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Spatially Resolved Studies of Grain-Boundary Effects in Polycrystalline Solar Cells Using Micro-Photoluminescence and Near-Field Microscopy

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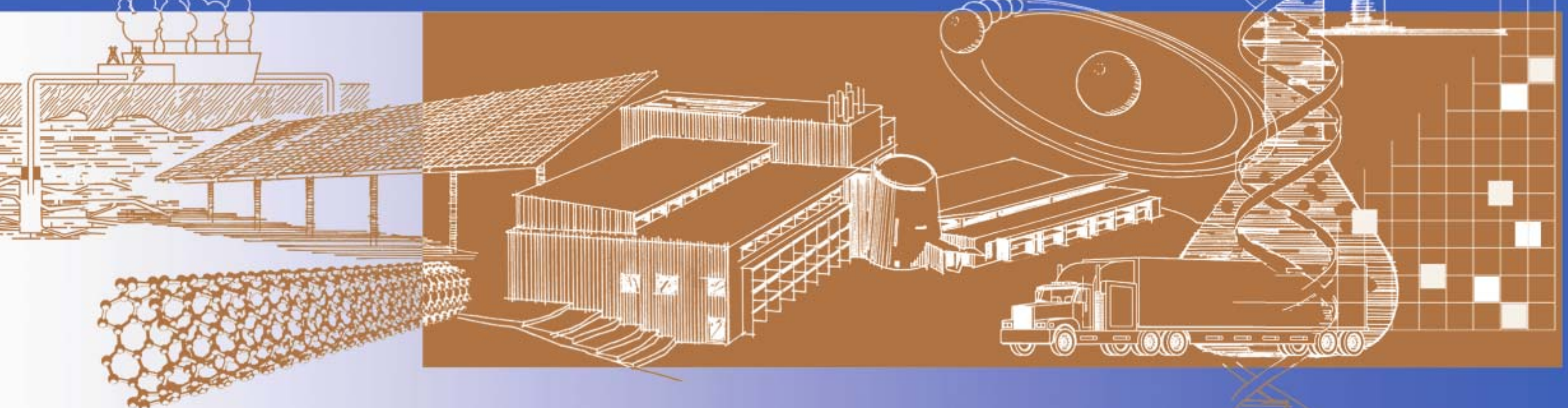

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Spatially Resolved Studies of Grain-Boundary Effects in Polycrystalline Solar Cells Using Micro-Photoluminescence and Near-field Microscopy

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ABSTRACT

Photoluminescence and photocurrent spectroscopies combined with diffraction-limited and sub- diffraction-limited spatial resolution are achieved via micro-photoluminescence (-PL) and near-field microscopy (NSOM). These methods are used to examine the photo-response of individual grain boundaries in thin-film, polycrystalline solar cells at room and cryogenic temperatures. A systematic -PL study of the effect of $CdCl_2$-treatment on recombination in CdTe/CdS solar cell structures of varying thickness directly reveals the grain-boundary and surface passivation action of this important post-growth processing step. We achieve 50nm (/10) spatial resolution in near-field Optical Beam Induced Current imaging (n-OBIC) of polycrystalline silicon solar cells using NSOM, at varying stages of silicon nitride grain-boundary passivation, and measure lateral variations in photo-response of CdTe/CdS solar cells with subwavelength spatial resolution.

1. Objectives

Grain-boundary passivation is a key step in all thin-film photovoltaic technologies, as it substantially improves the efficiency and useful life of these devices. However, a microscopic picture of grain-boundary passivation is still lacking in most thin-film solar cell materials. The goal of this work is to explore the optoelectronic and spectroscopic consequences of post-growth grain-boundary passivation at the nanometer length-scale, via novel, high-resolution optical techniques capable of probing the properties of individual grains and grain-boundaries. The ability to distinguish between these two spatial regions in polycrystalline thin-film materials is critical to understanding the mechanisms of this important post-growth treatment and its' effect on thin-film device performance. The work is in support of the Fundamental and Exploratory Research: Basic Science task, as stated in the Solar Program Multi-Year Technical Plan.

2. Technical Approach

Using low-temperature, -PL, we investigate a series of CdTe/CdS heterostructures of varying thickness subjected to post-growth $CdCl_2$-treatment. By varying film thickness, we control grain size and therefore the relative contribution of grain-boundary versus intra-grain regions to the -PL spectra. Spatial resolution up to 0.67 m was verified with this system[1], while the largest grains exceeded 2 m in diameter. We thus expect high sensitivity to the spectral constituents associated with grain-boundaries. The experimental apparatus was identical with that described in reference 1. Briefly, all photoluminescence spectra (PL) were recorded at 4.2K using a microscope cryostat and dispersed via a 0.46m single-grating spectrometer onto a liquid-nitrogen cooled CCD. Spatial scans in one direction were achieved via computer-controlled micro-positioners. The n-OBIC measurements were made using a commercial NSOM system in conjunction with phase-sensitive detection of photocurrent in the transimpedance configuration at select wavelengths.

3. Results and Accomplishments

To investigate the relative contributions of surface and grain-boundary passivation of post-growth $CdCl_2$-treatment on CdTe/CdS solar cells, we fabricated a series of CdTe/CdS heterojunctions grown on standard $Glass/SnO_2/CdS$ substrates, where the CdTe layer thickness was varied from 0.4 - 3.4 m. It is well-known that the final grain size in CdTe polycrystalline films increases with film thickness, and we confirmed this by AFM measurements of these samples. As the grain size becomes larger, the relative effect of grain boundaries on recombination should become less important. To quantify this effect, we examined the low-temperature PL before and after the $CdCl_2$-treatment of said series of samples. Figure 1 shows a plot of the relative increase in radiative recombination as a function of film thickness, defined as in equation 1:

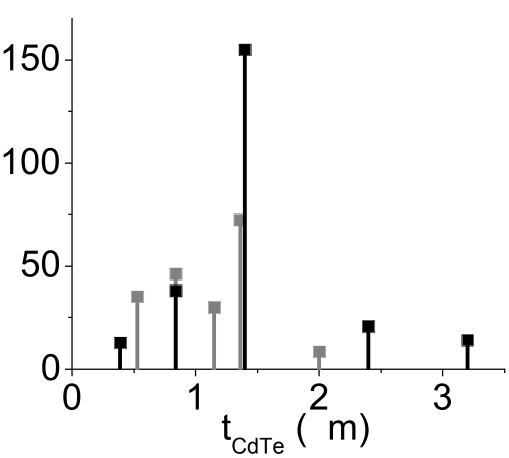

Fig.1: Relative enhancement factor   as a function of film thickness for CdTe/CdS heterojunctions studied for two series of samples of varying thickness.

$$\eta = \frac{I_{CdCl_2\ \ treated}(\lambda, x)d\lambda dx}{I_{as\ \ grown}(\lambda, x)d\lambda dx} \qquad (1)$$

This quantity reflects the relative increase in radiative efficiency averaged over the spatial region sampled. As the grain size exceeds the diffusion length, we expect this quantity to approach that of a free surface and become independent of grain size. Indeed, this is observed for thicknesses greater than ~ 1.4 μm. Thus these values of η reflect the contribution of surface-passivation.

For thinner films, an increase in η with film thickness was observed. This likely reflects the close proximity of the CdTe/CdS heterojunction and the density of grain boundaries and strain-related defects, which both decrease with film thickness. It is likely that such defects cannot be fully-removed by $CdCl_2$-treatment, and below a critical thickness, η is dominated by these defects. Thus the values of η at lower thickness reflect the effectiveness of grain-boundary and defect passivation, and possibly the effect of alloying on radiative efficiency. It is interesting to point out that the critical thickness observed is identical to the proximity of a minima in radiative lifetime observed in cross-sectional time-resolved μ-PL measurements in similarly prepared samples[1]. In that work, an increase in impurity concentration at that thickness was proposed. Whether such an impurity layer is affected by $CdCl_2$-treatment and it's importance to device operation should be a focus of further study.

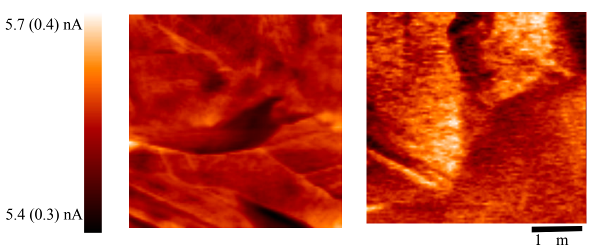

Fig. 2: n-OBIC images of poly-silicon solar cell before and after silicon-nitride passivation treatment (color scale for rightmost image in parentheses).

Figure 2 shows a comparison of spatially-resolved photocurrent using n-OBIC before and after silicon-nitride grain boundary passivation. With ~ 50nm diameter NSOM probe, variations in photocurrent commensurate with the probe diameter are observed, and grain-boundary effects on photo-response are revealed. Generally, much of the fine structure in the photocurrent maps was lost after silicon-nitride treatment. Such an effect could be interpreted as evidence of grain-boundary passivation. Additionally, overall contrast in each image decreased by a factor of 2 after silicon-nitride treatment, a further proof of passivation. However, the measurements were complicated by an apparent degradation in photo-response likely due to compromise of the contacts during processing.

Figure 3 shows the results of n-OBIC measurements taken on a specially-processed CdTe/CdS solar cell. Here,

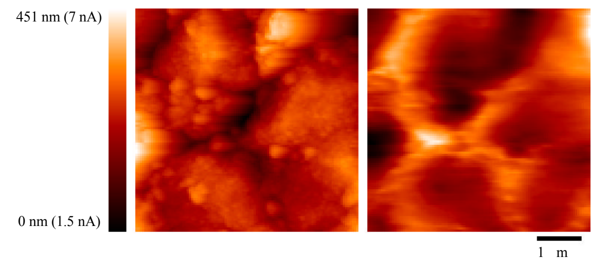

Fig. 3: Simultaneously acquired topographic and n-OBIC images of CdTe/CdS solar cell taken with back-contact selectively etched over 500 μm window.

we selectively etched away ~ 500 μm diameter window in the Ti back contact in order to inject carriers directly into the CdTe grains (a ~ 50nm p-ZnTe layer was transparent to the exciting light, λ=635nm). Because the device is fully depleted, we collect current even when illuminating the cell at the back contact. The leftmost image in the figure shows the topography, where grain boundaries are clearly observed. The rightmost image reveals a relative increase in photocurrent at grain boundaries, substantially larger than might be induced by topographic elements. It has been proposed that grain boundaries in these devices may separate charges due to band-bending at the boundaries[2]. Such charge separation may lead to increased photocurrent. As seen in Fig. 3, we observe an increase in photocurrent at grain boundaries, in support of hypotheses put forth in reference 2 and other works.

4. Conclusions

We observed the effects of grain-boundary passivation in polycrystalline thin-film solar cells with nanometer spatial resolution. Our results further the understanding of this important device processing step by illuminating the effect of $CdCl_2$ and silicon-nitride treatments on individual grain boundaries.

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PV; spatially resolution; photoluminescence; photocurrent spectroscopic; diffraction-limited; sub- diffraction-limited; via micro-photoluminescence (μ-PL); near-field microscopy (NSOM); grain boundary; solar cells; polycrystalline silicon;

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