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Nano-scale Optical Spectroscopy of PV materials

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Abstract: A variety of novel high-spatial resolution techniques, including micro-PL, solid immersion lens microscopy and near-field microscopy have been used to characterize the low-temperature photoluminescence of photovoltaic materials and devices with sub-micron spatial resolution. The spatial variation of the energy and time-resolved photoluminescence spectra along the cleaved-edge of CdTe/CdS solar cell structures showed an enhancement in low-energy emission offset an estimated 1-2 microns from the material heterojunction for $CdCl_2$ treated devices, concomitant with a decrease in PL decay time at the CdTe exciton peak. Substantial spatial variations in PL spectra of $Cu(In,Ga)Se_2$ solar cells were also observed to occur on a micron length scale.

Introduction: Most low-cost, polycrystalline solar cell materials are inhomogeneous on a micron length-scale, how this inhomogeniety affects carrier energetics and transport in these materials, and the devices in which they are incorporated, is an important issue in the advancement of PV technologies. Optical spectroscopy combined with high spatial-resolution directly addresses the need to investigate material and device opto-electronic properties on these length-scales. Towards this end, we have developed a variety of techniques and instrumentation with the aim of investigating the spatial variation in the optoelectronic properties of important PV materials. These techniques include near-field microscopy, solid immersion lens imaging and micro-PL. This report will focus on micro-PL results obtained in a cross-sectional study of CdTe/CdS heterojunctions and a plan-view study of $Cu(In,Ga)Se_2$ solar cells.

Experimental: All micro-PL measurements were made at a nominal temperature of 4.2K using a low-profile optical cryostat (Oxford Instruments MicroStat-HiRes) using high-NA corrected optics. The MicroStat was mounted on a computer-controlled precision XY stage, affording linear translations with sub-micron accuracy. The impulse response of the system was verified by scanning the focused spot across a sample patterned with a reflective half-plane, which was compared to the convolution of a gaussian spot with a reflective half-plane as shown in figure 1. As the match is quite good, we estimate the achieved spot size to be approximately 0.67µm FWHM, which is very nearly the diffraction limit for the experimental conditions (660nm).

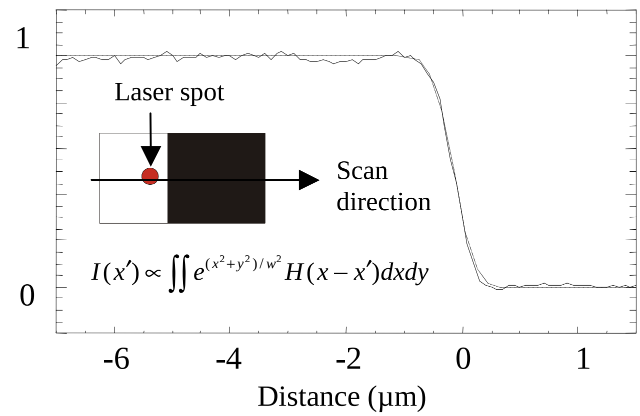

Figure 1: Experimentally obtained (solid line) and theoretically predicted (dashed line) linescans of a reflective half-plane. The former obtained by scanning the focused spot across a sample patterned with aluminum, the latter obtained by the equation shown in the inset.

The CdTe/CdS heterojunctions were deposited on silicon substrates to facilitate cleaving, and otherwise grown under similar conditions as actual CdTe/CdS solar cells. The CIGS sample was a small piece of a working CIGS solar cell.

Cross-sectional low-temperature micro-PL of CdTe/CdS heterojunctions: A study of the spatial variation in the energy and time-resolved low-temperature PL (T=4.2K) along the cleaved edge of a $CdCl_2$-treated CdTe/CdS solar cell (see figure 2) was performed using the apparatus described above. CW and pulsed excitation were focused to approximately 0.67µm, the sample was scanned in 0.7µm intervals along the growth direction and subsequent energy and time-resolved spectra were acquired at each point in the scan. The CdTe excitonic PL intensity vs position (inset B) should closely map the device structure and correlates well with our expectation based on the known growth conditions: this emission is approximately constant with a slight decrease due to increased defect concentration and possible partial alloying with sulfur as the excitation spot is scanned toward the heterojunction. A dramatic decrease in this signal indicates the presence of the CdTe/CdS interface. The below-gap PL (inset C) peaks approximately 1.4µm before this minimum of the CdTe excitonic PL. This suggests an increased defect or impurity concentration offset from the material heterojunction by over a micron. The carrier lifetime (inset D) also is a minimum in this region. Similar experiments were performed on an untreated CdTe/CdS sample, where the strong enhancement in the below-gap PL was not observed and PL lifetimes did not vary significantly

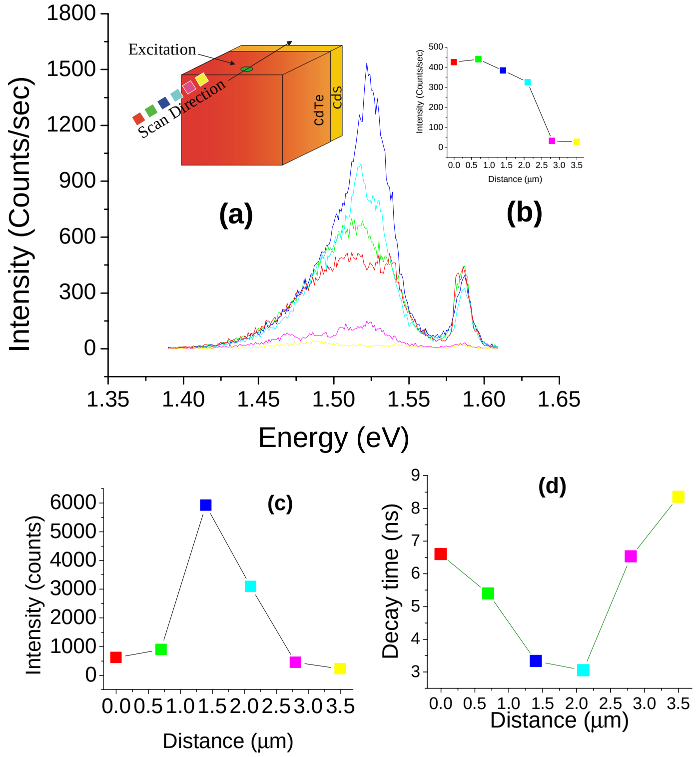

Figure 2 Above: PL spectra spatially-resolved along cleaved-edge of CdTe/CdS solar cell (see inset A). Inset B shows excitonic PL intensity along scan direction. Lower Left: Peak PL intensity along scan direction, Lower Right: Excitonic decay times along scan direction

with distance. The results suggest $CdCl_2$ treatment produces or modifies an impurity layer in these devices well separated from the material heterojunction.

Low-temperature micro-PL of CIGS solar cells: Combining the spatial resolution of the micro-PL technique with an InGaAs diode array, we were able to spatially-resolve the low-temperature (5K) photoluminescence spectra (centered near 1.0eV) in CIGS solar cells, revealing substantial spatial inhomogeneity on a micron length scale. The observed length scale is commensurate with the grain size in these devices. Further work is planned to isolate the effects of the various layers and growth stages and their relative contributions to the observed inhomogeneity

Summary: We have developed a variety of techniques to probe the optoelectronic properties of PV materials on a sub-micron length scale. The micro-PL technique offers reasonably high spatial resolution, is relatively easily implemented, and is amenable to a variety of spectroscopic techniques. The measurements discussed represent significant contributions to an area which is largely uncharted territory, however, further work is necessary to obtain a detailed understanding of the phenomena reported here.

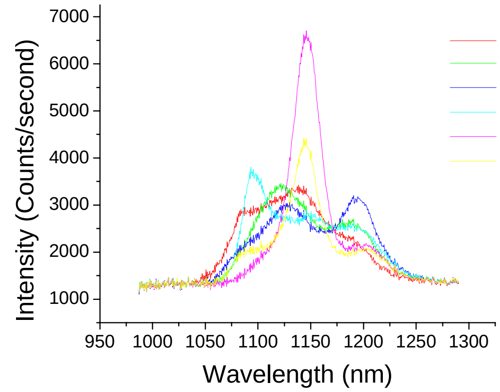

Figure 3: Sequence of 6 spectra taken sequentially during a 5 micron linear scan along the surface of a CIGS solar cell.