BAPVC Annual Project Report
Project Title: Advanced Materials Characterization
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Summary:

The Toney Group at SSRL characterizes photovoltaic materials with X-ray techniques. SSRL has developed several in-situ thermal processing chambers that have been utilized on projects with members of the BAPVC. The rapid thermal processing (RTP) chamber has been utilized by the Milliron group to characterize CZTS and CIGS nanoparticles as they transition to sintered films. The in-situ annealing chamber and in-situ Se annealing chamber have been utilized by several projects in the Bent group. An investigation has also been done into the chemical character of the Cl remaining in Cl derived perovskites both in-situ and ex-situ X-ray absorption spectroscopy (XAS). Diffraction and XAS has been utilized to better understand the CuZnS TCOs developed by the Ager group. The work of the Salleo group within BAPVC focuses on using sensitive sub-gap measurements to characterize optical absorption and defects in photovoltaic materials and entire PV stacks.

Key Accomplishments:

The RTP chamber developed under a Bridge proposal can heat samples at a rate of 100°C/s to a temperature of 1200°C taking XRD every 100ms and is a powerful tool for measuring PV materials under industry relevant conditions. The Milliron group has used this to study the kinetics of their CZTS and CIGS nanoparticles sintering into films during annealing. With the RTP, the phase transition from Wurtzite to Kesterite can be seen as a function of temperature Fig1.

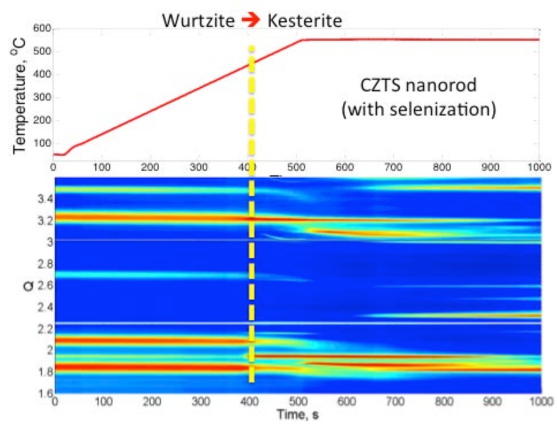

Figure1: In-situ annealing of CZTS nanoparticles shows the Wurtzite to Kesterite transition.

The Ager group at LBL is developing $Cu_xZn_{1-x}S$ alloys as a promising p-type transparent conductor. Initial studies by the Ager group suggested that their films were amorphous; however, the Toney group has been able to determine that the films are nanocrystalline and to determine the crystalline structure of these films. X-ray diffraction patterns of $Cu_xZn_{1-x}S$ films are shown in Fig. 2. The XRD shows that the films contain both sphalerite and wurtzite ZnS phases with predominantly wurtzite at x=0.30, which corresponds to a peak in conductivity.

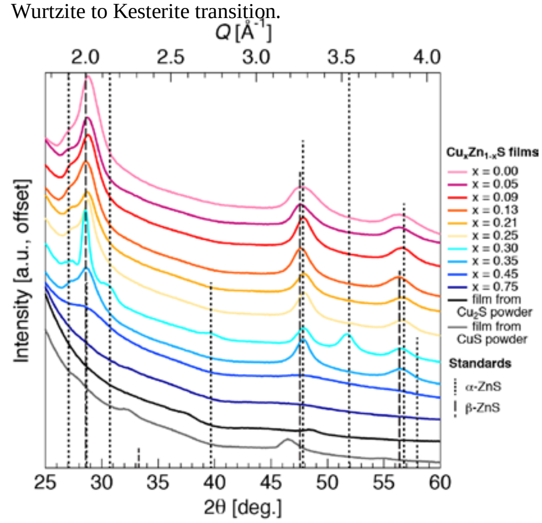

Figure 2. XRD of $Cu_xZn_{1-x}S$ films deposited on quartz at room temperature for $0 \le x \le 0.75$. Films contain a mix of sphalerite (β) and wurtzite (α) ZnS, with wurtzite dominant in the $x = 0.30$ film.

Work has been done on hybrid perovskite solar cell absorbers to understand the role that Cl plays in improving the performance of Cl derived $MAPbI_{3-x}Cl_x$ (MA = methyl ammonium) solar absorbers. XAS has verified that Cl remains in the films after typical annealing. Comparing the spectra of Cl of fully converted (to $MAPbI_{3-x}Cl_x$) films to

XAS of MACl and $PbCl_2$ standards, we showed that the remaining Cl is not the precursors remaining in the film. Further work is needed to understand where in the film the Cl is incorporating.

Measurements implemented by the Salleo group include: below-gap photocurrent measurements (FTPS) in photovoltaic stacks to characterize defects and locate whether they are found in the active layer or in other regions of the stack; true absorption (i.e. excluding scattering) above gap using photothermal deflection spectroscopy (PDS) in thin and thick layers; and absorption below-gap in active layers using PDS to characterize defects. In 2014 through the spring of 2015, Salleo group collaborations with BAPVC members on FTPS measurements increased significantly, including ones with GE/First Solar, the University of Oregon (Mark Lonergan's group), the Colorado School of Mines (CSM - Colin Wolden), and 3-Sun.

In cadmium telluride cells, the appearance of defects in the sub-gap region of the semiconductor can be related back to variations in processing. Thus, FTPS is an important characterization tool to understand the changing materials properties with processing. The EQE over 7-8 orders of magnitude was measured for several sets of GE cells. These cells showed substantial variation in both height and width of the sub-gap absorption region, as well as substantial variation in PCE. Correlation of the sub-gap absorption to changes in PCE is ongoing. The Salleo group also characterized cadmium telluride cells made at CSM as part of a round-robin comparison effort to measurements done at the U. of Oregon.

3Sun operates an a-Si:H/ micromorph tandem facility. As an extension of work from the previous year, measurements have begun on the tandem cells in order to identify defects that occur when the entire stack is deposited. The Salleo group has developed a biased-light FTPS measurement, the results of which are shown in Fig. 3. The biased-FTPS measurement mirrors the monochromatic EQE of the individual cells, but can measure many more orders of magnitude.

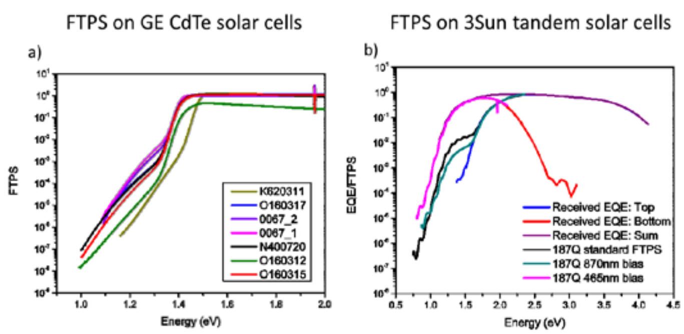

Figure 3. a) FTPS on several CdTe cells from GE of varying efficiency and sub-gap absorption. b) FTPS on tandem cells. The black line indicates the FTPS measurement with no bias light. The IR-biased and blue-biased spectra are overlaid with the monochromatic EQE measured by 3Sun for the top and bottom cells respectively.

Future Work:

The Toney group will continue collaborating with members of the BAPVC in order to better understand PV materials structure-function relationships and processing routes to formation. Work is ongoing with the Milliron group using the RTP and the Bent group using the in-situ Se annealing chamber. Future work will be done with the Ager group to determine the location of the Cu atoms by utilizing resonant x-ray diffraction (REXD). This will allow determination of whether the Cu atoms in the samples are substituted for the Zn atoms in the ZnS lattice or are a disordered component of the film. Work is just starting up with the Wladek group investigating the $(SnTe)_x(CdO)_{1-x}$ alloy systems. These films appeared to be amorphous at approximately $x = 0.35$ to $x = 0.69$; however, initial XRD studies at SSRL suggest there may be a nanocrystalline component of these films. Future work will include XAS and small angle x-ray scattering (SAXS). In the Salleo group work is ongoing to use biased-FTPS to identify subgap states in the higher-band gap cell.