U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

Surface Analysis

Sally Asher, Joel Pankow, Craig Perkins,
Robert Reedy, Glenn Teeter, and Matt Young

DOE Solar Energy Technologies Program Peer Review

Denver, Colorado

April 17-19, 2007

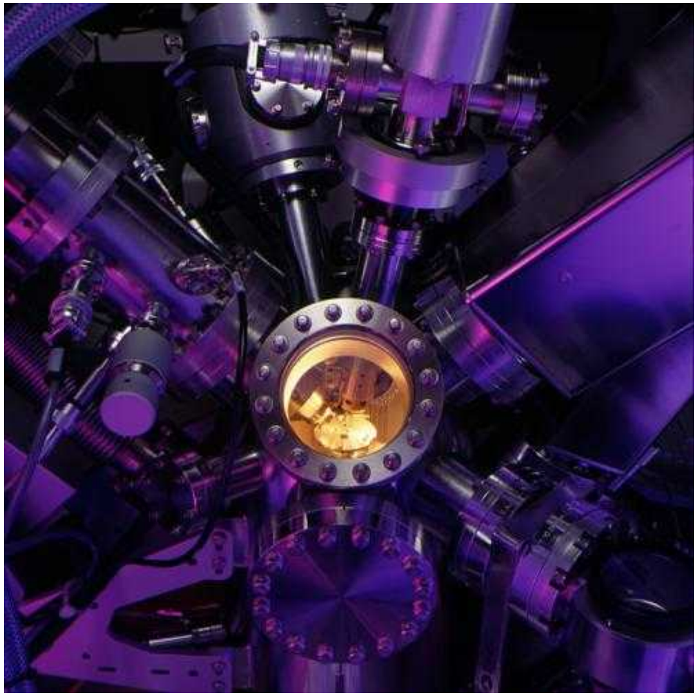
Overview

Advance the understanding of photovoltaic materials and devices by employing surface science techniques to investigate surface and interfacial properties.

- **W**ork with Solar America Initiative (SAI) TPP awardees and other PV researchers to identify and solve research and manufacturing problems.
- **C**ollaborate with DOE SETP researchers to solve key problems faced in the development and reliability of PV materials.
- **D**evelop new tools and improved methodologies for *in-situ* study of PV surfaces and interfaces.
- **D**isseminate research results through publications, presentations, and regular interactions with other researchers in photovoltaic and surface-science disciplines.

Major Analytical Methods

- Auger Electron Spectroscopy (AES)
- X-ray and Ultraviolet Photoelectron Spectroscopy (XPS/UPS)
- Surface Analysis Cluster Tool
  - UHV Transfer System
  - AES/XPS/UPS
  - UHV Deposition Tool
    - Thermal Desorption Mass Spectrometry (TDMS)
    - LEED, RHEED, SE capable
  - Controlled Ambient Glove Box
- Secondary Ion Mass Spectrometry (SIMS)
  - Dynamic (double-focusing magnetic sector)
  - Static (time-of-flight)



Phi 5600 XPS/UPS System

Budget History

October 1, 2005 to January 1, 2007

Project Task(s)	Total Value
PVA6.3301	$1,380,000
PVB6.5133	$100,000
PVA7.3301	$478,663*
Grand Total	$1,959,663

FY06 - 5.88 FTE's
FY07 - 5.65 FTE's

*Amount in FY07 Plan under continuing resolution pro-rated for 1/3 year

FY2006/7 Activities

Support Research and Development

- Worked with at least 17 different PV manufacturers
- Considerably larger number of NREL and academic researchers
- >800 samples, >3000 separate measurements
- All materials technologies

Collaborative Research and Development

- Study reaction kinetics and electronic structure of nano-scale Cu_xTe films for CdTe back contact applications
- Study relationship between moisture barrier deposition fundamentals and barrier performance
- Co-inventor of one issued US patent

FY2006/7 Activities

Tool Development for PDIL

- Large-area Auger tool development
- Liquid-Phase Quartz Crystal Microbalance (LP-QCM)
- Automated chemical reactor for wet-processing
- Theoretical calculations for flux uniformity and combinatorial deposition
- Large-Area XPS tool development

Publications and Presentations

- 8 - Oral presentations - external (2 invited)
- 2 - Oral presentations - internal
- 12 - Publications

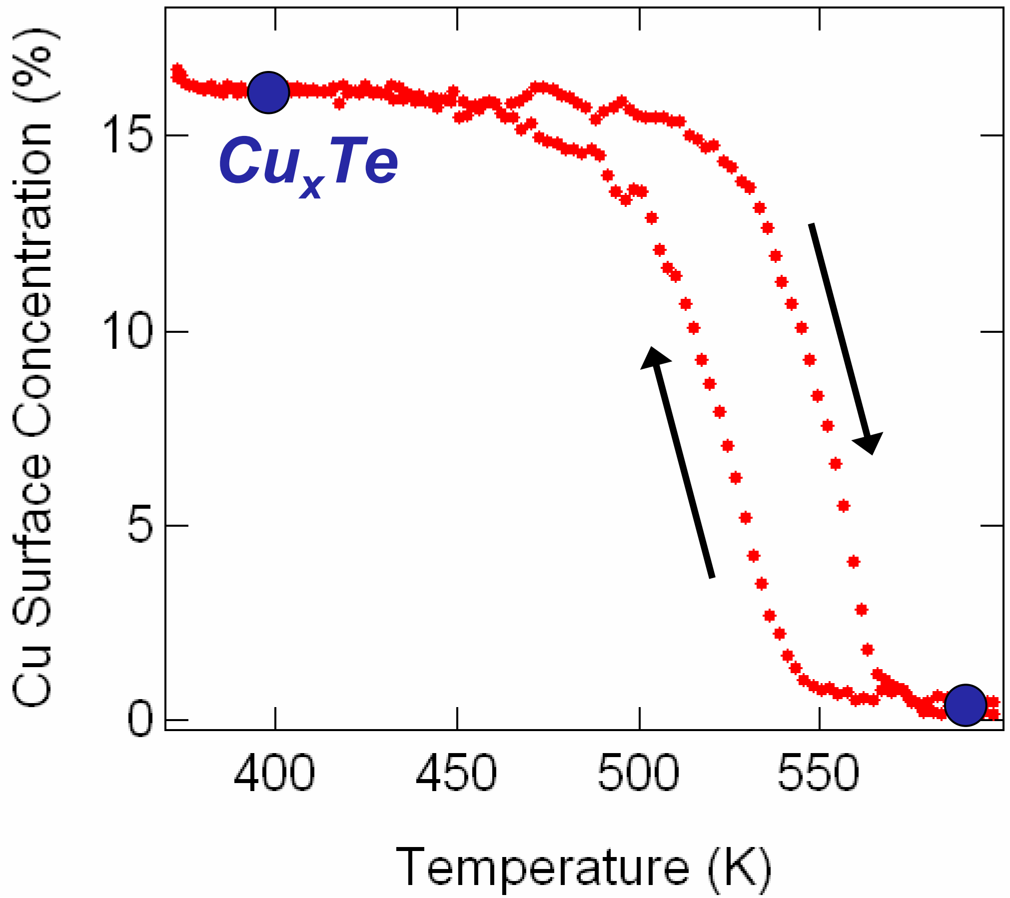
Accomplishments

Collaborative Research

Task: Study the reaction kinetics of nanoscale Cu_xTe films

Cu-doped CdTe: Temperature-Reversible Cu_xTe Surface Precipitation

Temperature-Programmed XPS Measurement



dT/dt = 2 K/min.

Hysteresis
→ nonequilibrium

XPS, AES show Cu_xTe at surface

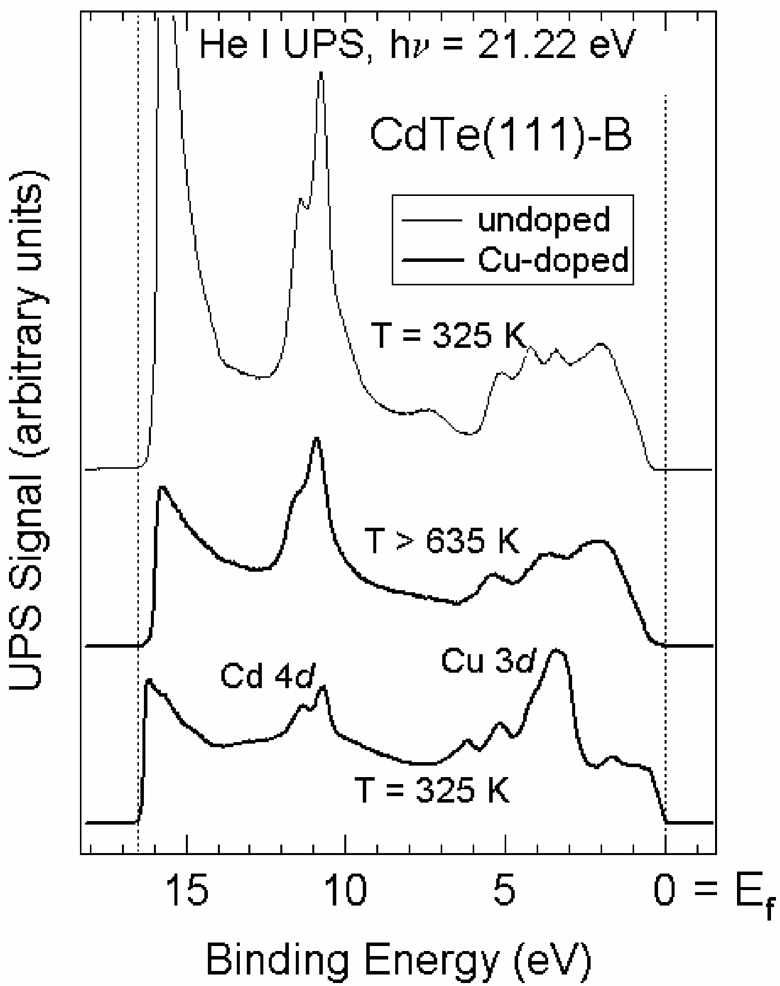
Precipitation—driven by Cu-CdTe solubility

Accomplishments

Collaborative Research

Task: Study the electronic structure of nanoscale Cu_xTe films

Ultraviolet Photoelectron Spectroscopy and Band Alignments



CdTe(111)-B substrate	SEC (eV)	VBM (eV)	I_S (eV)
w/o Cu, T=325 K	15.98	0.45	5.69
w/ Cu, T > 635 K	16.06	0.37	5.53
w/ Cu, T=325 K	16.38	0.00	4.84
Est. uncertainty	±0.03	±0.03	±0.06

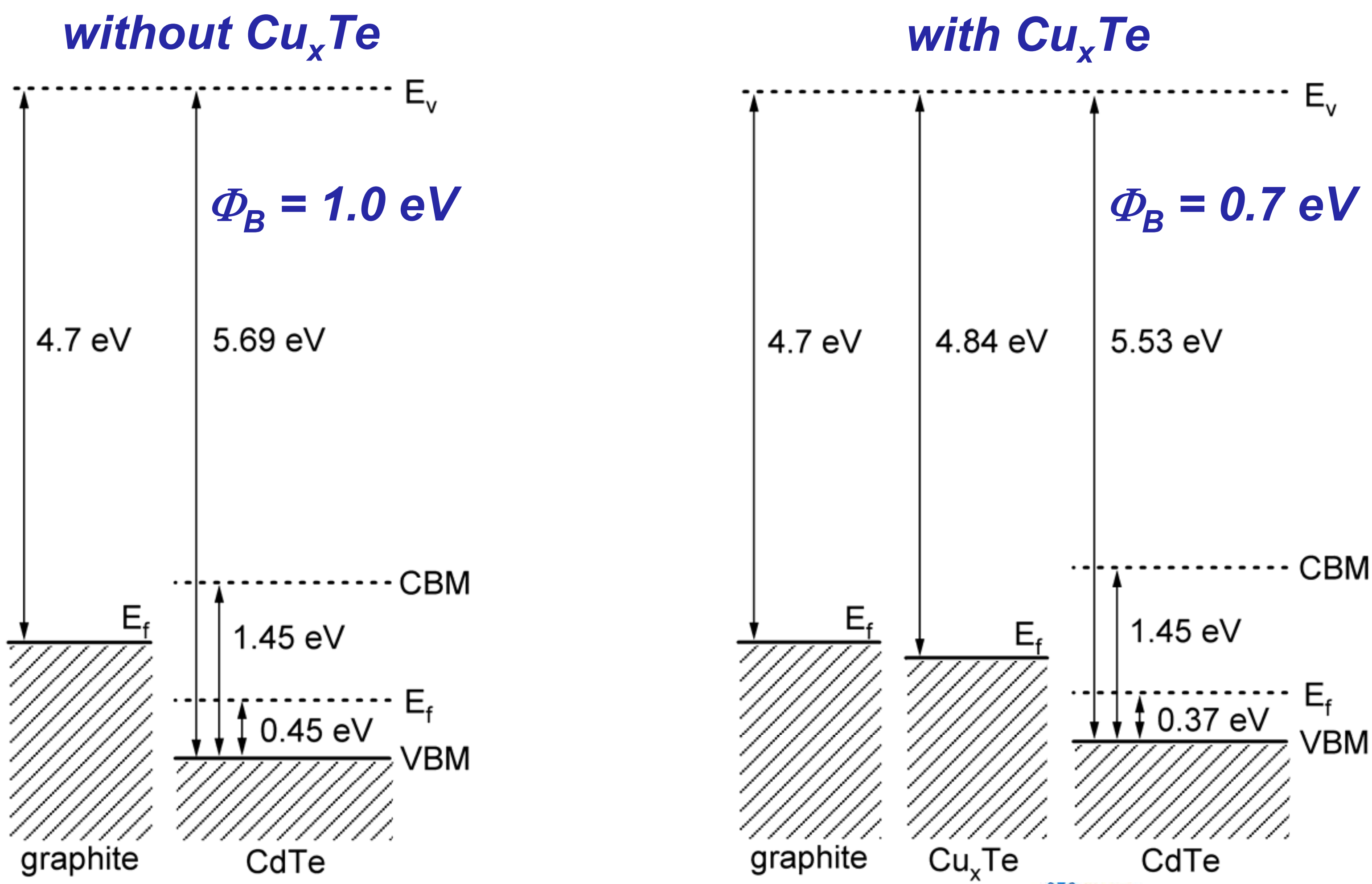
Heavy Cu doping does not dramatically alter valence-band or I_S.

Precipitated Cu_xTe lowers I_S by about 0.9 eV.

Accomplishments
Collaborative Research

Task: Study the reaction kinetics of nanoscale Cu_xTe films

Ultraviolet Photoelectron Spectroscopy and Band Alignments



G. Teeter, poster at this meeting

Accomplishments

Collaborative Research

Task: Study the electronic structure of nanoscale Cu_xTe films

Ultraviolet Photoelectron Spectroscopy and Band Alignments

Φ_B = 0.7 eV → still too large to provide ohmic contact.

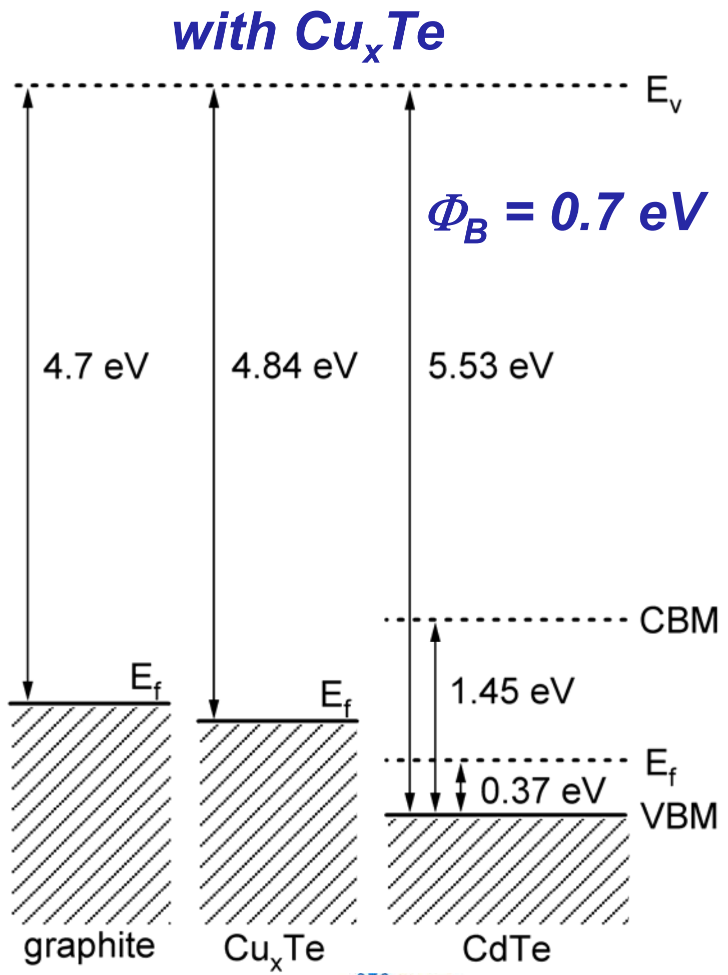
Schottky-Mott theory for MS interfaces:

$$\Phi_B = \phi_M - I_S$$

interface dipole term can decrease barrier:

$$\Phi_B = \phi_M - I_S + eV_{int}$$

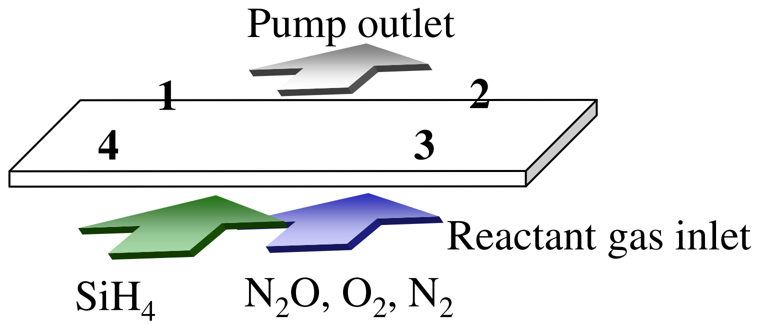
Interface effects could change Φ_B



Accomplishments

Collaborative Research

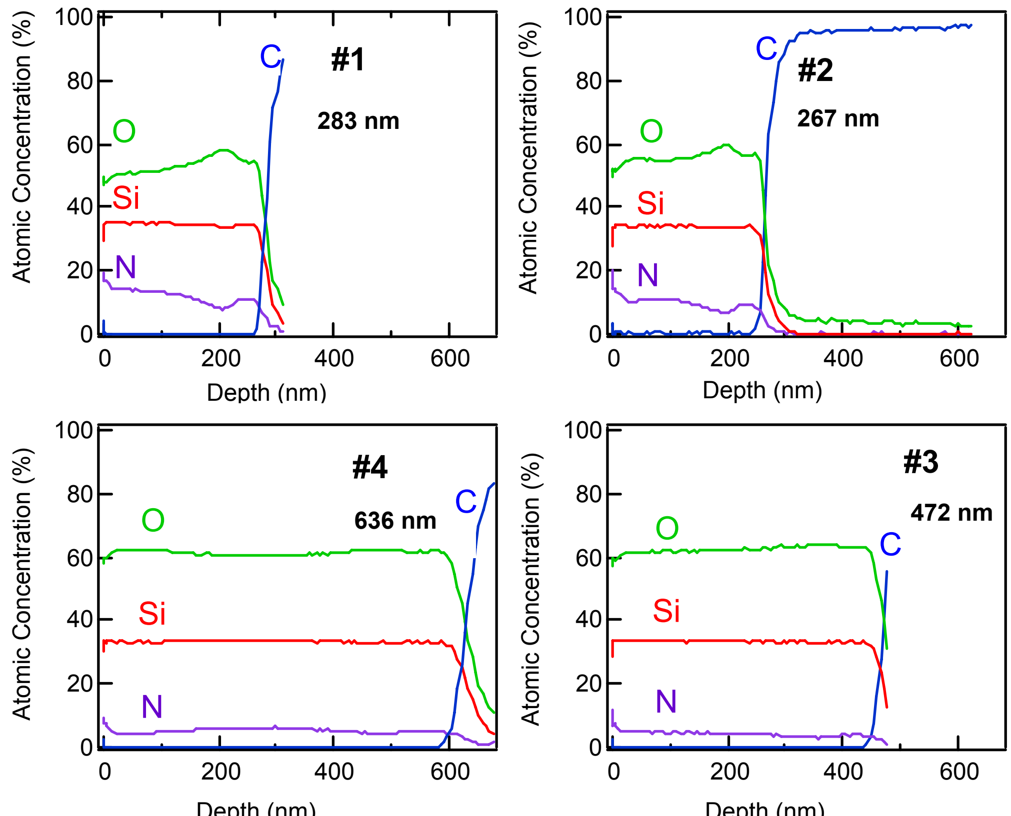
Task: Study relationship between moisture barrier deposition fundamentals and barrier performance characteristics



SiO_xN_y Moisture Barriers on PET[1]

- PECVD over 12” x 12” Deposition Area
- Substrate Temperature
  - –Heater setting ≠ T_{Dep}
  - –No *in-situ* annealing of PET
- Film (Non)-uniformity measured by XPS Depth Profiling
  - –Thickness variation
  - –Compositional variation
- *Use the film non-uniformity to perform combinatorial-type experiments for adhesion and WVTR properties.*

Still unknown what barrier properties are necessary to protect a solar cell



1. J.W. Pankow and S.H. Glick, 2006 *IEEE 4th World Conference on Photovoltaic Energy Conversion*, p. 2250.

Accomplishments
Collaborative Research

Task: Study relationship between moisture barrier deposition fundamentals and barrier performance characteristics


Small Area MOCON Cell

SiO_xN_y Moisture Barriers on PET
- Develop Small Area WVTR MOCON Cell
  – Improved design with better thermal control and monitoring

Status as of 01/2007
- Barriers exhibit good dry adhesion (cohesive failure of test coupon rather than delamination of barrier)
- Excellent barrier properties to ~60°C in damp heat (no detectable H_2O permeation)
- ~>60°C lose adhesion => barrier fails
- Performance appears independent of thickness and composition over the range studied
- *Weak interface between barrier and PET suspected to be responsible for failure*
  – plasma damage during deposition
  – Artifact of measurement protocol

  Films are allowed to dry prior to each temperature change resulting in dimensional changes in the PET

Sample/ Location	Barrier Composition	Thickness (Å)	T (°C)	WVTR (g/m^2day)	Peel Strength (N/mm)[1]
ST504	N/A	N/A	40	3.6	NA
			60	12.5	
			85	61.0	
Inlet	$SiO_{1.8}N_{0.15}$	5540	40	<0.05	0.5
			50	<0.05	
			60	3.67	
Center	(2)	(2)	50	< 0.05	(2)
			60	< 0.05	
			70	8.5	
Outlet	$SiO_{1.6}N_{0.32}$	2755	50	< 0.05	0.3
			60	3.7	

1. After 250 h damp heat
2. To be determined
N/A=not applicable, uncoated

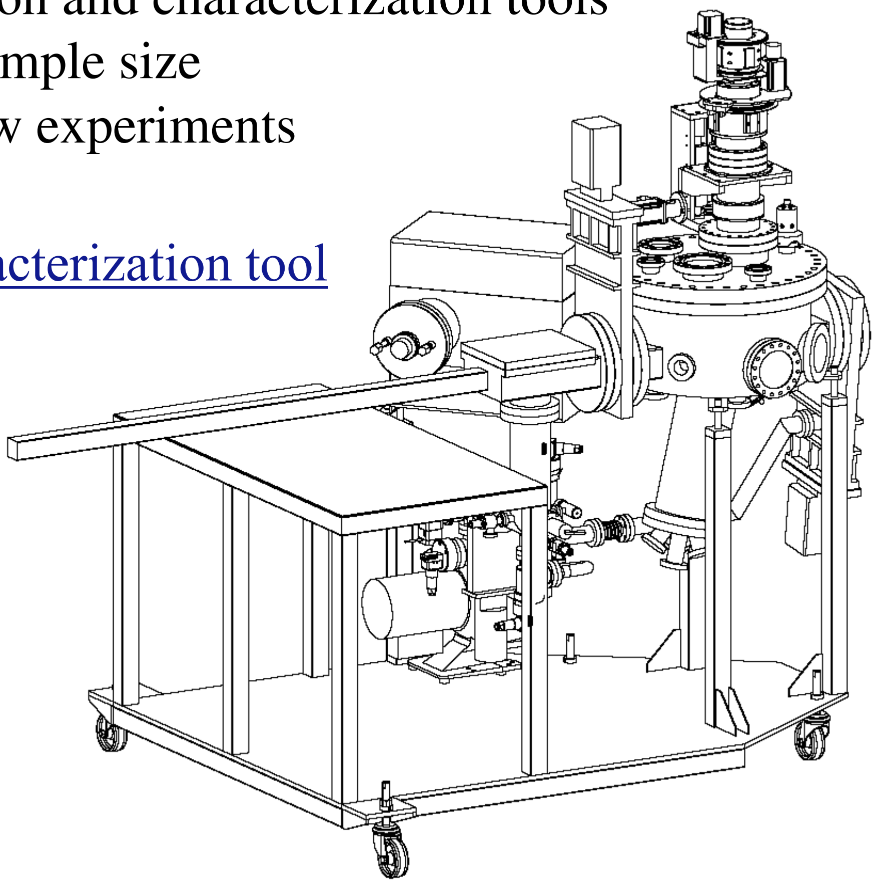
Accomplishments

Tool Development for PDIL

Task: Design and specify a cart-based Auger electron spectroscopy tool for use in the Science and Technology Facility

Process Development and Integration Laboratory - PDIL

- Flexible platforms with integrated deposition and characterization tools
- Standard transfer interface with 6” x 6” sample size
- Rapid reconfiguration of platforms for new experiments



Large-area Auger Tool - first dedicated characterization tool

- **W**hole platen analysis
- **H**ighly Automated Data Acquisition
  - Rapid depth profiling, composition
  - Stage mapping
- **V**ersatile chamber
  - Ports for future experiments
- **S**tatus as of 01/2007
  - Plans approved
  - Under construction
  - Expected delivery 06/2007

Accomplishments
Tool Development for PDIL

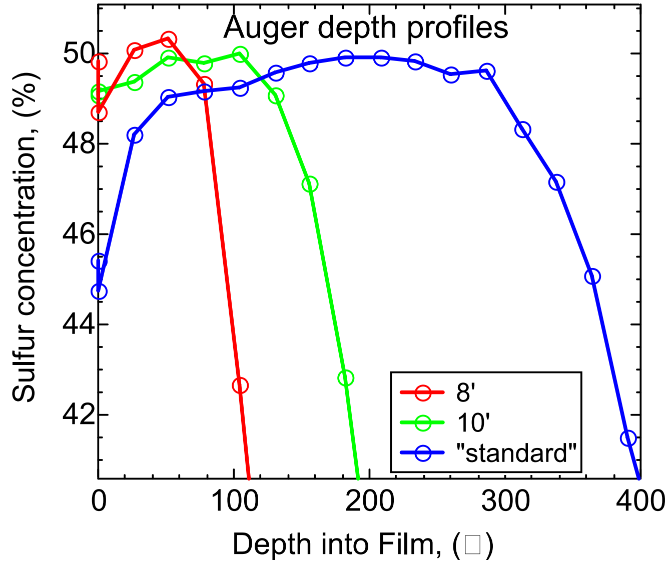
Task: Study wet-chemical processing of PV material surfaces leading to better control of deposition processes

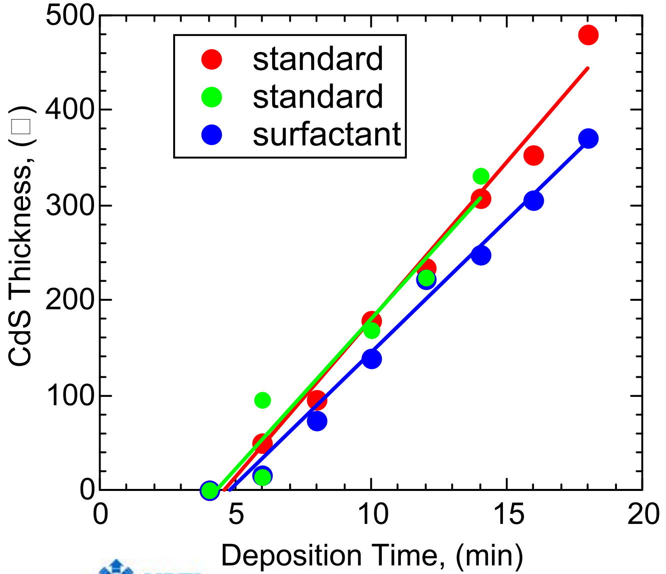
Liquid-Phase Quartz Crystal Microbalance (LP-QCM)

<u>Motivation-study CBD CdS surface chemistry</u>

- CdS thickness has strong effect on device performance (CdTe and CIGS). Thickness reproducibility critical.[1]
- Post-growth thickness measurement is tedious
  - Upper right graph-Auger depth profiles from three different CdS film growths
  - Bottom right graph-three growth rate calibration curves generated from 22-separate depth profiles (represents 22 different films grown!!)
- Accuracy is poor for thinnest films
- No method for *in-situ* measurement of film growth

In-situ measurement required if PDIL tools are to be automated with endpoint detection for film growth.





1. C.L. Perkins and F.S. Hasoon, *J. Vac. Sci. Techn. A*, 24(3) 2006, 497.

Accomplishments

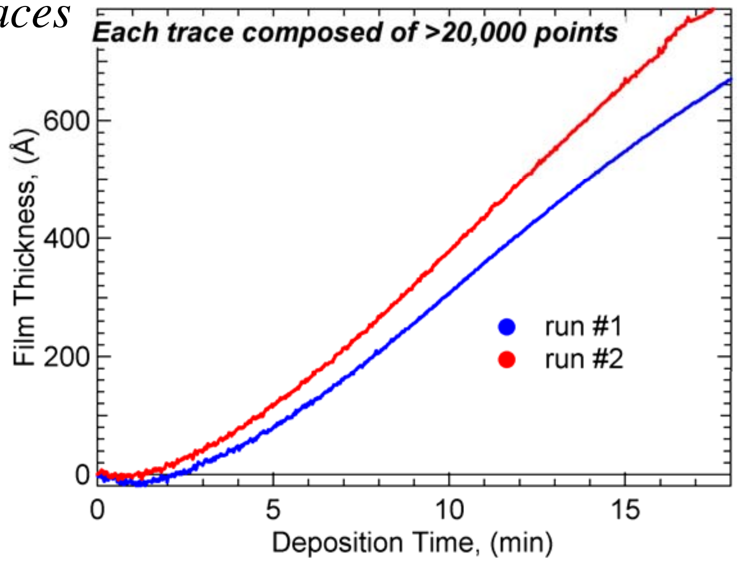
Tool Development for PDIL

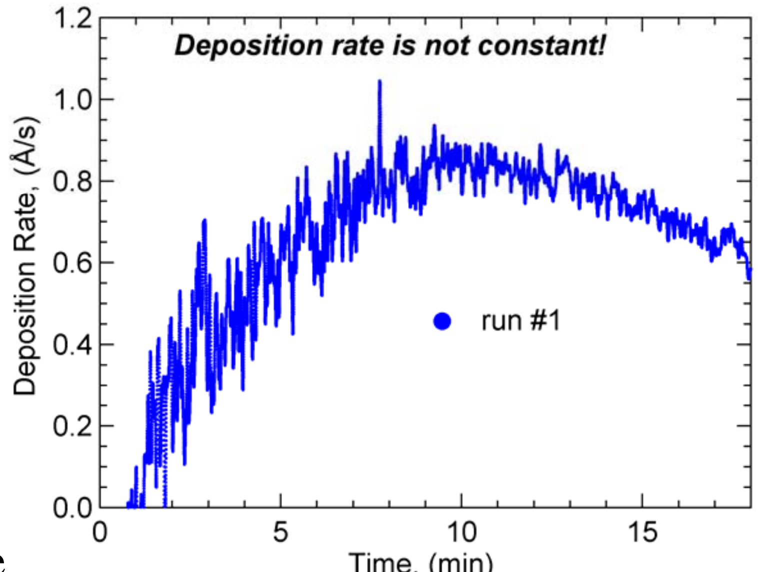
Task: Study wet-chemical processing of PV material surfaces leading to better control of deposition processes

Liquid-Phase Quartz Crystal Microbalance (LP-QCM)

Simple Equipment with complex interactions in CBD

- **Considerations for use**
  - –Deposition on both sides of the crystal
  - –Temperature dependent properties of system
  - –Changing hydraulic pressure
  - –Sensitivity to stirring
  - –Bubble formation
  - –Poor nucleation on sensor
  - –Different reaction rates between crystal and substrate
  - –Surface roughness
  - –Non-rigid film
  - –Film-induced stress on sensor
- High sensitivity to changes in growth rate
  - **A**bility to discern both thickness and rate during deposition
  - **R**ate is not constant throughout deposition
  - **H**owever, locally linear portions of thickness vs. time useable for endpoint detection





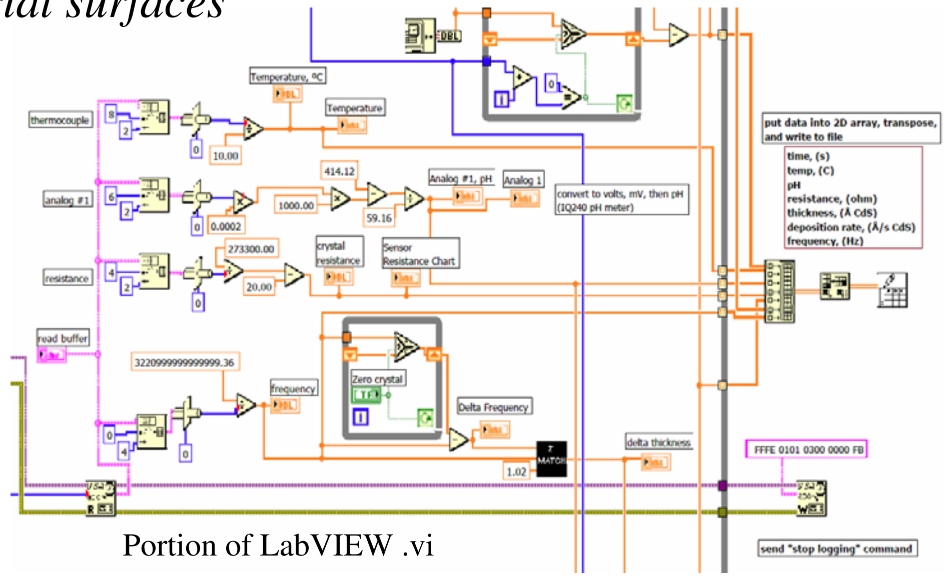
Accomplishments

Tool Development for PDIL

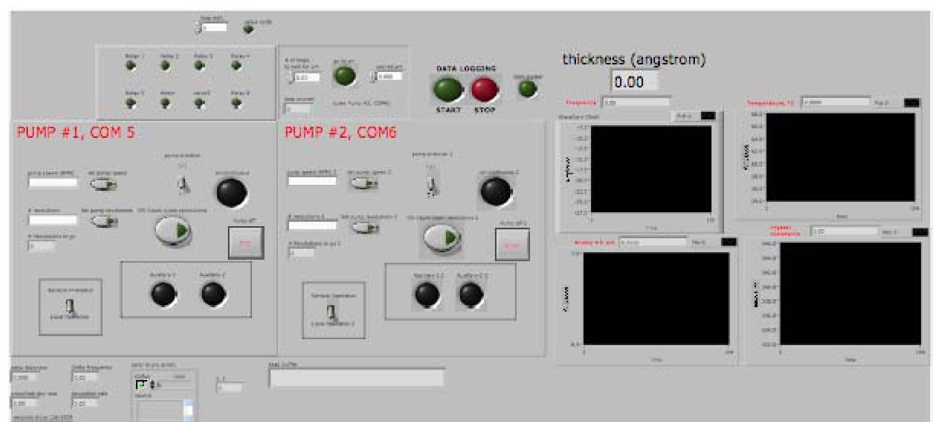
Task: Study wet-chemical processing of PV material surfaces leading to better control of deposition processes

Automated Reactor with LP-QCM Control of CBD Film Thickness

- **D**esigned a custom reactor for use in Surface Analysis cluster tool glove box
- **D**eveloping LabVIEW-based control software
- **C**ustom hardware and software interface controls:
  - QCM sensor
  - two chemical metering pump
  - Thermocouple
  - pH meter
  - six-solenoid mixing valve
  - spare analog inputs/outputs for expansion



Portion of LabVIEW .vi



Front panel for LabVIEW QCM and CBD control

<u>Status as of 1/2007</u>

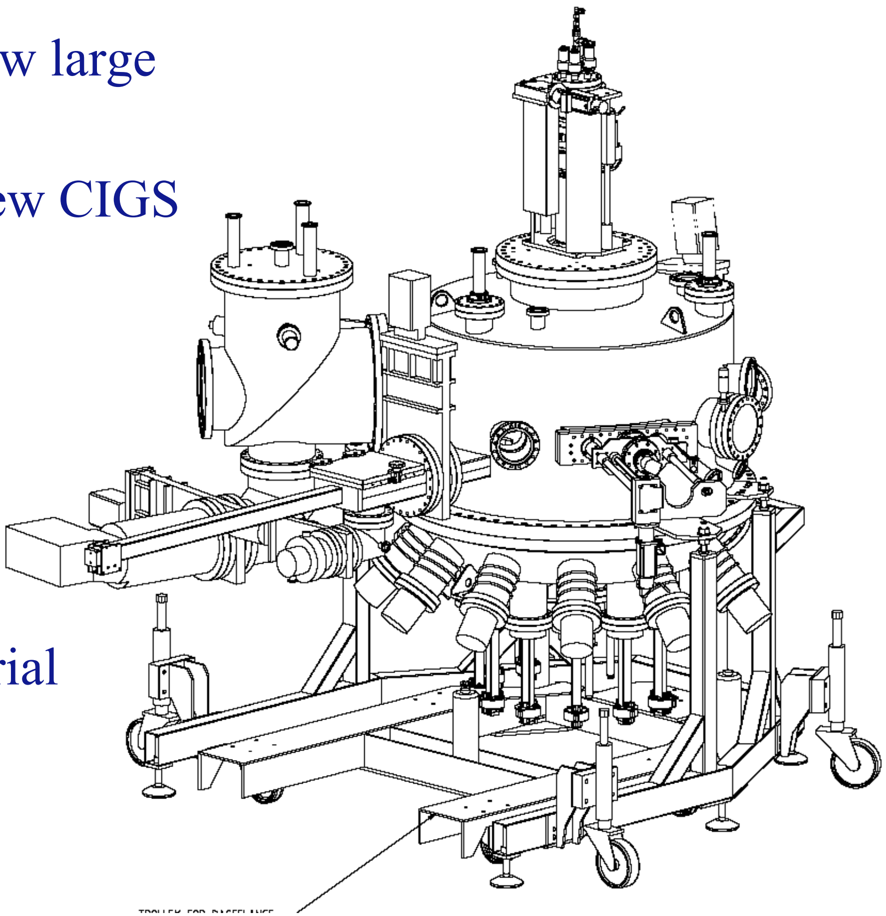
- LP-QCM is operational
- **S**oftware controls most hardware items
- **R**eactor design is finalized and awaiting construction

Accomplishments

Tool Development for PDIL

Task: Perform theoretical calculations for flux uniformity and combinatorial deposition

- **W**ork was performed in anticipation of new large area deposition tools[1-2]
- **P**rinciples were used in specification of new CIGS deposition tool
- **A**pplicable to other deposition tools slated for development



Status 1/2007

- CIGS tool drawings have been approved
- Location of sources will allow combinatorial deposition per this work

G. Teeter, *J. Vac. Sci. Technol.* A, 24(4), (2006) 1112.
G. Teeter, *J. Vac. Sci. Technol.* A, 24(4), (2006) 1119.

Schedule of Major Events/Milestones

- **Move Surface Analysis Cluster Tool to S&TF (FY06)**
  - Completed. Tool operational September 2006
- **Large-area Auger tool for PDIL (FY06 & FY07)**
  - Tool order met FY06 milestone, Sept. 2006
  - *Delivery expected June 2007, on track for FY07 milestone*
- **Large-area XPS tool for PDIL (FY07)**
  - Design specification process on track to meet FY07 milestone, Sept. 2007
- **Study wet-chemical processing of PV material surfaces leading to better control of deposition processes (FY06 & FY07)**
  - LP-QCM test and evaluation met FY06 milestone, Sept 2006
  - Progress on components of automated reactor (hardware and software components) on track to meet FY07 milestone, Aug. 2007
- **Study the reaction kinetics of nanoscale Cu_xTe films (FY06 & FY07)**
  - Completed study of Cu and Te reaction kinetics, publication 2006
  - Developing model to describe surface segregation of Cu
- **Study relationship between moisture barrier deposition fundamentals and barrier performance characteristics (FY06 & FY07)**
  - Deposition system characterized, June 2006
  - Small area MOCON cell, relationship between deposition location and barrier and adhesion properties, September 2006-ongoing
  - Deposition on Al-mirrors for barrier testing, April 2007
  - Report/project assessment due Sept. 2007
- **Investigate materials chemistry of CIGS on flexible substrates leading to an improved understanding of long-term reliability (FY07)**
  - NREL generated test samples evaluated, correlated with commercial films Nov 2006
  - Additional samples in progress
  - Report due Aug 2007

Future Directions

- Continue support of, and research with SAI TPP awardees and other members of the PV community
  - Work with M&C and NCPV management to develop prioritization and scheduling guidelines
- Design and specify new tools for PDIL
  - Large-area XPS tool (tool order to be placed by Sept 2007, delivery 3rd quarter FY2008)
  - Characterization cluster tool components (if funded), including wet processing station and plasma etching/thermal processing station (tools specified by Aug 2007, delivery FY2008)
- Initiate collaborative surface science research using new large-area Auger tool
- Implement concepts developed from LP-QCM and automated wet-processor research into PDIL tools, specifically, semi-automated CBD CdS reactor under development by CIS task
- Complete quantitative model of Cu surface segregation in CdTe. Apply model to back-contact design.
- Determine cause for damp heat failure of barrier film interfaces. Improve coatings based on new knowledge. Recent results are promising.
- Investigate the effect of excess Na on the surface chemistry of CIGS, and the effect on CdS growth.
- Dependent on funding, upgrade surface analysis cluster tool and SIMS equipment