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Final results are described for a seed project focusing on the development of inorganic, nanostructured semiconductor-based composite thin films intended for use as heterojunction elements or photoactive contact materials for photovoltaic energy conversion devices. The project demonstrated the successful production of quantum-size, semiconducting CdTe nanoparticles (light absorption, charge generation material) within a ZnO (transparent conductive oxide, charge transport matrix) using sequential rf-sputtering deposition. Unique to this study, the deposition approach allowed the spatial distribution of the semiconductor phase within the host matrix to be controlled, resulting in nanostructure-tunable optical absorption and carrier transport behavior of significant impact to the intended application of these materials for spectrally enhanced thin film photovoltaic performance and other optoelectronic technologies. Transmission electron microscopy, x-ray diffraction, and vibrational spectroscopy confirmed the identity of the phases participating in the composite as well as the variation in nanostructural characteristics as influenced via deposition control and thermal annealing. The work demonstrated the development of nanocomposite thin films that exhibit tunable, quantum-confinement induced modification in spectral absorption based on the manipulation of extended semiconductor phase connectivity. The control of semiconductor phase assembly was also used to optimize photocarrier transport behavior (generated within the CdTe nanophase) as evidenced by spectrally resolved photoconductivity measurement.

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Final Technical Report:
Optoelectronic Nanocomposite Materials for Thin Film Photovoltaics

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Abstract:

Final results are described for a seed project focusing on the development of inorganic, nanostructured semiconductor-based composite thin films intended for use as heterojunction elements or photoactive contact materials for photovoltaic energy conversion devices. The project demonstrated the successful production of quantum-size, semiconducting CdTe nanoparticles (light absorption, charge generation material) within a ZnO (transparent conductive oxide, charge transport matrix) using sequential rf-sputtering deposition. Unique to this study, the deposition approach allowed the spatial distribution of the semiconductor phase within the host matrix to be controlled, resulting in nanostructure-tunable optical absorption and carrier transport behavior of significant impact to the intended application of these materials for spectrally enhanced thin film photovoltaic performance and other optoelectronic technologies. Transmission electron microscopy, x-ray diffraction, and vibrational spectroscopy confirmed the identity of the phases participating in the composite as well as the variation in nanostructural characteristics as influenced via deposition control and thermal annealing. The work demonstrated the development of nanocomposite thin films that exhibit tunable, quantum-confinement induced modification in spectral absorption based on the manipulation of extended semiconductor phase connectivity. The control of semiconductor phase assembly was also used to optimize photocarrier transport behavior (generated within the CdTe nanophase) as evidenced by spectrally resolved photoconductivity measurement.

Introduction:

The need for increased energy security and efficiency drives the development of new photovoltaic (PV) technologies for portable and site-based renewable power sources. Coupled with the broad range of environments and unique performance requirements dictated by the Naval field of operations, new options for tailored energy generation performance, beyond that typical of commercial localized or distributed PV systems is required.

The present work addresses the need for materials possessing tunable optoelectronic response (optical absorption, charge generation and transport behavior) with the potential to serve as the basis for heterojunction photovoltaic devices with tailored spectral performance. Semiconductor (SC) nanostructures, embedded within inorganic, thin film photovoltaic (PV) heterojunctions, offer a means to achieve these objectives, providing options for improved energy conversion efficiency while tailoring PV device spectral sensitivity and electronic characteristics through manipulation of SC composition and phase assembly (multilength scale structure). In this context, the dramatic impact of collective phenomena on the electronic structure of a quantum-dot (QD) ensemble is of prime interest. The manipulation of ensemble behavior through control of SC-phase extended structure thus becomes an enabling materials engineering opportunity for the development of non-traditional PV operational characteristics.

The project focuses on the sequential RF-magnetron sputter deposition of semiconductor-host nanocomposite thin films possessing a range of structural topologies, ranging from isolated semiconductor nanocrystals embedded within the host to interconnected semiconductor and host phases. In this case, a model nanocomposite system, based on a II-VI semiconductor (CdTe) and an

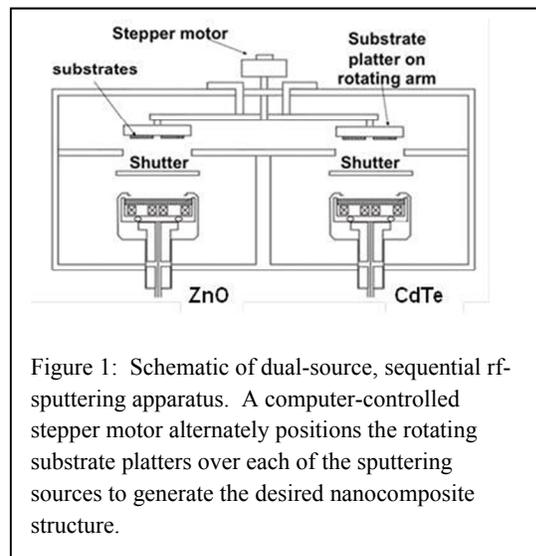
electrically active embedding phase (ZnO), is under study. Results confirm the efficacy of using thin film deposition controls to influence the extended semiconductor phase distribution with the matrix and to use this as a means to modify the resulting nanocomposite optical absorption and photocarrier transport behavior. In the context of the eventual application of these results, these investigations emphasize materials and processes with proven utility for large-scale, thin-film PV production (providing a line-of-sight to the rapid scale-up and application of these results) while providing a fundamental basis from which to engineer new nanocomposite systems with unconventional spectral sensitivity through variation in SC and matrix composition and processing conditions.

Results and Discussion:

a. Thin Film Deposition and Processing

Subsequent to a preliminary series of studies to confirm optimal deposition conditions for both CdTe and ZnO single-phase thin films, nanocomposite films were produced via a multisource sequential rf-sputtering technique (Figure 1). The overall volume fraction and spatial distribution of CdTe was varied by changing the relative exposure times to each source using a computer-controlled stepper motor to position the substrate platter over each gun. Total film thicknesses were attained by iterative cycling of the substrate over each of the CdTe and ZnO sputtering sources for the required exposure times. All films presented here were deposited to a nominal total thickness of approximately 500 nm.

Two suites of nanocomposite specimens were produced to manipulate CdTe phase connectivity both within the film plane and along the film growth direction (film normal). In order to probe the influence of CdTe connectivity within the plane of the film, CdTe layers were produced with exposure times equivalent to the deposition of 0.5 nm and 1.5 nm of CdTe per cycle. The 0.5 nm layer exposure was intended to produce a more discontinuous film with the subsequent deposition of ZnO effectively interrupting the development of CdTe islands in the early stages of layer formation. Conversely, the longer CdTe exposure was intended to produce a more continuous, interconnected in-plane semiconductor film structure. To probe the potential for physical interconnection and/or collective behavior arising between adjacent CdTe layers (i.e. along the film growth direction), the exposure time of the substrate to the ZnO source was also varied. This control of the CdTe and ZnO layer thicknesses, used to define the repeated deposition cycle, dictates the longer length scale nanostructural characteristics of the composite film.

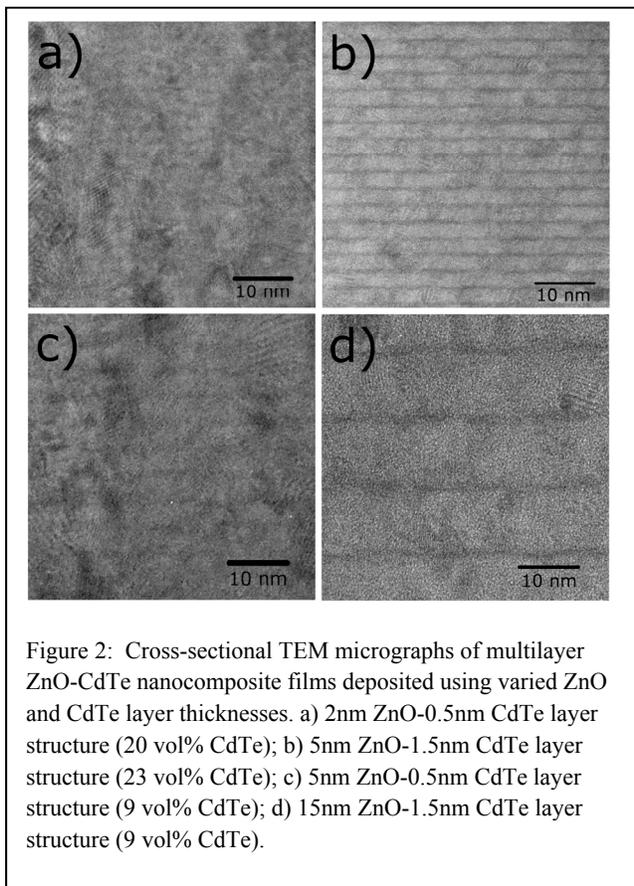


The use of post-deposition annealing was used to further explore the impact of processing on phase distribution as well as phase crystallinity and stability. Specimens consisting of a 15 nm ZnO – 1.5 nm CdTe multilayer (ML) design were thermally treated in a muffle tube (fused silica process tube) furnace under a flowing Ar atmosphere. The effects of five-minute isochronal anneals at temperatures ranging from 300 C to 800 C were examined.

Spectrally resolved photoconductivity (SRPC) was examined in films produced within an transparent, ITO contact sandwich structure thus allowing an applied bias field to be applied along the film normal. SRPC was monitored with modification in CdTe phase connectivity achieved through modification of ZnO layer thickness, as described above. The CdTe deposition cycle time was held constant, equivalent to 0.5 nm/cycle.

b. Structural Studies

Figure 2 contains representative cross-sectional TEM micrographs illustrating the range of multilayer (ML) CdTe-ZnO designs explored in the study. The darker layers correspond to the CdTe



phase while the light layers are the ZnO. The visibility of the layer structure is influenced by both the limited atomic number contrast afforded by the materials systems involved as well as the absolute thicknesses of the ZnO and CdTe layers. Combinations of thinner CdTe and ZnO layers (e.g. 2 nm ZnO-0.5 nm CdTe ML; Figure 1a) tend to produce images with a more uniform contrast across the field of view while multilayer designs of thicker layers (e.g. 15 nm ZnO – 1.5 nm CdTe ML; Figure 1d) more readily show the multilayer nature of the deposition process. Additional contrast in these micrographs also arises from diffraction effects, particularly observable in the ZnO majority phase of the composite.

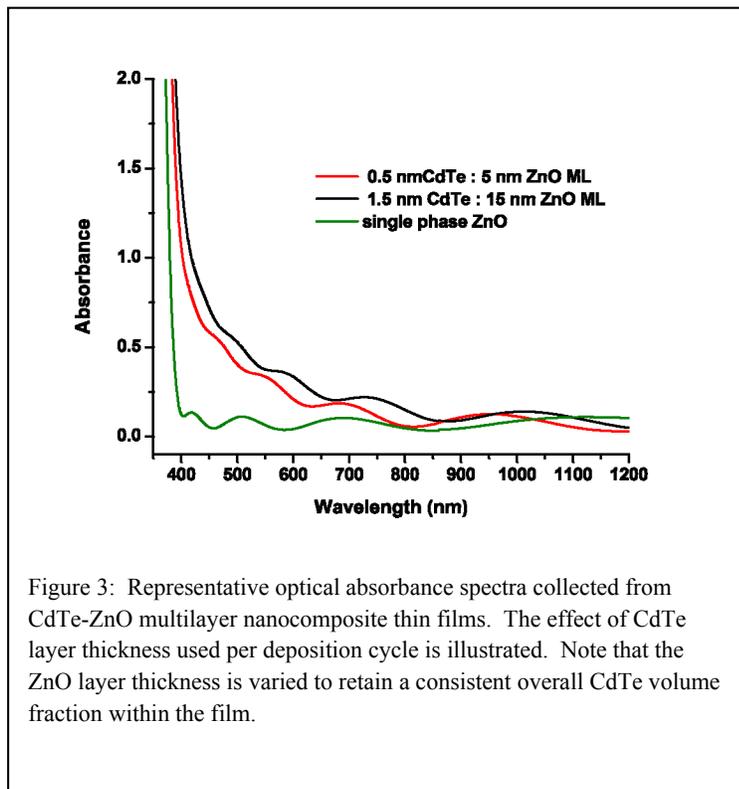
X-ray diffraction confirmed the presence of ZnO phase crystallinity (wurtzite, JCPDS # 36-1451, (002) preferred orientation) in these as-deposited materials. Raman investigation also confirmed the presence of crystalline CdTe and ZnO phases in the as-deposited specimens. In this case, a CdTe LO-phonon resonance is

observed in all samples near 160 cm^{-1} and a dominant feature at 575 cm^{-1} is associated with grain boundary structure in polycrystalline ZnO.

In general, post-deposition processing under the lower temperature, short-time isochronal conditions used, produced no significant modification nanostructural assembly or spectral absorption behavior in the films examined. Within the temperature range 200 C to 550 C, a gradual increase in crystalline phase quality for both the CdTe and ZnO components was confirmed by Raman spectroscopy. At annealing temperatures greater than 700 C, significant ZnO grain growth was observed, confirmed by TEM and x-ray diffraction Debye-Scherrer line broadening analysis. With increased temperature, Raman analysis revealed the development of Te-Te vibrational modes indicating the decomposition of the CdTe phase. The study thus also provided initial confirmation of thermal processing limits for the CdTe-ZnO thin film system under these conditions.

c. Optical Absorption

The films produced in the present study consistently exhibited an absorption onset, associated with the CdTe nanophase, at higher energies than that of bulk CdTe. This blue-shift in absorption onset



is associated with the quantum confinement of photocarriers within the CdTe phase and implies the presence of an interfacial structure/chemistry sufficient to provide a barrier to electron and hole motion.

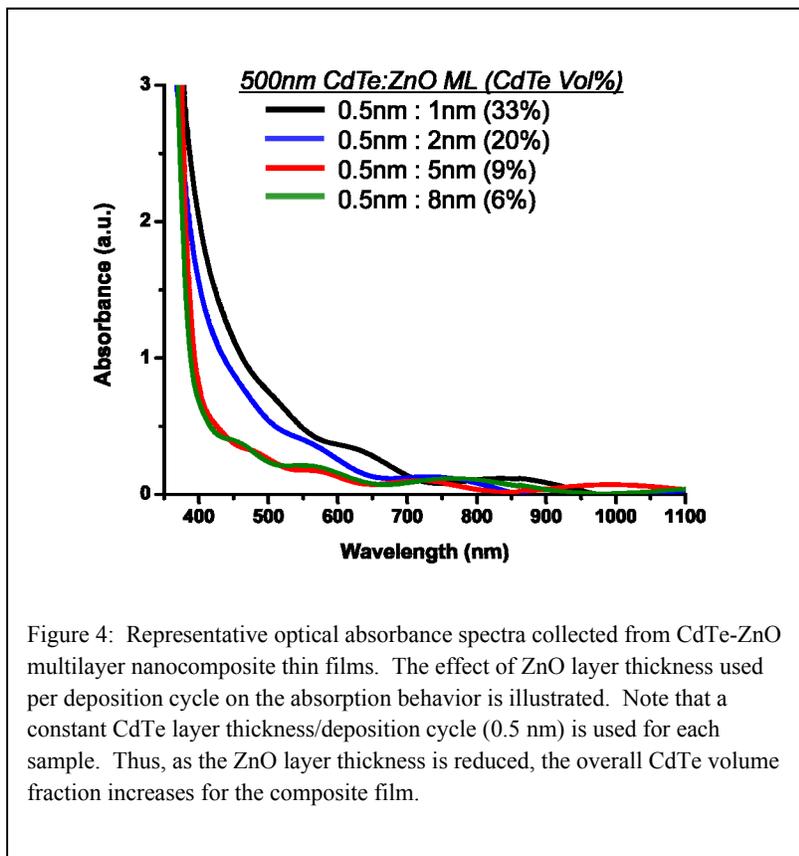
Representative optical absorption spectra for the samples examined are provided in Figures 3 and 4, illustrating the effect of varied CdTe layer thickness and ZnO layer thickness in the multilayer designs used, respectively. In Figure 3, spectra obtained from a 0.5 micron thick single-phase ZnO film is provided for comparison with the nanocomposite film results. In general, all nanocomposite films exhibit an absorption onset over the energy range between the absorption onsets observed for the CdTe single phase film

(1.18 eV) and the ZnO film (3.18 eV). While the nanocomposite spectra typically exhibit Fabry-Perot interference fringing that limits a quantitative analysis of absorption edge position or its variation with deposition conditions, the spectra of Figure 3, for example, do exhibit a clear red-shift in the absorption onset for the films of approximately 0.3 eV with increasing CdTe layer thickness used in generating the

multilayer film. Similarly, Figure 4 also shows a blue-shift in absorption onset (0.25 eV) as the thickness of the ZnO layer is increased.

CdTe phase distribution within the ZnO embedding phase can be correlated with the quantum-size induced CdTe absorption onset observed in Figures 3 and 4. In Figure 3, shorter CdTe exposure times resulted in more discontinuous CdTe layers, and the production of isolated nanoparticles of the semiconductor (see Figure 1) that corresponded to higher energy absorption onsets. Conversely, longer CdTe deposition time specimens, exhibiting more continuous CdTe layers, produced a red-shifted (lower energy) absorption onset. The more isolated CdTe nanoparticles in the shorter exposure time films produce a reduced carrier confinement volume, resulting in a general increase in the lowest optical transition energy observed in the absorption spectrum for the semiconductor ensemble.

The influence of phase assembly control, this time along the growth direction of the nanocomposite thin film, is examined in Figure 4 which highlights the evolution of spectral absorption with variation in ZnO layer thickness. Absorption below 400nm is generally associated with the ZnO phase ($h\nu > \text{ZnO } E_g$) while the absorption beyond 400nm is due to inhomogeneously broadened band gap absorption from the polydisperse-CdTe nanoparticle phase. While interference from Fabry-Perot fringes precludes a more quantitative evaluation of the CdTe phase absorption edge position, a clear



red-shift in the CdTe absorption onset with increased CdTe volume fraction (i.e. decreasing ZnO thickness) is observed. This trend was also verified using absorption coefficient data (not shown).

Modification in spectral absorbance is associated with the CdTe phase connectivity produced by control of the deposition schedule. Consistent blue shifts in absorption onset over the bulk CdTe band gap energy (1.5 eV) are interpreted in terms of quantum confinement of photocarriers in the CdTe phase. The ZnO thickness contributes to the potential for physical and/or carrier-tunneling interactions between adjacent CdTe nanoparticle layers in the composite, thus influencing the

ensemble contribution to carrier confinement effects within the semiconductor phase. Increasing the ZnO layer thickness per deposition cycle decreases the CdTe phase connectivity which serves to further

blue shift the CdTe absorption as interaction (and ensemble-related effects on quantum confinement) between adjacent CdTe nanoparticle layers is decreased. The thickest ZnO layers examined in this study effectively preclude interactions between adjacent CdTe layers which results in an absorption response more consistent with a collection of isolated CdTe nanoparticle layers and a saturation in the blue-shift in CdTe absorption onset with increasing ZnO layer thickness (Figure 4).

d. Spectrally Resolved Photoconductivity

By examining the changes in the photoconductivity response with respect to overall film nanostructure, the combined effects of absorption, photocarrier generation and charge carrier transport can be interpreted in terms of semiconductor phase extended structure and its contribution to

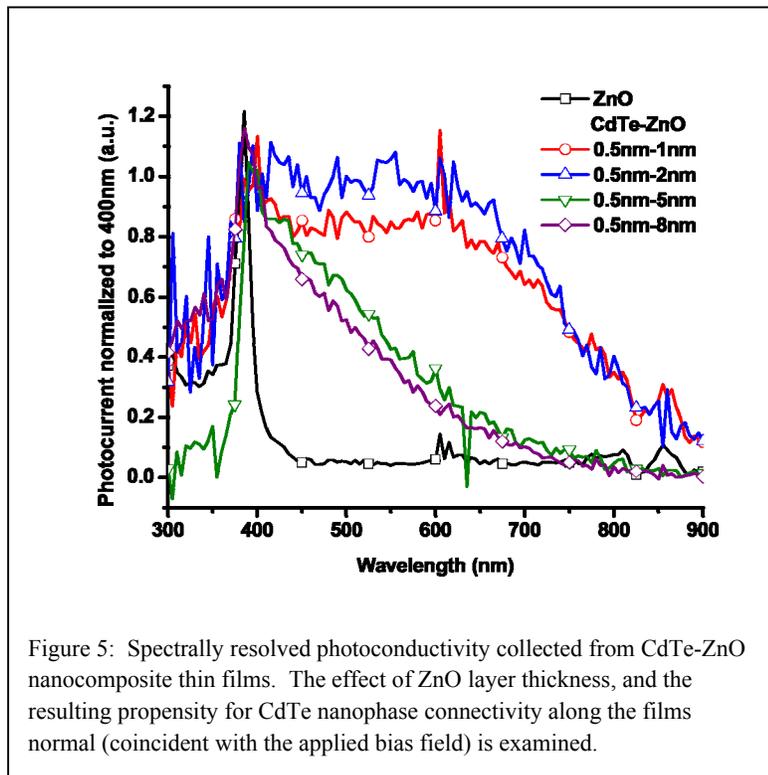


Figure 5: Spectrally resolved photoconductivity collected from CdTe-ZnO nanocomposite thin films. The effect of ZnO layer thickness, and the resulting propensity for CdTe nanophase connectivity along the films normal (coincident with the applied bias field) is examined.

CdTe interparticle interactions. . Representative photoconductivity spectra for the samples analyzed are given in Figure 5. Included is the photoconductivity of a single phase ZnO film deposited under identical conditions for comparison. The photoconductivity spectrum of the ZnO film exhibits a peak around 400nm, which corresponds to the absorption onset of that material. No measurable photocurrent at longer wavelengths is observed in these single-phase ZnO films. The low power output of the Xe arc lamp source contributes to the sharp drop off in photocurrent at wavelengths shorter than 380nm. Noise in these data is generally attributed to trapped charge carriers and the

buildup of space charges within this nanoheterogeneous material system.¹⁴

In contrast, the photoconductive response of the nanocomposite CdTe-ZnO films extends beyond 400nm to longer wavelengths. For an extended CdTe nanophase structure favoring increased potential for interaction between adjacent layers of nanoparticles, (i.e. nanocomposites produced with 1nm and 2nm ZnO layer thicknesses per cycle) the photocurrent exhibits a broadened band centered near 625 nm in addition to the ZnO-related peak observed at 400 nm. This longer wavelength photocurrent is coincident with the spectral range for CdTe nanoparticle optical absorption (Figure 4) and thus confirms the generation and long-range transport of photocarriers associated with the nanophase semiconductor.

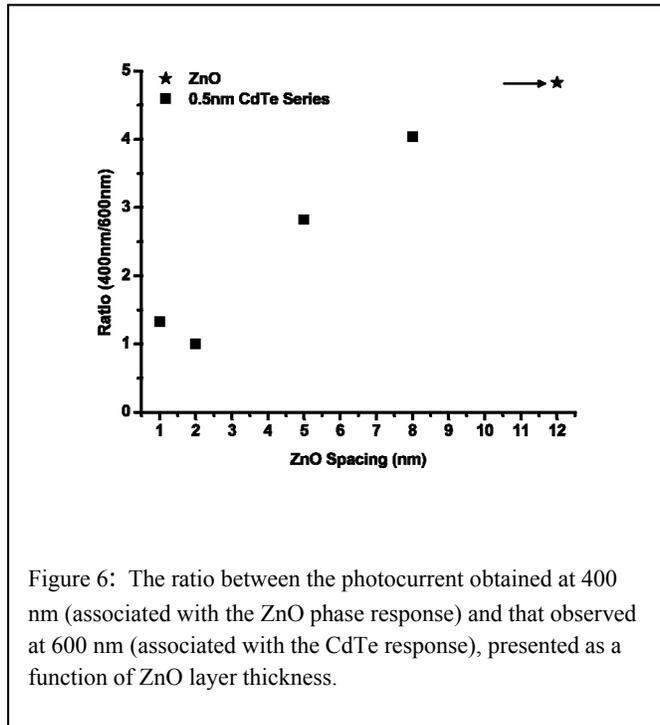


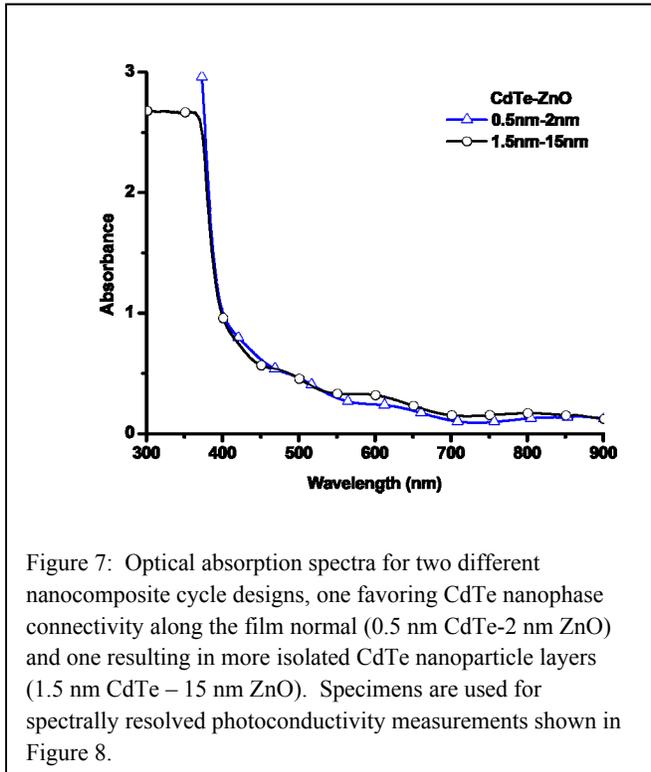
Figure 6: The ratio between the photocurrent obtained at 400 nm (associated with the ZnO phase response) and that observed at 600 nm (associated with the CdTe response), presented as a function of ZnO layer thickness.

Beyond confirmation of the role of the CdTe phase in the photoconductive response, Figure 5 also shows that nanocomposites with more limited potential for interaction between adjacent CdTe nanoparticle layers along the applied field direction (i.e. those produced using 5nm and 8nm ZnO layer thicknesses per cycle) exhibit a reduced photocurrent in this longer wavelength range. The responses in Figure 5 have been normalized to the photocurrent value at 400nm to help highlight the difference in the relative CdTe contribution to the total photocurrent with changes in the CdTe nanostructure. To help further illustrate the changes in relative contributions to photoconductivity from each phase of the nanocomposite, Figure 6 depicts the ratios of the photocurrent values at 400nm (associated

with the ZnO phase) and at 600nm (associated with the CdTe nanophase) with respect to the ZnO spacing thickness.

Referring to Figure 6, as the ZnO thickness increases there is a corresponding increase in the photocurrent ratio that is consistent with a decrease in the relative contribution of the CdTe phase to the total photoconductivity of the nanocomposite. As mentioned above, the increasing ZnO layer thickness is associated with a decrease in CdTe phase connectivity that contributes to a blue shift in absorption onset and a concomitant reduction in absorption strength in the long wavelength spectral range. The change in response at the longer wavelengths can be attributed to either change in the ensemble absorption characteristics, as seen in the absorption response, or lack of more continuous (or higher mobility) carrier paths in the CdTe phase, as both phenomena are anticipated to contribute to the photoconductivity observed.

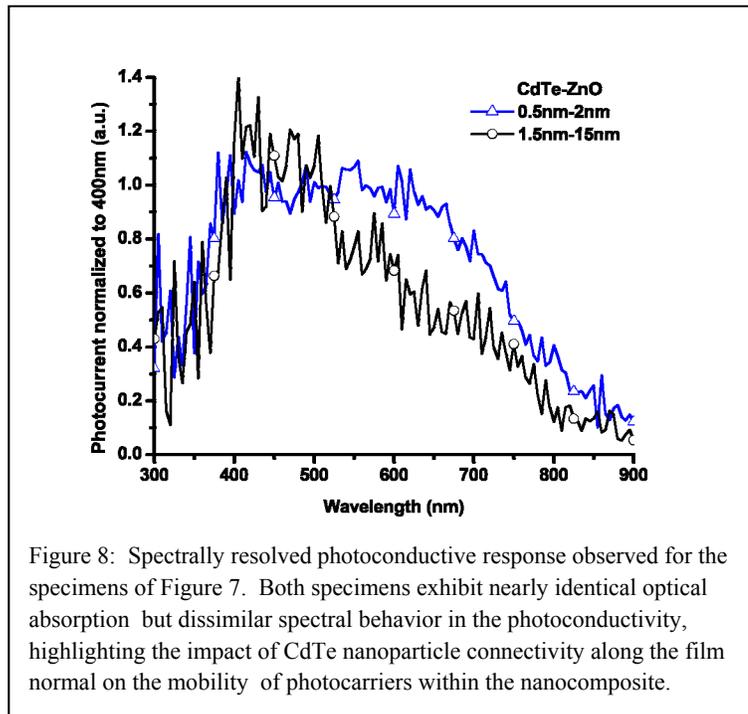
In order to decouple the effects of absorption and charge carrier path mobility, a set of films was produced with similar absorbance spectra but with CdTe nanostructure providing different degrees of phase connectivity along the film growth (applied field) direction. In this way, the effects of photocarrier generation could be more effectively isolated from the transport behavior. Specifically, nanocomposite films with a ZnO layer thickness of 15 nm per cycle and a CdTe effective deposition thickness of 1.5 nm per cycle were produced. These films exhibited an optical absorption response similar to the 0.5nm CdTe – 2nm ZnO film (Figure 7) but will have increased separation (and reduced potential for nanoparticle interaction) between adjacent CdTe layers along the film normal when compared to the 2 nm ZnO per cycle specimens.



Since the absorption responses from the CdTe nanophase are similar between the two samples, and if comparable quantum efficiency for photocarrier generation is assumed for the two specimens, differences in photoconductivity can be attributed to changes in the carrier transport efficiency. Figure 8 contains the spectrally resolved photoconductivity for the 0.5nm CdTe – 2nm ZnO and 1.5nm CdTe – 15nm ZnO films, again normalized to the photocurrent value at 400nm (i.e. that associated with the ZnO phase). The 1.5nm CdTe – 15nm ZnO film photoresponse contrasts that of the 0.5nm CdTe – 2nm ZnO film and is similar to that observed in other films that also were produced a larger ZnO layer thickness (and reduced interaction between adjacent CdTe layers), in that it exhibits a reduced photocurrent at longer wavelengths.

Summary and Outlook:

This seed project has demonstrated the development of CdTe-ZnO nanocomposite thin films exhibiting nanostructure-mediated optical absorption and photocarrier generation and transport. The sequential sputtering process has been used to produce a range of as-deposited extended semiconductor structures within the ZnO host matrix. Samples were produced that have highlighted the potential for tailoring the semiconductor phase connectivity both within the film plane and along the film growth direction. Further, the optical absorption onset of the semiconductor phase and



photocarrier transport behavior within this nanoheterogeneous material has exhibited a correlation with the extended structural connectivity of the CdTe phase.

Optical, electronic, and nanostructural results thus support the role of multilength scale material structural control on the quantum confinement and long range transport behavior exhibited by on photocarriers within the CdTe nanophase. These phenomena, coupled with the control of extended semiconductor phase assembly, have the potential to provide an alternative means to tune the spectral response of the material while maintaining viable conduction and photocurrent generation – key factors in determining the energy conversion performance of a heterojunction PV device based on these thin films. In this context, the nature of the CdTe-ZnO interface, that defines the energy barrier to photocarrier motion within the semiconductor, becomes an important contributor to the optical performance of these materials. Similarly, the impact of the interfacial component as a contributor to carrier scattering and efficient long-range charge transport is also of interest. Such study will have significant impact on the continued assessment and application of these novel systems for PV and other optoelectronic applications.

Finally, incorporation of such semiconductor-TCO nanocomposite films as spectral sensitizer elements within an established thin film photovoltaic device architecture remains an important next step in verifying the effective transfer of the intrinsic, nanostructure-mediated material optical and electronic behavior, that served as the focus for this seed project, to the targeted application technology. The materials selected for the current project are widely employed within established (and industrially relevant) thin film photovoltaic device architectures as heterojunction elements for absorber and window layers. The inherent materials and process compatibility offered by the materials strategy described above offers a readily scalable path for the application of the structures and phenomena explored in the project to photovoltaic energy conversion and related optoelectronic technologies.