimum In concentration (Fig. 4). The Se concentration decreases within the copper containing section of the layer and this is consistent with the formation of $Cu_{2-x}Se$ as it has a higher metal-to-chalcogen ratio than In_2Se_3. The depth profile of the Selenized sample is broadly homogenised, though a slight increase in the concentration of indium throughout the depth of the sample is observed. EDX measurements on this selenized sample indicated a Cu:In:Se composition of 21.3:30.9:47.8 at%.

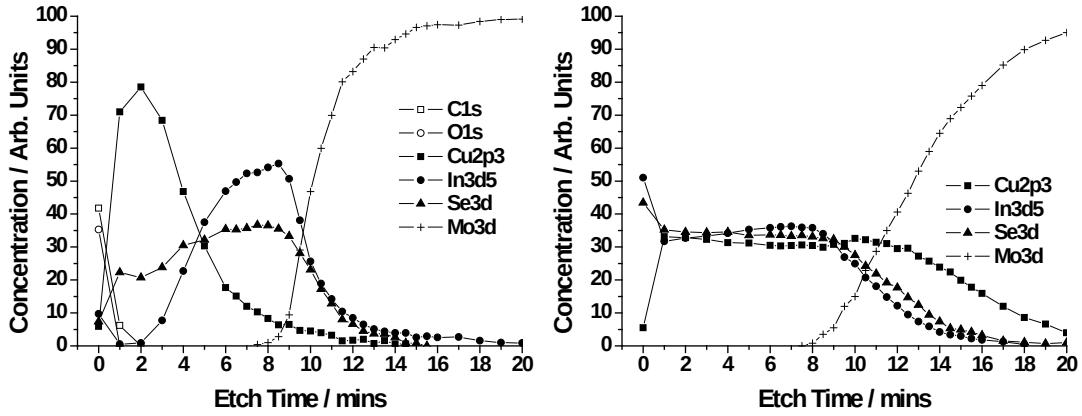

Figure 4: *XPS depth profiles of a copper in-diffused In_2Se_3 layer before (left) and after (right) the heat treatment in selenium atmosphere.*

Solar cells processed from selenized precursor films have so far exhibited efficiencies of up to 4%. The I-V curve of a solar cell processed from a selenized layer with a Cu:In:Se composition of 20.6:32.6:46.8 at% is shown in Figure 5. Relative to high-performance co-evaporated $CuInSe_2$ solar cells, these cells exhibit low open circuit voltages and fill factors.

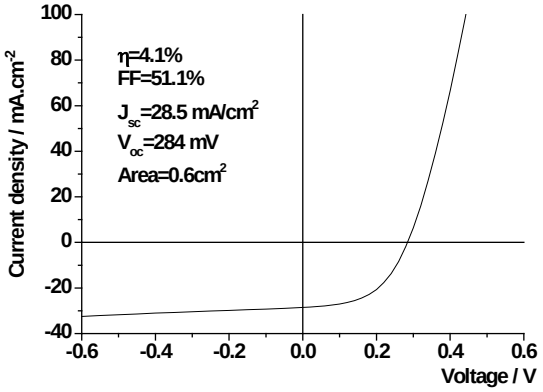

Figure 5*: I-V curve of the CIGS solar cell prepared using ion exchange in aqueous solution.*

Ion exchange in ethylene glycole solutions [6, 7]

Corrosion of the Mo back contact prevented In_2Se_3 layers of the desired thickness from being successfully processed in the Cu solution and so alternative solutions were investigated to prevent the corrosion. Organic solvents were investigated as alternatives to water and ethylene glycol was found to be a good choice as it exhibits a high dissociation constant for CuCl and does not react with free Cu ions. In order to use solutions with a very large excess of Cu ions (so that the effective Cu content of the bath remained constant even after processing many films) whilst maintaining a controlled reaction speed, a complexant, NaCl, was added to the solution.

The higher temperatures during the ion-exchange reaction in the 2nd approach allow faster copper in-diffusion und therefore a shorter processing time (Fig. 6). The problems with dissolving uncovered molybdenum during the exchange reaction was not observed with the new solution.

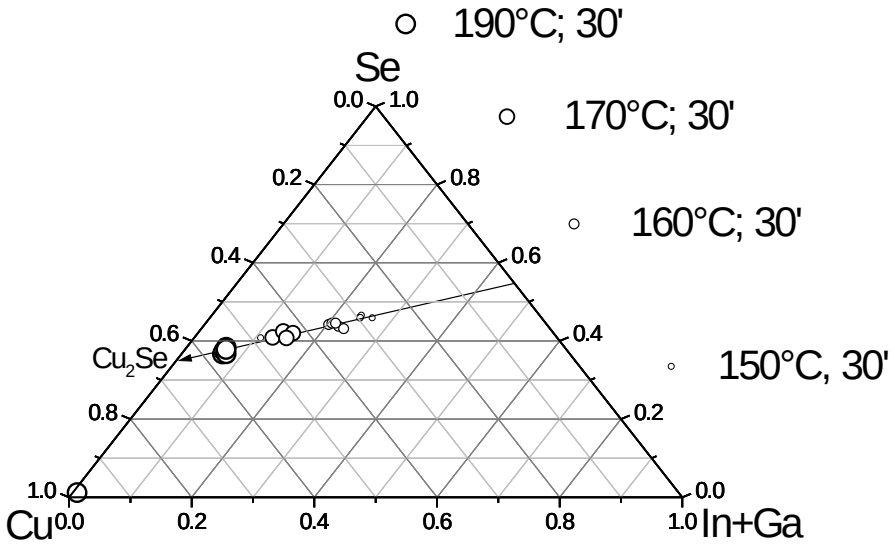

Figure 6: *Copper concentration in the (In, Ga)$_2$Se$_3$ precursor layer as a function of solution temperature during ion-exchange in ethylene glycole solution*

Morphology and depth profiles were then investigated by SEM and EDX measurements. Figure 7 shows that the ion exchange reaction does not change the initial morphology. In SEM images some agglomeration and definition of grain boundaries can be seen. The EDX measurements again confirm that the copper concentration is higher near the layer surface.

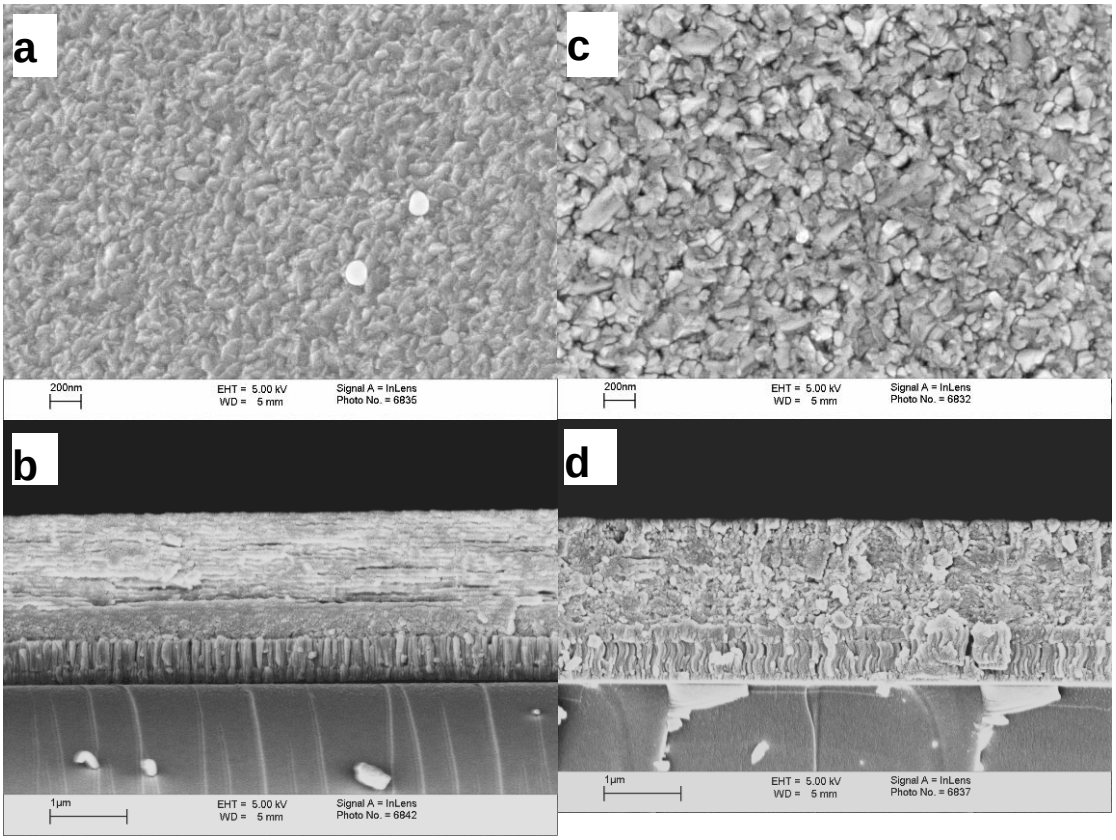

Figure 7: *SEM images showing the morphology and cross-section of the untreated (InGa)$_2$Se$_3$ substrate (a and b) and the Cu ion-exchanged layer (c and d).*

Depth profiles of layers at various stages of processing were studied by SIMS (Fig. 8). The composition of the as-deposited IGS layer (A) is homogeneous throughout its depth, however a regular oscillation in Ga/In signal strength ratio is observed. Since the number of oscillations corresponds to the number of passes that the substrates made back and forth across the sources, they are attributed to incomplete mixing of the In and Ga during deposition. The layer analyzed following Cu treatment (B) indicates that Cu is incorporated from the surface and that loss of In occurs in preference to loss of Ga, explaining the higher than expected Ga content in the annealed CIGS layers. The fact that Ga-Se compounds have greater enthalpies of formation than their In-Se analogues is a possible explanation for Cu ions exchanging more rapidly for In ions than Ga ions. The depth profiles measured from the annealed layers, both with preheated Se source (C) and delayed Se supply (D) indicate broadly homogenised depth profiles. However, in both cases there is a decrease in Ga signal towards the front of the layer which is slightly more pronounced for the layer annealed with delayed Se supply.

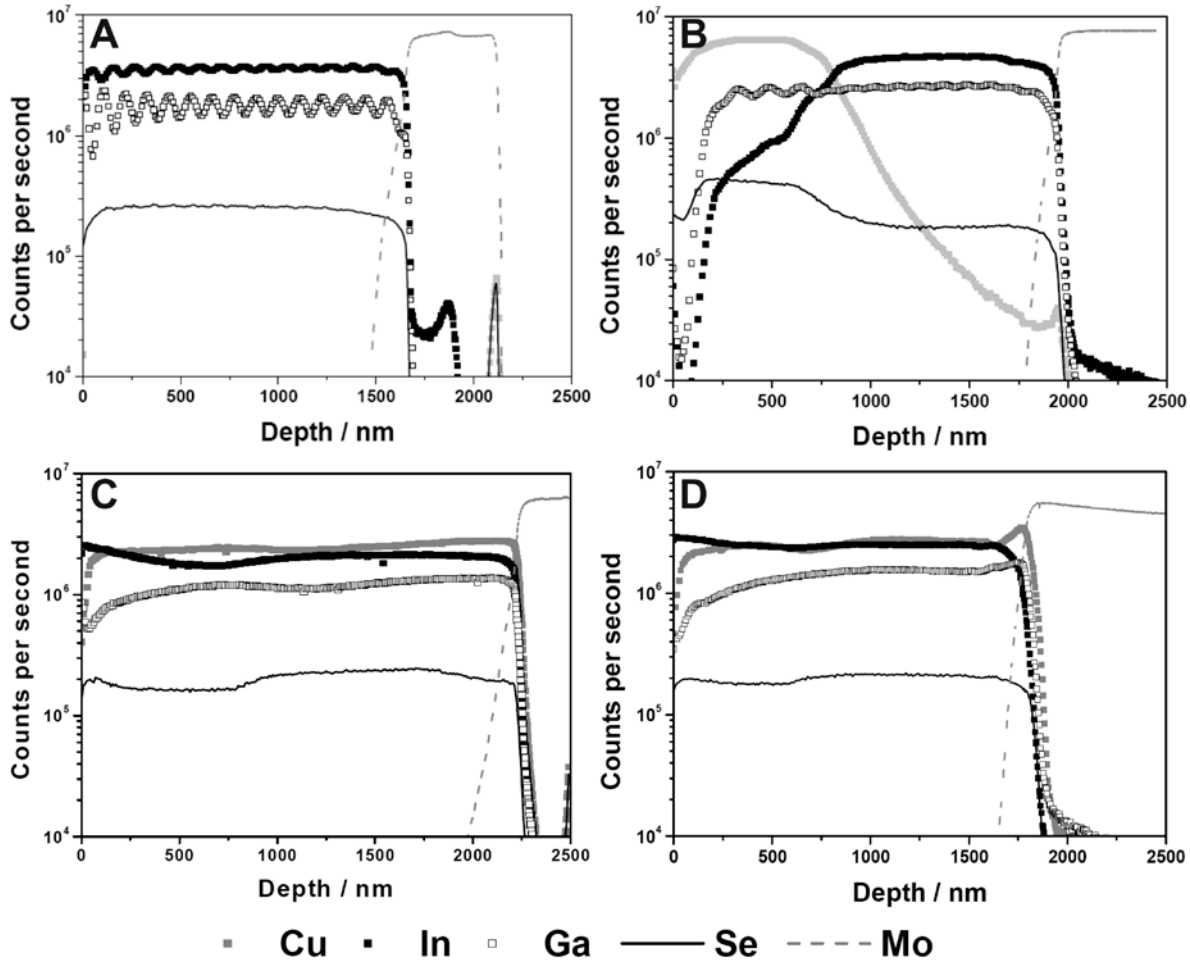

Figure 8: *SIMS depth profiles of as-deposited IGS (A), Cu-treated IGS (B) and layers annealed at 575°C with Se supplied throughout the entire annealing process (C) and only once substrate temperature reached ≈400°C (D). Oscillation in the In and Ga signals in A and B result from substrate movement during precursor deposition.*

After selenization the crystal structure recrystallizes and forms large grains. Generally InGaSe matrices have a defect wurtzit structure which during the annealing should be converted into the chalcopyrite CIGS phase. The phase transformation allows for a complete change of the morphology and grain structure. Figure 9 presents cross sectional and surface images of ion-exchanged and annealed CIGS thin films. The cross sections depicted here is a complete solar cell.

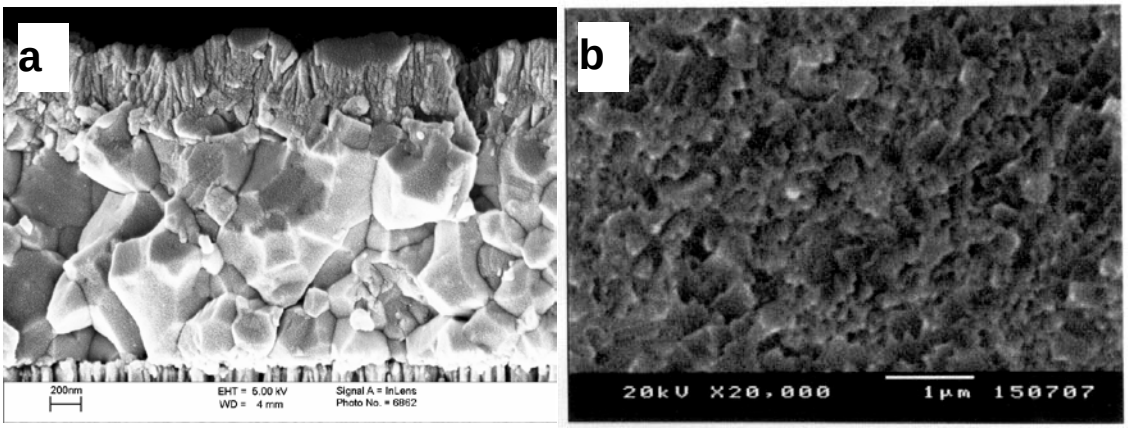

Figure 9: *SEM images showing the cross-section and morphology of the selenized layers which formed large grains during the annealing.*

Solar cells made by the 2nd approach of chemical copper incorporation treatments resulted in efficiencies of up to 3.5%. Even though the 2nd approach is more reliable than the 1st approach, the performance of the solar cells could not be improved yet. This may be due to the non-optimal interface region between the CIGS and buffer layer. Although the layers present a good cross-section structure, the CIGS surface shows a small grained pattern which is unusual for CIGS layers. Further the selenization conditions used have not evenly distributed the copper concentration in the layer depth. Having a copper poor bottom layer is not beneficial for forming efficient absorber layers.

Approach II. Paste coating with or without alternative binders

Baseline experiment with cellulose binder

In order to reproduce the previous "state-of-art" experiments, a series of 20-25 samples were prepared using EC as the organic binder and solar cells were processed. Within a short term an efficiency of 4% was achieved (Fig. 10a). As expected, the residual carbon layer is visible between the CIGS layer and Mo contact (Fig. 10b).

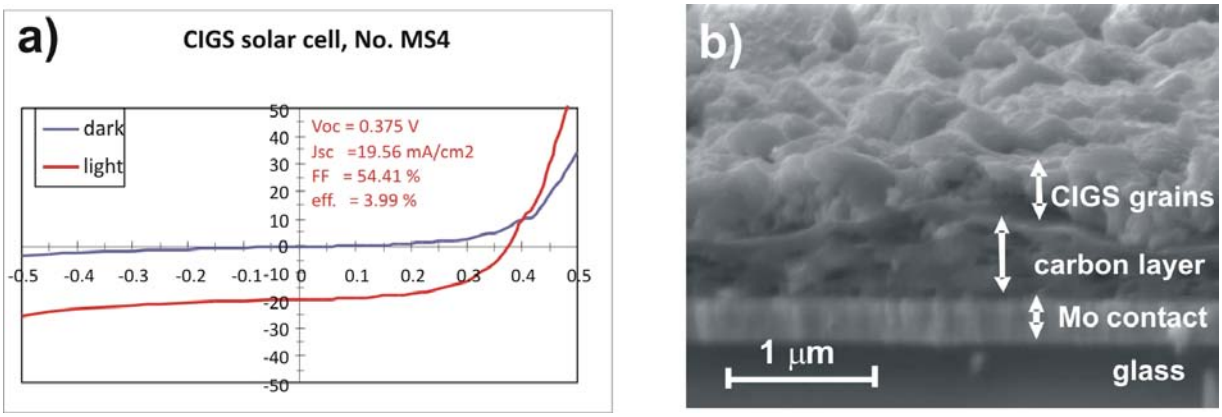

Figure 10: *(a) I-V curve of a "baseline" CIGS solar cell prepared by doctor-blading the paste with EC binder. (b) SEM picture with cross-section of the "baseline" solar cells.*

Using a pre-deposited Se layer

It is worth noting that despite its undesirable formation, the carbon layer apparently forms a quasi-ohmic contact to CIGS and serves as charge collecting contact together with Mo. Additionally, the EC matrix protects the Cu, In and Ga from oxidation and hydration during pre-heating step on a hot plate [4].

In order to (i) employ useful properties of EC binder and (ii) avoid the presence of the carbon residue at the CIGS-Mo interface, an option of paste coating on Se-on-Mo substrate was tested. Three Mo-glass substrates were covered with a thin, 0.5-1.7 μm, layer of elemental Selenium. Then the EC-containing paste was applied and heated at 180-330^{o}C. This induces the preferential nucleation of CIGS grains but not the carbon layer at the CIGS/Mo interface (Fig. 11a). By allowing sufficient time on a heating plate, a complete consumption of the SE layer can be achieved and all paste is converted into CIGS phase (Fig. 11b). In all cases, the resulting CIGS layer was, however, very porous and not suitable for solar cell processing. Moreover, severe cracking of the paste was observed during all experiments, triggered by high vapor pressure of Se and thermal expansion mismatch.

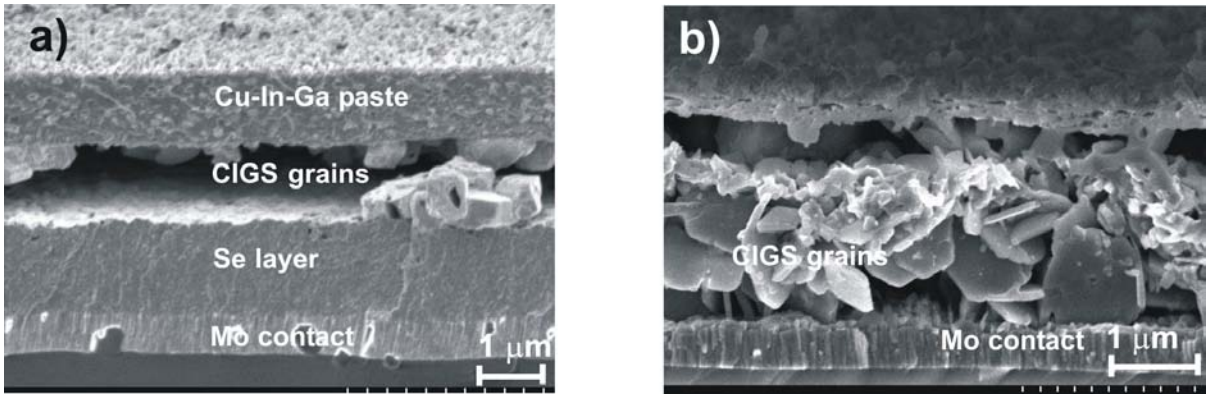

Figure 11: *SEM pictures of CIGS pastes applied onto Se layer on Mo-coated glass and pre-heated at 330^{o}C for 1 minute (a) and 15 minutes (b). The complete consumption of selenium layer is observed in (b) and no intermediate carbon layer is formed although the CIGS layer is not compact.*

Poly(methyl methacrylate) (PMMA) as binder

PMMA was tested as an alternative binder material, which theoretically should leave no char residues upon thermal degradation at temperature higher than 350 ^{o}C. In this case the paste was prepared by dissolving PMMA in chloroform (CH) and then mixing it in different ratio with methanol solution of inorganic salts. The pastes with lower content of PMMA yielded uniform doctor-bladed pastes, comparable to EC-containing ones (Fig. 12).

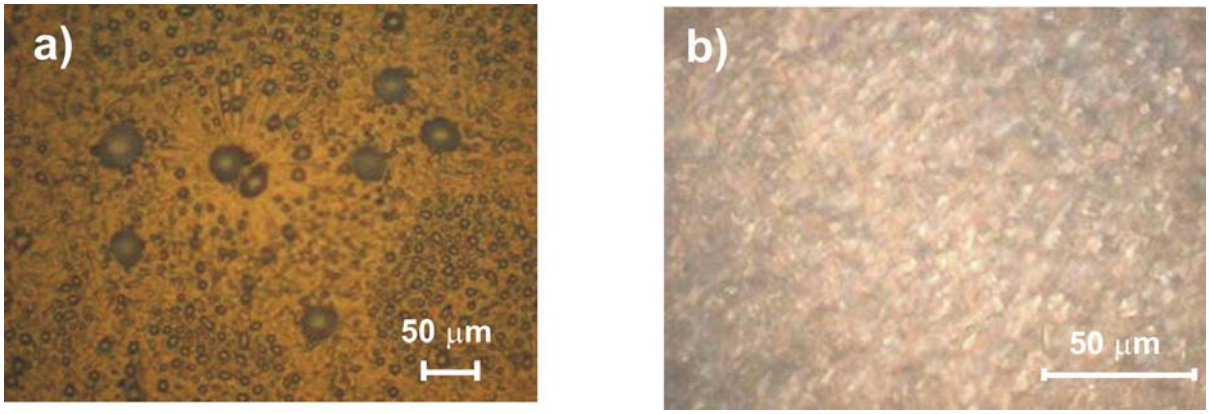

Figure 12*: Optical pictures of doctor-bladed pastes containing (a) 80% of PMMA in CH and (b) 25% of PMMA in CH. Paste (a) is not uniform and exhibits needles of crystallized CuCl. Paste (b) has higher methanol content and is more homogeneous.*

The selenization of as-coated and preheated pastes produced CIGS-containing layers. The amount of carbon in the final layer was reduced but not entirely. The CIGS grains formed on top of the organic matrix during selenization prevent the complete evaporation of the PMMA. In addition, the increased evaporation of organic matrix gives rise to increased porosity of the layer and no sufficient electrical contact to the Mo back contact is formed (Fig. 13). Grains on

top are CIGS as confirmed by XRD (Fig. 13b), as well as several parasitic phases, in particular indium oxide, were also detected.

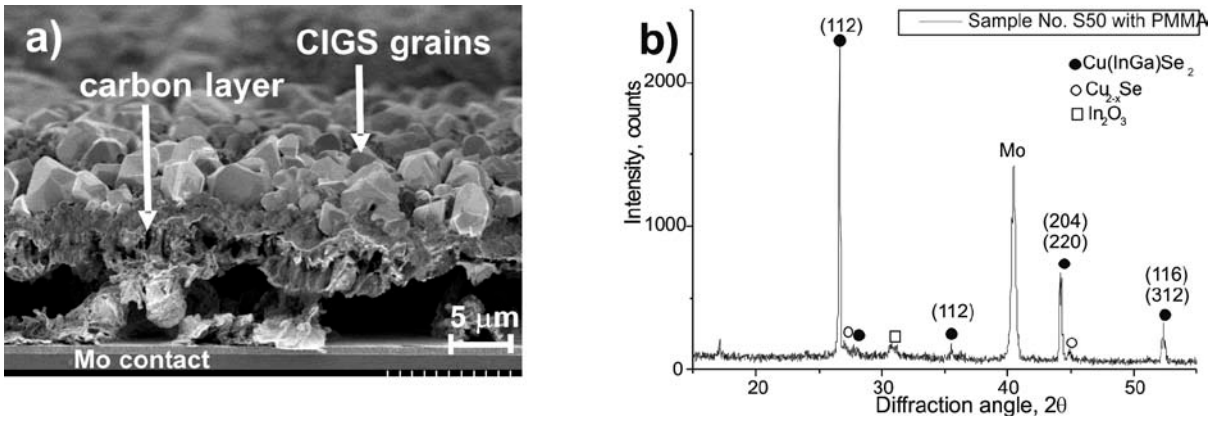

Figure 13: *(a) SEM picture of selenized PMMA paste. (b) XRD of the obtained CIGS layer.*

Experiments without organic binder

In order to completely avoid the formation of the carbon layer, pastes without organic binders were prepared. A quite dense layer with local inclusions of big CIGS grains was produced (Fig. 14). Although doctor-bladed layers were non-uniform because of high surface tension and low viscosity of methanol solutions, no residual carbon layer was spotted at CIGS/Mo interface.

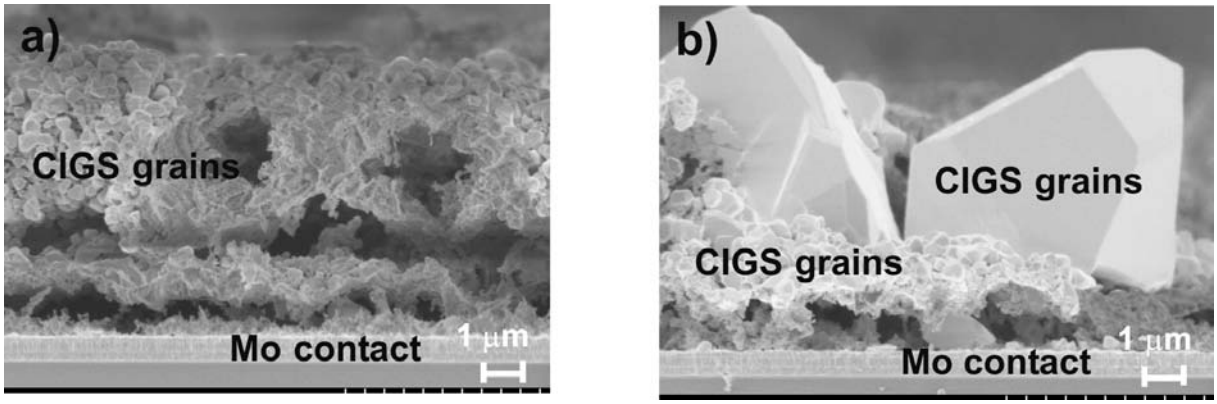

Figure 14: *SEM pictures of CIGS layers produced from binder-free pastes. The layer is generally porous (a) and some big lump grains of CIGS are often formed.*

5. Conclusions

Two different solution-based approaches have been investigated in view of developing a non-vacuum low-cost deposition of CIGS layers for thin film solar cells. The first approach considers incorporation of Cu into In_2Se_3 or $(In,Ga)_2Se_3$ precursor layers by ion-exchange from aqueous or organic solutions. The second approach involves paste coating of Cu,In, and Ga-containing salt solution mixed with appropriate organic binder. The principal research findings are summarized as follows:

- The ion exchange approach results in thin films with a graded composition containing the crystalline phases β-$Cu_{2-x}Se$ and γ-In_2Se_3. Annealing the films in selenium atmosphere forms chalcopyrite $CuInSe_2$ and homogenised the depth profile of the films. Solar cells processed from selenized precursor films exhibit efficiencies of up to 4.1%. The use of aqueous solutions is, however, destructive to the Mo back contact and attempts to use alternative contacts resulted in no incorporation of Cu into the

In_2Se_3 films. The corrosion problems can be solved by using ethylene glycole solutions, also ensuring higher ion-exchange rates. Even though the organic solution recipe gives reproducible Cu incorporation, respective solar cell efficiencies are limited to 3.5%, probably because of the non-optimal interface between CIGS and CdS.

- Paste coating is a convenient one-step approach to deposition the Cu-In-Ga precursor, which is further annealed and selenized into the CIGS layer. Organic binder material serves to obtain suitable paste rheology and also protects the metal species from oxidation. Ethyl cellulose as binder yields solar cells with of 4% efficiency and the residual carbon layer between CIGS and Mo is formed. Preferential nucleation of CIGS layer instead of carbon layer can be promoted by using a pre-deposited layer of selenium although the resulting layers are porous. PMMA can be used as the alternative binder, where more complete evaporation of the organic matrix is achieved but parasitic oxide phases and evaporation of In and Ga salts are observed. Non-binder solutions produce almost carbon-free pastes although the layers are non-uniform because of high surface tension and low viscosity of alcohol solutions. Further improvement should be possible using more viscous solvents and amine-based complexing agents to diminish oxide formation.

A patent on the ion-exchange method has been formulated together with a specialised patent attorney and was filed (PCT application number PCT/EP1007/059422). The response of the patent agency has been received, indicating that most of the proposed ideas are novel indeed although a further administrative processing is required to finalize the patent filling.

6. National and international collaboration

Thanks to the valuable research results obtained during this project, the LTPV group at Empa has been qualified to participate in the EU FP7 project “NOn-Vacuum processes for deposition of CI(G)S active layer in PV cells (NOVA-CIGS)”, Project Nr. 228743, starting 01.01.2010. The project involves 8 partners (Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Flisom AG, Corus, Pemco, Würth Solar GmbH & Co (WS), EMPA, TNO, WUT) from 5 European countries, which will work together on developing non-vacuum processes for CIGS deposition.

The Solaronix SA company based near Lausanne and specialized in novel thin-film solar cells participated in “baseline” experiments and provided Mo- and FTO-coated substrates. Solaronix is interested in further investigation of this CIGS fabrication method.

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