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Flexible CIGS solar cells on large area polymer foils with in-line deposition methods and application of alternative back contacts

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The contents and conclusions expressed in this report are those solely of the author.

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Abstract

This project progress report summarises the work performed within this project and also in synergy with other projects that helped to make a significant contribution to the development of $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells on flexible substrates such as polymer foils. The project aim was to learn about the up-scaling issues and demonstrate our ability for processing of layers on large area (up to 30 x 30 cm^2) polyimide foils for flexible CIGS solar cells. The solar cell processing on large area substrate required deposition of Mo back contact by dc sputtering and and ZnO/ZnO:Al front contact by rf sputtering on in-line moving substrate. For deposition of CIGS layer on in-line moving substrate modifications were essential for obtaining uniform and controlled evaporation fluxes of In, Ga, Cu, Se elements evaporated from linear evaporation sources.

Custom-built evaporators were designed and constructed in-house; successive rounds of improvements in their construction were implemented after simulations and analysis of the uniformity of deposited layers and finding reasons of failure of the linear sources. Evaporators were tested in terms of evaporation profiles for uniformity of layer thickness and composition across the substrate area. A set of linear evaporators were configured for deposition on in-line moving substrates. Reasonable homogeneity of deposited layers was obtained over a substrate width of at least 25 cm. However, because of the limited size of the vacuum chamber it was not possible to arrange the evaporation sources for optimum growth of CIGS and there was no space available for integrating Na source in the chamber.

The chemical bath deposition (CBD) equipment for CdS layer was designed for large area substrates. The construction of the CBD reactor was designed for minimal wastage of chemicals/solvents by confining the chemical solution in a small volume reactor. A commercial system was not affordable because of the high price; therefore a simple home-made reactor and rocking mechanism for solution intermixing were constructed in-house. Engineering of the substrate heating, rocking mechanism for intermixing and uniform solution movement across the large area substrate provided reasonably uniform layers CdS layers, but not of enough satisfactory quality on flexible foils. Solution chemistry (concentration ratios of constituents) was modified to overcome the problems of particulate deposition and non-uniform precipitation in the rocking reactor.

The CIGS system for in-line deposition was modified also for roll-to-roll deposition in a collaborative effort. Tests were performed to assess which CIGS process can be implemented best considering the limitations of small vacuum chamber. CIGS depositions were made on several meter long rolls using roll-to-roll deposition but because of non-availability of ZnO/ZnO:Al sputtering system it was not possible to deposit TCO front contact layers on large (30x30 cm^2) size substrates. Therefore front electrical contacts were grown in a sputtering system where maximum substrate size is limited to 5x5 cm^2 only. Samples of CIGS/Mo/polyimide were cut off from the web and then solar cells with the standard structure were completed.

The composition ratio of CIGS obtained depends on growth conditions and the recipes used. Using CIGS layers (without Na doping) coated in a roll-to-roll system provided up to 8% efficiency (V_{OC}=439mV, J_{SC}=29.5mA/cm^2, FF=61.9%) solar cell. These solar cells have lower efficiencies compared to our high efficiency cells of 10-14% achieved with static methods because of absence of Na in CIGS. It is known that Na incorporation in CIGS improves the efficiency significantly mostly caused by increase in Voc and FF.

Alternative electrical back contacts to conventional Mo were evaluated on flexible polyimide foils. Preferred materials were transparent conducting oxides (ITO) and metal-nitrides covered with a thin buffer

layer facilitating tunneling of carriers across the CIGS-back contact interface. The deposition processes were developed and properties of layers and interfaces were investigated. For the first time bifacial flexible CIGS solar cells were developed. Flexible solar cells of 12% were achieved where both, the front and back electrical contacts are based on transparent conducting oxide layers.

In order to overcome the well known problems of the conventional Mo back contact, efforts were made to employ Ti/TiN as an alternative back contact because of several attractive features of this system, especially for flexible substrates. The R&D work for feasibility study was performed in collaboration with two companies in Switzerland and the encouraging results (13.1% efficiency) gave rise to the initiation of a CTI project “Multifunctional back electrical contact for flexible thin film solar cells” started in June 2009.

1. Objectives

One objective of the project, as stated in the proposal that time, is to improve the CIGS vacuum deposition equipment as well as the CdS chemical bath deposition equipment to develop solar cells on large area substrates and optimise a process for high efficiency and reliability. It is difficult to predict the efficiency potential of the in-house developed equipment but our endeavour will be towards 12% efficiency cells on in-line moving polyimide foils. This efficiency target is somewhat lower than our own world record of 14.1% achieved on a “small static deposition” equipment, but the 12% efficiency target is still higher than the current state of the art of worldwide competing groups on this topic.

The second objective is to develop high efficiency flexible CIGS solar cells on polyimide foils coated with alternative electrical back contacts for CIGS instead of the well established Mo layers. There is three-fold motivation behind the development of flexible CIGS solar cells using alternative materials such as transparent conducting oxides as back contact:

i) to overcome the performance instability problem associated with the oxidation of conventional Mo layer;

ii) to provide multi-functionality in solar cell and for futuristic multi-junction (tandem) solar cells;

iii) to reduce the thickness of the CIGS absorber by applying back contacts with higher reflectivity than of Mo layer.

Successful development of highly efficient CIGS solar cells may solve the problems of degradation of the back contact in moisture, micro-cracking and de-lamination, especially in flexible cells, and open further possibilities for device engineering.

2. Results

Improvements of in-house developed evaporation sources

A typical CIGS deposition system in research labs is configured with a rotatable substrate holder at a fixed position and point sources (effusion cells) for evaporation of Cu, In, Ga, Se elements for CIGS compound formation and a NaF evaporation sources for addition of Na in CIGS. Such a deposition system called “static deposition system”, shown in figure 1 is suitable for small area substrates (5x5 cm^2 in our case). However for large area deposition, in-line moving substrates and long boat shaped evaporation sources are required. The evaporation source could be a series of point sources (effusion cells), or a linear evaporator with number of small openings (orifice for effusion), or a linear source with a linear long slit for evaporation of materials (figure 2).

Typical point evaporation source profiles lead to substantially reduced layer thickness towards the edges of the deposition zone. This becomes very critical for large area substrates and therefore new configurations of evaporators have to be developed for homogeneous material deposition and layer thicknesses. Therefore linear evaporators were designed and used to improve the evaporation profiles in the deposition zone.

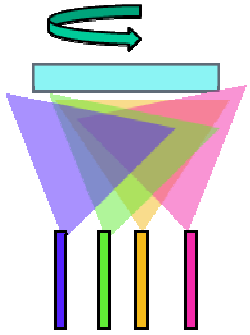


Figure1: CIGS deposition system with point sources (effusion cells) for thermal evaporation of Cu, In, Ga, Se, NaF, suitable for small area substrates in lab. Substrate at a fixed position with respect to the evaporation sources, however substrate rotation can be applied for better uniformity.

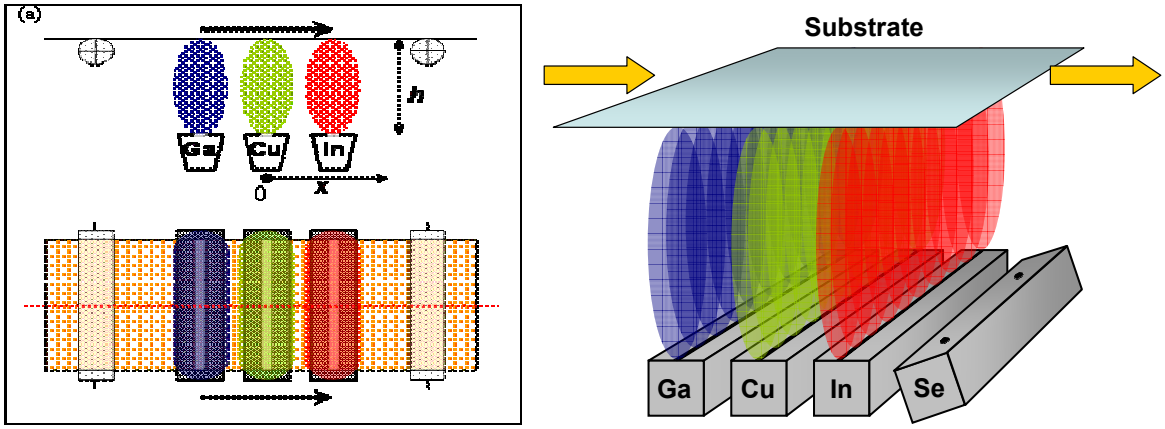


Figure 2: Schematics of a CIGS deposition system with linear evaporators and in-line moving substrate showing configurations in top-view (upper) and side-view (lower) in the left side figure (a). The linear evaporator can consist of a number of point sources or long slit for overlapping evaporation fluxes on moving substrate (right side figure).

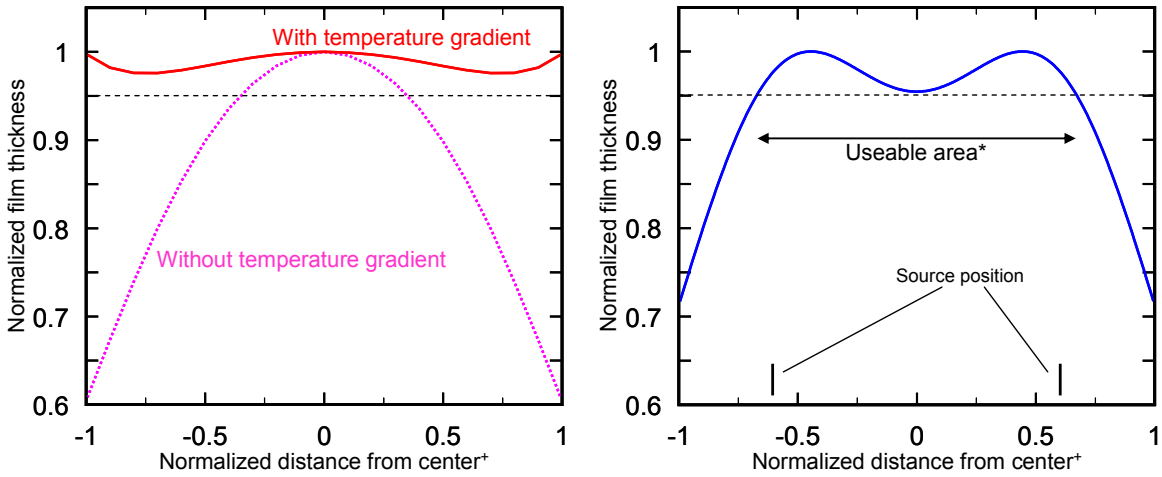


Figure 3: Simulations showing thickness uniformity and variations for three specific configurations.

Figure 3 shows results of simulated thickness uniformity proving guidelines for designing of the evaporators. Line source can be designed to offer excellent homogeneity of film thickness and a high utilization of materials (possibility of the short distance from sources to substrate), but their design and construction is difficult in view of control of the source temperature and heating arrangement. Point source offer simplicity of the design, construction and the temperature control but with limited area of uniformity and low utilization of materials.

Figure 4 shows the results of a successful source design for selenium evaporation. Se layer was deposited on 30x30 cm^2 size substrate and thickness measurements at various positions in the deposition zone (25 cm, to exclude for the edge effects) were recorded; corresponding points lying on the same line perpendicular to the substrate movement direction were linked to display the evaporation profiles in this direction. The flatness of the lines expresses homogeneous deposition thickness. For CIGS growth selenium is normally evaporated in excess than actually required in the CIGS layer to account for its relatively low sticking coefficient. Similar thickness profiles were recorded for the other evaporated materials. As described below we show the elemental uniformity of the CIGS components (see figure 5) where a slightly selenium deficient layer was grown to prove a homogeneous selenium incorporation achieved with an optimized selenium evaporator.

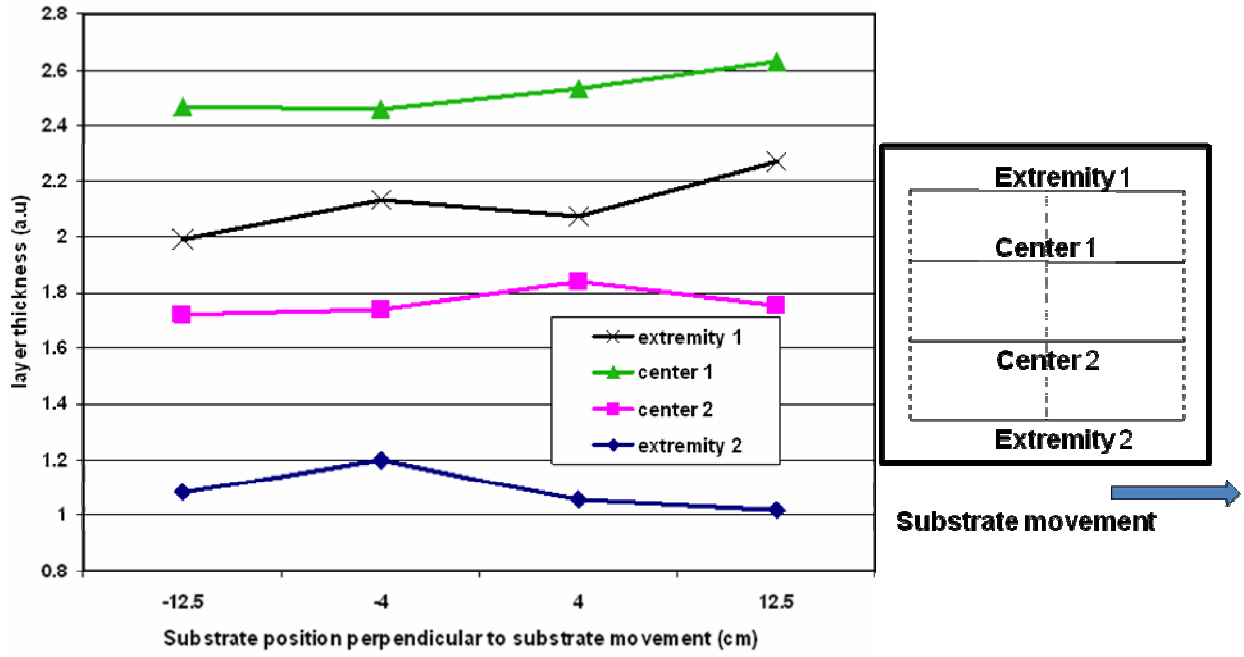


Figure 4: Selenium flux distribution perpendicular to substrate movement direction. Flat lines indicate a homogeneous flux profile over a distance of 25 cm in the width of the substrate. Each line represents a different position in the direction of the substrate movement. The highest flux of selenium is obtained near the centre of the deposition zone where at the same time the metals are deposited to form the CIGS compound. Se source is not in-line with the metal sources, but is tilted along an axis.

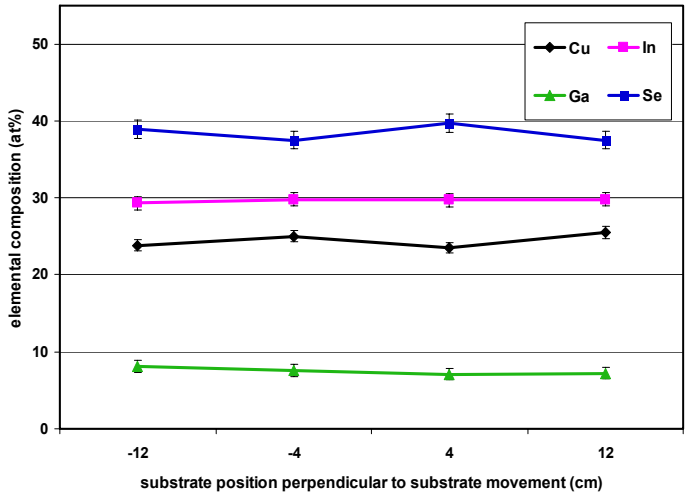


Figure 5: Elemental distribution over 25 cm long distance perpendicular to the in-line moving direction (refer to figure 2) as measured by energy dispersive X-Ray Analysis. Homogeneity across the deposition width is reasonably good taken into account the measurements accuracy of the EDX system.

Testing of thickness, chemical composition of CIGS layers grown on in-line moving substrates

For the testing of the chemical composition and thickness of the layers grown on in-line moving substrates the sample-holder was divided into several sections to accommodate large number of small area substrates so that thickness measurements could be measured. Thickness measurement profiles were analyzed after the CIGS deposition step. To test the suitability of the evaporation source the most interesting parameter is the compositional profile perpendicular to the substrate movement direction since the homogeneity in the direction of the moving substrate can be expected to be homogeneous (which was confirmed as well). Figure 5 presents a processed sample with a typical compositional distribution across the direction perpendicular to the substrate movement. As it can be seen, variations are rather small if the measurement accuracy of +-3% is taken into account.

Even though compositional homogeneity (ratio of constituent elements, e.g. Cu/[In+Ga]) is of prime importance, layer thickness also needs to be controlled over the width of the substrate and should not show differences of more than +-10%. The thickness profile is investigated by scribing (removing) fine lines of the CIGS layer and recording step sizes with a stylus profiler. Table 1 shows the measured layer thickness across the substrate width. All these measurements of composition with EDX and XRF, and thickness with stylus profiler were very much time consuming for measurements to plot the uniformity profiles over large area substrates.

Table 1: CIGS layer thickness measured over a distance of 25 cm perpendicular to substrate movement direction showing good thickness uniformity after improvement of the evaporation source profiles.

Distance from centreline (cm)	-12.5 cm	-4	4	12.5
Layer thickness(nm)	1500	1520	1570	1560

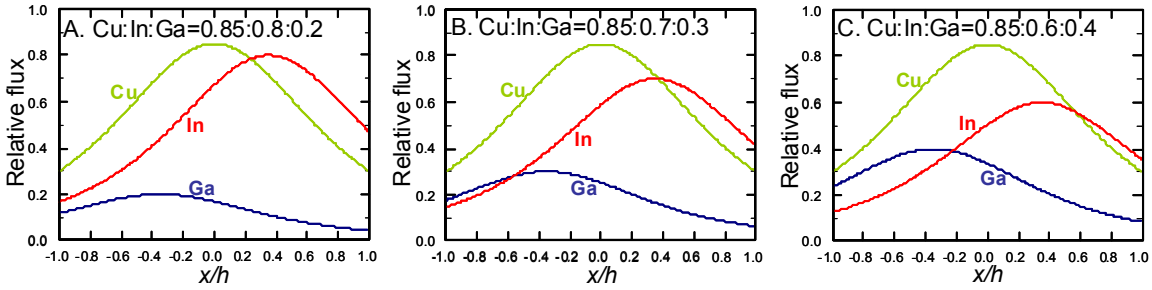


Figure 6: Elemental evaporation fluxes of Ga (blue), Cu (green), and In (red) depending on the spatial evaporation position for different final composition ratios of Cu:In:Ga in layer as marked A, B, C inside the figures. Only layers with [Ga]/[In+Ga]=0.3 or lower (figures marked A and B) go through a Cu-rich phase during growth. Here, x is the position in deposition zone with reference to the evaporation source location and h is the gap between the evaporation source and the substrate.

Evaporation profiles for CIGS deposition

During growth of the CIGS absorber layer the relative composition of Cu, In, and Ga can vary over a wide range. In order to achieve high quality CIGS and have reasonably large grains of about one micron, for this purpose it is desired that the growing layer goes through a Cu-rich composition during its complete growth, i.e. Cu/[In+Ga] > 1. The formation of CuxSe phase helps in achieving large grain. However after the growth of the CIGS layer the overall composition of CIGS should be Cu-deficient with respect to (Ga+In) concentration.

Depending on the setup of evaporation sources we have simulated the composition profiles of the layer formation for an in-line deposition process. Figure 6 shows a simple one dimensional simulation for relative thickness distribution by plotting the estimated flux rate, from Ga, Cu, and In sources. For this analysis, following equation, which is so-called cosine dependence of film thickness from surface source, is adapted.

$$\frac{d}{d_{max}} \propto \frac{1}{\left[1+(x/h)^2\right]^{1.5}} \qquad (1)$$

The main difference in figures A, B, C grouped together in figure 6 comes from different values of Ga ratio i.e. [Ga]/[In+Ga] included in the film. By varying the final Ga composition of the layer for constant Cu content, i.e. varying the [Ga]/[In+Ga], the film sees different possibilities for Cu-excess. Figure 6 shows the element/fluxes of Cu, Ga, and In for different final compositions. One can see that depending on the final Ga-content the film is going through a Cu-rich phase or not. For a Cu-rich growing phase a final composition equal or lower than [Ga]/[In+Ga]=0.3 is needed. This simulation also shows that one has to be careful when interpreting results of solar cells with different final composition since not only the bandgap changes because of different In:Ga ratio, but also the growing history and phase formation differs.

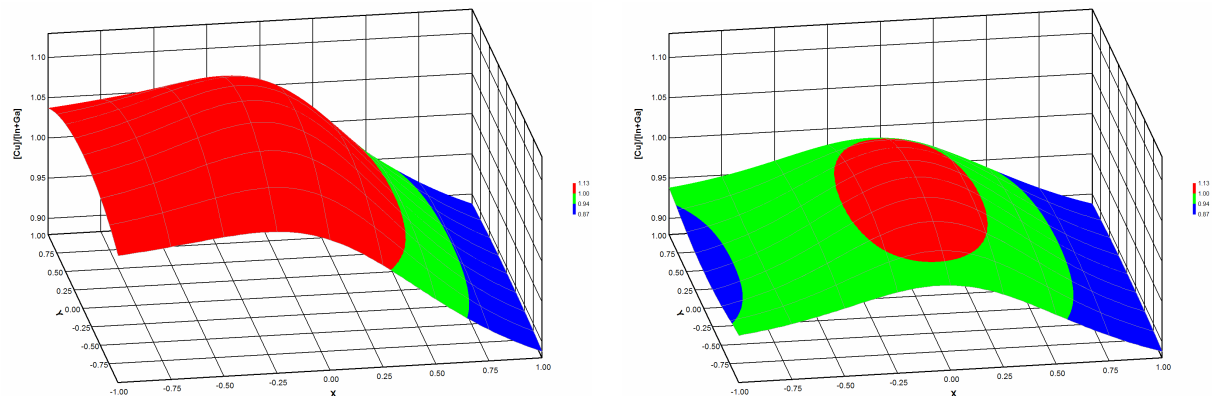


Figure 7: 2-dimentional simulations to analyse the Cu composition during an in-line process for a configuration of linear sources. Left is for Ga/[Ga+In]=0.2 and right is for Ga/[Ga+In]=0.3.

The composition homogeneity during the in-line deposition of CIGS on roll-to-roll system was investigated through two-dimensional 2D simulations for a specific configuration of evaporation sources and recipe. Figure 7 shows 2D analysis of history of Cu stoichiometry [Cu]/[In+Ga] during such a deposition process. For this analysis, Eq. (1) is extended to 2D. It should be noted that the temperature gradient of source was appropriately chosen to get uniform film thickness and composition for the simplicity. The red parts in figure 7 represent the Cu-excess film composition. For [Ga]/[In+Ga]=0.2, the composition of whole film starts from Cu-excess composition and then reaches Cu-poor device composition at the end. On the other hand, for [Ga]/[In+Ga]=0.3, not all film reaches Cu-excess composition. Therefore, concerning the history of Cu stoichiometry during the deposition process, [Ga]/[In+Ga]<0.3 could be more suitable for roll-to-roll deposition system.

In-line CIGS deposition system without Na incorporation treatment

It is well known that addition of Na in CIGS can increase the efficiency of flexible solar cells by more than 30-50%. We have also reported earlier that due to a post-deposition Na incorporation in CIGS layers the efficiency of low temperature grown CIGS cells increased from 7-9% to 12-14%. However, due to the limited size of the deposition equipment the sodium source could not be unfortunately incorporated in an appropriate manner. Being essential for high cell efficiencies a suitable solution remains to be found for the doping step in existing equipment otherwise a new deposition chamber with more space for incorporation of evaporators is required.

Development of an improved CdS chemical bath deposition system for 30 x 30 cm^2 foils

Up-scaling of the chemical bath deposition (CBD) step required a complete redesign of the deposition equipment in order to reduce the precursor concentrations per area of deposited layer. This is of special importance due to the usage of toxic Cd acetate solutions. The newly designed setup allowed a reduction of the precursor concentrations by a factor of ~10 while still yielding good surface coverage. This could be achieved by substantially reducing the contact area of the solution with parts other than the solar cell surface. A flexible heating system was installed and optimized to control the temperature during the deposition reaction.

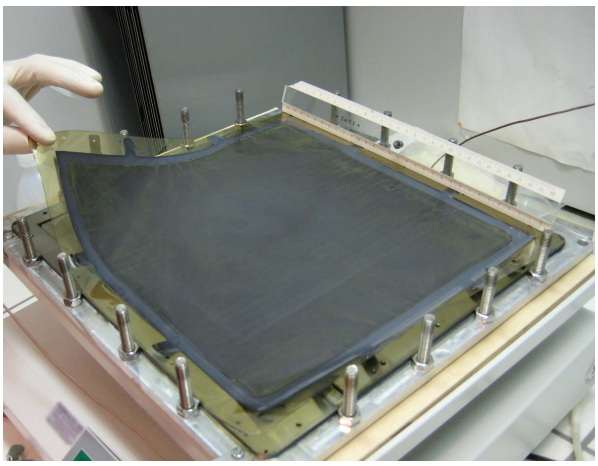


Figure 8: Large area solar cell covered with thin buffer layer. The buffer layer (~40nm) is deposited in a chemical bath where the reaction of the precursor leads to the formation of a homogenous thin layer on the absorber surface with excellent coverage.

Optimization of CdS CBD process in the system for 30 x 30 cm^2 foils

A further optimization of the deposition reaction was required to enhance the thickness homogeneity of CdS and to reduce particle generation which occur during the later stage as a precipitation of Cd(OH,S) particles. By modifying the concentration of precursor solution, adapting the movement speed for optimal solution mixing rate, and fine-tuning of the temperature control, homogenous CdS layers could be achieved on 25x25 cm^2 big surfaces (see figure 9)

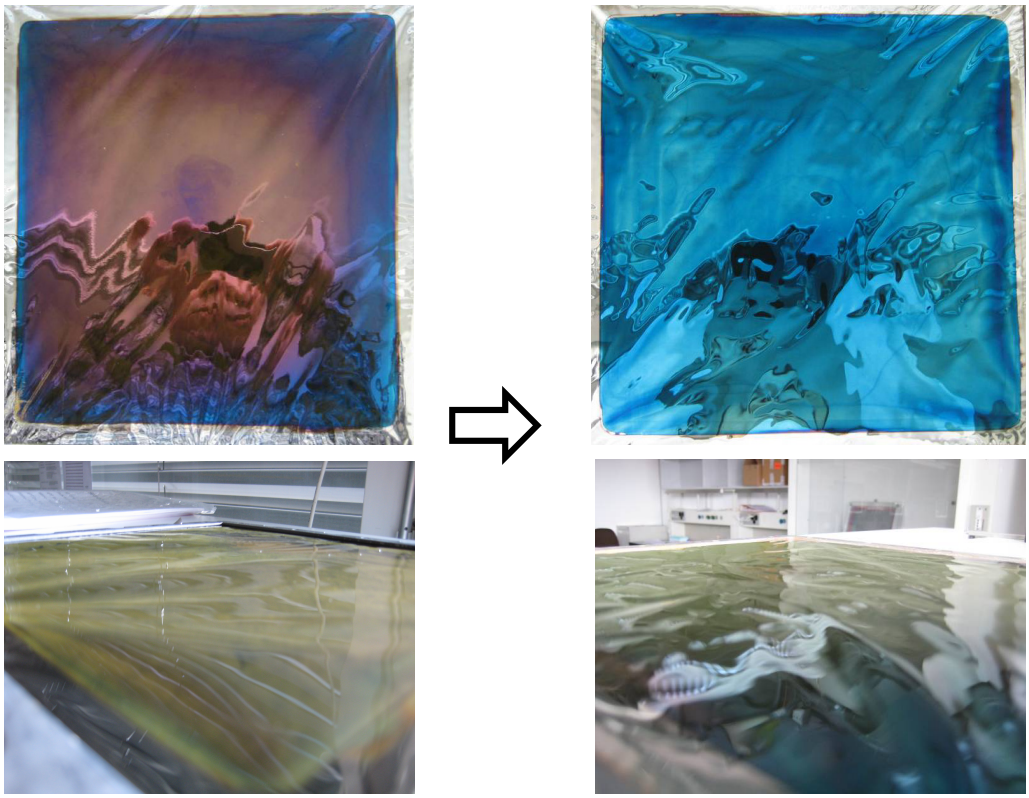


Figure 9: Left: Initial inhomogeneous layers with particle precipitation. Right: Homogeneous layers without particle precipitation after optimization of several parameters. (Top: Top views; Bottom: side views)

Roll-to-roll deposited CIGS layers and flexible solar cells on polymer films

The CIGS system for in-line deposition was modified also for roll-to-roll deposition in a collaborative effort. Tests were performed to assess which CIGS process can be implemented best considering the

limitations of small vacuum chamber and available space for incorporation of evaporation sources and other mechanisms. Options of single pass and multiple scanning pass CIGS depositions were experimentally evaluated. CIGS depositions were made on several meter long rolls using roll-to-roll deposition but because of non-availability of ZnO/ZnO:Al sputtering system it was not possible to deposit TCO front contact layers on large (30x30 cm^2) size substrates. Our group has a very old second-hand MRC sputtering machine which suffers from several problems and is extremely difficult to operate in a consistent manner. Therefore front electrical contacts were grown in a sputtering system where maximum substrate size is limited to 5x5 cm^2 only.

After the deposition of CIGS layers on 3 meter long Mo/polyimide web, several samples of CIGS/Mo/polyimide were cut off from the web and then solar cells with the standard structure and processes were completed using substrate holders for 5×5 cm^2 size. The composition ratio of CIGS obtained depended on growth conditions and the recipes used.

Table 2: Average solar cell properties of flexible CIGS solar cells where the absorber layer is grown with a "specific process-I" in the in-line deposition system and the **CIGS layer does not contain Na which is known to significantly increase the efficiency** of solar cells.

Sample	Effi. (%)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	Rp (Ω)	Rs (Ω)	Substrate heater power (substrate temp.)
M277_01	4.9	421	27.6	41.4	1400	5.7	0 (430°C)
M277_02	6.4	423	29.0	51.7	1713	2.6	0 (430°C)
M277_03	7.4	431	29.4	58.5	1412	2.1	15 (480°C)
M277_04	7.0	426	28.6	57.6	1365	2.4	15 (480°C)

Table 2 shows average solar cell properties of those devices with an area of 0.6 cm^2 using CIGS absorber from a series with composition: [Cu]/[In+Ga]~0.82, [Ga]/[In+Ga]~0.11. The low average efficiency of sample M277_01 is related to the high series resistance due to the high resistance of Mo back contact. The best performance cell was found in M277_03 and its efficiency is 8.0 % (V_{OC}=439mV, J_{SC}=29.5mA/cm^2, FF=61.9%). These solar cells have lower efficiencies compared to our high efficiency cells of 10-14% achieved with static methods. The reasons for lower efficiency are:

(i) CIGS without Na doping: it is known that Na incorporation in CIGS improves the efficiency significantly mostly caused by increase in Voc and FF.

(ii) Non-optimal Ga grading in CIGS layers due to the recipe and system configuration: it seems the CIGS surface is depleted of Ga while most of the Ga is located towards the Mo back electrical contact.

(iii) We don't have enough experience with web coating and lack several tools. However, despite the limitations and lack of resources the achieved efficiencies are quite high for flexible cells based on CIGS without Na.

Table 3: Deposition condition of Mo and the resistance of Mo film.

Sample	Mo condition	R (Ω)
M285_05	w/ tension, w/ plasma etching, 1kW	1.07
M285_06	w/ tension, w/o plasma etching, 2kW	1.05
M285_07	w/ tension, w/ plasma etching, 2kW	0.73
M285_12	w/ tension, w/o plasma etching, 3kW	0.67
M285_13	w/ tension, w/ plasma etching, 3kW	0.61
M285_14	w/o tension, w/ plasma etching, 3kW	0.58

It was observed that the properties of CIGS layers and solar cells strongly depend on the properties of Mo layers and surface treatment methods. Mo films were deposited on a polyimide web with different conditions. The deposition conditions and the resistance of each of Mo films are listed in Table 7. The

parameter of Mo deposition is (1) tension of polyimide web during the deposition, (2) plasma etching before the deposition, and (3) sputtering power for Mo deposition. The change of resistance depending on the Mo deposition condition is observed in Table 3. Currently ongoing work suggests Mo back contact process is also quite important for achieving high efficiency solar cells and reproducible results.

Alternative Back Contacts

Because of the multilayer structure of the CIGS solar cells and the different thermal expansion coefficients of the involved materials and the substrates (especially flexible ones), the search for ideal materials and processes for stress reduction and adhesion improvements remains very crucial. The conventionally used electrical back contact (BC) consists of a molybdenum (Mo) layer, since it has shown the best results so far. However there are several motivations to replace the Mo back contact with alternative materials. One important motivation is surely to find a material that overcomes the disadvantages of Mo, like its expensive price or its inadequate thermal expansion coefficient for CIGS and most of the substrates, which would increase the adhesion of the absorber onto the back contact. Mo can also contribute to reduced performance stability due to easy oxidation in air, which is especially a troublesome matter for monolithically interconnected solar modules, due to corrosion of exposed Mo after the P2 scribing step.

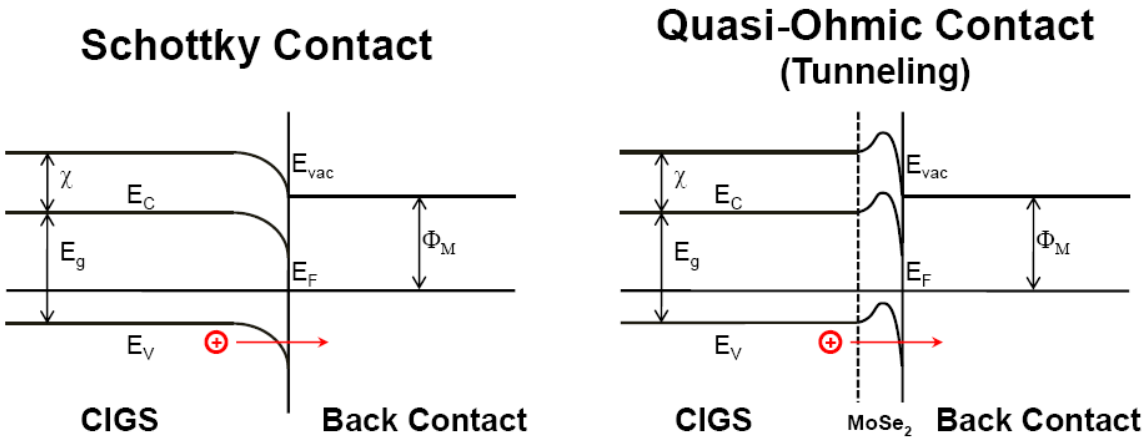


Figure 10: Principle of the quasi-ohmic contact. $MoSe_2$ helps in narrowing down the depletion layer width of the blocking barrier, which allows tunneling of carrier giving quasi-ohmic contact.

In addition to improve the adhesion and corrosion properties, an alternative material can also offer multifunctionality. A back contact layer with a high reflectivity in the red or near infra-red spectrum would enable multiple light scattering for thickness reduction of CIGS layer without losses in conversion efficiency. The advantage of having thinner absorber layers would result in saving material, time and eventually costs. At the same time that BC layer can act as a diffusion barrier against impurities during CIGS deposition and moisture during the lifetime of the solar cells. Transparent and conducting back contacts, like transparent conductive oxides (TCO), would make back illumination possible in addition to front illumination and are indispensable for the development of multijunction solar cell. Those are needed to further improve the photovoltaic conversion efficiencies to very high values by better utilization of the solar spectrum in stacked solar cells based on different absorbers.

A large number of metals or semi-metals can be considered as an alternative to Mo, and the selection of prospective materials could be narrowed down by considering the following criteria:

$$\Phi_m > E_g + \chi$$

for p type semiconductors, where F_m is the BC work function, E_g the bandgap and c the electron affinity of the absorber. However, unfortunately none of those alternative back contact forms ohmic contact with the CIGS absorber layer because of incompatibility of work-function and/or interface related problems. In previous work we have shown that a very thin $MoSe_2$-layer, which forms automatically on Mo BCs during CIGS growth, is responsible for forming quasi-ohmic contact at the interface of the hetero-

junction, suggesting that $MoSe_2$ may be used as an interface layer between CIGS and other metals/semimetals as long as the layers remain chemically compatible and electrically stable.

We had already tested several alternative back contact materials on glass substrates in previous work and developed CIGS solar cells with similar efficiencies to conventional CIGS solar cells (i.e. with Mo back contacts) by using very thin $MoSe_2$ interface layer. Therefore we decided to apply the two most promising back contact material, ITO and TiN, on flexible polyimide and to process them to complete devices.

ITO back contacts on polyimide substrates and development of bi-facial flexible CIGS cells

Transparent and conductive ITO (Indium Tin Oxide) layers have been deposited by RF sputtering to be used as electrical back contacts. In order to maintain a good conductivity of the ITO and because of the limited temperature resistance of the polyimide, we deposit the CIGS layers at low temperature (i.e. <450°C). Even with major difficulties due the scribing of the cells, conversion efficiencies up to 11.9% could be achieved (figure 11, Table 4).

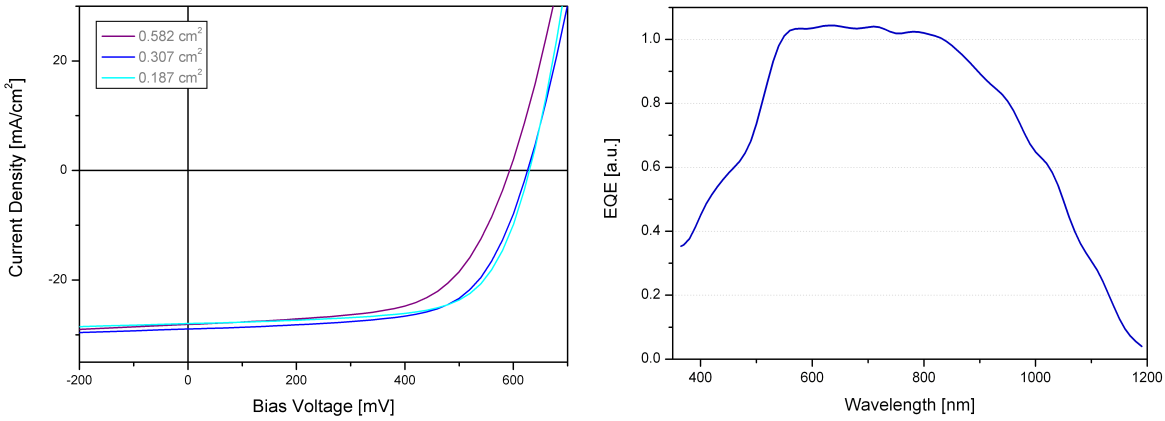


Figure 11: J-V curve (left) and external quantum efficiency (right) of the best CIGS solar cell, with 11.9% efficiency, on flexible polyimide substrates with ITO back contacts.

Table 4: Photovoltaic properties of CIGS solar cells on flexible polyimide substrates with ITO back contacts.

Area	Voc [mV]	Jsc [mA/cm^2]	FF [%]	Efficiency [%]
0.582	593	28.1	61.3	10.2
0.307	626	28.9	64.8	11.7
0.187	629	28.0	67.2	11.9

TiN/Ti as alternative back contacts for flexible solar cell on polyimide substrates

In a first approach TiN layers were tested for their mechanical suitability for flexible solar cells. This material has already successfully been tested on glass substrates (see LARCIS project report) the chemical properties were already proven to be suitable for CIGS cells with higher chemical inertness against corrosion. The deposition of the TiN is done by reactive sputtering with titanium targets in controlled nitrogen plasma. The TiN (typically 70nm) was grown on top of a Ti layer stack which was used to improve the electrical resistance. A sheet conductance of 1 Siemens per square area is required for high efficiency solar cells with minimized serial resistance. Figure 12 shows the conductivity in function of the layer thickness. Layer stacks having a thickness of 450nm and more are therefore required for the desired conductivity.

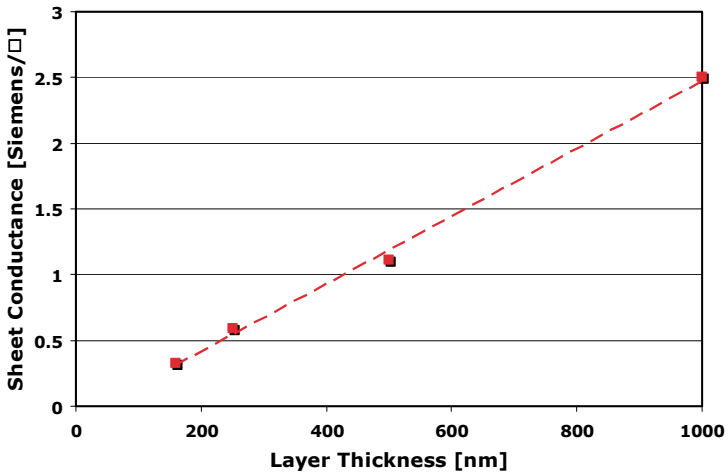


Figure 12: Sheet conductivity of Ti/TiN layer stacks in function of the layer thickness.

Internal layer stress is an important factor during the preparation of the back contact on flexible substrates. High thermal expansion mis-match could lead to buckling and ultimately to layer cracking. Optimization of the deposition conditions to reduce the structure internal stress and sandwich structures by double sided coating were the used approaches to reduce substrate buckling (figure 13). The new solar cell structures would give benefits by the higher reflectivity and improved chemical stability of the new materials.

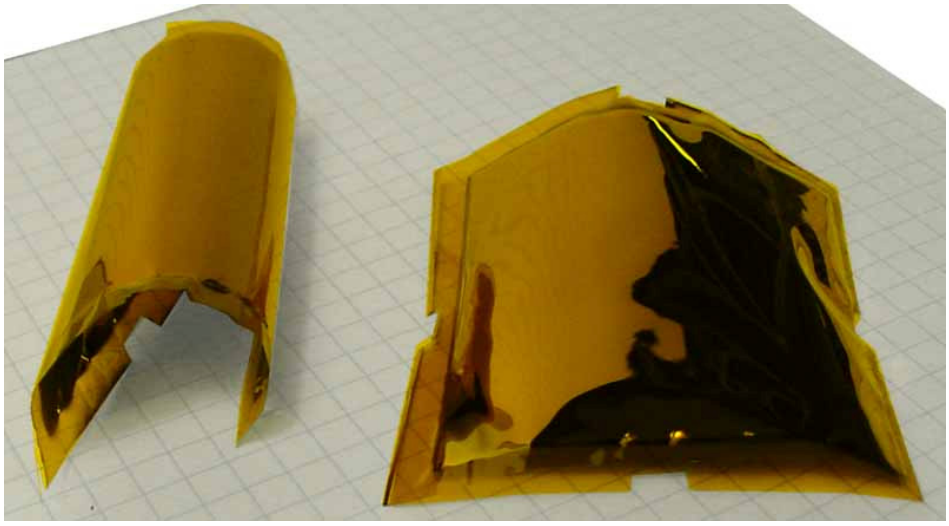


Figure 13: Ti/TiN coated polyimide foil showing the typical golden colour of the TiN compound. Layer internal stress leading to pronounced buckling of the polymer substrate for single side coated samples (left). Double side coating reduces the buckling significantly (right).

In Figure 14 the cross-section of CIGS solar cells with a TiN/Ti bilayer back contact is shown. The TiN layer and the Mo interface layer is clearly visible and the polycrystalline grains of the CIGS layer form a good interface to the back contact (the grains have a reasonably large size even at the back-contact interface) what leads to low recombination at this interface.

We observed a better adhesion of the back contact on the substrate and of the absorber on the back contact. After the TiN/Ti deposition process optimization also no cracks and no film stress could be observed, which we attribute to the more suitable thermal expansion coefficient (CTE) with respect to the CTE of CIGS and the used substrates.

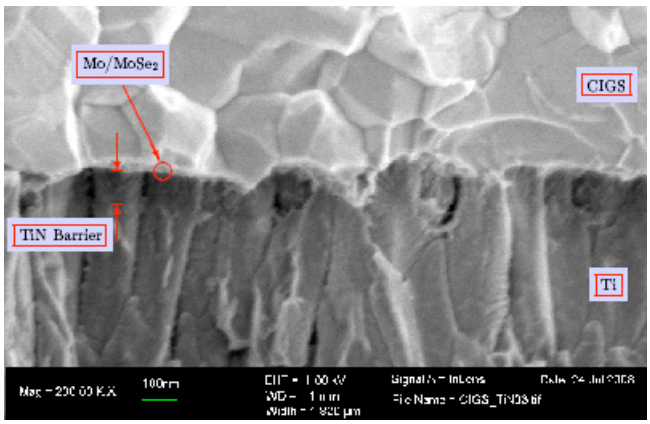


Figure 14: Cross-section scanning electron microscope image of a CIGS solar cell with TiN/Ti back contact and a very thin $MoSe_2$ interface layer.

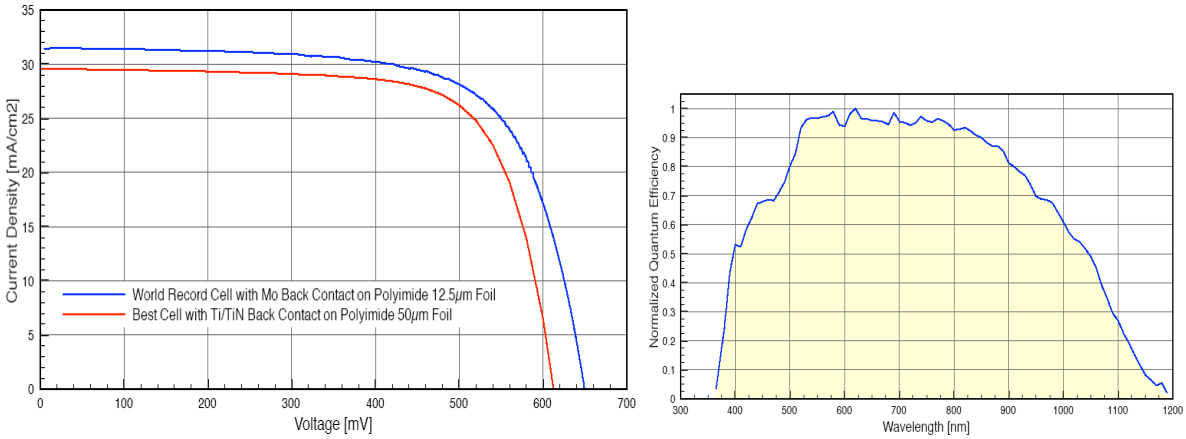


Figure 15: J-V curve and comparison with world record cell (left) and external quantum efficiency (right) of the best CIGS solar cell on flexible polyimide substrates with TiN/Ti back contacts.

A conversion efficiency of 13.1% (V_{OC} = 613mV, J_{SC} = 29.6mA/cm^2, FF = 73.7%) could be achieved for a small cell area of 0.16 cm^2, by using a Ti/TiN bilayer stack and a Mo interface layer. It should be mentioned that only a few solar cells could be processed in this preliminary work, and most of the solar cells of typical area of 0.5 cm^2 were in the range of 8 to 10% efficiency. In figure 15 the comparison with the best reported conversion efficiency of 14.1% (V_{OC} = 649mV, J_{SC} = 31.5mA/cm^2, FF = 69.1%) on polymer foil [1] is shown along with the J-V curve of 13.1% efficiency cell on alternative contact. Even if the best cell efficiency achieved with a TiN/Ti back contact is for the moment slightly lower than the world record cell, this result shows the potential of this back contact to reach as high or even higher efficiencies than on Mo back contacts. TiN offers additionally the advantage of higher stability against oxidation and corrosion, a higher optical reflectivity and impurity diffusion barrier properties

3. Conclusions and outlook

The project has helped to gain experience on the scale-up issues of various deposition processes, implementing CIGS growth on in-line moving substrates as well as in the development of a large area CBD reactor for growth of buffer layers on large area substrates.

Improvements in the design of the evaporators were achieved and the simulation of evaporation fluxes provided in-depth knowledge on the evaporation behavior and uniformity profile for large area deposition of layers. A chemical reactor was designed and constructed in-house for deposition of the CdS

buffer layer. The chemical bath deposition process was improved for defect reduction and waste minimisation.

Flexible solar cells on polymer films with CIGS layers **without Na** grown in a home-build web coating system exhibited efficiencies in the range of 7-8% range. **Obviously efficiencies of flexible cells with Na containing CIGS absorbers will be significantly higher**. Improvements in deposition equipment and/or upgrading of old equipment are essential for speedy progress of the technology and to maintain international lead. However, unfortunately, this requires investment which often is difficult to find despite successful results and great potentials and international excellence achieved,

Successful development of high efficiency flexible solar cells with alternative electrical back contacts based on TCO and TiN/Ti is of particularly interest for further advancement in the field. Industrial involvement to support this research idea was especially encouraging. Although still in a preliminary development stage flexible CIGS solar cell of 13.1% efficiency achieved with alternative back contact is an important milestone for further innovation. These alternative stacked back contacts offer several advantages for manufacturing as well as for long term performance stability of flexible solar cells. However, a large amount of R&D is necessary to understand the scientific and technological issues of this unconventional heterostructure. There is a significant industrial and academic interest to pursue this type of work. FLISOM AG and Blösch AG have provided valuable support and supported the initiation of a new CTI project “Multifunctional back electrical contact for flexible thin film solar cells” started in June 2009.

Up to now the research results mentioned above indicate good progress in the state of the art and the advancements show even further potentials for development of highly efficient and stable solar flexible solar cells. Further research is needed to solve the challenging issues of growth processes in dynamic mode (in-line moving substrates) where the growth kinetics of layers and interface properties are expected to be different from the static mode of deposition. This would require development of deposition equipment and revisiting the material science of layers and interfaces.

Flexible CIGS solar cells are known to have excellent potential (with estimated production cost below 0.5 $/Wp) to provide cost competitive solar electricity.

4. National and international collaboration

Some aspects of this project benefit from the collaboration with FLISOM AG, an ETHZ spin-off company and other national and European projects in the research group. Support of Blösch AG on alternative back contact work is gratefully acknowledged.

5. Publications describing project results

1. Effects of target bias voltage on indium tin oxide films deposited by High Target Utilisation Sputtering. Sonya Calnan, Hari M. Upadhyaya, Sandra E. Dann, Mike J. Thwaites, Ayodhya N. Tiwari. Thin Solid Films, 515, 8500 (2007).
2. Flexible CIGS solar cells and technologies, A. N. Tiwari, D. Bremaud, Proc. 22nd European Photovoltaic Solar Energy Conference, 3-7 September 2007, Feira Milan, Italy.
3. Highly Productive Manufacturing of CIS-Based Large-Area Modules, M. Powalla, F. Kessler, A. N. Tiwari & D. Brémaud, M. Edoff, L. Stolt, B. Dimmler, R. Klenk & H.-W. Schock, O. Kerrec, P. P. Grand, D. Lincot & N. Naghavi, A. Perez-Rodriguez, S. Auvray, Proc. 22nd European Photovoltaic Solar Energy Conference, 3-7 September 2007, Feira Milan, Italy.
4. Manufacturing development and prospects of flexible CIGS solar cell, A. N. Tiwari, 3rd Workshop on the Future Direction of Photovoltaics, 8-9 March 2007, Tokyo, Japan (Invited talk).