RF-Sputtered Ge-ITO Nanocomposite Thin Films for Photovoltaic Applications

C.G. Allen, G. Shih, and B.G. Potter, Jr.

Materials Science and Engineering Department, University of Arizona, Tucson, AZ 85721

Objectives and Motivation

Nanophase photovoltaic (PV) cell architectures containing distinct absorption and carrier transport phases offer new opportunities to individually tailor the spectral capture and carrier collection functions necessary for efficient PV energy conversion.

The current effort focuses on the development of inorganic nanocomposite structures in which a semiconductor "sensitizer" phase is introduced at a thin film PV heterojunction. Nanostructured semiconductors are of increasing interest in the context of photovoltaics as their absorption characteristics can be tuned through both composition and quantum size effects for more effective matching to the solar spectrum. ***Multilength scale structural control, however, critical in achieving desired properties.***

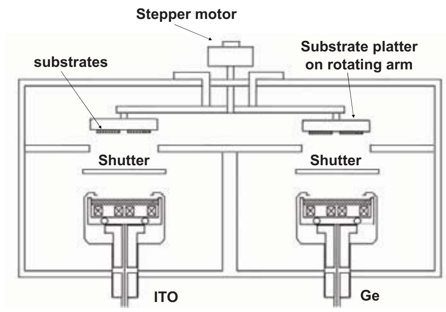
Dual-source, sequential RF-sputtering technique:

✓ *Manipulation of semiconductor-embedding phase assembly* to influence nanocomposite optical and electronic performance.

✓ Incorporate *electrically active embedding phase* to mediate the extraction of photocarriers and their transport within the nanocomposite.

Both ***deposition conditions and post-deposition thermal treatments*** produce a range of semiconductor nanostructures resulting in tunable spectral absorption and increased free carrier formation, key aspects of photovoltaic function.

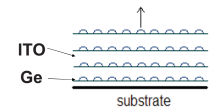
Sequential RF-Magnetron Sputter Deposition



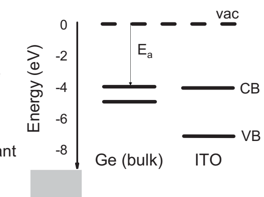
Dual-source deposition chamber schematic

Nanocomposite Design:

✓ **Multilayer Ge:ITO:**
- Layer designs examined:
  0.4 nm Ge:15 nm ITO;
  1.5 nm Ge:15 nm ITO



✓ **Electronic Structure:**
- Close match in bulk electron affinities (E_a)
- limited photoexcited electron confinement in Ge quantum-size structures anticipated.
- interfacial chemistry and electronic structure important to photocarrier extraction and transport in ITO



Approach:

✓ Alternating exposure to Ge and ITO sputter sources. Control exposure time over each source to define: relative volume fraction of each phase in nanocomposite, distribution of phases along film growth direction, phase assemblage (e.g. discontinuous vs. continuous layers)

Post-deposition thermal anneal:

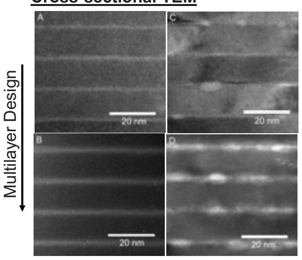
✓ Isochronal anneals: 5 minutes at 250 – 650 C in air for initial evaluation.

Substrates:

✓ Silica and p- and n-type Si.

Microstructural Analysis

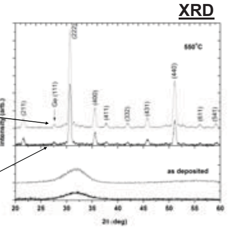
Cross-sectional TEM



0.4 nm Ge:15 nm ITO
smaller average Ge nanocrystal size (2-8 nm), more equiaxed morphology.

1.5 nm Ge:15 nm ITO
larger, higher aspect-ratio Ge crystals produced (lengths: 10-12 nm, widths: 5-6 nm).
Ge contrast overlap – potential interconnected semiconductor phase topology.

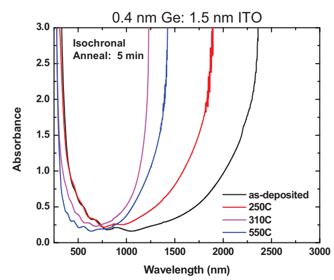
XRD

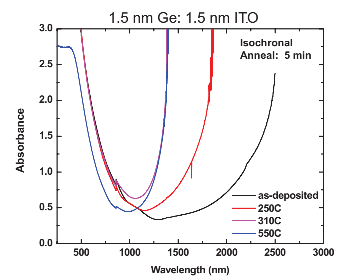


XRD and Raman (not shown) confirm formation of crystalline Ge phase, concurrent with ITO crystallization, upon thermal anneal.

✓ Thermal treatment promotes the break-up of the as-deposited Ge layers, producing Ge nanocrystals whose number density varies along film deposition direction with a periodicity determined by the initial alternating layer structure.
✓ Thinner initial Ge layer thickness promotes smaller, more equiaxed Ge nanocrystal population upon anneal. Thicker Ge layer – larger, elongated nanocrystal population.
✓ Potential for control of final connectivity of semiconductor phase to influence collective behavior of semiconductor ensemble – optical absorption, carrier transport.

Optical Absorption: Layer Design and Annealing Effects



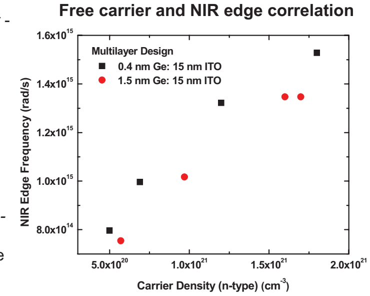


Nanocomposite absorption dramatically impacted by both layer design and annealing

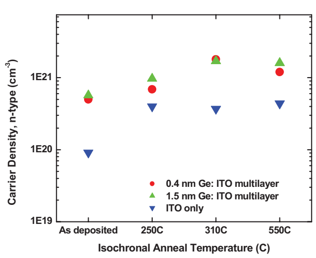
High energy absorption onset: Ge band-edge absorption.
- *Blue-shift in Ge-phase absorption onset* - consistent with formation of smaller Ge domains upon annealing (increased confinement-induced modification of Ge electronic structure) - potential impact of interfacial blocking layer.

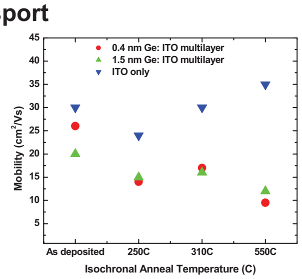
Near-IR transmission edge: associated with free-carrier plasma resonance (Drude behavior)
- *NIR edge correlated with free carrier (n-type) density measured via Hall effect.*
Carrier density increases with isolated Ge nanocrystal phase formation and increased ITO crystal quality.

Free carrier and NIR edge correlation



Carrier Generation and Transport





✓ Hall Effect measurements indicate n-type majority carriers in all films (as expected).

✓ Majority carrier density enhanced by the presence of the Ge phase and thermal treatment, saturation at approximately 10^{21} cm^{-3} after annealing at 550 C. Insensitive to multilayer design. Consistent with limited carrier confinement in Ge nanocrystals embedded within ITO.

✓ Carrier mobility in all nanocomposite films reduced below ITO-only film. Degradation in nanocomposite mobility with increased annealing temperature contrasts enhancement in mobility in ITO-only specimen as crystallization proceeds. Associated with carrier transport through high interfacial area, nanoheterogeneous matrix in Ge:ITO composite.

Summary

✓ Ge-ITO nanocomposites of interest for thin film photovoltaics were produced via sequential RF-magnetron sputtering.

✓Successful manipulation of nanocomposite structure through both deposition control and post-deposition thermal annealing resulted in optical and electronic behaviors attributed to quantum size effects and an enhanced free carrier density associated with the Ge nanophase.

✓ Variation in Ge fundamental absorption with phase assemblage of Ge nanocrystalline phase illustrates the importance of ensemble behavior associated with the extended structure of these quantum-scale systems.

✓ Introduction of the Ge-nanocrystalline phase into ITO increases free carrier population, in agreement with anticipated bulk energy band offsets at Ge:ITO interface, limited carrier mobility consistent with increased interfacial area (carrier scattering/trapping).

THE UNIVERSITY OF ARIZONA

Acknowledgements

✓State of Arizona TRIF Solar Initiative
✓Arizona Research Institute for Solar Energy (AzRISE)
✓Dept. of Defense SMART Scholarship Program
✓J. Madocks, M. George, H. Chandra – General Plasma Inc.
✓K. Weiss, K. Mossman - LeRoy Eyring Center for Solid State Science at Arizona State University.

mse
The University of Arizona