

RECENT PROGRESS AND CRITICAL ISSUES IN THIN FILM POLYCRYSTALLINE SOLAR CELLS AND MODULES

Robert W. Birkmire
Institute of Energy Conversion, University of Delaware
Newark, DE 19716

ABSTRACT

Thin film CdTe and CuInSe₂ based solar cells have reported efficiencies of over 15% and 17% respectively for small area laboratory devices and over 10% for prototype modules. In the present article, an approach to translate laboratory results to the development of large scale module manufacturing facilities is discussed, and critical issues associated with the development of CuInSe₂ and CdTe thin film polycrystalline module manufacturing are identified. For CuInSe₂ based PV, the analysis and modeling used in the design and development of a continuous, commercial scale deposition system is presented. For CdTe based PV, the issues associated with the back contact are discussed with particular emphasis on the development of a diffused Cu contact.

BACKGROUND

In the 1960's, the development of PV technology was driven by the need for space power systems. A multi-million dollar program was initiated through JPL and, as a result, crystalline silicon technology was successfully developed to meet the space power requirements. In the 1970's, in part driven by the oil embargo, PV for terrestrial applications began to emerge initially for specialized power application. Large scale central power PV facilities were envisioned and the challenge to make PV cost competitive with conventional sources of electricity began. Monolithically integrated thin film modules were identified as having the greatest potential to reduce the cost of PV electricity. Thin film PV, in principle, could take advantage of high volume manufacturing processes to drive the cost down.

Remarkable progress was made on the development of thin film PV in the early 1980's. In 1980, the first 10% efficiency thin film solar cell was reported based on Cu₂S/CdS [1]. Several companies started to develop manufacturing facilities to produce Cu₂S based PV modules and in 1981, the first deposition of a PV material, CdS window layer, was achieved on a continuously moving web [2]. However, the development of the Cu₂S/CdS PV was discontinued because of stability issues. Also, again in 1981, the first 10% CuInSe₂ solar cell was reported [3]. In 1982, small area laboratory solar

cells based on both a-Si and CdTe with efficiencies over 10% were reported [4, 5]. Many companies during the 1980's and into the 1990's indicated their plans to manufacture modules based on these thin film PV technologies but, as of today, the only commercial production has been that of a-Si based modules. In the U.S., Amoco/Enron [6] and ECD/USSC [7] are presently developing 10 and 5 MW a-Si facilities, respectively. By 1993, the performance of small area thin film polycrystalline laboratory cells was increased to over 15% for both CuInGaSe₂ and CdTe solar cells [8, 9], still without having a commercial manufacturing facility in operation.

Why aren't there thin film polycrystalline manufacturing facilities?

The translation of the laboratory results to large scale manufacturing has been much more difficult than expected due to the complexity of the processes involved for making thin film polycrystalline PV modules. This is compounded by the limited scientific basis to complement R&D since polycrystalline thin films are primarily used for PV. Further, most of the research activities were driven by the need to improve device performance and not to develop the fundamental scientific base required to properly engineer manufacturing equipment. The key issue, as in the 1970's, is the cost for the electricity as compared to more traditional alternatives while meeting, at the same time, the performance standards set by the crystalline silicon PV modules. For polycrystalline thin film PV to be a viable technology it must meet the 'standards' set by silicon: 1) module efficiencies of 12 to 15%; 2) demonstrated performance and stability; and 3) be an environmentally 'friendly' technology. In terms of cost, a recent economic analysis for a 25 MW multicrystalline production facility indicated that the module cost would be less than \$2/W [10]. To give a perspective of the manufacturing requirements for polycrystalline thin film PV technologies, for a 25 MW facility, an 80 W (~2 x 4 ft²) module would need to be produced every 1 min [11].

APPROACH

At IEC, a particular scale-up approach, summarized in Figure 1 [12], has been emphasized and is being used to

guide our research activities. A 'sufficient' scientific base of information is developed regarding a processing step to provide the required data needed for a quantitative engineering analysis. Mathematical models are developed and used for the design of commercial scale equipment. In most case, this leads to the identification of areas that require additional experimentation. The entire approach is iterative.

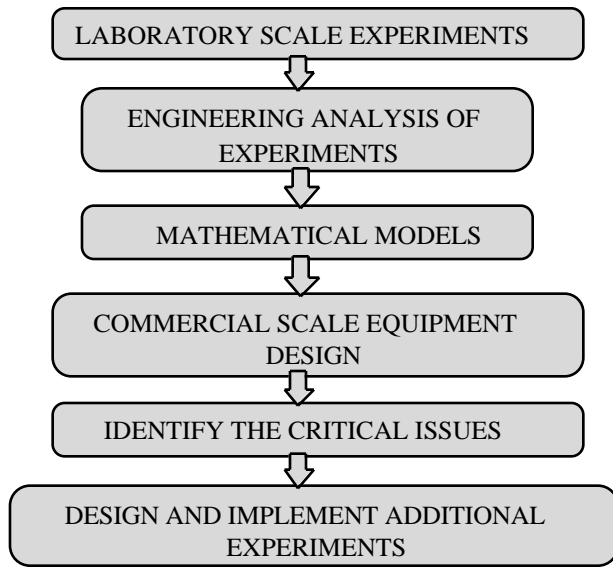


Figure 1. Approach to scale-up

CuInSe₂ BASED PV

CuInSe₂-based solar cells and modules have demonstrated the highest performance of any of the thin film PV technologies and a summary of cell and module results are shown in Table 1 [13]. These results should be viewed as proof of concept, pointing to the manufacturing potential of this material.

Critical Issues: CuInSe₂

The primary issues that have inhibited the development of manufacturing processes for CIGS based PV modules are:

- The design, operation & control of commercial scale equipment required for the deposition of the CuInSe₂ need to be custom designed, with little or no previous technology to draw upon.
- Analytical instrumentation for monitoring film growth is lacking due to the fact that the fundamental properties of the CuInSe₂ films which can predict the quality of the material and performance of the modules are not well known.
- Difficulty of maintaining uniformity of materials & device properties over large areas:

Na incorporation: diffusion of Na from the glass substrate can cause variation in performance across the module.

thin window layer: the thickness of the window layer is usually less than 50 nm and is difficult to control across the textured surface of the CuInSe₂.

- Low V_{oc} resulting in increased area loss.

Table 1. Status of Polycrystalline Thin film

Material	Area [cm ²]	V _{oc} [V]	Eff. [%]	Process Lab
<i>Laboratory Cell Results</i>				
Cu(In,Ga)Se ₂	0.414	0.674	17.7	NREL
Cu(In,Ga)Se ₂	0.38	0.647	17.6	Uppsala Univ./IPE
Cu(In,Ga)Se ₂	0.48	0.655	17.6	Matsushita
Cu(In,Ga)Se ₂ InOHS/ZnO	0.38	0.594	15.4	Uppsala Univ./IPE
Cu(In,Ga)Se ₂ (E _g = 1.34 eV)	0.4	0.729	14.3	IEC
Cu(In,Ga)Se ₂ (E _g = 1.47 eV)	0.4	0.804	11.5	IEC
CuGaSe ₂	0.38	0.870	9.3	IPE
CuInS ₂	0.38	0.735	12	IPE
<i>Modules</i>				
CuIn(Ga)Se ₂	3830		11.2	SSI: selenization
Cu(In,Ga)Se ₂	3100	30.95	7.7	EPV
CuIn(Ga)(S,Se) ₂	50.2	6.7	14.1	Showa Shell: selenization
Cu(In,Ga)Se ₂	90.6	9.3	13.9	IPE, ZSW: evap.

Design of a CuInGaSe_2 continuous deposition system

CuInGaSe_2 film growth by elemental source deposition is a robust process and has been used to produce high efficiency laboratory solar cells, over 17% [14]. It is used by many laboratories and provides a means of directly incorporating Ga into the films to control the bandgap. The growth and properties of the CuInGaSe_2 film are controlled by substrate temperature and the incident flux of Cu, In, and Ga. The effusion rates of the sources are controlled during the film growth so that: 1) the $\text{Cu}/(\text{In}+\text{Ga})$ ratio is varied from greater than 1 during the early stage of film growth to less than 1 in the final stage so that the $\text{Cu}/(\text{In}+\text{Ga})$ in the final film is less than 1; and 2) the $\text{Ga}/(\text{Ga}+\text{In})$ ratio determines the bandgap and can be varied during growth to grade the bandgap. Figure 2 is a schematic of a typical laboratory deposition system.

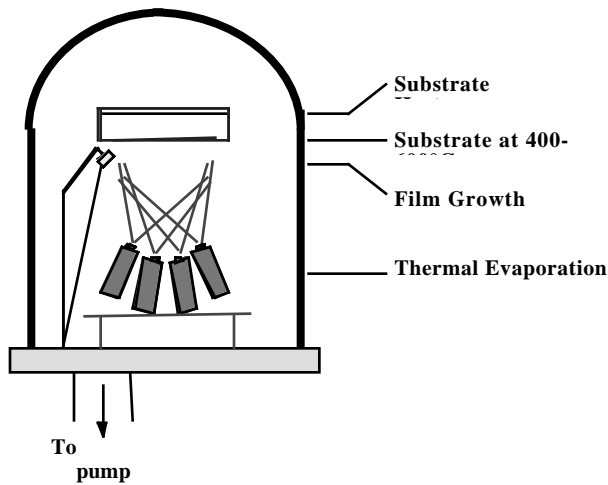


Figure 2. Schematic of laboratory deposition system for CIGS films.

For an in-line commercial system, it is desirable to translate the time dependent flux profiles used in the laboratory systems to spatial variation of the fluxes from

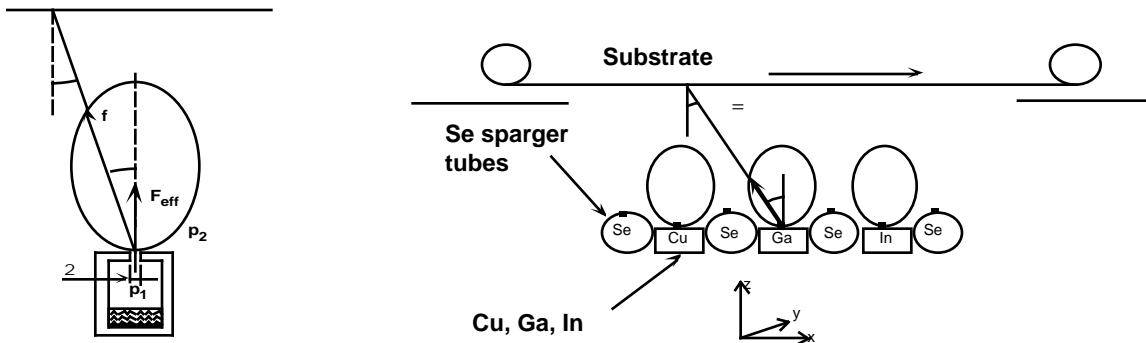


Figure 3. The effusion sources operate in the free molecular flow regime where the Knudsen number, K_n , is less than 1.

distributed sources onto the moving substrate [15]. Such a process is currently under development and the engineering analysis leading to the process design is discussed below [16].

The preliminary design criterion for the process were:

- $\text{Cu}(\text{InGa})\text{Se}_2$ thickness and composition uniformity: $\pm 5\%$
- Uniform Se flux throughout the deposition zone
- Uniform Cu, In and Ga fluxes across the substrate to give uniform thickness and composition
- Location of individual sources determines Cu, In & Ga fluxes along the direction of the web to control incident flux composition and thus film growth.

The primary issue was the delivery of the Cu, In, and Ga to the surface of a moving substrate which can be either glass plates or a continuous web. Based on the operation of laboratory effusion sources, on the fundamental expression for vapor pressures, and on models for evaporant flow through an orifice and angular distribution of the evaporant plume developed at IEC in the 1980's [17], sources were modeled and designed to meet the above criterion. Figure 3 is a schematic of the continuous deposition system including a schematic of an effusion source. Equation 1 is the expression for evaporation from free surface and Equation 2 is the expression for the total flux through the nozzle in the free molecular regime. Equation 3 gives the flux per unit area on the substrate at any point in the deposition zone.

$$F = \frac{M}{2 RT} \sqrt{\frac{2\pi}{M}} (p^{\text{sat}}(T) - p) A \quad \text{in units of mass.time}^{-1} \quad (1)$$

$$F = \sqrt{K} \frac{M}{2 RT} \sqrt{\frac{2\pi}{M}} (p_1 - p_2) \quad \text{in units of mass.time}^{-1} \quad (2)$$

$$f_{\text{eff}} = \frac{3F}{2 r^2} \cos^2 \theta \cos \phi \quad \text{in units of mass.time}^{-1} \text{.area}^{-1} \quad (3)$$

The surface temperature of liquid metal controls P_1 and the pressure differential, $P_1 - P_2$, across the nozzle and the nozzle diameter, $2r$, control the effusion rate. A system based on this design is currently operational and the model developed for the source design and operation has been validated in the case of flexible polyimide substrate. The composition evolution in the deposition zone matches model predictions and the thickness uniformity across the substrate is about 2%. Small area solar cells have been fabricated and cell efficiencies over 9% have been achieved.

CdTe BASED PV

CdTe based solar cells and modules have demonstrated high performance as summarized in Table 2 [18]. The variety of techniques employed to deposit CdTe cells should be noted. In CdTe the deposition process in general is not as critical as the post deposition processes that are employed (see below). Again, these results should be viewed as proof of concept pointing to the manufacturing potential of this material.

Critical issues: CdTe

The primary issues that have inhibited the development of a CIGS facility are:

- Optimal design, operation and control of a CdTe reactor.

- Analytical instrumentation for monitoring film growth is lacking due to the fact that the fundamental properties of the CdTe films which can predict the quality of the material and performance of the modules are not well known.

- Difficulty of maintaining uniformity of materials and device properties over large areas:

Interdiffusion of CdTe-CdS

Back contact

- Back contact stability.
- Environmental concerns with Cd.

CdTe back contact

All high efficiency CdTe solar cells ($> 10\%$) have been made using a superstrate device configuration where the CdTe is deposited on the window layer (heterojunction partner) leaving a free CdTe surface for the back contact. The fabrication process always has a high temperature, 400°C or greater, processing step in the presence of O_2 and a Cl species.

In order to form the back contact, the CdTe surface is first modified, most commonly by a chemical etch, to form a Te-rich surface. The contact material, generally incorporating a p-type dopant such as Cu, is then applied, followed by a heat treatment to diffuse the dopant. Typical contact materials used are: 1) Cu/Au, used only as a 'diagnostic tool' since it is unstable over time; 2) graphite plus dopant such as Cu or HgTe; 3) diffused Cu plus a metal, and 4) ZnTe(Cu).

Table 2. CdTe based solar cells and modules

CdTe Deposition Process	Academic Interest	Industrial Interest	Efficiency / Area
Compound Sublimation and Vapor Transport (CSS)	USF[1], NREL, IEC, Stanford	SCI, Antec[3]	15.8% / 1.05 cm^2 [4] 8.4% / 7200 cm^2 [5]
Electrodeposition	CSM, Queensland	BP Solar, A.D. Plating	14.2% / 0.02 cm^2 8.4% / 4540 cm^2
Atomic Layer Epitaxy		Microchemistry	14.0% / 0.12 cm^2
Screen printing	KAIST, U. Gent[7]	Matsushita	12.8% / 0.78 cm^2 8.1% / 1200 cm^2
Spray/sinter		Golden Photon	14.7% / 0.3 cm^2 8.1% / 832 cm^2
MOCVD	GIT, USF, U Durham, RPI[8]		11.9% / 0.08 cm^2 [9]
PVD - vacuum evaporation	IEC, Univ Parma, New Castle-on-Tyne, Stanford		11.8% / 0.3 cm^2 [10]
Laser Driven PVD	U Toledo		10.5% / 0.1 cm^2 [11]
MBE	NREL[12], Swiss Fed. Inst. Tech, GIT		10.5% / 0.08 cm^2 [13]
Sputtering	NREL, U Toledo		10.4% / 0.1 cm^2 [11]
APCVD	USF[14]	Batelle[15], SCI[16]	9.9% / 1 cm^2 [14]

At IEC the diffused copper contact has been under development for several years [19]. The contact procedure consists of depositing 5-20 nm of Cu onto the surface of CdTe. The cell is then annealed to diffuse Cu into the CdTe and etched to remove excess Cu as well as approximately 10 nm of CdTe. A conductor such as Ni, Cr, Pt, Mo, carbon paste or indium-tin oxide (ITO) is then deposited to act as the primary current carrying part of the contact. This contact has been evaluated using CdTe/CdS deposited by a variety of techniques, and the results are summarized in Table 3.

Recent analysis of the back contact, with Cr as the contact metal, by glancing-incidence XRD indicated the

presence of Cu_2Te . Figure 4 shows the XRD pattern for an X-ray incidence angle of 3° .

The process has been further modified to include an etch of the CdTe, *prior* to Cu deposition, in: 1) bromine-methanol, 2) dichromate solution, and 3) hydrazine (BDH etch). This modification results in an improvement in the fill factor of the solar cells. Analysis of the CdTe surface after the BDH etch indicates the presence of Te, and the analysis after the contact is completed indicates the presence of a thicker Cu_2Te layer. Based on this analysis, an all dry contact process is currently under development to eliminate the wet chemistry step.

Table 3. Cell results using Cu contact on samples from different groups

Group	CdTe Deposition Technique	Eff (%)	FF (%)	V_{oc} (mV)	$(dV/dJ)@V_{oc}$ ($-\text{cm}^2$)
Colorado School of Mine	Electro	8.82	64.5	754	6.3
IEC	Physical Vapor	10.97	66.2	853	7.3
Solar Cell Inc.	Elemental Vapor	11.73	74.5	789	3.1
Univ of Toledo	Sputtering	11.43	65.0	796	8.5
Univ of South Florida	Close-Spaced Sublimation	14.68	71.2	845	3.7

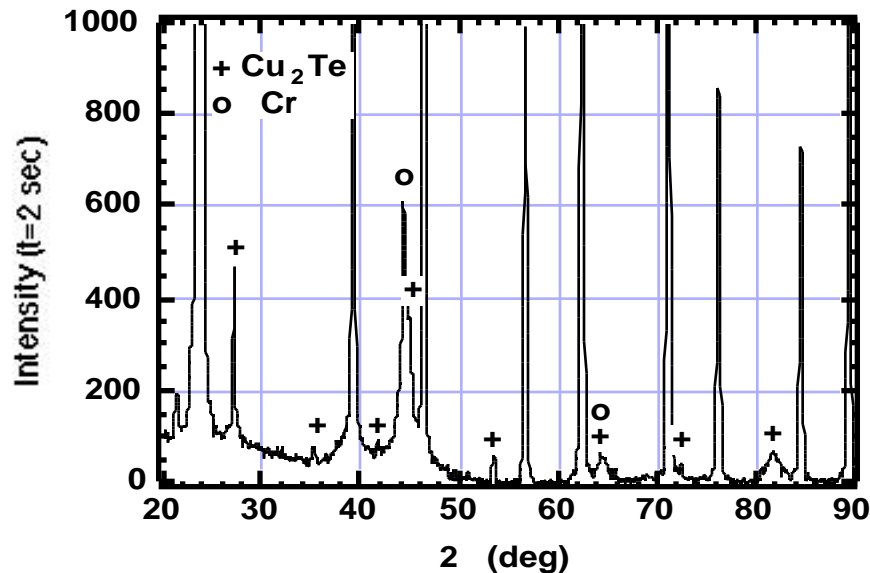


Figure 4. Glancing-incidence XRD pattern (X-ray incidence angle of 3°) showing Cu_2Te at the back contact.

DISCUSSION

Translation from the laboratory to pilot production of the complex processes used to make polycrystalline CuInSe_2 based and CdTe solar cells requires detailed understanding of the individual processes to provide the basis for an effective engineering reactor design. Reactor independent parameters controlling film growth (reaction analysis) must be determined, and uniform delivery of species and heat transfer (reactor analysis) modeled. This type of analysis is multidisciplinary in nature and makes it difficult for a single organization to develop manufacturing processes. Consortium or team efforts can greatly accelerate progress towards developing such a manufacturing facility.

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