1 **Innovation Highway: Breakthrough Milestones and Key Developments in Chalcopyrite**

2 **Photovoltaics from a Retrospective Viewpoint**

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26

1   Abstract:

2   The present contribution is a summary of an event that was organized as a special evening

3   session in Symposium V "Chalcogenide Thin-Film Solar Cells" at the E-MRS 2016 Spring

4   Meeting, Lille, France. The presentations in this session were given by the coauthors of this

5   paper. These authors present retrospectives of key developments in the field of

6    $Cu(In,Ga)(S,Se)_2$ solar cells as they themselves had witnessed in their laboratories or

7   companies. Also, anecdotes are brought up, which captured interesting circumstances in that

8   evolutionary phase of the field. Because the focus was on historical perspectives rather than a

9   comprehensive review of the field, recent developments intentionally were not addressed.

10

11   1. Introduction

12   Research and development of solar-cell devices based on chalcopyrite-type absorber layers

13   has been conducted for more than 40 years. Since often in science, past findings and

14   knowledge fall into oblivion if reported too long ago, it was the motivation of a special

15   session organized at the recent 2016 E-MRS Spring Meeting (Symposium V on

16   "Chalcogenide Thin-Film Solar Cells") to have a retrospective view of some important

17   milestones and key developments in chalcopyrite-type solar cell absorber layers and

18   corresponding devices. The presentations by the coauthors of this paper during the special

19   session, which included also video recordings of colleagues absent at the session, were

20   focused describing the circumstances and issues relevant at that time, while looking back to

21   the evolution of the field. Unfortunately, the circumstances allowed for only limited

22   contributions in terms of number and time.

23   The presentations started with the invention of $CdS/CuInSe_2$ photodetectors and solar cells in

24   1974, via thin-film solar cells with the same structure, to CdS/Cu_2S and $CdS/Cu(In,Ga)(S,Se)_2$

25   cells on the laboratory scale and early phase of industrial efforts. Other presentations on

26   different topics included unintentional incorporation of Na in $Cu(In,Ga)Se_2$ introduced from

27   soda-lime glass substrates, native point defects in the absorber materials, transition from

28   evaporated CdS to chemical-bath-deposited buffer layers, insight into industrial

29   developments, and the challenges of $CuInS_2$ solar cells. The intent was not to give a

30   comprehensive review of the field, but only a selection, limited mostly to the activities of the

1 presenting authors. Therefore, various important contributions were omitted. The present

2 summary is restricted to this limited selection of retrospective factual views.

3

4 2. Invention of the first photodetectors and solar cells based on CdS/CuInSe$_2$ heterojunctions

5 In the beginning of the 1970s, the development of light-emitting diodes was a hot topic in

6 semiconductor device research. At that time, S. Wagner and colleagues at Bell Telephone

7 Laboratories developed green light-emitting diodes based on heterojunctions made of *n*-type

8 CdS and *p*-type CuGaS$_2$ [1], which exhibits a band-gap energy of 2.5 eV. Since GaAs lasers

9 (photon energy of 1.4 eV) were also studied at that time as light sources for fiber optics, S.

10 Wagner and colleagues were looking for semiconductor materials with band-gap energies of

11 about 1 eV, to fabricate photodetectors for the GaAs lasers. This is how CuInSe$_2$ came into

12 focus. Based on the CdS/CuGaS$_2$ heterojunctions, which they had already fabricated, S.

13 Wagner and colleagues invented the CdS/CuInSe$_2$ heterojunction photodetector [2].

14 After measuring the quantum-efficiency spectrum over the entire wavelength window, S.

15 Wagner and colleagues realized that what they had produced performed well as a solar cell

16 [3]. Thus, they started paying attention to raising the open-circuit voltage (V_{oc}), reducing the

17 series resistance, and evaluating complete photocurrent-voltage characteristics. With just a

18 few experiments, they demonstrated a conversion efficiency of 12% [4].

19 The CdS/CuInSe$_2$ heterojunctions were based on what appeared under the optical microscope

20 to be CuInSe$_2$ single crystals. They were ultra-precious, since their growth in sealed quartz

21 ampoules by horizontal directional solidification of stoichiometric melts took several weeks.

22 The melt crystallized by random nucleation on the quartz wall, with the largest crystallites

23 forming at the top of the boule, with (112) Se surfaces. The largest crystals were selected by

24 visual inspection and then cut out in ~1-mm-thick pieces, with ~1 mm^2 surface areas of the

25 single crystals. The crystals were polished, etched, annealed in Se vapor to raise the p-type

26 conductivity, polished and again etched. The diode was completed by coevaporation of Cd

27 and S to form a 5-10-µm-thick CdS layer. After electroless deposition of Au for the CuInSe$_2$

28 back contact and soldering indium as a front contact to the CdS layer, the device was

29 evaluated.

30 First, current-voltage, capacitance-voltage, and quantum efficiency measurements were

31 conducted at zero-to-low bias voltages. Then, the applied voltage was increased to see how

1 far it was possible to go into forward and reverse bias, until the device shorted. Since the

2 CuInSe$_2$ single crystal was so precious, it was recycled by stripping the In contact and the

3 CdS layer, and by etching the CuInSe$_2$ crystal to obtain a fresh surface for fabricating a new

4 diode. The device was the result of a typical Bell Labs interdisciplinary collaboration: Horst

5 Kasper grew the CuInSe$_2$ crystals, Joe Shay and Piero Migliorato were solid-state physicists

6 who learned device physics on the fly, and Sigurd Wagner fabricated the solar cells.

7 In 1974, the CdS/CuInSe$_2$ heterodiode was one of four solar-cell concepts that realized

8 power-conversion efficiencies of more than 10%. Further research on solar cells with

9 chalcopyrite-type semiconductors included Cu$_2$CdSnS$_4$, a forerunner of earth-abundant

10 semiconductors, in the CdS/Cu$_2$CdSnS$_4$ heterojunction [5].

11

12 3. First thin-film solar cells based on CdS/CuInSe$_2$ heterojunctions

13 Soon after the success of S. Wagner and colleagues, in 1976, L.L. Kazmerski, then at

14 University of Maine, demonstrated 4-5% conversion efficiency for CdS/CuInSe$_2$ solar cells

15 based on CuInSe$_2$ thin films deposited by evaporation from CuInSe$_2$ and Se sources [6]. In

16 1980, R.A. Mickelsen and W.S. Chen from Boeing Aerospace Company won a proposal with

17 the Solar Energy Research Institute (which became later the National Renewable Energy

18 Laboratory) in Golden, CO, U.S.A. These researchers based the proposed development of

19 CdS/CuInSe$_2$ thin-film solar cells on earlier work that they had performed on Cu$_2$S/CdS solar

20 cells (see section 4 below) under NASA contract. Like other researchers at that time, they

21 found that CdS/Cu$_2$S devices would decompose under bias. One of the ideas Mickelsen and

22 Chen had to stabilize these devices was introducing impurities into the crystal, of which one

23 option was In. Combining this approach with the earlier work by L.L. Kazmerski described

24 above (who used evaporation of CuInSe$_2$ from the compound), they proposed coevaporation

25 from the elements as a technique to obtain better control of the process. Thus, Mickelsen and

26 Chen demonstrated the first 10% efficient CuInSe$_2$ thin-film solar cell in 1982 [7].

27 Until 1985, the conversion efficiencies of CuInSe$_2$/CdS solar cells were improved to almost

28 12%, mainly by using (Cd,Zn)S instead of CdS as n-type counterpart to the p-type CuInSe$_2$

29 [8]. Soon thereafter, Mickelsen, Chen, and colleagues demonstrated the first Cu(In,Ga)Se$_2$

30 thin film solar cells with conversion efficiencies of more than 10%, using a [Ga]/([Ga]+[In])

31 ratio of 0.25 [9]. Adding Ga to CuInSe$_2$ provided flexibility to either fabricate absorber layers

with band-gap energies matching the solar spectrum (low Ga concentrations) or to produce high-gap partners for $CuInSe_2$ in a tandem solar-cell device (high Ga concentrations). The conversion efficiencies for $CuInSe_2$ and $Cu(In,Ga)Se_2$ thin-film solar cells were improved to 14.1% and 12.9% by Mitchell et al. at ARCO Solar [10], mainly by reducing the thickness of the evaporated CdS buffer layer from few µm to about 50 nm, and by using a 1.5-3-µm-thick ZnO window layer.

As an interesting incident during the initial development period of $Cu(In,Ga)Se_2$ thin film solar cells at Boeing Aerospace Company, the power packs for the substrate heaters on the $Cu(In,Ga)Se_2$ evaporation system failed. The power thyristors shorted, and a thermal run-away in the system occurred. At that time, the solar-cell stacks were deposited on borosilicate glass. The substrate temperature went very high, much higher than normal. When the $Cu(In,Ga)Se_2$ thin films were imaged by electron microscopy in cross-section, the researchers found that the grain sizes were much larger than normal. This incident gave rise to growth recipes for $Cu(In,Ga)Se_2$ thin films with much higher temperatures than commonly used for $CuInSe_2$ at that time.

4. Development of CdS/Cu_2S and $CdS/CuInS_2$ thin-film solar cells

It is noteworthy that in the two decades before the first $CdS/CuInSe_2$ photodiodes were produced, a related technology had already been developed and studied intensively by several research groups. In 1954, the photovoltaic effect was found in rectifiers composed of Cu contacts and CdS single crystals [11], at about the same time that Si homojunction solar cells were first reported [12]. Initially, CdS-based photovoltaic thin-film devices relied on a heterojunction of Cu_2O and CdS, with illumination through the rather thick (up to 100 µm) CdS layer (the backwall configuration). During the subsequent years, the design of CdS thin-film solar cells was modified by the deposition of thin (few µm) p-Cu_2S layers on the n-CdS layers (see stacking sequence given in Fig. 1) and by switching to a frontwall configuration (illumination through the Cu_2S layer). Most of the incident light is absorbed in the Cu_2S layer (band-gap energy of about 1.2 eV [13]).
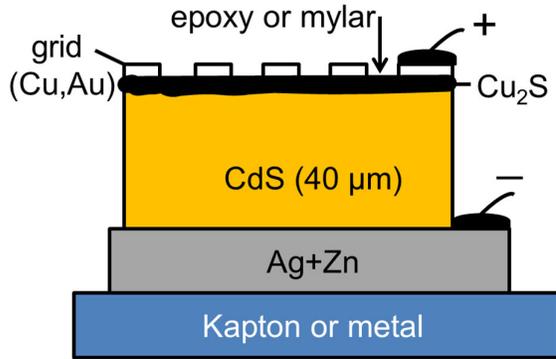
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2   Figure 1: Stacking sequence of CdS/Cu$_2$S solar cell with a front-wall design (adapted from

3   Ref. [14]).

4

5   Both the Si and CdS/Cu$_2$S technologies were considered equally important owing to the

6   demonstrated conversion efficiencies of 5-8% (for CdS/Cu$_2$S in the 1960s [15,16]). While the

7   Si devices soon showed progress towards 10% and higher efficiencies, they were also found

8   to be vulnerable to radiation damage, which was a substantial problem for application of these

9   devices in space, e.g., on satellites. Similar to other thin-film technologies developed during

10   that time, such as CdTe solar cells [17], CdS/Cu$_2$S heterojunction devices were demonstrated

11   to be inherently far more stable to the whole spectrum of proton and electron radiation in

12   space environment (see Ref. 18 and references therein).

13   Until the 1980s, conversion efficiencies of up to more than 9% were achieved with CdS/Cu$_2$S

14   solar cells [19], and more than 10% by the addition to Zn to the CdS layer [20]. However, as

15   heterojunction devices, CdS solar cells exhibit substantial limitations on their device

16   performances via trapped charge densities near the CdS/Cu$_2$S interface, which causes a

17   persistent increase in junction capacitance (photocapacitance) and plays a significant role in

18   determining carrier transport properties [21]. Also, the Cu$_2$S layer was found to decompose

19   into other, Cu-poorer Cu-S phases for bias voltages of larger than about 0.3 V [22], leading to

20   an intermediate Cu-S layer between Cu$_2$S and CdS with a larger band-gap energy (1.8 eV)

21   than that of chalcocite Cu$_2$S (1.2 eV), hence substantially deteriorating the *p-n* junction

22   performance [23].

23   As mentioned above in Sec. 3, one solution to this problem was to introduce indium to the

24   Cu-S compound, in order to stabilize the structure. This approach led to the development of

CdS/CuInS$_2$ heterojunctions, which were considered as promising alternatives to CdS/CuInSe$_2$ heterojunctions (Sec. 3) and will be discussed in the following.

A first report on this topic was published by L.L. Kazmerski et al. in 1975 [24], encouraged by their work on CuInSe$_2$ (see Sec. 3). Apart from solving the problem of stabilizing the structure of Cu$_2$S/CdS p-n junctions, their motivation was also to replace costly Se and to obtain devices with larger band-gap energies in the absorbing layers. Achieving a conversion efficiency of 10% was considered a challenging milestone. However, first devices were far below this performance level [25]. In 1988, solar cells based on mm-sized CuInS$_2$ crystals in contact with a redox electrolyte came close to this milestone (conversion efficiency of 9.7% [26]), while a patent on this device concept was issued already in 1979 [27]. However, it was not possible to grow crystals reproducibly by this specific technique.

In 1993, the milestone of 10% conversion efficiency was reached eventually by a joint effort of scientists at the Hahn-Meitner Institute, Berlin (now Helmholtz-Zentrum Berlin) and at the Institute for Physical Electronics, University of Stuttgart, Germany. A Cu-rich ([Cu]/[In]>1), coevaporated CuInS$_2$ film with standard CdS/ZnO emitter exhibited a conversion efficiency of 10.2% [28], but at the same time also a large V_{oc} deficit (i.e., difference with respect to the corresponding value at the Shockley-Queisser limit [29]) of about 0.8 V. Secondary phases of Cu-S due to Cu-excess were etched away by cyanide treatment prior to emitter deposition [30]. Soon it became clear that ZnO/CdS/CuInS$_2$ photovoltaic devices were limited by enhanced recombination at the CdS/CuInS$_2$ interface – unlike the Cu(In,Ga)Se$_2$ devices, which, at that time, exhibited conversion efficiencies of around 15% with a V_{oc} deficit of only about 0.5 V (see also the further sections below). Attempts to copy the concept of Cu-poor ([Cu]/[In]<1) growth applied for CuInSe$_2$ thin films failed because of the very low resulting conductivity [31] and Cu-Au defect ordering [32], leading to enhanced recombination [33] in the CuInS$_2$ layers.

Further progress with CuInS$_2$ grown under Cu-rich conditions was achieved by the application of sequential phase formation [34] and by the addition of Ga [35]. The company Sulfurcell (later Soltecture) in Berlin, Germany, was able to commercialize the CuInS$_2$ technology in full-size modules with conversion efficiencies of around 10% [36]. In the meantime, the Asahi Kasei group revised the Cu-poor Cu(In,Ga)S$_2$ formation with the aim of avoiding the cyanide treatment prior to emitter deposition [37,38]. These colleagues achieved around 10% conversion efficiency, for which an increase in conductivity by Na doping and

Ga addition appeared to be the key. It was not until 2015 that this effort was resumed by scientists from Solar Frontier, Japan, who reached the next milestone of 15% by detailed growth optimization and a novel ZnMgO buffer layer [39]. The V_{oc} deficit was reduced to 0.6 V. This result may now lead to revived interest in Cu(In,Ga)S$_2$ solar cells.

5. A short history of point defects in Cu(In,Ga)Se$_2$

In the previous sections, research and development of Cu(In,Ga)(S,Se)$_2$ solar cells has been described as driven by the goal to improve the conversion efficiency. Fundamental studies on the electronic structure of Cu(In,Ga)(S,Se)$_2$ absorber layers themselves had been rare and not very systematic until the late 1990s. One evident reason for this fact is that understanding the electronic defects may lead to substantial improvement of the device performance only very indirectly and with a long delay. However, the Cu(In,Ga)(S,Se)$_2$ material used in solar cells – a solid solution of CuInSe$_2$, CuGaSe$_2$, CuInS$_2$, and CuGaS$_2$, which is Cu-poor (i.e., substoichiometric with [Cu]/([In]+[Ga]) < 1) and highly compensated – is not really suitable for (optical) defect spectroscopy.

Nevertheless, there is a growing insight into the importance of shallow defects, which govern the doping levels of the Cu(In,Ga)(S,Se)$_2$ absorber and thus the *p-n* junction formation, as well as deep defects which are responsible for recombination of photogenerated carriers as well as for metastable behaviour of the solar cells. Comprehensive reviews on this topic can be found in Refs. 40 and 41. In the present overview, we will concentrate on shallow (doping) defects in Cu(In,Ga)Se$_2$.

In contrast to Si, the doping behaviors of CuInSe$_2$ and CuGaSe$_2$ are dominated by intrinsic defects, i.e., cation antisite defects, vacancies, and interstitials. A specific property of CuInSe$_2$ and CuGaSe$_2$ compounds is that their ternary characters give rise to extremely low defect formation energies [42]. Shallow (doping) defects are usually investigated by photoluminescence (PL) spectroscopy or by the activation energies determined from Hall measurements. The interpretation of corresponding measurement results is easier when obtained on ternary compounds (i.e., CuInSe$_2$ and CuGaSe$_2$), because the alloy disorder present in Cu(In,Ga)Se$_2$ can be avoided [43].

1 Unfortunately, energy values for defect levels in CuInSe$_2$ and CuGaSe$_2$ single crystals or thin

2 films reported in the literature [40] almost fill the whole energy ranges of the corresponding

3 band gaps. One problem in the interpretation of PL measurements is that the Cu-poor

4 ([Cu]/[In]<1) Cu(In,Ga)Se$_2$ layers used in high-efficiency solar cells do not exhibit narrow

5 transitions in the PL spectra, which may be interpreted in terms of defect levels, but rather a

6 broad, red-shifted luminescence peak, even at low temperatures. Already in early 1976 [44], it

7 was discussed that this broad luminescence peak in CuInSe$_2$ is due to potential fluctuations,

8 and rediscovered in 1998 during PL investigations in Meyer's lab at the University of Giessen,

9 Germany, when analyzing Cu(In,Ga)Se$_2$ absorbers fabricated at the company Siemens Solar

10 (now Avancis) [45]. Defect spectroscopy on CuInSe$_2$ with narrow PL lines is only possible on

11 layers grown under Cu-rich ([Cu]/[In]>1) conditions [46]. The same behavior was found in

12 Cu-poor and Cu-rich CuGaSe$_2$ [47].

13 Still, on the Cu-rich side of both materials, several different transitions were detected in

14 different samples, which made the interpretation difficult in terms of defect energies.

15 Clarification of this dependence of defect levels on the process conditions was possible by

16 using epitaxial films grown in the Siebentritt group (in M.C. Lux-Steiner's department at

17 Hahn-Meitner Institute, Berlin) by metal organic vapor epitaxy, by which the composition can

18 be well controlled. It was shown that both, CuInSe$_2$ and CuGaSe$_2$, are dominated by three

19 shallow acceptors and one shallow donor [40,48,49]. For both materials, the shallowest

20 acceptor dominates near stoichiometry ([Cu]/([In]+[Ga])=1) and disappears with increasing

21 [Cu], whereas the second acceptor increases with increasing [Cu]. The third acceptor is rather

22 composition independent and has been related to structurally damaged material [50]. All

23 defects exhibit energy levels which are slightly deeper in the band gap for CuGaSe$_2$ than for

24 CuInSe$_2$.

25 Although a corresponding analysis is difficult for Cu(In,Ga)Se$_2$ since alloy disorder broadens

26 the emission peaks in the PL spectra, it seems that a continuous transition exists between

27 defect energies (see Fig. 2) [43]. For the interpretation of the chemical nature of these defects,

28 comparison with calculations based on ab-initio density functional theory is necessary [42].

29 Here, the discussion is still ongoing, with substantial improvements concerning the applied

30 functionals in the recent years [51,52,53,54]. Structural, experimental evidence is available

31 for the Cu vacancy V_{Cu} as well as for the In$_{Cu}$ antisite defect and the Ga interstitial Ga$_i$

1   [55,56], and also for a V_{Se}-V_{Cu} double vacancy [57], which has been reported to be the origin

2   for various metastabilities in Cu(In,Ga)Se$_2$ [58,59].

3   In addition to intrinsic defects, doping in Cu(In,Ga)Se$_2$ thin films can be influenced by defects

4   related to impurities. These may be intentionally introduced [60] or diffuse into the layers

5   from the substrates of the solar-cell stacks (e.g., Na, O, and K from soda-lime glass; Fe from

6   steel foils); see also Sec. 6 below. Charged point defects play an important role on surfaces of

7   CuInSe$_2$ and CuGaSe$_2$ thin films, where they stabilize polar configurations by atomic

8   reconstructions [61]. Similar reconstructions have also been identified to occur at planar

9   defects (i.e., stacking faults, ramdomly-oriented grain boundaries) in polycrystalline

10   Cu(In,Ga)Se$_2$ thin films (see Ref. 62 for a recent review on this matter).
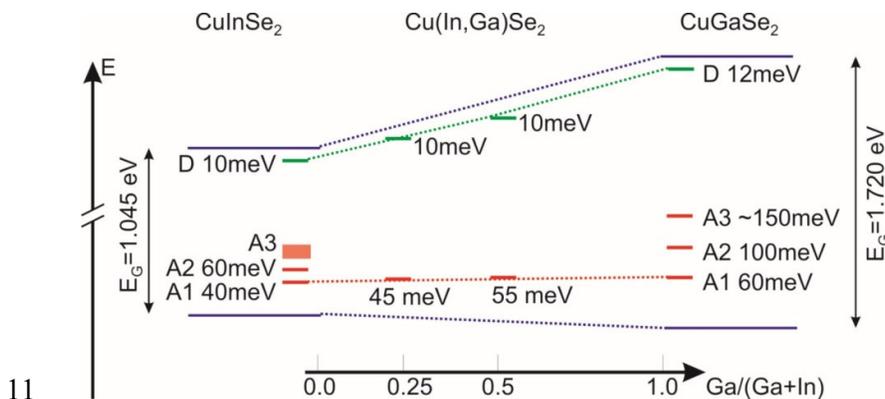
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12   Figure 2: Shallow acceptor (A1, A2, A3) and donor (D) levels, with energy differences given

13   with respect to the valence and conduction band edges, determined by means of

14   photoluminescence spectroscopy on Cu(In,Ga)Se$_2$ layers grown at four [Ga]/([In]+[Ga])

15   ratios (adapted from Ref. [43]).

16

17   6. The role of alkali metals in Cu(In,Ga)Se$_2$ solar cells: from the old Boeing days to the

18   present

19   Apart from native point defects in Cu(In,Ga)Se$_2$ treated in the previous section, defects related

20   to impurities may also affect the photovoltaic performance of Cu(In,Ga)Se$_2$ solar cells. A

21   particular role is played by Na, which can diffuse into the growing Cu(In,Ga)Se$_2$ layer when

22   using substrate materials such as (e.g.) soda-lime glass, from a precursor layer (e.g., NaF)

23   deposited between the substrate and the Mo back contact, or via a post-deposition treatment

24   (for an overview, the reader is referred to the very good work by D. Rudmann [63]).

1   Experiences with the effects of Na on the growth of CuInSe$_2$ thin films were already obtained

2   at Boeing Aerospace Company in the 1980s. At that time, B.J. Stanbery and coworkers

3   implemented monolithic integration in the solar-cell stack for module production [64], and

4   they used borosilicate glass substrates (not containing Na). In order to selectively etch the

5   molybdenum to form the P1 base metal contact isolation pattern, these colleagues used,

6   among other etchants, a hot aqueous solution of NaOH. They observed that this etching

7   solution lifted the photoresist off at the end of the Mo etching process, without requiring a

8   separate photoresist stripping process, which was a very attractive process simplification. The

9   conversion efficiency of the completed device was not extraordinary. However, the grain size

10   in the CuInSe$_2$ thin films was much larger than in processes for which no NaOH was applied

11   as an etchant. In spite of this astonishing result, this matter was not followed up any further

12   since a contract milestone-deliverable had to be reached in due time, and NaOH was no

13   longer used as the Mo etchant for monolithic integration.

14   It was indeed many years later when work of L. Stolt and colleagues at the University of

15   Uppsala, Sweden, showed that Na from soda-lime glass indeed is a very important impurity

16   for growing large-grain CuInSe$_2$ layers [65]. At this institution, CuInSe$_2$ solar-cell stacks were

17   deposited on sintered alumina substrates in the 1980s. This substrate material is tough,

18   temperature resistant, inert, and exhibits a thermal expansion coefficient similar to that of

19   CuInSe$_2$ (and Cu(In,Ga)Se$_2$). However, the supply of alumina substrates was limited, and

20   therefore, substrate materials with enhanced availability were required. This is why, among

21   other materials, soda-lime glass was tested, which is less tough, less temperature resistant, less

22   inert, but cheap, accessible, and has a thermal expansion coefficient which is similar to

23   CuInSe$_2$ (and Cu(In,Ga)Se$_2$).

24   At about the same time, H.-W. Schock and colleagues at the Institute of Physical Electronics,

25   University of Stuttgart, Germany, ran out of Na-free Corning 7059 glass substrates and used,

26   accidentally, "dirty" soda-lime glass. These scientists found increased oxygen concentrations

27   at the CuInSe$_2$ surface using photoelectron spectroscopy, which is (as we know today) related

28   to the Na diffusion from the soda-lime glass into the CuInSe$_2$ layers, and allowed fabrication

29   of devices with conversion efficiencies of 12.4% using this glass type in 1991 [66]

30   (collaborative work within the EUROCIS project). By 1992, conversion efficiencies of almost

31   15% were achieved using CuInSe$_2$ absorber layers and soda-lime glass as substrates [67],

1   which improved to 16.9% in 1993 with Cu(In,Ga)Se$_2$ absorbers [68] (both results also

2   obtained within the EUROCIS project).

3   The influence of Na on the grain growth of Cu(In,Ga)Se$_2$ thin films has been related to the

4   formation of Na polyselenides during the growth process [69], which act as a source of Se. In

5   addition, Cu(In,Ga)Se$_2$ phase formation via Cu$_2$Se binaries is favored in the presence of Na,

6   which was suggested to lead to larger grains owing to the templating function of the large

7   Cu$_2$Se crystallites (formed during the Cu-rich stage of the growth process) [70]. The main

8   effect of Na in Cu(In,Ga)Se$_2$ thin films on the device performance has been attributed to the

9   effective annihilation of In$_{Cu}$ point defects (donors) [71,72], which results in an overall higher

10   net doping concentration [73], thus, leading to higher open-circuit voltages [74].

11

12   7. Early years of chemical bath deposition of buffer layers

13   While in the previous sections, the focus was on the technological development and the

14   properties of the Cu(In,Ga)(S,Se)$_2$ absorber layer, the main issue of the solar-cell device was

15   the optimization of the *p-n* junction. For this purpose, the use of various materials systems as

16   *n*-type counterparts to the *p*-type Cu(In,Ga)(S,Se)$_2$ have been elucidated. Moreover, these

17   materials have been also deposited using a variety of methods, ranging from (co)evaporation,

18   sputtering, chemical vapor deposition, and atomic layer deposition, to deposition from a

19   chemical bath. From all these research efforts during the past decades, it was found that

20   chemical bath deposition (CBD) is particularly suitable for a controlled and well-adapted

21   junction formation of various *n*-type materials with the *p*-type Cu(In,Ga)(S,Se)$_2$. Therefore, a

22   specific section is dedicated to this topic.

23

24   7.1. Historical overview

25   The CBD of semiconducting sulfide, selenide, and oxide thin films was introduced a long

26   time ago, already in 1884, when J. Emerson-Reynolds reported the deposition of lead sulfide

27   by a reaction between lead tartrate and thiourea under basic conditions [75]. In addition, lead

28   sulfide and lead selenide devices prepared by CBD were even used at the industrial level as

29   infrared detectors during the Second World War. Thereafter, this deposition method for

30   semiconducting films has then been mostly ignored for decades also owing to the rapid

1   development of deposition methods from the gas phase (physical and chemical vapor

2   deposition).

3   A revival of research efforts into CBD-CdS thin films in the beginning of the 1980s originated

4   from the work of Prof. Chopra's group in New Delhi, India, who provided a detailed review

5   and an in-depth study on the CBD of CdS thin films [76], first reported in 1961 [77]. In 1989,

6   when working on CuInSe$_2$ solar cells within the European EUROCIS project, interest arose at

7   the Ecole Nationale Superieure de Chimie Paris in trying the CBD method developed by Prof.

8   Chopra's work to prepare CdS films for CuInSe$_2$ solar cells, as an alternative to the

9   evaporation methods applied up to that date. D. Lincot and coworkers repeated the

10   experiments described by Prof. Chopra's publication and eventually found appropriate

11   conditions for optimal CBD of CdS, after having broken several tens of glass tubes. This

12   allowed for rapidly testing a broad range of experimental parameters and to select those

13   leading to heterogeneous instead of homogeneous deposition of CdS films on the inner glass-

14   tube surface [78]. At about the same time, R. Birkmire and coworkers at the Institute of

15   Energy Conversion at the University of Delaware, U.S.A., reported first experiments on the

16   use of CdS buffer layers synthesized by CBD for solar cells [79].

17   The key finding by D. Lincot and coworkers was that the deposition proceeded according to a

18   well-defined, surface-controlled mechanism, independent of the hydrodynamic regime. These

19   researchers also found that CBD solutions with an excess of thiourea resulted in good

20   coverage properties of the CdS thin films at low thicknesses (20 nm). Joint studies

21   immediately started within the EUROCIS project, in particular in collaboration with the group

22   of H.-W. Schock at IPE, Stuttgart, Germany, using such recipes with high thiourea

23   concentrations. These efforts resulted in a considerable breakthrough with solar-cell

24   efficiencies exceeding those of devices with sputtered or evaporated buffer layers. Not only

25   increased current densities, but also higher open-circuit voltages were achieved [80,81] (see

26   Fig. 3), which indicated a better interface quality between the CuInSe$_2$ absorber and the CdS

27   buffer layers. This work on the improvement of CBD-CdS buffer layers contributed

28   substantially to the record conversion efficiency published by the EUROCIS group in 1993

29   (see Sec. 6 above).

30   Soon thereafter, it was found by analyzing the surface chemistry of Cu(In,Ga)Se$_2$ thin films

31   after the CBD process that the CBD solution cleans selectively and changes the composition

32   of the Cu(In,Ga)Se$_2$ surface, involving in-diffusion of Cd by surface-exchange reactions [82].

1   In the following, CBD became the standard technology for CdS buffer layers [83].

2   Fundamental mechanistic studies demonstrated in parallel that the growth mechanism relies

3   on well-defined and successive reaction steps at the atomic level at the $Cu(In,Ga)Se_2$ surface,

4   as also occurring when depositing thin films by means of chemical-vapor deposition methods

5   [84]. This fact was confirmed by the occurrence of epitaxial growth of CBD-CdS on various

6   substrates, including $CuInSe_2$ [85].

j-V	V_{oc} (mV)	j_{sc} (mA/cm^2)	FF (%)	η (%)
(1)	400	32.4	68	8.8
(2)	424	38.5	70	11.5
(3)	450	38	68	11.7

ELII-illumination 100mW/cm^2
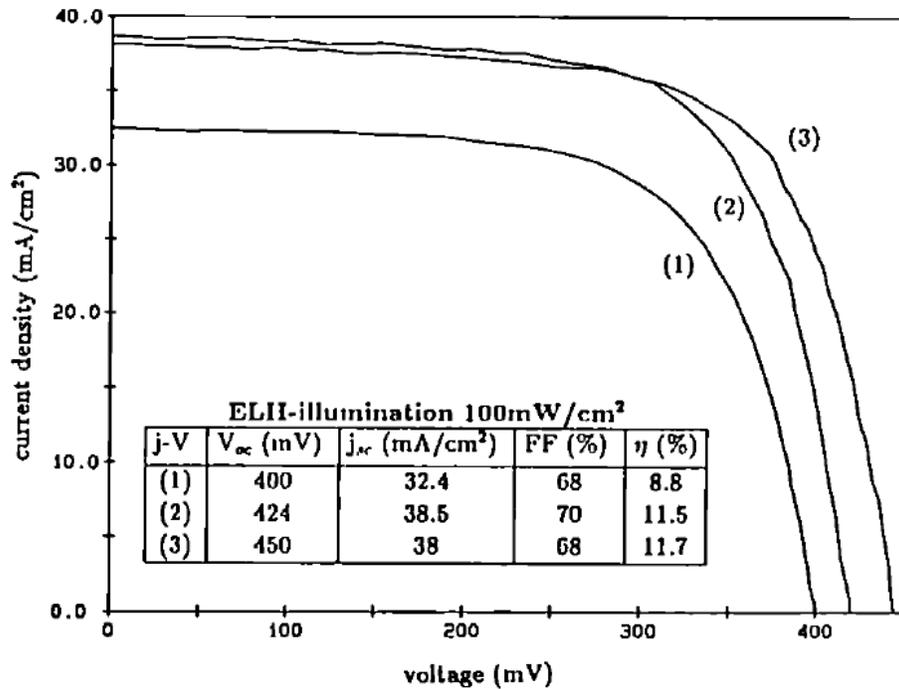
7

8   Figure 3: Key results of the EUROCIS consortium concerning the use of CBD-CdS buffer

9   layers from 1991. Current-voltage characteristics of a $Cd_{0.85}Zn_{0.15}S$-$CuInSe_2$ standard device

10   (1) and corresponding ZnO-CdS-$CuInSe_2$ devices with sulfide-based and iodide-based CBD-

11   CdS buffer layers. Reproduced with permission from Ref. 80.

12

13   In 1994, another challenge was met within the follow-up of the European network project

14   EUROCIS (EUROCIS-M), which was devoted to the large-scale manufacturability of solar-

15   cell devices. One of the problems with CBD processes performed in beakers was the

16   enormous loss of material by homogeneous precipitation, which was why CBD was initially

17   not considered as a possible method for large-area deposition. This obstacle was solved by

18   using large substrates oriented face-to-face with each other, with rubber rings, having a

1   thickness of 1-2 mm, as separators. The reacting solution was poured into the spacing

2   provided by the rubber rings. The walls of the beaker were covered by the substrates. In the

3   first successful attempt, on substrate areas of 30x30 cm^2, due to the lack of larger rubber

4   rings, the window glasses were separated by soft telephone cables.

5   Modifications of this configuration, termed "two-plates configuration" or "closed-space"

6   CBD, were developed also for CdS deposition in CdTe solar modules by the companies BP

7   Solar and Shell Solar (using multiplates in back-to-back pairs of substrates). However,

8   mechanical breaking problems arose in the EUROCIS project when upscaling the plate area,

9   owing to a bending effect induced by thermal stress during the deposition of the $Cu(In,Ga)Se_2$

10   layer at high temperature. In 1993, a flat reactor concept with the substrate at the bottom and

11   an oscillating wave to insure the renewal of the solution at the surface was presented by D.

12   Lincot [86], which was called the "photographic" process and which was further developed

13   within the EUROCIS M project. It was successfully transferred to the industry and is sold

14   nowadays as standard equipment for solar-module manufacturers. This success was

15   unpredictable in 1989 during the "test tube breaking" period.

16   In the early 1990s, the CBD method was developed also for other buffer-layer materials,

17   especially for Zn-based semiconductors (see the excellent review by D. Hariskos [83]). In

18   1992, a recipe for a ZnS buffer layer based on thioacetamide was presented, which resulted in

19   solar-cell efficiencies of 9%. However, the devices exhibited a considerable light-soaking

20   effect [87]. In a subsequent publication, the formation of zinc hydroxyl sulfide in an ammonia

21   thiourea bath was reported [88]. However, the real breakthrough for Zn-based buffer layers

22   was achieved by using $Zn(OH)_2$ / $Zn(O,S,OH)_x$ by K. Kushiya and coworkers at Showa Shell

23   Sekiyu in Japan (today: Solar Frontier) (Ref. 89; for more details, see Sec. 7.2 below).

24   Apart from CBD, atomic layer deposition (ALD) has also been used successfully as a

25   deposition method for buffer layers in $Cu(In,Ga)(S,Se)_2$ solar cells, particularly successful for

26   In_2S_3 buffers [90]. Although ALD is nowadays also considered scalable and thus suitable for

27   industrial module production, CBD as buffer-deposition method still remains in a strong

28   leadership position with conversion efficiencies of up to more than 22% reached by Zn-based

29   CBD buffers, for devices with both, coevaporated $Cu(In,Ga)Se_2$ [91] and sequentially

30   processed $Cu(In,Ga)(S,Se)_2$ [92] absorber layers. The success story that started in the late

31   1980s, followed by ten years of golden pioneering period [93,94] is still continuing.

32

1   7.2. Motivations for the development of a Cd-free $Zn(O,S,OH)_x$ buffer layers

2   Showa Shell Sekiyu K.K. joined the Japanese New Energy and Industrial Technology

3   Development (NEDO) Solar Research and Development project in 1993. Within this project,

4   it was not planned to use a CdS buffer layer for the solar modules, although CdS had, up to

5   then, been the main material for this application. In the following, the circumstances for the

6   development of a Cd-free $Zn(O,S,OH)_x$ buffer are described in detail.

7   CdS exhibits a rather small band-gap energy of 2.42 eV. First, ZnO was selected owing to its

8   wider band gap (> 3.3 eV). Also, it is of the same material as the window layer applied (i.e.,

9   doped ZnO), but with high resistivity being undoped. However, Zn is well known as an

10   amphoteric element, i.e., it was very difficult to annihilate the $Zn(OH)_2$ content completely by

11   dehydration of $Zn(OH)_2 \rightarrow ZnO + H_2O$ in a strong, caustic (pH>10) solution of a CBD

12   process. The chemical stability of the $Cu(In,Ga)(S,Se)_2$ based absorber layer allowed for the

13   usage of a strong caustic condition given by an ammonia solution. However, it led to the

14   formation of a complex with a Zn ion. Due to the larger molecular size of $Zn(OH)_2$, the

15   colloid formation reaction was accelerated. Therefore, a higher bath temperature of 85

16   degrees C, compared with 65 degrees C, for CdS was employed to increase the growth rate

17   [89,95].

18   To reduce the $Zn(OH)_2$ content further and to enhance the resistivity of the buffer layer,

19   thiourea dissolved in a deionized water was added to the CBD solution. As a result, a mixture

20   of ZnO, ZnS and $Zn(OH)_2$ (termed $Zn(O,S,OH)_x$) as a high-resistivity buffer layer was

21   deposited on the $Cu(In,Ga)(S,Se)_2$ absorber. Owing to the $Zn(O,S,OH)_x$ band-gap energy of

22   more than 3.3 eV, the short-circuit current densities j_{sc} were enhanced by at least 2 mA/cm^2,

23   without any loss in absorption, within the wavelength range from 300 to 520 nm [95].

24   As one of the disadvantages of a wet CBD process for CdS deposition, in which the

25    $Cu(In,Ga)(S,Se)_2$ surface layer/$Cu(In,Ga)Se_2$ absorber/Mo/glass stack is immersed completely

26   into the solution, it was recognized that it required an extra step to wipe off the CdS-deposited

27   edge and rear sides of the substrate by ethanol. This extra work was understood as a

28   substantial disadvantage for commercialization. In contrast, ZnO was employed as a buffer

29   layer because it was an essentially high-resistivity material, and the additional cleaning step

30   was not necessary.

1   The resistivity of $Zn(O,S,OH)_x$ is about ten times larger than that of CdS. Therefore, CBD

2   techniques have been employed in order to not only deposit $Zn(O,S,OH)_x$ films with good

3   coverage on the $Cu(In,Ga)(S,Se)_2$ absorber layers, but also to realize substantially smaller

4   thicknesses (around 5 nm) than normally applied for CdS buffer layers (50 to 100 nm). Such

5   small thicknesses were expected to enhance the tunneling of charge carriers through the

6   barrier.

7   When depositing CBD-CdS buffer layers, large amounts of Cd-containing, liquid waste have

8   to be dealt with in commercialization, and the corresponding waste disposal of the CBD

9   solution is rather expensive, substantially increasing the manufacturing costs. In contrast, for

10   baseline processes with $Zn(O,S,OH)_x$ buffer layers, the same CBD solution can be used at

11   least six times, resulting in equally good solar modules, although the colloid formation

12   reaction proceeds continuously. At Showa Shell Sekiyu K.K., a waste-disposal process was

13   developed for the caustic CBD solution containing ZnO, ZnS and $Zn(OH)_2$. In this process,

14   ammonia was at first removed from the heated solution by discomposing with a catalyst, in

15   order to neutralize the waste CBD solution, and then, dry-solid powders of ZnO and ZnS were

16   collected, which were treated as industrial waste.

17   Maintenance of the CBD equipment used for CdS deposition always requires full protection

18   clothing, as well as other safety goods because of the use of a dilute acidic (e.g., HCl)

19   solution. In order to avoid such extra expenses, and for enhanced safety conditions in the

20   workplace, Cd-free materials for the buffer layer were selected, even in the early stage of

21   research and development.

22   The hardness of ZnO-based buffer layers is larger than that of CdS. As a result, CdS did not

23   work well as a suitable shock absorber against the sputtering process applied for the doped

24   ZnO window layer. Thus, owing to damage on the surface of the $Cu(In,Ga)Se_2$ absorber, it

25   was not possible to control the junction quality, although researchers tried to reduce the

26   impact of the sputter bombardment. Therefore, deposition techniques based on metal-organic

27   chemical vapor deposition (MOCVD) were applied for a ZnO:B (BZO) transparent

28   conductive oxide window [96]. One of the advantages of the MOCVD-BZO window was that

29   an insufficiently doped, high-resistivity ZnO thin layer was deposited at the initial stage of its

30   hetero-growth on a $Zn(O,S,OH)_x$ buffer layer [97]. The thickness of this initial layer was

31   controlled by adjusting the timing of the doping. This technique had been, for the first time,

32   developed by ARCO Solar, Inc. (ASI) [98], where a MOCVD-BZO window was deposited on

a CdS buffer layer. Then, based on this growth model, the window design was modified by depositing a high-resistivity ZnO layer between the Cu(In,Ga)Se$_2$ absorber and the conductive ZnO:Al (AZO) window layer.

The finding of a light-soaking effect of the baseline Zn(O,S,OH)$_x$ buffer layers was key to achieve enhanced conversion efficiencies. The sensitivity to light soaking is believed to correlate strongly with the concentration of hydroxide in the CBD buffer layer. CBD-CdS, in contrast, does not exhibit a strong light-soaking effect, probably since the hydroxide concentration is substantially smaller (less than a few mol%, as measured by means of X-ray photoelectron spectroscopy) [99].

8. Production processes for Cu(In,Ga)(S,Se)$_2$ photovoltaic industries: from ARCO Solar to the present day

Eventually, research efforts performed at the laboratory scale are supposed to be transferred to industrial production of Cu(In,Ga)(S,Se)$_2$ solar modules. Therefore, it is essential to look into the development of industrial production during the past decades in this final section of the present contribution.

8.1. Development of stacking sequences during the past three decades

Fig. 4 gives an overview of this development. For a recent review on industrial Cu(In,Ga)Se$_2$ processes and stacking sequences of the corresponding solar modules, the reader is referred to Ref. 100. The first 10% efficient solar-cell produced at Boeing Aerospace Company in 1982 consisted of a CdS:In(2-4 µm)/CdS(0.5-1.5 µm)/CuInSe$_2$(2-6 µm)/Mo thin-film stack on a borosilicate glass substrate, where CuInSe$_2$ was deposited as a high-resistive/low-resistive bilayer [7]. Back then, SiO$_x$ was used as antireflection coating, instead of MgF$_2$ as applied nowadays. During the following years, the CdS:In/CdS window was replaced first by evaporated CdZnS [8], then by a thin (50 nm) CdS layer, grown by CBD, which was introduced by ARCO Solar Inc. [10] (see also Secs. 3 and 7 above). Further improvements in the window layers of the solar-cell stack were achieved by using a high-resistivity/low-resistivity ZnO:Al bilayer, which was sputtered on the CdZnS buffer layer. The high resistivity part was realized by an undoped, intrinsic (i-)ZnO layer of few tens of nanometers

1 in thickness [101]. Using this approach, a 13.7% efficiency record was reached at Boeing

2 Aerospace Company, applying a bilayer process for $Cu(In,Ga)Se_2$ deposition, during which

3 first a Cu-rich, and then a Cu-poor Cu-In-Ga-Se layer was coevaporated, resulting in an

4 overall Cu-poor composition. In contrast, 13% solar cells were produced at ARCO Solar Inc.

5 using a sequential $Cu(In,Ga)Se_2$ process, i.e., first sputtering of Cu, In, Ga, and then

6 selenization of these precursors in H_2Se gas [10].

7 In 1994, researchers at NREL developed a three-stage process for $Cu(In,Ga)Se_2$ layer

8 deposition. It comprises the deposition of an In-Ga-Se precursor, then coevaporation of Cu-Se

9 until excess Cu-Se forms on top of the $Cu(In,Ga)Se_2$ layer, and finally In-Ga-Se in order to

10 consume the excess Cu-Se again, resulting in a $Cu(In,Ga)Se_2$ layer with overall Cu-poor

11 composition [102]. The beneficial role of the Cu-Se phase was discussed by Klenk et al.

12 [103].

13 Introducing Na during or after $Cu(In,Ga)(S,Se)_2$ layer deposition improved the

14 $Cu(In,Ga)(S,Se)_2$ solar-cell performance even further (see Sec. 6 above). One option is that

15 Na diffuses from the Na-containing glass substrate. Alternatively, a diffusion-barrier layer

16 (e.g., Si-N, Si-O) prevents Na diffusion from the glass, and a Na precursor (e.g., a thin NaF

17 layer) is deposited on top of the Mo/barrier/substrate stack (or Na is already incorporated in

18 the Mo layer), prior to the $Cu(In,Ga)(S,Se)_2$ layer deposition. By the end of the 1990s, $MoSe_2$

19 formation between Mo and $Cu(In,Ga)(S,Se)_2$ has attracted substantial attention [104], and

20 efforts have been made in order to control its thickness and other properties in order to

21 optimize the electrical properties at the back contact.
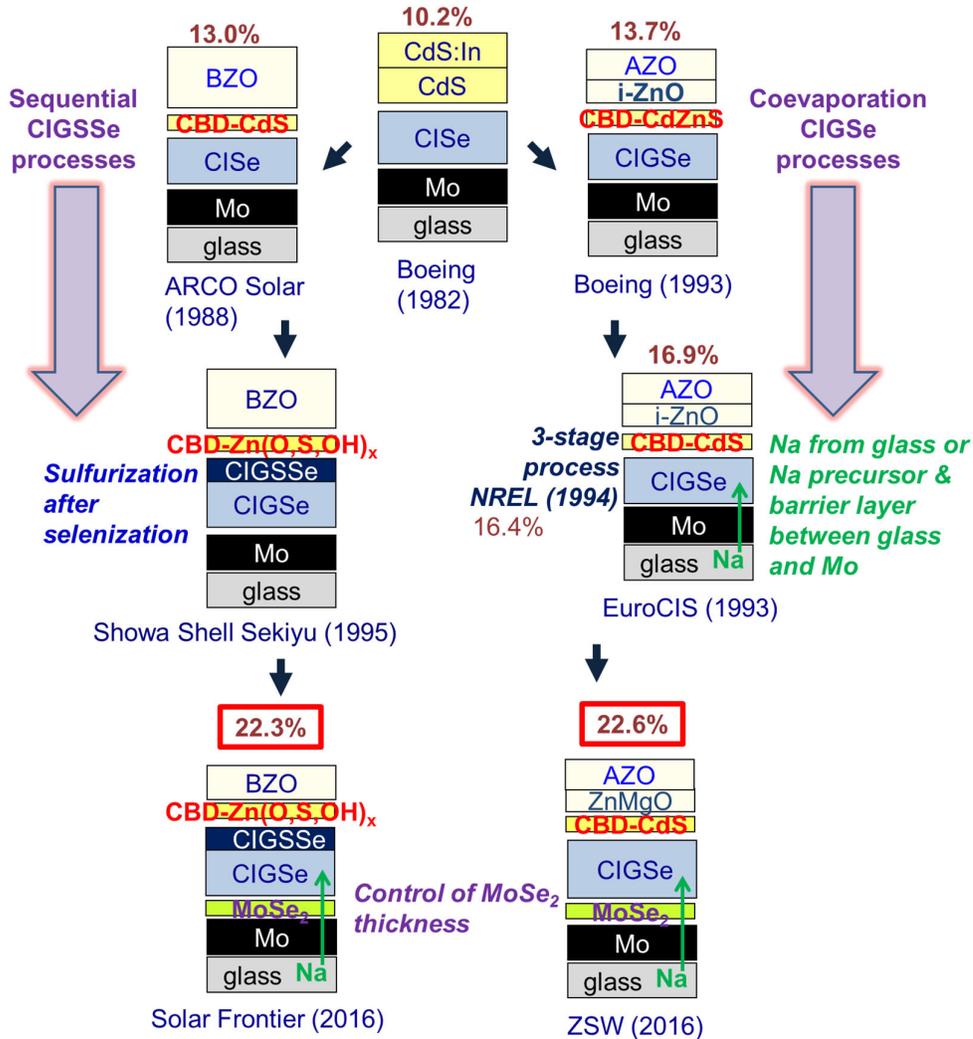
Figure 4: Development of stacking sequence in Cu(In,Ga)(S,Se)$_2$ solar cells for industrial application through the past four decades.

8.2 ARCO Solar

ARCO Solar Inc. (ASI) was founded as Solar Technology International in 1975, and by 1980, it was the world's largest photovoltaic manufacturer with a crystalline silicon capacity of about 1 MW/yr. ASI began work on CuInSe$_2$ photovoltaic devices in late 1981, soon after Boeing Aerospace Company had reported a 10% thin-film CuInSe$_2$ solar cell (see Sec. 3 above). Early ASI work on CuInSe$_2$ focused on elemental coevaporation, but the company also explored sputtered binary selenides and electroplated elemental metal stacks with

1 subsequent H_2Se selenization as pathways to lower-cost commercialization. The challenges of

2 uniform precision electroplating on large areas at high rates motivated a shift to sputtering of

3 Cu and In precursor stacks, from which world record cells (13% in 1988 [10]) were produced.

4 A key enabling advance was a first-order Cu-In hydride-selenization model, based on an

5 adaptation of Si-oxidation models [105].

6 Early two-step $CuInSe_2$ films often featured poor adhesion at both the Mo/substrate and the

7 $CuInSe_2$/Mo interfaces. Overall, the adhesion improved substantially by upgrades in substrate

8 cleaning, implementation of adhesion layers (e.g., Cr), adjustments to the Mo properties (via

9 the sputter conditions), and tuning of the selenization parameters, which probably also

10 affected the properties of the intermediate $MoSe_2$ layer (as discovered only later, see Sec.

11 8.1). Ga was added by using Cu-Ga sputter targets with the aim of producing $Cu(In,Ga)Se_2$

12 films exhibiting larger band-gap energies; however, the selenization processes of that time

13 yielded strong Ga concentration gradients, i.e., the effective band-gap energy of the

14 $Cu(In,Ga)Se_2$ absorber layer was largely unchanged. However, the presence of a high Ga

15 concentration near the Mo further improved the adhesion at the $Cu(In,Ga)Se_2$/Mo interface

16 and broadened the selenization processing ranges, which in turn led to larger average grain

17 sizes in $Cu(In,Ga)Se_2$ films.

18 $Cu(In,Ga)Se_2$ solar cells at ASI initially comprised evaporated CdS/CdS:In transparent

19 electrode stacks, similar to contemporaneous solar cells at other manufacturers. The

20 photocurrent densities of these devices were increased by decreasing the optical absorption in

21 the CdS layer, first by replacing CdS:In with metal oxides exhibiting larger band-gap

22 energies, and second by replacing evaporated CdS with thin, dense, and conformal chemical-

23 bath-deposited buffer layers. A low-temperature, chemical vapor deposition process was

24 developed to deposit ZnO:B as a low-cost, controllably-textured transparent conductor.

25 Improvements in $Cu(In,Ga)Se_2$/Mo adhesion and $Cu(In,Ga)Se_2$ film quality increased the

26 stable cell efficiency and sparked a shift to work on larger, commercially-relevant substrate

27 sizes as well as the development of manufacturing tools, processes and infrastructure,

28 including large-area selenization systems. A mishap with a selenization tool interrupted this

29 progression; the focus shifted to vapor-phase and solid-state selenization. Eventually hybrid

30 chalcogenization processes incorporating solid-state Se and hydride gases were developed,

31 e.g., H_2Se to improve the optoelectronic properties of $Cu(In,Ga)Se_2$, and H_2S to produce

32 $Cu(In,Ga)(Se,S)_2$ films. Sulfurization of the surface of the synthesized $Cu(In,Ga)Se_2$ layer

1   resulted in an increased band-gap energy at the $Cu(In,Ga)(S,Se)_2$/CdS interface, which

2   improved the open-circuit voltage of the device substantially.

3   In 1990, ASI was taken over by the European joint-venture partner Siemens Solar, and in

4   1998, the first worldwide commercial series production of $Cu(In,Ga)(S,Se)_2$ solar modules

5   (with 40 W_p of nominal power) was started in Camarillo, California. The Siemens Solar

6    $Cu(In,Ga)Se_2$ research team in Germany realized various additional advances, including, most

7   notably, rapid thermal processes, which were subsequently commercialized at Avancis,

8   Germany. Also at ASI's Asian joint venture partner Showa Shell Sekiyu, progress in module

9   manufacturing was achieved, mainly by a "sulfurization after selenization" $Cu(In,Ga)(S,Se)_2$

10   process as well as by a $Zn(O,S,OH)_x$ buffer layer, commercialized later by Solar Frontier (see

11   Secs. 7.2 above and 8.3 below).

12   ASI's 1980s work on electroplating and atmospheric-pressure selenization, on chemical bath

13   deposition of buffer layers and on chemical vapor deposition of transparent conductors

14   indicated that non-vacuum processes may yield $Cu(In,Ga)Se_2$ solar-cell devices with good

15   qualities. Various groups further explored non-vacuum $Cu(In,Ga)Se_2$ processing with the aim

16   of reducing the capital cost of production tools and facilities as well as the materials costs of

17   manufacturing. These groups included Unisun and International Solar Electric Technologies,

18   which independently developed non-vacuum processes based on nanoparticulate materials.

19   Unisun focused on core-shell, mixed-metal oxide nanoparticles formed by aerosol pyrolysis,

20   on precursor layer deposition by spraying, dipping, spinning, or printing, and on $Cu(In,Ga)Se_2$

21   film formation by reactive annealing and on-demand, in-situ hydride generation. Unisun

22   technology was licensed to Nanosolar, which in turn went on to develop low-cost mechanical

23   milling of mixed-metal nanoparticles, high-speed roll-to-roll slot-die printing of precursor

24   layers on metal foil, and non-hydride selenization to form large-area cells. SoloPower

25   developed roll-to-roll Cu-In-Ga electroplating, solid-state chalcogenization, and light-weight

26   flexible modules. In France, an electroplating route for $Cu(In,Ga)Se_2$ was initiated in the

27   beginning of the 1990s within the EUROCIS and EUROCIS-M projects, which was then

28   further developed at IRDEP at the beginning of the 2000s and led to the founding of the start-

29   up company Nexcis. These non-vacuum strategies provide a high-return-on-capital

30   alternative to vacuum-based $Cu(In,Ga)Se_2$ technologies.

31

8.3 Solar Frontier, Japan

The baseline process for production of $Cu(In,Ga)Se_2$ absorber layers with a very thin surface layer of $Cu(In,Ga)(S,Se)_2$ at Solar Frontier is depicted in Fig. 5. The absorber synthesis by "sulfurization after selenization" (SAS) is described in detail further below. A $Zn(O,S,OH)_x$ buffer layer instead of CdS, and a ZnO:B window layer (BZO, originally developed by ARCO Solar Inc.), instead of a ZnO:Al (AZO, introduced by Boeing Aerospace Company), are used in order to reduce absorption losses in the short-wavelength and plasma regions.
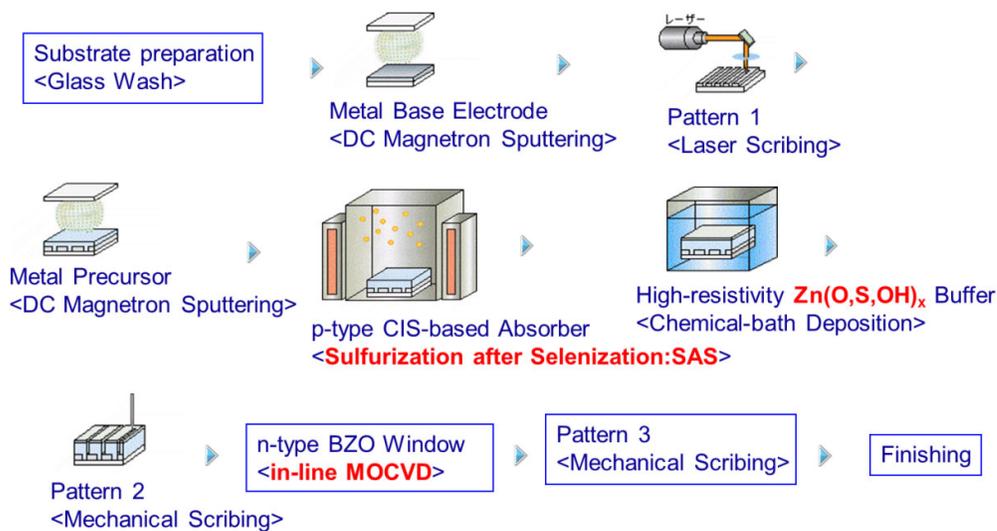
Figure 5: Baseline process of $Cu(In,Ga)(S,Se)_2$ solar modules transferred to commercial production at Solar Frontier.

The "sulfurization after selenization" process (Fig. 6) comprises sputtering of a Cu-Ga-In precursor layer using Cu-Ga alloy and In targets, selenization using dilute H_2Se gas and finally a sulfurization step using dilute H_2S gas in the reaction furnace, which results in a $Cu(In,Ga)(S,Se)_2$ surface layer on top of a $Cu(In,Ga)Se_2$ absorber [106,107]. Goushi et al. showed that Ga diffusion towards the $Cu(In,Ga)(S,Se)_2$ surface is enhanced when using higher substrate temperatures and longer holding durations for the sulfurization step [108]. It was also revealed that it is possible to increase the sulfur content incorporated into the Ga-graded $Cu(In,Ga)Se_2$ absorber by properly selecting the growth parameters [108,109].

1　The use of dilute instead of pure reactive gases has the advantage of reduced gas

2　consumption; thus, reduced production costs. The thicknesses of the complete

3　$Cu(In,Ga)Se_2/Cu(In,Ga)(S,Se)_2$ layers are about 1.2-1.5 μm. Used sputtering targets can be

4　recycled, because they are not contaminated considerably in the baseline process.
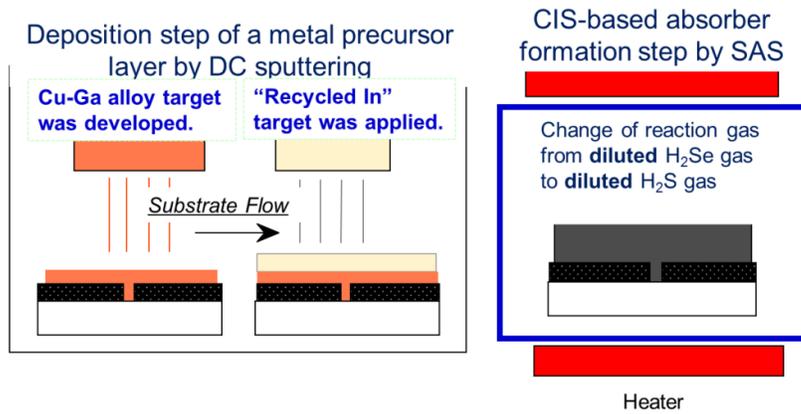
5

6　Figure 6: Schematics of the "sulfurization after selenization" (SAS) process at Solar Frontier

7　K.K..

8

9　9. Conclusions

10　The present work provides a historical retrospective on several milestones and key

11　innovations in the research and development of $Cu(In,Ga)(S,Se)_2$ solar cells, as witnessed and

12　presented by the coauthors working in their laboratories or companies at that time. It becomes

13　apparent that one is well advised to remain open minded, even when concentrating on very

14　specific issues in daily research work. Taking the example of the first $CuInSe_2$ solar cells,

15　which were produced by chance when actually aiming at developing broad-band

16　photodetectors for optical communication, it was shown that innovative technologies for a

17　specific application may arise from developments in a different field. Other insights simply

18　resulted from accidents or by chance in the experimental work, as, e.g., the issue of Na from

19　the soda-lime glass substrate. Moreover, very often, the observation of an unexpected result or

20　effect gets overlooked and receives no further attention for investigation or analyses, owing to

21　restricting boundary conditions, such as project milestones. Here, it is recommended to

22　always pay attention to things one does not understand, study them and analyze them, because

23　this is where breakthroughs come from.

1    $Cu(In,Ga)(S,Se)_2$ solar-cell efficiencies have improved to remarkably high values of more

2   than 22%. There are good prospects for further improvement as progress continues. However,

3   industrial production of correspondingly high-efficiency solar modules with low production

4   cost requires overcoming additional challenges. In this context, further work is necessary,

5   especially for the development of simple and robust deposition methods along with device

6   structures requiring less complexity for processing and less stringent conditions of large-area

7   uniformities, without sacrificing the efficiencies. New directions of research, such as flexible

8   solar cells on low-cost substrates, cells with thinner absorber layers, device concepts based on

9   passivated surfaces and point contacts or tandem solar cells, microcells among others, offer

10   interesting options for further developments. The historical developments described in the

11   present summary may provide motivation for finding innovative and unconventional

12   solutions.

13

14   Acknowledgements:

18

19   References:

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