

Compound Polycrystalline Solar Cells: Recent Progress and Y2K Perspective

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Abstract

A historical perspective on the development of polycrystalline thin film solar cells based on CdTe and CuInSe₂ is presented, and recent progress of these thin film technologies is discussed. Impressive improvements in the efficiency of laboratory scale devices has not been easy to translate to the manufacturing environment, principally due to our lack of understanding of the basic science and engineering of these materials and devices. "Next-generation" high performance thin-film solar cells utilizing multijunction device configurations should achieve efficiencies of more than 25% within ten years. However, our cost-effective manufacturing of these more complex devices will be problematic unless the science and engineering issues associated with processing of thin film PV devices are addressed.

Keywords: CdTe, CuInSe₂, Solar cells, Thin films

1. Introduction

As the demand for more electric power increases and present power plants reach end-of-life, the need for an environmentally benign means of generating electricity becomes imperative. Conversion of sunlight directly to electricity using photovoltaics is a means of generating electricity without causing changes to the environment because the fuel consumed is external to the Earth. Photovoltaic technologies are still in their infancy, but have the potential to play an important role in meeting electric power needs in the next century, provided that PV systems can be made competitive with conventional power generation and other emerging renewable energy technologies.

Present-day crystalline-Si technology is approaching its lower limit in terms of production costs. Thin-film photovoltaic modules can be produced by economical, high-volume manufacturing techniques, dramatically reducing cost, and are in a premanufacturing development stage. However, unlike crystalline Si, equipment for these technologies is largely unique and custom designed. In addition, the processes involved for making large-area, high-volume, thin-film PV modules are very complex. As a result, the translation of the laboratory results to large-scale manufacturing has been much more difficult than expected. Presently, several manufacturing facilities in the 1 to 10 MW range based on a-Si, CdTe and CuInSe₂ technologies are in the start-up stage. A critical

issue in developing these thin-film facilities has been the limited scientific and engineering basis available to effectively and rapidly scale up laboratory processes. In most cases, there are no quantitative relationships between critical process parameters, film growth, film properties and device performance. In this paper, recent progress in the development of polycrystalline thin film technologies, based on CdTe and CuInSe₂ materials, is discussed with respect to advances in basic science and engineering, device performance, module performance, and manufacturing. In addition, “next-generation” high-performance thin-film solar cells will also be assessed, along with critical issues associated with their development.

2. CuInSe₂ based devices

2.1. Historical perspective

Much of the fundamental knowledge of the CuInSe₂-based ternary compounds had already been established by 1980. The electrical, optical and structural properties of the semiconducting ternary chalcopyrites, (Cu,Ag)(Al,Ga,In)(S,Se,Te)₂, were examined in the 1960’s and 1970’s [1–3]. Then, in 1974 S. Wagner *et al* produced the first high efficiency (12.5%) CuInSe₂/CdS photovoltaic device by evaporating n-type CdS onto a single crystal of p-type CuInSe₂ [4]. However, there was limited interest in this p-n junction device [5,6] until the first high efficiency (9.4%) polycrystalline thin film solar cell was made from these materials [7]. Then by using the alloys of Cu(Ga,In)Se₂ [8] and CuIn(S,Se)₂ [9] wider energy band gaps and higher open circuit voltages were achieved. Finally, graded energy band gaps were produced from the alloys of CuIn(S, Se)₂ [10] to increase the open circuit voltage while maintaining short circuit current.

The energy band gaps and lattice structure of these ternary compounds and their associated alloys were examined from theoretical band structure calculations beginning in the mid 1980’s [11]. These studies demonstrated that a continuous alloying similar to that done with the III-V materials was also possible with the ternary chalcopyrites. Work is still ongoing in examining the defect physics of these materials [12].

A basic understanding of how these polycrystalline p-n heterojunctions worked as photovoltaic devices began to be established in the 1980’s [13-15]. Device measurements and analyses have showed that these high efficiency polycrystalline thin film solar cells are controlled by recombination within active light absorbing material, i.e., CuInSe₂ and its alloys [16]. This is because the absorber material inverts (i.e., changing from p to n-type) near the junction which eliminates interface recombination as a loss mechanism. The recombination is then controlled by states within the energy band gap in this region. The loss of minority carriers to grain boundary recombination in the polycrystalline absorber is also reduced because the grain boundary edges are more heavily doped than the bulk.

2.2. Operational aspects

There has been increasing insight into the science and engineering fundamentals of the Cu(Ga,In)Se₂ films and devices as researchers have utilized a variety of techniques to probe the structural and electrical properties. One area of focus has been the Cu(Ga,In)Se₂/CdS interface to understand better the role of the CdS film formation, particularly with chemical bath deposition of the CdS, on the device performance [17, 18]. Diffusion of In or Se into CdS and S into Cu(Ga,In)Se₂ have been shown by x-ray emission and photoelectron spectroscopies [19] while transmission electron microscopy [20] and secondary ion mass spectroscopy [21] measurements indicated Cd diffusion into the Cu(Ga,In)Se₂ film.

While a variety of measurements and analysis have indicated that Cu(Ga,In)Se₂ device performance is limited by recombination of minority carriers in the space charge region of the Cu(Ga,In)Se₂ absorber layer, detailed characterization of the trap states and their effect is only recently coming to light. Recently published results have shown that metastable effects in the electronic transport properties can be explained by the same trap states in the Cu(Ga,In)Se₂ [22,23]. The nature and origin of the defects that provide the recombination sites is a critical issue in controlling device performance. Admittance spectroscopy and deep level transient spectroscopy measurements reveal a distribution of trap states centered ~300 meV above the valence band [24]. There is evidence that these states may be associated with defect clusters rather than isolated point defects [25,26].

The beneficial effect of sodium incorporated into Cu(Ga,In)Se₂ films has been well established regardless of whether the Na is provided via diffusion from a soda lime glass substrate [27], from a Na-containing precursor layer deposited prior to the Cu(Ga,In)Se₂ film [28,29] or by Na introduced simultaneously with the Cu(Ga,In)Se₂ [30,31]. It has been shown that Na enables the films to achieve increased grain size, more strongly oriented texture [28] and higher conductivity [32]. Still, despite many studies of the structural, chemical, and electronic effects of Na impurities and several models proposed, the nature of the beneficial effect on devices is unclear. Only recently has it become clear where the Na impurities lie in the Cu(Ga,In)Se₂ film when high-resolution measurements have shown that Na migrates preferentially to the grain boundaries [33] and surfaces [34]. Oxygen is another impurity whose effect on Cu(Ga,In)Se₂ films and devices has been well studied but not clearly understood. It has recently been proposed that the roles of Na and O are related [35,36].

The relation between the structural properties of the Cu(Ga,In)Se₂ films and their electronic and device behavior is another area of research where recent efforts are beginning to shed new light. A quantitative study of growth parameters, including substrate temperature, on grain size has found that the correlation between grain size and device performance is not a simple one [37]. Similarly, the relation between Cu(Ga,In)Se₂

film orientation and both growth conditions and device performance have been explored without the emergence of a clear picture [38,39].

There has been considerable effort focussed on alloys of CuInGaSe_2 for the purpose of increasing the bandgap (E_g) with the primary emphasis on the addition of Ga and S. This can be achieved by introducing an additional source to the physical vapor deposition system or by post deposition annealing of suitable precursor films. The former is the most common method of obtaining $\text{Cu}(\text{Ga},\text{In})\text{Se}_2$ films. The latter is more suitable for the introduction of sulfur into the selenide films. Introduction of Ga and S into the precursor films by annealing has been investigated at some length at IEC. These investigations have resulted in the determination of the chemical reaction kinetics of the formation of $\text{CuIn}(\text{SeS})_2$ films, and of the diffusional kinetics involved in the intermixing of CuInSe_2 and CuGaSe_2 films [40,41]. The best cell efficiencies to date for the ternary materials CuInS_2 ($E_g = 1.5\text{eV}$) and CuGaSe_2 ($E_g = 1.5\text{eV}$) are 12.5% [42] and 9.3% [43]. Many other candidates for chalcopyrite thin films with higher bandgap could be developed, as discussed below.

2.3. Cell and module performances

Among CuInGaSe_2 based devices the most successful one incorporates a CuInGaSe_2 absorber layer containing 20% to 30% Ga with respect to $\text{In}+\text{Ga}$. NREL has been the leader in the development of small area devices of this type and has demonstrated record efficiencies that have been increasing steadily over the years [44]. The absorber film is deposited by co-evaporation from elemental sources on to Mo coated soda-lime glass. The latest record efficiency reported by NREL has been 18.8% for an area of 0.44 cm^2 . They have also reported 43.9 cm^2 area device with an efficiency of 13.7%. Other notable achievements by NREL that have significance for large scale manufacturing are: (1) a Cd free device of 15% efficiency, and (2) a device on stainless steel substrate of 17.4% efficiency. These performances establish the present state-of-the art for this class of PV devices.

In the industrial sector a number of companies are pursuing commercial development of CuInGaSe_2 based PV modules using a variety of process technologies and product designs depending on their perception of production costs and market demands. Of these, Siemens Solar, Inc. (SSI) is at the most advanced stage, having 4 different sizes (5W, 10W, 20W, 40W) of CuInGaSe_2 based 12V modules presently offered to customers [45]. In 1997, SSI installed a 1 kW array of 29 modules at the NREL testing facility with an average efficiency of 9% and the highest efficiency of 11.1% for module aperture areas of 3665 cm^2 [46]. The highest module efficiency reported so far by SSI is 12.1%. The process used by SSI for the deposition of the Ga containing absorber on to soda-lime glass is described as a non-vacuum “selenization/sulfurization” type, the details of which are proprietary. A potant and a tempered glass top cover are used to encapsulate the modules.

Another company, Würth Solar GmbH, is also developing a glass-to-glass encapsulated in-line Cu(Ga,In)Se₂ module manufacturing operation. The substrate is again Mo coated soda lime glass but the absorber deposition process is physical vapor deposition from elemental sources on to moving substrates. At the present time, the highest efficiency reported is 12.8% for an aperture area of 731 cm² [47,48]. Pilot production of 30 cm x 30 cm modules gives an average efficiency of close to 12% over 50 consecutive modules. An efficiency of 7% was obtained for a Cd free module of the same size.

Global Solar Energy (GSE), on the other hand, is developing flexible module manufacturing systems using polyimide or stainless steel as substrates. Using Cu(Ga,In)Se₂ deposited in a prototype web system at GSE, small area device efficiencies of 10% were obtained on both types of substrates at IEC within the framework of a technology development consortium. Also as part of this program, IEC has obtained a small area device efficiency of 12% [49] on stationary polyimide substrates..

In addition to the organizations mentioned above, there are a number of companies which are at early stages of commercialization of CuInGaSe₂ based modules. Energy Photovoltaics, Inc. is pursuing a technology based on physical vapor deposition of the CuInGaSe₂ based absorber and is planning to build CuInGaSe₂ manufacturing lines with 1MW capacity in New Jersey, 10MW in Germany and 5 MW in California. EPV utilizes its own *FORNAX* vacuum process for CuInGaSe₂ formation [50] with source materials delivered by linear source evaporation. ISET [51] and Unisun are each developing a new non-vacuum process. Their technologies involve spraying/printing of precursor powders on to a Mo coated glass substrate followed by reactive sintering. Such an absorber film from Unisun was recently processed into a device at IEC and resulted in an efficiency of 11.7% [52].

3. CdTe based solar cells

3.1. Historical context

The foundation for understanding the electronic nature of CdTe single crystals was first elucidated by D. A. Jenny and R. H. Bube [53] and F. A. Kroger and D. de Nobel [54] in the mid-1950's. The relationship between Cd-Te phase equilibria and defects to CdTe semiconducting properties was subsequently developed by D. de Nobel [55] in 1959 and refined by other research groups during the 1960's [56].

Solar cells based on n-type CdTe single crystals and polycrystalline films were developed in the early-1960's by reacting the surface in an acidic copper salt solution to form a CdTe/Cu₂Te junction [57–59].

Photoconverters based on p-type CdTe single crystals in conjunction with evaporated n-type CdS films were first prepared in the mid-1960's [60,61] and achieved modest conversion efficiency by the mid-1970's [62,63]. At that time, efficiencies of cells using CdTe single crystals were ~10% and exceeded efficiencies obtained with all-polycrystalline thin-film CdTe/CdS cells. The fundamental issues confronting researchers of this period were laid out by D. Bonnet in 1972 [64]: doping efficiency; abrupt versus graded junctions; active versus passive grain boundaries; and low-resistance contacts. By the early 1980's, processing schemes were refined, leading to conversion efficiencies approaching or exceeding 10% for superstrate thin-film CdTe/CdS devices made by different deposition technologies, such as close-space vapor transport [65], screen-printing and sintering [66] and electrodeposition [67]. Common to these processes were thermal treatment of the layers in the presence of oxygen and application of gold to obtain a low-resistance back contact. In the late 1980's, the beneficial role of cadmium chloride during thermal treatment [68,69] and addition of minute quantities of copper in the back contact [70,71] were demonstrated.

Considerable emphasis was directed towards the development of scalable fabrication processes for thin film CdTe/CdS modules, but for each fabrication technology, module performance lagged behind "best-cell" performance by about 2-to-1 [72].

3.2. Achievements over the past decade

Advances in CdTe cell processing in the 1990's resulted in conversion efficiencies exceeding 15% [73–76] in spite of little additional developments in understanding of the fundamental properties of polycrystalline CdTe. Measurements of isolated CdTe films, powders or crystals do not provide relevant information regarding operational characteristics of the CdTe/CdS junction in these devices. Recently, measured band-offsets, optical bowing and miscibility gaps in the CdS-CdTe alloy system have been calculated from band structure theory shedding light into our understanding of the junction operation [77]. Also, electronic and materials analyses of polycrystalline CdTe/CdS solar cells and solar cell structures have facilitated a qualitative understanding of the device and continue to feed into processing refinements. In present-generation devices, approximately 85% of the available photons can be collected as carriers, yielding short circuit current densities up to 26.5 mA/cm². However, open circuit voltage and fill factors fall short of predicted values, and the diode current in CdTe/CdS devices appears to be limited by recombination through a distribution of states in the space-charge region of the CdTe [78]. The best performance has been obtained by high temperature processes, suggesting that high process temperatures are required to reduce density of these defect states. A more complete picture is expected from research directed towards understanding the polycrystalline nature of the device with regards to: junction operation with vanishingly-thin CdS [79,80]; CdS-CdTe interdiffusion [81–83]; CdTe doping [84]; CdTe contact surface preparation [85,86] and penetrative effects [87]; stress effects on junction and contact stability [88,89].

Advances in process development at laboratory scale have been gradually transferred to large-scale deposition and cell fabrication. In 1998, total shipments of CdTe cells and modules were 1.2 million MW, primarily owing to products manufactured by Matsushita, based on a screen-print technology [90]. In the United States, a hybrid form of evaporative deposition was developed at Solar Cells, Inc., now First Solar, and has resulted in the production of ~3 foot wide modules [91]. Close space sublimation is being developed for module production by Antec in Germany [92]. The electrodeposition process first developed in the 1980's at Monosolar was further refined by the Standard Oil Company of Ohio, eventually leading to British Petroleum's 1 ft² Apollo production line. This technology has been extended to production of 5.9 ft² modules with aperture area efficiency of 8.1 to 8.3% at the BP Solarex facility in Fairfield, California [93].

4. Next generation: High performance, >20% polycrystalline solar cells

For PV to make a truly significant contribution to the energy supply and to an improved environment in the 21st century, the development of modules with higher performance is required. One option is to produce thin film modules using multijunction device structures. De Vos has determined the limits of efficiency for solar cells with multi-junctions, and the results are summarized in Table I for unconcentrated sunlight [94]. As the number of junctions increases from 1 to infinity, the thermal loss due to absorption of light with energy greater than the bandgap goes to zero, resulting in a thermodynamic performance limit of 68%. In Table II, the best efficiency for present-day multijunction solar cells is compared to the thermodynamic limit. Based on this, it is reasonable to predict that III-V single-crystal multijunction solar cells with conversion efficiencies of near 40% and thin-film multijunction solar cells of more than 25% should be achievable during the next 10 years. However, the real question will be: Can the increased complexity in fabricating these high-performance devices be cost effective when translated to commercial high-performance modules?

Table I. Thermodynamic Efficiency Limits for Unconcentrated Sunlight and the Optimum Bandgaps

# of Junctions	Efficiency	E _g (eV)
1	30%	1.3
2	42%	1.9 - 1.0
3	49%	2.3 - 1.4 - 0.8
4	53%	2.6 - 1.8 - 1.2 - 0.8
Infinity	68%	

Table II. Solar Cell Efficiency Records, Unconcentrated Sunlight

Device Structure	Efficiency	Organization	% of Thermodynamic Efficiency Limit
GaInP/GaAs (monolithic)	30.3%	Japan Energy [ref. 95]	70%
GaAs/CuInSe ₂ (4-terminal)	25.8%	Kopin/Boeing [ref. 96]	60%
a-Si/CuInSe ₂ (4-terminal)	14.6%	ARCO [ref. 97]	35%
a-Si/a-Si/a-SiGe (monolithic)	14.5% (unstabilized)	USSC [ref. 98]	30%

Current thin-film technologies can be separated into two categories: multijunction a-Si-based modules and single-junction polycrystalline modules. The multijunction a-Si device structure was developed to provide an engineering solution to a fundamental stability issue with a-Si materials. The best laboratory device is a three-junction cell with a stabilized efficiency of 13% [98]. Although a-Si-based materials can be made with bandgap from 1 to 2 eV, it is difficult to project significant improvements in performance without a major breakthrough in the fundamental properties of a-Si and its alloys.

In the polycrystalline thin-film area, CdTe-based solar cells have achieved a single-junction efficiency of ~16% [99]. CdTe solar cells, with a bandgap of ~1.4 eV, would be appropriate for the middle cell of a triple-junction device. Although the bandgap of CdTe can be controlled by alloying with other II-VI materials, to date there has been limited success at making solar cells with varied bandgap.

CuInSe₂-based solar cells have achieved a single-junction efficiency of 18.8% [44], which is comparable to that of the best multicrystalline silicon devices of 19.8% [100]. Thus, CuInSe₂-based solar cells are a real alternative to crystalline-silicon technologies. The I-III-VI chalcopyrite materials can be compared to the III-V materials in that there is a set of multinary compounds that form a continuous solid solution. In this group of materials, the bandgap can be varied from 0.9 to 2.7 eV for the Cu-based chalcopyrite and from 0.6 to 3.1 eV for the Ag-based materials (as summarized in Table III). This set of materials provides a design basis for developing multijunction thin-film polycrystalline solar cells. High-performance cells with low bandgap have been demonstrated, and continuous progress with wider bandgap materials has been made. The critical issues that need to be addressed for a tandem-cell structure are: (1) development of wide-E_g materials

(1.5 to 1.8 eV) for the top cell, with efficiencies exceeding 15%; (2) compatibility of the bottom cell to the growth process needed for the top cell; and (3) an effective transparent interconnect between top and bottom cells. These issues include a myriad of nontrivial scientific and technical problems, many of which interrelate and interact in the device realization. However, the PV technology has advanced to the point that these more complex devices should be considered—especially with their potential place in the coming generation of photovoltaic devices.

Table III. Candidates for Quaternary Alloys

Low Bandgap		High Bandgap	
Material	eV	Material	eV
CuInSe ₂	1.0	CuAlSe ₂	2.71
CuInTe ₂	1.0 - 1.15	CuInS ₂	1.53
CuInTe ₂	1.0 - 1.1	CuAlTe ₂	2.06
CuGaTe ₂	1.23	CuAlTe ₂	2.06
CuGaTe ₂	1.23	CuGaSe ₂	1.7
CuGaTe ₂	1.23	CuGaS ₂	2.5
AgInSe ₂	1.2	AgGaSe ₂	1.8
AgInSe ₂	1.2	AgAlSe ₂	1.66
AgInSe ₂	1.2	AgInS ₂	1.8
AgGaTe ₂	1.1 - 1.3	AgGaSe ₂	1.8
AgGaTe ₂	1.1 - 1.3	AgGaS ₂	2.55
AgAlTe ₂	0.56	AgAlS ₂	3.13

5. Discussion

Thin-film polycrystalline solar cells can play an important role in generating electricity in the next century, provided:

- A fundamental science and engineering base is developed so that an effective transfer of laboratory results can be achieved.
- In-line diagnostics and real time processing controls are developed for manufacturing facilities.

Further, next-generation thin-film technologies, using multijunction device configurations, will be needed if PV is to be an important contributor to power generation in the next century.

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