PROCESS DEVELOPMENT FOR HIGH V_{OC} CdTe SOLAR CELLS

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OBJECTIVE

The main objective of this project is:

to investigate new materials, device structures, and processes, in order to advance the open-circuit voltage (V_{OC}) of CdTe solar cells beyond the present state-of-the art levels of 840-850 mVs

Focus Areas

A: Front Contact/Window Layer: study the effect of buffer layers and CdS "doping" on device performance

- TiO_2 buffer
- Indium doping of CdS

B: Absorber (CdTe) Impurity Effects: study the effect of impurities in CdTe on solar cell characteristics

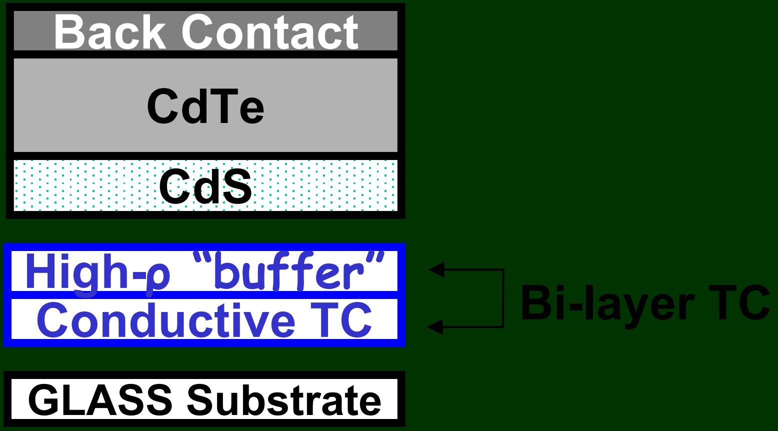
- CSS Ambient – the effect of O_2
- "Doped" Source Material (CdTe:P)
- Sb-diffusion (post-deposition)

C: Back Contact: develop deposition methods for high work function materials and utilize as back contacts to CdTe solar cells

- $TiSe_2$ by selenization

Buffers

Buffers or high-ρ transparent films are being used in CdTe cells to “sustain” high V_{OC}’s (in particular when CdS is thin)



For this Project TiO_2 has been deposited by RF sputtering and used as the high-ρ buffer

“BUFFER” REFERENCES

“High-Efficiency $Cd_2SnO_4/Zn_2SnO_4/Zn_xCd_{1-x}S$/CdS/CdTe Polycrystalline Thin-Film Solar Cells”, *X. Wu, R. Ribelin, R.G. Dhere, D. Albin, T. Gessert, S. Asher, D. Levi, A. Mason, H. R. Moutinho, P. Sheldon, Proc IEEE PVSC 2000, VOL 28, pp. 470-474*

“The Structural and Electrical Properties of Zn-Sn-O Buffer Layers and their Effect on CdTe Solar Cell Performance”, *S. Gayam, S. Bapanapalli, H. Zhao, L. Nemani, D. L. Morel and C. S. Ferekides, in print Journal of Thin Solid Films*

“Transparent Conducting Oxide Thin Films of Cd_2SnO_4 by RF Magnetron Co-sputtering of the Constituent Binary Oxides”, *R. Mamazza, D. L. Morel, and C. S. Ferekides, Thin Solid Films, 484, 1-2, (2005), pp. 26-33*

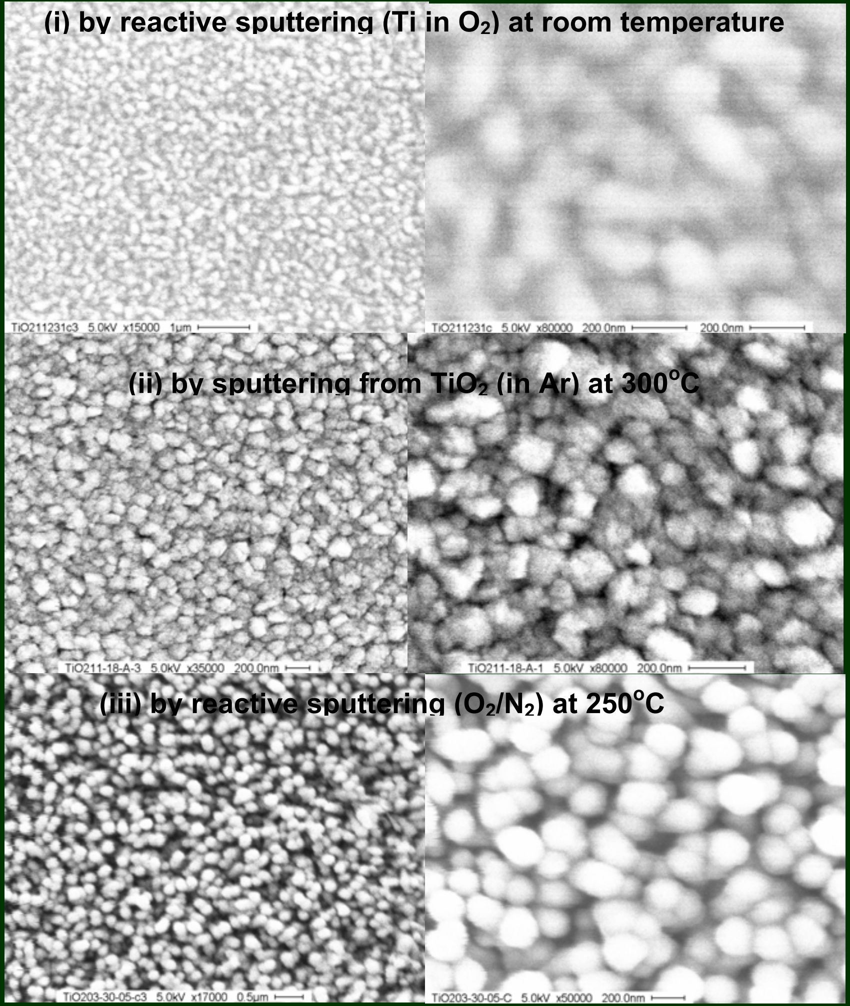
“Transparent Conductors and Buffer Layers for CdTe Solar Cells”, *C. S. Ferekides, R. Mamazza, U. Balasubramanian, and D. L. Morel, Thin Solid Films, 480-481, (2005) pp. 224-229*

TiO_2 Films

TiO_2 Films were prepared by Sputtering under various deposition conditions:

Deposition Process Variations:

- From TiO_2 ceramic target
- From Ti (in O_2)
- In N_2-Containing ambient
- T_{SUB}=RT-300°C
- Post-deposition annealed at high temp. (>600°C) in air

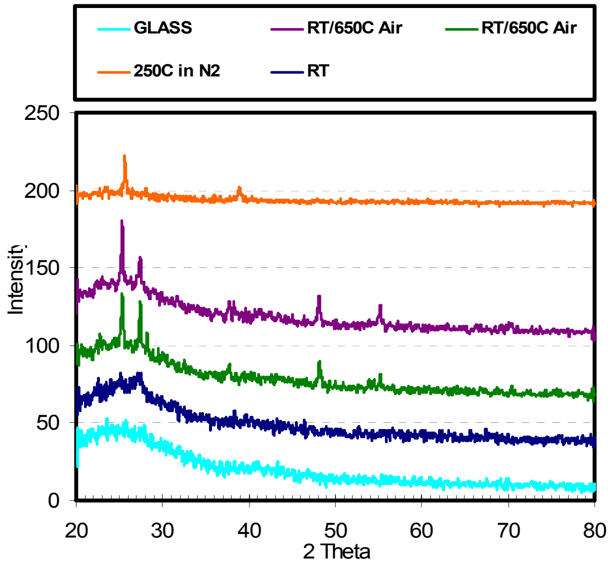

(i) by reactive sputtering (Ti in O_2) at room temperature

(ii) by sputtering from TiO_2 (in Ar) at 300°C

(iii) by reactive sputtering (O_2/N_2) at 250°C

- SEM & XRD Analysis
- Solar Cell Fabrication

TiO_2 – Structural Analysis



- All TiO_2 Films appeared to contain both TiO_2 phases (Anatase and Rutile)
- High Temp annealing improved crystallinity
- Electrical Resistivity VERY high and unmeasureable by simple 4-point probe measurements
- Optical transmission high and essentially unaffected by deposition conditions

Sample	2 Theta [°]	d-spacing [Å]	FWHM	Rel. Int. [%]	ID
T_{DEP}=RT	25.329	3.5164	0.2362	89.65	(101) A
Ann. 650°C/Air	27.422	3.2526	0.1181	100	(110) R
(green data)	48.179	1.8888	0.3149	38.26	(200) A
	54.593	1.6797	2.304	6.49	(211) A
T_{DEP}=RT	25.346	3.5141	0.1574	100	(101) A
Ann. 650°C/Air	27.343	3.2617	0.4723	45.44	(110) R
(purple data)	48.105	1.8915	0.2362	43.45	(200) A
	55.18	1.6632	0.576	24.81	(211) A
T_{DEP}=250°C (O_2&N_2)	25.626	3.4763	0.1181	100	(101) A
(orange data)	38.908	2.3148	0.4723	33.66	(200) R

CdTe/CdS/TiO_2/SnO_2:F Solar Cells

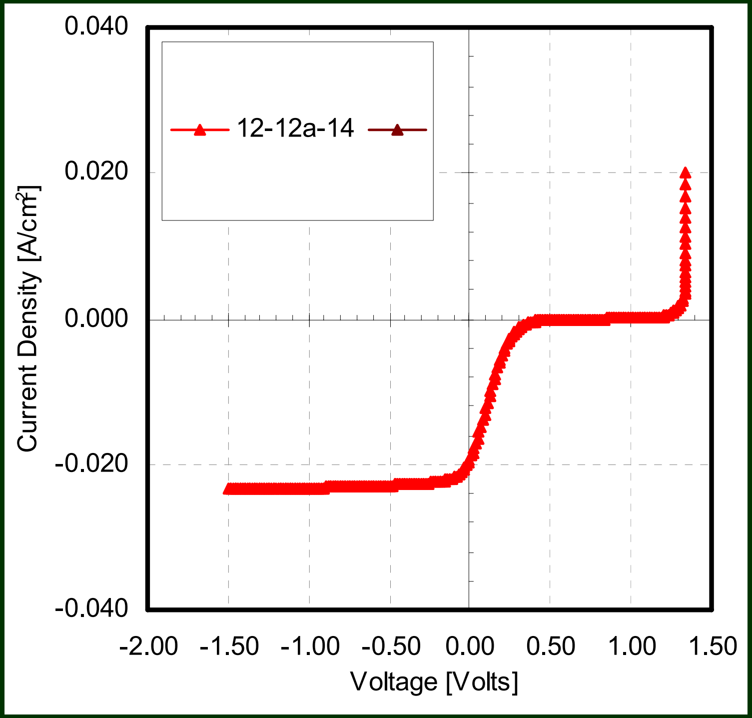
TiO_2 Deposition Conditions					V_{OC} [mV]	FF Range [%]
Ar [mT]	N_2 [mT]	O_2 [mT]	T [°C]	Thickness [nm]		
4.5	1.5	-	180	30	***880***	5-25
4.5	1.5	-	180	10	840	8-27
4.5	1.5	-	180	20	790	13-22
1	-	4	250	30	780	10-12
-	-	5	250	30	820	7-9

V_{OC} values represent HIGHEST measured at given conditions

- A max V_{OC} of 880 mV measured
- Highest V_{OC}'s measured for TiO_2 films deposited in N_2
- FF's below 25% in all cells fabricated to-date
- Highest V_{OC}'s typically accompanied by lowest FF's
- Significant scattering in the data

- Poor performance may be in part due to high resistivity of TiO_2
- Potential formation of microdiodes (data scattering)

$CdTe/CdS/TiO_2/SnO_2$:F Solar Cells Typical J-V Characteristic



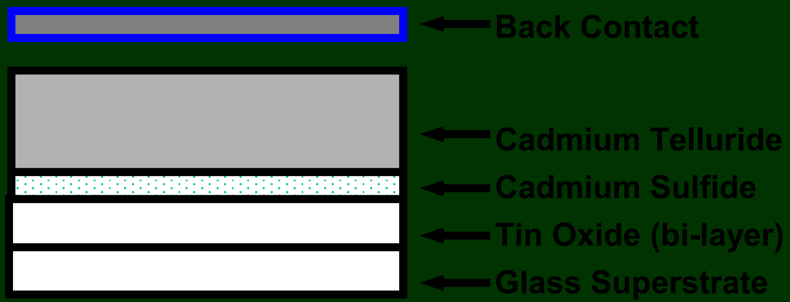
- Is the high resistivity of TiO_2 the limiting factor?
- If yes - Can TiO_2 films be doped for lower resistivity?
- Other buffers utilized successfully in the past have exhibited resistivity in the 1-10 Ω-cm range

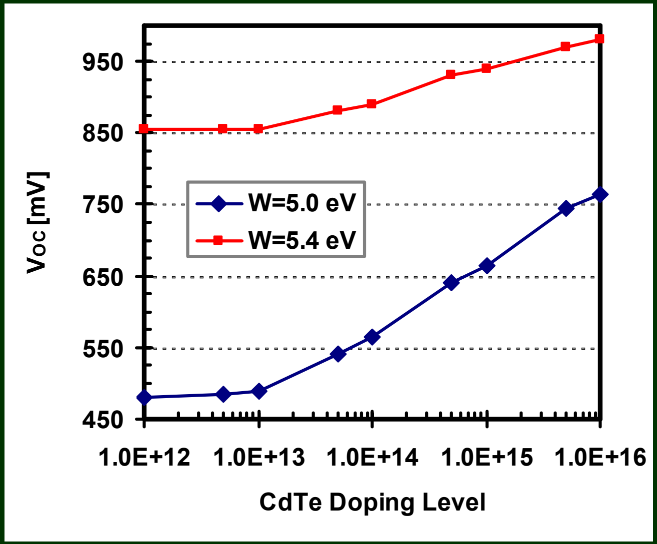
Large Work Function Materials

Key device parameters that limit V_{OC} are: doping in CdTe and energy of back contact (see fig. below)

If interfacial effects can be eliminated (@ back contact/CdTe interface), large work function materials could lead to improved V_{OC} and solar cell performance

For this Project $TiSe_2$ has been prepared by selenizing Ti





Results from modeling of CdTe solar cells using MEDICI ©

REFERENCES on Large Work Function Materials

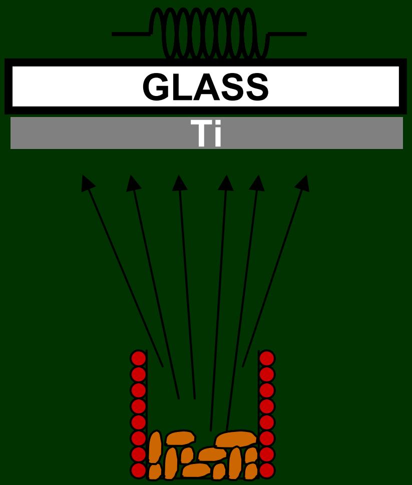
"Preparation and Electrical Properties of Niobium Selenide and Tungsten Selenide", *R. Kershaw, M. Vlasse and A. Wold, Inorganic Chemistry 6 (8), pp.1599-& (1967)*

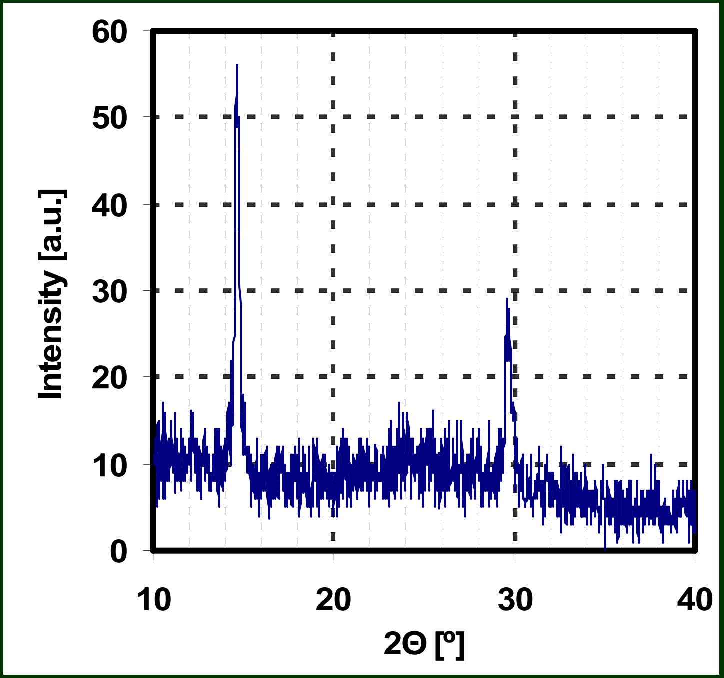
"The Transport-Properties of Vanadium-Doped $TiSe_2$ under Pressure", *R. H. Friend, S. S. P. Parkin and D. Jerome, Journal of Physics C-Solid State Physics 15 (25), pp.L871-L874 (1982)*

"Alternative back contacts for CdTe solar cells: a photoemission study of the VSe_2/CdTe and $TiSe_2$/CdTe interface formation", *D. Kraft, U. Weiler, Y. Tomm, A. Thissen, A. Klein and W. Jaegermann, Thin Solid Films, Volumes 431-432, 1 May 2003, Pages 382-386*

$TiSe_2$ by Selenization of Ti

Ti films deposited on glass (by sputtering) were selenized in a Se flux (by evaporation) in high vacuum @ elevated substrate temperatures





- The $TiSe_2$ Phase was identified in films selenized at temperatures over 400°C
- To-date no solar cells have been made with this material as the back contact
- Problem: $TiSe_2$ formation temperature (& vacuum environ.) lead to evaporation of CdTe
- Must explore compatible $TiSe_2$ deposition process

Effect of Impurities in CdTe

One of the tasks of this project is to study the role of impurities in CdTe in order to be able to increase its net carrier concentration and therefore the built-in potential and V_{OC}

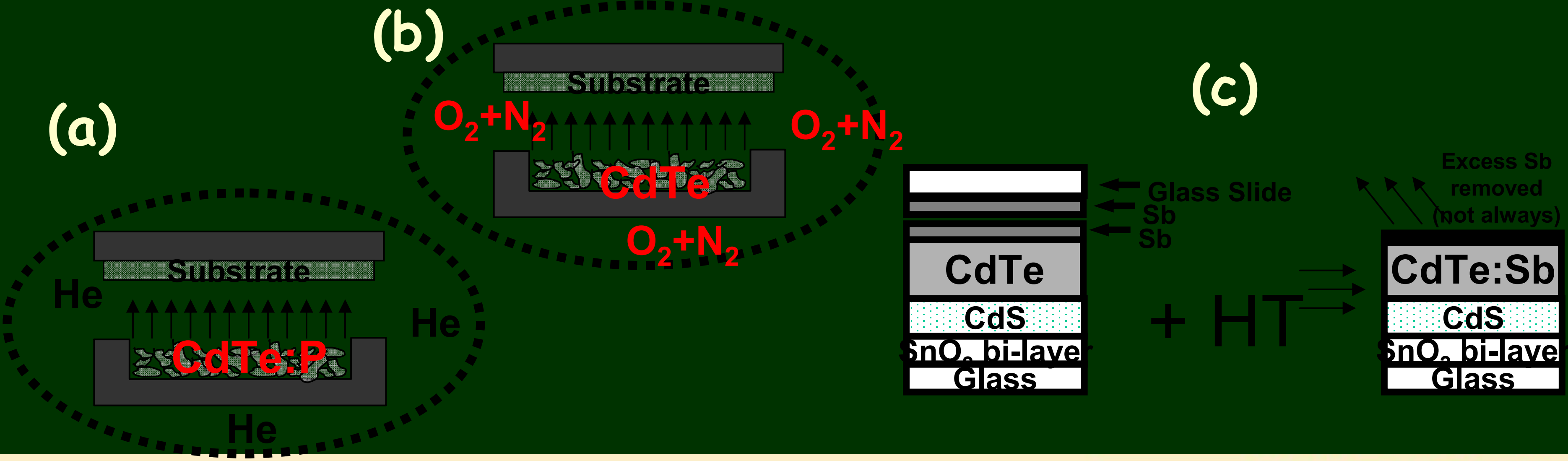
To-date:

(a) Incorporated Phosphorous (P) in the CSS-CdTe source material

(b) Studied the effect of O_2 partial pressure in the ambient of the CSS process

(c) Diffused Sb (post-deposition) into CdTe

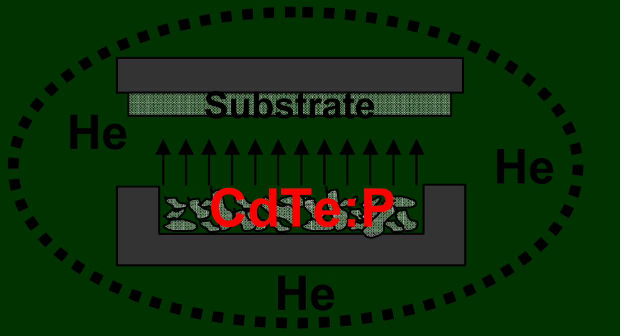
……… Fabricated cells with all of the above

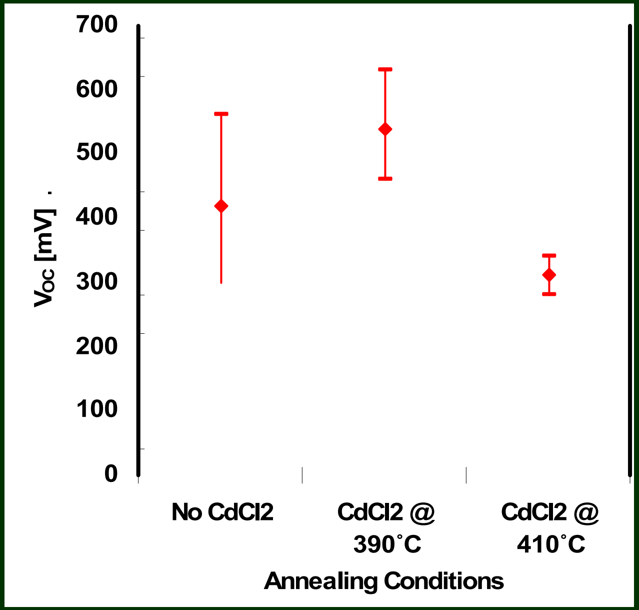


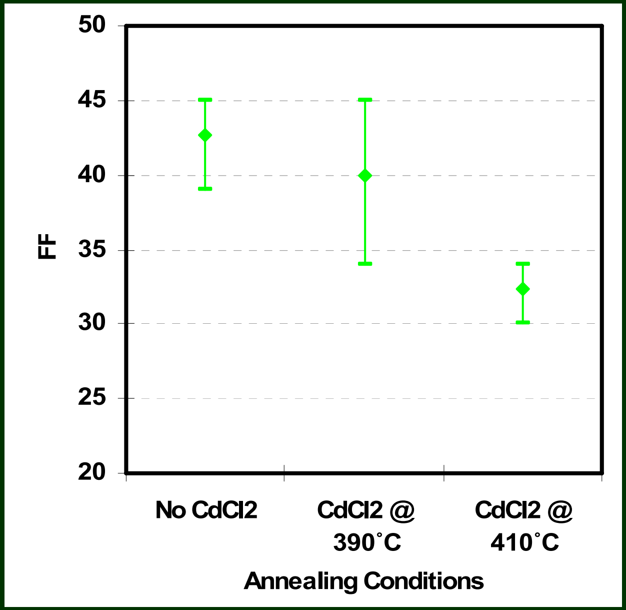
CdTe:P

- Introduced Phosphorous into CdTe by mixing CdTe + Cd_2P_3 powders in a quartz ampoule and heating at high temp. (5% at. P)
- Used “mixed powder” as source material during CSS deposition process
- Evidence of “P transport” during CSS (using EDS measurements)
- However, it appears that the source gets depleted of P within the first 2 depositions
- Solar Cell results were very poor and only improved (slightly) after $CdCl_2$ heat treatment

(a)



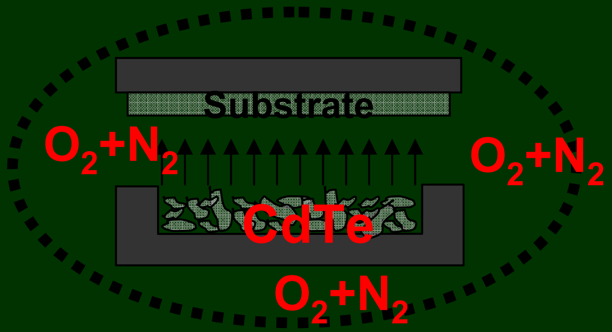


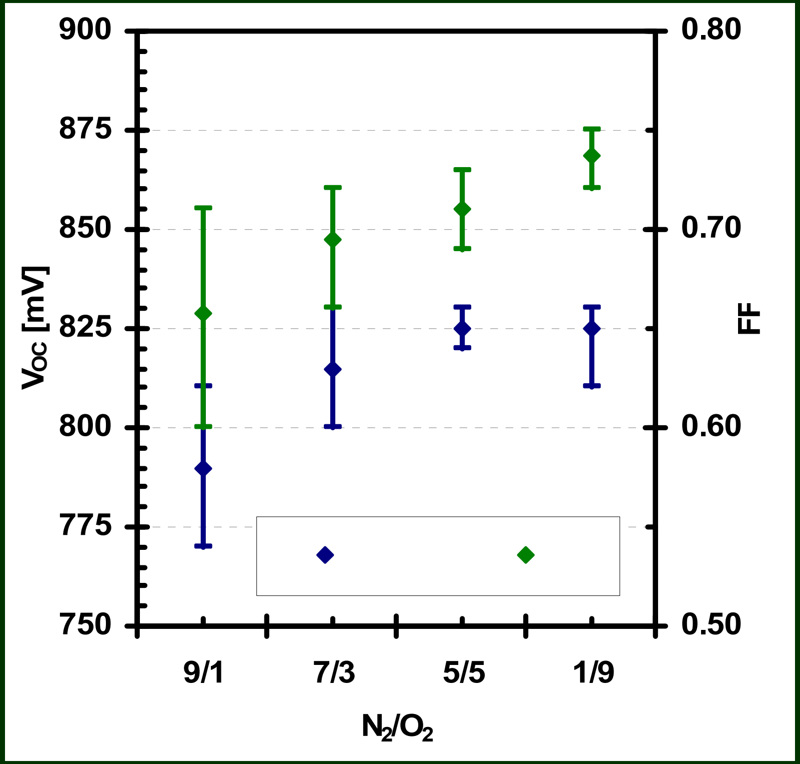


Effect of CSS-Ambient: Oxygen

- Varied amount of O_2 during CSS deposition
  - Total pressure; 10 torr
  - N_2/O_2: 9/1; 7/3; 5/5; 1/9
  - T_{SUB}/T_{SRC}: 550/630°C
  - Cells contacted with graphite paste

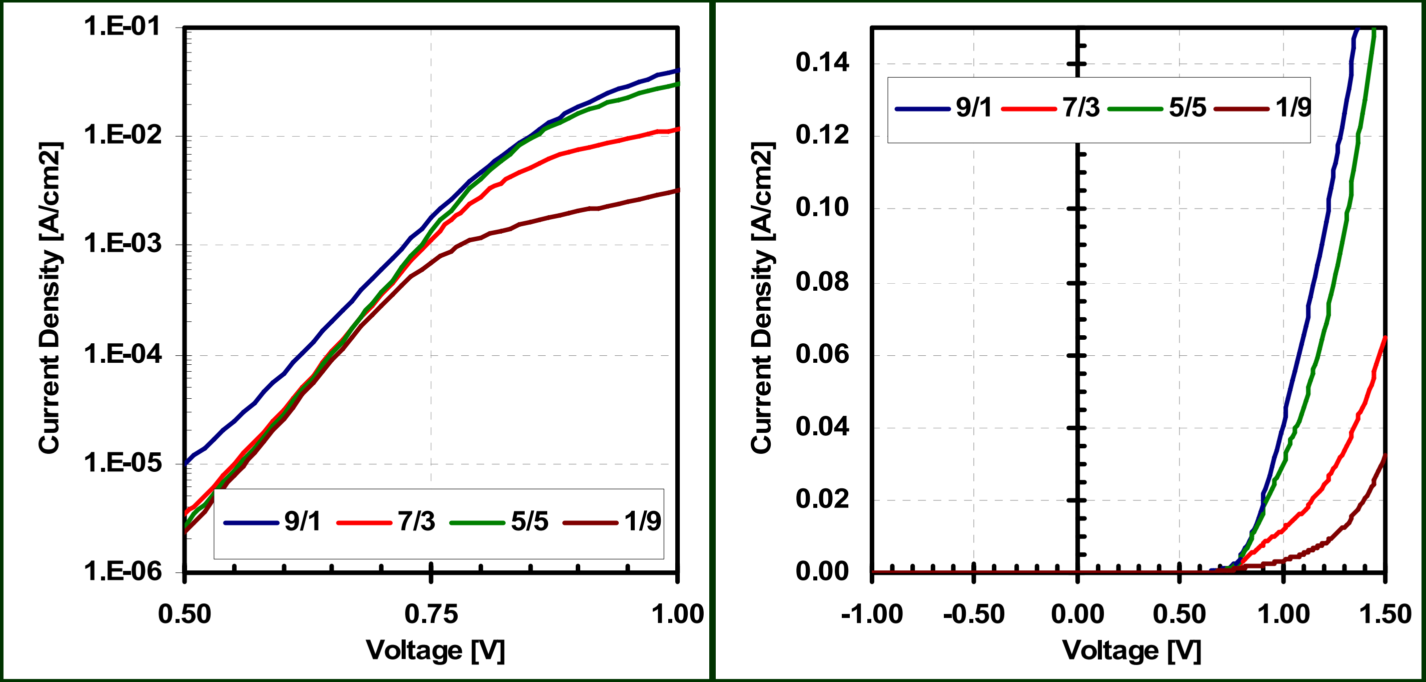
(b)





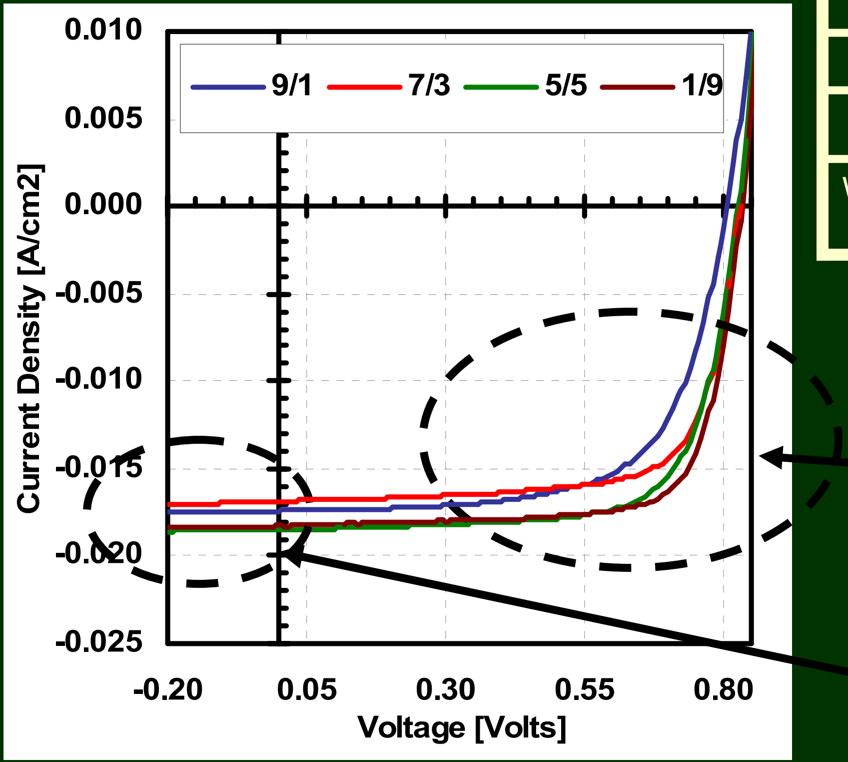
Effect of CSS-Ambient: Oxygen

- Increasing O_2-partial pressure results in decreasing J_O (Improved V_{OC}'s)
- Turn-on dark characteristics suggest CdS characteristics vary among the cells (become more resistive and photoconductive in cells with high oxygen partial pressure)



Effect of CSS-Ambient: Oxygen

- Increasing O_2-partial pressure leads to increased net carrier concentration – which however seems to "saturate" in the 10^{14}cm^{-3} range
- FF improves as O_2 pp increases due to improved collection
- Oxygen appears to have multiple effects (on CdTe p-concetration and on CdS photoconductivity)



	N_2/O_2			
	9/1	7/3	5/5	1/9
N_A-N_D [cm^{-3}]	1.98 x 10^{14}	2.77 x 10^{14}	3.46 x 10^{14}	3.4 x 10^{14}
W_D @0 Volts [µm]	3.03	1.82	1.98	2.03

Calculated from C-V measurements

- FF losses most likely due to collection

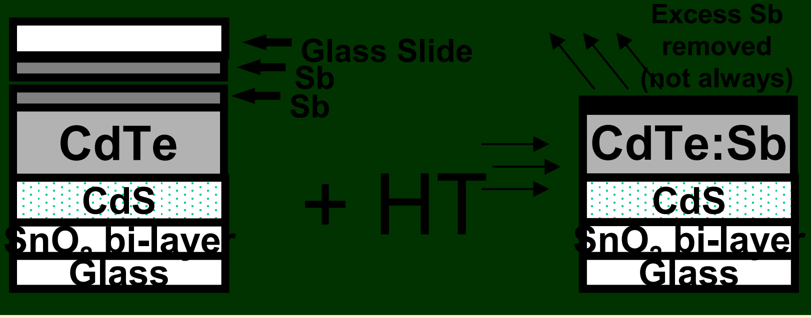
- Similar shunt resistances

CdTe:Sb

The $CdCl_2$ heat treatment (HT) was included for the fabrication of most CdTe:Sb based cells due to the large impact it has on device characteristics

Sample ID	"A"	"B"	"C"	"D"
CdTe	O_2 ambient; thickness 5-6 μm			
Sb Thickness on CdTe [nm]	20			
Heat Treatment (Sb Diffusion) T[°C]/time[min]	400/25	450/25	430/25	430/25
$CdCl_2$ HT	*None*	*None*	*Yes*	*Yes*
Contact	Sputtered Mo			
V_{OC} [mV]	710-730	740-750	800-810	810-830
FF [%]	37-41	41-44	61	61-62

(c)

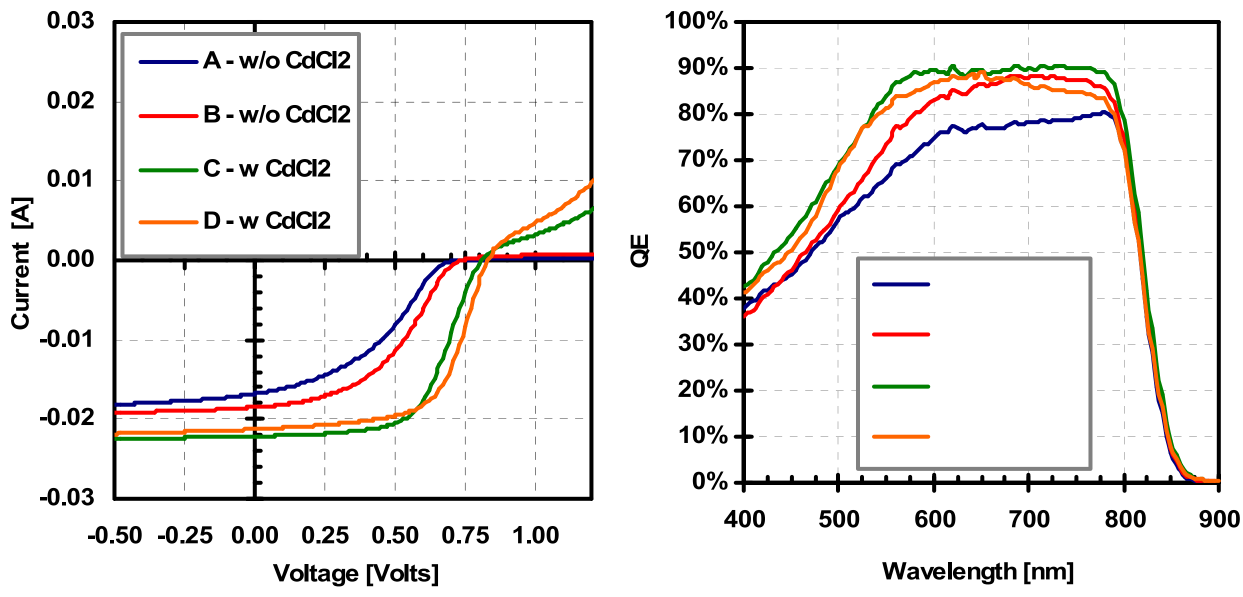


The Need for the $CdCl_2$ HT

The effect of the $CdCl_2$ HT on device performance (for the specific set of devices) is on the order of 5% (i.e. efficiencies improved from 6-7% to 11^+%)

Device performance improves in several ways:

- improved collection
- improved back contact performance (i.e. reduction in back barrier)
- higher V_{OC}s



Effect of “Excess Surface” Sb

Sb_2Te_3 has been previously used for the fabrication of effective back contacts

Therefore Sb remaining on the surface of the CdTe after the diffusion heat treatment could influence the solar cell characteristics

HCl etch was used to remove excess Sb from the CdTe surface

Device results DO suggest that NOT removing Sb yields better performance

Sample ID	**“400/HCl”**	**“400/NO HCl”**	**“450/HCl”**	**“450/NO HCl”**
CdTe	In O_2 ambient; thickness 5-6 μm			
Sb Thickness on CdTe [nm]	20			
Heat Treatment (Sb Diffusion) T[°C]/time[min]	***400/25***	***400/25***	***450/25***	***450/25***
HCl Etch	***Yes***	***No***	***Yes***	***No***
$CdCl_2$ HT	None			
Contact	Sputtered Mo;			
V_{OC} [mV]	680-690	710-730	630-680	740-750
FF [%]	37-38	37-41	32-37	41-44

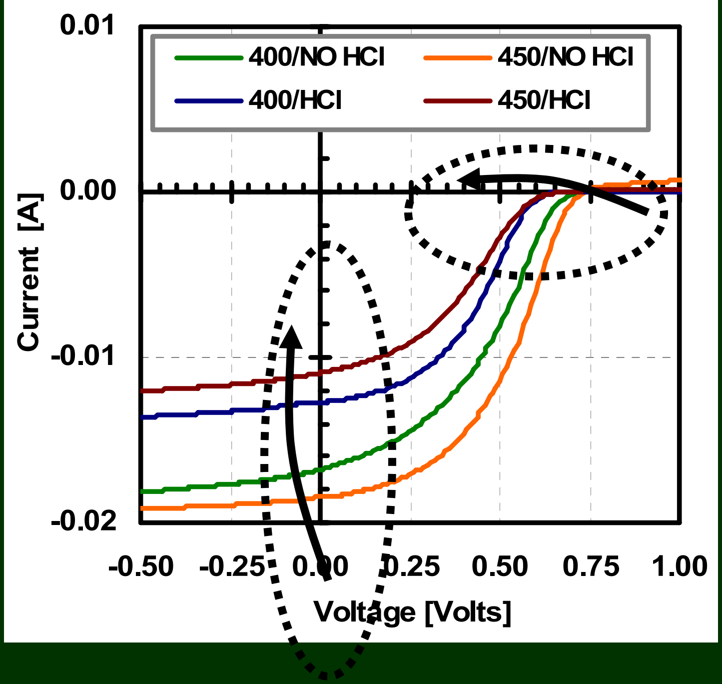
REFERENCE on Sb_2Te_3 Back Contact

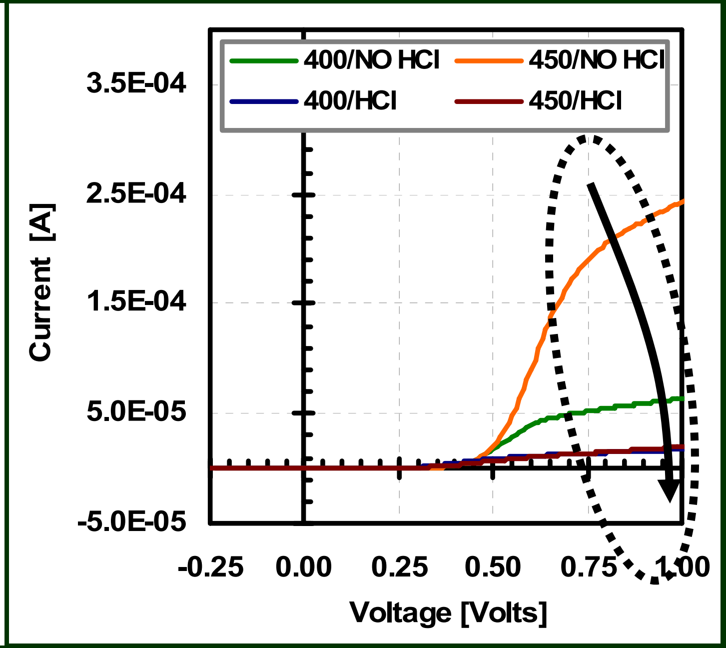
“Development of efficient and stable back contacts on CdTe/CdS solar cells”, D. L. Bätzner, A. Romeo, H. Zogg, R. Wendt, A.N. Tiwari Thin Solid Films, 387, 1-2, (2001) pp. 151-154

Dark and Light J-V

Cells etched with HCl exhibit lower J_{SC}, lower V_{OC} and their forward dark currents are significantly lower than those in un-etched samples

The observed behavior points to Sb influencing the back contact region of the device (either as a “contact material” or by increasing the p^+ doping at the back surface of CdTe)





The Effect of Sb-Diffusion Process

Sb-diffusion Time:

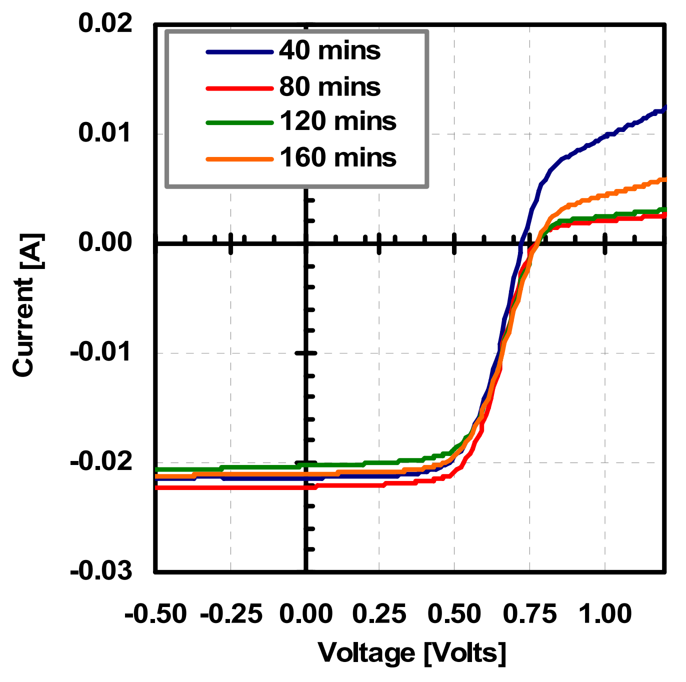
- Longer Sb-diffusion times result in improved V_{OC} by approximately 30-50 mV
- However, performance seems to "level off"

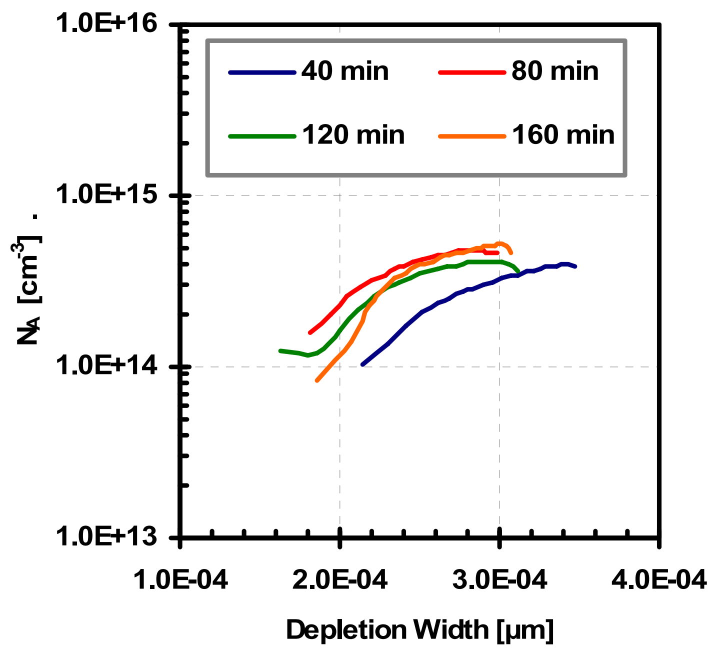
Sample ID	**"40"**	**"80"**	**"120"**	**"160"**
CdTe	In O_2 ambient; thickness 5-6 µm			
Sb Thickness on CdTe [nm]	30			
Heat Treatment (Sb Diffusion) T[°C]/time[min]	***400/40***	***400/80***	***450/120***	***450/160***
$CdCl_2$ HT	YES			
Contact	Sputtered Mo;			
V_{OC} [mV]	700-730	750-770	730-770	740-770
FF [%]	58-63	60-62	61-63	61-64

The Effect of Sb-Diffusion Process

Sb-diffusion Time:

- *C-V measurements indicate an increase in doping profile*
- *Doping levels "saturate" and are well within the "typical" CdTe doping levels (i.e. 10^{14} cm^{-3})*

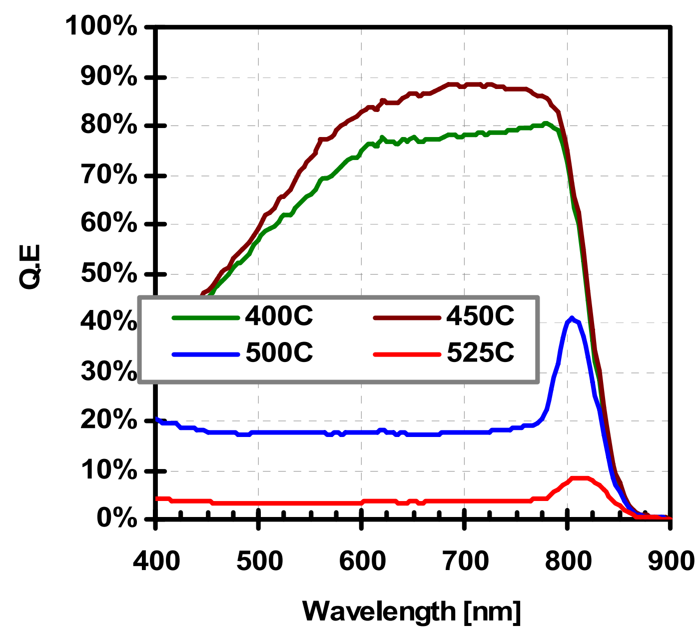




The Effect of Sb-Diffusion Process

Sb-diffusion Temperature:

- In general, performance improves up to 450°C
- SR for high T indicative of interfacial recombination
- Optimum diffusion temperatures in the 400-450°C range

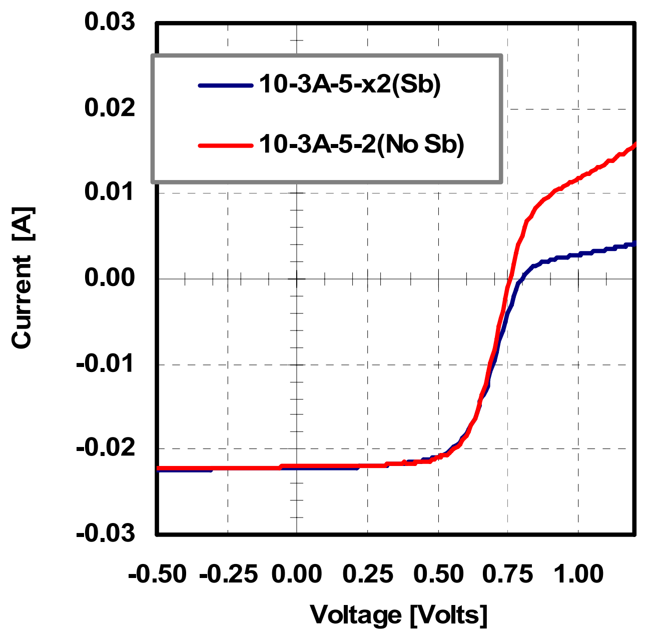


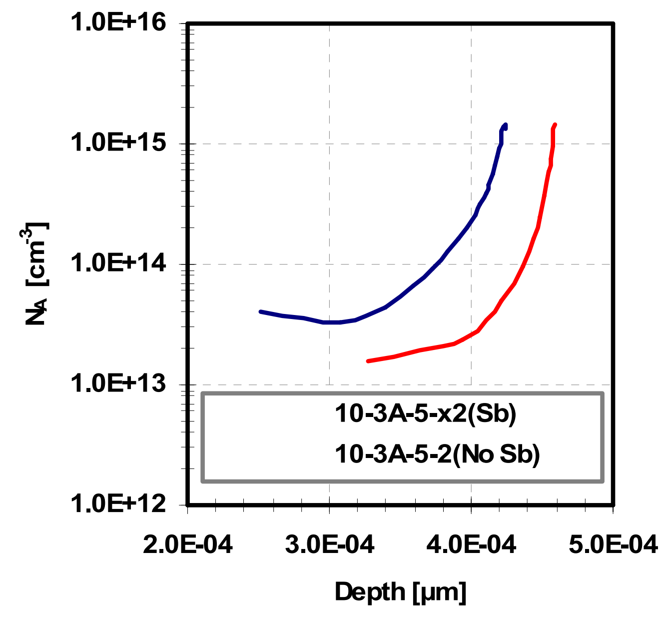
CdTe:Sb vs. CdTe

<u>SAME CELL RESULTS</u>

One half of the substrate fabricated with Sb-diffusion
Second half w/o Sb

Higher V_{OC} (50 mV) and higher doping profile for Sb-diffused sample

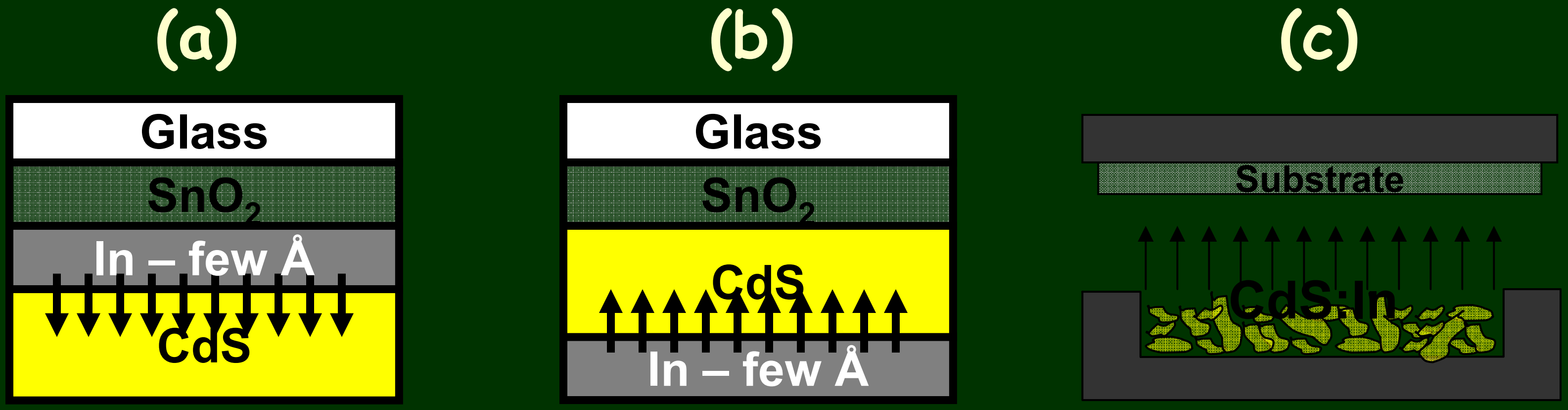




Indium Doping of CdS

Three process variations:

- Apply a thin In film prior to CSS-CdS deposition
- Apply a thin In film after the CSS-CdS deposition (heat treat)
- Use In-doped CSS-CdS source (purchased with 500 ppm In)



Indium Doping of CdS

Three -Variations

- Apply a thin In film prior to CSS-CdS deposition
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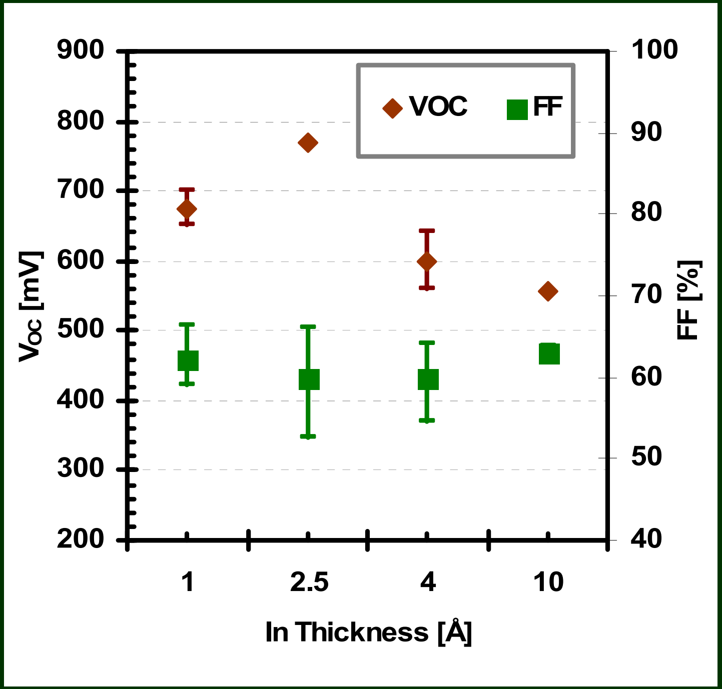
Preliminary solar cell results for process (b):

post CdS deposition In-diffusion



Summary

- Deposited TiO_2 films by rf sputtering under various conditions
  - Evaluated structural properties of TiO_2
  - both Anatase and Rutile phases are present in all instances
  - Incorporated TiO_2 films in CdTe cells as buffers
  - Measured 880 mV V_{OC}, HOWEVER …
  - "TiO_2" cells suffer from extremely low FF's (<25%) presumably due to the high electrical resistivity of TiO_2

- Investigated three potential p-type dopants for CdTe: Sb, O, P
  - Dopant transport during the CSS process is not efficient (P-experiments)
  - Sb and O "doping" suggest an increase in the net hole concentration in CdTe, HOWEVER …
  - Doping levels always appear to saturate in the 10^{14} cm^{-3} range
  - $CdCl_2$ HT is indeed a necessary process step (at this time) …

- Prepared $TiSe_2$ films by selenization of Ti to use as back contacts to CdTe
  - Ti-selenization process incompatible with CdTe solar cell
  - Must develop a process compatible with CdTe films (solar cell structures)

- Initiated work on Doping of CdS
  - Device results are still preliminary