Review of the Solar Cells Based on CIGS Film

by Guobin Zhang

16/10/2008

基于CIGS薄膜的太阳能电池综述

- 薄膜太阳能电池概况

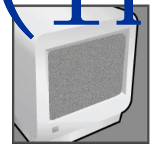
- 太阳能电池原理
- 基于CIGS薄膜的太阳能电池

  特点　结构　制备方法

- 挑战&探索

  研究的具体方向

CIGS[Cu(In,Ga)Se2]



I-III-VI2

薄膜太阳能电池概况

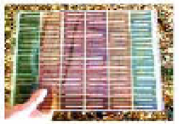
DOE National Lab module research balances various materials thru joint industry R&D and long-term research

4% | Organic PV

Customizing organic molecules for optimal cell efficiency in materials that can be processed without expensive vacuum chambers

1% | Dye Sensitized Cells

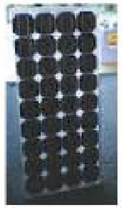
Advancing the efficiency and stability of inexpensive dye-based solar cells with novel nanostructures

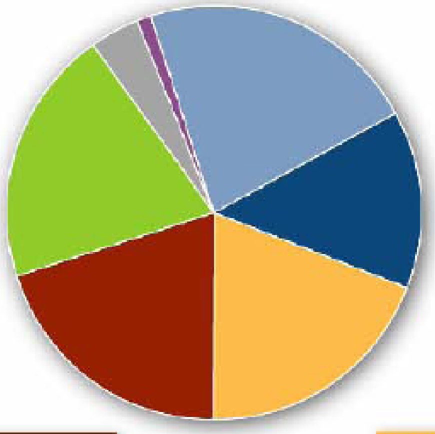


22% | Wafer Silicon

Combining thin amorphous and wafer silicon to make high efficiency cells with smaller total amounts of silicon

Developing new ink-jet printing methods for silicon electrical contacts

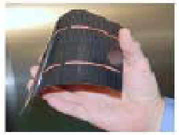




20% | Thin Films (CIGS)

Supporting the novel manufacture of CIGS cells from ink-based precursors

Transferring discovery that highest performance material has nanostructured patterns into a fast and uniform manufacturing process



14% | Concentrator PV

Devising strategies for making quicker, easier, less precise cells but maintaining record performance

Achieving record efficiencies (33.8%) even without concentration

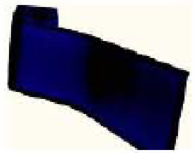
20% | Thin Films (CdTe)

Produced thinner films with same cell performance

Discovered a more durable way to make electrical contacts

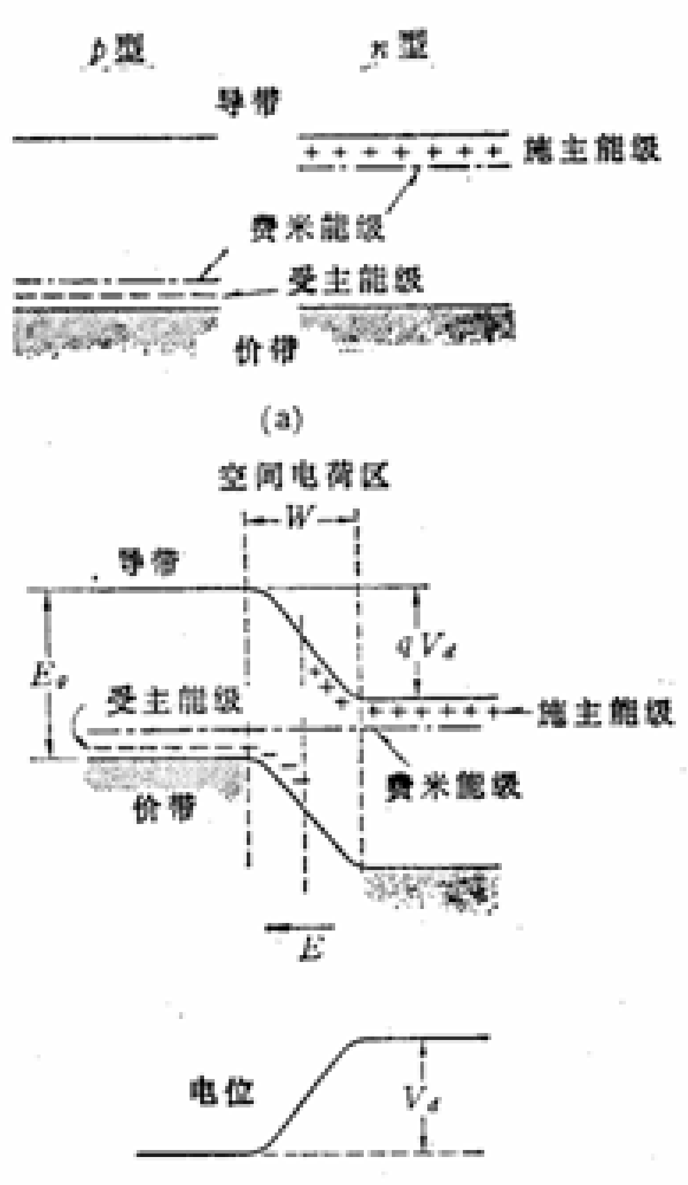
19% | Thin Films (Silicon)

Developing methods of making thin silicon film solar cells on inexpensive glass and at low processing temperatures



太阳能电池原理

- PN结



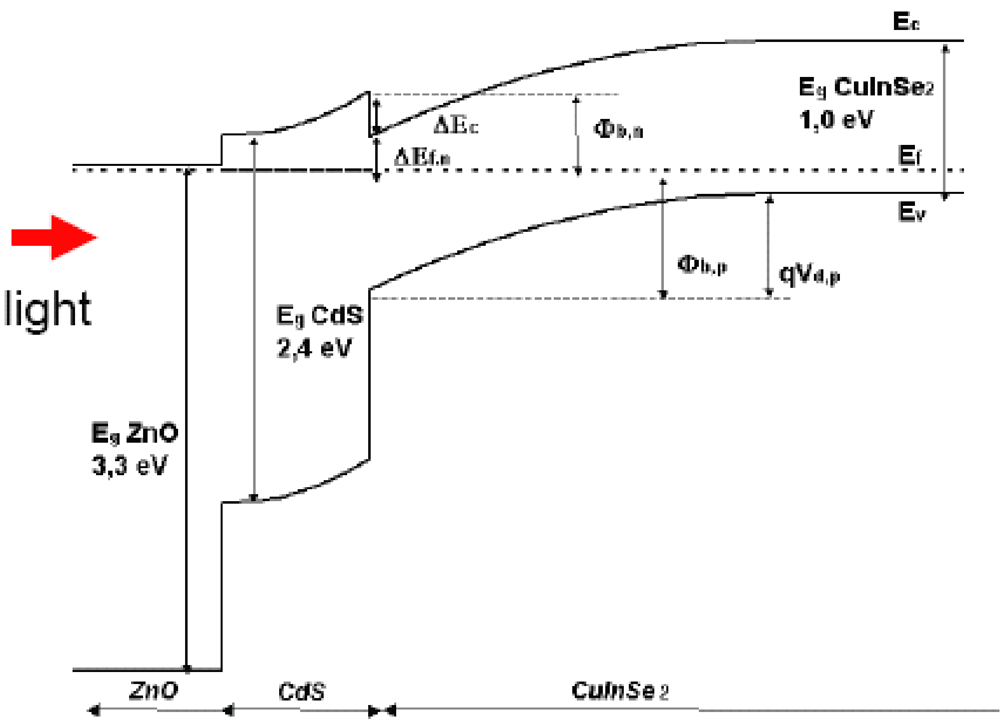
p型
n型
导带
施主能级
费米能级
受主能级
价带
(a)
空间电荷区
W
导带
qVd
Eg
受主能级
施主能级
费米能级
价带
E
电位
Vd

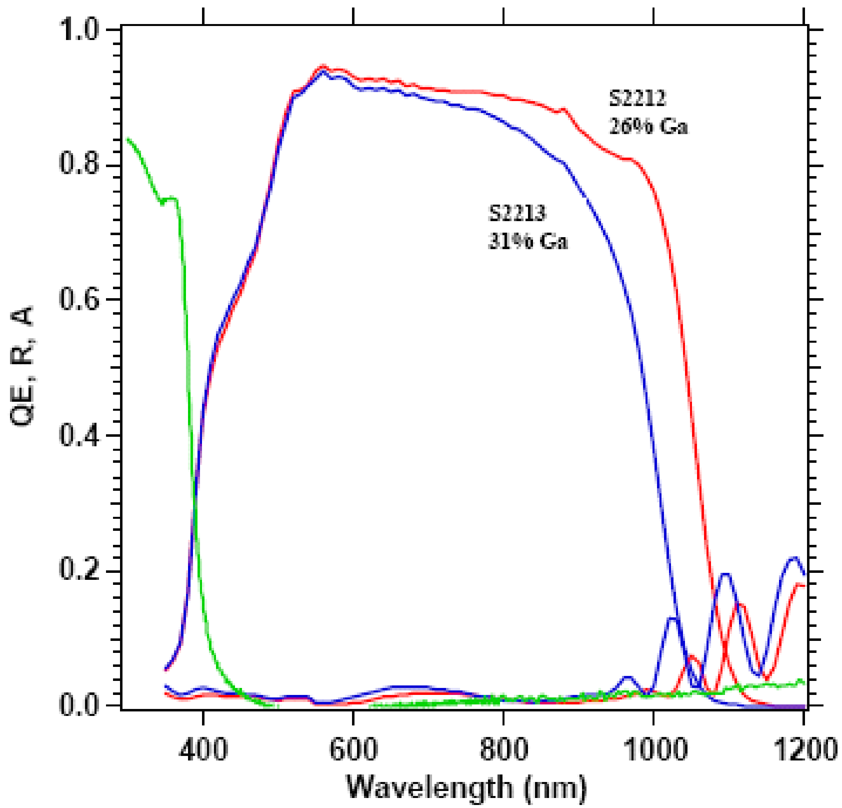
太阳能电池原理

- 光生伏特效应

　当用适当波长的光照射非均匀半导体(p-n结等)时，由于内建电场的作用（不加外电场），半导体内部产生电动势（光生电压）；如将p-n结短路，则会出现电流（光生电流）。这种由内建电场引起的光电效应，称为光生伏特效应。光生伏特效应是光电池的基本原理。

CIGS 太阳能电池能带图及光电流产生机理





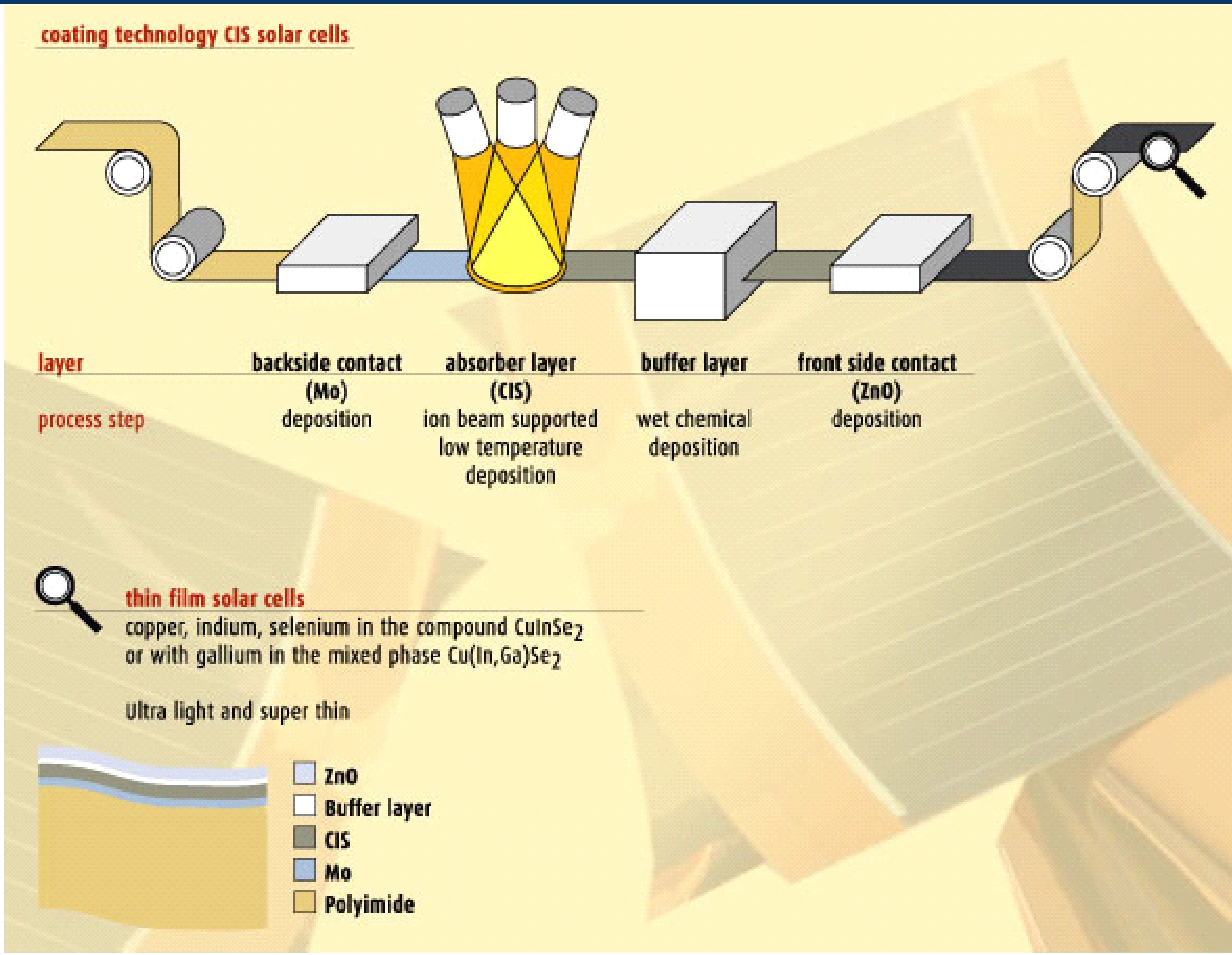
By Courtesy of Dr. K. Ramanathan et al., NREL, EMRS 2004

影响太阳能电池的因素

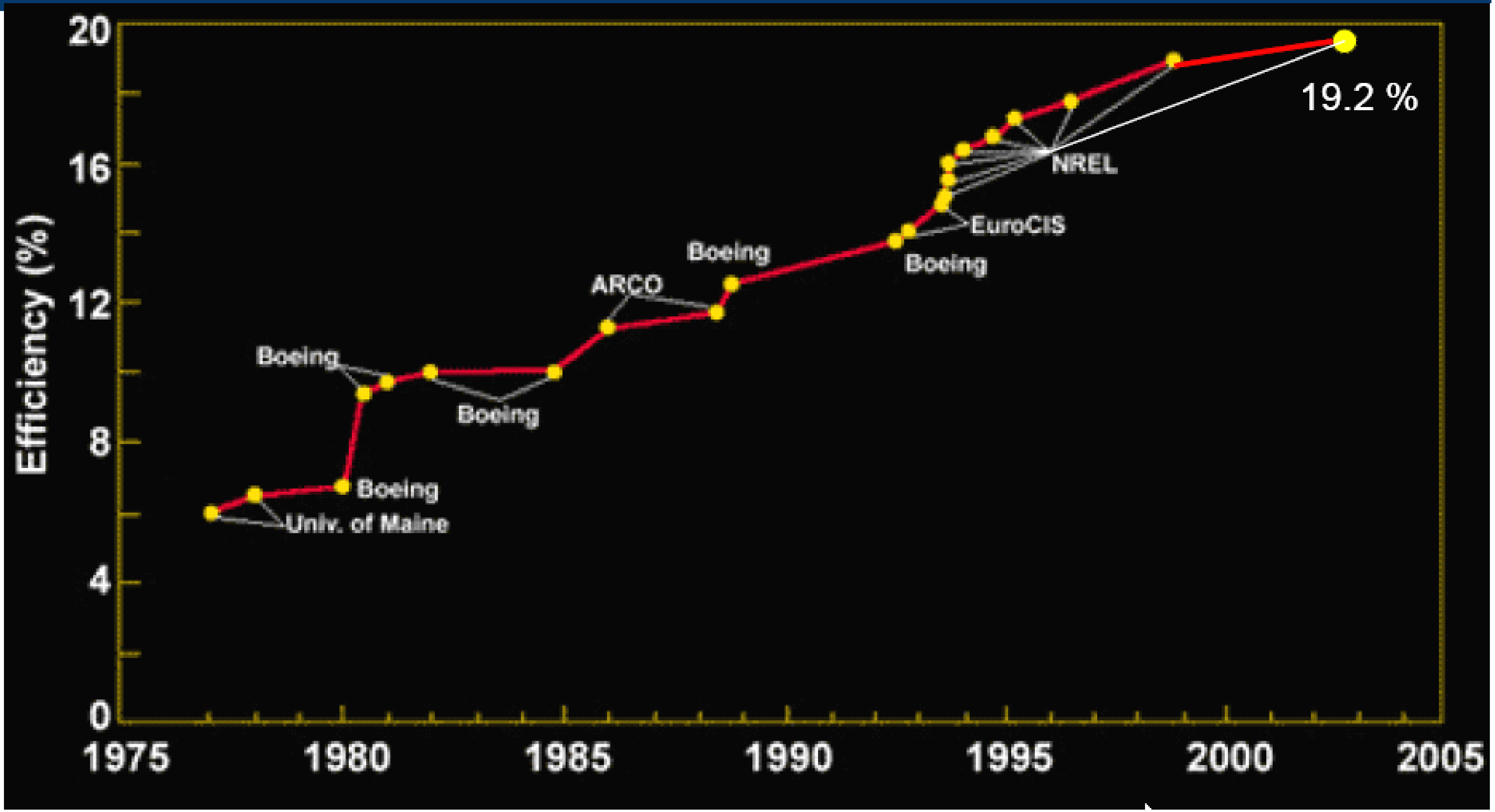
- 禁带宽度
- 复合寿命
- 光强
- 串联电阻
- 金属栅和反射光

基于CIGS薄膜的太阳能电池

CIGS电池生产的工艺流程

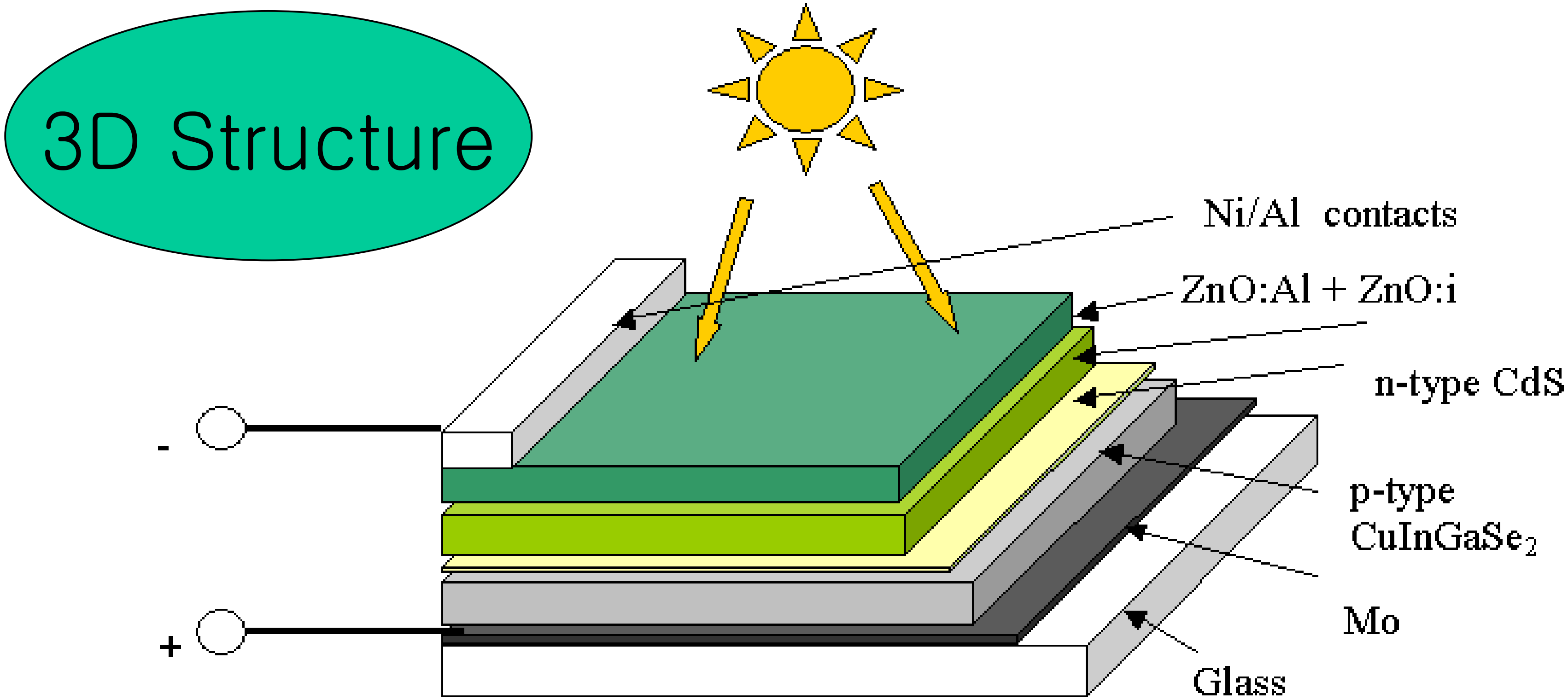


40years Rearch: Trails, Errors, Success !

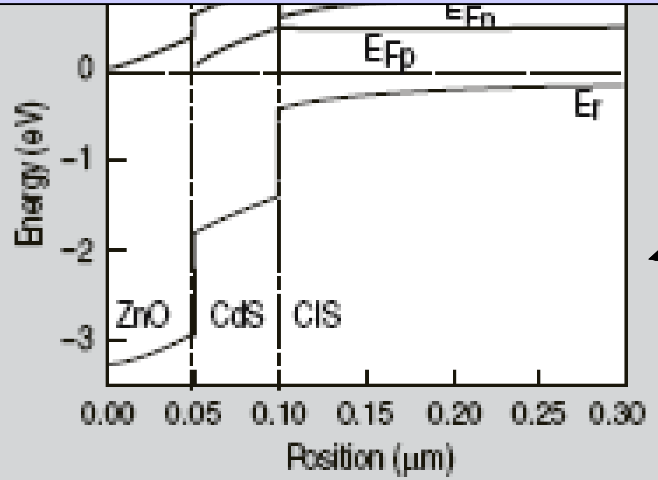


FROM:Web Site of National Renewable Energy Lab

典型结构(Typical Structure)

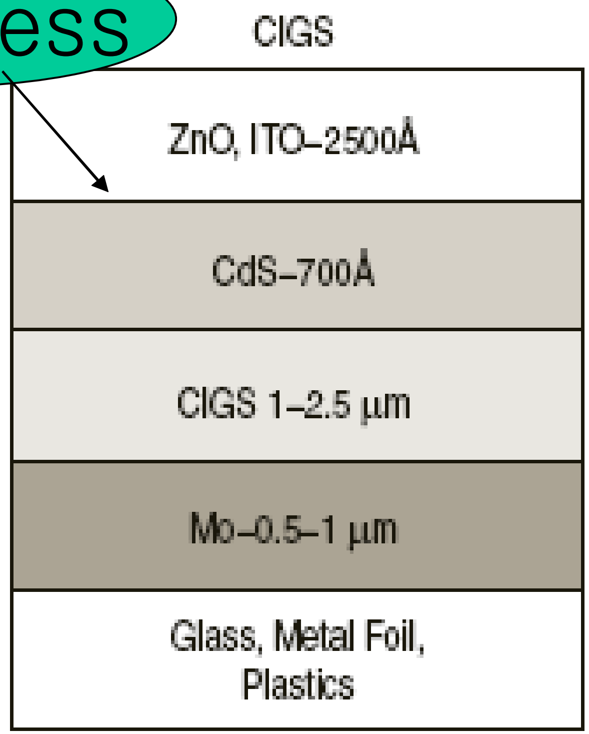


FROM: Materials Challenges for Terrestrial Thin-Film Photovoltaics
Alvin D. Compaan

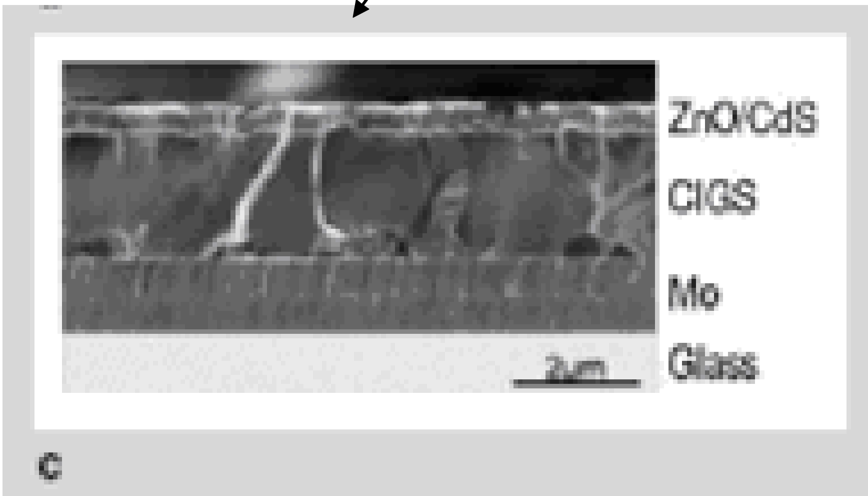


Energy level digram

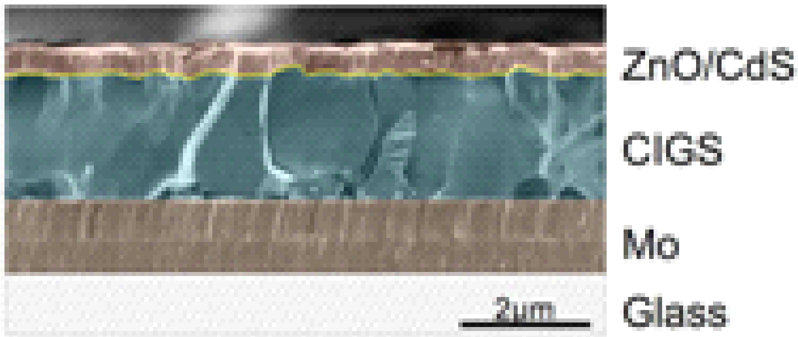
Thickness



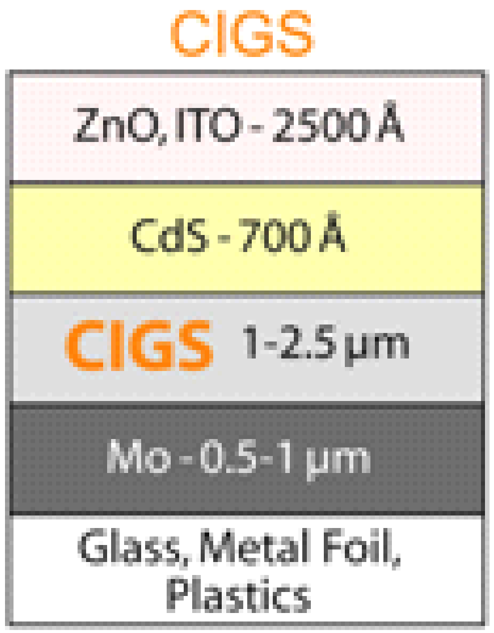
Cross-section SEM



各功能层概述



2μm
ZnO/CdS
CIGS
Mo
Glass



CIGS
ZnO, ITO - 2500 Å
CdS - 700 Å
CIGS 1-2.5 μm
Mo - 0.5-1 μm
Glass, Metal Foil,
Plastics

衬底(Substrate)

- 低的离子浓度
- 优良的导热性
- 热膨胀系数：稍大于CIGS膜
- Na离子的含量控制

背电极Mo（Back Contact）

- 金属Mo是CIGS薄膜太阳电池背接触层的最佳选择

良好的电特性、与玻璃接近的热膨胀系数

与衬底良好的附着性、无化学反应

- 用溅射双层Mo的效果比较好。高压强Ar下溅射0.1um,然后在低气压下再溅射0.9um.

CIGS薄膜特点

- 直接禁带半导体：1.04eV

Adjusted by rati of Ga/(In+Ga) 1.04~1.65eV

梯度带隙半导体、“V”字型带隙分布

- 很高的吸收系数：105---106/cm

Highest

- CIGS吸收层厚度只需1.5-2.5μm，整个电池的厚度为5-6μm

节省原材料

- 无光致衰退效应（S-W Effection）

吸收层CIGS薄膜的生长方法

- 溅射+硒化法
- 共蒸发： 3-Stage Process

  Highest Eff.,by NREL

- 电化学沉积

  Large area, Low cost

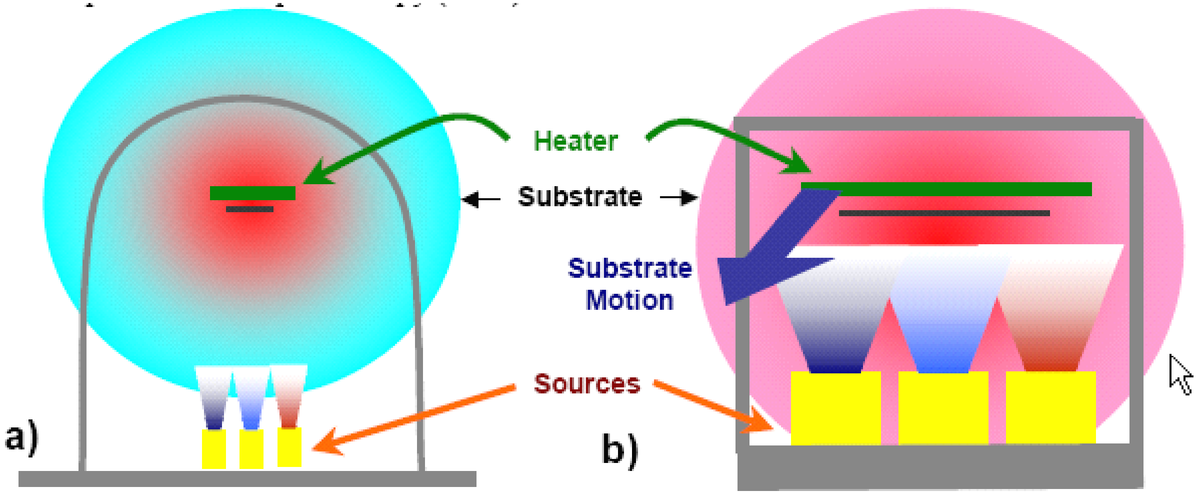
- 化学水浴沉积(CBD)
- 旋涂（Screen Printing）

  Expected Champion Low Cost

COST REDUCING

3-Stage Process

a: laboratory *b:production*



FROM:June 2003 • NREL/SR-520-34314

Tolerance of Three-Stage CIGS Deposition to Variations Imposed by Roll-to-Roll Processing

3-stage process

The NREL protocol for Nowadays High Efficiency Cells

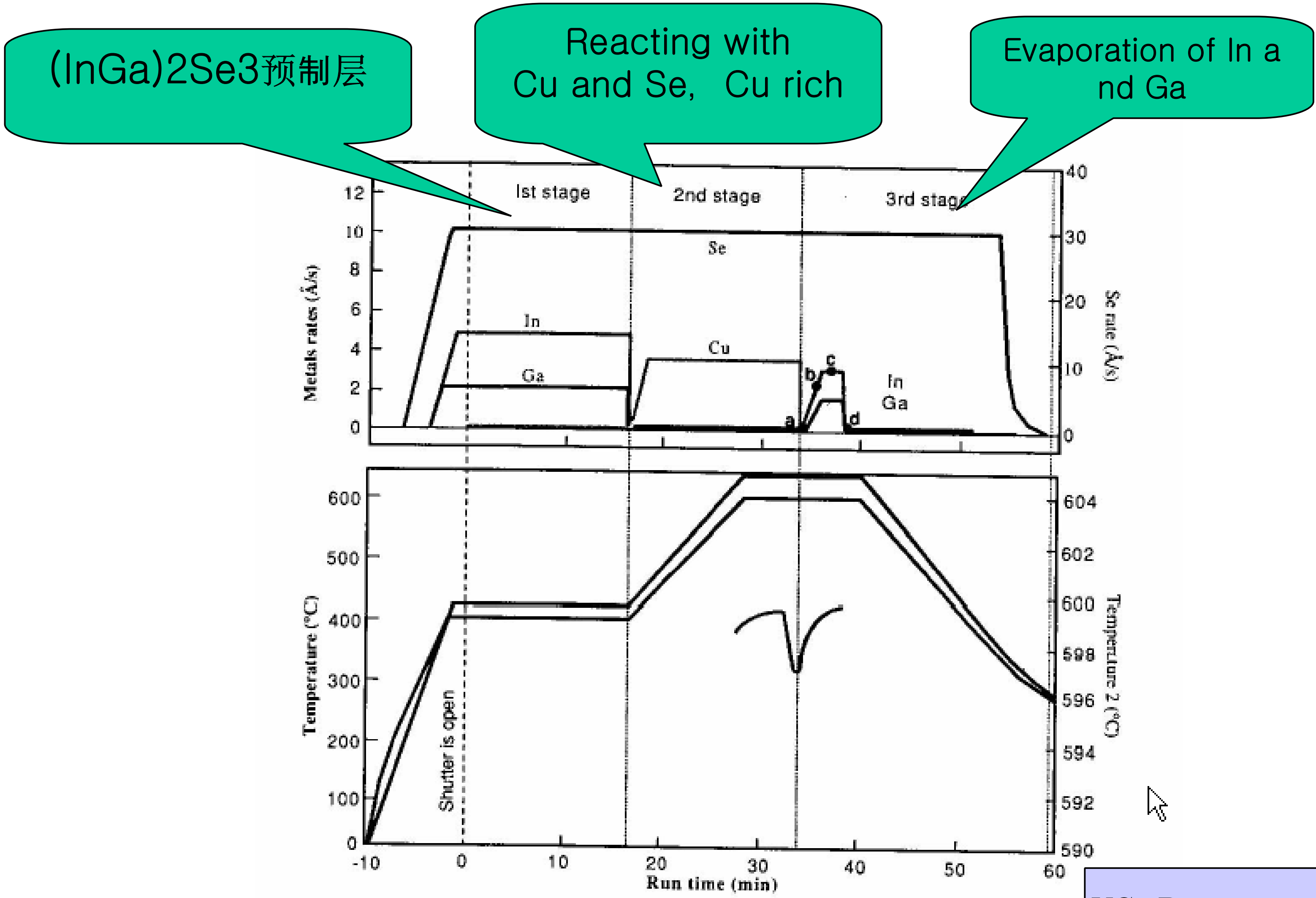


Figure 1. Schematic profile of the 3-stage process.

US Patent 5,441,897

Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe2 Thin-film Solar Cells

- PARAMETER

By NREL, 2003

Sample	Device	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (%)	Efficiency (%)	Remarks
S2051A1	1	0·689	35·71	78·12	19·2	New record
	2	0·685	35·68	77·91	19·1	
	3	0·680	36·11	77·64	19·1	
C1068-2		0·678	35·22	78·65	18·8	Previous record

FROM:PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2003; 11:225–230 (DOI: 10.1002/pip.494)

The highest eff.

Ga-poor, In-rich

Reduce Recombinati

19.9%

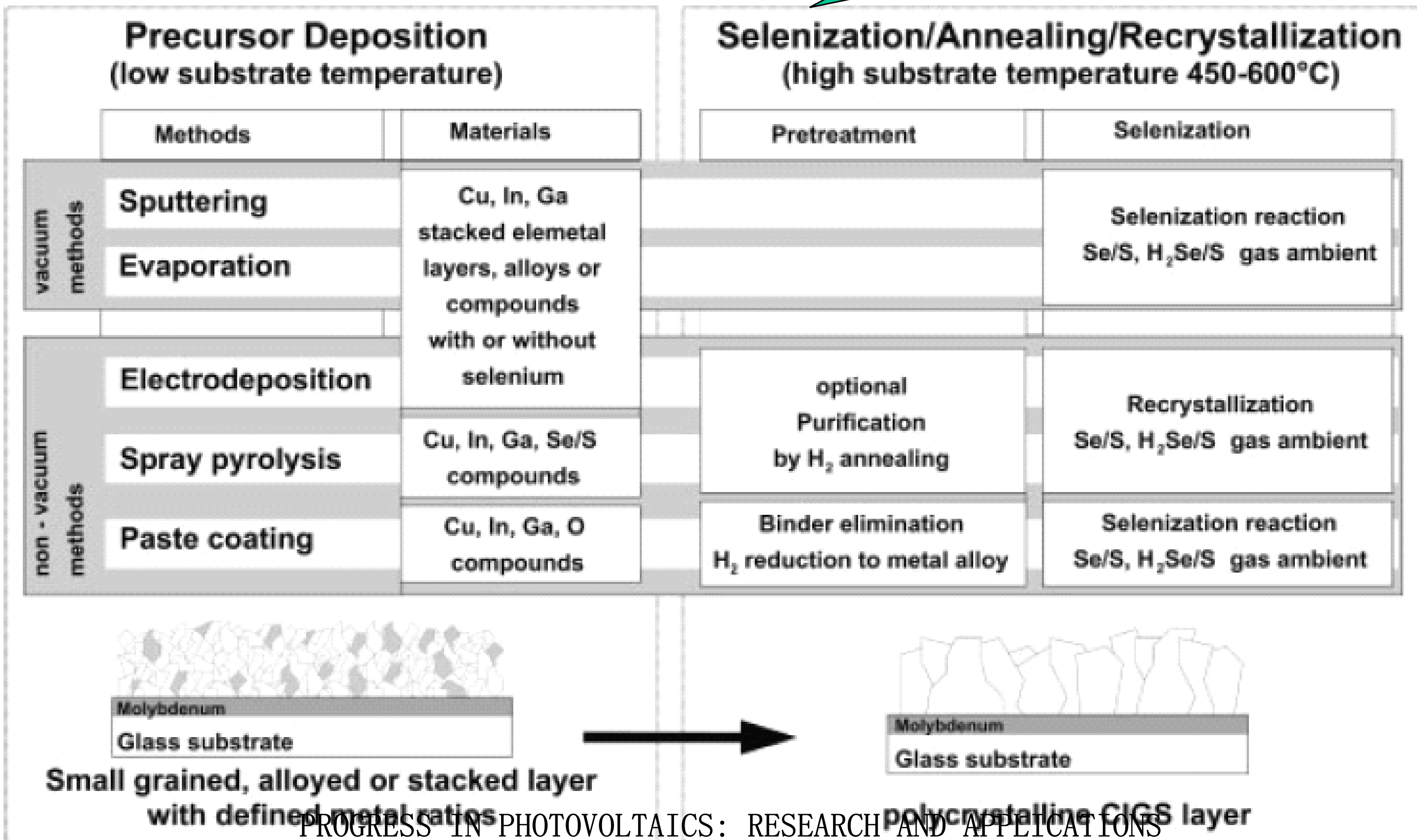
By NREL, May,2008

Device Name	Area (cm^2)	η (%)	V_{oc} (mV)	FF (%)	J_{sc} (mA/ cm^2)	Official Measurement?
[illegible]	0.419	19.9	690	81.2	35.4	Yes
[illegible]	0.416	19.9	697	80.0	35.7	[illegible]
[illegible]	0.417	19.8	714	79.1	35.1	Yes
M29[illegible] 11#4	0.419	19.7	690	81.2	35.1	Yes
M2992-11#6	0.419	19.7	690	81.1	35.3	Yes
C2183-12#4	0.417	19.7	695	80.0	35.5	Yes
C2200-22#1	0.420	19.6	725	80.6	33.6	No
C2213-[illegible]	**0.994**	19.2	716	80.4	33.4	Yes

From:Characterization of 19.9%-Efficient CIGS Absorbers

硒化法 (Selniza

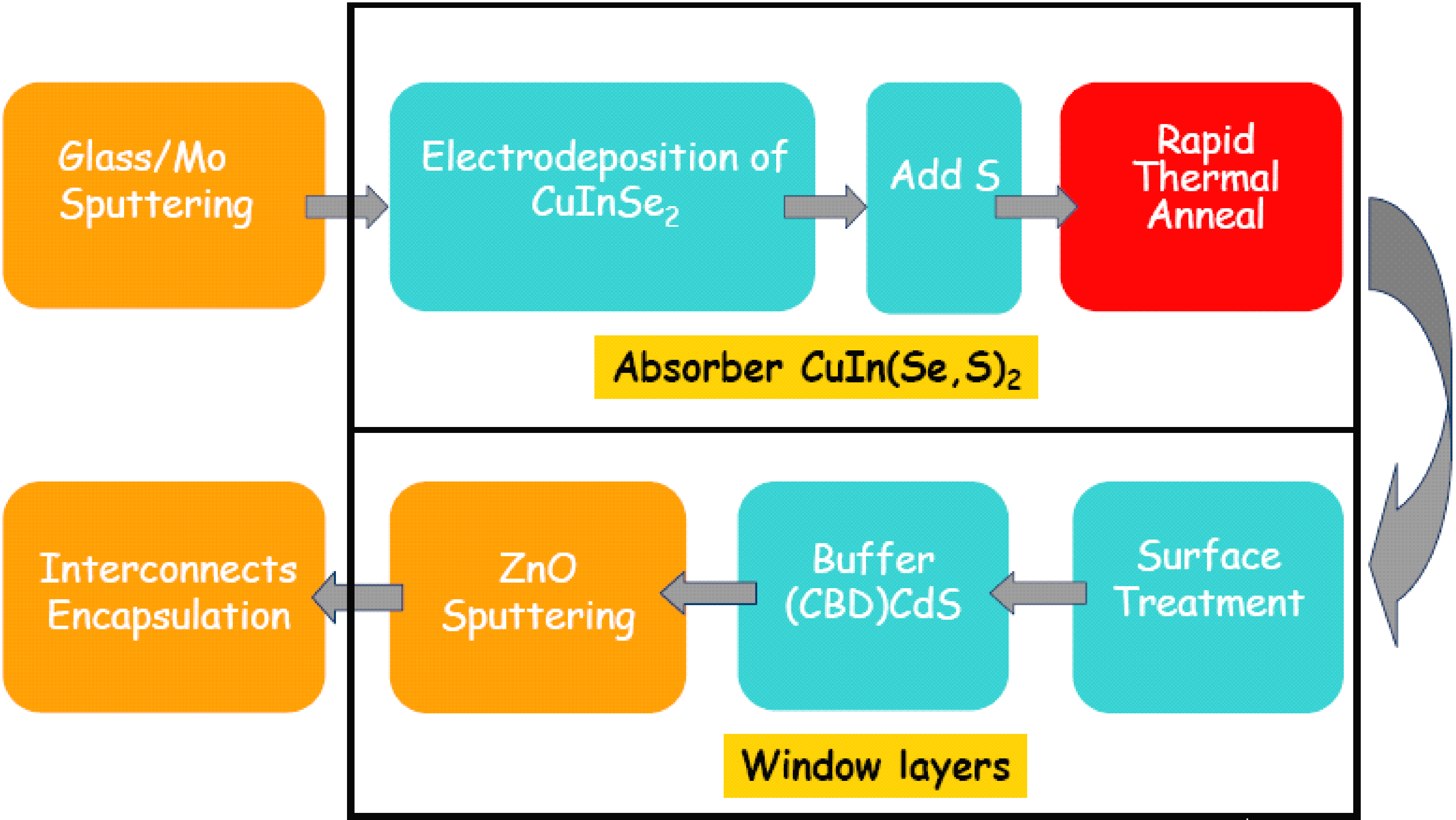
H2Se剧毒， 易挥发！



PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2004; 12:93－111
(DOI: 10.1002/pip.527)

电化学沉积法

11.4%



The processes are "mastered" for 5x5 cm^2 and 30x30 cm^2

电化学沉积原理

$$Cu^{2+} + 2e \Leftrightarrow Cu$$

$$E = 0.34 + 0.0295 \log \left(\alpha_{Cu}^{2+} / \alpha_{Cu}\right)$$

$$In^{3+} + 3e \Leftrightarrow In$$

$$E = -0.34 + 0.0197 \log \left(\alpha_{In}^{3+} / \alpha_{In}\right)$$

$$Ga^{3+} + 3e \Leftrightarrow Ga$$

$$E = -0.56 + 0.0197 \log \left(\alpha_{Ga}^{3+} / \alpha_{Ca}\right)$$

$$HSeO_2^+ + 4H^+ + 4e^- + OH^- \Leftrightarrow H_2SeO_3 + 4H^+$$

$$+ 4e^- \Leftrightarrow Se + 3H_2O$$

$$E = 0.74 + 0.0148 \log(\alpha_{HSeO2}^{+} / \alpha_{Se}) - 0.0443pH)$$

FROM:J MATER SCI 41 (2006) 1875–1878

电化学沉积（Example）

- **实验装置**: a Potenciostat/Galvanostat EG&G Princeton Applied Research model 263, which was coupled to a PC, 50ml single compartment cell；
- **工作电极**: ITO on glass, aluminum, 304 steel;
- **反电极**：Pt bar;
- **参比电极**: saturated Ag/AgCl(KCl saturated);
- **电解液**：prepared with ultrapure water (18 MΩ) and the Reagents were of analytic grade.
- **电解媒质**: 0.6M nitric acid+ 0.3 M dietilelentriamine ; 3 mM $Cu(NO_3)_2$, 3mM $In(NO_3)_3$, and 5mM SeO_2.

电化学沉积（Example）

- **PH值**：adjusted to 8.5, using HNO3 and NaOH ;
- **祛氧气**：bubbling argon gas for 5 min;

From:J Solid State Electrochem (2007) 11:407–412
DOI 10.1007/s10008-006-0162-7

电化学沉积（Example）

- 工作电极：镀有Mo层的钠钙玻璃衬底 ；
- 反电极：Pt；
- 参比电极：饱和 Ag/AgCl(KCl saturated)；
- 电解媒质：CuCl2、InCl3、GaCl2、H2SeO3;
- PH值：调节为 1.5，using HCl(volume10%)；
- 温度：水浴温度25℃;
- 祛氧气：bubbling argon gas for 5 min;
- 共沉积过程反应条件：饱和甘汞电极（SCE）应用电势范围-0.6到-0.8V，沉积时间60min;

不同反应浓度下的CIGS组分比

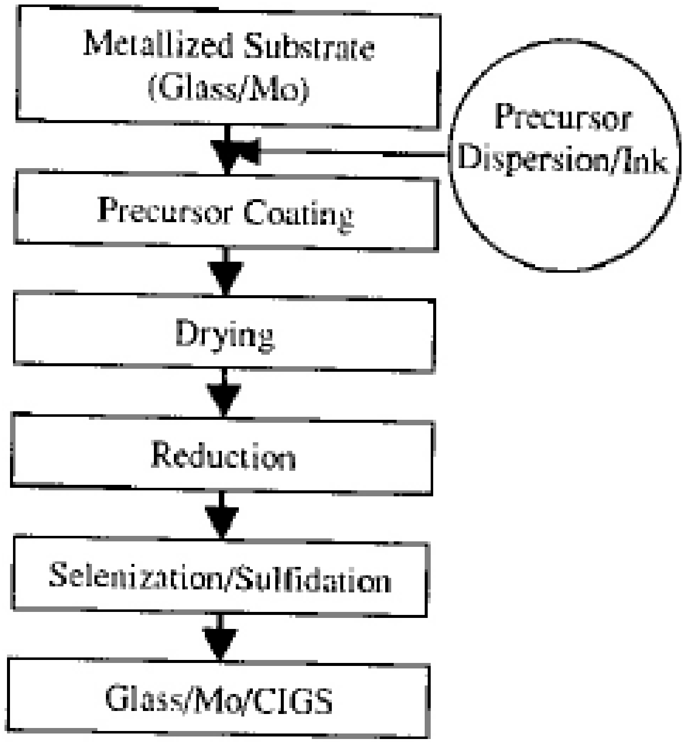
Sample no	Bath concentration/mM				Composition/(at%)				Cu/(In+Ga)	Ga/(In+Ga)
	$CuCl_2$	$InCl_3$	$GaCl_3$	H_2SeO_3	Cu	In	Ga	Se		
a	2.5	50	65	15	13.65	23.85	7.70	54.80	0.43	0.24
b	3.0	45	65	15	21.92	18.20	7.76	52.12	0.84	0.30
c	5.0	50	70	10	27.21	20.72	9.77	42.30	0.89	0.32
d	2.5	45	70	10	13.27	17.19	9.69	59.25	0.48	0.35

目前最高效率电池Ga的含量是30％Ga/(In+Ga），
此时带隙大约为1.12ev

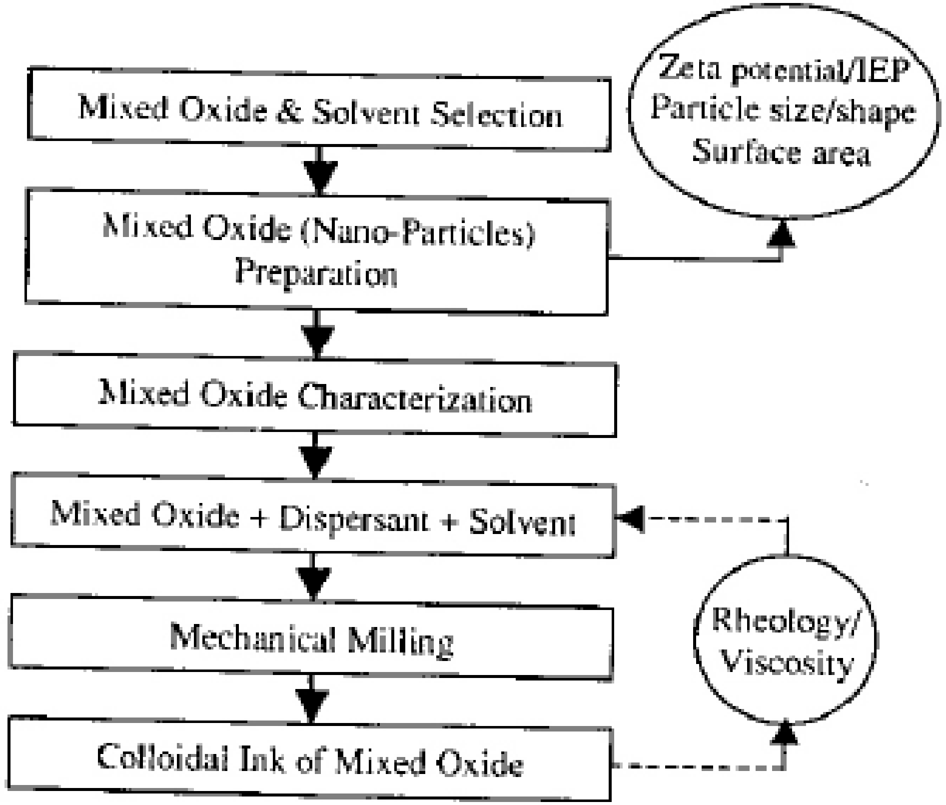
FROM:J MATER SCI 41 (2006) 1875–1878

低成本制备CIGS太阳能电池的方法

Screen Printing



Non-vacuum CIGS Deposition

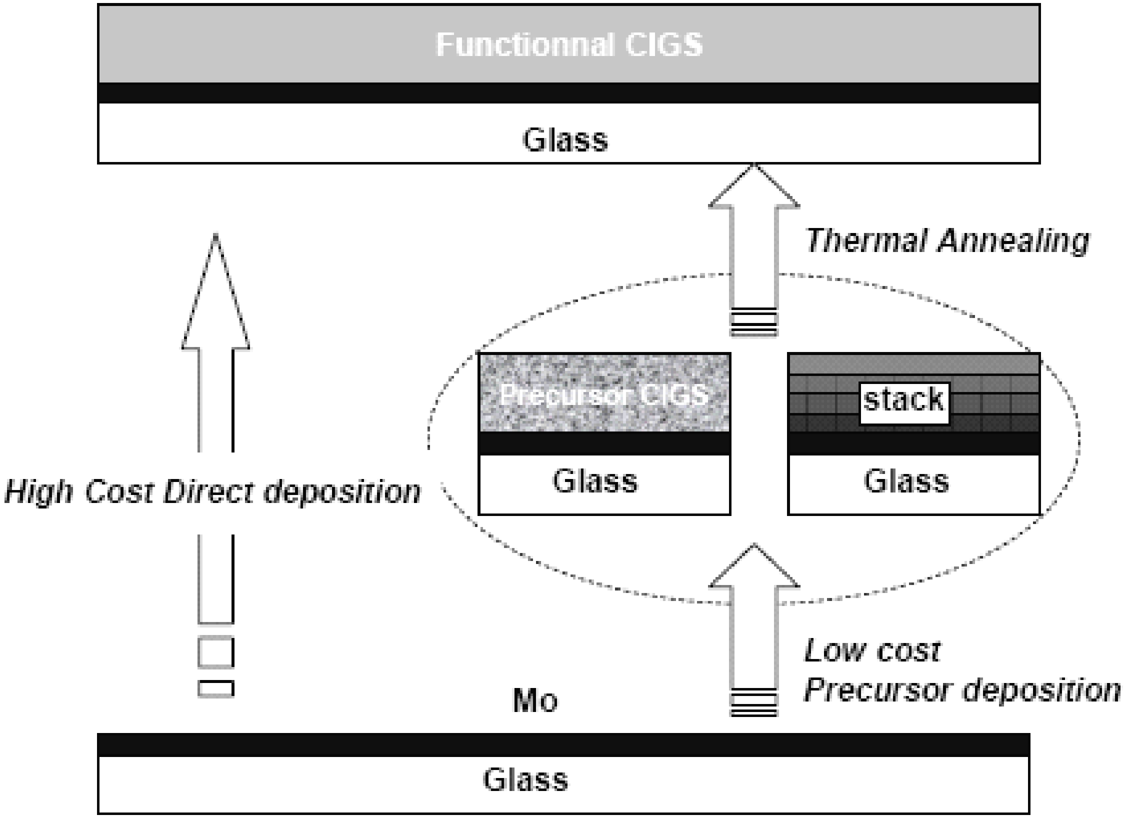


Non-vacuum Process Ink Preparation

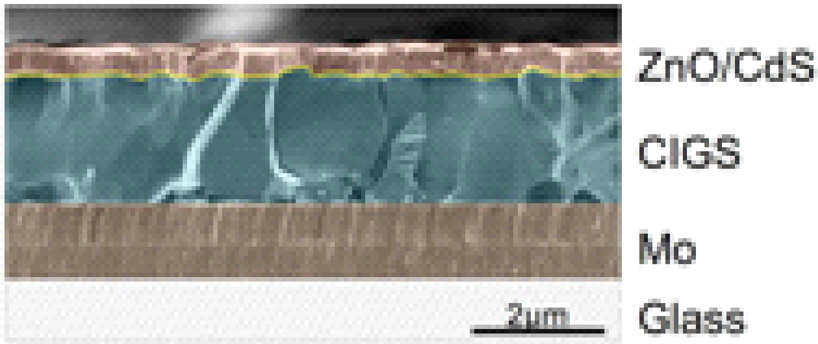
低成本制备CIGS太阳能电池的方法

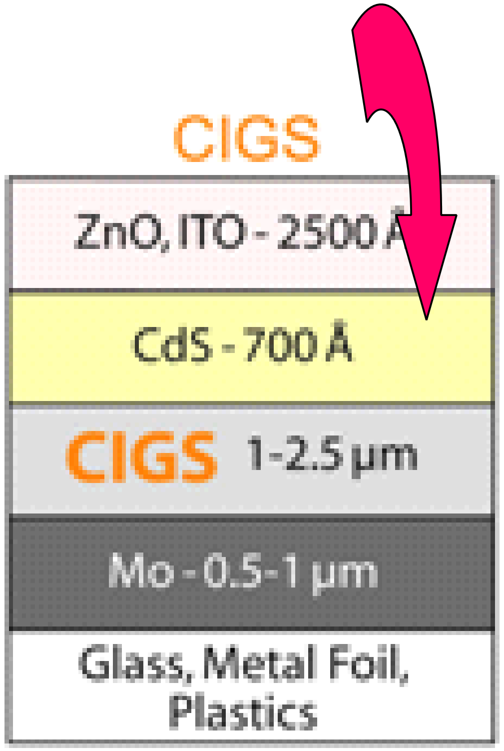
From the 3 stage process to Multistep Processes

…….A new consequence of CIGS « Softness »



缓冲层CdS (Baffer layer)





CdS的制备方法：CBD(Chemical Bath Depositon)

- 原理：原理是在去离子水配制的溶液中和的反应；
- 反应试剂：CdCl2、硫脲(SC(NH2)2)、triethynolamine(TEA)、氨水（可以调节溶液的PH值），CdCl2与硫脲质量之比为1:1；
- 薄膜沉积温度：60～90℃， PH值：PH值范围是9～11，衬底是垂直放置在水浴溶液中的，时间为30min；

CdS thin films from two different chemical baths—structural and optical Analysis Journal of Crystal Growth 285 (2005) 41 - 48

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CdS thin films from two different chemical baths—structural and optical Analysis Journal of Crystal Growth 285 (2005) 41 - 48

Possible Reasons for CdS Alternatives

(1) Basic Performance.

Higher current from improved blue photon collection (generally realized), while maintaining equal voltage (generally not realized).

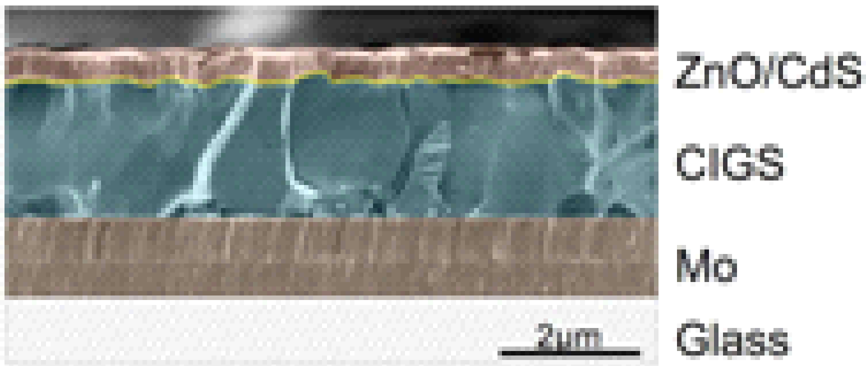
(2) Conduction-Band Offset Considerations

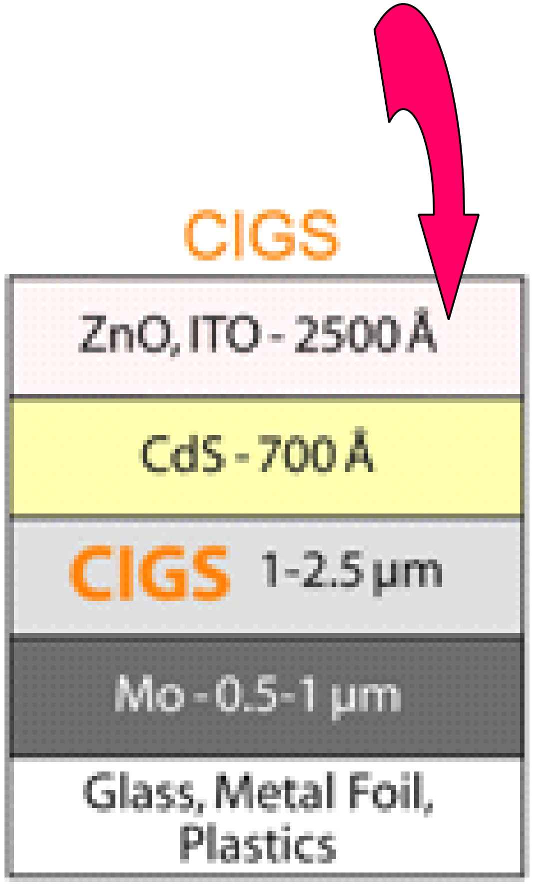
(a) Better match to CIS, especially when no blue photons present (current issue). (b) Better match to wide band-gap CIGS (voltage issue).

FROM: CIS Team Meeting
Alternative Junctions Subteam Report by Jim Sites

TCO (Transprent Conducting Oxide)

- **High Conductivity and Transparency**





挑战&探索

目 标

- 减少原材料的使用量，降低成本
- 提高光电转换效率

当前研究方向

热点一

CIGS电池的理论研究

结构方面

采用第一性原理（First Principle）的计算，如CIGS各种化合物的形成能。CIGS四元相图的标定。

电学特性

CIGS材料中点缺陷的研究（近百种电学缺陷），P-N异质结的理论分析。CIGS电池的亚稳特性等。

当前研究方向

热点二

Cd-free缓冲层的探索

Cd-free缓冲层的探索

- 用ZnS、InS等材料替代CdS

Buffer Layer	Efficiency
CdS	19.5% (2004)
ZnS(O,OH)	18.6% (2003)
InS(O,OH)	16.2% (2003)
Cd-PE	15.7% (2003)
ZnO	15.0% (1999)
$ZnIn_2Se_4$	14.5% (1998)
ZnSe	14.2% (2000)

FROM:1 March 8, 2005 Alternative Junctions Subteam Alternative Junctions Subteam Report by Jim Sites

Cd-free缓冲层的探索

- 可以**尝试**用有机材料做缓冲层

Inoganic/Oganic
hybrid Struc.

当前研究方向

热点三 →

Na在CIGS吸收层中的作用机理

实验验证 ⟷ 理论模型

Increased ~50%!

ble I: Device performance parameters of the matched CIGS devices with and without N

Cell	Voc (V)	Jsc (mA)	FF (%)	Eff (%
34017.12 – 1 (Na)	0.624	32.9	74.0	15.2
34017.32 – 4 (Na-less)	0.494	33.6	64.3	10.7

From: Study of the Electronic Properties of Matched Na-containing and Na-free CIGS Samples Using Junction Capacitance Methods

Peter T. Erslev[1], Adam F. Halverson[1], J. David Cohen[1], and William N. Shafarman[2]
[1] Department of Physics, University of Oregon, Eugene, OR 97403 U.S.A.
[2] Institute of Energy Conversion, University of Delaware, Newark, DE 19716 U.S.A.

Na的在CIGS薄膜中的缺点

稳定性差

Na本身的迁移析出量会随玻璃原料的不同和时间而大有差异

High Eff.的解释:

Na的存在降低了CdS/CIGS界面处的缺陷密度

From: Study of the Electronic Properties of Matched Na-containing and Na-free CIGS Samples Using Junction Capacitance Methods

“Alkali-silicate Glass ThinLayer（ASTL）法”

柔性CIGS太阳能电池单元转换率突破17.7%

By:日本的产业技术综合研究所

当前研究方向

热点五

In、Ga等稀有金属元素的替代

In、Ga等稀有金属元素的替代资源对电池大规模发展的制约。寻找可替代的元素也是研究热点：比如Cu2ZnSnS4等材料。

当前研究方向

热点六

带隙梯度太阳能电池

方法及解释

在CIGS薄膜的厚度方向上形成Ga/(In+Ga)成梯度

迎光表面一侧至背电极一侧的禁带宽度梯度

扩大从红外到可见光相应光谱的范围，
同时可以使能量较高的短波光子得到有效利用

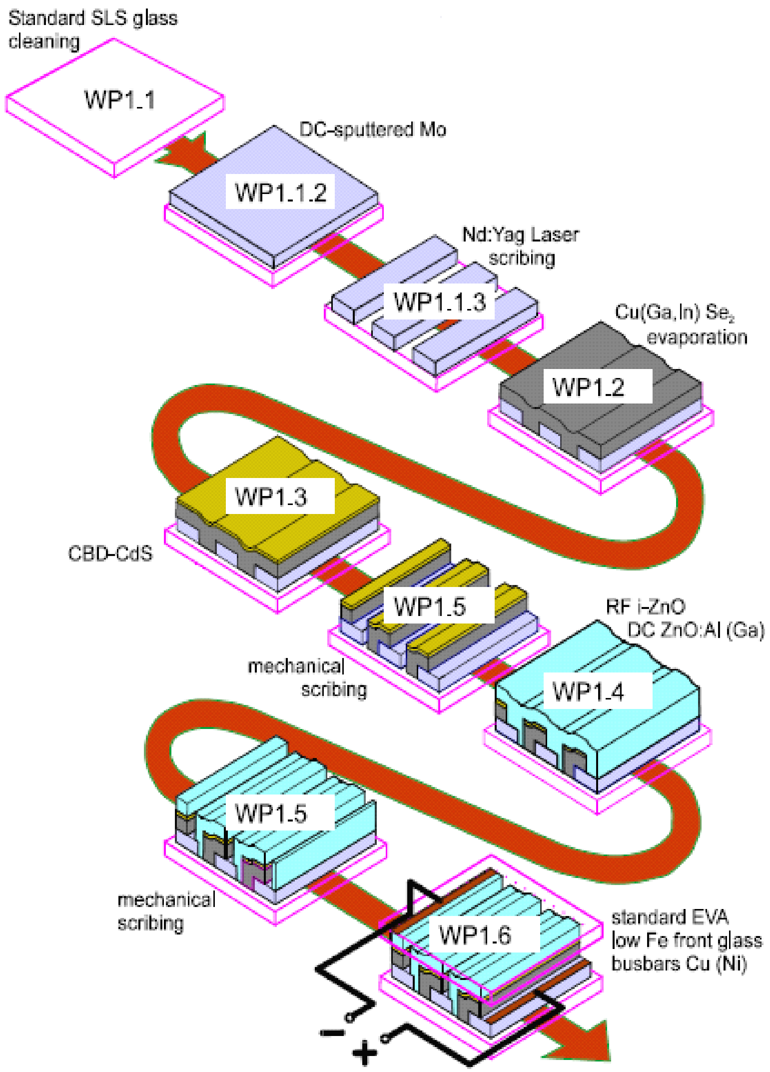
无限多结电池

50%？？？

FROM: Advanced Materials Industry No.4,2005,
CIGS薄膜太阳能电池研究现状及发展前景
庄大明，张弓 清华大学机械工程系薄膜实验室

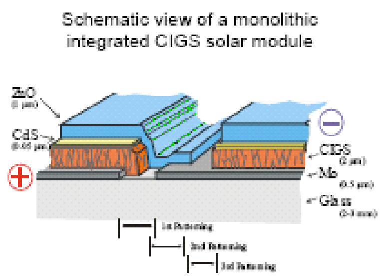
展望

产业化（Idustrialisation）



Par Courtoisie : Dr. Hans W. Schock (HMI, Berlin)

Mode d'interconnection



Flexible CIGS Solar Cells

公司	衬底	技术	效率（％）	面积	
GSE	不锈钢 30、48cm 宽	Roll to roll 共蒸发	12.5 小电池 10.7 组件	3716cm2	2007：40MW
Miasole	不锈钢 0.6-1m 宽	Roll to roll 共溅射	10.52	2.42 cm2	www.miasole.com 50 MW/年
Odersun AG	铜带 1cm 宽	Roll to roll 电沉积,用 S	11	1cm2	100-400 MW/年
Daystar	不锈钢 10×10 cm2	Roll to roll 溅射－硒化	16.9	1.1 cm2	
Nanasolar	Al 和不锈钢片	Roll to roll 印刷 纳米粒子	13.95 14.6	0.47 cm2	www.Nanosolar.com 2010 年，400MW

公司	衬底	技术	效率（%）	面积	
ISET	玻璃和柔性衬底	印刷納米粒子	13.0 Mo, 10.4 PI, 9.6 SS, 9.5 Ti, 13.6 玻璃.	0.08 cm2	2007,3MW
Scheuten	玻璃珠 0.2mm		5	0.06 mm2	2012 年，1GW/年
Solarion	PI 20cm 宽	共蒸发	7.5	1cm2	大于 10MW
Ascent solar	PI	Roll to roll 共蒸发			2007, 0.5-1.5MW
Heliovolt	玻璃，金属，PI				
[illegible]					

公司	衬底	技术	效率（%）	面积	
Matsushita	不锈钢	Roll to roll 共蒸发	17.1 12.6	0.96 cm2 91.1 cm2	
Flisom	PI	Roll to roll 共蒸发	14.1	0.595 cm2	

共蒸发是技术主流

走在前列的公司/国家

Manufacturer	Capacity in MW_P/a	Substrate (m × m)	Efficiency max./mea
	CIS		
Johanna Solar, Germany	30 (2008)	0.5 × 1.2	–/9.4% [20]
Würth Solar, Germany	14.8 (2007)	0.6 × 1.2	< 13%/11.7%
Global Solar, USA	4.2 (2006)	metal foil 1 ft wide	10%/8%
Showa Shell, Japan	20 (2007)	0.6 × 1.2	14.2%/11.8%
Honda Soltec Co. Ltd., Japan	27 (2007/2008)	0.8 × 1.3(0.2 × 0.2)	13%/10%
Sulfur Cell, Germany	5 (2007/2008)	0.65 × 1.25	8.2%/∼7%
AVANCIS, Germany	20 (from 2008)	0.6 × 1.2	13.1%/12.2%
Solibro GmbH (Q-Cells), Germany	25–30 (2009)	0.6 × 1.2	—

国内研发情况

- 与国外相比，国内对CIGS太阳能电池的研究研究微不足道
- 基础研究资金投入不足
- 研究单位极少
- 研究成果：实验室最高效率记录10%

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美好蓝图

Würth Solar (site web)

Shell (web)

50 kWp , 42,5 MWh produits par an

利用太阳能是解决能源与环境两个问题的最佳选择。

THANK YOU!