RTSE Studies of the Fabrication of High Efficiency CdTe PV

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ABSTRACT

This project performed at the University of Toledo is distinctive in its application of magnetron sputtering to CdS/CdTe solar cell fabrication. This method permits highly controllable and low temperature deposition of TCOs (transparent conducting oxides), HRTs (high resistivity transparent layers), CdS, CdTe and alloys of these materials. A major new capability established over the project period is the application of the techniques of spectroscopic ellipsometry (SE) to materials and cell fabrication and processing. These techniques can be applied in situ and in real time to characterize the evolution of structure and optical properties, as well as in an ex situ depth profiling mode in conjunction with a CdTe layer-by-layer etching procedure, both for correlation with device performance and an improved understanding of process-property relations.

1. Objectives

The overall objective of this project is to establish a transferable knowledge and technology base for the improvement of high-efficiency CdTe and related alloy solar cells that supports NREL Technology Partners in the manufacture of a 10% efficiency CdTe production module. As described in the DOE Solar Energy Technologies Program (SETP) Multi-Year Program Plan, the goal of this project is to assist technology partners in lowering direct manufacturing costs to \$0.90 Wp (\$90/m^2) for 10% CdTe by 2011.

2. Technical Approach

In the development of RTSE as probe for CdTe solar cell optimization, a step-by-step research program is being undertaken to separate out the complexities that occur in the fabrication process. It is important to characterize these complexities first under ideal RTSE conditions chosen for high sensitivity. In this way, databases can be established that enable a complete real time analysis in the actual solar cell structure -- which may be less than ideal in terms of sensitivity, usually due to substrate roughness that propagates throughout the structure. The results of such analyses can then be applied to optimize solar cell performance based on a better understanding of the fabrication process. The following lists the strategy being applied:

(1) *CdTe growth on ultrasmooth c-Si substrates held at different temperatures.*
Such depositions avoid substrate-induced roughness, and as a result, the smoothest film surfaces occur after the nucleation and coalescence processes. Under these circumstances, the dielectric functions of the growing CdTe film can be determined with the greatest accuracy and precision. From the dielectric functions, film characteristics can be extracted such as temperature, stress, and grain size or defect density.

(2) *CdS growth on ultrasmooth c-Si substrates held at different temperatures.*
The motivation for these studies is the same as that for CdTe growth. The goal is to extract the dielectric functions of the CdS with the greatest confidence. The added capability that may be possible for CdS is the determination of the degree of preferential orientation of the *c*-axis relative to the film normal. This can be obtained because the stable phase of CdS is hexagonal, and thus optically uniaxial with different dielectric functions for optical field directions parallel (e) and perpendicular (o) to the *c*-axis.

(3) *CdS/CdTe growth on ultrasmooth c-Si with film thickness and temperature control.*
The goal of these studies is to develop a dielectric function database versus measurement temperature for the full metastable compositional range of $CdTe_{1-x}S_x$, as well as for the equilibrium compositions achieved by annealing the deposited sample at temperatures up to the $CdCl_2$ treatment temperature. By controlling the ratio of the CdS:CdTe thicknesses as well as the processing temperature profile, single phase films of the desired composition can be obtained. The ultimate goal is to establish the compositional evolution during interface formation.

(4) *CdS/CdTe growth on ZnO-coated glass under different deposition conditions for the CdS and CdTe.*
This structure includes the complication of substrate-induced surface roughness that is avoided in studies (1)-(3). This roughness propagates throughout the entire structure, weakening sensitivity to the interfaces. The motivation for this set of studies is to correlate the process conditions, e.g., substrate temperature, Ar pressure, plasma power, with the RTSE-deduced structural evolution and optical properties as well as with solar cell performance. The final goal is to use this information to optimize the cell fabrication process based on an improved understanding of the process.

(5) *Post process treatments of films and devices.*
At each step (1)-(4), it is important to establish the effects of post-deposition treatments including both thermal annealing and $CdCl_2$ treatments on the thin films or devices. Post-processing can influence both the film structure and optical properties, and the goal is to explore the role of the key parameters of process temperature and time. Real time studies of these post-processing treatments are of interest; however, due to the complexity of the final film or device to be studied, a more effective approach is a Br_2-methanol etch-back procedure that enables depth profiling. This procedure allows one to perform time-reversed spectroscopic ellipsometry while maintaining a smooth surface as the layers of the structure are etched away.

3. Results and Accomplishments

In research undertaken thus far, experiments have been completed for Steps (1)-(3), data analysis has been completed for Step (1), and is in progress for steps (2) and (3). In addition, upon development of the time-reversed measurement approach, initial studies in Step (5) have been performed. This brief report presents results for Steps (1) and (5).

Figure 1 shows the step-wise evolution of void fraction in the first 3300 Å of magnetron sputtering of CdTe (Ar pressure: 18 mTorr) on Si wafer substrates held at different temperatures, as obtained by RTSE performed in Step (1). In these studies, a minimum in void fraction is observed at the end of the deposition at a temperature between 215 and 237 °C

For deposition at 188°C, the abrupt increase in void fraction is attributed to void generation which relaxes compressive stress building up in the deposition process. At higher substrate temperature where the mobility of film precursors is higher, the initial void fraction is large enough (and increasing) so that the initial stress is lower and the abrupt transition to lower density film growth is not observed. This interpretation is supported by the results in Figure 2, which shows the room temperature fundamental band gap at a thickness of 1000 Å, i.e., before the stress-induced transition in Fig. 1. Here it is clear from the band gap data that the initially growing films at low temperature are under much higher compressive stress.

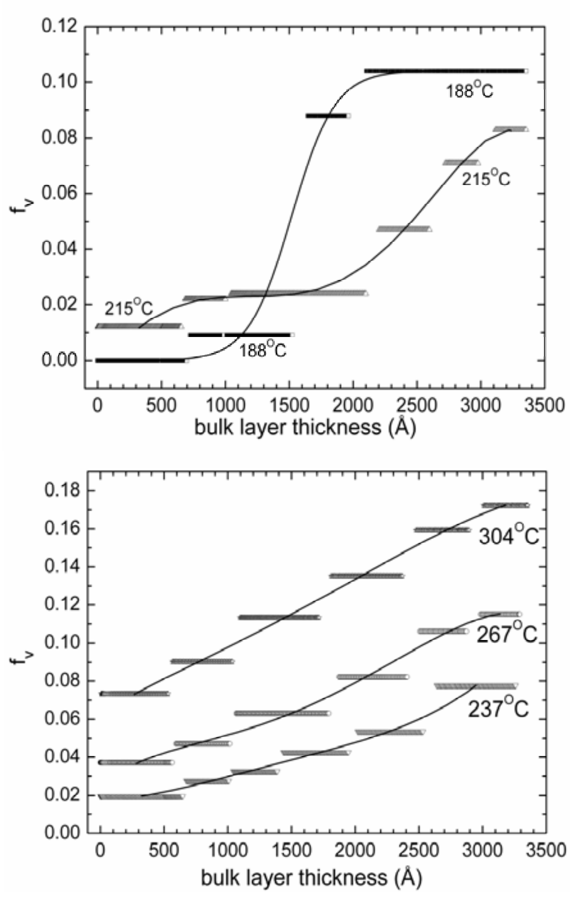

Fig. 1 Void volume fraction versus thickness for CdTe obtained by RTSE using a step-wise optical model.

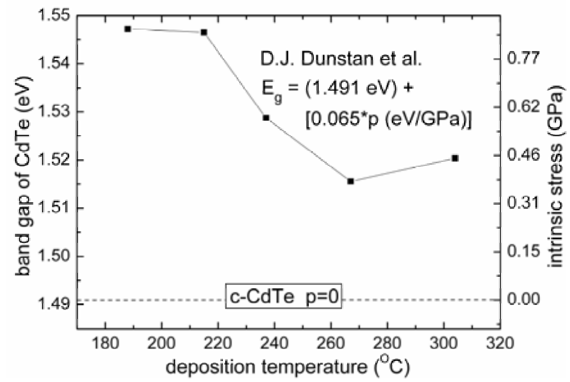

Fig. 2. Room temperature fundamental band gap and deduced compressive stress at a thickness of ~1000 Å plotted vs. deposition temperature.

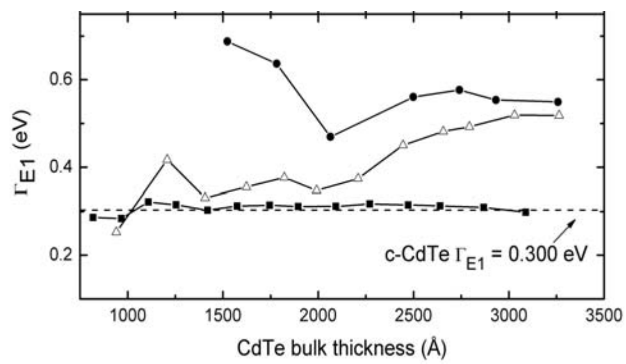

Fig. 3. Broadening parameter vs. CdTe bulk layer thickness during Br_2+methanol etching for an as-deposited film (upper), a film annealed at 387°C for 30 min in Ar (center) and for 5 min in $CdCl_2$ vapor (lower).

Figure 3 shows the E_1 critical point broadening energy Γ_{E1} as a function of CdTe layer thickness obtained during Br_2-methanol etching of a ~3000 Å thick CdTe films prepared at 188°C and processed under different conditions. This energy is expected to vary with grain size R according to $\Gamma_{E1}(R) = \Gamma_0 + (hv/R)$ where h is Planck's constant and v is the electron group velocity. Thus, it is clear that $CdCl_2$ treatment generates a uniform grain size through the top 2000 Å of the film; in contrast, annealing in Ar leads to a larger grain size in the bulk, but smaller at the surface.

4. Conclusions

In this project, RTSE has been applied to problems in thin film CdTe solar cell fabrication that may limit achievement of the goals of the SETP Multi-Year Plan. Significant progress has been made applying this method for CdTe film growth and post-deposition $CdCl_2$ process development.[1]

ACKNOWLEDGEMENTS

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REFERENCE

[1] For an up-to-date review of recent results see Mater. Res. Soc. Symp. Proc., Symp. Y (2007, in press).