



Fabrication and Physics of CdTe Devices by Sputtering

Wright Center on Photovoltaics Innovation and Commercialization
The University of Toledo

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Univ. of Toledo is an R & D Partner in the Solar Cell Optimizer Category for both **a-Si** and **CdTe**

- “Fabrication and Characterization of Advanced Triple-Junction Amorphous Silicon Based Solar Cells”
- “Fabrication and Physics of CdTe Devices by Sputtering” (this presentation)

The CdTe project objectives--

- Use magnetron sputtering to find the limits CdTe thickness, improve morphology, improve deposition speed, lower process temperature
- Develop techniques and instrumentation for in-situ, real-time process control especially spectroscopic ellipsometry
- Improve the understanding of CdTe thin-film device physics

Technical work plan:

- **Task 1: Device Fabrication**
 - **Buffer and interface layers**
 - **Thin CdTe, light trapping**
 - **High rate sputtering**
 - **Effects of morphology/grain boundaries**
- **Task 2: Device physics and modeling**
 - **MIS model of CdTe cells**
 - **Defect assisted tunneling—back contacts**
 - **Non-uniformity loss in solar cells**
 - **Shunting phenomena**
 - **Bias-dependent adhesion**
- **Task 3: Device diagnostics**
 - **Optical spectroscopies of deep levels (Phase III)**
 - **Real time spectroscopic ellipsometry (RTSE)**
 - **AFM and STM**
 - **EXAFS**
- **Task 4: Device degradation and stability**
 - **Degradation modes (w/ and w/o Cu)**
 - **ALT and laser-ALT**

Major Accomplishments (Phases I and II):

- Established that increasing the magnetron deposition rate by the factor of 2.5 does not reduce the cell performance when the post-deposition treatment is properly optimized (more to follow)
- Established the relationship between the CdTe film thickness and device efficiency in the range of 2.5 - 0.45 micron, in particular demonstrated high efficiency devices of thickness well below 1 micron (more to follow)

Major Accomplishments continued--

- Developed RTSE (real-time spectroscopic ellipsometry) through a systematic approach by sputter growth on ultrasmooth, oxidized c-Si substrates of CdTe, CdS, and CdS/CdTe layers followed by chloride treatments (more to follow)
- Through collaborative efforts, used XAFS (at APS) to establish predominance of Cu-O bonds at the back contact and grain boundaries and XES (with UNLV/ALS) to show that S-O bonds increase in CdS after Cu diffusion
- Developed pyrrole as a substitute for aniline treatment for shunt passivation of CdTe cells

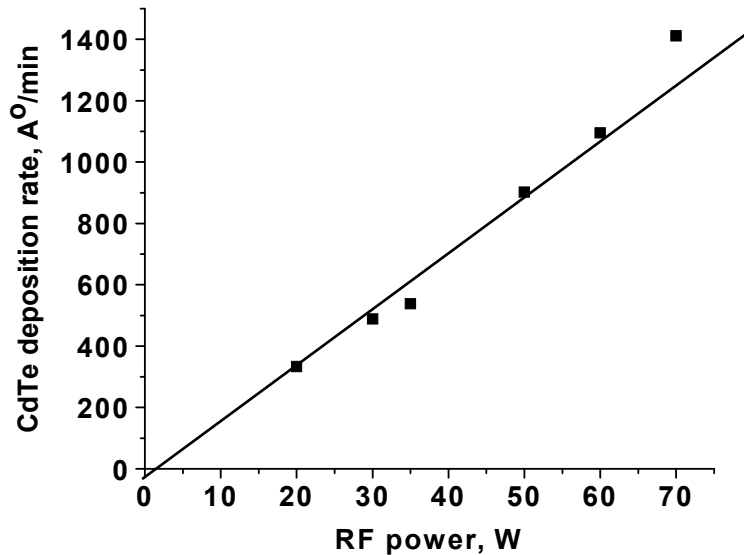
Major Accomplishments continued--

- Developed a model of field reversal in the CdS layer that predicts a variety of phenomena, such as the lack of carrier collection from CdS, buffer layer effects, light-to-dark current-voltage curve crossing and rollover
- Developed a theory of long-range random potentials in thin-film PV in which the lateral screening due to the conducting electrodes leads to a screening length close to the structure thickness
- Analyzed the physical properties of ultrathin photovoltaics with thickness smaller than both the depletion width and diffusion length, applicable to amorphous, polycrystalline, and nanostructured devices

Basic sputter characteristics

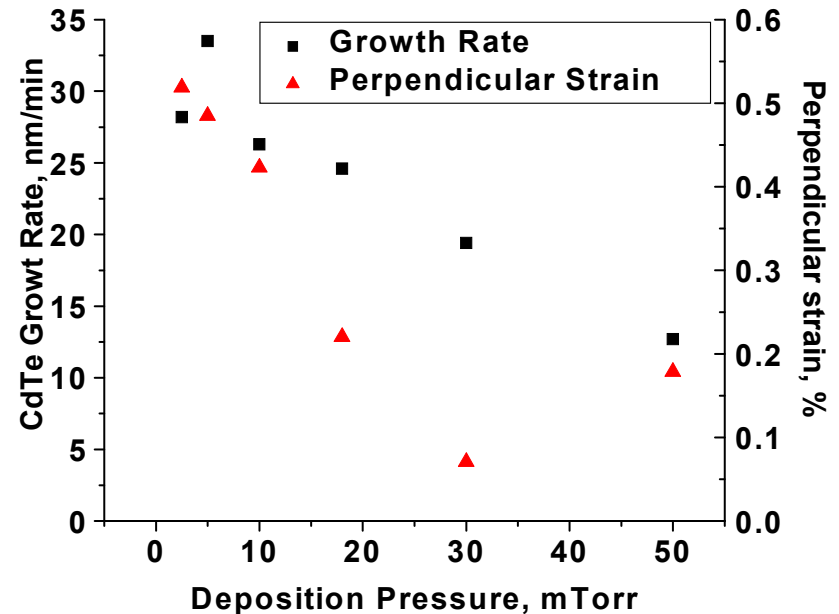
(dependence on rf power, pressure, angle)

Linear dependence on RF power through 70 W (3.5 W/cm²)



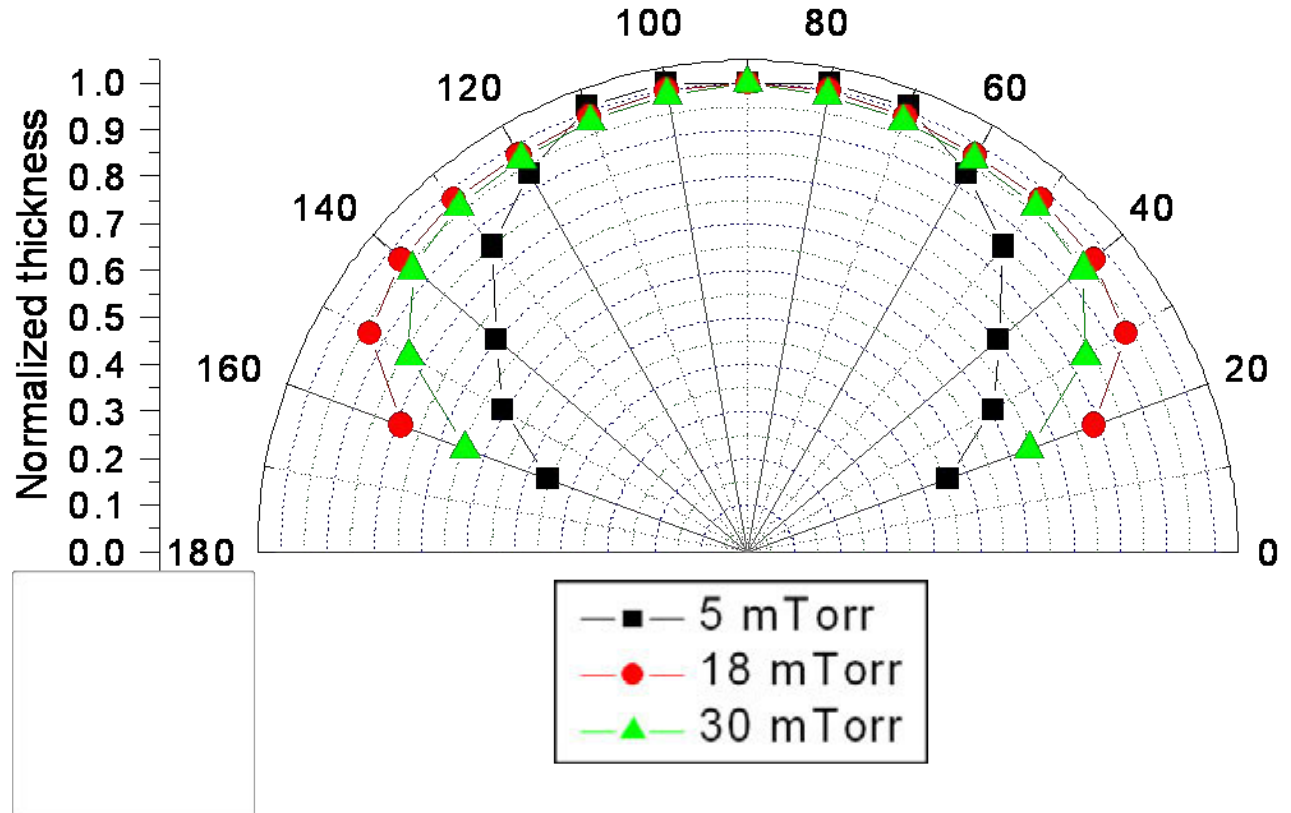
Pressure dependence--

- Compressive stress at low p
- Reduced growth rate at higher p



Angular dependence of sputtering vs. Ar pressure

- low pressure (5mT) sputtering gives more forward directed flux — better utilization
- Higher pressures — less stress but lower deposition rate



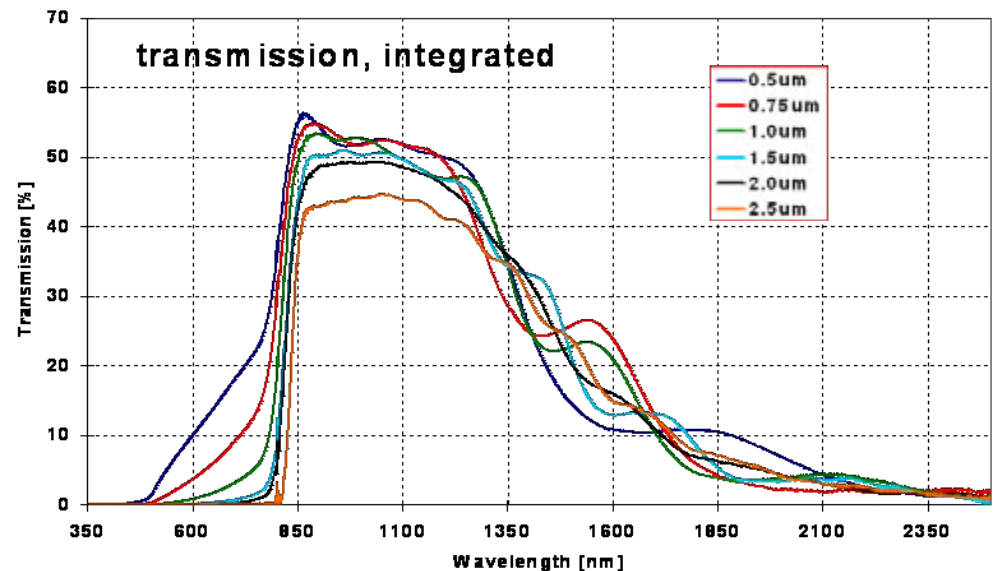
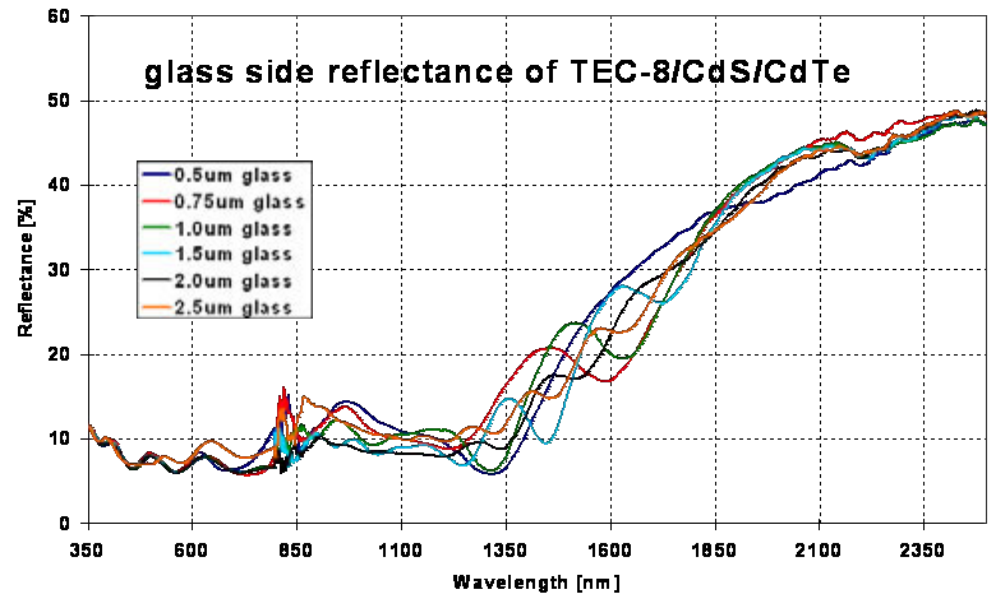
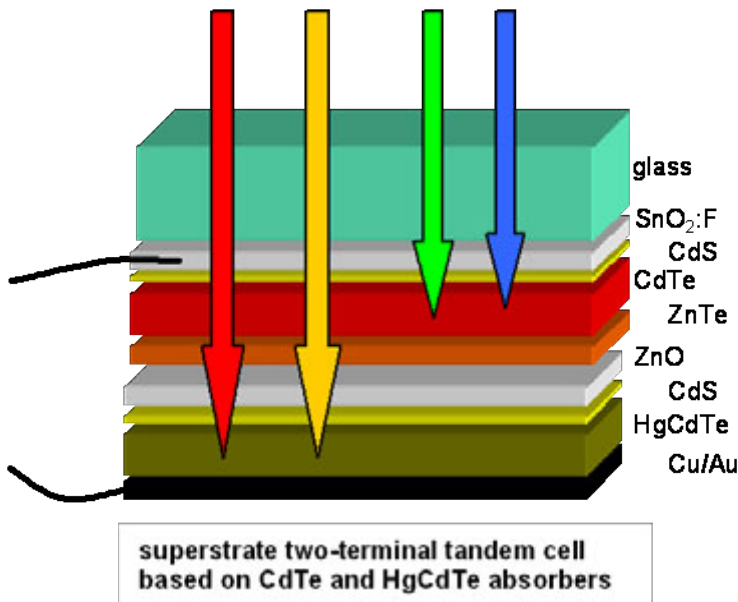
I-V Performance of Best Thin Cells on Pilkington TEC-7 glass



Sam. ID	CdS (μm)	CdTe (μm)	CdCl ₂ (min.)	Back Cont. (Cu / 200Å Au)	Diff. Time (min)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	Eff. (%)
980A2	0.13	2.3	30	30Å	45	807	22.3	72.3	13.0
184A1	"	1.28	30	30Å	30	714	21.3	65.9	10.0
184B1	"	"	10	30Å	"	710	22.3	61.4	9.7
184B2	"	"	"	15Å	18	767	22.1	66.8	11.3
190A1	0.08	0.5	30	30Å	30	484	20.1	44.1	4.3
190B1	"	"	10	15Å	18	708	20.5	64.6	9.4
189A1	0.13	0.87	10	15Å	18	772	22.0	69.7	11.8
225A1	0.05	0.7	"	"	10	750	21.7	69.2	11.2
187A1	0.07	0.94	"	"	"	762	22.6	67.4	11.6
188A1	0.13	1.04	"	"	"	795	21.2	70.8	11.9

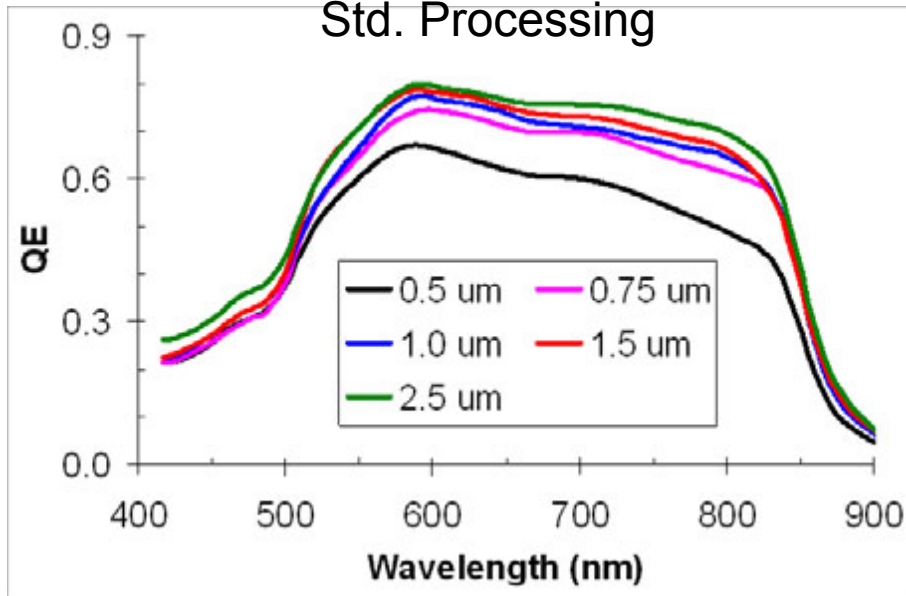
Semitransparent, thin CdTe top cells

reflectivity and
transmission through
TEC-8/CdS/CdTe
structures for several
CdTe thicknesses

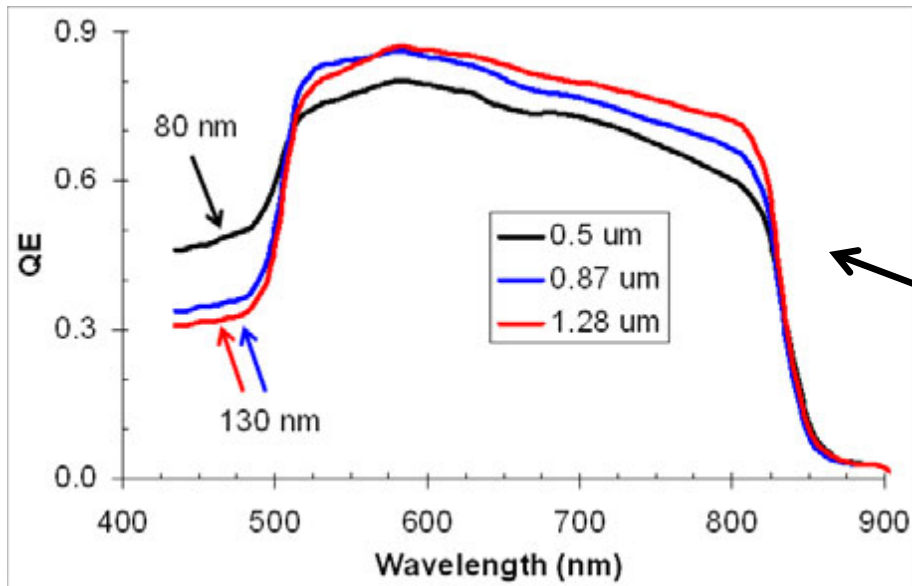
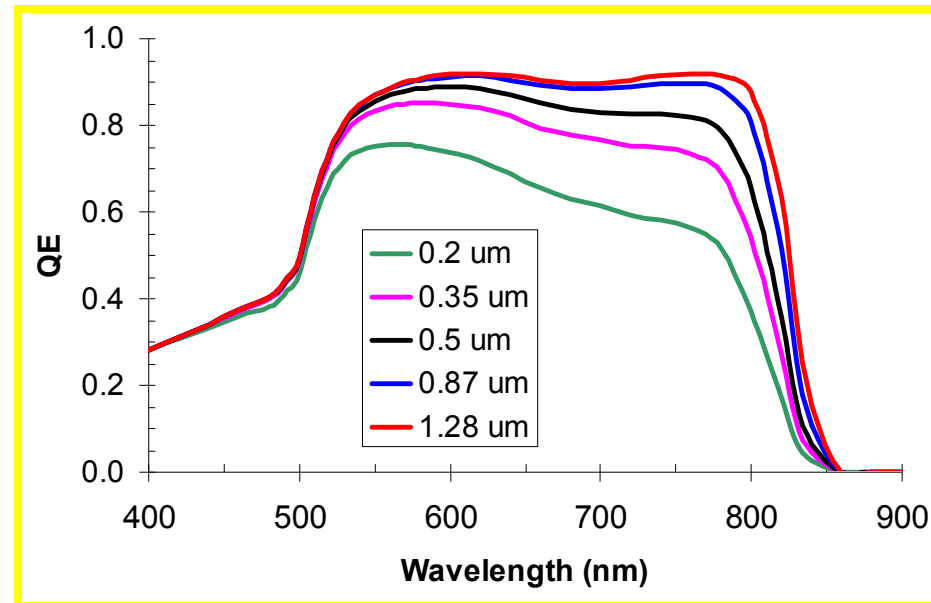


Effect on QE of post-deposition optimizing

Std. Processing



AMPS-1D Simulated



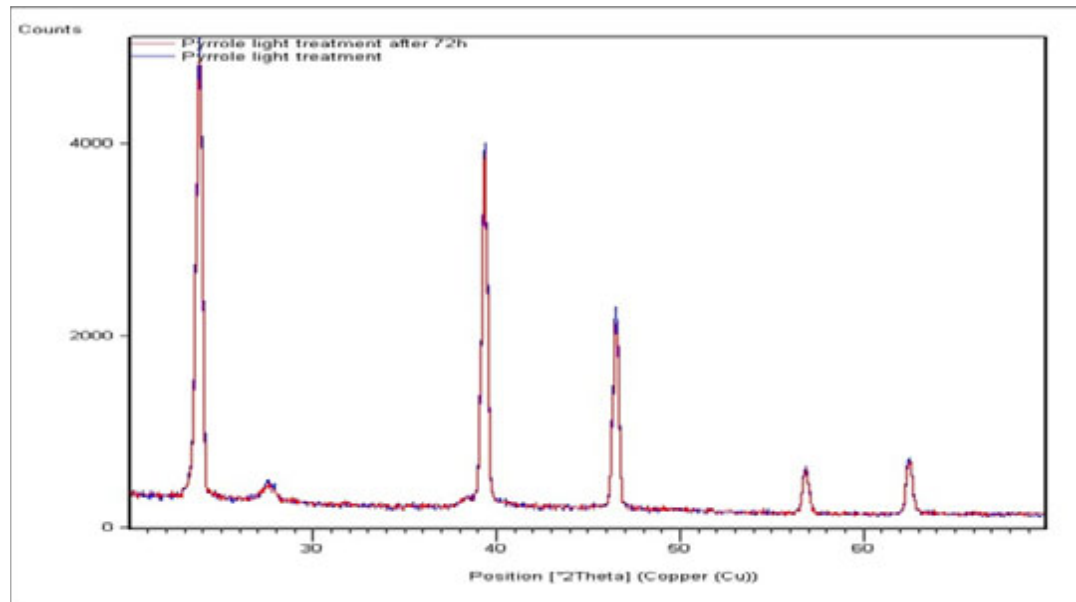
Re-opt. Processing

Pyrrole Post-Deposition Treatment of CdTe Surfaces

- Aniline post-deposition increases efficiency
however, toxicity of aniline is a concern

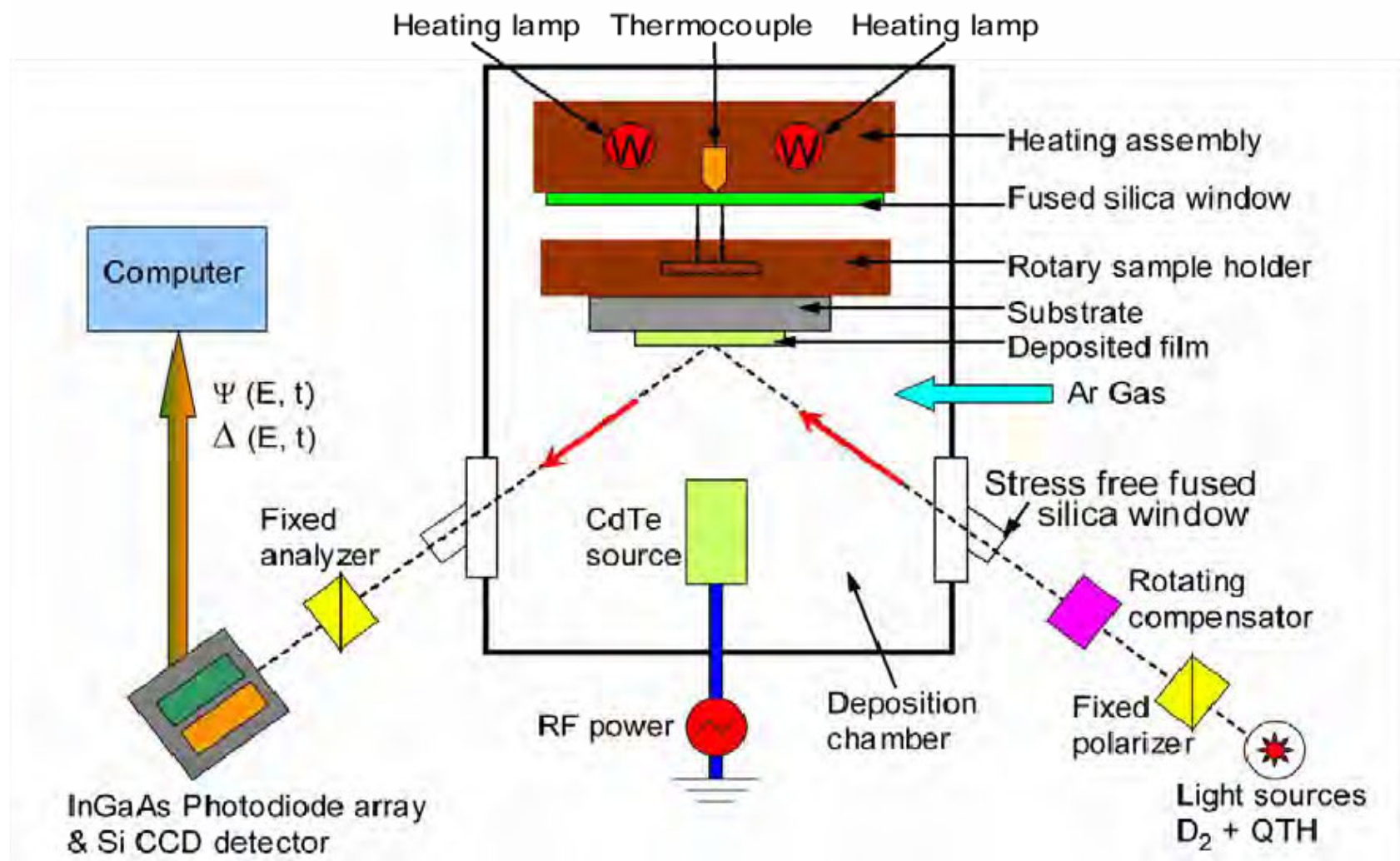
Y. Roussillon, et al, Appl. Phys. Lett., **84**, (2004), 616.

- Pyrrole treatment provides the same increase
 - toxicity of pyrrole is not a concern
- Pyrrole treatment gives Te(101) peak at 27.6°
 - Te is not observed on untreated CdTe devices
 - diffractograms obtained immediately after treatment and 72 hours later overlap
 - this contrasts other etches (e.g., BM or NP) where oxides form in a few hours



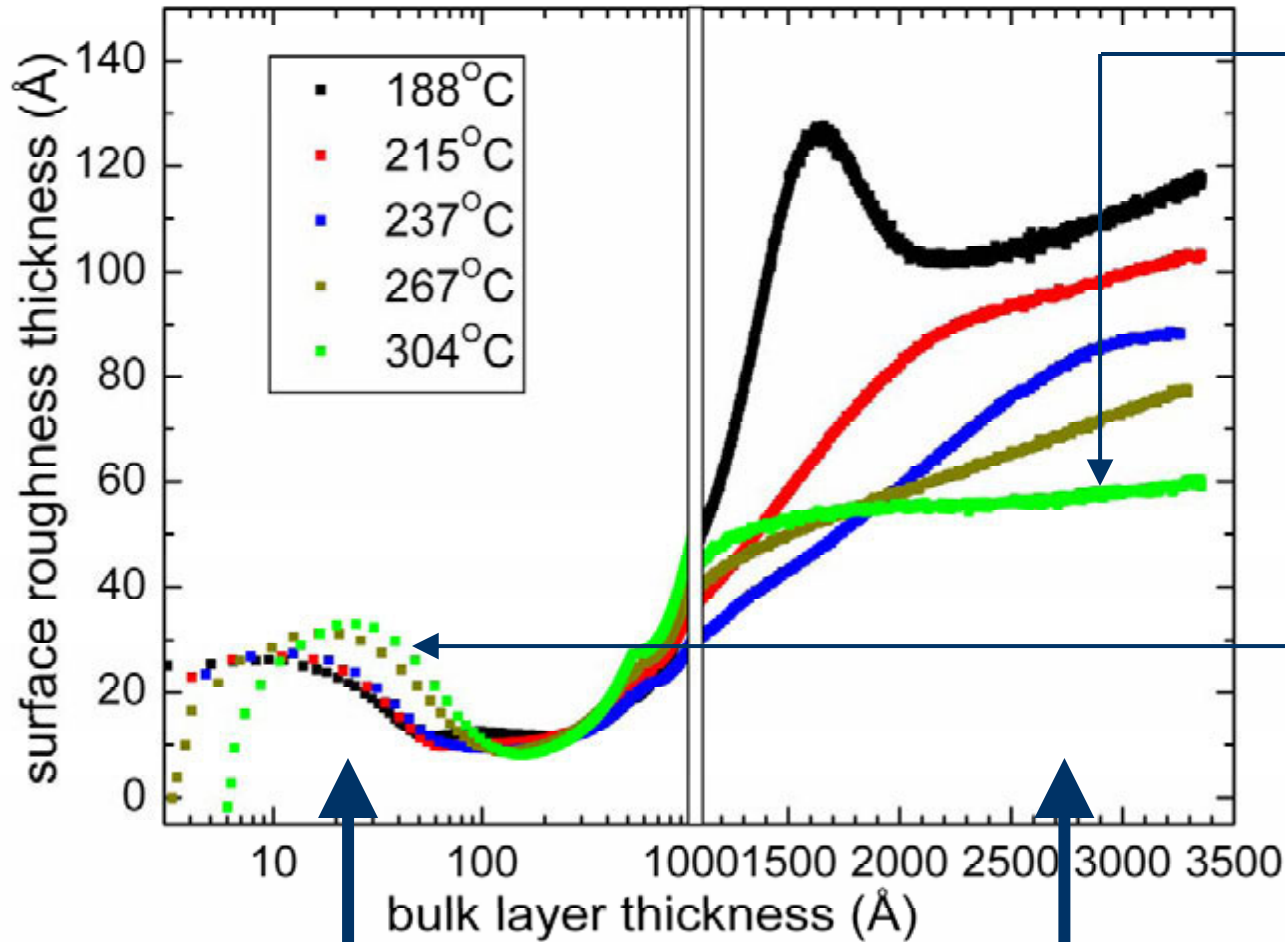
Experimental Details:

Analysis of Magnetron-Sputtered Thin-Film CdTe by RTSE



Multichannel spectroscopy: 0.75 ~ 6.5 eV; 706 spectral points
Fast spectral acquisition: $t_{acq} \sim 32$ ms (minimum)

Effect of growth temperature on structural and optical properties of sputtered CdTe: surface roughness layer thickness evolution



At higher temperatures the roughness increases more slowly and the surface is smoother.

At higher temperatures the onset of clustering shifts to larger bulk layer thicknesses, indicating Stranski-Krastanov (S-K) growth mode is favored.

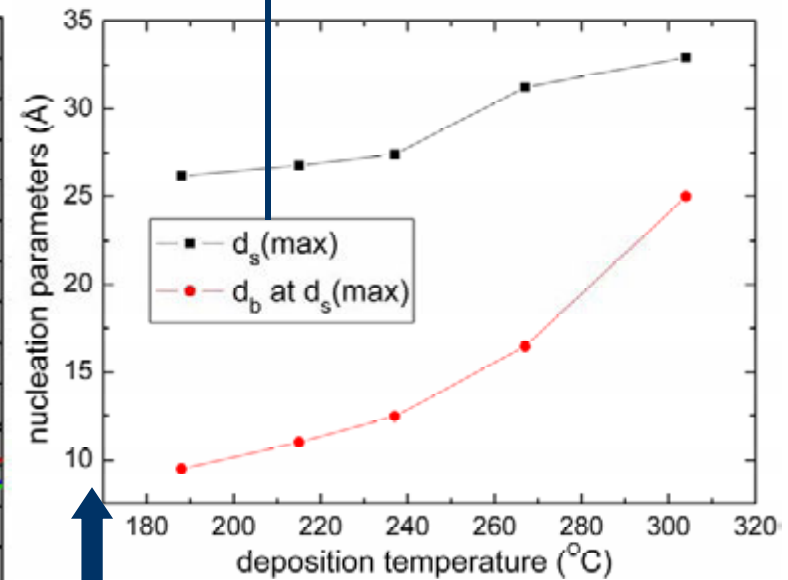
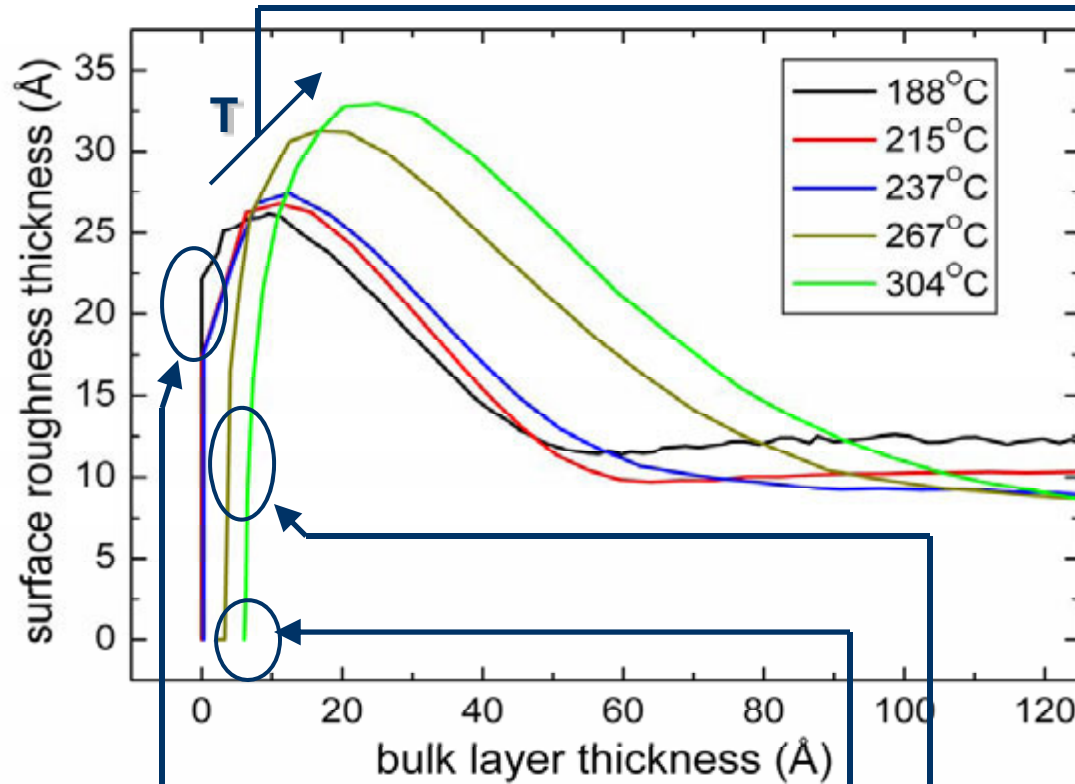


Both observations are likely due to enhanced surface diffusion at elevated temperature -- either on the substrate in the initial stages or on the film surface in the later stages.

The left half (0 ~ 1000 Å bulk layer thicknesses) was obtained in an analysis over the energy range of 0.74 ~ 6.5 eV and shows thin film nucleation and coalescence characteristics.

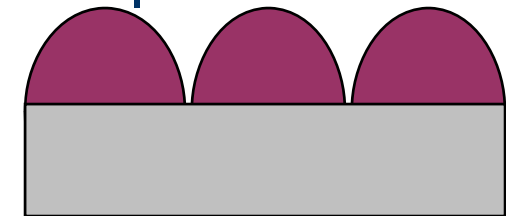
The right half used the higher energy range 3.5 ~ 6.5 eV and focuses on the surface roughness evolution.

Effect of growth temperature on structural and optical properties of sputtered CdTe: nucleation and different growth modes

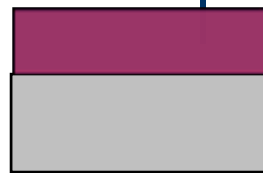


Higher deposition temperature causes enhanced roughness prior to coalescence. This initial roughness may control the subsequent void evolution in the film (next).

Three different nucleation modes



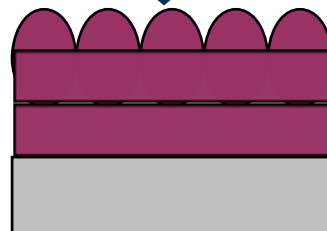
Volmer-Weber growth
 $\gamma_{\text{dep}} + \gamma_i > \gamma_{\text{sub}} : T < 240^\circ\text{C}$



Frank-van der Merwe growth

$\gamma_{\text{dep}} + \gamma_i < \gamma_{\text{sub}} :$

$260 < T < 300^\circ\text{C} ; d_b > 2 \text{ ML}$



Stranski-Krastanov growth

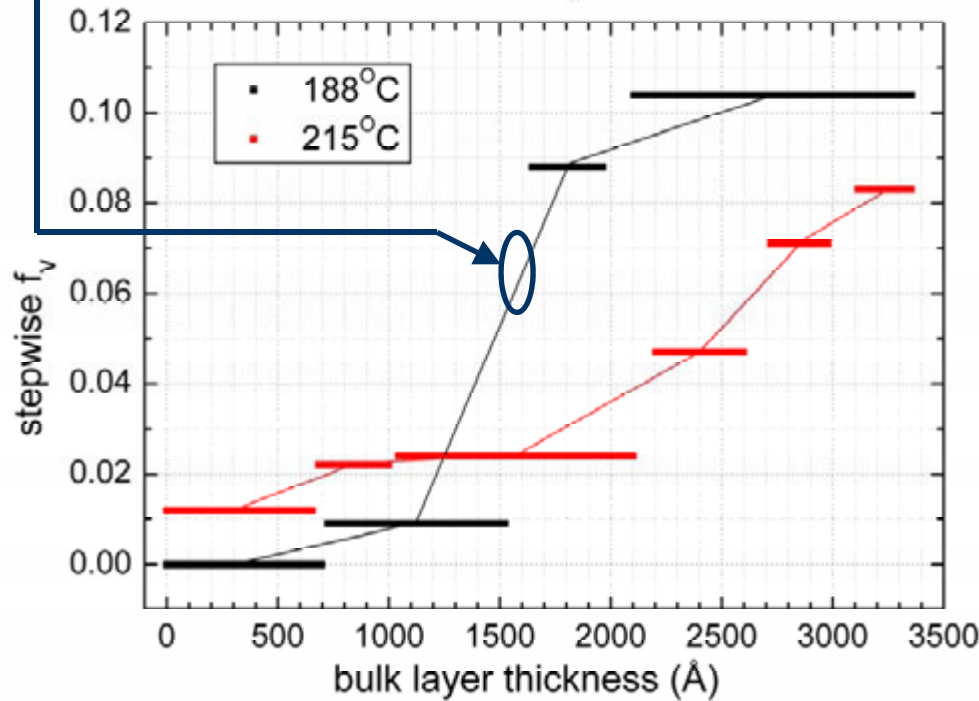
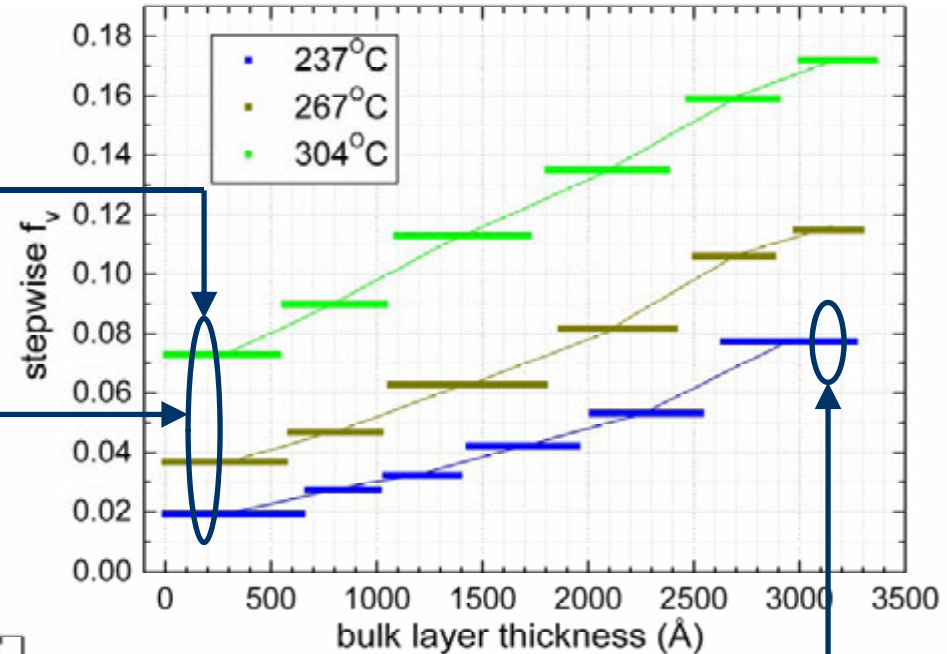
$\gamma_{\text{dep}} + \gamma_i \sim \gamma_{\text{sub}} :$

$T = 267^\circ\text{C} \Rightarrow 1 \text{ ML} ; T = 304^\circ\text{C} \Rightarrow 2 \text{ ML}$
 (for CdS/c-Si, transition $T \sim 160^\circ\text{C}$)

Effect of growth temperature on structural and optical properties of sputtered CdTe: bulk layer void volume evolution

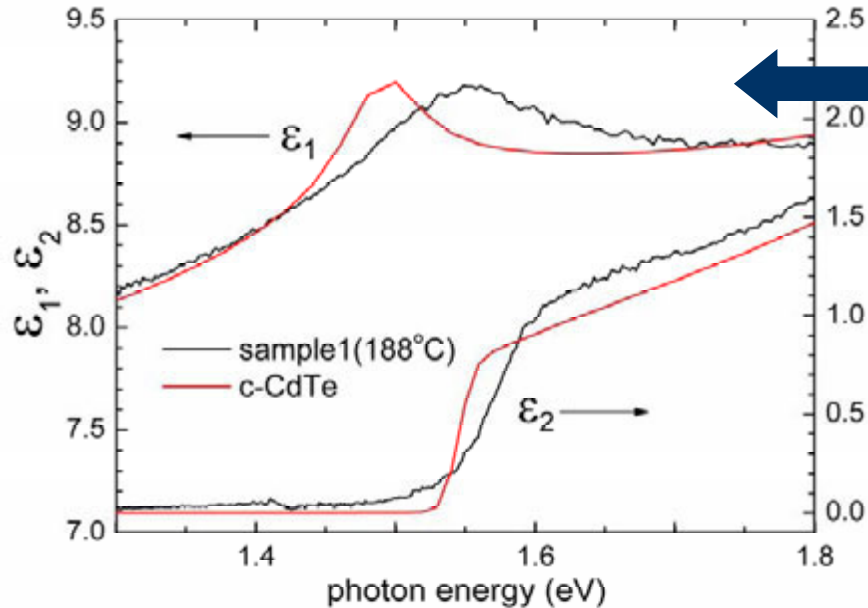
In the thin film regime ($d_b < 500 \text{ \AA}$), f_v increases monotonically with increasing deposition temperature.

The lowest T film exhibits an abrupt structural transition with thickness at $d_b \sim 1300 \text{ \AA}$. This transition is suppressed with increasing T and is attributed to the relaxation of strain that develops under low surface diffusion, low f_v conditions.



The lowest void fraction film (at $\sim 3000 \text{ \AA}$ thickness) is obtained for $T=237^\circ\text{C}$; here the structural transition is avoided, while f_v enhanced in the thin film regime at higher T is minimized. The deposition temperature for minimum void density approximates that for optimum solar cell performance.

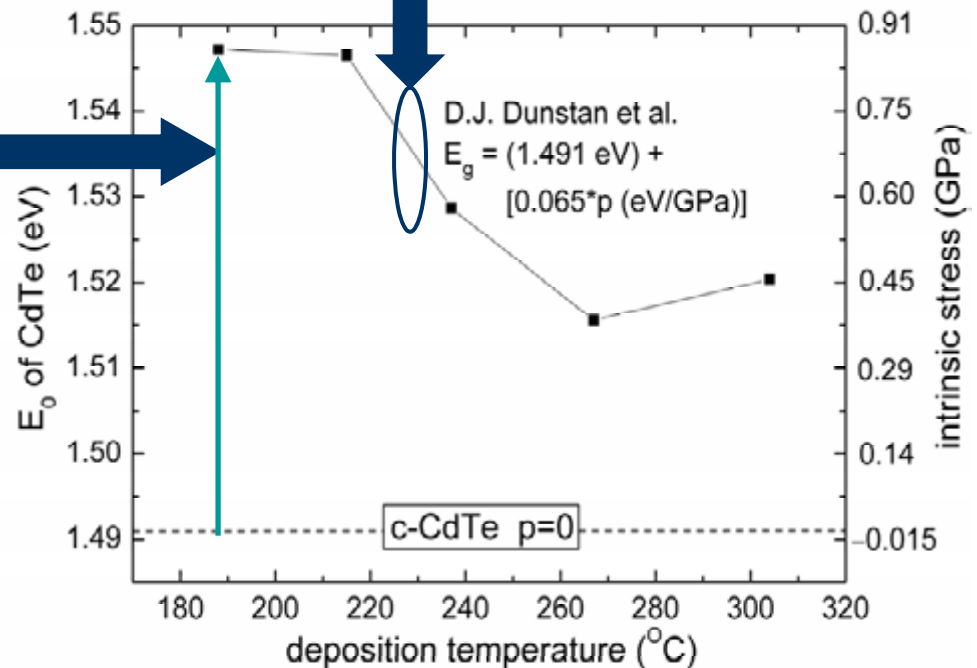
Effect of growth temperature on structural and optical properties of sputtered CdTe: intrinsic stress and band gap shift



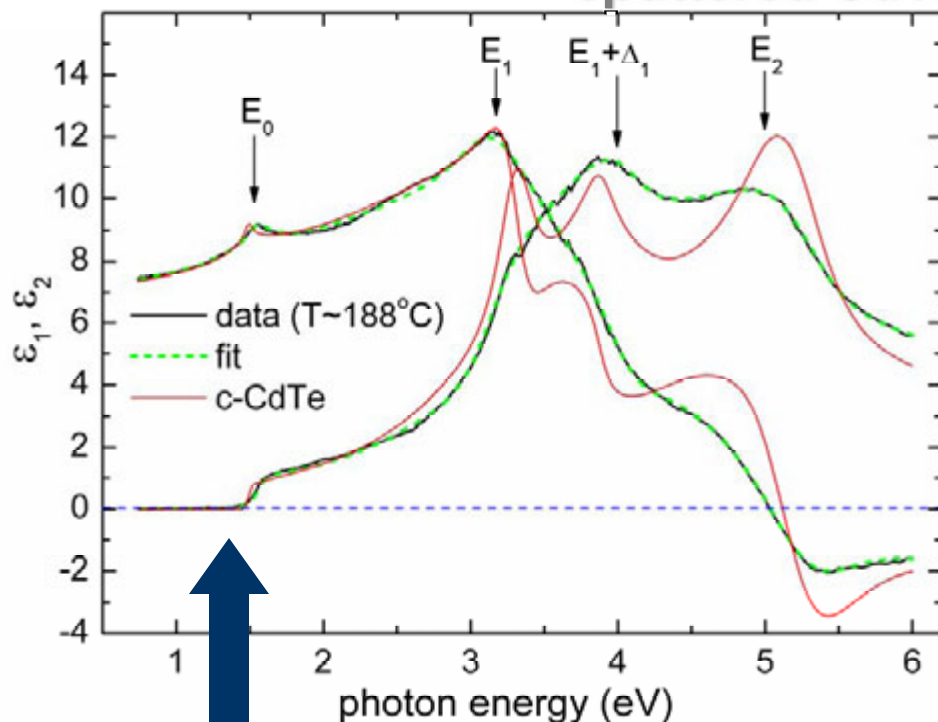
At room temperature, the E_0 band gap of low-T-deposited films are ~ 50 meV higher than that of single crystal CdTe. We attribute this to a strain effect due to film stress.

Strain relaxation occurs at a deposition temperature near 200°C which is close to $\sim 1/3$ of the melting temperature of CdTe, consistent with the observations of H. Windischmann for sputtered films.

An estimate of the associated stress can be made by comparing the E_0 gaps for the CdTe films with that of single crystal CdTe. Using the known hydrostatic pressure dependence of E_0 in crystal CdTe, stresses of ~ 0.9 and 0.4 GPa are obtained for the lowest and highest T films, respectively.



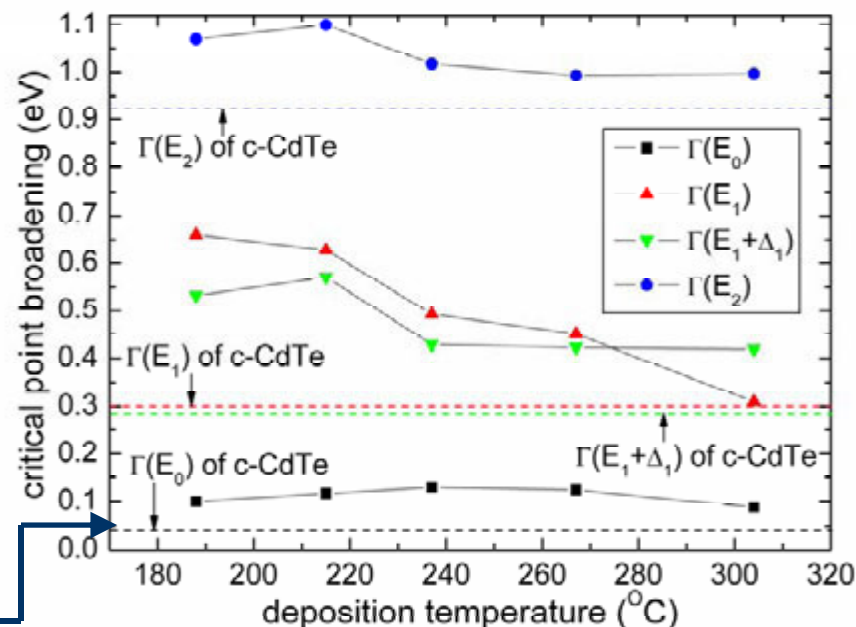
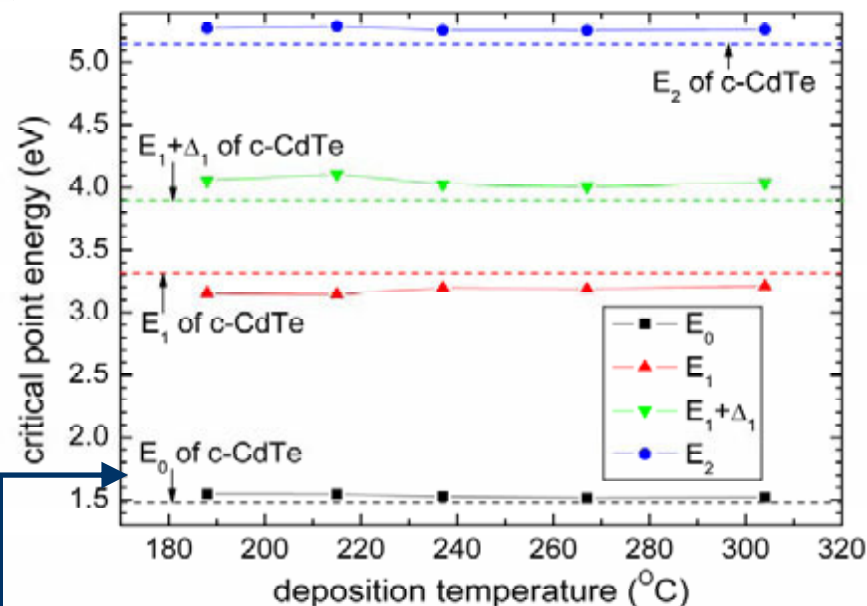
Effect of growth temperature on room temperature optical properties of sputtered CdTe: grain size effects



The complex dielectric function (ϵ_1, ϵ_2) of CdTe was fit with a model using the critical point (CP) parabolic band approximation:

$$\epsilon = \sum_n [A_n \exp(i\phi_n)] [\Gamma_n / (2E_n - 2E - i\Gamma_n)]^{\mu_n}$$

The critical point parameters differ from those of single crystal CdTe (horizontal broken lines) due to strain in the films and to electron scattering at defects and grain boundaries.

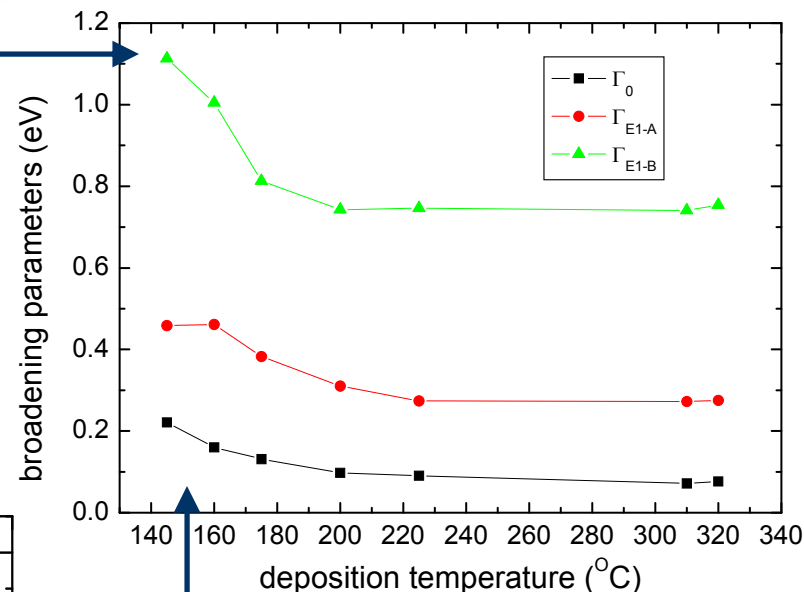
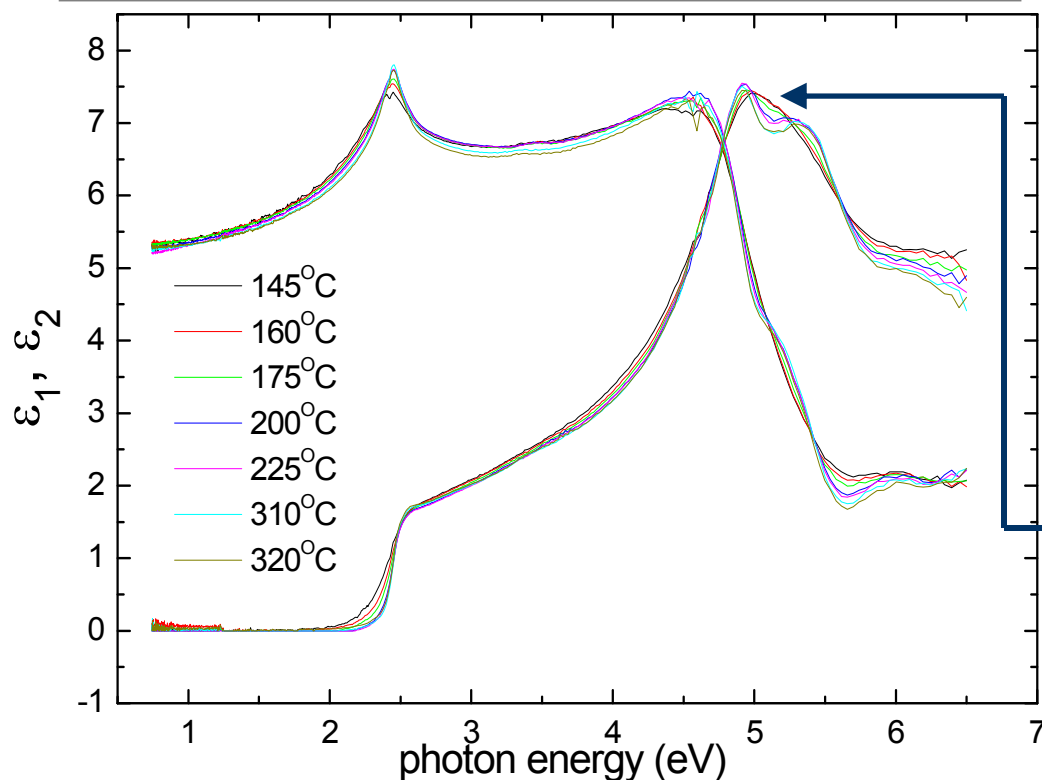


Effect of growth temperature on room temperature optical properties of sputtered CdS: grain size effects

The complex dielectric function (ε_1 , ε_2) of CdS was fit with a model using the critical point (CP) parabolic band approximation:

$$\varepsilon = \sum_n [A_n \exp(i\phi_n)] [\Gamma_n / (2E_n - 2E - i\Gamma_n)]^{\mu_n}$$

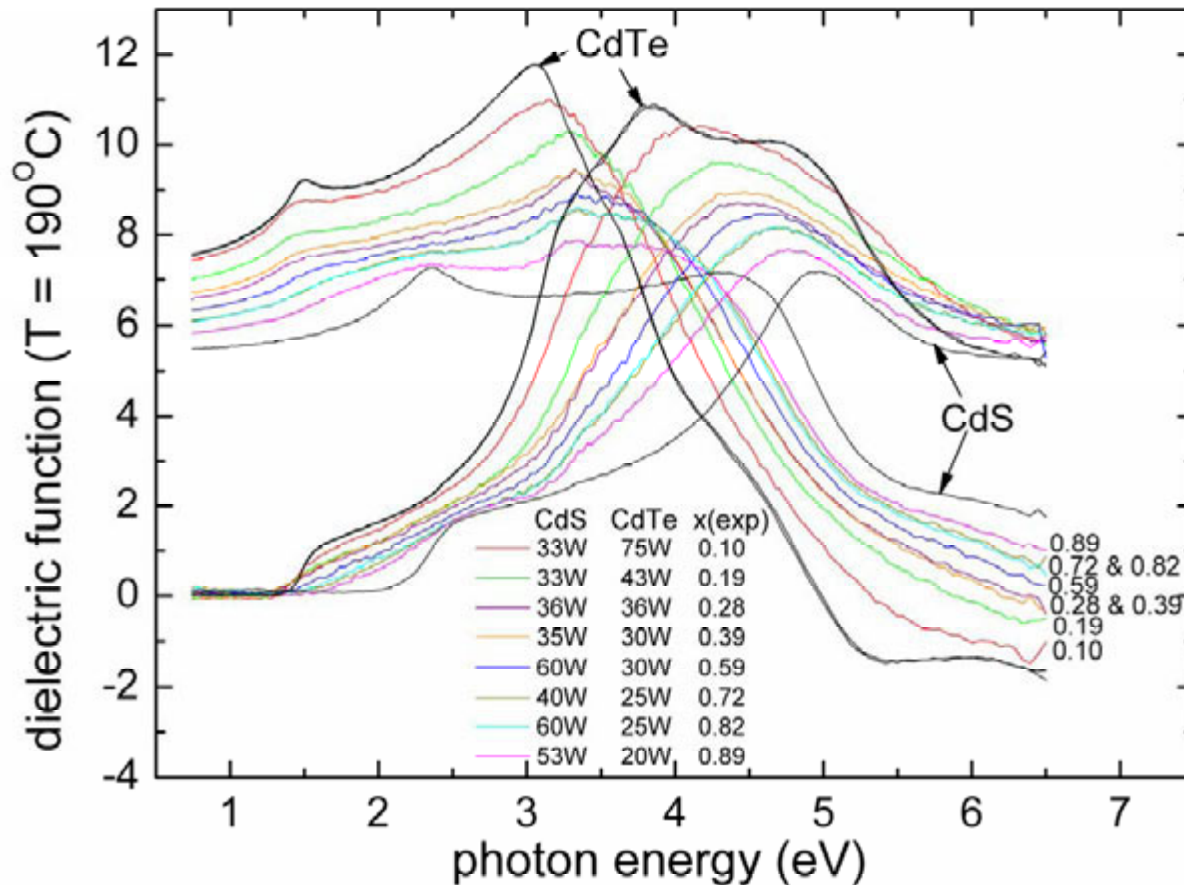
The broadening parameter Γ_n provides information on average grain size.



The CP features in the optical properties of CdS deposited at higher temperatures (T) show much sharper critical point (CP) features than lower T , indicating larger grain size at high growth T .

The resolved double peak structure (E_1-A , E_1-B) at ~ 5.2 eV clearly indicates the HCP lattice structure which is difficult to determine by XRD because of similar peak positions for HCP and cubic phases.

Optical properties of magnetron co-sputtered $\text{CdS}_x\text{Te}_{1-x}$: database for real time ellipsometry analysis of interface alloying



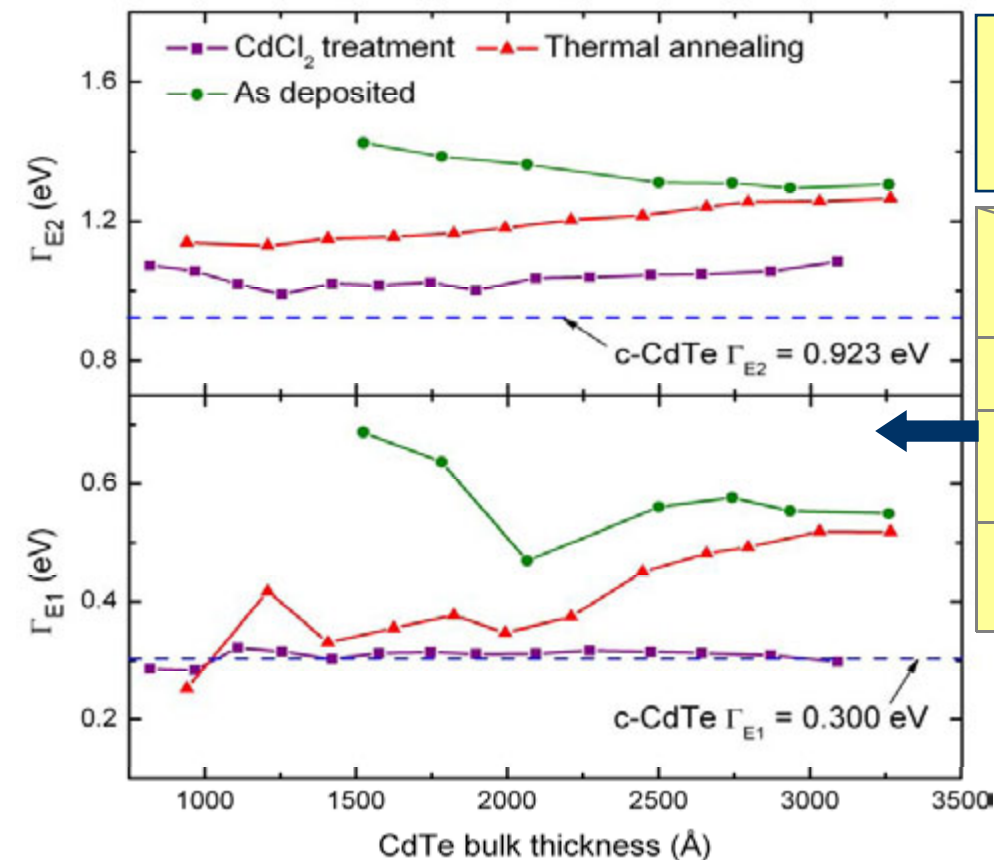
The complex dielectric functions (ϵ_1 , ϵ_2) of $\text{CdS}_x\text{Te}_{1-x}$ will be fit with a model using the critical point (CP) parabolic band approximation:

$$\epsilon = \sum_n [A_n \exp(i\phi_n)] x [\Gamma_n / (2E_n - 2E - i\Gamma_n)]^{\mu_n}$$

The free parameters $\{A_n, \phi_n, E_n, \Gamma_n, \mu_n\}$ will be given as polynomial functions of composition x and measurement temperature T .

Such results will be useful information for developing a database for investigating inter-diffusion and junction formation during solar cell fabrication

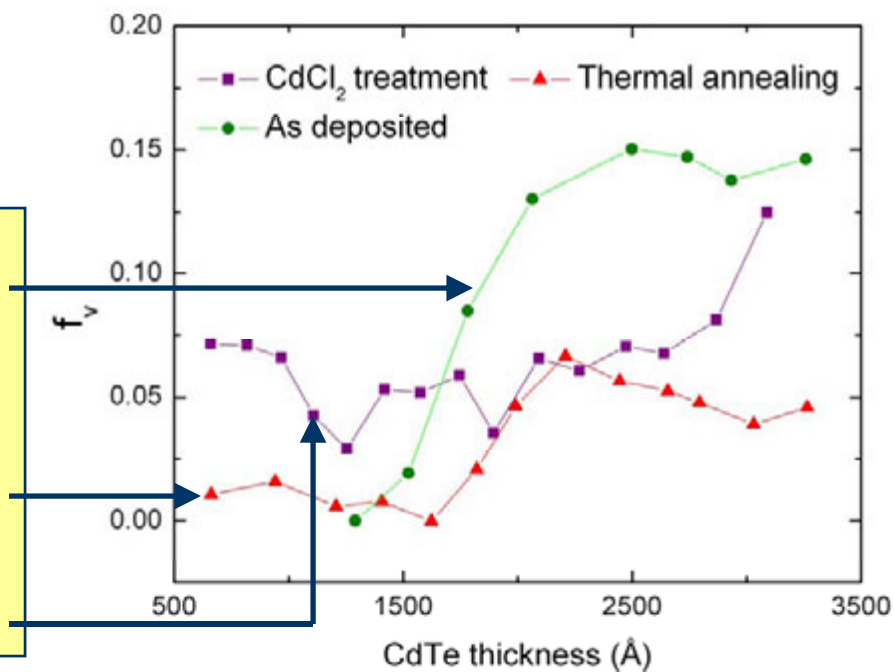
Ex situ etch back study for as-deposited and treated samples



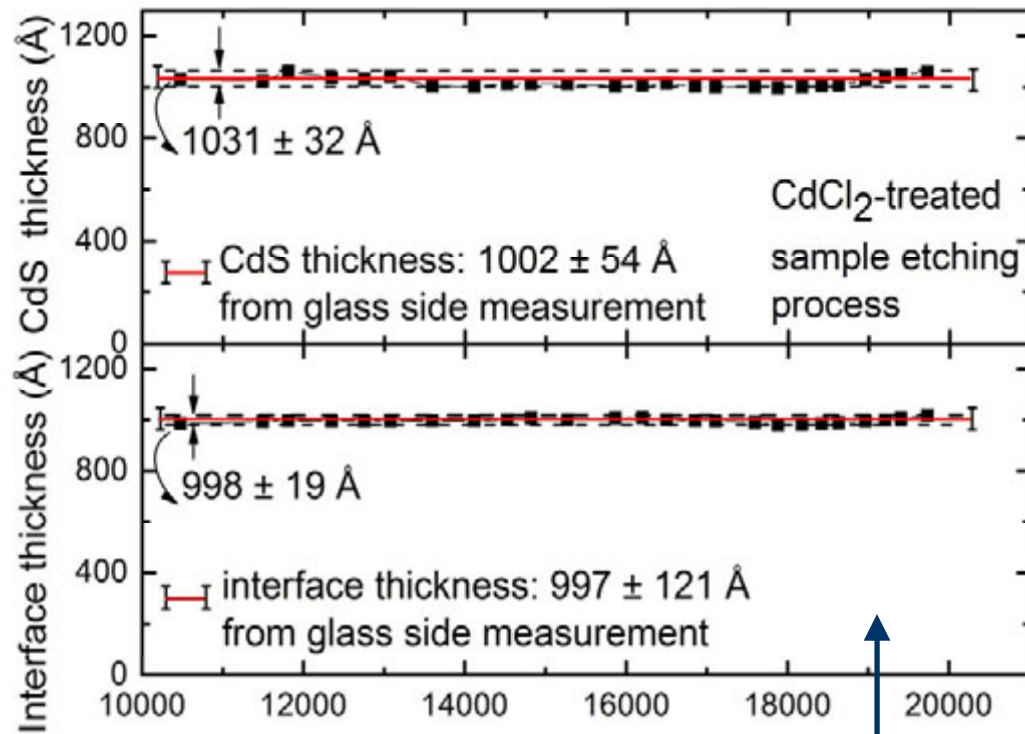
The T=188°C CdTe film was further treated and stepwise-etched to depth profile the grain size and void volume fraction.

	average grain size	depth profile
as-deposited	small	$r_{\text{sub}} < r_{\text{top}}$
thermal annealing (387°C, 30 min)	larger	$r_{\text{sub}} > r_{\text{top}}$
CdCl ₂ treatment (387°C, 5 min)	largest	uniform

The as-deposited film shows a similar depth profile in f_v as found by real time SE, i.e., an abrupt transition at 1500~2000 Å. This transition is preserved upon thermal annealing but with a significantly lower average f_v level. The CdCl₂ treatment led to a film with uniform f_v . The increased f_v for the near substrate region may be attributed to release of strain.

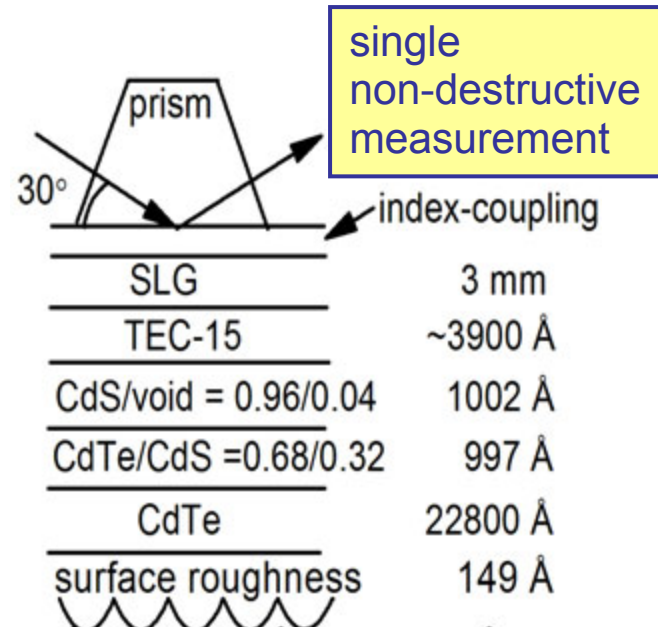
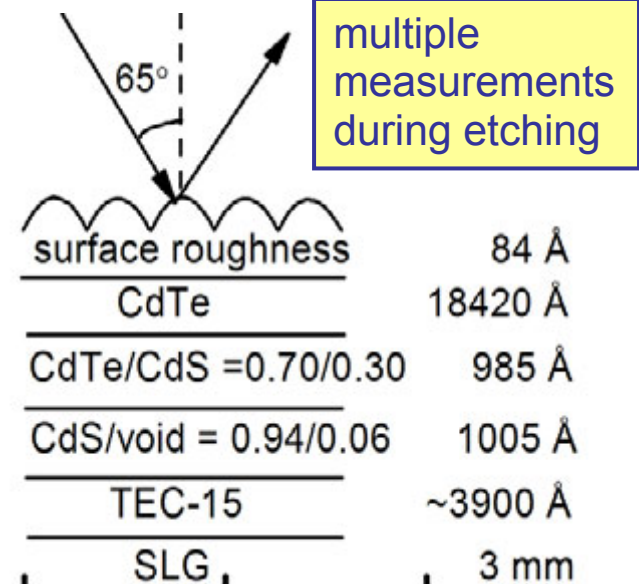


Ex situ etch back study for complete solar cell structure: measure from film side and from glass side with prism

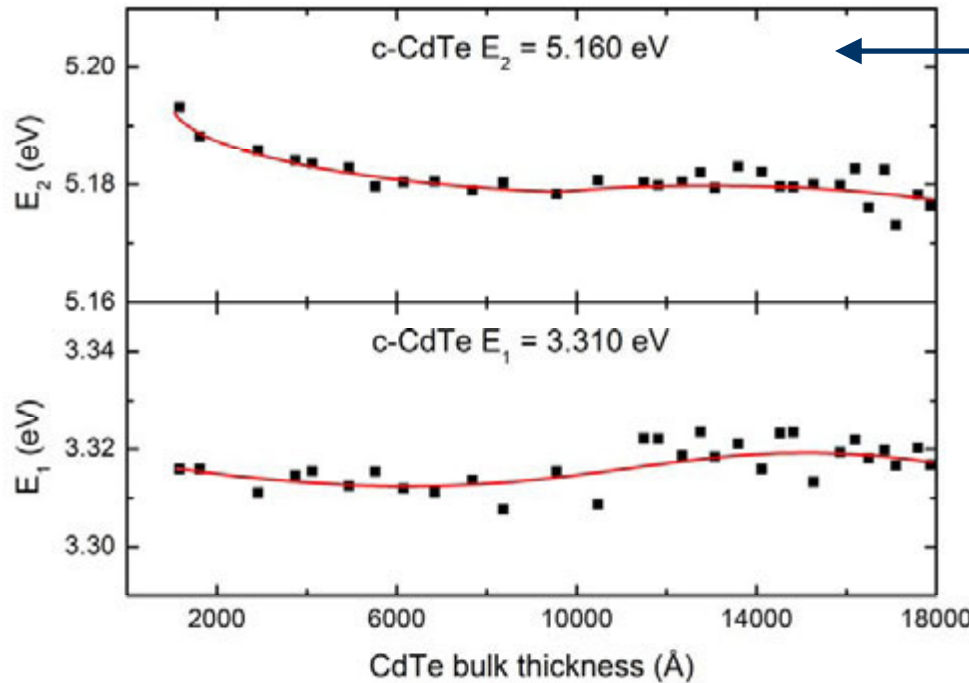


(Top) CdS layer and CdTe/CdS interface layer thicknesses deduced from spectra collected at the CdTe free surface in 24 successive etches exhibit $\sim 1\text{-}1.5\%$ deviations and the average values lie within the confidence limits of the analyses performed on spectra collected through the prism/glass.

The interface layer in this case is dominated by microscopic interface roughness between the CdS and CdTe induced in part by the roughness on the TEC-15.

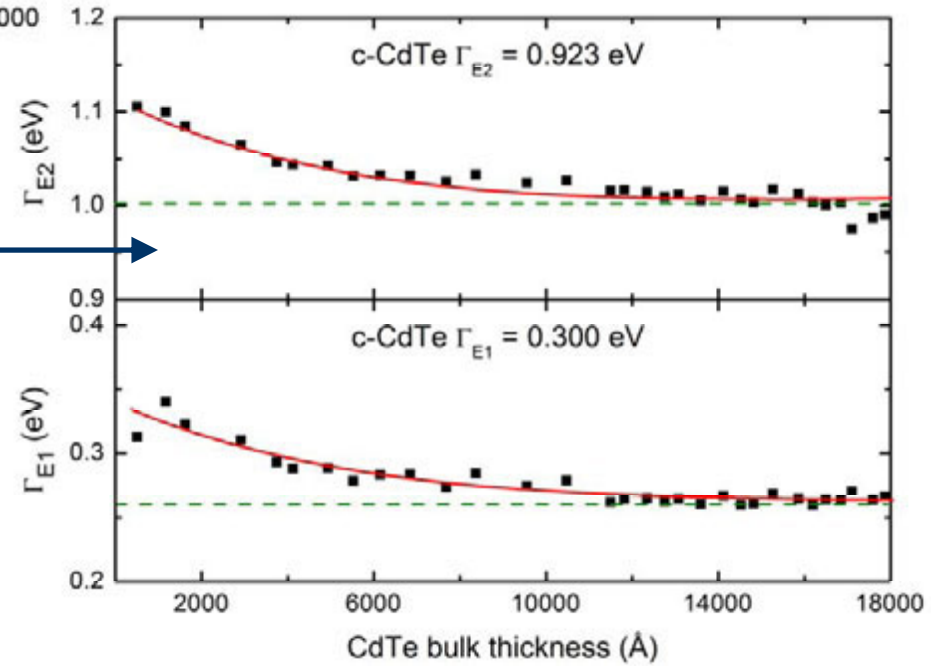


Ex situ etch back study for complete solar cell structure: CP parameters evolution versus CdTe film thickness



The energies of the E_1 and E_2 transitions versus CdTe thickness in successive etches show relatively weak variations; however, as the CdS interface region is approached, E_2 -- which appears to be a more sensitive indicator of structural deviations from the single crystal -- increases consistently, possibly due to interface strain or to in-diffusion of S.

The CP broadening parameters, Γ_n , corresponding to each critical point have been investigated, showing that Γ_1 and Γ_2 both increase gradually as the interface is approached. This may be due to S alloying, as in the case of the energies E_1 and E_2 , or to grain size reductions.



Conclusions

- Efficiency of 11.8 & 11.2% are achieved with 0.87 & 0.7 μm thick CdTe layers on TEC-7. Yield is poor (~20%) but use of water-white glass, improved TCO, HRT layer at front and shunt passivation should increase the performance and yield and facilitate large-area deposition
- Increased sputter deposition rate by factor of 2.5 with no problems. Ultimate limit still to be found.
- RTSE has proven to be a powerful tool for understanding and improving polycrystalline thin-film II-VI layers and for process control
- Progress in understanding grain boundary effects, the role of copper and oxygen in CdTe and CdS
- Advanced the understanding of the device physics of PV in defective and non-uniform thin films and how to ameliorate the deleterious effects of weak diodes and shunting

Future activities—Univ. of Toledo

- Continue to reduce deposition times through reduction in CdTe and increased rate.
- Improve performance of submicron CdTe devices.
- Fully utilize information from RTSE to improve devices (reduce void fraction and stress, control interdiffusion, stoichiometry of graded layers, etc).
- Extend work on device physics including non-uniformity loss in thin-film PV.
- Support entrepreneurial activities for scale-up to large-area deposition systems, low-temperature processing, flexible substrates, etc.
- Support the Wright Center on *Photovoltaics Innovation and Commercialization* and its activities along the full value-chain of the PV market.

