High open circuit voltages in CdSe ETA cells

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Extremely Thin Absorber (ETA) solar cells were made using electrodeposited CdSe as absorber, nanoporous TiO_2 as electron conductor and CuSCN as hole conductor. Electrodeposition of CdSe from a selenosulfate bath forms nanocrystals of about 4 nm which aggregate into 50-100 nm clusters sparsely distributed throughout the mesoporous TiO_2 (P25) film (figure 1).

The as-deposited CdSe results in very poor cells. Annealing in air improves the cells with particularly high values of V_{OC} (> 0.8 V and up to 0.9 V for mild light concentration) that are very dependent on annealing temperature (figure 2). Values of I_{SC} are low (typically of the order of 1 mA/cm^{-2}) probably due to recombination in the relatively large CdSe clusters, although several $mA \cdot cm^{-2}$ have been obtained in some cases. Our interest is focused on the cause of the relatively high V_{OC} (for CdSe). The fact that high values of V_{OC} are obtained even though the coverage by CdSe is poor implies that the TiO_2/CuSCN interface does not shunt the cell to any major degree.

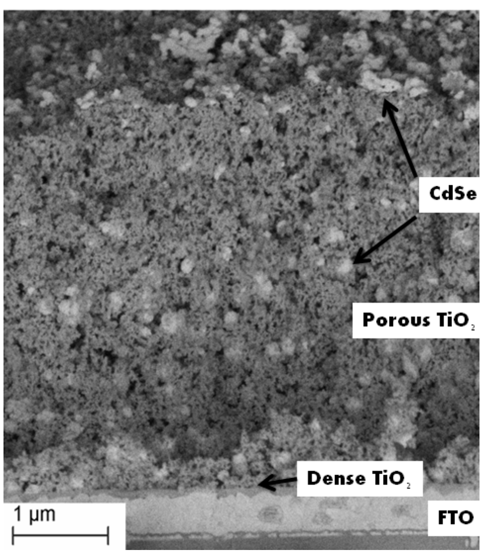

Fig. 1. Cross section back-scattered SEM image of FTO/TiO_2/CdSe. The CdSe clusters are seen as bright ~100 nm spots.

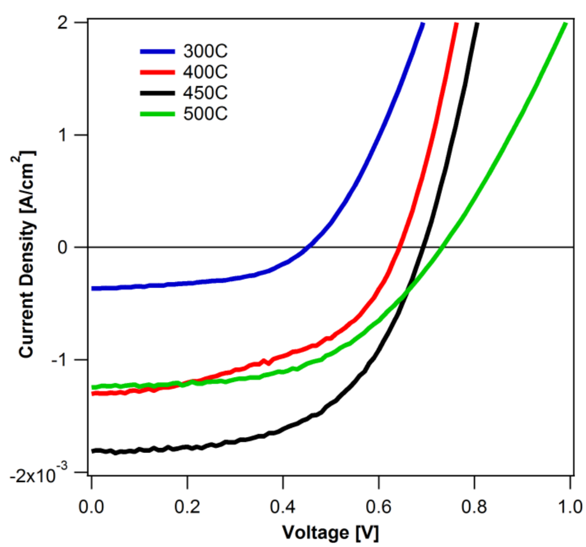

Fig. 2. J-V curves of cells (1 cm^2, 1 sun) annealed at various temperatures in air.

The variation of cell parameters with annealing temperature can be partially correlated to the CdSe grain size within a sensitizer cluster (figure 3). As the temperature increases, small grains coalesce into larger grains. The fewer grain boundaries the charge carrier has to pass before being extracted by the respective conductor, the lower the probability for recombination. However, it was found that grain size alone cannot explain the variation in V_{OC} When conducting similar experiment under inert conditions (N_2 flow), although the grain size increased at least as much as in air, the Voc was much lower and did not vary greatly with annealing temperature (figure 4).

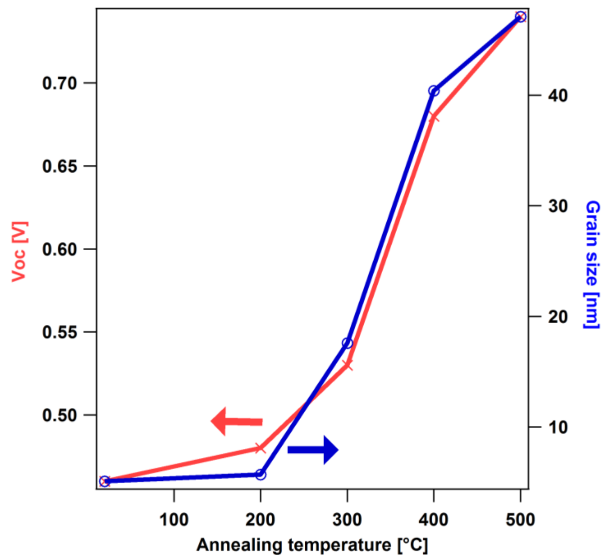

Fig. 3. Correlation of Voc and grain size with the annealing temperature.

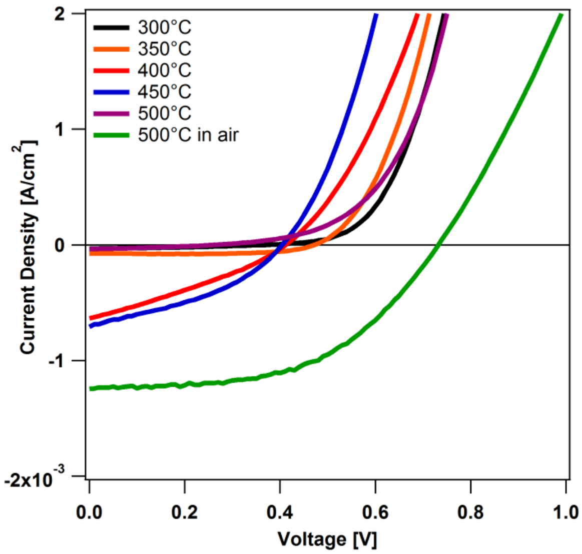

Fig. 4. As fig. 2, but annealed in nitrogen.

To elucidate these differences, we analyzed the chemical composition of the electrode surface using X-ray photoelectron spectroscopy. Annealing in air increases the cadmium to selenium ratio in the absorber, and also, as expected, forms an oxidized surface ($CdSeO_x$, possibly CdO), with increase in concentration of these oxidized species as the annealing temperature increases.

We therefore attribute the changes in the V_{OC} to these oxidized species. There are several possibilities for the mechanism of this effect. One is a buffer layer that prevents electrons (holes) from recombining with holes (electrons) in the CuSCN (TiO_2). Another is passivation of grain boundaries in the CdSe clusters to reduce recombination in the CdSe itself. However both these scenarios would be expected to improve current to a greater extend than seen. We are presently investigating other directions, such as the effect of air annealing on the cell band diagram.