

## Sensitization of Single Crystal Semiconductor Electrodes with Dyes, Quantum Dots and Polymers

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Recent results from our work on spectral sensitization of single crystal semiconductor electrodes will be presented.

ZnO single crystal electrodes were fabricated into internal reflection prisms to test our long-standing assumption that the photocurrent yields we measure for dye monomers and dye aggregates on the crystal surfaces were proportional to their coverage on the electrode surface or that monomer and aggregates had the same quantum yields for photocurrent production. Our initial results for a model dicarboxylated thiocyanine dye indicates that our assumption was valid at least in the case of this dye. We have also been studying the influence of the doping density of the semiconducting oxide substrate on the yields of sensitized photocurrents. Preliminary results indicate that there is an optimum doping level where the electrical field gradient from the space charge layer is high enough to rapidly separate the injected electron and eliminate the back reaction where the electron returns to the photo-oxidized dye. These results are being compared to a model developed by Spitler that predicted the yields and current voltage behavior<sup>1</sup>. Currently high temperature vacuum annealing or reduction with hydrogen is used to change the doping density of these crystals. Substitutional doping is the preferred method for doping these materials since it results in less strain and formation of trap states. We have had success with the growth of homoepitaxial layers of titanium dioxide with atomic layer deposition (ALD) where ordered single crystal layers are templated on either rutile or anatase substrates. Substitutional doping of these layers with niobium should produce higher quality substrates for fundamental studies of sensitization.

We will also discuss recent results from our collaboration with the Schanze Group at the University of Florida. We were able to verify that a poly(phenylene ethylene) conjugated polyelectrolyte, that was specifically synthesized to avoid aggregation, can photosensitize n-type zinc oxide (0001) single crystals and was demonstrated not to aggregate by both photocurrent spectroscopy and AFM imaging at the single polymer molecule level.

1. Spitler, M. T., J. Electroanal. Chem., 1987, 228, 69